ACS SYMPOSIUM SERIES 1122

Pioneers of Quantum Chemistry

EDITED BY

E. Thomas Strom and Angela K. Wilson

Pioneers of Quantum Chemistry

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

ACS SYMPOSIUM SERIES **1122**

Pioneers of Quantum Chemistry

E. Thomas Strom, Editor
The University of Texas at Arlington
Arlington, Texas

Angela K. Wilson, Editor
University of North Texas
Denton, Texas

Sponsored by the
ACS Division of History of Chemistry

American Chemical Society, Washington, DC

Distributed in print by Oxford University Press, Inc.

on February 21, 2013 | http://pubs.acs.org
Publication Date (Web): February 13, 2013 | doi: 10.1021/bk-2013-1122.fw001

Library of Congress Cataloging-in-Publication Data

Pioneers of quantum chemistry / E. Thomas Strom, editor, The University of Texas at Arlington, Arlington, Texas, Angela K. Wilson, editor, University of North Texas, Denton, Texas ; Division of History of Chemistry.
pages cm. -- (ACS symposium series ; 1122)
Includes bibliographical references and index.
ISBN 978-0-8412-2716-3 (alk. paper)
1. Quantum chemistry--Congresses. 2. Chemists--Congresses. I. Strom, E. Thomas, editor of compilation. II. Wilson, Angela K., editor of compilation. III. American Chemical Society. Division of History of Chemistry, sponsoring body.
QD462.A1P56 2012
541′.280922--dc23
2012042601

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48n1984.

Copyright © 2013 American Chemical Society

Distributed in print by Oxford University Press, Inc.

All Rights Reserved. Reprographic copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Act is allowed for internal use only, provided that a per-chapter fee of $40.25 plus $0.75 per page is paid to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. Republication or reproduction for sale of pages in this book is permitted only under license from ACS. Direct these and other permission requests to ACS Copyright Office, Publications Division, 1155 16th Street, N.W., Washington, DC 20036.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department

Preface

The field of quantum chemistry has grown so immensely that the importance of some of the earliest work and the earliest pioneers of quantum chemistry is unfamiliar to many of today's youngest scientists in the field. Thus, this book is an attempt to preserve some of the very valuable, early history of quantum chemistry, providing the reader with not only a perspective of the science, but a perspective of the early pioneers themselves, some of whom were quite interesting characters.

The symposium on which this book is based came about because one of the co-editors (ETS) came to a conviction that the contributions such as those by George Wheland to quantum chemistry and Otto Schmidt to free electron theory should be better appreciated and known. He organized a symposium in which quantum chemistry pioneers, both those celebrated by everyone and those seemingly overlooked by posterity, would be recognized. He sought out and received the help of a younger colleague (AKW) active in quantum chemistry, who also had interest in recognizing early contributions in the field, based upon her own experiences. Her Ph.D. advisor, Jan Erik Almlöf, was a prominent figure in the field, whose contributions have been core to many developments in molecular electronic structure theory, and, in many ways, is a more recent contributor than the pioneers featured in the present book. Unfortunately, he died in 1996 at a relatively young age. However, in seeing how many of today's youngest generation of quantum chemists are not familiar with his name, the need to provide the earlier history of the field has become ever more clear to her. *(Note, as Jan Almlöf, is a later contributor than most of the pioneers featured in the present book, there is no chapter in his memory.)*

As is evident from the list of chapters and contributors below, the symposium and book came together remarkably quickly with acceptances by noted quantum chemists and historians of chemistry, some of whom themselves are true pioneers of quantum chemistry. Present at the symposium was Nicholas Handy of Cambridge University, who was being recognized with the ACS Award in Theoretical Chemistry for his contributions to quantum chemistry, and a pioneer himself. Handy was interested in contributing to this book but was unable to do so because of his untimely passing on October 2, 2012. However, we were honored to have his presence during his last visit to the U.S.

While this volume is certainly not a history of quantum chemistry, it does cover many highlights over a period of about sixty years. This volume consists of chapters based upon ten of the presentations at the symposium "Pioneers of Quantum Chemistry" held March 28, 2011, at the 241st ACS National Meeting in Anaheim, CA. This symposium was organized by the ACS Division of the History of Chemistry (HIST) and co-sponsored by the ACS Divisions of Computers in Chemistry (COMP) and Physical Chemistry (PHYS).

The opening chapter on “Three Millennia of Atoms and Molecules” by Klaus Ruedenberg and W. H. Eugen Schwarz covers close to three thousand years, starting with the atomic hypotheses of Greek philosophers and finishing with the advances of the late 1970’s. The next chapter by István Hargittai, “Pioneering Quantum Chemistry in Concert with Experiment”, is a survey chapter also, but it starts in more recent times with G. N. Lewis and finishes with John Pople. In “George Wheland: Forgotten Pioneer of Resonance Theory”, E. Thomas Strom makes his case for Wheland being a significant figure in quantum chemistry. William Jensen goes into “The Free-Electron Model: From Otto Schmidt to John Platt”, covering the relatively unknown Schmidt and the more recognized group at the University of Chicago.

Michael Dewar was a colorful individual with a “take no prisoners” style in his oral presentations. Eamonn Healy contributes an equally colorful chapter on Dewar in “Michael J. S. Dewar, a Model Iconoclast”, Wes Borden discusses “H. C. Longuet-Higgins—The Man and His Science”, in his chapter, and Borden laments the fact that Longuet-Higgins left theoretical chemistry too soon after a career of just 25 years. In “The Golden Years at LMSS and IBM San Jose” Paul Bagus reflects on his time at the Laboratory of Molecular Structure and Spectra led by Robert Mulliken and C.C.J. Roothaan at the University of Chicago and at the Large Scale Scientific Computations Department at IBM in San Jose, CA, an effort led by Enrico Clementi. Those of us of “a certain age” remember well the Quantum Chemistry Program Exchange at the University of Indiana. Donald Boyd tells the tale of that incredibly useful endeavor. Many of us learned about molecular orbital calculations from Andrew Streitwieser’s *Molecular Orbital Calculations for Organic Chemists* published in 1961. In his chapter Streitwieser gives biographical material on Erich Hückel and Charles Coulson and then discusses his monograph/textbook on Hückel molecular orbital theory. The final chapter describes work of that giant of quantum chemistry, Nobel Laureate John Pople, as presented by his former student Janet Del Bene.

Many quantum chemistry pioneers are pictured in the main photo on the cover. This photo is that of the participants in the famous 1951 Shelter Island Conference on Quantum Mechanical Methods in Valence Theory. Those in the photo are identified in the corresponding figure in the chapter by Ruedenberg and Schwarz. The young man at the far left of the standees is Klaus Ruedenberg. The four smaller photos below the main photo show, respectively from left to right, quantum chemistry pioneers John Pople, Erich Hückel, H. C. Longuet-Higgins, and George Wheland.

We are grateful for financial support of the Anaheim Symposium by Q-Chem and also by HIST. We acknowledge additional presentations given at the symposium, including those by M. Katharine Holloway, Vera V. Mainz, Roald Hoffmann, and Henry F. Schaefer III. Thanks also go to Tim Marney and Arlene Furman at ACS Books for their encouragement, help, and advice, as well as to the many reviewers of the exciting chapters that follow.

The chapters that follow are clearly a selective rather than a comprehensive survey of quantum chemistry, but they do illustrate the many avenues to be explored. Read and enjoy!

E. Thomas Strom
Department of Chemistry and Biochemistry
The University of Texas at Arlington
Box 19065
Arlington, Texas 76019-0065

Angela K. Wilson
Department of Chemistry
University of North Texas
1155 Union Circle #305070
Denton, Texas 76203-5017

Chapter 1

Three Millennia of Atoms and Molecules

Klaus Ruedenberg*,[1] and W. H. Eugen Schwarz[2,3]

**[1]Department of Chemistry and Ames Laboratory USDOE,
Iowa State University, Ames, Iowa 50011, United States
[2]Department of Chemistry and Biology, University Siegen,
D 57068, Siegen, Germany
[3]Department of Chemistry, Tsinghua University, 100084 Beijing, China
*E-mail:ruedenb@scl.ameslab.gov**

The growth of human insight into the atomistic structure of matter is traced, starting with the conceptions of the Greek philosophers of Antiquity, through the slow advances in the Middle Ages, into the modern era of expanding natural sciences. It focuses on developments that have generated lasting scientific knowledge through creative speculation subject to the strictures of experimental corroboration as well as logical and mathematical consistency. Special attention is paid to the role of chemistry as well as that of physics in general and to the development of quantum chemistry in particular. The Table of Contents provides a chronological overview of the subjects treated.

In celebration of the centennial of the definitive recognition of the physical reality of molecules (see page 19)

Motivation

While for many of us time is filled by study and research that extends the current knowledge of matter, some of us may wonder in quiet moments how, over three millennia, human thinking arrived at the present understanding of matter in terms of atoms, molecules and bonds. The present overview was motivated by the intent to offer a brief guide to how these concepts evolved and to trace a

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

coherent story of the issues that came to the fore and interconnected at different times. We owe it to our scientific community to remain aware of the dedicated men and women to whose insights we are indebted in our work. Hopefully some of the many remarkable historical personalities on the following pages may arouse the interest of some readers to find out more about them, as well as about their contemporaries whose contributions, even though not mentioned here, were also important and influential.

Since the authors are not professional historians, much of the presented information is obtained from secondary historical sources. The perspective is that of active researchers in theoretical chemistry. It focuses on developments that have advanced lasting scientific knowledge through the synergism of creative speculation subject to the strictures of experimental screening and corroboration as well as logical and mathematical consistency. Some references to broader and deeper historical discussions are listed at the end. Much information can also be found on the internet.

Atoms in the Shadow of the Continuum of Elements in Antiquity (~ 1000 BC-500 AD)

Conception

Although the Greek historian Strabo (at the time of Augustus, ~ 0) mentions a legendary Phoenician atomist "living before the Trojan War" (~ 1200 BC), the roots of non-mythological scientific thinking about nature can be traced back to the teachings and writings of Greek philosophers during the classical period from the 7th to the 3rd century BC. Remarkable from the modern perspective is that, in trying to comprehend the relation between transience and permanence, two models of matter were advanced from the beginning, a "continuum model" and a "corpuscular model".

Various conceptions of the continuum model were developed between 650 BC and 400 BC by the Greek philosophical schools in Ionia on the eastern coast of present day Turkey, notably in Miletos, as well as in southern Italy, notably in Elea. Thales (~ 600 BC), Anaximander, Anaximenes and Herakleitos (~ 500 BC) belonged to the former group. Parmenides and his followers as well as Empedokles (around 550 – 450 BC) belonged to the latter group. Pythagoras (~ 550 BC) spent the first part of his life on the isle of Samos in the former region and the second part in southwest Italy. He also visited Egypt and Babylon. It was Empedokles, around 450 BC, who integrated the various ideas of prime substances to form the model of the four unalterable 'roots' or 'principles', *viz.* earth (solid), water (liquid), air (gaseous) and fire (heat), from which attracting and separating forces ('love and strife') generate all transient temporal phenomena. The word 'element' was likely coined a generation later by Plato.

During the same century, some philosophers of the eastern group conceived of the alternative corpuscular view. Anaxagoras (~ 450 BC) took the first step by imagining all matter to be composed of little "seeds" characteristic of each substance, yet ultimately containing the same material. But (according to

Aristotle) the real founders of the atomic theory were Leucippus (first half of 5th century BC) and, most notably, his student Democritus (Greek: Demokritos, 460-370 BC), one of the most incisive thinkers of his time.

In the next century Aristotle (Greek: Aristoteles, 384-322 BC) further elaborated the continuum model whereas, soon after him, Epicurus (Greek: Epikouros, 341-270 BC) made atomism an important part of his philosophical system. The philosophical differences notwithstanding, Aristotle respected Democritus highly as a scientist and most of our knowledge regarding the latter comes in fact from the former's writings.

Aristotle considered matter to consist of one primary substrate subject to two basic pairs of *formative powers* with opposite qualities, namely warm *versus* cold and dry *versus* wet, with Empedokles' four elements being prototype combinations. Phenomenological changes occur when the relative mixtures of these basic qualities undergo variations in specific situations due to four basic factors: the material of which an object is composed, the intrinsic structural forces of an object, the effect of an external agent, and the teleological purpose. Mathematical considerations were alleged to require the substratum to be continuous and a vacuum was held to be non-existent.

In the atomists' view, on the other hand, matter consists of an infinite number of hard indivisible atoms (a word created by Democritus) of different types, distinguished only by size, shape and weight, turbulently moving and colliding in the vacuum and at times mechanically entangling by small surface appendages to form various kinds of corpuscles. All observed phenomenological properties, as well as changes, are secondary consequences of these primary properties.

Reception and Impact

Aristotle's conception generally prevailed over that of Democritus for the next two millennia. One reason was the enormous scope and systematic layout of Aristotle's detailed and comprehensive work on the humanities, logic and natural sciences including biology as well as the earth sciences, all based on a multitude of accurate observations, dissections and penetrating analyses. It was the grandest and broadest synthesis and classification of natural phenomena achieved until then and much of it proved of lasting value. He was a true, and then unequaled, scientist, teaching and cooperating with talented students at the Lyceum, his school in Athens, a private research institute that survived him for about 250 years. Democritus by contrast, although widely traveled, working with comparatively few students in Abdera two hundred miles north east of Athens, made fewer physical investigations and founded no school.

Another, perhaps more important aspect was the universal intertwining between natural sciences and philosophy of life at the time. Of all the arguments Aristotle gave in favor of his model of matter, his most weighty dissent from Democritus sprang from his deep conviction that nothing in nature happens by accident and that everything has a recognizable ultimate purpose (τέλος), in particular in biology. In the atomists' view by contrast, most events in nature happen by chance even though atomic motions are governed by unknown, uncaring underlying physical laws (ανάγκη). Aristotle's teleological view of nature was more hospitable to metaphysical aspirations than Democritus' and Epicurus' materialistic and anti-transcendental stance.

These ideological differences provided the basis for many subsequent rejections of Democritus and Epicurus. Such judgments were made by the Stoic school, notably the major philosopher Seneca (1st century BC), as well as by the followers of Plato (424-348 BC, a younger contemporary of Democritus) in whose view the material world is merely a flawed shadow of a higher ideal world. A strong polemic against the Epicurean school was waged by the famous Roman orator, writer and politician Cicero (1st century BC) and, later, by many in the early Christian church including St. Jerome and St. Augustine of Hippo (both ~ 400 AD).

The atomic theory did not vanish however. The Epicurean school continued to hold atomistic notions of course. Even the leader of Aristotle's Lyceum after 288 BC, Strato of Lampsakos, recognized the weakness of Aristotle's physics and advocated an atomistic theory. This view also gained adherents among some of the practicing scientists of his time. The renowned engineers Ktesibius of Alexandria and Philo of Byzantium in the 3rd century BC as well as Hero of Alexandria in the 1st century AD discussed the atomic theory and the vacuum as the basis for the many hydraulic and pneumatic engines they invented. The Alexandrian physician Erasistratos of Keos (~ 300 BC) founded a medical tradition based on an atomistic physiology. According to one of his followers, the Roman physician Asklepiades of Bithynia (~125–40 BC), nutrition, digestion, physical growth, sickness and waste as well as the penetration of healing ointments through the skin are due to accumulation, depletion or propagation of corpuscular carriers.

These arguments are also found in the most famous exposition of atomism in Antiquity, *viz.* the epic six-book poem *De Rerum Natura (On the Nature of Things),* by the Epicurean Titus Lucretius Carus (~99–55 BC), a Roman contemporary of Asklepiades. As further physical evidence, he adduced, among other observations: the propagation of smells, even so subtle that only dogs are aware of them; the propagation of heat and of sound; the loss of strength of perfumes left open; the evaporation of liquids left unattended; the weight loss of plants or meat by drying; laundry hung near the coast getting humid on overcast days but drying in sun light; the loss of salt when saltwater flows through certain soils; the accumulation of sweet water in a vessel of certain porous clay when it is submerged in saltwater; the attrition of small metal objects by frequent handling; the dulling of plow blades by continued use; the wearing out of stones by walking on them or even by small but steady drops of water. Lucretius even offered a close to correct explanation for the Brownian motion of dust particles visible in a sunbeam. While many of these inferences are remarkably perceptive, a conclusive advance toward hard knowledge was impossible until the technical means for experimental testing and quantitative analysis began to become available over a thousand years later.

The mainstream authors in the Roman Empire, such as the naturalist Plinius (1st Century AD) and the physician Galen (2nd century AD), though generally respectful towards Democritus, continued to hold Aristotle's views. The latter also allowed for the transmutation between different substances, which was well in tune with the alchemists' obsession to produce gold and other valuable materials. Speculative ideas on the constitution of matter developed in India and China around that time had little, if any influence in Western Antiquity. No major shifts occurred until the collapse of the Western Roman Empire and civilization in the middle of the first millennium.

Atomism versus Aristotelian Scholasticism in the Middle Ages (~ 500-1600 AD)

Survival of the Sciences of Antiquity (~ 500-1400)

During the turbulent next half millennium, the knowledge that the Greek-Roman civilization had accumulated survived in the West essentially only in books and fragmentary documents preserved in libraries of churches and monasteries. A few scholars, notably Isidore Archbishop of Seville (~ 600), Bede of Northumbria (~ 700), Rabanus Maurus Archbishop of Mainz (~ 800), William of Conches (~ 1000) and Vincent of Beauvais (early 13th century), tried to maintain some awareness of what had been known to the ancients by composing encyclopedic summaries, all of which included brief sections on Aristotle's as well as Democritus' views.

In the Near East, on the other hand, Greek as well as Indian philosophies had a considerable impact on a number of Muslim scholars of the Islamic 'Golden Age' (about 750-1250). Among those who kept the Greek philosophy free of theological dilution were notably the Persian Ibn Sina (~ 1000, known as Avicenna in the West) and the Arab Ibn Rushd (12th century in Spain, known as Averroes in the West). They became highly expert in Aristotelian philosophy, pursued rational and empirical thinking and, via the Iberian peninsula, had a marked influence on the cultural revival in Western Europe.

As a new western civilization began to take shape in the 12th century under secular as well as ecclesiastic aegis, a desire to reconnect with the knowledge of Western Antiquity awoke. One of the first rediscovered major authors was Aristotle, in large part through contact with the Muslim civilization in Spain, but also through renewed studies of Greek manuscripts in Constantinople. Aristotle's teleological reasoning proved so persuasive that the Italian Dominican Thomas Aquinas (1225–1274) incorporated Aristotle's views of nature into his *Summa Theologica*, a major foundation of scholastic church doctrine. On the other hand, taking its cue from St. Augustine, the church proscribed Democritus' and Epicurus' atomism as atheistic. In 1347, the anti-Aristotelian atomist theologian Nicholas d'Autrecourt (1297–1369) saw his books publicly burned in Paris. In the Muslim civilization, interest in the Greek philosophers and the rational pursuit of the sciences did not revive after the sack of Baghdad by the Mongols in 1258.

Humanistic Revival of Atomism (~ 1400-1600)

In the West, confidence in the scholastic views of nature began to erode over the next two centuries. One reason was the steadily increasing number of classical manuscripts that continued to be discovered, such as Diogenes Laertios' *Lives* *and Opinions of Eminent Philosophers* (of the 3rd century). A notable influx of ancient Greek books into Western Europe occurred since the later part of the 14th century when wealthy citizens of Constantinople relocated with their libraries to Italy fearing the eventual success of the Ottoman siege, which indeed came to pass in 1453. The newly discovered European cultural heritage sparked broader studies of all Greek and Roman philosophers and led to the emergence of rational humanism.

A momentous event was the rediscovery of a copy of Lucretius' above mentioned atomist tract *De Rerum Natura* in 1417 in southern Germany or Switzerland by the early Italian humanistic scholar Poggio Bracciolini. Immediately, many copies were made and it became one of the first books printed in 1473 and again in 1486, 1495, 1500, 1511, 1512, 1514, 1531. (Niccolo Machiavelli (1469–1527) made a copy. A few hundred years later Molière made a translation, and Isaac Newton as well as Thomas Jefferson had copies in their libraries.) That atomistic views were making inroads into general thinking is apparent in the writings of the German Cardinal Nicholas of Cusa (1401–1464).

Among scientists, the Italian physician Girolamo Fracastoro (1478–1553) subscribed to atomism and held that epidemics are caused by aerial transmission of tiny spores over long distances. The Italian artist and engineer Leonardo da Vinci (1452–1519) wrote that the sky is blue because invisible tiny water atoms become luminous by absorbing the rays of the sun.

Beginnings of Chemical Atomism (~ 1300-1600)

Consequential regarding the present theme was that some alchemists found it expedient to introduce corpuscular models to account for various observations in their advancing chemical experimentations. They did so without abandoning their Aristotelian heritage by emphasizing certain, originally peripheral, passages in Aristotle's writings regarding *natural minima* that had been further elaborated by Muslim alchemists, who were then highly regarded in the West. Thus, the most influential alchemist book *Summa Perfectionis* (~1300), believed to be authored by the Italian Franciscan Paul of Taranto, alias Geber, makes frequent use of such *minimae partes* to explain how various metals consist of mercury and sulfur particles. While these experiment-related smallest entities were still posited as composed of the four Aristotelian elements, their substructures were of no practical consequence and in fact held unknowable by eminent Aristotelian scholars such as the Italian Julius Caesar Scaliger (1484-1558). Even though the attributes of the *minimae partes* differed considerably from those of Democritus' *atoms*, some 'chymists' tried towards the end of this period to fuse this empirical Aristotelian atomism with Democritus' ideas, notably the German Andreas Libavius (1555–1616) in his text *Alchemia*.

Impact of Technological Advances (1200 – 1600)

One reason for the gradual discovery of new (al)chemical reactions was the development of the strong mineral acids during this period. New chemical reagents were a part of the vigorous technological advances in Europe in the later Middle Ages (such advances also occurred in the Far East). Others were the manufacture of materials (e.g. iron working processes, glass, cloth, paper, gunpowder), the developments of new tools and mechanical contrivances (e.g. windmills, watermills, cranes, weaving looms), the construction of large buildings and ships, the inventions of sophisticated devices (e.g. mechanical clocks, spectacles, compasses) and numerous other innovations, such as the introduction of Hindu-Arabic numerals by Leonardo Fibonacci of Pisa (1170-1250). The perfection of the printing process led to wide and fast dissemination of new ideas. In the late 1400's the Americas were discovered. One impact of these achievements was a growing confidence that nature could be understood better through the human senses by appropriate physical experimentation and correlative quantitative analyses rather than on the basis of metaphysical scholastic *a-priori* axioms.

The Turn of the Tide (~1500-1700)

Aristotle's Authority Begins to Fade (~ 16th Century)

As the 16th century progressed, scholastic syllogism were increasingly perceived as barren and the appeal of the Aristotelian natural philosophy declined accordingly. Two strong theological critics of the scholastic constraints, the French humanist Pierre de la Ramée (1515–1572) and the Italian Dominican Giordano Bruno (1548–1600) paid with their lives for their vocal advocacy. But appreciation of a liberal inquiry into the world continued to grow and paved the way for the gradual removal of ideological injunctions against the rational and experimental approach to the natural sciences.

This was also the time when the Polish-German canon and astronomer Nicolaus Copernicus (1473–1543), the Danish astronomer Tycho Brahe (1546–1601) and the German astronomer Johannes Kepler (1571–1630) initiated the replacement of the geocentric Ptolemaic cosmology, which had also been Aristotle's, by the heliocentric planetary model, which the Greek mathematician Aristarchos of Samos had proposed 18 centuries earlier, and which the Italian scientist Galileo Galilei (1564-1642) was soon to defend.

The leading figures in guiding natural philosophy into the era of modern scientific methodology in the beginning of the 17th century were the Englishman Francis Bacon (1561-1626) and the Frenchman René Descartes (1596–1650), even though both were only partial atomists. The former forcefully formulated the program that the soundest basis for human knowledge is furnished by induction from the empirical findings of the natural sciences. The latter advocated a fully mechanistic and mathematical understanding of nature that must be separated from the spiritual and religious concerns of the human mind or soul.

Atomism Begins to Prevail (~ 17th Century)

In the spirit similiar to that of Decartes' dualism, atomistic explanations of natural phenomena became more and more prevalent among philosophers, physicians and natural scientists. The Dutch theologian David Gorlaeus

(1591-1612) and the devout German polymath and educator Joachim Jungius (1587-1657) published explicit atomistic theories. Passages by Galileo Galilei show that he entertained atomistic concepts, as do the writings of his French-Italian associate Claude Berigard (1578-1664). Recent research has suggested that Galileo's atomistic critique of Aristotle's doctrine of matter may have been as weighty a reason for his trial in 1633 as his advocacy of Copernicus' heliocentric cosmology.

In an influential book of 1649, the French Priest and philosopher Pierre Gassendi (1592-1655) put forth an atomistic view of nature on the basis of empirical observations with the goal of even creating a skeptical Epicurean attitude within a Christian framework. He wrote of 'molecules' composed of 'atoms'. In the book *Democritus reviviscens* (1646), the French-Italian Physician Johann Chrysostomus Magnenus produced the first quantitative atomic data ever: Upon examining the diffusion of incense burnt in a large church, he calculated the number of particles in the original solid kernel to be at least ~ 10^{18}, only about one order of magnitude short regarding the length of an incense molecule.

In chemistry the new outlook culminated in the work of the British polymath Robert Boyle (1627–1691), one of the leading English intellectual figures of the century. An experimentalist as well as theorist, he put forth and elaborated the 'mechanical philosophy' that all chemical phenomena are due to physical interactions between atoms that work in ways analogous to the operation of macroscopic machinery. His friend Isaac Newton (1643–1727), who also made chemical experiments, shared Boyle's atomistic views and speculated about short-range attractive and long-range repulsive forces between such particles.

A fatal blow to a fundamental Aristotelian tenet, namely the non-existence of any vacuum, was dealt by the Italian physicist and mathematician Evangelista Torricelli (1608-1647), when he created a natural vacuum by his famous barometer experiment in 1643, explaining that "we live submerged at the bottom of an ocean of air". In 1654 Otto von Guericke (1602–1686), mayor of Magdeburg and scientist, demonstrated publicly and spectacularly the artificial creation of a vacuum by using a pump he had invented, which was subsequently improved by Robert Boyle. Other inventions, such as the microscope (1600), the telescope (1608), the thermometer (1611) and the pendulum clock (1656), were instrumental in furthering the scientific advances during this time.

Chemistry Leads to Empirical Elements and a New Atomism (~ 1600-1810)

While there was increasing consensus in the 17th and 18th centuries to consider matter as consisting of invisibly small corpuscles, every one of the natural philosophers seemed to have his own ideas about the details of atomistic structures. Real *substantive progress* towards a solid empirical atomistic science of matter emerged from the *experimental advances that led from alchemy to chemistry* in these two centuries. With the use of new and more powerful tools and reagents, many new ways of decomposing and recovering old and creating new substances were discovered. By combining the implications of many interlocking experimental results of the various reactions to resolve ambiguities, it became gradually possible to disentangle what by the end of the 18th century came to be distinguished as elements (often called "principles") and compounds. It then became apparent that there were a great number of these *empirical elements* and, although this proliferation was found in some way disturbing, it laid to rest any remaining scientific interest in the Aristotelian elements and the alchemical principles by the end of the period. On this basis, a new atomism was then developed.

Rise of Systematic Chemical Empiricism

While the roots of this pragmatic approach go back to the alchemists of the beginning of the 14th century mentioned above, it was Daniel Sennert (1572–1637), Professor of Medicine in Wittenberg, who first pursued the empirical program systematically and consistently through many experiments and publications. The essential basis for his reasoning were *cyclic* experiments that exhibited the *'reduction to the pristine state'*, as exemplified by the widely quoted cycle of alloying silver with gold, dissolving the silver out of the alloy in nitric acid (aqua fortis), filtering the silver nitrate without leaving a residue, precipitating silver carbonate by adding potassium carbonate (salt of tartar) and finally *recovering the silver metal* by washing and heating. On the basis of this type of experimental evidence, he refuted the basic Aristotelian theory of chemical changes in terms of *generation and corruption of substantial forms involving the four elements* and concluded that all reactions between different substances are in fact the results of junctions and separations of tiny elementary indestructible atoms (he adopted Democritus' term) that are associated with each substance. Variations in observable properties of a substance are due to various spatial atomic arrangements. Only experiment can provide information regarding what types of atoms exist.

A generation later, the prolific Robert Boyle amplified and extended this experimental approach by conceiving and performing a vast number of experimental investigations from which he inferred evidence for various aspects of the atomic structure of matter. He presumed the existence of elemental substances but did not feel ready to identify any. He gave though experimental evidence that neither Aritotle's four elements nor Paracelsus' (1493–1541) three principles of mercury, sulphur and salt can be the ultimate constituents of everything. This basic *empirical* approach of Sennert and Boyle to deducing atomistic conclusions from macroscopic experimental chemical reactions, without regard to internal properties of atoms, subsequently became fundamental in chemistry.

When it came, however, to observable properties for which the available experiments could not provide explanations, notably manifest differences in bonding strengths between different types of atoms, but also electric and magnetic phenomena, Sennert fell back on Aristotle's concepts and attributed such interactions to the power of *immutable and unknowable Aristotelian forms within atoms.* Boyle, by contrast, firmly rejected any perpetuation of Aristotelian forms and advanced the 'mechanical philosophy' mentioned above to provide the interactions that account for *all* phenomena in the atomic realm. By severing the last connection with the Aristotelian philosophy, Robert Boyle's many books, notably *The Sceptical Chymist* (1661), mark the beginning of modern chemistry. They became the source of inspiration for subsequent scientific thinking, even though the vision of a fully physical basis of chemistry was only realized 266 years later after the advent of quantum mechanics.

Identification of the Empirical Elements

Successful on a shorter timescale was the further pursuit of the *chemical-experimental* approach that had begun with the alchemists of the 14th century and that Sennert and Boyle had perfected to the point of providing support for atomism. A limitation of the 17th century chemists had been that their experiments still focused mainly on material changes in condensed phases, in particular metals and salts, because they had only few and primitive means of monitoring the gases evolved during reactions. This inability had prevented a quantitative proof of the indestructibility of atoms by verifying the conservation of mass through *weighing.* That weight conservation should be taken as evidence for atomic indestructibility had been advanced by the Flemish chemist Johann Baptista van Helmont (1579–1644) and was accepted by Sennert and Boyle.

The route for progress on this problem was opened by the development of two new implements. Around 1727 the Englishman Stephen Hales (1677–1761) invented the pneumatic trough, which enabled the collection and quantitative analysis of gases produced in reactions above a liquid like mercury. Around 1750, the Scotsman Joseph Black (1728 –1799) developed the analytical balance by placing a light-weight beam on a wedge-shaped central fulcrum, which enabled far more accurate mass determinations than before. This ability to weigh gases escaping upon heating, burning, fermenting or other reactions, provided the prerequisite tools for determining the quantities of reactants and products. By the end of the century, close to two dozen different gases, elemental and compound, had been identified.

The leaders in isolating and characterizing gases were, in addition to Black, the English scientist Henry Cavendish (1731-1810), the German-Swedish pharmacist Carl Wilhelm Scheele (1742-1786), the English theologian and scientist Joseph Priestley (1733-1804) and the French administrator and chemist Antoine Laurent Lavoisier (1743-1794) in collaboration with his wife Marie-Anne Paulze (1758–1836).

On the basis of the information gained by these chemical experiments, Lavoisier recognized the fundamental role of oxygen in combustion and created the basic framework for modern chemistry. In the *Tableau des substances simples* of his *Traité élémentaire de chimie* (1789), he put forward the first list of elements: 22 metals and metalloids, 6 nonmetals and 3 gases (oxygen, nitrogen and hydrogen). Also included were however the massless agents heat and light. Defining elements operationally as "the last point that analysis is capable of reaching", Lavoisier considered his list provisional.

A New Atomism

In contrast to these chemical advances, no concrete new information emerged during the 18th century from attempts to develop the *physical* atomistic speculations of Newton and Boyle further, for instance through efforts of the French chemist Claude Louis Berthollet (1748–1822) and others to deduce forces between atoms from quantifications of 'chemical affinities', or through the ingenious theoretical models of the Croatian polymath Jesuit Ruđer Bošković (1711–1787). In the early 1800's, however, after Lavoisier's recognition of chemical elements became known, it was from the perspective of an atomistic physicist that the English meteorologist John Dalton (1766-1844) conceived that elements consist of atoms and compounds consist of molecules formed from atoms. He devised a way of extracting the *compositions of molecules in terms of atoms* from the results of *gravimetric chemical measurements*. He was the first to present formulas for molecules in terms of atoms and to deduce weights of molecules by assigning different weights to atoms of different elements.

In the final decade of the 18th century, followers of Lavoisier had become interested in finding regularities of the relative proportions in which elements combined. Thus, the French chemist Joseph Louis Proust (1754–1826) discovered in 1797 the law of definite proportions, viz. that elements combine only in small numbers of fixed ratios *by weight*. Relevant in this context was also that, from 1791 on, the German chemist Jeremias Benjamin Richter (1762–1807), although neither a follower of Lavoisier nor an atomist, had documented the law of equivalent proportions *by weight* for all neutralization reactions involving 18 acids and 30 bases.

Dalton, on the other hand, was trying to explain the homogeneity of gas mixtures, such as the atmosphere, in terms of Newtonian physical repulsions between the gas particles and, at one point, began to suspect the weight of the particles to be a relevant factor. He tried to deduce weights of molecules in gas mixtures from analytic data available from chemists and also using, to some degree, the assumption that equal gas volumes contain equal number of particles. He then began to carry out his own studies, first on various oxides of nitrogen and later on other gases. Around 1803 he inferred the law of multiple proportions and, shortly thereafter, he perceived the implications of his work for chemistry.

Dalton's seminal invention was a process of reasoning for *deducing simultaneously molecular formulas and relative atomic weights* from experimentally observed *mass ratios* found in chemical analyses. He embarked on an intrepid procedure for inferring the most likely molecular formulas from the available chemical and physical data using the "rule of greatest simplicity". Notwithstanding the manifest initial ambiguities, the approach proved in fact workable in the long run by merging information from many experiments as more and more data became available during the first half of the 19th century.

Dalton's *New system of chemical philosophy* (1808 and 1810) represents the first substantive step towards concretely intertwining the physical and the chemical approaches to molecules. His fundamental *atomistic* conception, together with Lavoisier's identification of *elements* and Boyle's original program of *physical* *and empirical* chemistry are generally credited to be the historical cornerstones of modern chemistry.

Chemistry Finds Rules for Molecule Formation (~ 1800-1870)

To turn Dalton's conceptual vision into a quantitative science, on par with the level of accuracy that had been achieved by gravimetric analyses, presented a daunting challenge, namely: To deduce complex conclusions regarding the microscopic atomic composition of molecules from macroscopic measurements. The results from many experiments had to be combined. In addition to the basic assumption of the indestructibility of atoms, two approximate empirical physical rules were invoked, whenever possible. For reactions involving gases there was a general tendency to assume that equal volumes contain equal numbers of molecules so that the relative weights of molecules could be deduced from the relative weights of equal gas volumes. For solids a similar purpose was served by a rule found in 1819 by the French physicists Pierre Louis Dulong (1785–1838) and Alexis Thérèse Petit (1791-1820), namely that all solids have the same heat capacity per atomic equivalent. To achieve a proper understanding of molecular structures took over half a century. The goal was reached through several stages of successive insights.

Inorganic Molecules, Electro-Polar Bonding versus Diatomic Elemental Gases

In the early part of the century, fundamental analytical techniques were developed for the accurate measurement of weight ratios in many chemical reactions that provided accurate data for determining atomic weights and molecular compositions. The premier figure of this period was the Swedish chemist Jöns Jacob *Berzelius* (1779–1848) with many seminal advances to his credit. His quantitative determinations were impeccable (in contrast to Dalton's). Six new elements were discovered in his laboratory. He introduced the chemical letter symbolism for atoms and molecules, which proved so fruitful for all subsequent chemical reasoning that it is still in use today. For many years from 1822 on, he wrote the authoritative annual report on the progress in chemistry.

A consequential complication arose regarding the elemental gases. On the basis of experimental evidence by many investigators, the French chemist Joseph Louis Gay-Lussac (1778–1850) concluded in 1808 that the volumes of reactants and products in gas reactions stand in very simple integer proportions. Three years later, the Italian physicist Amadeo Avogadro (1776-1856) pointed out that Gay-Lussac's data are compatible with the equal-volume = equal-number-of-molecules assumption only when the molecules of most elemental gases contain more than one atom, in particular O_2 and H_2. He proposed that this is in fact the case and thereby inferred the relative weights of many atoms. Although supported a few years later by the respected French physicist André Marie Ampère (1775–1836), it took the chemical community half a century to accept the general validity of this hypothesis.

The initial rejection was a consequence of the invention in 1800 of the electric battery and, hence, the availability of direct current in chemically useful amounts, by the Italian physicist Alessandro Volta (1745–1827). In the same year, the English chemists William Nicholson (1753-1815) and Anthony Carlisle (1768-1840) as well as the German chemist-physicist Johann Wilhelm Ritter (1776-1810) used the current to decompose water into its elements, which was simpler and more quantitative than previous attempts with an electrostatic friction generator. Starting in 1803, Berzelius as well as the English chemist Humphry Davy (1778-1829) began employing electrolysis to analyze acids, bases and salts and to discover further elements. These fruitful experiments led Berzelius to posit that bonding between atoms occurs because individual atoms are *permanently* electropositive or electronegative, a model that manifestly precluded bonding between atoms of the same element in a molecule in the gas phase as implied by Avogadro. The relationships between chemical equivalents and electric current, experimentally discovered in 1832/33 by the English scientist Michael Faraday (1791-1867), seemed to add weight to these views. In the context of inorganic chemistry, on which Berzelius focused, this dualistic theory of chemical bonding was useful. But the presumption of mono-atomic gases impeded the correct identification of atomic weights and, hence, of molecular formulas.

Organic Molecules, Covalent Bonding Structures

With the beginning of the second quarter of the 19th century, the German chemists Friedrich Wöhler (1800-1882) and Justus von Liebig (1803-1873) and the French chemist Jean-Baptiste Dumas (1800-1884), building on Berzelius' achievements, created laboratory techniques of greatly improved accuracy for accurate quantitative determinations of carbon, hydrogen, oxygen and nitrogen in substances that belonged to what came to be called organic chemistry. Wöhler's inorganic synthesis of urea marked the beginning of the end of the hypothesis that organic compounds could only be made by living organisms. Dumas devised a nitrogen determination that is still used. Liebig's *Five-Bulb-Kaliapparat* for carbon analysis proved of such universal importance for three-quarters of a century that it was chosen to grace the logo of the American Chemical Society ever since its founding in 1876. The accurate analytical data obtained by these techniques were essential prerequisites for developing the conceptual theoretical understanding of the molecules generated in this mushrooming experimental field.

Sorting out the vast number of new compounds and reactions turned out to be a monumental task. Among the many outstanding chemists involved in unraveling the complex relationships through experiments and conceptions were, in addition to Wöhler, Liebig and Dumas, the German chemists Hermann Kolbe (1818-1884), Wilhelm von Hoffmann (1818-1892) and Friedrich August Kekulé (1829-1896); the French chemists Auguste Laurent (1807-1853), Charles Friedrich Gerhardt

(1816-1856), Adolphe Wurtz (1817-1884), and Marcelin Berthelot (1827-1907); the English chemists Alexander William Williamson (1824-1904), Edward Frankland (1825-1899), and William Odling (1829-1921); the Scottish chemist Archibald Scott Couper (1831-1892); the Italian chemist Stanislao Cannizzaro (1826-1910); and the Russian chemist Aleksandr Mikhailovich Butlerov (1828-1886).

Many of the investigated reactions involved only the elements carbon, nitrogen, oxygen, hydrogen, sulfur and chlorine, and many similarities in the properties of compounds and analogies in reactions were observed. Isomorphism of inorganic crystals was discovered in 1818 by the German chemist Eilhard Mitscherlich (1794-1863). The discoveries of the allotropy of carbon by Davy in 1814 and of the isomerism between silver-fulminate and silver-cynate by Liebig and Wöhler in 1824 revealed early that, in addition to the elemental composition, the mutual arrangement of atoms in a molecule was also relevant.

By about 1840, it became apparent, notably in view of the substitution of chlorine for hydrogen in organic molecules, that Berzelius' universal electro-polar model of bonding had to be abandoned; *i.e.* the organic chemists discovered homopolar (covalent) bonding. Consequently, atoms of the same element could bond to each other and the objection against Avogadro's diatomic elemental gases vanished. Laurent, Gerhardt and Cannizzaro were instrumental in this development, which opened the path towards the correct assessment of atomic weights.

To account for the multitude of observations, a multiplicity of schemes came to be proposed and used regarding conjectured conserved groupings of atoms within molecules, denoted variously as radicals, equivalents, types, substitutions and combinations thereof - a situation as confusing to the contemporaries as it is in historical hindsight.

Between 1850 and 1860, the work of Gerhardt, Williamson, Frankland, Odling, Wurtz, Kekulé and others led to the perception that, in organic-chemical reactions, certain bonds (to use modern language) are broken or formed between *adjacent* groupings and that chemical reactions could therefore be used to pinpoint where bonds existed between groups of atoms. It was then recognized that such bonds can be associated with individual atoms in a molecule and that specific atoms possessed specific valencies (to use modern language), notably the monovalency of hydrogen and chlorine, the divalency of oxygen, the trivalency of nitrogen and the tetravalency of carbon (proposed by Kekulé in 1857). These conclusions finally led Couper, Frankland, Kekulé, Williamson, Butlerov and subsequently the Scottish chemist Alexander Crum Brown (1838-1922) to formulate "structure formulas", which represented what may be called the topology of bonding in a molecule. Kekulé also came to accept double bonds between carbon atoms and, in 1865, deduced the hexagonal bonding structure of benzene from its substitution reactions.

A milestone on the way to a consensus between the many different views was the Congress of Karlsruhe in 1860, attended by 140 chemists from a dozen countries, where Cannizzaro delivered the influential final lecture. It was the first *international* scientific congress ever.

The Periodic System

With the number of elements steadily increasing, chemists were searching for a systematic order. The clarification regarding atomic weights achieved in Karlsruhe opened the road towards the crowning achievement of chemical atomism: the discovery of the periodic system of the elements. Using Cannizarro's latest atomic weights, the French geologist Alexandre-Emile Béguyer de Chancourtois (1820–1886) showed in 1862 that elements with similar chemical and physical properties occur below each other when ordered according to increasing atomic weights on a cylinder; but his work appeared in a less accessible place. In 1862 and 1864 the German chemist Julius Lothar Meyer (1830-1895) designed a table of the main group elements. In 1865 the English chemist John Alexander Newlands (1837-1898) developed the "Law of Octaves" based on chemical similarities. In 1869 and 1870 finally, Meyer as well as the Russian chemist Dmitri Ivanovich Mendeleev (1834–1907) independently published periodic tables containing all elements known at the time. On the basis of his table, Mendeleev furthermore predicted as yet unknown elements and their properties. Only the column of the noble gases had to be added in 1894-98 when these elements, were discovered by the Scottish chemist William Ramsey (1852-1916) and the English physicist Lord Rayleigh (1842–1919).

Chemical Atoms versus Physical Atoms

The complex and convoluted chemical elucidations during the course of the 19th century sketched above furnished the essential experimental basis for developing the conceptual understanding of molecules in terms of atoms and, thereby, for the atomistic understanding of matter. Since the overwhelming chemical evidence was based only on the law of the conservation of mass, opinions among chemists varied widely as to whether the chemical letter symbols used in their formulas correspond in fact to real physical atoms and molecules with geometrical shapes existing in real three-dimensional space. While the physicalists in the tradition of Boyle, Newton and Dalton were certain of it, the extreme chemical empiricists, notably H. Kolbe, considered this question unanswerable and irrelevant. They viewed chemical formulas as mere symbolic bonding schemata (even for hexagonal benzene) and chemical equations as mere symbolic representations for mass ratios and reactions measured in continuous matter. A great diversity of notions on this subject was evident among the participants at the Congress in Karlsruhe.

Physical Reality of Atoms and Molecules (~ 1860-1912)

Kinetic Gas Theory and Statistical Mechanics

The firm establishment of the physical reality of atoms is closely connected with the recognition of the law of the *conservation of energy*. In 1797 the British-American physicist Benjamin Thompson, Count Rumford (1753– 1814) had observed that heat can be created by work when he supervised the boring of cannon barrels in Bavaria. The mechanical equivalent of heat was proposed and determined in 1842 by the German physician Julius Robert Meyer (1814–1878), and in 1845 by the English brewer and physicist James Prescott Joule (1818–1889). In 1847 the German physicist Hermann von Helmholtz (1821–1894) postulated the conservation of energy between *all* physical phenomena. In 1850 the German physicist Rudolf Clausius (1822–1888) formulated the first law and the second law in a memoir in which, according to the American scientist Josiah Willard Gibbs (1839-1903), “the science of thermodynamics came into existence”.

The realization of the mechanical equivalence of heat then led Clausius to implement between 1858 and 1860 the model that the Swiss mathematician-physicist Daniel Bernoulli (1700–1782) had proposed in 1738, namely that pressure and temperature of gases are expressions of the energy of motion of the molecules. Clausius’ development of the kinetic gas theory and the statistical extensions by the Scottish physicist James Clerk Maxwell (1831–1879) and the Austrian physicist Ludwig Boltzmann (1844–1906) between 1860 and 1871 not only placed the ideal gas law on a firm foundation but, impressively, made verifiable new physical predictions (e.g. the unexpected independence of the gas viscosity of the density). In addition, the theory enabled the Austrian physical chemist Josef Loschmidt (1821-1895) to deduce the actual sizes and weights of molecules and what is presently called the Avogadro or Loschmidt number (1865) from the macroscopic viscosity, thermal conductivity and condensation volume.

In 1908 the atomistic view of nature was visibly exhibited by the experiments of the French physicist Jean Baptiste Perrin (1870–1942) on the microscopically observable Brownian motion as well as barometric density distribution in colloidal solutions. His accurate detailed measurements confirmed the statistical-theoretical predictions the German physicist Albert Einstein (1879 –1955) had made in 1905 and yielded another determination of Avogadro’s number.

Stereochemistry

In the chemical community, too, the empiricist reservations regarding the actual physical reality of “chemical atoms” slowly lost ground. A notable success of the physical conception was the explanation of optical activity by the French chemist Joseph Achille Le Bel (1874-1930) and the Dutch chemist Jacobus Henricus van’t Hoff (1852–1911). Polarized light had been identified in 1690 by the Dutch physicist Christiaan Huygens (1629-1695). Between 1811 and 1821, work by the French physicists François Arago (1786–1853), Jean-Baptiste Biot (1774–1862) and the English astronomer John F. W. Herschel (1792–1871) revealed that enantiomeric quartz crystals rotate plane-polarized light in opposite directions and that turpentine solution rotates such light. In 1848 the French chemist Louis Pasteur (1822–1895) found that this property is maintained when he dissolved enantiomeric tartaric acid crystals, he had prepared, separately in water. He inferred that two possible mirror-imaged structural arrangements of atoms are possible *within the individual three-dimensional molecules*. In 1874, van’t Hoff and Le Bel independently proposed that atoms bonded to a four-valent carbon are in fact *physically* located at the corners of a tetrahedron and that chirality results when all substituents are different. Wider applications of these ideas by the German chemist Johannes Wislicenus (1835-1902) and others led to the development of organic stereochemistry. In 1905, the Swiss chemist Alfred Werner (1866-1919) extended the usefulness of physical stereochemical views to inorganic chemistry by introducing the concepts of three-dimensional coordination structures and isomerism for understanding the colorful transition metal complexes.

Atomic Spectra

Another strong indication of the physical existence of atoms came from the discovery of atomic line spectra. The resolution of white light into its colored components by means of a prism had been discovered by Isaac Newton in 1666. That different substances emit different spectra in flames was noted in 1752 by the Scottish physicist Thomas Melvill (1726–1753). A very thorough study of the solar spectrum was made from 1814 on by the German optician Joseph von Fraunhofer (1787–1826). Using a telescope, he found that this spectrum had a huge number of dark “lines” (the use of a *slit* for the incoming light had been introduced by W. H. Wollaston in 1802) and he measured hundreds of them accurately. In 1833 David Brewster and William Miller respectively suggested that Fraunhofer’s lines are due to absorptions by gases in the atmosphere and in the sun. John Herschel and W. H. Fox Talbot in 1826 and 1834 noted that chemical elements have characteristic spectra. In 1849, the French physicist Léon Foucault (1819–1868) showed that Fraunhofer’s dark D lines coincide exactly with certain emission lines from an arc spectrum. The extension of the solar spectrum into the ultra-violet region was found in 1852 by the English physicist George Stokes (1819–1903) using a quartz prism and photographic plates (photography had been invented in the late 1820s by N. Niépce and L. Daguerre in France).

That atomic spectra uniquely distinguish and precisely identify the elemental atoms was established by the extensive systematic investigations of the decade-long in-depth cooperation between the physicist Gustav Kirchhoff (1824–1887) and his chemist colleague Robert Wilhelm Bunsen (1811-1899) in Heidelberg. They developed the prism spectroscope, as well as the burner to dissociate molecules into atoms in a near-colorless flame. Starting in 1859, they showed the general identity of absorption and emission lines, they accurately identified and tabulated in great detail the line spectra of a great many elements and they foresaw the analytical importance and astronomical applications. Indeed, in 1868 a new element, helium, was first discovered through its lines in the solar spectrum by the English astronomer Norman Lockyer. Kirchhoff and Bunsen discovered cesium and rubidium in 1860 and 1861 and over a dozen other elements were discovered through their spectra during the 19th century.

From 1882 on, the capabilities of spectroscopic measurements were greatly broadened in scope and enhanced in accuracy by orders of magnitude by using, instead of prisms, the extremely accurate diffraction gratings that the American physicist Henry Augustus Rowland (1848–1901) was able to etch with the ruling engine he had invented. For over a generation, his gratings were essential instruments in spectroscopic laboratories around the world.

Demurrers

Remarkably, in spite of the various indirect indications, a few highly respected scientists did not accept the physical reality of atoms and molecules until the end of the century. Notably, the chemists Benjamin Brodie (1817-1880) in Oxford, Marcelin Berthelot (1827–1907) in Paris and Wilhelm Ostwald (1853—1932) in Leipzig as well as the physicists Ernst Mach (1838–1916) in Austria and Henri Poincaré (1854–1912) and Pierre Duhem (1861–1916) in France considered the available information to be insufficient evidence for the ontological existence of an atomistic world.

A similar reluctance persisted into the beginning of the 20th century among crystallographers with regard to exploring theoretically the consequences of placing chemical atoms and molecules as physical entities into the geometric Bravais lattices. Their hesitancy to speculate was comparable to that existing among earlier generations of chemists.

Crystal Structure

The first to write about explaining crystal shapes had been Johannes Kepler. Musing over the reasons why the snowflakes falling on his coat in the winter of 1610 were always hexagonal, he had analyzed the problem of closely packing tiny spherical water globules, even though he was not an atomist. Subsequently, many crystallographers and mathematicians contributed to unraveling the problems of crystal symmetry. In 1784, the French mineralogist René Just Haüy (1743-1822) argued that crystals are built from *periodically* stacked polyhedral blocks. In 1824, the German physicist L.A. Seeber replaced the polyhedra by uniformly spaced representative tiny spherical objects, which led to the model of *periodic space lattices*. In 1850, the German mathematician J. P. G. L. Dirichlet (1805-1859) introduced the construction of a primitive cell surrounding each lattice point. Through a penetrating analysis, the French physicist Auguste Bravais (1811-1863) derived in 1850 the 14 fundamental lattices that provided the basis for almost all subsequent work. Further analyses moved more and more toward the group theoretical elucidation, which culminated in the identification of all 230 space groups in 1891 by the Russian crystallographer Yevgraf Stepanovich Fyodorov (1853-1919), by the German mathematician Arthur Moritz Schoenfliess (1853-1928), and, in 1894, by the English geologist William Barlow (1845-1934).

In this highly successful crystal structure theory, the lattice points had become part of the *mathematical model* and the question of their possible relation to positions of physical atoms or molecules was avoided rather than explored. The connection was established only in 1912 when the German physicists Max von Laue (1879–1960) with his coworkers Paul Knipping and Walter Friedrich, influenced by the German theoretical physicist Paul Ewald (1888–1985), succeeded in scattering X-rays from copper-sulfate crystals, thereby simultaneously establishing the wave nature of X-rays and the physical atomistic structure of crystals. Still in the same year, the Australian-English physicists William Henry Bragg (1862–1942) and William Lawrence Bragg (1890–1971) began to develop this technique for chemical structure determinations. These experiments, performed exactly a hundred years ago, dispelled any remaining renitence regarding the physical reality of molecules. A year later, Niels Bohr explained the line spectrum of the hydrogen atom by quantizing the electron orbits around the nucleus.

Internal Structure of Atoms (~ 1895-1925)

Speculations

Since atoms of different substances were perceived as acting differently, some scientists had always speculated on the possibility of atoms having internal structure. In the 17th century Daniel Sennert had still ascribed properties of atoms to internal Aristotelian forms while Robert Boyle and Isaac Newton conjectured internal mechanisms. In 1758, Ruđer Bošković advanced the concept that atoms are centers of forces rather than impenetrable particles. In 1844, Faraday expressed agreement with Bošković's view. (Remarkably, Maxwell disagreed in 1875.)

In 1815, the English physician and chemist William Prout (1785–1850) had hypothesized that all atoms are composed of hydrogen atoms. Although Berzelius' accurate analyses had disproved the implication that all atomic weights are multiples of the weight of hydrogen, the approximate validity of this relationship over the periodic table remained intriguing. In 1884, the English physicist William Crookes (1832–1919) conjectured that this feature of atomic weights is due to the existence of what in modern language would be called mixtures of isotopes. The essence of his speculation was confirmed thirty years later when, from 1912 on, the Polish-German physical chemist Kasimir Fajans (1887-1975) and the English physical chemist Frederick Soddy (1877–1956) discovered the radioactive displacement law.

In 1874, the Anglo-Irish physicist George Johnstone Stoney (1826–1911) postulated an elementary charge defined by dividing the Loschmidt-Avogadro number into Faraday's equivalent and, in 1891, he called it the electron. He furthermore postulated that the number of electrons in an atom is equal to its valency and that spectral emissions and absorptions are due to periodic orbital motions of these electrons in an otherwise empty atom. Using the model of orbiting electrons, the Dutch physicist Hendrik Antoon Lorentz (1853–1928) was able to quantitatively explain in 1897 the splitting of atomic spectral lines by a magnetic field, which had been discovered by the Dutch physicist Pieter Zeeman (1865–1943) in 1896.

By the 1890's, many of the physicists interested in atoms surmised that atoms of various elements were made of the same ingredients, that they were penetrable and that they contained electrons. While the model of orbiting electrons was being considered, a manifest problem with such motions was that, within a short time, the electrons would lose all their energies by classical emission of electromagnetic radiation and fall into the center of attraction.

Conclusive information regarding these speculations finally came from two experimental sources: line spectra and electric discharges in rarified gases.

Line Spectra Systematics

In order to account for the observed atomic spectra, George Stokes in 1852, as well as James Clerk Maxwell in 1875, had surmised the existence of resonating vibrations inside atoms. The discovery of the regularities that govern the line spectra of the elements came however entirely about by empirical numerology. In 1885 the Swiss college mathematics teacher Johann Jakob Balmer (1825–1898) showed that the wavelengths of nine known lines of hydrogen form a series satisfying the formula that now bears his name and predicted seven more lines. By recasting this result in terms of wave numbers (inverses of wave lengths), the Swedish physicist Johannes Rydberg (1854–1919) was able to develop several generalizations in 1888, which accounted for the line spectra of a great number of atoms. The essential insight was the representation of the wave numbers of spectral lines as differences of "terms" that are proportional to denominators of the form $(m+\mu)^2$ where m can assume sequences of integer values (25 years later to be identified as quantum numbers) and μ is a constant fraction (later to become related to the quantum defect).

The generalization to the *Combination Principle* for all atoms was formulated by the Swiss physicist Walther Ritz (1878- 1909) in 1908. These conclusions were further confirmed when, in 1908, the German physicist Friedrich Paschen (1865-1947) extended the hydrogen spectrum into the infrared and, from 1906 on, the American physicist Theodore Lyman (1874-1954) extended it into the vacuum ultraviolet. While all of these empirical relationships were firmly established, they exhibited no recognizable relationship to any explanatory theory, vibrational or other, and spectroscopy remained a relatively inconspicuous branch of physics.

Electric Discharges in Vacuum

The observations that provided the key for developing an understanding of atomic structure came from a different experimental field, namely the discharge of electricity through rarefied gases. Francis Hawksbee, Isaac Newton's laboratory curator, had noted in 1705 that static electricity caused a glow in a vacuum (of about one Torr) that he created over mercury using a solid-piston pump improved from that of Robert Boyle. Michael Faraday observed in 1838 a small dark space near the cathode in addition to a glow in an air-filled discharge tube. Essential for the development of sophisticated experiments was the major technical advance towards lower pressures through the liquid-mercury-piston pump invented in 1858 by the German physicist Julius Plücker (1801–1868) and his glass blower Heinrich Geissler, which produced about 0.1 Torr. Steady improvements by various scientists, notably the use of mercury droplets to trap and remove gas, led to the achievement of about 10^{-6} Torr by the end of the century. Many observations were made by many physicists with many adaptations of these tubes.

The Electron

By 1870 the English physicist William Crookes (1832–1919) expanded Faraday's dark space to fill the entire tube and noted a fluorescence of the glass behind the anode. The German physicist Johann Hittorf (1824–1914) showed in 1869 that rays move in straight lines from the cathode to the anode. In 1895, Perrin proved that they carry a negative charge. Finally the English physicist Joseph John Thomson (1856–1940) showed in 1897, through the application of deflecting electric and magnetic fields, that the cathode rays are electric particles whose ratio of *(e/m)* was independent of the gas in the tube. Remarkably, this ratio was identical with the one deduced, around the same time, by Lorentz from his explanation of the Zeeman effect.

In 1895 the German physicist Wilhelm Conrad Röntgen (1845–1923) systematically investigated a new type of radiation generated by cathode rays impacting on solids, which he called X-rays. (Some of their effects had been noted but ignored earlier by others.) These rays were found to ionize gas molecules and form clouds around them whose charges could be determined from their movements under gravity. Assuming them to be small multiples of the same charge found in the cathode rays, Thomson determined the charge and hence the mass of the electron. Using oil droplets in ionized air, the American physicist Robert A. Millikan (1868–1953) made a much more accurate determination of the electron charge and hence mass by a similar approach in 1909. The mass of the electron was found to be surprisingly small (which had caused earlier physicists to dismiss similar observations.)

A possible implication was that almost the entire mass of an atom is associated with a compensating positive charge. From 1905 to 1911, Thomson advanced an atomic model consisting of electrons embedded in a positive charge plus mass that filled the atom uniformly. By contrast, the German physicist Philipp E. A. von Lenard (1862–1947) concluded that each atom was mostly empty space since he had shown in 1903 that even solids of heavy metals like platinum absorb the electrons of cathode rays only extremely weakly.

The Nucleus

In 1886 the German physicist Eugen Goldstein (1850–1930) discovered a beam of positive ions that travel away from the anode and, passing through channels in a perforated cathode, continued behind it. In 1898 the German physicist Wilhelm Wien (1864–1928) measured (e/m) ratios for various ions in these beams and identified hydrogen ions. While the electron and the hydrogen ion had the same charge, the latter was confirmed to be about 2000 times heavier than the former, which was in agreement with the approximate atomic masses corresponding to Loschmidt's deductions from kinetic gas theory.

The observations of ionization in gases suggested that atoms consist of light electrons and a heavy positive part, the total being neutral. For the scattering of electromagnetic radiation by a classically oscillating particle with the mass and charge of an electron, Thomson had derived the scattering length of 2.8×10^{-6} nanometer, which was taken as a measure of the (classical) electron radius. What then was the size of the positive part of atoms? The answer was found through the scattering of helium ions (alpha particles) fired at a very thin gold foil in an evacuated chamber, an experiment performed in 1909 by the German physicist Hans Geiger (1882–1945) and the English undergraduate physicist Ernest Marsden (1889–1970) under the direction of the New-Zealand-English physicist Ernest Rutherford (1871–1937) in Manchester. In his theoretical analysis of 1911, Rutherford concluded that the scatterings are caused by positive atomic centers with diameters less than 3.4×10^{-6} nanometer, implying $\sim 0.8\times10^{-6}$ nanometer for the proton since theory shows Coulomb scattering to be proportional to the cube root of the nuclear charge.

The Model of the Hydrogen Atom

As mentioned earlier, applying kinetic gas theory and statistical mechanics to macroscopic observations, Loschmidt, and later Perrin, had deduced that atomic radii are of the order of magnitude of nanometers. The electrons and the nucleus of an atom, both with diameters of $\sim10^{-6}$ nanometer, were therefore presumed to fill this otherwise empty space, forming a neutral unit. In order to maintain a stable state, classical electrostatics and mechanics required them to be in a *dynamic* equilibrium. Since the experiments with cathode and anode rays had shown the positive part of the hydrogen atom to be about 2000 times heavier than the electron, it furthermore followed that the electrons were mobile while the positive nucleus was very sluggish. Rutherford noted in his paper that, in 1904, half a decade before his experiments had determined the size of the nucleus, the Japanese physicist Hantaro Nagaoka (1865-1950) had theoretically shown the *mechanical* stability of an atomic model of electrons, assembled in ‘Saturnian rings’, circling a massive positive nucleus. (He had been inspired by Maxwell’s proof of the stability of the rings of Saturn in 1859.) Actually, Nagaoka had abandoned the model in 1908, mainly because of the aforementioned instability of orbiting electrons with respect to classical emission of radiation.

As it turned out, the problem was not with the model, but the problem was a basic inadequacy of classical physics that had recently come to light in other contexts. In 1859-1862, Kirchhoff had formulated the fundamental concept of the black body for understanding thermal radiation. Since then, difficulties had emerged in deducing the experimentally found frequency dependence of the energy density of the black body radiation from electrodynamics and statistical dynamics or thermodynamics. The correct dependence was obtained in 1901 by the German physicist Max Planck (1858–1947) who introduced a novel physical principle, namely: A material oscillator of frequency ν that is in equilibrium with the radiation can absorb/emit energy only in quanta of magnitude hν.

This innovation was carried further by Einstein who showed in 1905 that, by describing light as a stream of corpuscles having energies hν, he could account for the photoelectric effect. This effect had first been observed by Heinrich Hertz in 1887, and Thomson’s later discovery of the electron had revealed that the generated current was in fact due to electrons. The puzzling observation that the kinetic energy of the ejected electrons is directly proportional to the frequency ν of the incident light, but independent of its intensity, was explained by Einstein's approach. It showed that the proportionality constant is exactly Planck's constant h for all substances. In 1907 Einstein furthermore derived the first explanation of the temperature dependence of the heat capacity of solids by assigning to its atomic oscillators energies that are multiples of $h\nu_o$ (ν_o being a material characteristic frequency).

In 1913 the Danish physicist Niels Bohr (1885–1962), who then worked with Rutherford, conceived of a way to transfer the principle of quantization from oscillators to planetary motion and, thereby, was able to reproduce experimental spectra theoretically. (An unsuccessful, very different attempt to connect quantum concepts with planetary motions, which had been made by the English physicist J. W. Nicholson in 1910, is also discussed in Bohr's paper.) Bohr's innovation was *to postulate the general concepts of non-radiating stationary states and of radiation emitting/absorbing jumps between them*. He chose the stationary states as planar circular orbits determined by the condition that the angular momenta are integer multiples of $h/2\pi$, and he adopted the emission/absorption condition $h\nu = E_1 - E_2$ for radiation of frequency ν. Application of this model to the electron in the hydrogen atom recovered its spectrum: It explained the series structure of the spectrum and it yielded the quantitative values of its Rydberg terms within the accuracy allowed by the then available values of e, m, and h. (Serendipitously, the error due to assuming the lowest angular momentum to be $\ell=1$ instead of $\ell=0$ cancelled the error due to assuming a planar rather than a three-dimensional motion.)

Application to He^+ showed that additional spectroscopically observed series were due to He^+ and not to H^0 as had been previously thought. The difference of about 40 cm^{-1} between the $He^+(2s)$ and H(1s) levels was explained within a few cm^{-1} as due to the difference in the reduced masses, and similarly for higher He^+ levels. (The remaining deviations are due to relativistic spin-orbit coupling, velocity-mass effects, nuclear size and Lamb shift, which were then unknown.)

Models for Other Atoms

Further experiments by Geiger and Marsden for a number of elements implied that the number of elementary charges at the atomic centers is equal to about half the atomic weight, a value that agreed with the number of electrons per atom that the English physicist Charles Glover Barkla (1877-1944) determined by X-ray scattering in 1911. These results suggested the identity of the nuclear charge with the atomic number in the periodic table. The conclusion was dramatically confirmed for a large part of the periodic table by the thorough analyses of X-ray spectra of inner shells, using Bohr's model, which the English physicist Henry Moseley (1887–1915) performed in 1913-14. The identity had been conjectured in 1912 by the Dutch lawyer and physicist Anton van den Broek (1870-1926). Characteristic features of X-ray spectra were subsequently elucidated by the German physicist Walther Kossel (1888–1956).

In his papers of 1913, Bohr had also tried to elucidate the physics that underlies the regularities of the periodic table by proposing the formation of successive groups of electrons. He had distinguished outer and inner electrons and had proposed that the former give rise to optical spectra and the latter to X-ray spectra. In 1916, the German theoretical physicist Arnold Sommerfeld (1868–1951) completed Bohr's model by introducing quantum conditions for the three action integrals in the Hamiltonian analysis of the Kepler problem so that the states of the electron were characterized by the three spherical quantum numbers. On this basis, Bohr developed, from 1921 on, his earlier ideas further into the "Aufbau Principle" for the electronic shell structure in atoms, which rationalized much of the periodic system of the elements. Two years later, the Austrian physicist Wolfgang Pauli (1900–1958) remedied certain shortcomings of this model, in particular regarding spectra in magnetic fields, by positing a fourth two-valued quantum number and postulating the exclusion principle. The new quantum number was then interpreted in terms of the electron spin by the Dutch-American physicists George Uhlenbeck (1900-1988), Samuel Goudsmit (1902-1978) and Ralph Kronig (1904–1995).

Physics on the Atomic Scale (~ 1926-1935)

By the first quarter of the twentieth century, the corpuscular model of matter had become successful in elucidating not only chemistry in terms of atoms and molecules but also the internal structure of atoms. It had even made inroads into the theory of radiation. It proved however unable to provide a real theoretical physical, in particular quantitative understanding of larger atoms and of molecules. This goal was only achieved by the introduction of an entirely new theoretical description of matter that had continuum character.

Wave Mechanics of Matter

In 1924 the French physicist Louis de Broglie (1892–1987) suggested that matter may have wave character. In 1926, partly stimulated by de Broglie's paper, the Austrian physicist Erwin Schrödinger (1887–1961) developed a new general wave equation for the description of particles under the influence of forces. Applying it to hydrogen-like atoms, he showed that it led to an eigenvalue problem whose spectrum recovered exactly the quantized energy levels of these systems. In 1927, the experiments of the American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), as well as those by the English physicist George Paget Thomson (1892–1975), showed that free electrons are in fact diffracted like waves, similarly to X-rays, by the lattice structures of solids.

From the beginning, Schrödinger's wave equation was designed for many-particle systems, a formulation that subsequently also proved to be valid. Still in 1926, the English physicist Paul Dirac (1902–1984) as well as the German physicist Werner Heisenberg (1901–1976) showed that imposition of the antisymmetry requirement on Schrödinger's many-electron wave functions recovers Pauli's exclusion principle. In 1927 Pauli developed the theory of spin operators and spin functions for proper inclusion into the wave equation. In 1928 Dirac formulated the wave equation for an electron in the relativistic regime and showed that it entailed Pauli's spin theory.

The German physicist Max Born (1882-1970) pointed out since 1926 that the predictions obtained from wave mechanics for scattering as well as spectroscopic experiments must have probabilistic-statistical character.

These new theoretical concepts implied that space is not only filled with energy carrying electromagnetic waves but also with mass-carrying electron waves. Indeed, according to current theories, space is also filled by the fields of additional elementary particles. One is tempted to imagine that Aristotle would smile to learn that there is no true void after all.

Interaction of Matter with Radiation

In 1927, Dirac also developed the detailed quantum theory for interactions between the electromagnetic field and wave-mechanically described matter, i.e. for the emission and absorption of light by atoms and molecules. It not only provided a rigorous foundation for the earlier postulates of Bohr and Einstein but moreover covered a vastly greater range of phenomena.

The definitive establishment of the theoretical relations between structure and spectra in atoms and molecules turned experimental spectroscopy into a science of prime importance.

Wave Functions and Spectra of Atoms

In the years following these revolutionary discoveries, the Schrödinger equation was used extensively to elucidate the electronic structure and spectra of atoms. These analyses generated basic theoretical insights into the general structure of electronic wave functions. They moreover created a new general conceptual framework of physical interpretations that proved to be a solid and versatile foundation for the treatment of molecules.

The earlier Bohr-Pauli Aufbau Principle for the periodicity of the elements was now implemented via products of successively filled, radially modified hydrogen-type one-electron wave functions, termed orbital configurations. In 1929 the American physicist John C. Slater (1900–1976) showed how superpositions of determinantal functions formed from spin-orbital products furnish a highly effective basis for constructing the required antisymmetric wave functions. Remarkably, considerable elucidations of the electronic structure of many atoms were achieved by using superpositions of Slater determinants constructed only from what Mulliken later called *minimal basis set orbitals*.

The deduction of effective approximate wave functions for stationary atomic states proved possible because the conservation of angular momenta in spherical fields entails highly structured systems of energy levels, as well as very specific selection rules for emission and absorption. Strong inferences regarding atomic configurations could therefore be drawn by comparing the observed spectra with those predicted from the mentioned approximate wave functions. The construction of the latter was based on symmetry considerations presuming in zeroth order spherical potentials and obtaining corrections by a perturbation theory that had also been formulated by Schrödinger. This approach yielded energy levels in terms of few integrals, which were treated as parameters to fit the spectra or evaluated approximately, using for instance screened nuclear charges. Notable among the many physicists that elucidated the fundamentals as well as the intricacies of stationary states in many atoms within less than a decade were Friedrich Hund in Germany (1896-1997) and John Slater in the United States.

The consequences of the invariance of the Schrödinger equation with respect to *general* transformation groups, of which the antisymmetry requirement and the conservation of angular momentum are specific instances, were worked out by the German mathematician Hermann Weyl (1885–1955) and the Hungarian-American Physicist Eugene Wigner (1902-1995) between 1927 and 1930.

In addition to the aforementioned semi-quantitative analyses, progress was also made towards obtaining rigorous solutions of the many-electron Schrödinger equation with the aim of computing atomic properties. These calculations, which are antecedents to modern quantum chemistry, were generally based on the variation principle, which had also been formulated by Schrödinger in 1926. The most accurate work was that of the Norwegian physicist Egil Hylleraas (1898-1965) who obtained the ground state energy of the helium atom in 1928 with an error of less than 0.01 eV by introducing, in addition to the electron positions, also the inter-electronic distance as a spatial variable. For systems with many electrons, the English physicist Douglas R. Hartree (1898-1958) devised in 1928 the self-consistent-field method, which the Russian physicist Vladimir A. Fock (1898–1974) reformulated in 1930 so as to properly account for the antisymmetry requirement of wave functions. On the basis of statistical reasoning, the British physicist Llewellyn Thomas (1903-1992) and the Italian physicist Enrico Fermi (1901–1954) independently developed a precursor of the density functional approach in 1927 and 1928 respectively.

The achievements of this vigorous decade of innovations led to two authoritative summations: Volume 24,1 of the Handbuch der Physik, *Quantentheorie*, by H. Bethe, F. Hund, N. F. Mott, W. Pauli, A. Rubinowitz and G. Wentzel (1933) and *The Theory of Atomic Spectra*, by E. U. Condon and G. H. Shortley (1935).

Wave Mechanical Structure of Molecules

Potential Energy Surfaces (1927-1940)

The new problem encountered in molecules is that the motions of the nuclei relative to each other generate energy changes that, while usually smaller than electronic energy changes, are still sufficiently substantial to yield important information regarding molecular structures. Molecular wave functions must therefore contain nuclear as well as electronic coordinates. Max Born and the American physicist Julius Robert Oppenheimer (1904–1967) showed in 1927 that the full wave equation can be solved in two consecutive steps, the energy levels of the electronic wave equation for fixed nuclei, yielding the potential functions for the nuclear wave equation . A long range consequence of this divide-and-conquer approach has been the division of theoretical chemistry into two branches: stationary quantum chemistry, which deals with the electronic calculation and analysis of potential energy surfaces, and molecular dynamics, which deals with the nuclear motions on potential energy surfaces. The construct of the *potential energy surface*, which mediates between the two regimes, has therefore become a central concept in theoretical chemistry. (Certain basic questions regarding this approach still remain.)

Thus, between 1928 and 1935, the Hungarian–British polymath Michael Polanyi (1891–1976) and Eugene Wigner as well as the American chemical physicist Henry Eyring (1901–1981) developed a theory of reaction rates by focusing on the transition states of 'reaction paths' on potential energy surfaces. Trajectories on the potential energy surface of H_3 were calculated by the American chemical physicists Joseph Hirschfelder (1911–1990), Henry Eyring and Bryan Topley in 1936.

That it is necessary to use several potential energy surfaces simultaneously when they come close in energy was shown in 1932 and 1933 by the physicists Lev D. Landau (1908–1968) in Russia and Clarence Zener (1905–1993) in the U.S. A general theory of adiabatic and diabatic reaction processes was conceptualized in 1935 by the German physicist Hans G. A. Hellmann (1903–1938) and the Russian physical chemist Ya. K. Syrkin (1894-1974). The general use of coupled potential energy surfaces was formulated in 1951 by Max Born.

Hund postulated in 1927 the non-crossing rule for potential energy surfaces of the same symmetry and it was derived in 1929 by Wigner and the Hungarian mathematician John von Neumann (1903–1957). In 1937, the Hungarian-American physicist Edward Teller (1908–2003) showed however that, in molecules with more than two atoms, there can in fact exist conical intersections between states of like symmetry.

Spectra of Molecules (1927-1950)

The simultaneous excitations of nuclear and electronic motions render molecular spectra much more complex than atomic spectra. Nonetheless, the methods of analysis that had proven successful in atoms were successfully extended to diatomic molecules, most notably by the American chemical physicist Robert S. Mulliken (1896-1986) and the German-Canadian physicist Gerhard Herzberg, (1904–1999) as well as by Friedrich Hund in Germany. Although rigorous potential energy surfaces could not be calculated at that time and even though the symmetry is significantly lower in these systems than in atoms, a remarkable amount of information on ground state and excited state potential energy curves was deduced by extensive studies of the experimental spectra. The intricacies of the simultaneous electronic, vibrational and rotational energy changes were sorted out thorough analyses and insightful physical and chemical intuition in combination with group theory and the intensity selection criterion formulated in 1926 by the physicists James Franck (1882–1964) in Germany and Edward U. Condon (1902–1974) in America. A particularly seminal achievement was the perceptive invention of correlation diagrams for energy levels. Progress was also made by the same researchers in the elucidation of polyatomic spectra although they proved to present a considerably greater challenge.

Herzberg's monumental books *Molecular Spectra and Molecular Structure I, II, III* (1939, 1945, 1966), including tables on the spectra of small molecules have remained classics.

Chemical Bonding between Hydrogen Atoms (1927-1933)

Since the discovery of the electron in 1897 it had been generally surmised that chemical bonding is somehow connected to electronic rearrangements. In 1904 the German inorganic chemist Richard Abegg (1869–1910) distinguished electro-positive and electro-negative atoms. He documented extensively that the maximal positive and negative oxidation states (to use modern terminology) in the second and third row of the periodic table add up to eight and his explanatory hypotheses were essentially equivalent to attributing a special stability to electron octets on atoms. In 1916, Abegg's rule (as G.N. Lewis called it) motivated the German physicist Walther Kossel (1888–1956) to conjecture that *ionic* bonds result from electron *transfer* and, on the other hand, inspired the American physical chemist Gilbert N. Lewis (1875–1946) to imagine that *covalent* bonds result from electron *sharing*. A physical basis of bonding was still not found however: When Wolfgang Pauli as well as the Danish physicist Karel Niessen (1895–1967) independently applied the corpuscular quantum model of Bohr and Sommerfeld to the hydrogen molecule ion in 1922, it turned out not to be bound.

It was only with Schrödinger's wave equation that, in 1927, the German physicists Walter Heitler (1904–1981) and Fritz London (1900–1954) were able to deduce the covalent bond in the hydrogen molecule from first principles. In the same year, the Danish physicist Øyvind Burrau accomplished the same for the hydrogen molecule ion. In the next few years a number of very accurate calculations achieved theoretical binding energies for both systems that agreed with the experimental values within a fraction of kT at room temperature. Particularly notable was the calculation of the hydrogen molecule in 1933 by the American physicist Hubert James (1908-1986) and the American chemist Sprague Coolidge (1894-1977) using techniques that Hylleraas had pioneered in treating the helium atom.

It is apparent that the covalent bond is contingent on the *continuum* nature of wave mechanics and that this is one reason why the corpuscular Newtonian mechanics could not account for it.

Why Does Wave Mechanics Yield Chemical Bonding? (1933-1962)

While satisfactory numerical values for the strengths of covalent bonds in simple molecules could be calculated by wave mechanics, the question whether a *conceptual* physical mechanism could be associated with the *computational* results had remained unanswered.

Isaac Newton had conjectured in 1679 that there exist short-range attractive and long-range repulsive forces between atoms. At the beginning of the 19th century, Berzelius had imagined bonds to be due to electric charges on atoms and this was also the basis of Kossel's model a hundred years later. In the Faraday Lecture of 1881 at the Royal Institution in London, Helmholtz had raised the question how long-range electrostatics could give rise to short-range inter-atomic binding forces. Common to all these speculations is the notion that bonding is due to a *static* attraction between atoms, possibly derivable from some potential. It therefore seemed natural to carry over this static potential perception in trying to rationalize why wave mechanics yields chemical bonding.

Thus, since it was noted by many that bonding is typically associated with a wave mechanical accumulation of charge between atoms, it was often speculated, beginning with Slater in 1933, that the electrostatic attraction between this accumulated charge and the adjacent atoms generates a potential energy lowering that provides an 'electrostatic cementing effect'. This inference seemed to be consistent with the virial theorem, according to which bond formation will lower the potential energy and increase the kinetic energy.

Hellmann suggested however in 1933 (originally on the basis of the statistical Thomas-Fermi approach) that covalent bonding is connected with a lowering of the *kinetic* energy of shared valence electrons as is in fact the case in the Heitler-London treatment. The reason is that a larger potential well becomes available to their motions when atoms form a covalent bond. This spatial expansion will lower the kinetic energy according to Heisenberg's uncertainty principle (as exhibited *e.g.* by the kinetic energy lowering of a particle in a box upon extending the box length). Hellmann was aware of, but could not resolve the apparent inconsistency with the virial theorem.

The resolution was given only in 1962 in a series of independent analyses by the German-American theoretical chemist Klaus Ruedenberg (1920-). He emphasized that the conceptual understanding of the wave mechanical recovery of bonding requires a rigorous theoretical basis rather than simple analogies. Such a basis is provided by the variation principle, which determines the electronic ground state as the optimal compromise in the competition between the electronic kinetic pressure and the nuclear electrostatic potential pull. This analysis showed that covalent bonding occurs when the electron delocalization between atoms weakens the kinetic energy pressure and that this attenuation allows a greater charge localization in regions of lower potential energy, notably a closer attachment of the electron cloud to the nuclei. Thus, the *inter-atomic kinetic energy* lowering through delocalization is the *driver* even though an *induced intra-atomic potential energy lowering* becomes the negative part of the binding energy.

This analysis was subsequently extended by the American theoretical chemist William A. Goddard (1937-) and the German theoretical chemist Werner Kutzelnigg (1933-). The German theoretical chemist Eugen Schwarz (1937-) generalized it to other diatomic molecules using the pseudo-potential approach pioneered by Hellmann and the Hungarian physicist Pál Gombás (1909-1971) in the 1930's. From this perspective, covalent, ionic and correlation bonding result from modifications of the kinetic, the nuclear-electronic attraction or the electron-electron repulsion energy functionals, respectively.

Fritz London had shown in 1930 and elaborated in 1937, that the weak long-range attractions between atoms or molecules without electric multipoles are in fact caused by correlations between the electronic motions in different atoms ("dispersion bonding").

Bonding Models beyond the Hydrogen Atom (1929-1963)

As regards bonding in larger molecules, Dirac wrote in 1929: *"The underlying laws necessary for the mathematical theory ... of the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be solvable. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."* Several approaches along these lines during the next two decades led to very significant progress in the understanding of molecules.

Valence Bond Model

The valence bond (VB) approach was an attempt to formulate simple algorithms, built on the model of the Heitler-London expression, for constructing polyatomic wave functions directly from products of the atomic orbitals on the atoms. It was developed notably by John Slater and the American chemists Linus Pauling (1901–1994) and George Wheland (1907-1972). Initially, it attracted most attention because the formal expressions, involving only atomic orbitals, seemed to correspond naturally to the conception of molecules as being constituted of atoms. The model recovers covalent bonding through orbital overlap as well as some electron correlation through left-right electron exchange.

In the influential final version, laid out in Pauling's book "The Nature of the Chemical Bond" (1939) and Wheland's book (1944) "The Theory of Resonance", *comparative* conclusions regarding bonding in various molecules are deduced from the "resonance" between "valence bond structures", i.e. the presumptive effect of the variation principle with respect to the superposition of wave functions that are attributed to several competitive empirical chemical bonding patterns. This wave mechanical interpretation of chemical structure formulas yielded qualitative inferences that were often found helpful by experimental chemists.

Molecular Orbital Model

The molecular orbital (MO) approach was an outgrowth of the aforementioned highly successful elucidation of diatomic spectra by Mulliken and Hund and therefore had a manifest, semi-quantitative but solid relation to physical and spectroscopic reality. It was developed by Robert Mulliken, Friedrich Hund, and the English theoretical chemist Sir John Lennard-Jones (1894–1954). In the MO approach, one first constructs molecular orbitals (i.e. molecular one-electron functions) from atomic orbitals. Then many-electron wave functions are constructed from the molecular orbitals. This two-step approach has the advantage of a divide-and-conquer attack since the construction rules for both steps are quite transparent with respect to group theoretical assignment as well as the bonding and anti-bonding identification of orbital superpositions and spin couplings.

Because the connection to atoms seemed to be less direct in the MO model, as compared to the valence bond model, the MO approach initially appealed less to experimental, in particular organic chemists. Over time, it became however greatly appreciated, in particular in the simplified version in which the total energy is estimated as the sum of one-electron energies calculated from a parameterized effective Hamiltonian.

This independent particle model became a valuable tool for the understanding of π-electrons in systems with multiple and conjugated carbon bonds. In the 1930's, the German physicist Erich Hückel (1896-1980) had found this approach more effective than the valence bond model for such systems. In the forties and early fifties, the model was further developed by the English theoretical chemists Charles Coulson (1910-1974) and Christopher Longuet-Higgins (1923-2004), who also elaborated an analysis of the electron density in terms of charges and bond orders. The American physical organic chemist Andrew Streitwieser (1927-) and the Swiss physical chemist Edgar Heilbronner (1921-2006) established the power of the Hückel model in organic chemistry.

An intuitively elucidating aspect of the model is that Hückel orbitals have an extremely simple relationship to free-electron waves on the network of atoms, which facilitates their visual interpretation. This isomorphism was rigorously proved by Ruedenberg and Scherr in 1951. In fact, the free-electron model had first been suggested by the German Chemist Otto Schmidt in 1940. In the late forties and early fifties it was used by the Swiss-German physical chemist Hans Kuhn (1919-) as well as by the American physicist John Platt (1918-1992) to interpret the electronic spectra of many conjugated molecules. A conceptual relationship exists also to the structure of electron waves in periodic potentials that was formulated in 1928 by the Swiss American physicist Felix Bloch (1905–1983).

An effective generalization of the simple molecular orbital model to non-planar systems, involving σ as well as π orbitals, was devised in 1952 by the American theoretical chemists Max Wolfsberg (1948-) and Lindsey Helmholz through formulating a simple parameterization of very general interaction-integrals. Thereby, they were able to elucidate the spectra of tetrahedral transition metal oxides.

In 1963 the American theoretical chemist Roald Hoffmann (1937-) used the Wolfsberg-Helmholz-type interaction parameterization to formulate the "Extended Hückel Theory", which extended the range of the simple molecular orbital model to molecules with quite general bonding patterns and even to solids. The approach proved enormously fruitful in generating a deeper understanding of organic as well as inorganic molecular and solid state chemistry. A relativistic version of this approach for heavier elements was later developed by the Finnish theoretical chemist Pekka Pyykkö (1941-).

A triumph of the molecular orbital model was that it furnished the basis for powerful predictions regarding certain organic reactions, *viz.* the frontier orbital theory formulated in 1952 for aromatic molecules by the Japanese theoretical chemist Kenichi Fukui (1918–1998) and the stereochemical rules for pericyclic reactions formulated in 1965 by Roald Hoffmann and the American organic chemist Robert Burns Woodward (1917–1979).

Figure 1. Participants of the Conference on Quantum Mechanical Methods in Valence Theory, held September 8-10, 1951, at the Ram's Head Inn on Shelter Island, Long Island NY. Standing, left to right: K. Ruedenberg (U. Chicago), T.H. Berlin (Johns Hopkins U.), M.P. Barnett (Rayon Research Association, London), B.L. Crawford (U. Minnesota), D.A. MacInnes (Rockefeller Institute, New York), H. Margenau (Yale U.), K.S. Pitzer (U. California, Berkeley), G.E. Kimball (Columbia U.), Ch.W. Ufford (U. Pennsylvania), R.S. Mulliken (U. Chicago), J.H. Van Vleck (Harvard U.), P.O. Löwdin (U. Uppsala), J.E. Lennard-Jones (Cambridge U.), H. Eyring (U. Utah), J.C. Slater (MIT), Ch.A. Coulson, (King's College, London, in back, J.O. Hirschfelder (U. Wisconsin) in front, H. Shull (Iowa State U.), L.E. Sutton (Oxford U.), R.G. Parr (Carnegie Institute of Technology). Seated, left to right: J.E. Mayer (U. Chicago), W. Moffit (British Rubber Producers' Research Association, Herts), C.C.J. Roothaan (U. Chicago), M. Kotani (U. Tokyo). Not shown: G.W. Wheland (U. Chicago), who had left before the picture was taken.

Crystal Field and Ligand Field Models

Another approach resulted from the efforts to gain an understanding of the coordination complexes of transition metals that Werner had identified in 1905. On the basis of electrostatic considerations using Kossel's atomic ions, the French physicist Jean Becquerel (1878-1953) suggested in 1929 that many properties of such complexes can be considered as those of the central atom perturbed by the electric field of the crystal in which the atom is embedded. Simultaneously a thorough analysis by the German theoretical physicist Hans Bethe (1906–2005) laid out in detail the exact quantum mechanical changes that are induced in the wave function and energies of an atom when the perturbations by a crystalline environment change the spherical electrostatic potential into that of a lower symmetry group. From 1935 on the analysis was further developed by the American physicist John H. van Vleck (1899-1980) and in 1942-43 by the Italian-Israeli theoretical physicist Giulio Racah (1909-1965). Van Vleck and his collaborators worked out the consequences of this ‘crystal field theory’ for structure, stability, reactivity, spectra, and magnetic behavior, including spin-orbit coupling. They elucidated a wealth of details regarding these properties of open shell atoms and ions in crystals.

The English chemist Nevil Vincent Sidgwick (1873-1952) had used G.N. Lewis’ electron-sharing model to interpret coordination bonds as dative covalency since 1923, and Pauling integrated these ideas into the valence bond model beginning in 1931. While many magneto-chemical phenomena could be rationalized by this model, the impressive color phenomena of transition metal complex chemistry remained out of its reach.

The group-theoretical electrostatic crystal-field perturbation model, the qualitative valence bond model and the qualitative molecular orbital model were later combined by several groups: in 1946 by the German physical chemist Hermann Hartmann (1914−1984), in 1952 by the English chemist Leslie E. Orgel (1927-2007), since 1954 by the English quantum chemist William Moffitt (1925-1958) and in particular, from 1954 on, by the Danish physical chemist Carl J. Ballhausen (1926-). This approach was conceptually formulated within the molecular orbital framework including ligands and involved corresponding empirical parameters. In some versions the Wolfsberg-Helmholz interaction approach was used. This molecular orbital based *ligand field* theory greatly advanced the understanding of bonding and magnetic as well as spectral properties in coordination complexes.

Turn Towards Quantitative Rigor (1950-1970)

Shelter Island Conference

While the discussed approaches had deduced essential concepts from wave mechanics for understanding molecules, in the course of the 1940’s a number of molecular theoreticians came to the conclusion that further progress was contingent on explicit quantitative calculations. It was also believed that headway could be made beyond the limits anticipated by Dirac in 1929 because of promising advances in computational hardware, such as punch card machines and electronic computers, which were being developed at various institutions. The first commercial computers, IBM 701 and Univac I, became available in 1952. In response to a general perception that a meeting dedicated to the challenges posed by these aspirations would be beneficial, Robert Mulliken organized the *Conference on Quantum-Mechanical Methods in Valence Theory*, which was held on September 8-10, 1951, on Shelter Island, Long Island NY, under the sponsorship of the National Academy of Sciences with the support of the Office of Naval Research. The 25 participants, mostly major senior scientists and a few younger colleagues, are pictured in Figure 1. The variety of work presented at this symposium conveyed the anticipation of new developments.

Two problems had to be addressed more explicitly than had been done so far: The many-electron formalism including electronic interactions had to be implemented rigorously and the magnitudes of the electron interaction integrals between atomic orbitals had to be evaluated accurately.

Semi-Empirical Many-Electron Approach

A step in this direction had in fact been taken in the ligand field models, except that the integrals had remained parameterized. Another advance was a configuration interaction calculation of the lowest π-electron states and spectra in benzene in 1938 by the German-American physicist Maria Goeppert-Mayer (1906–1972) and the American physicist A.L. Sklar. They explicitly calculated the most important energy integrals by approximate methods. Several improvements of this work culminated in the calculation (1950) of the American theoretical chemist Robert G. Parr (1921-) and the Australian theoretical chemists David P. Craig (1919-) and Ian G. Ross, who calculated all integrals in this problem, although still using approximation formulas for part of them. It was in this paper that the phrase *ab initio* was introduced to indicate that the calculations of the two groups were done independently from scratch.

The effective *accurate* evaluation of all many-orbital electron repulsion integrals needed in polyatomic molecules remained however elusive in the 1950's. In view of the apparent absence of an immediate solution, a number of theoreticians bypassed this obstacle by limiting the atomic orbital bases to the *minimal* sets on each atom. As a consequence, all integrals had recognizable physical meanings, which were then exploited in order to devise approximations or assign physically meaningful parameters. Using this approach to the integral problem, a number of general schemes were devised in which the many-electron formalism of antisymmetric wave functions was no longer ignored but properly accounted for. This semi-empirical anchoring in reality proved quite effective. In some cases, semi-empirical methods were also used to construct and explore potential energy surfaces of reactions.

Atoms in Molecules

The starting point of the perceptive approach, which the English theoretical chemist William Moffitt (1925-1958) developed under the name "Atoms-in-Molecules" in 1951, is loosely related to the valence bond model. Expressing the molecular wave function as superpositions of antisymmetrized products of many-electron states of the bonded atoms, he obtained the molecular energy as a sum of large intra-atomic and small inter-atomic terms. The former were parameterized by reference to free atom values; the latter were considered as perturbations and calculated approximately. Moffit in fact clarified the electronic spectrum of oxygen. A more rigorous version of the method, called "Intra-Atomic Correlation Correction", was devised by the Australian theoretical chemist Andrew Hurley (1926-1988) from 1955 to 1963 and successfully applied to a number of diatomic molecules. Further developments were made later by the Japanese physicists Tadashi Arai and Hiroshi Nakatsuji (1943-) and by the American theoretical chemists Michael W. Schmidt and Klaus Ruedenberg.

Neglect of Differential Overlap

The "neglect of differential overlap" implies in most cases that all those electron repulsion integrals between atomic orbital products are neglected in which the orbital factors of at least one product are from different atoms. This leaves only integrals whose evaluation or credible approximation is practical. It was introduced in 1952 by Robert G. Parr in the context of the molecular orbital approach.

The approximation was used in 1953 by the American physical chemist Rudoph Pariser (1923-) together with Robert Parr and independently by John Pople to develop the "PPP" method for π-electrons in planar conjugated systems. It differs from the Hückel-type methods by correctly performing self-consistent-field as well as simple configuration interaction calculations in terms of a fixed minimal atomic pπ-orbital basis. The spectra of many conjugated π-systems were successfully elucidated by such calculations.

By appropriate generalizations of the integral approximations based on similar principles, Pople and coworkers developed, from 1965 through 1968 on, more general methods ("CNDO, INDO, NDDO") which allowed the treatment of molecules with any geometry and bonding pattern formed from atoms in the first two rows of the periodic table. These methods were the first ones to be available as "black-box programs" to non-theorists. In the hands of judicious users, who were aware of the approximate character and the limitations, the results often provided useful guidance for experimental work.

Through special purpose parameterizations and simplifications, this approach was adapted for use in large organic molecules by the English American chemist Michael J.S. Dewar (1918–1997). The resulting MOPAC program made a wide audience of organic chemists aware of the usefulness of theoretical methods.

Among the other semi-empirical approaches that were developed during this period, the PCILO method (1968-69) by the French theoretical chemist Jean-Paul Malrieu (1939-), combines the CNDO parameterization with a perturbation procedure.

Improved Ligand Field Approach

In ligand field theory, progress was made by accounting more rigorously for the one- and two-electron integrals between the central atom and the ligands. Notable advances were the set of relations and diagrams derived from the formulas of Racah by the Japanese physicists Yukito Tanabe and Satoru Sugano in 1954-56 and in the comprehensive book by John Stanley Griffith in 1961. These tools led to marked improvements in the understanding of ground and excited starts of transition metal complexes.

Ab Initio Quantum Chemistry (1950-1980)

As experience with the various semi-empirical approaches accumulated, it became apparent that, in many cases, the achievement of reliable accuracy for chemically useful predictions would require calculations in which all quantities were calculated by the book. The present account follows these developments until about 1980. The mushrooming, vigorous and fruitful work since then would require very much more space than is available here.

Ab Initio Wave Functions of Diatomic Molecules

The spearhead of the *ab-initio* effort in quantum chemistry in the 1950s was R. S. Mulliken's Laboratory of Molecular Structure and Spectra at the University of Chicago. Even though Mulliken's enormous experimental knowledge and legendary theoretical intuition regarding molecules kept generating a steady flow of new insights, he had nonetheless become convinced of the need for rigorous ab-initio calculations. It was his staunch advocacy that sustained and advanced the development of this approach at a time when skepticism was still widespread. It was in the early fifties that the term *ab initio* (first found in the above mentioned paper by Parr, Craig and Ross) began to be used to denote the absence of *any* empirical parameters. [K.R remembers Mulliken using the term *ab initio* in a physics colloquium that he presented at the University of Chicago between 1953 and 1955.]

The initial object of the *ab initio* effort in Chicago was the elucidation of diatomic molecules. The Dutch-American physicist Clemens C.J. Roothaan (1918-) was in charge of the enterprise and guided its progress. Early in 1951, he formulated an influential framework for the Hartree-Fock self-consistent-field (SCF) approach in terms of molecular orbitals constructed from atomic orbitals. Essential for success was furthermore that a solution be found for the evaluation of electron interaction integrals between exponential-type orbitals. This goal was achieved later in 1951 by the exchange integral work of Ruedenberg (a postdoctoral research associate at the laboratory from 1950 to 1955). With these tools, the American theoretical chemist Charles W. Scherr (1926-2005) carried through the first full ab initio self-consistent-field calculation in terms of Slater-type exponential atomic orbitals beyond H_2, *viz.* for the ground state of the N_2 molecule at the equilibrium distance (published in 1955).

While this calculation was still performed on electric-mechanical desktop calculators, the Chicago group converted to electronic computers after 1955. It also spawned close fruitful cooperative theoretical chemistry groups at Argonne National Laboratory and at the IBM Research Center in San José, California. The construction of many-electron wave functions advanced successively from the SCF approximation to configuration interaction built on multi-configuration-self-consistent-field reference functions. The many resulting investigations shed much interesting new light on diatomic molecules, notably by the work of the American theoretical chemist Arnold C. Wahl and that of the Chinese-American theoretical chemist Bowen Liu (1939-1997).

Interaction Energies between Atomic Orbitals

In the Proceedings of the Shelter Island Conference, 13 papers out of a total of 53, on 90 pages out of a total of 290, had been devoted to the subject of energy integrals between atomic orbitals. From 1938 on, the Japanese theoretical physicists Masao Kotani (1906 -1993), Ayao Amemiya (1907–1977) and coworkers had published extensive tables of certain of such integrals. But the accurate evaluation of electron-repulsion integrals between atomic orbitals on different atoms presented considerable mathematical difficulties. Moreover, very large numbers of them are needed in any one molecular calculation, which calls for extremely fast evaluations. At the time, this unsolved problem was widely seen as the major roadblock to progress.

The atomic orbitals were then generally assumed to be of the exponential type. These were perceived as providing the most effective basis for expanding molecular wave functions, because they furnish the best building blocks for generating *atomic* wave functions with the appropriate physical behavior very far from as well as very close to the nuclear singularity.

The first breakthrough came when, as mentioned above, the efficient wholesale evaluation of all two-electron integrals for exponential-type orbitals in a diatomic molecule was made possible as the result of a surprisingly straightforward reformulation that Ruedenberg achieved in 1951 by means of an integral transformation and the introduction of intermediate charge densities.

Unfortunately, this approach could not be extended to the three- and four-center electron repulsion integrals between exponential-type atomic orbitals that occur in polyatomic molecules. In fact, no satisfactory direct solution to the problem of fast evaluation of large numbers of these integrals was found, notwithstanding intensive high-powered efforts by the molecular integral community.

It was only over a decade later that an effective way out of this impasse became possible because, by then, electronic computers offered the means for manipulating large linear arrays efficiently. With this capability, it became practical to take up a proposal that the English theoretician S. Francis Boys (1911-1972) had made in 1950, namely to replace exponential-type atomic orbitals by Gaussian-type atomic orbitals because, for the latter, all multicenter integrals can be calculated straightforwardly. The POLYATOM program, which was developed in the late fifties and early sixties by M.C. Harrison, M.P. Barnett, I.G. Csimadia, J.W. Moskowitz and B.T. Sutcliffe in Slater's group, was the first major electronic structure program for general use on this basis. The applications indicated that very many Gaussian orbitals would be needed to obtain satisfactory energies.

As the computers of the 1960's became capable of processing such expansions rapidly, a number of research groups developed serviceable *contracted* Gaussian orbital sets from the mid-sixties on, most notably the Japanese-Canadian theoretician Sigeru Huzinaga (1926-), the American theoretician Thom H. Dunning (1943-) and the English theoretical chemist John A Pople (1925-2004). In fact, contracted Gaussians represent discretizations of exact closed-form Gaussian integral transforms of exponential-type functions. The *even-tempered* Gaussian discretizations developed by Ruedenberg in 1971 were proven to be near-optimal by the German theoretician Werner Kutzelnigg (1933-).

Several methods for the efficient evaluation of the integrals of Gaussian expansions were developed in 1976-1978: by the French American theoretical chemist Michel Dupuis (1949-) and the American theoretical chemists Harry F. King(1931-) and John Rys; by John Pople and Warren J. Hehre; and by the American theoretical chemists L. E. McMurchie and Ernest R. Davidson (1936-). These integral evaluation methods became in fact so efficient that the Swedish theoretical chemist Jan Erik Almlöf (1945-1996) overcame the storage bottleneck for very large molecules by devising a successful "direct SCF" method where all integrals between atomic orbitals are recalculated whenever needed during the SCF iterations.

As a result of these developments, the problem of integral evaluation finally lost its gravity in the overall scheme of things.

Electron Correlation

As production codes for integrals between exponential-type as well as contracted Gaussian-type orbitals became well established, attention shifted to the much greater challenge of constructing effective as well as manageable wave functions that can describe electron correlations with an accuracy sufficient for calculating chemically useful reaction and activation energies. The fundamental advances made in the two decades between about 1960 and 1980 created the basis for the productive development of quantum chemistry in the subsequent years.

In the early fifties, Frank Boys had formalized and used configuration interaction (CI) by superposing Slater determinants whereas Masao Kotani had had done so in terms of spin- adapted bases. For dealing with the very large expansions, which are invariably encountered, several major methodological advances proved essential. One was the iterative algorithm for finding the lowest eigenstates of very large matrices that Davidson devised in 1975, which was subsequently extended to non-Hermitean matrices by the Japanese theoretical chemists Hiroshi Nakatsuji and Kimihiko Hirao (1945-). A second was the "direct" CI method (1972) by the Swedish theoretical chemists Björn O. Roos (1937–2010) and Per E.M. Siegbahn (1945-), who showed how to calculate CI matrix elements from molecular orbital integrals on the fly (i.e. while executing the diagonalization iterations) rather than storing them. A third was the generation of spin-adapted configuration spaces through the graphical unitary group scheme created (1976-78) by the Czech-Canadian theoretical chemist Josef Paldus (1935-) and the American theoretical chemist Isaiah Shavitt (1925-). A fourth was the direct configuration interaction based on the string-based generation of full determinantal spaces developed (1984) by the English theoretical chemists Nicholas Handy (1941-2012) and Peter Knowles.

Most challenging proved the problem of judicious configuration selection so as to avoid carrying useless 'deadwood' in the CI expansion. To this end, many different approaches were pursued. A configuration selection by individual quantitative analyses was devised by the German theoretical chemist Sigrid D. Peyerimhoff (1937-) and the American theoretical chemist Robert J. Buenker.

A specific guiding aim in the search for effective configurations was to account preferentially for interactions between electron pairs in as much as the Hamiltonian contains only two-electron interactions and, additionally, the exclusion principle prevents more than two electrons from coming simultaneously close to each other. The first wave function of this type was the antisymmetrized product of strongly occupied geminals (APSG) proposed in 1953 by Hurley, Lennard-Jones and Pople, which was generalized by Parr in 1958. Calculations by Ruedenberg and the American theoretical chemists Ernest L. Mehler (1940-) and David M. Silver (1941-) in the sixties showed its inadequacy.

A general analysis of pair interactions was formulated by the Turkish theoretical chemist Oktay Sinanoglu (1934-). In depth studies of pair correlation theories by the German theoretical chemists Werner Kutzelnigg, Reinhart Ahlrichs (1940-) and Wilfried E. Meyer (1938-) in the sixties led to the effective CEPA approximation. An excellent simple estimate of the correlation energy was derived by Davidson in 1974 and has found wide use. The CEPA method as well as the Davidson correction turned out to be partial linearizations of the coupled cluster expansion, which the Czech-Canadian theoretical chemists Jiři Ĉižek (1938-) and Josef Paldus introduced into quantum chemistry in 1969 (It had originally been proposed in 1958-60 by the nuclear physicists Fritz Coester and Herman Kümmel). From the end of the seventies on, cluster methods were further particularly developed by Nakatsuji and Hirao, Pople, and in particular by the American theoretical chemist Rodney Bartlett (1944-). Subsequently, coupled cluster theories have spawned many effective electronic structure codes.

Another approach to the CI problem, namely through perturbation theory, using the Hartree-Fock wave function in zeroth order, had already been formulated in 1934 by the Danish physicist Christian Møller (1904 –1980) and the American physicist Milton Spinoza Plesset (1908–1991). From the early seventies on, Bartlett and Silver used diagrammatic many-body perturbation theory (which is formally related to coupled cluster theory) for a series of investigations of many diatomic molecules. In 1975, Pople adapted the Møller-Plesset perturbation theory to the quantum chemical framework. This approach proved highly successful and stimulated further vigorous activities in perturbation methods. On the other hand, Thom Dunning as well as the Danish theoretical chemist Poul Jørgensen showed that such perturbation expansions often do not converge.

Somewhat later, another very consequential advance was achieved, *viz.* a practical procedure for the linear inclusion of internuclear distances in the wave function of many-electron systems. Kutzelnigg and the Dutch-German theoretical chemist Wim Klopper (1961-) succeeded (1984) in this challenging generalization of the method that Egil A. Hylleraas' had invented and used for two-electron systems in 1929-30.

In the context of the described work, it became apparent that orbital optimizations are important to keep wave functions manageable and interpretable. The first molecular orbital optimizations beyond the Hartree-Fock model were performed for APSG wave functions in the above mentioned work by Ruedenberg et al. An effective orbital optimization in the framework of simple pair wave functions for larger molecules, the Generalized Valence Bond approximation, was devised by the American theoretical chemist William A. Goddard (1937-) and coworkers around 1970. Between 1965 and about 1975, several usable methods of increasing efficiency were developed for the *general* orbital-plus-configuration optimization of multi-configurational expansions (MCSCF method): by the American theoreticians Arnold C. Wahl and G. Das as well as Jürgen Hinze (1937-2008) and C.C.J. Roothaan; by the French theoretician Bernard Levy; by the German-Canadian theoretician Fritz Grein and T.C. Chang, by K. Ruedenberg and Lap M. Cheung; by W.E. Meyer; and by E. Daalgard and P. Jorgensen. MCSCF wave functions in full configuration spaces that are conceptually related to the minimal basis set concept proved particularly useful. This approach was begun in the sixties by Wahl and Liu and further elaborated in the seventies by Ruedenberg and by Roos.

A very different route towards the goal of obtaining electronic energies including correlation was proposed in 1964-65 by the Austrian-American physicist Walter Kohn (1923-), the French-American physicist Pierre Hohenberg (1934-) and the Chinese-American physcist Lu Jeu Sham: the density functional theory, which represents an orbital based extension of the earlier mentioned statistical treatment of Thomas, Fermi, Dirac, Gombàs, and a rigorous extension of the Xα method of Slater (1951). From about 1970 on, Robert Parr and the American theoreticians Mel Levy (1941-) and John Perdew (1943-) advocated this method for quantum chemistry. It proved to be considerably more accurate than many theoreticians originally expected and subsequently became a widely used approximation for the treatment of large molecules.

Along all of the mentioned avenues, vigorous and important further advances in the treatment of correlation have been achieved since the end of the seventies.

Are Atoms Embedded in the Continuum of Accurate Molecular Wave Functions?

The reason for generating complicated electronic wave functions is that they are required to predict reaction energies, activation energies, geometric structures and other properties with the accuracy that experimental chemists like to have available. On the other hand, experimental chemists also desire to be given – hopefully simple – interpretations of theoretical results in terms of atoms and bonds. These expectations call for the extraction of quasi-corpuscular models from complex continuum representations. That is to say, electronic wave functions have to be transformed in such a way that embedded atomistic structures and bonding patterns – if any – are brought to light. There exists some leeway in the *exact* choice of such transformations, a freedom that has its counterpart in the somewhat fuzzy character of many concepts in experimental chemistry. Nonetheless, the unique values obtained from a *specific* judicious theoretical definition scheme are expected to yield useful *comparisons* when applied to series of molecules. There are two aspects to this objective: an analysis of the electronic distribution and an analysis of the energy.

Instructive information regarding the electron *distribution* can be deduced from the first order density matrix of a wave function. As the Swedish theoretical chemist Per Olov Löwdin (1916–2000) pointed out in 1955, the spectral resolution of this matrix generates “natural orbitals” with rapidly decreasing occupation numbers. The most strongly occupied ones define an orbital space that, in fact, furnishes a rigorous embodiment of the minimal basis space that was conceptually and qualitatively envisaged in formulating the early semi-empirical approaches. In these orbital spaces various types of localized orbitals can be determined that represent chemically deformed atomic or bonding orbitals. On this basis, values can be obtained for quantities that had been qualitatively conceived to characterize bonding patterns in the valence bond model, the molecular orbital model and the semi-empirical models, such as valence hybridization, polarization, bond orders, atomic populations and others. Mulliken’s analyses of these quantities (1958) have become very influential. Orbital localization was first suggested by Hund in 1931. Criteria were given by Lennard-Jones and Pople in 1951 as well as by Boys in 1960 and by the American theoretical chemists Clyde Edmiston and Klaus Ruedenberg in 1963. The algorithm generally used for determining such orbitals was developed by Edmiston and Ruedenberg in 1963. The natural orbitals beyond the minimal basis set space provide the basis for the interpretation of dynamic correlations. An analysis of the role of the second order density in bonding was begun only later by the Czech theorist Robert Ponec.

The breakdown of molecular *energies* in terms of contributions from atoms and bonds is more demanding. A major challenge is posed by the problem of how to define the atoms in a molecule. There manifestly are atomic terms in the energy expression; but they cannot be simply identified with states of the free atoms as Moffitt had suggested in his Atoms-in-Molecules approach. The first rigorous resolution and analysis of the molecular energy in terms of atoms and interactions between them was formulated by Ruedenberg in 1963. Since the seventies several “energy decomposition analyses” have been advanced, notably by Kazuo Kitaura and Keiji Morokuma (1976), Tom Ziegler (1977), Frank Weinhold (1980), Richard Bader (1981) and, in the context of density functional theory, by Robert Parr in 1980.

The rigorous deduction of interpretative concepts from rigorous wave functions is nontrivial. While it can be fairly said that free atoms are now quite well understood, our insights into the nature of atoms in molecules are still preliminary and there is still much to learn. Robert Mulliken’s remark, made by at the Boulder Conference on Molecular Quantum mechanics (June 21-27, 1959), comes to mind: “I believe the chemical bond is not so simple as some people seem to think”.

Broadening of Quantum Chemistry

The seminal advances that were achieved during the sixties and seventies in constructing and understanding credible – if not yet perfect – quantitative electronic wave functions of molecules, in conjunction with the steadily increasing electronic computing power and algorithmic efficiencies, created the basis for tackling broader problems in molecular chemistry and physics.

The quantitative calculation of *bona fide* diatomic potential energy surfaces and spectra had already begun in the early sixties, notably by Bowen Liu and coworkers, and had yielded illuminating insights. In the following years, properties and potential energy surfaces of polyatomic systems became also the object of exploration. Among the theoretical chemists who contributed to these elucidations were notably Peyerimhoff, Davidson and the Italian theoretical chemist Enrico Clementi (1931-). The American theoretical chemist Mark S. Gordon (1942-) clarified many bonding patterns in the third period of the periodic table, identifying in particular consequential similarities and dissimilarities between silicon and carbon bonding. A very large number of chemical problems were addressed through *ab initio* calculations by the American theoretical chemist Henry Fritz Schaefer (1944-), who was notably effective in providing relevant elucidations to many experimentalists. These and other *ab initio* applications to concrete problems led to theoretical implications for the chemistry of main group elements, which Kutzelnigg integrated in an influential summary (1984).

With regards to the higher periods, especially transition metal atoms, new approaches were developed for the efficient treatment of relativistic effects in atoms and molecules, notably by the Finnish theoretical chemist Pekka Pyykkö (1941-).

Also developed in the sixties were basic formulations for intermolecular polarization interactions by the English theoretical chemist A. David Buckingham (1930-), and for solvation effects by the Italian theoretical chemist Jacopo Tomasi (1934-).

In addition to equilibrium structures and vibrational spectra, more demanding problems came to be studied as time progressed, such as transition states and reaction paths as well as excited states and electronic spectra. Essential in these contexts were the reaction path concept introduced by Kenichi Fukui in 1970 as well as the methods for calculating derivatives on potential energy surfaces developed by the Hungarian-American theoretical chemist Peter Pulay (1941-) at about the same time. In the seventies, the American theoretical chemists Donald G. Truhlar (1944-) and William L. Hase begun to interface electronic structure and molecular dynamics in order to follow the evolution of chemical reactions on potential energy surfaces.

Since the eighties, the applications to specific chemical problems soared. Realistic investigations of catalytic reaction mechanisms were undertaken. Photochemical excited-state reactions and radiationless transitions were examined. Non-adiabatic processes were investigated including conical intersections, which Teller as well as Herzberg and Longuet-Higgins had predicted in 1939 and 1963 to play important roles in photochemistry.

Since many chemical phenomena occur in condensed phases, a considerable amount of work has furthermore gone into extending electronic structure methods to supra-molecular systems such as solvation, surface reactions, biological environments, nano-structures and periodic systems.

It should also be noted that, over the last half century, strong advances in spectroscopy have produced a large amount of new information on atoms and molecules that is amenable to theoretical treatment.

Final Thoughts

The last quarter century has seen an explosive growth in significant theoretical as well as experimental information about atoms and molecules. It would vastly exceed the limits set for the present account if one were to attempt to do justice to the many important advances that have occurred during this span. The time around 1980 seemed therefore appropriate for concluding the present chronicle.

Over almost three millennia, human thinking about the properties of matter has moved from the early speculations regarding corpuscles and a continuum to the modern theories of quantized fields, elementary particles, atoms and molecules. The gradual advance in hard knowledge has been contingent on the closer and closer intertwining of several activities: careful and extensive experimental observations based on advancing technologies, mathematical analyses of increasing sophistication, and ever more imaginative hypotheses. In the course of this process, the overlap between chemistry, physics and mathematics has steadily increased.

The achievements have been the fruits of a joint enterprise, encompassing contributions of experimentalists and theoreticians from many disciplines concerned with many different properties of matter, often combining results and data obtained at quite different times or places and following unfashionable as well as fashionable avenues. Many times, imaginative speculations ran ahead of experimental observations, rightly as well as wrongly. On other occasions, existing evidence went for a time unnoticed before significant implications were perceived.

The long journey has involved the cooperation between many dedicated individuals from many countries, many cultures and many temperaments who all shared a sense of wonderment *de rerum natura*.

Acknowledgments

The authors thank their colleagues Reinhart Ahlrichs, Mark S. Gordon, Andreas Karachalios, Werner Kutzelnigg, Alan J. Rocke, Michael W. Schmidt and Alfred Stückelberger for kindly taking a look at the manuscript and offering their helpful comments. Part of the work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University through the Ames Laboratory.

Additional Reading

- Anders, U. *Early Ideas in the History of Quantum Chemistry*; http://www.quantum-chemistry-history.com, 2011.
- Andrade, E. N. da C. The Rutherford Memorial Lecture, 1957. The Birth of the Nuclear Atom. *Proc. R. Soc. London, Ser. A* **1958**, *244*, 437−455.
- Ballhausen, C. J. Bonding in Inorganic Complexes. *J. Chem. Educ.* **1979**, *56*, 215−218, 294−297, 357−361.
- Berne, B. J.; Miller, W. H.; Schaefer, H. F., III; Segal, G. A. *Modern Theoretical Chemistry*; Plenum Press: New York and London, 1977; 8 volumes.
- Brush, S. G. Dynamics of Theory Change in Chemistry. *Stud. Hist. Phil. Sci.* **1999**, *30*, 21−79, 263−302.
- Dingle, H. A Hundred Years of Spectroscopy. *Brit. J. Hist. Sci.* **1963**, *1*, 199−216.
- *Atoms in Chemistry: From Dalton's Predecessors to Complex Atoms and Beyond*; Giunta, C., Ed.; American Chemical Society: Washington DC, 2010.
- Giunta, C. *Classic Chemistry, a compilation*; http://web.lemoyne.edu/~giunta, Department of Chemistry, Le Moyne College, Syracuse, New York.
- Haase, W.; Temporini, H., Eds.; *Aufstieg und Niedergang der römischen Welt (ANRW) = Rise and Decline of the Roman World*, Part 2, Principate, Vol. 36: Philosophie, Wissenschaften, Technik. De Gruyter, Berlin, 1987−1994; see in particular Stückelberger 1990.
- Huff, T. E. *The Rise of Early Modern Science: Islam, China, and the West*; Cambridge University Press: Great Britain, 1993.
- Hund, F. *Geschichte der Quantentheorie*; Bibliographisches Institut: Mannheim, 1967; translated by Reece, G. The History of Quantum Theory; Harrap: London, 1974.
- *Griechische Atomisten*; Jürß, F.; Müller, R.; Schmidt, E. G., Eds.; Reclam: Leipzig, 1977.
- Klein, U. *Tools and Modes of Representation in the Laboratory Sciences*; Kluwer: Dordrecht, 2001.
- Lasswitz, K. *Geschichte der Atomistik vom Mittelalter bis Newton*; L. Voss: Hamburg, L. Voss: Leipzig, 1890.
- *Historical Atlas of Crystallography*; Lima-De-Faria, J., Ed.; Kluwer: Dordrecht, 1990.
- Mulliken, R. S. *Life of a Scientist*; Springer: Berlin-Heidelberg, 1989.
- Multhauf, R. *The Relationship between Technology and Natural Philosophy, ca. 1250-1650: as Illustrated by the Tech-nology of the Mineral Acids*; Ph.D. Dissertation, University of California, 1953.
- Neufeldt, S. *Chronologie Chemie: Entdecker und Entdeckungen (1800-2000)*; Wiley-VCH: Weinheim, 2003.
- Newman, W. R. *Atoms and Alchemy: Chymistry and the Experimental Origins of the Scientific Revolution*; University of Chicago Press: Chicago IL, 2006.
- O'Connor, J. J.; Robertson, E. F. *MacTutor History of Mathematics Archive*; http://www-history.mcs.st-and.ac.uk, University of St. Andrews-Scotland, 2012.

- Pabst, B. *Atomtheorien des lateinischen Mittelatlers*; Wissenschaftliche Buchgesellschaft: Darmstadt, 1994.
- Parascandola, J.; Ihde, J. History of the pneumatic trough. *ISIS (Univ. Chicago)* **1969**, *60*, 351−361.
- Park, B. S. *Computations and Interpretations: The Growth of Quantum Chemistry 1927−1967*; Bell & Howell: Ann Arbor MI, 1999.
- Partington, J. R. The Origins of the Atomic Theory. *Ann. Sci.* **1939**, *4*, 245−282.
- Partington, J. R. *A History of Chemistry*. MacMillan: London, 1961, 1962, 1964, 1970 (4 vols).
- Pauli, W. Die allgemeinen Principien der Wellenmechanik. In *Handbuch der Physik*; Geiger, H., Scheel, K., Eds.; Springer: Berlin, 1933; Vol. 24.1, 83−272.
- Pullman, B. *L'atome dans l'histoire de la pensée humaine*; Librairie Artheme Fayard: Paris, 1995.
- Redhead, P. A. *History of Vacuum Devices*; CERN Document OPEN-2000-287.-1999, 281-290, 2000.
- Redondi, P. *Galileo Eretico*; Giulio Einaudi: Torino, 1983; translated by Rosenthal, R. *Galileo Heretic*; Princeton University Press: Princeton NJ, 1987.
- Richtmyer, F. K.; Kennard, E. H. *Introduction to Modern Phyics*; McGraw Hill: New York, 1942.
- Rocke, A. J. *Chemical Atomism in the Nineteenth Century: From Dalton to Cannizzaro*; Ohio State University: Columbus, OH, 1984.
- Rocke, A. J. *Image and Reality: Kekulé, Kopp, and the Scientific Imagination*; University of Chicago: Chicago, IL, 2010.
- Russell, C. A. *The History of Valency*; Leicester University Press: Leicester, 1971.
- Simonyi, K. *A Fizika Kultúrtönténete*; Gondolat Kiadó: Budapest, 1978; translated by Kramer, D. *A cultural history of physics*; CRC Press: Bota Raton, FL, 2012.
- *Stanford Encyclopedia of Philosophy*; Zalta, E. N., Principal Editor; Center for the Study of Language and Information, Stanford University: Stanford CA, 2012; http://plato.stanford.edu/.
- *Antike Atomphysik, Texte zur Antiken Atomlehre*; Stückelberger, A., Ed.; Heimeran: München, 1979.
- Stückelberger, A. Die Atomistik in römischer Zeit: Rezeption und Verdrängung. In *Rise and Decline of The Roman World,* Part 2, 1990; Volume 36.4, pp 2561−2580.
- Van Melsen, A. G. M. *From atomos to atom; the history of the concept atom*; Pittsburgh, Duquesne University Press: Pittsburgh PA, 1952.
- Van Spronsen, J. W. *The Periodic System of Chemical Elements. A History of the First Hundred Years*; Elsevier: Amsterdam, 1969.
- *Dictionary of the History of Ideas: Studies of Selected Pivotal Ideas*; Wiener, P. P., Ed.; Scribner: New York, 1973; 4 Vols.; electronic ed. by University of Virginia Library, Charlottesville VA, 2003 [http://onlinebooks.library.upenn.edu/webbin/book/lookupid?key=olbp317].

Chapter 2

Pioneering Quantum Chemistry in Concert with Experiment

Istvan Hargittai*

Hungarian Academy of Sciences and Budapest University of Technology and Economics, P.O. Box 91, 1521 Budapest, Hungary
***E-mail: istvan.hargittai@gmail.com**

Computation and experiment perform best when they act in concert, and the pioneers of quantum chemistry kept this in mind from the start. Eugene P. Wigner considered the observation of coherence and regularities as the most important scientific approach. Qualitative models constituting often a bridge between theory and experiment served both. It was exemplary how Gilbert N. Lewis and Linus Pauling discussed theory and experimental information in a concerted way. A conspicuous case was when Pauling deduced the planarity of the peptide bond from the theory of resonance. The theory of resonance went through bumpy periods in the Soviet Union in the early 1950s and its proponents were made to suffer for their ostensibly succumbing to foreign ideologies. For a while there was a great battle between VB and MO approaches with the former being more eloquent and the latter more useful. Robert Mulliken and others showed the way to shift toward MO theory and applications. Walter Kohn and John Pople received their shared Nobel Prize for density functional theory and for computational methods in quantum chemistry, respectively. These approaches have become an integral part of chemical research. Pople pointed the way to estimating the "experimental error" of calculations. This is a necessary condition for quantum chemistry becoming truly an equal partner in the realm of all "physical" techniques of chemistry.

> *To understand the properties of molecules,*
> *not only must you know their structures,*
> *but you must know them accurately.*
> Linus Pauling (attributed)

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Introduction

I have been influenced by Eugene P. Wigner's characterization of scientific research. He expressed it eloquently in his Nobel lecture when he quoted his teacher, Michael Polanyi in that "…science begins when a body of phenomena is available which shows some coherence and regularities, [that] science consists in assimilating these regularities and in creating concepts which permit expressing these regularities in a natural way." Wigner (and Polanyi) saw in this the real transferability of the scientific approach, and more so than in transferring concepts, such as energy, for example, "to other fields of learning (*1*)." The beginning of my interactions with Wigner dated back to 1964 when he wrote me a long letter in response to an article I had published in a Hungarian literary magazine in reference to his essay on the limits of science. This article was my first ever publication and it was in the senior year of my university studies.

Wigner and Witmer's paper in 1928 contained the first application of symmetry considerations to chemical reactions. The Wigner–Witmer rules referred to the conservation of spin and orbital angular momentum in the reactions of diatomic molecules (*2*). Wigner in 1931 summarized his contributions to structural science in his German-language monograph about the applications of group theory to the quantum mechanics of atomic spectra. Three decades later the book was published in English translation (*3*).

Our interactions culminated in our meeting in person and extended conversations in 1969 at the University of Texas at Austin (Fig 1). In fact, Wigner was my mentor in my acquiring knowledge of applications of symmetry in chemistry.

Wigner introduced me to broad applications of the symmetry concept (*4*). We then remained in on–and–off correspondence throughout the years. The utilization of symmetry has become a characteristic feature of my and Magdolna Hargittai's work in structural chemistry (*5*). The present contribution is based on my presentation at the spring 2011 Anaheim meeting. It was supposed to augment the other contributions to the Symposium "Pioneers of Quantum Chemistry" rather than being a comprehensive survey. Emphasis was given to a few studies in which the concerted use of quantum chemical considerations whether via computation or not was used in frontier research, especially in the early periods.

I had been involved primarily with the experimental determination of molecular structure for about twenty-five years when about twenty years ago we invited Paul Schleyer to Budapest for a talk. He gave an excellent presentation during which he reciprocated our hospitality with a statement that we better throw out all our experimental equipment and do, rather, computational work. This did not sit well with the people who were supposed to allocate funding for our experimental projects, but, fortunately, they did not pay too much attention to it. Paul's statement reminded me of what Gay-Lussac said a hundred and fifty years before—and he did this politely—that the time was not far when everything would be possible to calculate in chemistry. Today, we could say the same. It is also true that nowadays it is easier to get graduate students for computation than for experimental work.

Figure 1. Eugene P. Wigner and the author on the campus of the University of Texas at Austin in 1969. (© I Hargittai.)

In this account, I would like to stress an additional component in chemical research, and that is chemical intuition and qualitative models, usually based on accumulated knowledge.

A Qualitative Model

Even in today's world of sophisticated quantum chemical calculations, qualitative models continue to play an important role in chemical research. As is known, successful models select one or a few of the properties of the systems they intend to describe and ignore the rest. A model is successful if it can be used for predicting properties not yet studied. The systems used for testing the model should be within the scope of applicability of the model. One of the most successful qualitative models in predicting molecular shapes, geometries, and even structural variations in series of substances has been the Valence Shell Electron Pair Repulsion (VSEPR) Model (*6*). It assumes that the valence shell of the central atom in the molecule is spherically symmetrical and the interactions among the electron pairs in this valence shell—taking into account all electron pairs regardless whether they are bonding pairs or lone pairs—are described by the potential energy expression $V_{ij} = k/r_{ij}^n$, where k is a constant, r_{ij} is the distance between the points i and j, and the exponent n is large for strong repulsions and small for weak repulsions, but they are generally stronger than simple electrostatic coulomb interactions.

The task is to look for the molecular shape for which the potential energy reaches its minimum. The exponent n is not known, but this is not an impediment, because as soon as it is larger than three, the results become insensitive to the choice of n. This insensitivity of the results to n is the secret of the wide applicability of the model. The resulting shapes of the arrangements of the electron pairs for two, three, four, five and six electron pairs in the valence shell will be linear, triangular, tetrahedral, trigonal bipyramidal, and octahedral, respectively. A set of sub-rules makes the model easily applicable for determining more subtle features of molecular geometry. Its applicability has limits, of course. Thus, for example, it is gradually less applicable with increasing ligand sizes relative to the size of the central atom, because for such structures non-bonded repulsions become gradually the dominating interactions (*7*). The popularity of the VSEPR model has been greatly enhanced by its successful application for predicting and explaining even some structures that initially appeared counter-intuitive.

An important feature of any model aiming at a realistic representation of structures is the inclusion of motion. The low-frequency, large-amplitude so-called deformation motions may lead to some of the experimental techniques yielding lower symmetry molecular shapes than the equilibrium structure that would correspond to the minimum position of the potential energy function. The relationship between average structures and the equilibrium structure has become a cornerstone consideration with increasing precision of the experimental determination and the enhanced sophistication of quantum chemical calculations of molecular geometry (*8*). Beyond certain precisions, the computed bond lengths, for example, and their experimentally determined counterparts cannot be the same, and any demanding comparison and meaningful discussion of such information requires considerations of the accuracy of structural information (*9*). The experimental results also depend on the way averaging over molecular motion happens in any given experimental technique. The impact of motion is only one of the possible origins of change in molecular symmetry. Various other effects have been uncovered and taken into account with the expanding scope of reliable structure determinations, including the Jahn–Teller effect (*10*).

The VSEPR model is a continuation of prior qualitative ideas about the nature of the chemical bond and its correlation with molecular geometry. G. N. Lewis's (Figure 2) covalent bond and his cubical atom models were direct forerunners (*11*). Lewis's approach permitted a resolution of the apparent contradiction between the two distinctly different bonding types, the shared electron pair and the ionic electron transfer bond. His cubical atoms were an example of useful though not necessarily correct application of a polyhedral model.

G. N. Lewis's contributions were trend-setters in the first half of twentieth century chemistry and his missing Nobel Prize has been rightly lamented about. In contrast, W. N. Lipscomb—showing more understanding toward the Nobel decision than the rest of the chemistry community—remarked that Lewis may have invented the covalent bond but he never understood it (*12*). Of course, the quantum chemical description of the covalent was given by Walter Heitler and Fritz W. London, but their rigorous treatment severely limited its utility for chemistry.

Heitler himself appreciated Lewis's forward-pointing contribution when he referred to it in his 1945 book *Wave Mechanics* (*13*):

> Long before wave mechanics was known Lewis put forward a semi-empirical theory according to which the covalent bond between atoms was effected by the formation of pairs of electrons shared by each pair of atoms. We see now that wave mechanics affords a full justification of this picture, and, moreover, gives a precise meaning to these electron pairs: they are pairs of electrons with antiparallel spins.

Another testimonial for the advanced nature of Lewis's theory was given by Robert S. Mulliken in his Nobel lecture. He described the relation of Lewis's theory to molecular orbital (MO) theory using chemical orbitals. Mulliken emphasized that "Lewis resolved the long-standing conflict between, on the one hand, ionic and charge-transfer theories of chemical bonding and, on the other hand, the kind of bonding which is in evidence in bonds between equal atoms… (*14*)"

Further, Mulliken writes, "for individual atoms, Lewis' electron shells were three-dimensional, in contrast to Bohr's planar electron orbits, in this respect being closer to the present quantum mechanics than the Bohr theory." Nonetheless, of course, Lewis's theory was "empirical, schematic, and purely qualitative," as Mulliken pointed this out as well (*15*).

Mulliken appreciated Lewis's contribution so much that he mentioned as a merit of the MO theory that it best approximates Lewis's theory. He writes, "…These localized MO's I like to call chemical MO's (or just chemical orbitals because of the fact thet some of the orbitals used are now really AO's [atomic orbitals]). In simple molecules, electrons in chemical MO's usually represent the closest possible quantum-mechanical counterpart to Lewis' beautiful pre-quantum valence theory… (*16*)"

Figure 2. Gilbert N. Lewis in 1912 at sea, during his honeymoon. (Courtesy of Edward S. Lewis.)

N. V. Sidgwick and H. M. Powell correlated the number of electron pairs in the valence shell of the central atom and its bond configuration in a molecule (*17*). Then Ronald J. Gillespie and Ronald S. Nyholm introduced allowances for the differences between the effects of bonding pairs and lone pairs, and applied the model to large classes of inorganic compounds (*18*). With coining the VSEPR name the model was ready in its initial formulation. It has since gone through improvements mainly by introducing additional subrules and defining its scope of validity.

There have been attempts to provide a quantum-mechnaical foundation for the VSEPR model. One direction in this has been, in part. to understand better the reason why the model works so well in large classes of compounds, but also to lend respectability to the rather rudimentary model, which, however, worked so well. Some basic tenets have been successfully interpreted by the Pauli exclusion principle. Another direction has been to encourage comparisons between sophisticated computations and the application of the model. It could have been expected that calculations of the total electron density distribution should mimic the relative space requirements of the various electron pairs. This was deemed though not too successful—apparently due to the core electron densities suppressing the minute variations in the valence shell. Closer scrutiny, however, revealed that the spatial distributions of the various electron pairs indeed showed distinguishing features in accordance with the expectations of the VSEPR model (*19*). A set of examples are shown in Figure 3.

It was then suggested to utilize approaches that would enhance the relative contributions of the valence shell electron density distributions. Thus, visualizing the second derivative of the electron density distribution led to success and the emerging patterns paralleled some important features predicted by the VSEPR model (*20*).

Resonance

Linus Pauling (Figure 4), arguably one of the greatest chemists of the twentieth century, went to Europe after having earned his doctorate at the California Institute of Technology. During the first third of the twentieth century it was often the case that young, ambitious scientists earned their doctorates at European centers of science or spent there a few postdoctoral years. Pauling learned a great deal during his European sojourn from great physicists like Arnold Sommerfeld in Munich and Erwin Schrödinger in Zurich. Pauling's aim was not to transform himself into a physicist; rather, his goal was to apply the latest discoveries in physics and in particular those in the new quantum mechanics to solving various problems in chemistry (*21*).

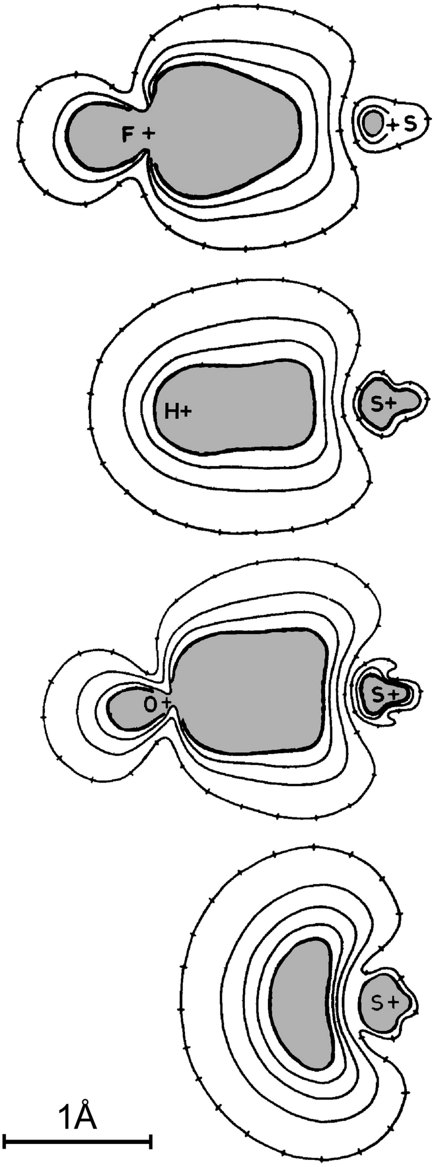


Figure 3. Localized molecular orbitals illustrating bonding electron pairs and a lone pair on sulfur; from top to bottom, representing S–F, S–H, S=O, and a lone pair, respectively. The contours denote electron densities of 0.02, 0.04, 0.06, etc., electron/bohr^3 from computations. The pluses indicate the positions of the atomic nuclei.

Pauling's main goal was the understanding of the nature of the chemical bond. He used the achievements of modern physics, the already available experimental information about molecular geometry, and his own intuition to create a theory.

He then kept refining it as new experimental information emerged. He also took it as his task to bridge the gap between the rigorous quantum mechanical description of the covalent bond by Heitler and London—not really applicable for anything more complex than the hydrogen molecule—and systems that chemists found to be of interest. He worked out a theoretical technique, for describing molecular structures, based on quantum mechanics, but simple enough for a broad circle of chemists. It was called the valence-bond or VB theory and it was one of the two major theoretical approaches to treat molecular structures over the decades—the other was the molecular orbital or MO theory. The VB theory built the molecules from individual atoms linked by electron-pair bonds. It appeared straightforward and had a great appeal to chemists; alas, it did not stand well the test of time. The MO theory has proved more amenable to computation and has become a major thrust in structural chemistry. However, for a long time, the VB theory dominated the field. Pauling was its emblematic figure, but by far not the only one among its proponents.

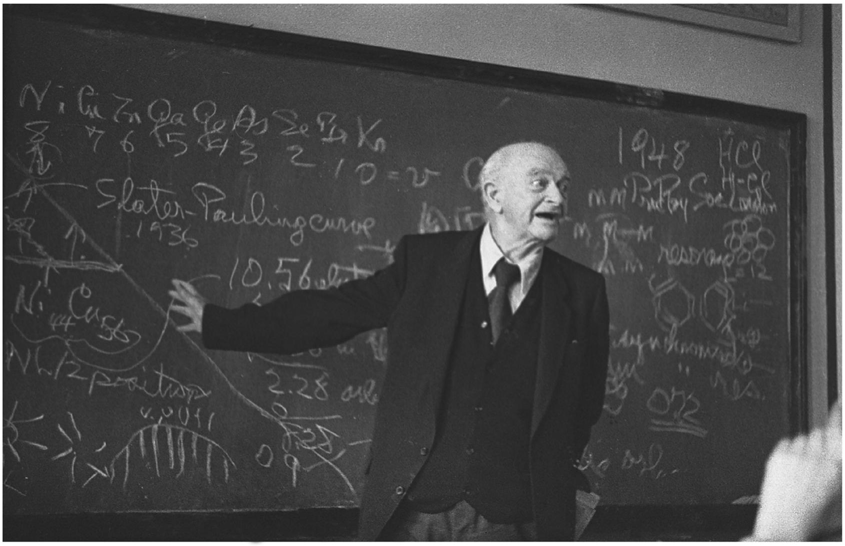


Figure 4. Linus Pauling lecturing in 1984 at Moscow State University. (Photograph by and courtesy of Dr. Larissa Zassourskaya, Moscow.)

An important feature of the VB theory was the description of molecular structure by a set of “resonating” structures. This did not necessarily mean that each structure represented in the set would be present individually; rather, it implied that the sum of the resonating structures would correspond to the real structure and hence would give its better description than any other approach at the time.

In the 1930s, Pauling wanted to explain, for example, why the structure of the benzene molecule could be equally well described by two equivalent structures with alternating single and double bonds. Such a pair of structures corresponded to Kekulé's hypothesis who pioneered it well before chemists understood the nature of chemical bonding. Pauling suggested that the two separate benzene structures might better represent reality if imagined as being in continuous resonance of going back and forth between the two. Hence the name of the theory of resonance. The critics of the theory of resonance argued that two different structures could not have co-existed and that the benzene molecule should be described by a single structure. Pauling took great pain stressing that his description was merely a model, a mathematical construction, but that did not pacify the opponents of the resonance theory.

The physicist Edward Teller was intrigued by Pauling's model and provided spectroscopic support for Pauling's approach. He and two co-workers published a paper in 1940 in which they showed that it was meaningful to describe the benzene molecule using Pauling's model (*22*). Teller was not the only physicist who was intrigued by the resonance model of the benzene molecule. Sixty-eight years later, in 2008, the Nobel laureate Philip Anderson also found modern means to give an interpretation to the resonance structures (*23*). He was oblivious of Teller's prior contribution to the problem (*24*).

We will see below how useful considerations of resonance structures would become, for example, in Pauling's quest for the protein structures. However, first we glimpse into a bizarre story of the resonance controvery around 1950 (*25*).

The Great Soviet Resonance Controversy

According to Soviet ideologues, Pauling's description of the benzene structure was not only meaningless, but was contrary to dialectical materialism—the philosophical foundation of communism. They organized a big meeting in Moscow on June 11–14, 1951, during which a group of vocal though scientifically weak chemists rejected the ostensibly harmful activities of the proponents of the theory of resonance. Some of those condemned were internationally renowned scientists who were forced to engage in humiliating self-criticism during the discussion. A thick volume of the minutes of the meeting was published in 1952 (*26*).

The meeting was organized by a most authoritative organization, the Chemistry Division of the Soviet Academy of Sciences and it had one topic only, the state of structure theories of organic chemistry. Four-hundred-and-fifty chemists, physicists, and philosophers attended the event from all over the country. A special commission of the Chemistry Division had compiled a report entitled "The status of chemical structure theory in organic chemistry." The presentation of this report was followed by forty-three oral contributions and an additional twelve contributions were submitted in writing. All were reproduced in the volume referred to above.

In keeping with the spirit of the time, the meeting accepted a resolution and sent a letter to I. V. Stalin, the supreme leader of the Soviet Union. The letter expressed self-criticism for the prior failure of appreciating sufficiently the role of ideology in chemical research. This is how they explained that the "foreign concept of resonance" could be spreading among Soviet scientists. They declared that the resonance concept was an attempt to liquidate the materialistic foundations of structure theory. However, the Soviet chemists pledged to wage a war against the ideological concepts of bourgeois science. Ironically—but resembling George Orwell's *Animal Farm* and *1984*—during the meeting there were repeated references to Stalin's teachings about the importance of letting different opinions collide and of the freedom of criticism.

The authors of the special report were from among the crème of Soviet chemistry. The report gave ample emphasis to Aleksandr M. Butlerov's teachings and stressed the importance of reaching back to the traditional values of Russian science. Of course, Butlerov had great merits in organic chemistry and in structural chemistry as well (*27*). For the latter, he contributed more with his suggestion of the term chemical structure than with new discoveries, but his contributions were forward looking. In his time, his teaching that every substance could be assigned a chemical structure was progressive. The critics of the resonance theory, however, turned around Butlerov's teaching and claimed that resonance contradicted Butlerov's maxim of each substance having one structure only.

The report singled out a few chemists, and Ya. K. Syrkin and M. E. Dyatkina (Figure 5) were named as the main culprits of disseminating the theory of resonance in the Soviet Union. True enough, Syrkin and Dyatkina had recently published a modern monograph about structural chemistry which was soon translated into English and praised in Western literature (*28*). The two authors were accused of having further developed Pauling's and George Wheland's erroneous concepts. The accusations included Syrkin's and Dyatkina's relying on and citing foreign authors. Others were also named although the accusations toward them were milder. However, it characterized the severity of the situation that the president of the Soviet Academy of Sciences, the organic chemist A. N. Nesmeyanov was among the accused along with his associate R. H. Freidlina. Their sin was that they interpreted the diverse reactivity of chlorovinyl compounds of mercury and others by the resonance between their covalent and ionic structures.

The report was followed by a question-and-answer period in which the most important question referred to the alleged idealism of the theory of resonance. It was obvious that the explanations read a lot of ideological content into the theory that Pauling and Wheland could not have dreamt of. The discussion that followed reflected the fact that it was only a small though very vocal group that attacked blindly and viciously the theory of resonance and with that they attacked quantum chemistry and all of the science of the West. By the same token they prescribed the return to historical Russian achievements and advocated their own, obviously worthless, theories. Many of the participants subjected the theories of this group to criticism, but they also painstakingly dissociated themselves from the theory of resonance. One gets goosebumps when reading the humiliating self-criticism of some excellent scientists.

Figure 5. Ya. K. Syrkin (1894–1974) and M. E. Dyatkina (1914–1972). Photographs courtesy of the late Lev Vilkov, Moscow.

At times the discussion looked like bidding at an auction of criticism of Western science. A philosopher declared Schrödinger to be a representative of modern physical idealism, which made him a relative of Pauling's. He stated that Dirac's superposition principle was as idealistic as Heisenberg's complementarity principle and even more idealistic than Pauling's theory of resonance. A writer accused the protagonists of the resonance theory as being the spokesmen of Anglo-American pseudoscience and praised the infamous T. D. Lysenko who proved that Mendel's work had nothing to do with biology.

The last entry in the volume of the minutes of the meeting was by E. A. Shilov, and it was one of the contributions that was not given as oral presentation during the meeting. This very brief entry is noteworthy, because it is very different from most of the others. It is critical of the report and the resolution and suggests that instead of scholastic debates looking back to the past, the community should be concerned with new teachings and new results He writes disparagingly of the subject matter of the discussions and promotes valid and productive work instead.

The resonance controversy revealed the insecurity of the Soviet scientific establishment mirroring the general political atmosphere. There was fear of everything coming from the West. The discussion looked more like a staged trial than a meaningful exchange. There could be reasons to dislike the theory of resonance, but no reason to elevate it to the level of assigning it to be a subversive tool in the hands of Western imperialists. Some outstanding Soviet chemists lost their jobs as a consequence of this witch-hunt.

A different interpretation is also possible of the events related to the theory of resonance in the Soviet Union. Although jobs were lost as a consequence, but not lives as was the case in similar ideological struggles in biology. Incidentally, at some point, an ideological attack against the Soviet physicist community had also been considered and prepared in 1948. It was then decided against when the Soviet leadership understood that such actions might cost them the nuclear weapons that were already being developed in the Soviet Union.

There was healthy criticism of the un-scientific group of chemists that finally did not succeed in forcing their will upon the larger community even if some outstanding scientists had to be sacrificed—though, again, in case of chemistry, sacrificed not in a physical sense. A long-range negative consequence of the Soviet resonance controversy was that for decades young and aspiring chemists in the Soviet Union frowned upon seeking a career in quantum chemistry and in theoretical chemistry in general. It seemed too hazardous if not outright dangerous.

There was an ironic quirk in the Soviet controversy about the theory of resonance in that Pauling had leftist leanings and friendly sentiments toward the Soviet Union, and this was known in the United States. However, it took some time for the Soviet bureaucrats to learn about it. There was some parallelism between the witchhunting in the ideological struggles in the Soviet Union and McCarthyism in the United States at about the same time. It is true though that the consequences of the former were much harsher than those of the latter, but the former was a totalitarian state and the latter a democracy.

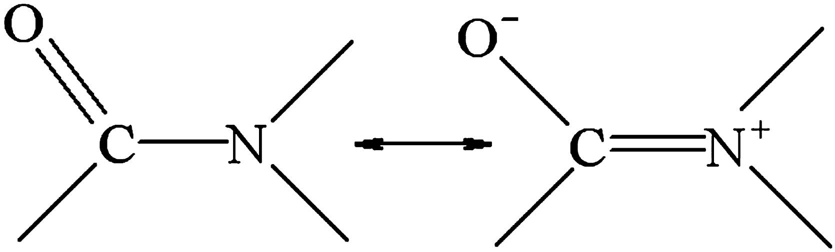
One question remains, and that is about how Pauling himself must have viewed the controversy about his theory in the Soviet Union. It is possible though hardly probable that he might have not followed the developments in Moscow.

When I asked him about this in the fall of 1993, that is, not long before his death, his answer puzzled me: "It took several years, from about 1949 to 1955, for the chemists in the Soviet Union to get a proper understanding of the resonance theory (*29*)." In a live conversation it would have been easier to bombard him with a follow-up question, alas, this was part of a correspondence. Pauling's response hurt Syrkin and Dyatkina along with others who recognized the usefulness of the resonance theory and utilized it and had to pay a price for having done so. They did not need those years Pauling indicated for "a proper understanding." On the other hand, the opponents of the theory of resonance maintained their opposition for decades without losing their influence. It is true though that with the Soviet officialdom recognizing a political ally in Pauling, the attacks on the theory of resonance soon lost their personal character. Ironically, at the time, Pauling was having trouble with the US State Department about his foreign travels for his leftist poilitics. Pauling's enemies might have felt *Schadenfreude* when observing the troubles of his teachings in the Soviet Union. At the time there were reports in the American press about the meeting of the Soviet chemists. The title of the account in *TIME* magazine in 1951 was "Science: Resonance Heresy." It warned that "From now on, Soviet chemists will have to watch their test tubes more carefully than ever: heresy may be lurking in any one of them (*30*)." By all indication *TIME* had a better appreciation of the situation in the Soviet Union in 1951 than Pauling seemed to have according to his statement in 1993.

Quest for the Protein Structure

The most spectacular application of the theory of resonance occurred in Linus Pauling's own oeuvre. In the 1930s he was advancing systematically in building up structural chemistry. He determined a host of inorganic structures relying primarily on X-ray crystallography and eventually also on gas-phase electron diffraction. Following the success with inorganic substances, he turned to organic structures. He often found molecules in which the bond lengths were intermediate between single bonds and double bonds, and the theory of resonance found useful applications in interpreting these results. Then, from the mid-1930s he decided to make an attempt at the determination of the structure of biopolymers, and in particular proteins. It was at the time when nucleic acids were not yet considered representing great interest as Phoebus Levene's hypothesis about the tetranucleotide structure of DNA was still generally accepted. According to this hypothesis, based on an erroneous observation, the four nucleotides in DNA were present in equal amounts. Thus the DNA molecule was not thought to be capable of carrying any great amount of information (*31*).

By the time Pauling joined protein research, there had been X-ray crystallography studies that had established the existence of two principal types of protein structure. Keratin fibers belonged to one and silk to the other. William T. Astbury had shown that keratin had two versions, the normal one, alpha keratin, and the stretched one, similar to silk, and he called it beta keratin. Pauling embarked on determining the structure of alpha keratin in 1937 and used X-ray crystallography together with his experience in model building. From numerous structures of protein building blocks he had information about the characteristic sizes of the group linking the amino acid units in the protein chain. Especially important was that the C–N bond in the peptide linkage was not simply a single bond although it was not a purely double bond either. His resonance theory taught him that the emerging structure of the peptide bond could be represented by the following two resonating structures:



As the C–N bond had considerable double bond character, again, from his accumulated knowledge about structures as well as from his quantum chemical considerations, he deduced that the peptide bond configuration, that is, all the bonds around the C–N bond, should be in the same plane. This was a very important piece of information, because this meant a constraint that vastly reduced the number of possible models in describing the structure of alpha keratin. At this time though he stopped this research for a while because he could not find a structure that would correspond to both his intuition and the X-ray crystallographic evidence.

He resumed his quest after World War II. In the meantime, Robert Corey, the outstanding X-ray crystallographer joined his laboratory. Pauling's students continued the determination of structures of amino acids that further enriched his data base of building blocks of protein structures. His approach to the problem had also undergone some chage. Earlier he was bothered by the fact that he had to find a structure in which twenty different amino acids might figure. At this time, in 1948, he decided to ignore their differences and for the purpose of his model, he assumed their equivalence. He then remembered a mathematical theorem that the most general operation to convert an asymmetric object—an amino acid in his case—into an equivalent asymmetric object is a rotation–translation whose repeated application produces a helix. The amount of rotation was such that took the chain from one amino acid to the next while the peptide group was kept planar, and this operation was repeated virtually infinite times. There was one additional stipulation to keep the adjacent peptide groups apart to such a distance that corresponded to hydrogen bonding between them.

Pauling's model thus had features that represented restrictions as well as relaxations. His model, for example, did not prescribe that the turn of the protein chain should involve an integral number of amino acids. His approach was very different from the British group which at the same time was also trying to determine the protein structure. It was the British school of crystallography—J. Desmond Bernal in 1934 in Cambridge—that had produced the first X-ray diffraction pattern of a protein, and Puling's competitor was a star-studded group in Cambridge: W. Lawrence Bragg, Max Perutz, and John Kendrew. But they did not have Pauling's approach of using modeling and, even more significantly, they were not aware of the planarity of peptide bonding. Whereas Pauling could reduce the number of possible models to two, the British group had no way of a priori eliminating a large number of models. They had to consider them all, and ended up communicating a large number of possible structures of which none turned out to be correct. The story of the discovery of alpha helix has been described (*32*).

Robert Mulliken, Friedrich Hund, Charles Coulson

Robert S. Mulliken (1896–1986) was both an experimentalist and a theoretician, but his name has become virtually equivalent with molecular orbitals. Here we present a brief account about him following mainly R. Stephen Berry's biographical memoir (*33*). Mulliken's quiet demeanor was the opposite to Pauling's flamboyance. In high school he considered both philosophy and science for his career and chose science. He received his undergraduate degree in chemistry at MIT. During World War I he did research on poison gases under the direction of James B. Conant for the US Chemical Warfare Service. He did his doctoral work at the University of Chicago between 1919 and 1922 where one of his interests was in isotope separation. He did war service during World War II in the framework of the Metallurgical Laboratory, the Chicago section of the Manhattan Project.

Like many of his peers, Mulliken spent a few postdoctoral years in Europe where he met and interacted with many big names in chemistry and physics. Close interactions developed between him and Friedrich Hund (1896–1997). They first met in 1925 Göttingen at the time when Hund was Max Born's assistant in the mid-1920s. They shared interest in understanding the structure of matter and the nature of the chemical bond. Further meetings strengthened their cooperation, which thrived though they never published a joint paper. In Göttingen in 1927 Hund and Mulliken generalized the ideas of atomic orbitals, the concept of molecular orbitals was born, and they wrote their first respective papers about it in 1928.

It seemed for a while that the Heitler–London–Slater–Pauling valence-bond theory would dominate the world of chemistry in the quest for the understanding and describing molecular structures. There were though difficulties from which the Hund–Mulliken molecular orbital theory did not suffer. Mulliken was critical not only and not so much of the valence bond theory, but rather of the way Pauling publicized it. He stated that "Pauling made a special point in making everything sound as simple as possible and in that way making it [the VB theory] very popular with chemists but delaying their understanding of the true [complexity of molecular structure] (*33*)."

Incidentally, Mulliken did not like the expression "valence-bond method," because it implied "emphasis in chemical bonding on a few pairs of electrons holding atoms together in the Heitler–London manner, whereas actually the interactions of many of the electrons often have very important effects on the stability of molecules (*34*)."

The merits of the MO theory and Mulliken's contributions were recognized in 1966 by the Nobel Prize in Chemistry "for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method." As up to three persons may share a Nobel Prize in any given category, Hund's omission from this award has been a puzzle. Mulliken gave ample exposure in his Nobel lecture to Hund's contributions. He described, among others, Hund's works on applying quantum mechanics to the understanding of atoms and their spectra and molecules and their spectra (*35*):

> Using quantum mechanics, he [Hund] quickly clarified our understanding of diatomic molecular spectra, as well as important aspects of the relations between atoms and molecules, and of chemical bonding. It was Hund who in 1928 proposed the now familiar Greek symbols *Σ*, *Π*, *Δ*, for the diatomic molecular electronic states which I had been calling S, P, and D. Molecular orbitals also began to appear in a fairly clear light as suitable homes for electrons in molecules in the same way as atomic orbitals for electrons in atoms. MO theory has long been known as the Hund–Mulliken theory in recognition of the major contribution of Professor Hund in its early development.

Friedrich Hund (1896–1997, Figure 6) remained active almost to the very end of his long life and his annual lectures in Göttingen were always a great scientific event.

Figure 6. Discussion panel—Friedrich Hind speaking—at the 40th annual meeting of physicists in 1976 in Bonn (courtesy of the Archives of the German Physical Society). From left to right, Carl Friedrich von Weizsäcker, Hund, Hans-Joachim Queisser (then president of the DPG), Rudolf Peierls, and Victor Weisskopf. (Courtesy of the DPG, the German Physical Society.)

Robert Mulliken's (Figure 7) career back home started with an assistant professorship in physics at New York University, followed by an associate professorship in physics at the University of Chicago. Chicago then remained his base for the rest of his career. During the second half of the 1920s and in the

1930s he made several trips to Europe. On the occasion of his 1930 visit he met again with Hund, but this time in Leipzig where Hund had been appointed to a professorship. This is where Mulliken met with Edward Teller for the first time and they became colleagues at Chicago after World War II. The recently married Mulliken and his wife visited Budapest where Teller acted as their host. Teller was Heisenberg doctoral student in Leipzig between the fall of 1928 and the spring of 1930 and had just completed his doctorate. However, he was already Hund's assistant since the end of 1929 and stayed in this appointment until his departure for Göttingen in the spring of 1931 (*36*).

Figure 7. Robert Mulliken and his wife, Béla Pogány (a professor at the Budapest Technical University) and Edward Teller in Budapest, probably in 1930. (Courtesy of the late George Marx.)

Mulliken wrote series of articles throughout his career and through them he influenced the development of chemical science and the spreading of his molecular orbitals approach. He built up a unique reprint collection in the field of his interest, and he met with a huge number of influential scientists over the years. R. Steven Berry concluded his Mulliken obituary with the following evaluation, "He was ready for the unexpected, but he was in tune with nature, and knew inside himself what was real and deserving his acute thought. He set a style and a standard that are as much his legacy as the body of scientific understanding he created (*33*)."

Charles A. Coulson (1910–1974, Figure 8) was an early hero of molecular orbital theory. He is known to have started as an enthusiast of Pauling's VB theory for its good predictions for organic structures. However, he noted the missing interpretation and the lack of providing any approach for numerical calculations (*37*). He was educated at Trinity College of Cambridge University and graduated with excellent qualifications both in mathematics and physics. He did his PhD work under John Lennard-Jones on the molecular ion, H_3^+. His work was published in 1935 and it was the time when Linus Pauling's VB theory was very much in vogue and Coulson noticed that "Molecular orbital theory was not getting a fair deal, it was not well accepted by chemists, who were—by and large—uncritical in their adoption of "resonance" theory (*38*)."

Coulson started making molecular orbital calculations and introduced and utilized such basic concepts as bond order, thereby enhancing the interest in establishing correlations between a great variety of molecular and bond properties. He became engaged in writing well-received books that were aids to researchers and were popular among the less narrowly specialized scientists as well. His books, such as *Waves* and *Valence* were considered pedagogical masterpieces. Both these books were republished repeatedly. It was especially a recognition of his work on the applications of the molecular orbital theory that in 1950 he was elected to be Fellow of the Royal Society (London).

Figure 8. Robert Mulliken and Charles Coulson in 1953. (Photograph by and courtesy of John D. Roberts, Pasadena.)

After having served in Oxford and in London in other capacities, he was appointed to the prestigious Rouse Ball Chair of Mathematics at the University of Oxford in 1952. About twenty years later, shortly before his untimely death, he left this position and was appointed to be Professor of Theoretical Chemistry at the same university. It was a position that he had been informally practicing for a long time. He dealt with a plethora of chemical problems at the theoretical level, including his pioneering theoretical studies of hydrogen bonding.

Coulson noticed that researchers in theoretical chemistry tend to be part of one of two groups. In Group 1 were those who wanted to calculate small molecules very accurately and in Group 2 were those whose goal was the observation of correlations and patterns. He seems to have succeeded in keeping together these two groups. He set the goal of quantum chemistry modestly when he stated that "Chemistry is an experimental subject whose results are built into a pattern around quite elementary concepts. The role of quantum chemistry is to understand these concepts and show the essential features of chemical behaviour (*38*)." Coulson certainly contributed a great deal to a much enhanced role of quantum chemistry in today's chemistry.

He had a deep interest in the application of the symmetry concept. I have long admired his approach, which was both a recognition of the possibilities of the utilization of the symmetry concept and a recognition of its limitations at the same time. He gave a Faraday lecture on symmetry and he stated in its conclusion, "Man's sense of shape—his feeling for form—the fact that he exists in three dimensions—these must have conditioned his mind to thinking of structure, and sometimes encouraged him to dream dreams about it." However, Coulson issued a caveat that "we must not carry this policy too far. Symmetry is important, but it is not everything." He quoted Faraday's warning in this connection and Coulson added to it his own, "It is when symmetry interprets facts that it serves its purpose: and then it delights us because it links our study of chemistry with another world of the human spirit—the world of order, pattern, beauty, satisfaction. But facts come first. Symmetry encompasses much—but not quite all (*39*)!"

Computational Revolution

It was a long anticipated recognition when in 1998 Walter Kohn (1923– , Figure 9) and John A. Pople (1925–2004, Figure 10) were awarded a shared Nobel Prize in Chemistry "for his development of the density-functional theory" and "for his development of computational methods in quantum chemistry," respectively.

John Pople was born in Burnham-on-Sea, Somerset, England, and received his degrees in mathematics from Cambridge University. He was Carnegie Professor of Chemical Physics between 1964 and 1974 and John Christian Warner Professor of Natural Sciences between 1974 and 1993 at Carnegie-Mellon University in Pittsburg. From 1993 to the end of his life he was Board of Trustees Professor of Chemistry at Northwestern University. He was introduced to computational electronic structure theory by his graduate advisor, John Lennard-Jones. He then returned to this area of reseach only after he had done theoretical—statistical mechanics—work on the structure of liquids, and then worked on the theory of NMR spectroscopy.

Figure 9. Walter Kohn in December 2001 in Stockholm, at the time of the centennial celebrations of the Nobel Prize. (Photograph and © 2001 by I. Hargittai.)

Figure 10. John A. Pople in his office at Northwestern University in 1995. (Photograph and © 1995 by I. Hargittai.)

In his career in computational chemistry Pople was first instrumental in the introduction and dissemination of semiempirical techniques, and contributed to the development of a whole set of successful methods that gained broad acceptance and applications. Eventually he embarked on developing ever improving approaches to non-empirical, *ab initio*, computations. There is a tremendous literature about his contributions that have remained essential for current research. Here, I present a selection of his views based on a conversation we had in 1995. It represents his concerted approach to theoretical chemistry in which he constantly looked out for the needs of both the computational and the experimental chemists (*40*).

Pople formulated the essence of computational chemistry “as the implementation of the existing theory, in a practical sense, to studying particular chemical problems by means of computer programs.” He stressed not to draw a distinction between computational chemistry and the underlying theory, because the computer only enabled the theory to be applied more broadly than was possible before.

At the time of our conversation, Pople was developing theories to include the density functional theory and he aimed to treat quantum mechanical problems more efficiently than before. He emphasized the importance of the possibility to make comparisons with experimental information. From this point of view, the density distribution of electrons is the same thing what X-ray diffraction provides, that is, the electron density distribution. In reality, when plots of the total electron density are calculated or measured the features of bonding (or the features of nonbonding electron pairs) are not directly discernable because the total electron density distribution suppresses the fine information related to them. There have been techniques that help us make the bonding features (as well as nonbonding electron pairs) visible and one such approach is mentioned here. When the total electron density of the molecule is measured or computed, the measured or computed electron densities of the atoms constituting the molecule may be subtracted from it yielding the features sought.

Pople saw the advantage in density functional theory versus the quantum chemical methods in that the former dealt with a function of three dimensions whereas to get the full wave function of the electrons, a problem in $3n$ dimensions had to be considered (with n being the total number of electrons).

I found Pople very sensitive to the question of experimental error in computational work, which is a cornerstone issue for a meaningful comparison of experimental and computational results. Because if its importance, I communicate his response to my question about it in full:

> This is a good question. The way I like to do this is to set up a theoretical model. You apply one theoretical model essentially to all molecules. This model is one level of approximation. Then you apply this one level of calculation to a very large number of different molecules. In fact, one level of approximation is applied to all molecules, giving you an entire chemistry corresponding to that approximation. That chemistry, of course, would not be the same as real chemistry but it would approach

> that chemistry and if it is a good model, it will approach real chemistry well. What I try to do is to take a given model and then to use that model to try to reproduce a lot of well-known facts of experimental chemistry. For example you try to reproduce the bond lengths in a number of simple organic molecules, or the heats of formation for that set of molecules, in a situation where the experiment is beyond question.Then you can actually do statistics and say that this theory reproduces all known heats of formation to the root-mean-square accuracy of 2 kcal/mol. When you've done that you build some confidence in the level of theory. If you then apply the same theory in a situation where experiment may not exist, you know the level of confidence of your calculations.

Pople fully agreed that it should always be an objective in computational work to indicate experimental errors. He envisioned an ideal relationship between experimental and computational work in which any chemist could use computations. He was not shy in admitting that he, more than anybody else, was responsible for transforming chemistry and making it a computational science, as far as electronic structure was concerned (he added this qualifying expression). Our conversation was recorded three year before his Nobel Prize.

As if responding to Gay-Lussac's challenge, in 1966 Mulliken concluded his Nobel lecture with the following words: "I would like to emphasize strongly my belief that the era of computing chemists, when hundreds if not thousands of chemists will go to the computing machine instead of the laboratory for increasingly many facets of chemical information, is already at hand (*41*)." If we look around today, Mulliken's evaluation has proved correct many times over.

Acknowledgments

I am grateful to E. Thomas Strom (University of Texas at Arlington) for many years of "pen pal" friendship, for the invitation to be part of this Symposium, and for his critical reading of this manuscript. I appreciate Robert F. Curl's (Rice University, Houston) kindness in helping me to secure permission from Edward Lewis to reproduce the photograph of the young Gilbert N. Lewis (his father).

References

1. Wigner, E. P. City Hall Speech—Stockholm, 1963. In *Symmetries and Reflections: Scientific Essays of Eugene P. Wigner*; Indiana University Press: Bloomington, IN, 1967; p 262.
2. Wigner, E.; Witmer, E. E. Über die Struktur der zweiatomigen Molekelspektren nach der Quantenmechanik. *Z. Phys.* **1928**, *51*, 859–886.
3. Wigner, E. *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren*; Vieweg: Braunschweig, Germany, 1931. English translation: Wigner, E. P. *Group Theory and Its Application to Quantum Mechanics of Atomic Spectra*; Academic Press: New York, 1959.

4. Hargittai, I. Learning symmetry from Eugene P. Wigner. In *Eugene Paul Wigner Centennial*; Marx, G., Ed.; Roland Eötvös Physical Society: Budapest, 2002, pp 124–143.
5. Hargittai, M.; Hargittai, I. *Symmetry through the Eyes of a Chemist*, 3rd ed.; Springer: New York, 2009 (hard cover), 2010 (soft cover).
6. Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn & Bacon: Boston, 1991. Reprint edition: Dover Publications, Mineola, New York, 2012.
7. For references, see Hargittai, I.; Menyhárd; D. Further VSEPRing about molecular geometries. *J. Mol. Struct.* **2010**, *978*, 136–140.
8. *Accurate Molecular Structures*; Domenicano, A.; Hargittai, I.; , Eds.; Oxford University Press: Oxford, U.K., 1992.
9. Hargittai, M.; Hargittai, I. Experimental and computed bond lengths: The importance of their differences. *Int. J. Quant. Chem.* **1992**, *44*, 1057–1067.
10. Hargittai, M. Structural Effects in Molecular Metal Halides. *Acc. Chem. Res.* **2009**, *42*, 453–462.
11. Lewis, G. N. The Atom and the Molecule.*J. Am. Chem. Soc.* **1916**, *38*, 762–785; Lewis, G. N. *Valence and the Structure of Atoms and Molecules*. Chemical Catalog Co.: New York, 1923.
12. Hargittai, I. William N. Lipscomb. In *Candid Science III: More Conversations with Famous Chemists*; Hargittai, M., ed.; Imperial College Press: London, 2003; pp 18–27.
13. Heitler, W. *Wave Mechanics* as quoted by K. J. Laidler, Lessons from the History of Chemistry. *Acc. Chem. Res.* **1995**, *28*, 187–192; actual quote on p. 190.
14. Mulliken, R. S. Spectroscopy, molecular orbitals, and chemical bonding. *Nobel Lectures Chemistry 1963–1970*; World Scientific: Singapore, 1999; p 131.
15. Mulliken, R. S. Spectroscopy, molecular orbitals, and chemical bonding. *Nobel Lectures Chemistry 1963–1970*; World Scientific: Singapore, 1999; p 144.
16. Mulliken, R. S. Spectroscopy, molecular orbitals, and chemical bonding. *Nobel Lectures Chemistry 1963–1970*; World Scientific: Singapore, 1999; p 142.
17. Sidgwick, N. V.; Powell, H. M. Bakerian Lecture. Stereochemical Types and Valency Groups. *Proc. R. Soc. London, Ser. A* **1940**, *176*, 153–180.
18. Gillespie, R. J.; Nyholm, R. S. Inorganic Stereochemistry. *Quart. Rev. Chem. Soc.* **1957**, *11*, 339–380.
19. Schmiedekamp, A.; Cruickshank, D. W. J.; Skaarup, S.; Pulay, P.; Hargittai, I.; Boggs, J. E. Investigation of the Basis of the Valence Shell Electron Pair Repulsion Model by ab Initio Calculation of Geometry Variations in a Series of Tetrahedral and Related Molecules. *J. Am. Chem. Soc.* **1979**, *101*, 2002–2010.
20. Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. Bonded and Nonbonded Charge Concentrations and Their Relation to Molecular Geometry and Reactivity. *J. Am. Chem. Soc.* **1984**, *106*, 1594–1605.

21. Hargittai, I. Spirit of Competition: Structure of Proteins. *Drive and Curiosity: What Fuels the Passion for Science*; Prometheus Books: Amherst, New York, 2011; Chapter 4, pp 86–105.
22. Nordheim, G.; Sponer, H.; Teller, E. Note on the Ultraviolet Absorption Systems of Benzene Vapor. *J. Chem. Phys.* **1940**, *8*, 455–458.
23. Anderson, P. Who or what is RVB?. *Phys. Today* **2008**, 8–9. (RVB = Resonance Valence Bond). Anderson was not aware of Teller's prior work: I learned this from Anderson in our e-mail exchange in the summer of 2008.
24. Private communication from Philip Anderson to the author by e-mail in 2009.
25. Hargittai, I. The Great Soviet Resonance Controversy. In *Candid Science: Conversations with Famous Chemists*; Hargittai, M., Ed.; Imperial College Press: London, 2000; pp 8–13.
26. *Sostoyanie teorii khimicheskogo stroeniya v organicheskoi khimii* (in Russian, State of Affairs of the Theory of Chemical Structure in Organic Chemistry); Izdatel'stvo Akademii nauk SSSR: Moscow, 1952. More on the great Soviet controversy related to Pauling's theory of resonance, see, for example: Hargittai, I.; Hargittai, M. *In Our Own Image: Personal Symmetry in Discovery*; Kluwer Academic/Plenum Publishers: New York, 2000; pp 84–88.
27. Hargittai, I. Aleksandr Mikhailovich Butlerov and chemical structure: Tribute to a scientist and to a 150-year old concept. *Struct. Chem.* **2011**, *22*, 243–246.
28. Syrkin, Y. K.; Dyatkina, M. E. *Structure of Molecules and the Chemical Bond*; Interscience Publishers: New York, 1950. For a review, see, for example: Longuet-Higgins, H. C. *Acta Crystallogr.* **1951**, 154–155.
29. Hargittai, I. Linus Pauling. In *Candid Science: Conversations with Famous Chemists*; Hargittai, M., Ed.; Imperial College Press: London, 2000; pp 2–7.
30. Science: Resonance Heresy. *TIME* 1951, September 10.
31. Hargittai, I. The teranucletide hypothesis: a centennial. *Struct. Chem.* **2009**, *20*, 753–756.
32. Hargittai, I. Linus Pauling's Quest for the Structure of Proteins. *Struct. Chem.* **2010**, *21*, 1–7.
33. Berry, R. S. Robert Sanderson Mulliken 1896–1986. *Biographical Memoirs*; The National Academy Press: Washington, DC, 2000; Vol. 78, pp 146–165.
34. Mulliken, R. S. Spectroscopy, molecular orbitals, and chemical bonding. *Nobel Lectures Chemistry 1963–1970*; World Scientific: Singapore, 1999; p 137.
35. Mulliken, R. S. Spectroscopy, molecular orbitals, and chemical bonding. *Nobel Lectures Chemistry 1963–1970*; World Scientific: Singapore, 1999; p 141.
36. Hargittai, I. *Judging Edward Teller: A Closer Look at One of the Most Influential Scientists of the Twentieth Century*; Prometheus: Amherst, New York, 2010.
37. Roberts, J. D.; Braude, E. A.; Coulson, C. A. *Chem. Intell.* **2000**, *6* (4), 58–59.
38. Address given by Roy McWeeny, Professor of Theoretical Chemistry at University of Sheffield, which opened the Fifth Canadian Symposium

on Theoretical Chemistry, held at University of Ottawa in June, 1974, dedicated to the memory of Charles Coulson, F.R.S. McWeeny, R. *Coulson: The Man and the Scientist*. http://www.quantum-chemistry-history.com/Coulson1.htm.

39. Coulson, C. A. Symmetry. *Chem. Br.* **1968**, *4*, 113–120.
40. Hargittai, I. John A. Pople. In *Candid Science: Conversations with Famous Chemists*; Hargittai, M., Ed.; Imperial College Press: London, 2000; pp 178–189.
41. Mulliken, R. S. Spectroscopy, molecular orbitals, and chemical bonding. *Nobel Lectures Chemistry 1963–1970*; World Scientific: Singapore, 1999; p 159.

Chapter 3

George W. Wheland: Forgotten Pioneer of Resonance Theory

E. Thomas Strom

Department of Chemistry and Biochemistry,
University of Texas at Arlington, Box 19065, 700 Planetarium Place,
Arlington, Texas 76019-0065
E-mail: estrom@uta.edu

George W. Wheland, although little remembered by the general chemistry public today, is forever linked to resonance theory through three seminal papers written with Linus Pauling and through two substantial monographs (1944 and 1955) on resonance. At the University of Chicago he carried out research on organic acids and bases, while continuing to publish papers on quantum chemistry. He also wrote three editions of a highly regarded text on "Advanced Organic Chemistry." Sadly, his scientific career ended long before his death when he contracted multiple sclerosis. This chapter gives an overview of his career, writings, and research in quantum chemistry.

Introduction

"Let us now praise famous men, and our fathers in their generations." Ecclesiasticus 44:1. Author Jesus ben Sirach in his book from *The Apocrypha* takes great pains and plenty of space to describe great figures from the Old Testament, because he knew full well that the famous men of one generation are the forgotten men of another. Consider the species below (Figure 1), shown appropriately enough as a superposition of three resonance structures.

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

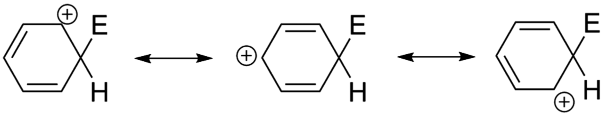


Figure 1. A Wheland Intermediate.

Readers with more recent exposure to organic chemistry will call it a sigma complex. Other readers might name it more precisely as an electrophilic-substituted cyclohexadiene cation or perhaps an arenium ion However, chemists of a certain age will call this species a Wheland intermediate. This term harkens back to a landmark paper by George Wheland, in which he used molecular orbital theory (surprise!) to study the potential intermediates in electrophilic, nucleophilic, and free radical aromatic substitution (*1*). In Figure 2 we see Wheland during his time as a faculty member at the University of Chicago at the time this landmark paper was written.

Figure 2. Wheland in his Chicago faculty days.

In this paper Wheland noted that chemists such as Ingold, Hughes, and Robinson had previously postulated such structures. Indeed, in his blog Henry Rzepa states that Henry Armstrong fifty years before had proposed a similar structure (*2*). Wheland's great contribution was to show by simple molecular orbital calculations that the orientation of substituent placement could be qualitatively reproduced. Around 20 years ago Hubig and Kochi actually observed a Wheland intermediate for aromatic nitrosation (*3*). A few years later Kochi and coworkers used theoretical calculations to demonstrate that their observed Wheland nitrosation intermediate probably occurred at a saddle point, but this same set of calculations also demonstrated that the Wheland intermediate was a true minimum for aromatic nitration (*4*). Of course, the mechanism they invoke is far different from that found in the usual organic textbook.

I believe that Wheland's contributions are little appreciated by the organic chemists of today, although historians of chemistry such as Park (*5*), Simoes, and Gavroglu (*6–8*) certainly give Wheland his due. Because of his early association with resonance theory and with Linus Pauling, Wheland's contributions tend to be swallowed up by his association with Pauling. Ganymede may be the largest of Jupiter's moons, but, when you're looking at Jupiter, it's hard to notice Ganymede. Thomas Hager, whose biography of Pauling covers Pauling's science the best, talks about Pauling setting out to solve the structure of benzene via resonance treatments with his student Wheland (*9*), a characterization that must have made any post-doc reading the book wince. Wheland was a National Research Postdoctoral Fellow and during his time at Cal Tech published articles on resonance and other topics independently of Pauling (*10–14*). Still, when Linus Pauling is your co-author, you must accept being overlooked.

In writing about the career of Wheland, two subjects must be dealt with, if only briefly. 1. What is resonance anyway, and is it related to the earlier concept of mesomerism? 2. Has valence bond/resonance theory, to which the name of Wheland is so closely coupled, been totally eclipsed by molecular orbital theory? Each subject would make up a long chapter, one which I'm not qualified to write, but I will make a few comments about each. For a good account of the connections/differences between mesomerism and resonance, I recommend the books by Nye (*15*) and Brock (*16*).

It's generally accepted that Pauling's original use of the term resonance was derived from Heisenberg's electron exchange idea to account for the interchangeability of electrons (*17*). The usual definition of mesomerism describes the situation wherein the correct character of a particular species can only be captured by using more than one Lewis structure. Isn't that what is generally meant by resonance? Yes, it is, and C. K. Ingold, who coined the term mesomerism, concluded that mesomerism and resonance were essentially the same (*18*). However, resonance does have something more. One can actually put numbers to the enhanced stability derived from a species having more than one possible Lewis structure, although the way the numbers are chosen can be arbitrary even if plausible. Wheland put matters this way in his first monograph on resonance (*19*). *"Resonance always has the effect of increasing the stability, or, in other words, of decreasing the energy of any molecule in which it occurs. ----**The resonance energy**, which is defined as the quantity obtained by subtracting the actual energy of the molecule in question from that of the most stable contributing structure, is therefore always positive. This new principle is probably the most important addition to chemical theory made within the last twenty years."* Resonance is mesomerism with numbers, or, put another way, mesomerism on steroids.

My discussion about the triumph of molecular orbital theory over resonance/valence bond theory has to be longer, because I firmly come down on both sides of the issue. The consensus is that molecular orbital theory has triumphed. Certainly two factors that came into play were the rise of organic photochemistry in the '50's and 60's and the increasing use of visible-uv spectroscopy to characterize compounds. Both of these require discussion of excited electronic states, something far more natural to molecular orbital theory than resonance/valence bond theory.

Pauling's biographer Hager likens the situation to the fable of the tortoise and the hare, with the slower molecular orbital tortoise finally catching the hare (*20*). At the end of the 20th century, Brush gave an overview of this contest as it played out in explaining the special stability of benzene (*21*, *22*). His overall conclusion was that molecular orbital theory was currently the victor. However, the 21st century sees some revival of valence bond methods. An interesting conversation on the rivalry involving Roald Hoffmann, Sason Shaik, and Philippe Hiberty appeared in 2003 in *Accounts of Chemical Research* (*23*) with rejoinders by Roberts (*24*) and Streitwieser (*25*). A recent book by Shaik and Hiberty makes the case that reports of the death of valence bond/resonance theory may have been exaggerated (*26*).

Nevertheless, I can give some personal testimony as to why many chemists favored molecular orbital treatments over valence bond/resonance treatments. In the early 1960s I was carrying out graduate work on electron spin resonance studies of anion radicals. Such radicals, particularly those of aromatic hydrocarbons, could be treated very well by Hückel molecular orbital theory. The hyperfine splitting of such radicals could be accurately given by the McConnell equation (*27*), using a simple direct proportionality between the hyperfine splitting and the Hückel spin densities. A modification of theory by McLachlan (*28*) to allow for the calculation of negative spin densities broadened the scope of such molecular orbital treatments even further. Then came the publication in 1961 of Andy Streitwieser's marvelous book on Hückel molecular orbital calculations (*29*). I devoured the book and taught myself to solve the secular equations to calculate Hückel energies and coefficients by hand. With the judicious use of group theory I could handle pretty large systems, and for even larger systems I could use the main frame computer to diagonalize the appropriate matrices.

Contrast that with the use of resonance/ valence bond theory to carry out comparable calculations. I bought a book, which shall remain nameless, on the topic and found that a calculation on naphthalene would entail dealing with 42 canonical structures, while a similar calculation on anthracene would necessitate the use of 429 canonical structures. I silently screamed and closed the book forever. The mathematical difficulties undoubtedly turned many people off quantitative calculations with resonance/valence bond theory.

Brush surveyed the teaching of aromatic chemistry in a number of textbooks, and he concluded that the increased use of molecular orbital theory in organic textbooks to explain benzene chemistry marked the triumph of molecular orbital theory in the last 30-40 years of the 20th century (*22*). The molecular orbital treatment that gave a satisfactory explanation for aromaticity was carried out by Erich Hückel back in 1931 (*30*), although appreciation by organic chemists for Hückel's accomplishments was many years coming. I mentioned Hückel molecular orbital theory above, and elsewhere in this book Andrew Streitweiser tells something of Hückel's insights in his chapter. A number of years ago Jerome Berson wrote an appreciative article on Hückel (*31*), which he later expanded in a section of a book (*32*). Very recently Andreas Karachalios wrote a full-fledged biography of Hückel (*33*). To give Hückel's results briefly, his treatment explained the aromaticity of benzene, the high acidity of cyclopentadiene, the lack of aromaticity of cyclobutadiene and cyclooctatetraene, and predicted aromaticity for cycloheptatriene cation. Aromaticity occurs when the molecular orbitals are completely filled, *i.e.* closed shell. This happens for systems with 2, 6, 10, etc. pi electrons. Most people attribute the snappy 4n + 2 description of this situation to Doering and Detert (*34*), although they reversed the numbers (2 + 4n).

My experience teaching organic chemistry leads me to believe that Brush claims a bit too much for molecular orbital theory. I think you readers need to know the rest of the story. Of course, my survey covers only ten organic texts, five of which I have taught from, and it is mostly limited to recent years (*35*). Generally resonance is treated right at the beginning of the texts in a very traditional manner. Usually no names are connected to the principle of resonance, but when a name is mentioned, it is Pauling, not Pauling and Wheland. When the chapter on aromatic systems appears, all the texts teach Hückel's Rule (4n + 2), and earlier there is often enough exposition about the molecular orbitals of polyenes that the Woodward-Hoffmann Rules can be justified. However, the descriptions of benzene normally start with the two Kekulé structures, which are denoted as resonance structures. The extra stabilization of benzene as compared to cyclohexene is duly noted, and some texts call this stabilization energy resonance energy. When the following chapters treat substituent effects on electrophilic aromatic substitution, molecular orbital theory is completely thrown into the ditch. The typical treatment shows the three resonance structures of the Wheland intermediate, and activation, *ortho/para* orientation are justified by a substituent stabilizing one of the resonance structures (alkyl groups) or providing a fourth resonance structure (alkoxy and amino groups). In the same fashion, deactivation, *meta* orientation are justified by a substituent (nitro, cyano, etc) destabilizing one of the resonance structures of the Wheland intermediate for reasons of positive charges being uncomfortably close to each other.. Later in the texts the acidity of enolate anions is completely explained by showing the two resonance structures---one with the negative charge on the alpha carbon; the other with the negative charge on the oxygen. To sum up, resonance explanations are alive and well in the normal organic textbook. Organic chemistry textbook authors are a pragmatic lot, and when molecular orbital theory works best, *i.e.*, 4n + 2, they use it; and when resonance theory works best, they also use it.

The main point of this introductory section has been to show that the supposed triumph of molecular orbital theory has resulted in a perception that Wheland's accomplishments occurred in a back water of quantum chemistry. The following sections will deal with Wheland's life and career, his books, and his research in quantum chemistry. To jump ahead to some of my conclusions, this chapter will point out that Wheland was perfectly able to use molecular orbital theory when he felt it was justified, that resonance theory still has great utility, and the great tragedy was that Wheland's illness struck him down just at the time when computer advances were greatly enlarging the scope of quantum chemistry.

Wheland's Life and Career

The two nouns in the heading for this section were chosen with some care. A life is not the same thing as a career. Of course, for some people their career is their life. Wheland had a successful career, sadly shortened by illness, but he did have a life outside of chemistry.

Figure 3. The very young Willard Wheland.

George Willard (Bill) Wheland was born on April 21, 1907, in Chattanoga, TN (*36*). The first syllable of the last name is pronounced “whee” rather than “whey”. He was the youngest child of Zenas Windsor Wheland (known as Win) and Lena Wheland. He had three older sisters: Mary, Dorothy, and Betty, all of whom were college educated. His father had a mechanical engineering degree from Cornell, and Win and his brother ran the Wheland Company, a foundry in Chattanooga. Wheland was normally called Willard in articles in his home town newspaper, and later he was referred to as Bill, although Linus Pauling referred to him as George in correspondence. Figure 3 shows Wheland as a young boy.

Wheland’s father may have influenced his liking for mathematics. His father was interested in mathematical proofs that 1 = 2, and Wheland maintained an interest in these faulty proofs the rest of his life. Later when he was a resident associate at Cal Tech, a local paper published an article on his collection of eight such “proofs”, with his noting the fallacy in each.

For preparatory school Wheland attended Baylor Military Academy in Chattanooga. This school had the usual college preparatory courses of the time, with Wheland taking four years of Latin, two years of Spanish, ancient, American, and Biblical history, plus the mathematics courses normally available in the high school curriculum. Figure 4 shows Wheland in his Baylor uniform. He was the valedictorian of his class, and his address was published in the Chattanooga paper. His address was idealistic, as one would hope, and I reproduce a small section below.

“Just as a nation attains a place among the nations of this world by striving for high ideals, so a school becomes known for its high ideals. Baylor has risen to her high prominence in this community, and, indeed, throughout the entire south, by her constant devotion to her noble ideal---the development of boys for Christian citizenship. We have been taught that man has a threefold nature---that there is the physical, the mental, and the moral man---and Baylor has endeavored to develop her boys physically, mentally, and morally.”

Wheland entered Dartmouth in the fall of 1924, and his career there was sterling indeed. I did not realize that universities had valedictorians, but at that time Dartmouth did; and Wheland was the valedictorian, graduating *summa cum laude*. He was a Rufus Choate Scholar all four years. In his freshman year he won the Churchill Award, given to the class member who most nearly measured up to ideals expressed by the donor---*“honesty with oneself, fairness to others, sensitiveness to duty and courage in its performance. These qualities make character, and on character rests the structure of society.”* In his sophomore year he won the Thayer Prize in mathematics, an award open to students in all four years of math studies. He was elected to Phi Beta Kappa in his junior year. In his senior year he won the Hazeltine Award in chemistry and physics, the Warren Prize scholarship award given to the highest ranking student in the senior class, and the Charles O. Miller, Jr. Memorial Fellowship, which paid for two years of graduate work at the university of his choice. He was a member of Alpha Sigma Phi fraternity and a member of the university rifle and fencing teams. Figure 5 shows Wheland as a member of the fencing team.

Figure 4. Wheland in his Baylor uniform, probably in his junior or senior year.

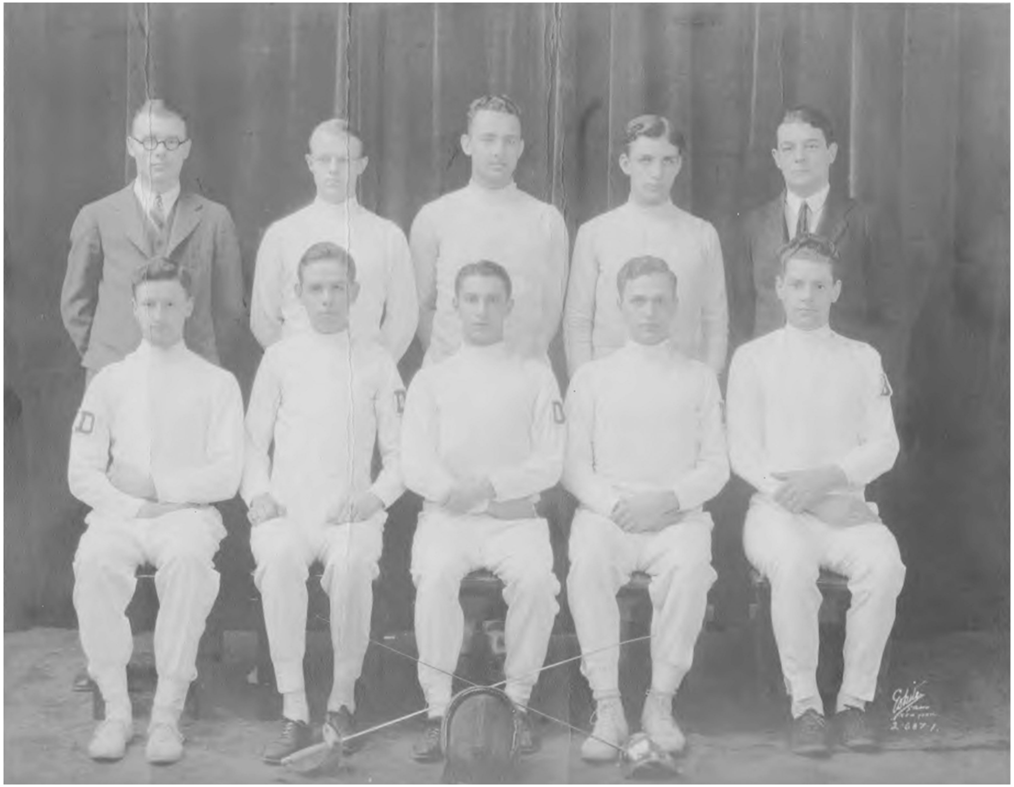


Figure 5. The Dartmouth fencing team. Wheland is second from the right on the front row.

Wheland did receive a B in quantitative analysis, but he received A's in every other chemistry course, every physics course, and every mathematics course. He had three years of mathematics courses, two years of physics courses, and three years of German plus the usual chemistry curriculum. His mathematics courses included statics, calculus, analytical geometry, advanced calculus, and differential equations. His physics courses included a year of general physics---mechanics, sound, heat, electricity, magnetism, and light---and a year of experimental physics on the preceding topics. There seems to be no indication that he had a course in quantum mechanics. Compared to the usual chemistry curriculum of that day, Wheland clearly was exposed to much more mathematics and physics, a background that would serve him well working with Linus Pauling.

In the fall of 1928 Wheland entered graduate school at Harvard, choosing to do his Ph.D. with noted faculty member and soon to be Harvard president James Bryant Conant. Frank Westheimer states that in those days there was a pipeline from the Dartmouth chemistry department to James Conant at Harvard, a path that Westheimer also traveled (*37*). Wheland received his M.A. degree in 1929 followed by a Ph.D. in 1932 (*38*). He had his Miller Fellowship for the first two years, and the last two years he taught, probably serving as the equivalent of a present day teaching assistant. His thesis on organic acids resulted in his first publication jointly with Conant (*39*). He studied extremely weak acids ranging in acidity from acetophenone to dimethylphenylmethane, ranking them in order of acidity and making rough estimates of their pK's. This involved working under strictly anhydrous conditions under a nitrogen atmosphere, the type of studies we would do nowadays in a glove box. This work perhaps inspired his later work on organic acids and bases. I found no evidence that Wheland had taken any quantum mechanics courses at Harvard, because the Harvard registrar informed me that Wheland's transcript was missing. Westheimer notes that the physical chemistry course at Harvard was taught by Kistiakowsky, and the only quantum mechanics given was Bohr theory, no Schrödinger equation (*37*). Possibly Wheland taught himself quantum mechanics, and he certainly could have audited the appropriate courses at Cal Tech.

In 1932 Wheland received a National Research Fellowship, and he used it to become a post-doctoral fellow with Linus Pauling at Cal Tech. I can only guess at the reasons for this choice although probably interactions between Conant and Pauling played a part; but I would also imagine the thought of spending winters in Southern California instead of New England would be attractive. Even more attractive would be the idea of working with Linus Pauling. Pauling had won the Langmuir award in 1931. This award later morphed into the ACS Award in Pure Chemistry, probably still the most prestigious award for a young chemist. Pauling was rightly regarded as the most brilliant young chemist in the country and working with Pauling was likely to lead to great things, and so it proved.

Wheland's time at Cal Tech was productive indeed. Eight publications resulted, three of them written with Pauling, four by Wheland alone, and a single experimental paper written with Doescher on magnetic susceptibility of metal ketyls (*12*). Pauling was extremely pleased with Wheland. In an early letter to Conant (*40*), he stated *"I am grateful to you for recommending Wheland. He is a very able man in mathematics and quantum mechanics, only one of my men being* *his equal."* (I wonder who that was.) In a later letter Pauling commented (*41*)," *Dr. Wheland is still with me. He is a very good man in theoretical work."* The net result was that Wheland was regarded as a "comer," likely to land a faculty position at a first rate university. His marketability was only enhanced by his winning a Guggenheim Fellowship in 1936 for study in England.

Wheland met his wife Betty Babson Clayton during his California stay. They met at a party given by a friend of Betty's mother. This friend was also a friend of Wheland's mother back in Chattanooga. This friend thought that young Willard Wheland should have a social life and meet some young ladies, so she threw a party and invited Wheland, Betty Clayton, and Betty's mother among others to the party. Wheland asked Betty out, and they became a couple. Wheland planned a romantic proposal---a drive up Mt. Wilson where he would propose as they looked over Los Angeles. But LA was fogged in that evening. He proposed on another evening when there was a view. When they married, they lived on Wheland's $1800 yearly salary. Their apartment was across from the Los Angeles Symphony practice hall. Since they both loved classical music, they greatly enjoyed that location. Figure 6 shows the young couple on April 1, 1934, as they enjoy Wheland's new car. They were married on August 11, 1934.

Figure 6. George Wheland and fiancé Betty Clayton, April 1, 1934.

Wheland's year in Europe with his Guggenheim Fellowship is covered well on pp. 36-37 of Park's article (*5*). He spent time at University College London visiting with Christopher Ingold and at Oxford where he worked with Cyril Hinshelwood. He also visited such luminaries as Sommerfeld, Hückel, and Lennard-Jones. Park says that Wheland received an offer of an assistant professorship at the University of California at Los Angeles and could have gone back to Cal Tech as a post-doc, but he chose to become an instructor at the University of Chicago. At present, the accepted path for a young academician is to join a faculty at the assistant professor level, hopefully to ascend the path to full professor, while instructors are usually lecturers with no research duties. Back in the 1930s, starting as an instructor as a way toward becoming a full professor was not unusual.

At the time Wheland joined the Chicago faculty in 1937, the fine inorganic chemist H. I. Schlesinger was the de facto chair of chemistry, although his title was Secretary. Chicago President Robert Maynard Hutchins hated scientists and science and in particular Schlesinger, so he refused to allow him to be called Chairman (*37*). Pauling wrote a very strong letter of support for Wheland to Schlesinger (*42*), stating that *"---his knowledge of descriptive and theoretical organic chemistry being especially extensive. He also has a grasp of quantum mechanics comparable with that of the leading theoretical physicists."* However, the key figure in hiring organic faculty was the ground-breaking free radical chemist, Morris Kharasch. Kharasch intended his organic faculty to be physical organic chemists before the term came into existence. Wheland joined a junior organic chemistry staff of Frank Westheimer, Frank Mayo, and Weldon Brown. When H. C. Brown joined the organic faculty in 1939, Gortler (*43*) maintains that *"this was probably the largest group of first rate physical organic chemists ever assembled at a single institution."* I personally doubt that any faculty since has matched that array of physical organic chemists.

Wheland fit in very well with that bright group of organic chemists, and they were pleased to have him in their midst. Westheimer (*37*) recalls that *"I especially enjoyed Bill Wheland, whose mind was built on precision lines, and didn't let anything shoddy slip by. A marvelous person with whom to talk---."* Westheimer also says, *"My great and good friend George Willard (Bill) Wheland, who was sick most of the years I knew him, was, I'm convinced, one of the brightest people who has ever lived on the earth."* Frank Mayo (*44*) mentions how amazed he was that Kharasch was able to bring Wheland into the faculty. Westheimer had an office across the hall from Mayo, and Wheland had an office on the floor below. Mayo says they would often meet in Mayo's office for lunch, as Mayo had the biggest office.

Wheland progressed through the ranks from instructor (1937 to assistant professor (1943). His publications, then and later, followed a pattern. He published in two areas, quantum chemistry, in which he was often but not always the sole author, and physical organic chemistry, in which the experiments were carried out by graduate students. His relationship with the *Encyclopaedia Brittanica* began sometime after his promotion to assistant professor. The *Brittanica* tended to use faculty of the University of Chicago as resources and editors. Wheland was the Editor of the Chemical Section of the encyclopedia and the author of the sections on Isomerism and Stereochemistry. I wonder if his very clear explanations of such topics in his advanced organic chemistry textbooks came about because of the need to write explanations for a more general readership. His children remember that the new year would begin with the arrival of a new, complete set of the *Encyclopaedia Britannica*. At the end of the year, they would have to ship the now old set back, but it would soon be replaced with a completely new set.

In 1944 Wheland published his first landmark book on resonance. Wheland's books will be discussed in more detail in the next section, but this book provided a much-cited example of his vivid writing, in which he tried to make a distinction between tautomerism and resonance (*45*). *"The significance of the above distinction between tautomerism and the newer concepts can be made clearer with the aid of an analogy. A mule is a hybrid between a horse and a donkey. This does not mean that some mules are horses and the rest are donkeys, nor does it mean that a mule is a horse part of the time and a donkey the rest of the time. Instead, it means that a mule is a new kind of animal, neither horse nor donkey, but intermediate between the two and partaking to some extent of the character of each. Similarly, the theories of intermediate stages and of mesomerism picture the benzene molecule as a having a hybrid structure, not identical with either of the Kekulé structures, but intermediate between them."*

Park (*5*) points out on p. 38 of his article that a book on resonance was to be written together by Pauling and Wheland. For some reason this project never came to fruition. Perhaps Pauling decided to focus instead on his classic *The Nature of the Chemical Bond*. Wheland did dedicate his book to Pauling, and it was well received. Wheland's promotion to associate professor followed in just two years.

Right after the completion of the book on resonance, Wheland put his notes from his class on advanced organic chemistry into a book with that title. This first edition was mainly for student use and was published by the University of Chicago bookstore in two parts in 1946 and 1948 (*46*). This book was transformed in 1949 into the second edition of *Advanced Organic Chemistry* (*47*). Perhaps coincidently, perhaps not, that same year Wheland was promoted to full professor. This textbook will be discussed in more detail later in this chapter.

Wheland's visibility as a prime promoter of resonance theory attracted attention from overseas. Perhaps this attention was not the type that most of us would like, but it amused Wheland. Both Pauling and Wheland came under strong attack from Communist Russia. Russell (*48*) describes the situation as follows. *"Soviet science took up arms against the resonance hypothesis (variously associated with the names of Pauling Wheland and Ingold) and declared it to be ideologically unacceptable. The use of imaginary ideal "structures" to describe real molecules was incompatible with the dialectical materialism of Marx, Engels, and Lenin.----- a strong attack on resonance came in an article "On a Machist theory in chemistry and its propagandists" by V. M. Tatevskii and M. I. Shakhparanov. Other articles appeared in Pravda and elsewhere in celebration of Stalin's 70th birthday demanding reforms in chemical thinking. Matters reached a climax with conferences in 1950 and 1951, in which the second of which an all-Union resolution was passed replacing the theory of resonance by a "theory of mutual influences.""*

For those of us who don't read Russian (which is most of us), an article was published by Hunsberger (*49*) in *J. Chem. Educ.* which summarized many of the Russian attacks. However, the flavor of the controversy is best captured by István Hargittai in his article "When Resonance Made Waves" (*50*). This piece was later reprinted in a book (*51*). An excellent historical account of the Soviet attacks on resonance theory is that by Graham (*52*). From present day perspectives with fewer people remembering the cold war, the Russian reaction seems bizarre.

What brought about the fuss---perhaps paranoia coupled with a fear of foreign influences?

The Russians called for a return to the principles of their great chemist Butlerov, who proposed that the structure of a compound be described by a single formula, which showed how every part was linked to every other. There is no doubt that Butlerov was a significant figure, whose contributions have been overlooked by western scientists. There is an interesting coincidence that makes me wonder if Wheland's previous research could have raised Russian ire. The second part of Wheland's Ph.D. thesis (*38*) deals with studies of Butlerov's acid (Wheland used the alternative spelling Butlerow). Wheland showed that Butlerov's proposed structure was incorrect, and the supposed pure compound contained two compounds. However, to my knowledge this second part of the thesis was never published in the open literature.

The late 40's also saw a disagreement, dispute would be too strong a word, between Pauling and Wheland over the exact meaning of resonance. The question was whether the various Lewis structures making up a resonance hybrid had any sort of "real" existence, or were they merely a mathematical artifice, forced into being by the requirements of the variation theorem. Hager describes how these disagreements came into the open via a three way correspondence between Pauling, Wheland, and Kasimir Fajans from the University of Michigan about the meaning of resonance (*53*). Pauling seemed to still attribute some sort of physical reality to the various resonance structures, while Wheland seemed to come down on the side of the structures being a mathematical aid. The subtleties and nuances of the Pauling/Wheland disagreement are brought out nicely on pp. 35-45 of Park's article (*5*).

Despite his uses of various Lewis structures (canonical structures) in Wheland's papers, I believe Wheland was firmly in the camp of the structures merely being a mathematical artifice. First, I need to give a brief description of the variation method, which is an approximation method. If it is not possible to know the true wave function for a particular complex system, then you can make a guess at a trial wave function. When the Hamiltonian acts on that function, the energy obtained will either be the true energy (best case but not likely) or greater than the true energy. If you then put several adjustable parameters into your trial wave function, you can come closer and closer to the true energy quicker than you can approach the true wave function. The successful use of the variation method involves being able to make shrewd choices for the trial wave function.

With that in mind, I want to discuss a mathematical analogy Wheland placed in all three editions of his *Advanced Organic Chemistry* (*46*, *47*, *54*) in the chapters on "The Theory of Resonance" and his use of the analogy to suggest that the canonical structures do not have any physical significance. In all three editions this segment runs around ten pages, and it is essentially identical in all three editions. Since the first edition was basically Wheland's course notes, he must have been using this analogy for several years before publishing the first section of his text in 1946.

The analogy is as follows: there are two equal line segments AB and BC that are attached to rigid supports A and B. The two segments meet in the middle at C. If you exert a fixed force F at position C through a new line segment CD, what is the force P exerted on the supports A and B as a function of the angle between the chords AC and BC? The solution can be solved exactly through the laws of statics, but Wheland posits that the imaginary physicist involved in solving the problem doesn't know either statics or trigonometry. For low bond angles, P = ½ F, while for really large bond angles P goes to infinity. Wheland shows an empirically derived equation, incorporating the behavior of the system at both low and high bond angles, but consisting of two sections with identical absolute values but opposite signs gives results coming very close to those of the exact solution. I can't imagine that the usual organic chemistry student could relate to this example very well, but it is a good introduction to the uses of the variation procedure. The coefficients for the two sections of the empirical equation were identical, and Wheland goes on to equate them to the two Kekulé structures for benzene. I'd best quote Wheland in full at this point (*55*). Concluding this section by referring to molecular orbital treatments, Wheland says *"mention should be made of at least one relatively satisfactory method for the quantum-mechanical treatment of molecular structure (the so-called molecular-orbital method), which makes no explicit use of the concept either of structure in the familiar chemical sense or of resonance among different structures. This method will not be employed, nor mentioned further, in this course, but the fact of its existence is of considerable theoretical interest in that it makes apparent the arbitrariness of the approach which is based upon the principles of the classical structural theory, and which will be employed in this course. Since, for the reasons given, the structures among which resonance is presumed to occur in any given instance are merely intellectual constructions devoid of physical significance, it is apparent that no meaning can be assigned to the relative amounts of time which the molecule spends in each of the structures involved. In other words, one cannot legitimately speak of the molecule as passing back and forth from one resonating structure to another, and one cannot assign any definite frequency to such a transition."*

Wheland seems very clear on this point. Since mathematical statics was one of the math courses he took at Dartmouth, I speculate his exposure to this course may have led to his taking an agnostic's position on the reality of various Lewis structures involved in resonance.

It is certainly possible that in the early 1950s Wheland became discouraged as to future possibilities in quantum chemistry. In his scientific autobiography (*56*), Klaus Ruedenberg states *"In view of my background, I thought it might prove fruitful to combine my training in chemistry and in quantum theory. Serendipitously, Robert S. Mulliken, then one of the few leaders in this field, was also a member of the physics department and willing to accept me as a postdoctoral fellow. On the other hand, the physical organic chemist George Wheland strongly advised me against this career choice because, as he put it, "you will never be able to calculate anything useful." In view of the then available means for quantitative computations, he was absolutely right, and I would have come to regret my decision to disregard his counsel had it not been for the revolutionary subsequent development of electronic computers."* Later Ruedenberg stated that he was unable to persuade Wheland to give a seminar to the Mulliken group (*57*). *"I was particularly interested in learning about resonance theory from him. However, he declined saying "I have nothing to say." I remember his very words and I also remember being very disappointed."* This was in the 1952-1954 time period. Reudenberg goes on to say *"I remember that Mulliken and Platt, as well as everybody else, had great respect for him. But they were not surprised, it seemed, that he did not want to give a seminar to us. Of course, we were in the physics department and he was in the chemistry department. For all these reasons I never got to know him better although I would have liked to know him more closely. Personally, he struck me as kind, unassuming, serious, but no-nonsense tolerating."*

In 1954 Wheland's alma mater, Dartmouth, recognized his achievements by giving him an honorary Doctor of Science degree. The citation read by Dartmouth President Dickey describes Wheland's honors at Dartmouth and quotes a letter written in 1938 by Linus Pauling to a Dartmouth chemistry teacher of Wheland's, Professor Hartshorn, "*there is no other man in the world who has a similar grasp of both organic chemistry and the quantum mechanics."*

The multiple sclerosis that later struck Wheland down showed up in the late 1950s, although Frank Westheimer, who left Chicago for Harvard in 1953, saw signs of illness even earlier (*37*). Graduate students taking his advanced organic chemistry course in the 1957-58 academic year noticed that he would step out of the room briefly in the middle of his lecture or stand silently beside the podium for a short time. There was only one paper after 1956, although he did finish his second resonance book in 1955 and the third edition of his textbook in 1960. Somewhere around 1963 or 1964 he became unable to function as a faculty member, although he never officially retired.

Wheland was an avid photographer, and he also enjoyed hiking. As the multiple sclerosis progressed, he was unable to do those things. However, he and his wife Betty would listen to classical music on FM radio and share good reading and good conversation. Eventually the illness caused almost total paralysis. Wheland died on December 28, 1972. Funeral services were held at St. Paul Union Church in Chicago. He was cremated, and much later interment services were held on June 2, 1973, in his home town of Chattanooga. At the funeral, tributes from his former faculty associate Frank Westheimer, his Chicago colleague Clyde Hutchison, and his last graduate student William LeNoble were read.

Westheimer wrote, *"Bill was a great man. He made enormous contributions to theoretical chemistry, and his two books set standards of intellectual rigor that continue to inspire other writers, even if they cannot come up to his mark. He was a fine man, a friend, and a reliable colleague. Despite his outstanding position in science, he was no prima donna, but met his day-to-day obligations like the rest of us. He had a marvelous sense of humor, but it was not biting unless perhaps when he was engaged in making fun of himself. That such a man should be struck down by an unknown neurological illness was a major tragedy for science and for his friends, as well as to himself. The courage with which he faced that illness was in keeping with his character."*

Hutchison noted that *"For me it was a pleasure to have known Bill, to have talked with him at length concerning scientific matters, and to have published a paper with him. I have always regarded him as one of the profoundest and most intelligent thinkers in the field of quantum chemistry."*

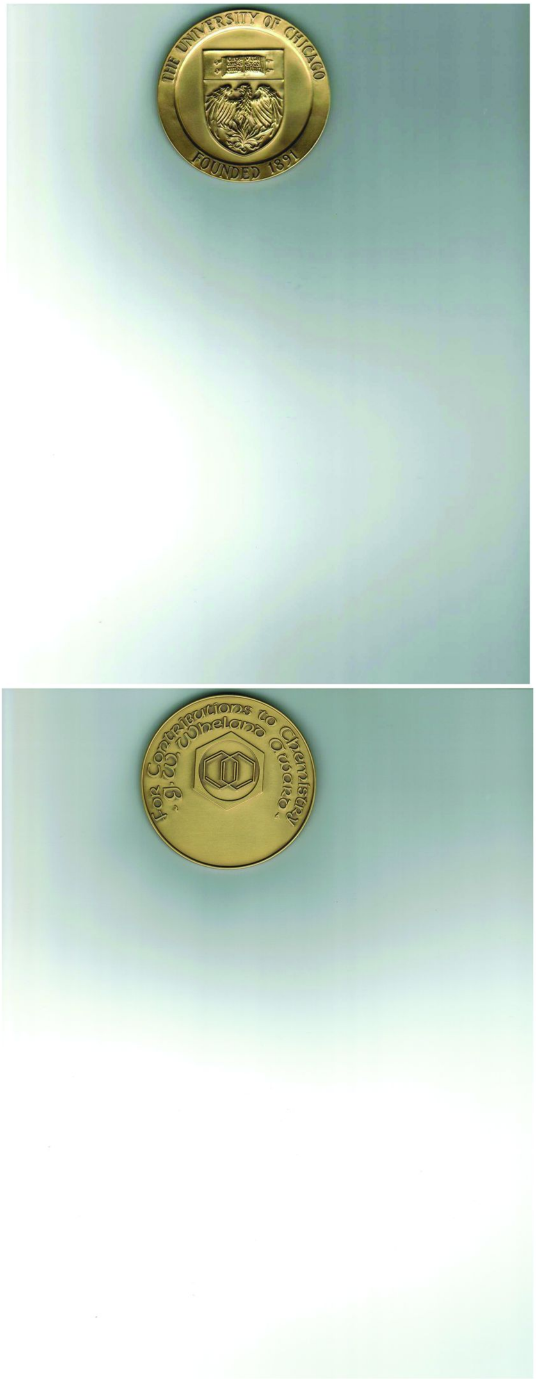


Figure 7. The two sides of the Wheland Medal.

William LeNoble contributed *"I hope you will find consolation in the fact that he achieved so much in his career. He achieved this especially through his books. Unlike most writings in organic chemistry, which are already partly out of date when they appear, his books have a quality of scholarliness that makes them timeless. They are still among the most quoted in the journals now, and as time goes by it will be clear that they richly deserve their description as classics.*

I would also like to assure you that his passing is not just a loss for you and your family alone. His students and the many scientists who knew him universally and genuinely liked him, not only because of his scholarly and incisive insights into the nature of our work, but also because of his fine personal qualities. His gentleness, his even temper, his wry sense of humor made him unique to us. I really don't believe I've ever known a man with a personality quite like his."

Wheland's fellow faculty member Stuart Rice spearheaded an effort to create an award honoring Wheland. With support from Wheland's colleagues, his former students, and his family, an endowment was obtained to support a Wheland lecture with an honorarium plus a Wheland medal. Rice and Wheland's faculty colleague Gerhard Closs designed the medal. One side of the medal shows, quite appropriately, two overlapping hexagons with the two Kekulé structures. Figure 7 shows the two sides of the Wheland Medal.

The first Wheland Award Ceremony was held on November 10, 1976. Fittingly, Wheland's great friend Frank Westheimer made the opening remarks. In these remarks Westheimer spoke of Wheland's research accomplishments, but I will just quote what Westheimer said about Wheland, the scholar, because in preparing this chapter I have become convinced that over and above being an outstanding researcher, Wheland was a scholar to the bone.

"He was a true scholar who had made his name through highly original creative research but who then turned to work of scholarship that raised the level of understanding of chemists throughout the world. Science cannot now utilize many pure scholars. It needed Wheland at least in part because he was such an extraordinary one. His first and perhaps most impressive work of scholarship was his book on "The Theory of Resonance" published in 1944. The second edition entitled simply "Resonance in Organic Chemistry" was published in 1955. Both books were careful and precise expositions written for mathematically semiliterate organic chemists by an expert who was in control of all the needed mathematical sophistication. The rapid understanding of the application of quantum chemistry to organic chemistry that grew up around the world was a product in considerable measure of Wheland's books. His next text "Advanced Organic Chemistry" provided lucid, thorough, logical—above all intellectually honest explanations of phenomena of organic chemistry. For generations organic chemists had been regarded as cooks. Wheland's text helped immeasurably to convert it to a science.

The first winner of the Wheland Medal was University of Chicago faculty member Michael Dewar. Like Wheland, Dewar was well known for his applications of quantum mechanics to organic chemistry. Wheland's career is summarized in Table 1, while Table 2 lists the winners of the Wheland Medal thus far. The 19 winners are indeed an illustrious crew, and three of the winners received their medals prior to winning the Nobel Prize in chemistry: Frederick

Sanger, John Pople, and Robert Grubbs. Sanger had won the prize in 1958, but he won it again in 1980, two years after receiving the Wheland Medal.

Finally, other voices should be heard about their impressions of George Wheland, some more of his peers, some of the students from his class, his last two graduate students, and his children. John D. Roberts (*58*) comments *"I met with Westheimer and Wheland several times in Chicago, and we had a lot of long and hard talks about resonance and Hückel MO theory, where Wheland and I did most of the friendly arguing and Frank Westheimer tended to be a referee. Wheland was very knowledgeable about MO theory—"* Roberts states that back in 1934 Wheland (*11*) showed that molecular orbital theory gave a better explanation of the low acidity of 1,3,5-cycloheptatriene than resonance theory. Stuart Rice (*59*) states *"Wheland was an underappreciated but important contributor to the development of modern interpretations of organic reactions. This information should be made more widely available."*

Gerhard Closs told an interesting story about Wheland relayed to me through Roy Olofson (*60*). The area around the University of Chicago was a high crime area in the 1950s and 1960s. Indeed, that is the reason that Frank Westheimer cites for his move from Chicago to Harvard (*37*). Apparently Wheland had been mugged a couple of times. He told Closs the ideal amount of cash to carry, which was $12, all in one dollar bills. He said the number of muggers would likely be from one to four. Dividing $12 by either one, two, three, or four would always give an even amount per mugger, so they were likely to be satisfied with that amount and let you leave with no further damage. Who says mathematics can't be practical?

Figure 8. George Wheland in his University of Chicago office.

Table 1. A Brief Overview of the Career of George Willard (Bill) Wheland

Born: April 21, 1907, Chattanooga, TN, Youngest of four children and the only son

Education:

Baylor Military School, Chattanooga, 1924, Valedictorian

Dartmouth, Freshman, Churchill Prize; Sophomore, Thayer Prize for Distinction in Mathematics; Junior, Phi Beta Kappa; Senior Valedictorian, Fellowship for Graduate Study, BS, 1928

Harvard, MA, 1929, Ph.D., 1932, Mentor, James Bryant Conant

Career Summary:

1932-1936 National Research Fellowship at Cal Tech with Linus Pauling

1936 Guggenheim Fellow, University College London and Oxford

1937-1943 Chemistry Instructor, University of Chicago

1943-1946 Assistant Professor, University of Chicago

1944 Author, *The Theory of Resonance*

1946-1949 Associate Professor, University of Chicago

1946, 1948 Author, *Advanced Organic Chemistry*, 1st Edition

1949 Author, *Advanced Organic Chemistry,* 2nd Edition

1949-1972 Professor, University of Chicago

1955 Author, *Resonance in Organic Chemistry*

1960 Author, *Advanced Organic Chemistry*, 3rd Edition

Miscellaneous:

1954 Honorary Doctor of Science Degree, Dartmouth College

Editor of the Chemical Section of the *Encyclopaedia Brittanica*

Member ACS, APS, Sigma Xi, AAAS, Wheland Medal named In his honor, 1976 and continuing

Personal Information:

Married Elizabeth (Betty) Clayton, August 11, 1934

Children: Dr. Margaret Wheland Couch (1941), Dr. Robert Wheland (1944)

Died: December 28, 1972

I obtained descriptions of Wheland's teaching style in his advanced organic chemistry class from Roy Olofson (*60*), Leon Gortler (*61*), Tom Curphey (*62*), and Henry Paulus (*63*). This three quarter course had lectures four times a week plus a discussion section on Monday. The course was supposed to cover synthetic organic chemistry as well as physical organic chemistry. Since Wheland did not lecture on synthetic chemistry, each week he assigned the class several pages out of the synthesis textbook by Wagner and Zook (*64*). The class would then take a weekly quiz on the synthesis readings in their Monday discussion section. Olofson remembers the exams on the lectures as having long questions involving discussion. Curphey remembers that Wheland's lectures were not dramatic but very clear and ordered. Gortler remembers that students were told they could look over Wheland's notes in his office if they so desired. Gortler did so on several occasions and remembers that the office seemed like a very *long* closet, poorly lit with two desks, each having a single desk lamp. Olofson remembers Wheland sitting in a large overstuffed chair. The ceiling was very high, and the walls were filled with book shelves from top to bottom. Paulus remembers Wheland as being a low-key person who presented the material with great conviction. He also remembers an amusing incident in which Wheland's second resonance book, *Resonance in Organic Chemistry*, was listed in the University library catalog as "Renaissance in Organic Chemistry," a title thought quite appropriate. Figure 8 shows Wheland in his office.

Table 2. Winners of the Wheland Medal

1976 M. J. S. Dewar	1997 Paul Sigler
1978 Frederick Sanger	2000 Edward Solomon
1981 John Pople	2003 Harry Gray
1983 Joseph Chatt	2006 Makoto Fujita
1986 Frank Westheimer	2007 James Barber
1988 Harden McConnell	2008 George Whitesides
1991 Nelson Leonard	2009 Christopher Walsh
1992 Robert Grubbs	2010 Stuart Schreiber
1994 Fred Wudl	2011 E. W. (Bert) Meijer
1995 Robert Baldwin	

Wheland's son Robert has the following memories of his father's office (*65*). *"My recollection of my father's office is that it was large, dark, undecorated to the point of feeling unfinished (pipes showing, everything faded), and crammed with row after row of utilitarian metal shelves loaded to capacity with books and journals, the biggest office library I have ever seen. The collection ranged from monographs to series such as a complete Beilstein. And, it smelled fascinatingly of chemicals, not because there were chemicals in the office, but because the U of C chemistry building was ancient, rich with wood well marinated by decades of pre-OSHA bench top chemistry."*

Wheland never had very many graduate students, never more than two at a time. Fortunately, I was able to receive information from the remaining two, Dewey Jones (*66*) and William LeNoble (*67*). Jones says about Wheland *"He was a quiet, reserved man. A great adviser on a Ph.D. project, i.e., he was always available for advice, but otherwise left one alone to work on his own. He was an excellent lecturer---made things crystal clear. I, and everyone I know who worked for him liked him very much. Why did I pick Wheland to work for? Well, there were three choices: Kharasch, Brown, and Wheland. I interviewed with all three. Then I talked with some of the graduate students for all three. I guess what finally swayed me was Wheland's ability to lecture in organic chemistry. I thought I would get the best advice and help when needed. I am sure I was right."* Jones went on to say that Wheland offered him a project on the benzidine rearrangement that Jones snapped up. Jones completed it so quickly that Wheland thought he needed to do some additional research. This resulted in a paper on the alkyl guanidine problem, which Jones also completed quickly. Jones wrote the thesis, and Wheland wrote the two papers.

The perception, which seems to be correct, was that Wheland did not apply for grants. Of course, there weren't many grants to be had in the early 1950s. This meant that, if you worked for Wheland, you had to have a fellowship with outside funding, or else be a teaching assistant all of your graduate career. LeNoble guesses why Wheland didn't apply for grants (*67*). "*Writing grant proposals, as you surely know, involves not only an experimental or calculational program, but also subtle suggestions about how successful one's career has been, and how important the proposed research is. Wheland had a very laid-back personality, with little overt ambition and no aggressive streak at all."*

LeNoble goes on to say, *"He did not have a principled objection to the proposal and grant system; in any case, in 1958 when I was at Rohm & Haas, I toyed for a time with the idea of going back to Chicago as his post-doc. He wrote back that this might not be the best way to pursue a career, but if I needed to be back in Chicago, he would be glad to have me back. But he added that he had no money, and I would need to write a research proposal. I did so, and he made some suggestions to improve it, but it never went out."* In the interim LeNoble received a post-doc offer from Kornblum at Purdue which he accepted.

So far as Wheland as a research director, LeNoble states *"These three years in Wheland's lab were among the best for me. He let me work completely independently; in all that time, he stopped by perhaps a half dozen times to see if I was making any progress or needed any help. On the other hand, his office was always open to me; while we never scheduled meetings, he was available for consultation whenever I felt the need for it. The result of this independence was that I made many mistakes and wandered down several blind alleys, but I found it a great way to learn. Some of my most memorable sessions with Wheland came after I gave him a draft of my thesis. What he did on subsequent meetings with me was to read the entire document out loud, sentence by sentence, chapter by chapter, including the dedications and the references. After every sentence, he would stop and say something like "Now what does that mean?" or "Now how does that follow?" or "What experiment supports this?" I was so embarrassed by the obvious inadequacy of my draft that after the first chapter, I asked for a long* *time-out so that I could come up with an improved version. My guide line for the revised version was that every sentence should be able to withstand the questions I knew Wheland would raise."*

It is a testimony to Wheland's personal life and character that both his children followed him into organic chemistry, both receiving Ph.D.s. His daughter Margaret remembers her path to chemistry as follows. *"I thought that Father had chosen an attractive field. By the time I had left high school, it was obvious to me that I was not destined for the liberal arts fields. They were boring. I took things much too literally (the "deep inner meanings" found in literature were incomprehensible to me). Of the sciences I studied, chemistry was the most interesting. Organic was more attractive because it was not super mathematical (and because Father was an organic chemist). I think Father was quietly pleased with my choice of chemistry. It was my mother who asked a number of times whether I was happy in chemistry. And I was."*

Wheland's son Robert remembers his choice of chemistry as follows. *"I went into chemistry because I enjoyed explosions, smells, and later the challenge of organic synthesis. I started off with fireworks and then moved on to burning questions such as what is the best water temperature and the best-sized chunk for a good sodium explosion, what special effects can be created with* $TiCl_4$ *in a squirt bottle, or what might make a worse smell than n-butyl mercaptan (alkyl dithio carboxylic acids made by reacting Grignard with* CS_2 *---somewhat a matter of taste rather than a clear winner as it turned out).*

Once my father knew I was interested in chemistry, he was quietly encouraging, throwing the occasional chemistry book my way, the keys to the University of Chicago chemistry library, providing a balance and basic glassware, and politely not noticing when I would return from downtown Chicago heavy with chemicals and equipment that would surely have worried my mother. He and I seldom talked about chemistry. I can remember his twice asking me questions about chemistry and then they were factual, once to balance a fancy redox reaction and another time a trick question on the aldol condensation of benzaldehyde. He seemed mildly pleased when I answered correctly, commenting that some graduate students at Chicago would have had problems with the questions. Another time I had noticed that an elderly solution of KOH in ethanol had turned spontaneously viscous and red, and we had an interesting discussion about mechanism, polymers, and adventitious catalysts. I do not remember his ever commenting on chemistry as a career choice for either me or my sister. By the time I got to college, the transition from chemistry as a hobby to chemistry as a career was barely noticeable."

Despite their differing views on the reality of resonance structures, relations between Wheland and Pauling remained warm. Wheland's wife Betty remembered from their days at Cal Tech that Wheland found Pauling to be dynamic, a font of ideas, and generous in sharing scientific credit.

Early on the Wheland family lived in an apartment in the Hyde Park neighborhood, two blocks from Wheland's office. This was a rough neighborhood. Around 1953 they moved to a house about seven miles from campus. Margaret says that their mother was the main disciplinarian in the family, and their father backed her up. They could occasionally get around their mother but never their father. Usually one month in the summer would be spent at their Grandfather Wheland's home in Chattanooga. The children would be left with their grandfather and their Aunt Mary, while their parents went hiking in the Smokies.

Wheland was very much into photography, especially pictures of flowers, and had probably 3000 slides. He had a great sense of humor and enjoyed spouting humorous poems, like "Cannabel Lee", a take-off on Poe's "Annabel Lee."

To sum up, Wheland's life was a well-lived life, but his scholarly efforts ended probably ten years too soon because of his illness. When musing on the end of a creative life, I tend to think in terms of composers of music. We all know the deaths of Mozart, Schubert, and Gershwin in their '30's deprived the world of a number of masterpieces. Still, there is also a loss when a mature person at the top of his game passes on too soon. The analogy to Wheland that occurs to me is the French composer Maurice Ravel. In 1931 at age 56 Ravel composed two absolutely marvelous piano concertos. Then early in 1932 Ravel was in a taxi accident where he received a severe blow to the head. Except for just a few songs right after the accident, Ravel was unable to compose again. He died in 1937 at age 62 with all his music locked up in his head. The advances in computer technology in the 1960s would have allowed Wheland to treat increasingly complex systems, but his illness intervened, with losses to scholarship that we can only guess at.

Wheland's Books

George Wheland is associated with essentially two editions of a monograph on resonance in organic chemistry and three editions of a textbook on advanced organic chemistry. Since the publication dates of the last editions of each date back to 1955 and 1960, respectively, is there anything worthwhile to say about them? My view is that a well-written monograph does have lasting value. Paul Flory's *Principles of Polymer Chemistry* was published in 1953, but it can still be read with profit today. A good monograph summarizes the progress in an area up to the date of the monograph's publication, so it gives the reader a running start in learning the past research in that area. Old textbooks, if they are good, may also have much value for us, though for a different reason. They provide the foundations that change much more slowly than the frequency of publishing new editions of textbooks would suggest.

My exposition will be a broad brush treatment, hitting just a few of the significant aspects of the two types of books. Wheland's first book on resonance (*19*), *The Theory of Resonance and its Application to Organic Chemistry*, filled a definite void. There had been no monograph on this new, exciting theory, so Wheland's book met a distinct need. The book was subject to wartime paper restrictions, but its mere 296 pages covered in depth a number of topics that are dear to organic chemists. The first three chapters on theory of resonance, valence, and resonance energy were pedagogic in nature, while the last five chapters covered the impact of resonance on steric effects, dipole moments, molecular spectra, chemical equilibrium, and chemical reaction in satisfying detail. An eleven page appendix of inter atomic distances completed the book.

Wheland began the chapters on dipole moments and molecular spectra with clear explanations of the physical chemistry involved. He made no attempt to go into mathematical detail about the quantum chemistry needed for resonance calculations. He did build on Ingold's analogy between pendulums and resonance (*18*). Overall, however, he sought to give the organic chemist useful qualitative ideas about the impact of resonance in a number of areas.

Table 3. Chapter Page Lengths for *the Theory of Resonance* (1944) and *Resonance in Organic Chemistry* (1955)

	1944	*1955*
Chap. 1, "The Theory of Resonance"	28	29
Chap. 2, "The Nature of Valence"	23	45
Chap. 3, "Resonance Energy"	36	78
Chap. 4, "Steric Effects of Resonance"	26	47
Chap. 5, "Resonance and Dipole Moments"	29	44
Chap. 6, "Resonance and Molecular Spectra"	21	93
Chap. 7, "Resonance and Chemical Equilibrium"	52	77
Chap. 8, "Resonance and Chemical Reaction"	70	130
Chap. 9, "Mathematical Basis of Resonance"	--	151
Appendix	11	105
Total pages less index	296	799

Wheland returned to the topic of resonance in 1955 with what was essentially a second edition of the first book. Like the first book, this volume was also dedicated to Linus Pauling. The book, *Resonance in Organic Chemistry* (*68*), had grown to almost 800 pages in accordance with the popularity of its topic. It contained the same first eight chapter topics of the first book, all of them expanded; but it also contained a 151 page ninth chapter on the mathematical basis of resonance. In this chapter Wheland went into the mathematics of resonance calculations in excruciating detail; but he also covered molecular orbital calculations and the free-electron model. (See William Jensen's chapter on the free-electron model elsewhere in this volume.) The book ended with a 105 page appendix on bond lengths and bond angles. A comparison of the chapter lengths in the two books is given in Table 3.

In the introduction to the 1955 volume, Wheland mentions that one reason for the expansion of the book is his increasing use of molecular orbital descriptions. He goes on to say (*69*) *"I have continued, however, to lay much the greater emphasis upon the resonance concept. My reason for thus relegating the molecular-orbital viewpoint to a secondary role is not that this viewpoint is of relatively little value; actually, it is at least as important as the resonance* *viewpoint, and, in a number of specific applications, it is more useful. The point is instead that, as an organic chemist, I believe that the resonance approach is clearer and more congenial to the great majority of other organic chemists than is the alternative one."* Wheland does take note of the Soviet attacks on the theory of resonance. He characterized the attacks as almost entirely of personal and political invective, and those attacks with scientific content based on a misinterpretation of the theory.

In the first chapter he tries to prevent the interpretation of the Kekulé structures as real entities. Thanks to the work of Vollhardt and his team (*70*), we now have a picture of what a true 1,3,5-cyclohexatriene looks like. Vollhardt's team apparently applied the maxim "nature abhors a cyclobutadiene," as that work involved imbedding the cyclohexatriene in a C_3-symmetric [4]phenylene. A 'normal' 1,3,5-cyclohexatriene is still a fiction. Wheland felt that his previous analogies to a horse, donkey, and mule quoted earlier in this chapter could be misinterpreted, because those entities are real; and the Kekulé structures are not. He first called on John Roberts' analogy of describing a rhinoceros, a real animal, as an intermediate between a dragon and a unicorn, both mythical creatures. Finally he used a literary analogy (*71*). *"For example, if we say that a certain actually existing man, John Doe, is a cross between Sherlock Holmes and Don Quixote, we give a fairly clear picture of the real John Doe, even though neither Sherlock Holmes nor Don Quixote ever lived."*

In Chapter 2, "The Nature of Valence," the descriptions of one electron, three electron, two electron, and hydrogen bonds are very similar to that of the earlier book. The main reason for the expansion of Chapter 2 in the second book is the addition of 13 pages on molecular orbital theory in which the hydrogen molecule, 1,3-butadiene, and benzene are the examples used. The chapter ends with a discussion of the binding forces in addition compounds.

In Chapter 3, "Resonance Energy," any perceptions of Wheland being wedded to valence bond/resonance theory are dispelled. In the 1955 version the early part of the chapter follows the 1944 format closely, although a lot more data is treated. The new section of the chapter is called "The General Theory of Aromatic Systems." In this section Wheland correctly concludes that cyclopentadiene anion and tropylium cation are aromatic, while the cyclobutadiene and cyclooctatetrene systems are not. It is worth quoting his grand conclusion (*72*). *"Just as the especially stable and unreactive atoms of the rare gases are obtained when each electronic shell that is occupied at all is completely full, so also the most stable and least reactive molecules may be expected to result when there are no partially occupied groups of orbitals with the same energy, or, in other* words, ***when the total number of aromatic electrons is equal to 2 + 4n, where n = 0, 1, 2, ---."*** **(emphasis by me)**. Sound familiar? He cites ethylene as an example of n = 0, the work of Breslow and Yuan on triphenylcyclopropenyl cation (*73*) not yet having been carried out. Benzene, pyrrole, pyridine, thiophene, and cyclopentadienyl anion are cited as examples of n = 1. He concludes that azulene and naphthalene may be n = 2 examples. Wheland does mention that he comes to these conclusions through free electron theory rather than through molecular orbital theory.

In Chapter 4, "Resonance and Steric Effects", the format in the two books is the same with the expansion in the 1955 book coming from the existence of more experimental data. The same could be said of Chapter 5, "Resonance and Dipole Moments," although the unexpectedly high dipole moments of azulene and fulvene are discussed in the 1955 volume in 4n + 2 terms.

In Chapter 6, "Resonance and Molecular Spectra," we see a more than four-fold expansion of the 1955 chapter over the 1944 chapter. The 1944 volume focused on visible-uv spectra of mostly hydrocarbons and dyes. In 1955 the chapter had a much expanded section on electronic spectra of hydrocarbons and dyes, in keeping with additional data of the past eleven years. However, additional sections were added on spectra of aldehydes, ketones, alcohols, phenols, and their various analogs plus a new section on molecular compounds. Solvent effects were also examined as well as theoretical calculations. The chapter concluded with a brief section on force constants.

The topics discussed in Chapter 7, "Resonance and Chemical Equilibrium," in the 1944 volume were acidity, basicity, steric inhibition of acidity and basicity, addition to double bonds, radicals, diradicals, and tautomerism. In the 1955 volume all the same topics appeared, although diradicals had a name change to biradicals, and each section was expanded in keeping with the greater amount of experimental data available. The section on acidity benefited by the introduction of the Hammett equation and its sigma-rho treatment. The only new classification was a short section on radicals of short life.

Chapter 8 on "Resonance and Chemical Reaction" was another chapter significantly expanded in the 1955 book over the 1944 volume. In both volumes the chapter started out by giving a general description of the activated complex and how resonance theory would fit in with that description. Then came treatments of addition of acids to carbon-carbon double bonds of both normal and abnormal orientation. The descriptors Wheland used in the first volume were "normal additions of acids---" and "abnormal additions of acids---." In the later volume the descriptors were "proton-initiated additions of acids---" and "free radical additions---.," thus reflecting the more modern views of these reactions. In both editions other standard organic reactions were covered. However, about half of the 60 page expansion of this chapter in the 1955 volume came from an increase in coverage of just two topics, orientation of substituents in aromatic systems and molecular rearrangements. Regarding the first topic, Wheland again refers to the Hammett equation and also to recent theoretical work using molecular orbital theory he had done with S. L. Matlow on competition between different substituents on aromatic systems (*74*). I will discuss the Matlow-Wheland paper later in this chapter.

Chapter 9 on "Mathematical Basis of Resonance" was probably placed at the end of the book to avoid scaring off organic chemists. The chapter starts with the Schrödinger Equation, goes on to the particle in a box, the hydrogen atom, and eventually the variation principle. Without my going into further detail, I believe a person who had mathematical training through differential equations and applied him/herself diligently to understanding this chapter could teach him/herself a great deal of quantum chemistry.

Wheland's textbook, *Advanced Organic Chemistry*, did not fill a void in the way that his first book on resonance did. There were other books available on this topic. William Jensen (*75*) notes comparable books by Cohen, Henrich, Waters, Watson, and Remick. However, the book by Wheland stands out among the group for the thoroughness of the coverage and the clarity of the writing. Testimony from two individuals, Kurt Mislow and William LeNoble, demonstrate the impact of the book. In an interview conducted by István Hargittai (*76*) Mislow tells of seeing the mimeographed first edition of Wheland's text when he first joined New York University. Mislow stated *"Wheland's uncluttered and logical way of thinking about stereochemistry opened my eyes to the power of symmetry arguments. It was a revelation to me that symmetry and chirality were at the heart of stereochemistry. So Wheland's book had a tremendous influence on my thinking and was a real inspiration. I became fascinated by stereochemistry, and it permanently changed the direction of my research.---Wheland's book inspired the first paper I published at NYU."* Mislow went on to discuss Wheland's definition of diastereomers being stereoisomers that are not enantiomers. In the 1950s and the 1960s that definition was not the accepted one. Mislow fought to get the Wheland definition accepted by the establishment, and he was ultimately successful. Now that definition is the one that appears in organic chemistry textbooks. Fourteen years later Mislow still says (*77*) *"In that interview with Hargittai, I expressed my own unbridled admiration for GW's scholarly analysis of complex problems that had befuddled lesser minds, and for the lucid exposition of his reasoning. Through his text, he was an inspiration to me, a true role model."* As a tribute, Mislow and Siegel dedicated a 1984 *J. Am. Chem. Soc.* paper on "Stereoisomerism and Local Chirality" to Wheland (*78*).

William LeNoble was Wheland's last graduate student. He actually was taught the advanced organic chemistry course by Weldon Brown, but the text for the course was Wheland's. LeNoble (*67*) says *"Brown's course was sheer pleasure, the reason being that he used Bill Wheland's book Advanced Organic Chemistry. From this beautifully written book, I learned that organic chemistry was not just a compilation of organic compounds and their reactions, but that it was a pure, modern science. In fact, it resembled nothing so much as an exciting detective story, leaving its readers itching to become part of the story. By the end of the quarter, although I had never met Wheland, I resolved to do my thesis work with him; luckily for me, he was also a member of the department."*

Table 4. Comparison of the Three Editions of Wheland's *Advanced Organic Chemistry*

1st Edition	*2nd Edition*	*3rd Edition*
1. Introduction, 32 pp.	1. Some Fundamental Concepts, 36 pp.	1. Some Fundamental Concepts, 37 pp.
2. Addition Compounds, 33 pp.	2. Addition Compounds, 35 pp.	2. Structural Isomerism, 47 pp.
3. Modern Concepts of Acids and Bases, 13 pp.	3. Modern Concepts of Acids and Bases, 13 pp.	3. The Theory of Resonance 51 pp.

Continued on next page.

Table 4. (Continued). Comparison of the Three Editions of Wheland's *Advanced Organic Chemistry*

1st Edition	*2nd Edition*	*3rd Edition*
4. Structural Isomerism, 43 pp.	4. Structural Isomerism, 47 pp.	4. Addition Compounds, 48 pp.
5. Stereoisomerism, 31 pp.	5. Stereoisomerism, 31 pp.	5. Modern Concepts of Acids Bases, 11 pp.
6. The Configuration of Carbon Compounds, 62 pp.	6. The Configuation of Carbon ompounds, 69 pp.	6. Stereoisomerism, 32 pp.
7. The Stereochemistry of Carbon 66 pp.	7. The Stereochemistry of Carbon 99 pp.	7. The Configuration of Carbon Compounds, 79 pp.
8. The Stereochemistry of Elements Other Than Carbon. Strain Theory, 47 pp.	8. The Stereochemistry of Elements Other Than Carbon 36 pp.	8. The Stereochemistry of Carbon 127 pp.
9. The Theory of Resonance 48 pp.	9. Strain Theory and Steric Hindrance, 22 pp.	9. The Stereochemistry of Elements Other Than Carbon 41 pp.
10. Molecular Rearrangements The 1,2-Shift, 102 pp.	10. The Theory of Resonance 47 pp.	10. Strain Theory, Steric Hindrance, and Conformational Analysis, 41 pp.
11. Molecular Rearrangements Further Types, 52 pp.	11. Electrostatic Effects in Organic Chemistry, 17 pp.	11. Electrostatic Effects in Organic Chemistry, 21 pp.
12. Tautomerism, 75 pp.	12. Molecular Rearrangements The 1,2-Shift, 84 pp.	12. Molecular Rearrangements The 1,2-Shift, 86 pp.
13. Free Radicals, 113 pp.	13. Molecular Rearrangements Further Types, 45 pp.	13. Molecular Rearrangements Further Types, 41 pp.
Total pages less index, 717	14. Tautomeriism, 67 pp.	14. Tautomerism, 71 pp.
	15. Free Radicals, 103 pp.	15. Free Radicals, 92 pp.
	Total pages less index, 749 pp	Total pages less index, 822 pp

I will not go through the three editions of Wheland's *Advanced Organic Chemistry* in the same detail that I discussed his monographs on resonance. Instead I will deal with the broad features, which remained fairly constant through all three editions. Wheland stayed away from the descriptive organic chemistry found in other advanced tests. Instead he focused more on what we would call today physical organic chemistry, with whopping amounts of stereochemistry. Four of the thirteen chapters in the 1st edition dealt with stereochemistry , making the book roughly 30% stereochemistry. That proportion stayed roughly the same in the next two editions. Table 4 compares the chapter headings and lengths for the three editions.

The first edition of Wheland's textbook consists of 8' by 11' sheets mimeographed on only one side and apparently bound by the University of Chicago Bookstore (*46*). It was published in two volumes. Copyright for the first nine chapters was assigned to the University of Chicago in 1946. The copyright for the last four chapters was assigned to the University in 1948. The title page of the first volume described the work as *Syllabus for Advanced Organic Chemistry 321*. The second volume had an identical title except the course number was 322. The dedication of the first volume states *"The Advanced Organic Class of 1946 wishes to express its appreciation to Professor George W. Wheland whose generosity and kindness have made possible the publication of his notes. Dr. Wheland extended his services gratis and worked tirelessly to prepare this volume for the benefit of his students."* I conclude that this volume started out, as the dedication says, as a way of giving Wheland's students a complete set of lecture notes to supplement his lectures. Once the two parts of syllabus were printed, it was a logical step and comparatively easy task to publish these notes in 1949 as the second edition of *Advanced Organic Chemistry* (*47*).

When one compares the chapter lengths of the first edition and the second edition, it seems at first glance that certain chapters were carried over from the first edition to the second essentially unchanged. However, this comparison is misleading. In the first edition all references were accumulated at the end of the chapter in regular type size. In the second edition the references are at the bottom of each page in much smaller type size. Chapter 3 on acids and bases looks like an exact carryover from the first edition to the second edition. For the most part it is, although an occasional word is changed. However, Wheland has significantly expanded the discussions of the leveling effect and acid/base nomenclature. In the second edition Wheland gave strain theory a chapter of its own. Overall, I think it is fair to say that the second edition was essentially based on the first edition with some tweaking and a little expansion necessary because of discoveries made since the 1946 printing of the first part. The most significant change is the addition in the second edition of a chapter on "Electrostatic Effects in Organic Chemistry," a chapter which also appeared in the third edition. No copyright is claimed for this chapter, which the introduction states is based on a memorandum written by Frank Westheimer.

In his interview with Gortler (*37*), Westheimer confirms that he had written the memorandum, but he doesn't say why. However, it is possible to make an intelligent guess based on information earlier in the Westheimer interview. Westheimer had taken advantage of John Kirkwood overlapping him one year on the Chicago faculty to work with Kirkwood on the problem of electrostatic effects on organic acids. That work resulted in two publications (*79*, *80*). Wheland, realizing that he had an in-house expert on the subject, perhaps felt it was more efficient to pick Westheimer's brains for the chapter than to do exhaustive study on the topic himself. Of course, a chapter on this new topic further enhanced the value of the book.

There was not a huge expansion of the book from edition to edition. Text for the first edition ran 717 pp.; that for the second edition 749 pp. ; and text for the third edition 822 pp. The third edition in 1960 saw the addition of material on molecular orbital theory in the chapter on "The Theory of Resonance." New topics added were conformational analysis, esr and nmr, inclusion and charge-transfer compounds, and the Hammett rho-sigma relationships. My impression is that Wheland's work on his second book on resonance spilled over into the choice of topics in the third edition of his textbook.

Besides advanced organic chemistry, Wheland is listed in what is the equivalent of the University of Chicago 1957-58 graduate catalog (*81*) as teaching a course titled "Modern Theories of Valence." The course description says *"Contributions which quantum mechanics have made to our understanding of valence discussed from a qualitative and descriptive point of view. Both the valence-bond (resonance) and molecular-orbital approaches are employed."* Frank Mayo (*44*) states that in the 1930s Wheland was teaching a course on quantum mechanics in the chemistry department (and Wheland did not recommend that Mayo take it). I wonder if this was a later version of the course. I have been unable to find any detailed information on the course, and I know of no course textbook.

Wheland's books, particularly his resonance books, played a large role in gaining him national recognition. His wife felt they played a significant role in his being promoted to professor, and the timing of his promotion and their publication looks about right. His daughter Margaret remembers his working at a card table with many little slips of paper, each with a word or phrase on them. He was working on the index for one of the books and told Margaret *"Never write any book that needs an index."* I think the chemical profession should be glad that Wheland never took his own advice.

Wheland's Papers on Quantum Chemistry

Wheland's paper on the intermediates in aromatic substitution (*1*) noted on the very first page of this chapter was undoubtedly his best known paper not published with Linus Pauling. However, two of his three papers coauthored with Pauling achieved even more recognition. In this section I will discuss his papers with Pauling as well as his other quantum chemistry papers. These treatments will normally be brief except in a very few cases.

Wheland's first paper with Pauling (*82*), which was his second paper overall, appeared in *J. Chem. Phys.* and was titled, "The Nature of the Chemical Bond. V. The Quantum-Mechanical Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals" These systems were treated by valence bond/resonance methods. Actually, more space in the article was given to hydrocarbon radicals than the benzene and naphthalene molecules. However, it is the benzene result that everyone remembers. Their conclusion was that the two

Kekulé-type canonical structures accounted for 80% of the special stabilization of benzene with the three Dewar-type canonical structures accounting for the other 20%. They refer to the 1931 Hückel paper (*30*), but they say their treatment was simpler. The problem was that Hückel had treated benzene two different ways, one by valence bond methods, the other by Hückel's molecular orbital treatment. Pauling and Wheland had ignored the latter. Hückel quite rightly took exception to Pauling ignoring his second method, the more significant of the two. In his Hückel biography, Karachalios discusses the Hückel-Pauling correspondence and their disagreements about this paper (*83*). Karachalios notes that Pauling mistakenly thought that Hückel's MO treatment did not fully obey the Pauli exclusion principle. He also points out that Pauling in some way believed in the reality of the individual resonance structures, while Hückel did not. Of course, as I have said earlier in this chapter, I believe that Wheland also did not believe in the reality of the individual resonance structures.

The second joint publication of Pauling and Wheland was a single page article, "Remarks on the Theory of Aromatic Free Radicals," in *J. Chem. Phys.* (*84*). They discuss the valence bond treatment of the benzyl system, noting that valence bond and molecular orbital treatments give similar results. They show canonical structures for the benzyl radical and the anion. These structures consist of two Kekulé structures with the radical or anion fixed on the benzylic carbon and three structures in which the radical or the anion are delocalized at the ortho and para positions. The results are rather anticlimactic, as they say some of the important integrals cannot be calculated.

I can't help but guess that Wheland had considerable influence on the choice of topic for their final joint paper in *J. Am. Chem. Soc.*, "A Quantum Mechanical Discussion of Orientation of Substituents in Aromatic Molecules," as this is organic through and through (*85*). They attempted to rationalize the ortho-para or meta directing effect of various substituents on a benzene ring through molecular orbital calculations! They justify this choice on the basis of the MO calculations being better for quantitative calculations. This is a very ambitious paper, as they treat a benzene ring with methyl, trimethylammonium, carboxylic, aldehydic, keto, amino, hydroxyl, and fluoro substituents plus heteroaromatic systems such as pyridine, furan, thiophene, and pyrrole plus naphthalene for good measure. Using 21st century 20-20 hindsight, we might criticize the work for focusing almost solely on ground states, neglecting reaction intermediates, but for its time and place it was a remarkable effort. By and large their results, with suitable parameterization, did duplicate the directive effects of substituents. In the course of the paper they take a couple of shots at Hückel. Karachalios has discussed this particular paper and its conflicts with Hückel's views in his Hückel biography (*86*).

I find that Wheland authored 15 quantum chemical papers independently of Pauling. They are listed in Table 5. I am excluding two Wheland publications that I consider review papers rather than research papers. Wheland coauthored a review paper in 1950 on "Theories of Valence" with Longuet-Higgins (*87*), who was at Chicago doing a post-doc with Robert Mulliken. This was a very objective review in which both valence bond and molecular orbital methods are given equal treatment. In 1950 Wheland also published on "The Chemical Bond in Hydrocarbon Molecules" (*88*), but I have not been able to obtain a copy of that material. Also, I don't count a 1933 *J. Chem. Phys.* paper (*10*), because the resonance energies cited in this publication seem to come from earlier papers.

Table 5. Wheland's Individual Papers on Quantum Chemistry

1. "The Quantum Mechanics of Unsaturated and Aromatic Molecules: A Comparison of Two Methods of Treatment," *J. Chem. Phys.*, **1934**, *2*, 474-481.

2. "Quantum-Mechanical Treatment of Molecules by the Method of Spin Valence," *J. Chem. Phys.*, **1935**, *3*, 230-240.

3. "The Number of Canonical Structures of Each Degree of Excitation for an Unsaturated or Aromatic Hydrocarbon," *J. Chem. Phys.*, **1935**, *3*, 356-361.

4. "Valence Bond Treatment of the Oxygen Molecule," *Trans. Faraday Soc.*, **1937**, *33*, 1499-1502.

5. "The Electronic Structure of Some Polyenes and Aromatic Molecules. V. A Comparison of Molecular Orbital and Valence Bond Methods," *Proc. Royal Soc., A*, **1938**, *164*, 397-408.

6. "Quantum Mechanical Basis of the Stability of Free Radicals," *Ann. New York Acad. Sci.*, **1940**, *40*, 77-90.

7. "Resonance Energies of Unsaturated and Aromatic Molecules," *J. Am. Chem. Soc.*, **1941**, *63*, 2025-2027.

8. "A Quantum Mechanical Investigation of the Orientation of Substituents in Aromatic Molecules," *J. Am. Chem. Soc.*, **1942**, *64*, 900-908.

9. "Hyperconjugation in Paraffin Hydrocarbons," (with J. T. Pinkston, Jr.), *J. Chem. Phys.*, **1944**, *12*, 69.

10. "Molecular Constants and Chemical Theories," *J. Chem. Phys.*, **1945**, *13*, 239-248.

11. "The Dipole Moments of Fulvene and Azulene," (with D. E. Mann), **1949**, *17*, 264-268.

12. "Some Comments on the London-Brooks Treatment of Diamagnetic Anisotropy," (with S. L. Matlow), *Prod. Nat. Acad. Sci.*, **1952**, *38*, 364-371.

13. "Modified Valence Bond Treatment of Unsaturated and Aromatic Compounds," *J. Chem. Phys.*, **1955**, *23*, 79-83.

14. "Orientation in Aromatic Substitution. A Theoretical Study of the Competition between Groups," (with S. L. Matlow), *J. Am. Chem. Soc.*, **1955**, *77*, 3653-3655.

15. "Some Semiempirical Quantum-Mechanical Calculations for Ammonia and Diimide," (with P. S. K. Chen), *J. Chem. Phys.*, **1956**, *24*, 67-70.

Wheland's 1934 *J. Chem. Phys.* paper (*11*) compares valence bond and molecular orbital treatments of unsaturated and aromatic molecules. He refers to the valence bond treatment as the Heitler-London-Slater-Pauling (HSLP) method and the molecular orbital treatment as the Hund-Mulliken-Hückel (HMH) method. While Wheland thought that the HSLP method gave overall better agreement with experimental results, he also found that HMH method also gave reasonable agreement with experiment. The big deviations were for cyclobutadiene and cyclooctatetraene. Wheland cites his preference for HSLP over HMH, because of their differing results for cyclobutadiene. HSLP predicted resonance stabilization, while HMH did not. From the perspective of 88 years later, we know that Wheland was wrong. It's more interesting to focus on what Wheland got right in that paper. In my opinion, the most significant achievement of HMO theory is not in predicting the special stability of benzene over cyclobutadiene and cyclooctatetraene, but in rationalizing the spectacular difference in acidity between cyclopentadiene and cycloheptatriene, Their difference in acidity is 10^{20}! Yet one can write five equivalent resonance structures for cyclopentadienyl anion and seven equivalent resonance structures for cycloheptatriene anion. Of course, the former is a 4n + 2 system, and the latter is a 4n system. Wheland's HMH calculations showed definitely that cyclopentadiene should be much more acidic than cycloheptatriene.

In 1935 along with his last two joint publications with Pauling, Wheland published two individual papers in *J. Chem. Phys.* (*13*, *14*). The first paper showed that the method of spin valence could be made equivalent to the Slater method for treating molecules. The procedure was illustrated by applying it to benzene. The second paper gave procedures for obtaining the canonical structures for each degree of excitation for a large number of aromatic hydrocarbons.

The next two papers in Table 5, Nos. 4 and 5, are fruits of Wheland's Guggenheim Fellowship. Both papers were submitted for Wheland by Lennard-Jones, and the Roman numeral V in the second paper links it to a series of papers by Lennard-Jones and coworkers. The first paper involved valence bond calculations on the oxygen molecule, showing that taking account of covalent functions gave a triplet state of lower energy than the singlet, in correspondence with experiment (*89*). The second paper revisited (*90*) valence bond and molecular orbital calculations for cyclobutadiene that Wheland had made before in his 1934 *J. Chem. Phys.* paper (*11*). The results were the same. The valence bond calculations showed resonance stabilization for cyclobutadiene; the molecular orbital calculations did not. Wheland went into the MO calculations a little more deeply this time and convinced himself that the normal type of MO calculation neglected a resonance effect, although he hedged his bet by saying no definite conclusion could be reached.

In the 1940 paper, free radicals were discussed from the valence bond approach (*91*). Wheland's results on free radicals in this paper were those of his 1934 *J. Chem. Phys.* paper, except they were all multiplied by a factor of 2. The 1941 note from *J. Am. Chem. Soc.* dealt with calculations on the resonance energies of unsaturated and aromatic hydrocarbons (*92*), but there were also calculations on resonance energies of free radicals. The new MO calculations used a non-orthogonality integral, what we would call nowadays an overlap integral, and consequently were more rigorous than the calculations Wheland used in his 1934 paper (*11*).

Next we come to the paper with the "Wheland intermediate" (*1*). Now there is no comparison of valence bond and molecular orbital results. This paper is molecular orbital all the way. Wheland treats benzene, chlorobenzene, phenol/

aniline, nitrobenzene, and nitrosobenzene plus pyridine, 2-naphthol, naphthalene, and 2-hydroxyhydrindene for the cases of electrophilic, nucleophilic, and free radical substitution. The species involved is the Wheland intermediate for either cation attack, nucleophile attack, or free radical attack. The overlap integral is assumed to be 0.25, and Wheland makes generous use of adjustable parameters for the Coulomb and resonance integrals of heteroatoms plus an auxiliary inductive parameter when needed. Of interest to me was Wheland's treatment of toluene. The methyl group is treated via hyperconjugation with the use of an auxiliary inductive parameter. I note with interest that some 25 years later Lazdins and Karplus (*93*) had to couple hyperconjugation with an auxiliary inductive parameter to get a correct explanation for the electron spin resonance behavior of the toluene anion radical. The overall result is that Wheland was able to give a convincing demonstration that this very simple treatment rationalized the orientation for these three different types of aromatic substitution. One part of Wheland's nomenclature may seem very strange to us now, the reluctance to use the word carbocation. Back in the early 40's carbocations were still not regarded as real in some quarters. Like many of his contemporaries, Wheland used the euphemism "open sextet."

Wheland's Letter to the Editor on hyperconjugation in paraffins explored whether resonance energies would affect the linearity of heats of combustion (*94*). The result was that they did not. The next paper refutes a series of papers that attacked modern ideas of valence (*95*). While this paper certainly discusses molecular orbital theory, no new calculations are performed.

Wheland and Mann's paper (*96*) on the dipole moments of fulvene and azulene looks superficially like just an experimental paper. Previous MO calculations of these dipole moments gave large values, albeit with the dipole in the right direction. The authors measured the dipole moments of some fulvene derivatives, which could be manipulated to give the dipole moment of fulvene (about 1.2 D), and they measured the dipole moment of azulene (1.0 D). However, this paper also had a short (a little over one page) mathematical appendix in which the authors came up with a way of introducing some electron repulsion within the simple HMO treatment. If the pi electron density at a carbon is less than one, the electron screening is reduced. If greater than one, the electron screening is increased. Wheland and Mann proposed that the value of the Coulomb integral should be linearly related to the charge; and this treatment entailed the use of one empirical parameter. In Streitwieser's discussion of this work (*97*), this procedure is called the omega (ω) technique. Wheland and Mann used a value of one for the parameter. Streitwieser used this procedure in molecular orbital studies of ionization potentials (*98*, *99*), finding that a value of 1.4 served best. Streitwieser wrote Wheland, asking him how he came up with a value of one (*100*). Wheland replied that it seemed like the right order of magnitude, but that he never did any further tests. Streitwieser notes that (*100*) "Wheland did have the right approximate magnitude just from his intuition." I should note that this method resulted in Wheland and Mann calculating a dipole moment for fulvene (1.9 D) much closer to the experimental result.

Elsewhere in this book, the chapter by Klaus Ruedenberg and W. H. Eugen Schwarz refers to the 1951 Shelter Island Conference. A picture of the participants at that conference is Figure 1 in that chapter, and it also appears on the cover of this volume. George Wheland attended the conference, although he left before the group picture was taken. The publication with Matlow published in *Proc. Nat. Acad. Sci.* was Wheland's presentation at that conference (*101*). Wheland used molecular orbital calculations to try to improve on previous methods for calculating diamagnetic anisotropy.

In his 1955 *J. Chem. Phys.* paper (*102*), Wheland returned to valence bond calculations on hydrocarbons. His efforts to make these calculations more empirically based resulted in more mathematical problems, such that he could only treat the smaller systems such as 1,3-butadiene, cyclobutadiene, and benzene. In his *J. Am. Chem. Soc.* note written with Matlow (*74*), he returned to the topic of his famous 1942 paper, again using MO theory with adjustable parameters. His goal this time was to deal with multiple groups, seeing if he could again reproduce the directing effects for electrophilic, nucleophilic, or free radical attack with more than one substituent present. The molecules studied were a nitro phenol, a nitro toluene, and a dimethoxy aldehyde. Wheland deemed the results satisfactory. Wheland's very last quantum chemistry paper was written with P. S. K. Chen (*103*). Here again he used molecular orbital calculations, this time of the semiempirical type.

With his graduate students, Wheland produced a number of papers in pure physical organic chemistry. Those papers are very interesting, but they are outside the scope of this volume. As you can see from this survey, in later years Wheland turned increasingly to molecular orbital treatments. His failing health prevented him from making the advances in MO theory that he had made with valence bond/ resonance theory, but there seems little doubt that he was capable of moving the field forward had his disease not interfered.

Summary

Photographs of a mature George W. (Bill) Wheland show a handsome, aristocratic individual, completely at home in the academic environment. The recollections of those who knew him testify that he had a brilliant mind and was a cheerful, witty companion. He was educated at excellent schools, and he had unusually good training in mathematics and physics for a chemistry major. When his big chance came to make a name for himself with Linus Pauling, Wheland took advantage of it. At the University of Chicago he only had about 25 publications. It is a tribute to the ability of the Chicago administration to evaluate quality as opposed to quantity that he progressed steadily through the academic ranks to full professor. Besides his scientific publications, he wrote several editions of two landmark books, one a monograph and one a textbook. His writing was known for its clarity and thoroughness. Despite his being linked by many solely with the valence bond/ resonance method, he was quite capable of creative work with the molecular orbital method. Nevertheless, he did focus on valence bond/resonance descriptions, because he knew that his fellow organic chemists could better relate to the structural pictures those methods brought to mind. Multiple sclerosis hit him in his early '50's and robbed him of ten years of creative accomplishments. Still, his work with resonance pervades the typical organic chemistry textbook, even if the authors and students are unaware of the source. His illness prevented him from doing more, but the world of chemistry should be grateful for what he was able to do. Bill Wheland was a true pioneer of quantum chemistry.

Acknowledgments

I started this project with a strong sense of purpose, and I finish this project with a strong sense of my own limitations. I wish I had remembered more of my quantum chemistry from graduate school, but I wish even more that someone else had started this project ten or twenty years earlier, when there were a lot more people around who knew Wheland. Still, if it couldn't have been done earlier, an evaluation of the accomplishments of Bill Wheland would only get harder in the future. More people would pass from the scene, and clippings, photos, etc. would get scattered or disappear. This chapter may not have been written at the ideal time, but it is being written at the best time possible now.

Most of all, I want to thank Wheland's children, Dr. Margaret Couch and Dr. Robert Wheland, for sharing their memories, photos, and clippings with me and for reading and commenting on parts of this chapter. I am grateful to Drs. Bill Jensen, István Hargittai, and Wes Borden for reading this manuscript and making helpful suggestions for its improvement.

With 100+ references for this chapter, it is obvious that I relied on much previous research. I want to mention two particularly helpful sources. I made a lot of use of Buhm Soon Park's excellent article (*5*) on "Chemical Translators: Pauling, Wheland, and their Strategies for Teaching the Theory of Resonance." I found Park's concept of viewing these two remarkable chemists as chemical translators a unique way of gauging their impact. Leon Gortler's interviews with Frank Westheimer (*37*) and Frank Mayo (*44*) gave me many useful insights as to Wheland's character and to the situation in the Chicago chemistry department in the 1930s. I urge historians of chemistry to make more use of the oral history resource at the Chemical Heritage Foundation.

Ms. Antoinette Nelson, Head of the Engineering and Science Library at my home institution of the University of Texas at Arlington (UTA), helped me at every step of the way of the two years it took to bring this project to completion. I also am grateful to Ms. Joeli Gomez from the UTA libraries for her help in obtaining crucial editions of Wheland's books. I thank Ms. Barbara Krieger, Archives, Rauner Library, Dartmouth College, for obtaining Wheland's transcript for me and informing me of the nature of the science courses taken by Wheland. I also thank Dr. Vera Dragisich of the University of Chicago for her help in obtaining information on the Wheland medal and in tracking down former Wheland graduate students. Dr. Stuart Rice of the University of Chicago was also a very valuable resource on Wheland's career at Chicago.

For their recollections of their time as Wheland graduate students I thank Drs. William LeNoble and Dewey Smith. For their memories of Wheland as a teacher, I am grateful to Drs. Leon Gortler, Roy Olofson, Tom Curphey, and Henry Paulus. I very much appreciate useful insights on Wheland obtained from Drs. Kurt Mislow, Andrew Streitwieser, Klaus Ruedenberg, Stuart Rice, and John D. Roberts. I want to thank Drs. Mahir Alrashdan and Martin Pomerantz, UTA, for their assistance in my original Wheland presentation at the ACS meeting in Anaheim. Finally, I am grateful to Mr. Tim Marney and Ms. Arlene Furman of ACS Books for their patience in seeing this chapter to completion.

References

1. Wheland, G. W. *J. Am. Chem. Soc.* **1942**, *64*, 900–908.
2. Rzepa, H. The Oldest Reaction Mechanism Updated. *Chemistry with a Twist*; http://www.ch.imperial.ac.uk/rzepa/blog/?tag=wheland-intermediate.
3. Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 8279–8288.
4. Gwaltney, S. T.; Rosokha, S. V.; Head-Gordon, M.; Kochi, J. K. *J. Am. Chem. Soc.* **2003**, *125*, 3273–3283.
5. Park, B. S. *Br. J. Hist. Sci.* **1999**, *32*, 21–46.
6. Simoes, A.; Gavroglu, K. In *Conceptual Perspectives in Quantum Chemistry*; Calais, J.-L.; Kryachko, E., Eds.; Kluwer Academic Publishers: The Netherlands, 1997; pp 383−413.
7. Simoes, A.; Gavroglu, K. In *Chemical Sciences in the 20th Century*; Reinhard, C., Ed.; Wiley-VCH: Weinheim, 2001; pp 1−23.
8. Gavroglu, K.; Simoes, A. *Neither Physics nor Chemistry. A History of Quantum Chemistry*; MIT Press: Cambridge, MA, 2012. For material on Wheland, see pp 121−124.
9. Hager, T. *Force of Nature. The Life of Linus Pauling*; Simon & Schuster: New York, 1995; p 168.
10. Wheland, G. W. *J. Chem. Phys.* **1933**, *1*, 731–736.
11. Wheland, G. W. *J. Chem. Phys.* **1934**, *2*, 474–481.
12. Doescher, R. N.; Wheland, G. W. *J. Am. Chem. Soc.* **1934**, *56*, 2011–2012.
13. Wheland, G. W. *J. Chem. Phys.* **1935**, *3*, 230–240.
14. Wheland, G. W. *J. Chem. Phys.* **1935**, *3*, 356–361.
15. Nye, M. J. *From Chemical Philosophy to Theoretical Chemistry. Dynamics of Matter and Dynamics of Disciplines 1800-1950*; University of California Press: Berkeley, CA, 1993; pp 194−207.
16. Brock, W. H. *The Norton History of Chemistry*; W. W. Norton and Co.: New York, 1992; pp 503−504.
17. Hager, T. *Force of Nature. The Life of Linus Pauling*; Simon & Schuster: New York, 1995; p 165.
18. Ingold, C. K. *Nature* **1938**, *141*, 314–318.
19. Wheland, G. W. *The Theory of Resonance and its Application to Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1944; p 52
20. Hager, T. *Force of Nature. The Life of Linus Pauling*; Simon & Schuster: New York, 1995; pp 325−329.
21. Brush, S. G. *Stud. Hist. Phil. Sci.* **1999**, *30*, 21–79.
22. Brush, S. G. *Stud. Hist. Phil. Sci.* **1999**, *30*, 263–302.
23. Hoffmann, R.; Shaik, S.; Hiberty, P. *Acc. Chem. Res.* **2003**, *36*, 750–756.
24. Roberts, J. D. *Acc. Chem. Res.* **2004**, *37*, 417–418.
25. Streitwieser, A. *Acc. Chem. Res.* **2004**, *37*, 419.

26. Shaik, S.; Hiberty, P. *A Chemist's Guide to Valence Bond Theory*; John Wiley & Sons: Hoboken, NJ, 2008.
27. McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 632, 764–766.
28. McLachlan, A. D. *Mol. Phys.* **1960**, *3*, 233–252.
29. Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; John Wiley & Sons: New York, 1961.
30. Hückel, E. *Z. Phys.* **1931**, *70*, 204–286.
31. Berson, J. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2750–2764.
32. Berson, J. A. *Chemical Creativity*; Wiley-VCH: Weinheim, Germany, 1999; Chapter 3.
33. Karachalios, A. *Erich Hückel (1896-1980) From Physics to Quantum Chemistry*; Springer: Dordrecht, 2010.
34. Doering, W. v. E.; Detert, F. L. *J. Am. Chem. Soc.* **1951**, *73*, 876–877.
35. This is a listing of the ten textbooks I surveyed to obtain my conclusions given in the text of this chapter. I have taught from the textbooks authored by Klein, McMurry, Wade, Morrison and Boyd, and Ternay, although not necessarily from the editions cited. The surveyed textbooks are: (a) Klein, D. *Organic Chemistry*, 1st ed; John Wiley and Sons: Hoboken, NJ, 2012. (b) McMurry, J. *Organic Chemistry*, 8th ed.; Brooks/Cole: Belmont, CA, 2012. (c) Wade, L. G., Jr. *Organic Chemistry*, 7th ed.; Prentice Hall: Upper Saddle River, NJ, 2010. (d) Carey, F. A.; Giuliaro, R. M. *Organic Chemistry*, 8th ed.; McGraw Hill: New York, 2011. (e) Jones, M., Jr.; Fleming, S. A. *Organic Chemistry*, 4th ed.; W. W. Norton & Co.: New York, 2010. (f) Smith, J. G. *Organic Chemistry*, 3rd ed.; McGraw Hill: New York, 2011. (g) Solomons, T. W. G.; Fryhle, C. B. *Organic Chemistry*, 9th ed.; John Wiley & Sons: Hoboken, N J, 2008. (h) Brown, W. H.; Foote, C. S.; Iverson, B. L.; Anslyn, E. V. *Organic Chemistry*, 6th ed.; Brooks/Cole: Belmont, CA, 2012. (i) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn and Bacon, Inc.: Newton, MA, 1983. (j) Ternay, A. L., Jr. *Contemporary Organic Chemistry*, 2nd ed.; W. B. Saunders: Philadelphia, PA, 1979.
36. Unless otherwise noted, all information and pictures in this section were obtained from Wheland's children, Dr. Margaret Couch and Dr. Robert Wheland.
37. Westheimer, F. H. Transcript of an Interview Conducted by Leon Gortler at Harvard University, January 4−5, 1979, The Beckman Center for the History of Chemistry.
38. Wheland, G. W. A Study of Certain Organic Acids. Ph.D. Thesis, Harvard University, Jan. 1, 1932.
39. Conant, J. B.; Wheland, G. W. *J. Am. Chem. Soc.* **1932**, *54*, 1212–1221.
40. Linus Pauling Day-by-Day, Special Collections, Oregon State University, Letter from Linus Pauling to James B. Conant, February 21, 1933.
41. Linus Pauling Day-by-Day, Special Collections, Oregon State University, Letter from Linus Pauling to James B. Conant, September 25, 1934.
42. Linus Pauling Day-by-Day, Special Collections, Oregon State University, Letter from Linus Pauling to H. I. Schlesinger, December 23, 1936.
43. Gortler, L. *J. Chem. Educ.* **1985**, *62*, 753–757.

44. Mayo, F. R. Interview by Leon B. Gortler at SRI International, Stanford, California, 21 January, 1981, (Philadelphia: Chemical Heritage Foundation, Oral History Transcript # 0031).
45. Wheland, G. W. *The Theory of Resonance and its Application to Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1944; p 3.
46. Wheland, G. W. *Advanced Organic Chemistry*, 1st ed. (Syllabus for Advanced Organic Chemistry, 321,322); University of Chicago: Chicago, IL, 1946, 1948.
47. Wheland, G. W. *Advanced Organic Chemistry*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1949.
48. Russell, C. A. *The History of Valency*; Leicester University Press: Leicester, England, 1971 (distributed in North America by Humanities Press Inc., New York); pp 307− 308.
49. Hunsberger, I. M. *J. Chem. Educ.* **1954**, *31*, 504–514.
50. Hargittai, I. *Chem. Intell.* **1995**, *1* (1), 34–37.
51. Hargittai, I. *Candid Science: Conversations with Famous Chemists*; Imperial College Press: London, 2000; pp 8−13.
52. Graham, L. *Science and Philosophy in the Soviet Union*; Knopf: New York, 1972; Chapter 8.
53. Hager, T. *Force of Nature. The Life of Linus Pauling*; Simon & Schuster: New York, 1995; pp 328−329, 657.
54. Wheland, G. W. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1960.
55. Wheland, G. W. *Advanced Organic Chemistry*, 1st ed. (Syllabus for Advanced Organic Chemistry, 321,322); University of Chicago: Chicago, IL, 1946, 1948; Chapter 9, p 29.
56. Reudenberg, K. *J. Phys. Chem. A* **2010**, *114*, 8490–8495.
57. Reudenberg, K. Private communication to E. T. Strom, Mar. 8, 2011.
58. Roberts, J. D. Private communication to E. T. Strom, Oct. 13, 2012.
59. Rice, S. A. Private communication to E. T. Strom, Oct. 27, 2012
60. Olofson, R. A. Private communications to E. T. Strom, Oct. 15 and Oct. 26, 2012.
61. Gortler, L. Private communication to E. T. Strom, Oct. 12, 2012.
62. Curphey, T. Private communication to E. T. Strom, Oct. 13, 2012.
63. Paulus, H. Private communication to E. T. Strom, Oct. 19, 2012.
64. Wagner, R. B.; Zook, H. D. *Synthetic Organic Chemistry*; Wiley: New York, 1953.
65. Wheland, R. Private communication to E. T. Strom, Oct. 13, 2012.
66. Smith, D. H. Private communication to E. T. Strom, Mar. 20 and Mar. 21, 2011 and Nov. 5, 2012.
67. LeNoble, W. Private communication to E. T. Strom, Nov. 21, 2010 and Mar. 23, 2011.
68. Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1955.
69. Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1955; p. viii.

70. Beckhaus, H.-D.; Faust, R.; Matzger, A. J.; Moohler, D. L.; Rogers, D. W.; Ruechardt, C.; Sawhney, A. I.; Verevkin, S. P.; Vollhardt, K. P. C.; Wolff, S. *J. Am. Chem. Soc.* **2000**, *122*, 7819–7820.
71. Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1955; pp 4−5.
72. Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1955; pp 145−146.
73. Breslow, R.; Yuan, C. *J. Am. Chem. Soc.* **1958**, *80*, 5991–5994.
74. Matlow, S. L.; Wheland, G. W. *J. Am. Chem. Soc.* **1955**, *77*, 3653–3655.
75. Jensen, W. B. Private communication to E. T. Strom, June 7, 2011 and June 29, 2012.
76. Mislow, K. M. Interview with I. Hargittai. *Chem. Intell.* **1998**, *4*, 16–25.
77. Mislow, K. M. Private communication to E. T. Strom, May 15, 2012.
78. Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319–3328.
79. Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506–512.
80. Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 513–517.
81. Announcements: Graduate Programs in the Divisions, University of Chicago, 1957−58; p 179.
82. Pauling, L.; Wheland, G. W. *J. Chem. Phys.* **1933**, *1*, 362–374.
83. Karachalios, A. *Erich Hückel (1896-1980) From Physics to Quantum Chemistry*; Springer: Dordrecht, 2010; pp 115−116, 127−132.
84. Pauling, L.; Wheland, G. W. *J. Chem. Phys.* **1935**, *3*, 315.
85. Pauling, L.; Wheland, G. W. *J. Am. Chem. Soc.* **1935**, *57*, 2086–2095.
86. Karachalios, A. *Erich Hückel (1896-1980) From Physics to Quantum Chemistry*; Springer: Dordrecht: 2010; pp 143−145.
87. Longuet-Higgins, H. C.; Wheland, G. W. *Ann. Rev. Phys. Chem.* **1950**, *1*, 132–150.
88. Wheland, G. W. *Phys. Chem. Hydrocarbons* **1950**, *1*, 1–53.
89. Wheland, G. W. *Trans. Faraday Soc.* **1937**, *33*, 1499–1502.
90. Wheland, G. W. *Proc. R. Soc. London, Ser. A* **1938**, *164*, 397–408.
91. Wheland, G. W. *Ann. N.Y. Acad. Sci.* **1940**, *40*, 77–90.
92. Wheland, G. W. *J. Am. Chem. Soc.* **1941**, *63*, 2025–2027.
93. Lazdins, D.; Karplus, M. *J. Am. Chem. Soc.* **1965**, *87*, 920–921.
94. Wheland, G. W.; Pinkston, J. T., Jr. *J. Chem. Phys.* **1944**, *12*, 69.
95. Wheland, G. W. *J. Chem. Phys.* **1945**, *13*, 239–248.
96. Wheland, G. W.; Mann, D. E. *J. Chem. Phys.* **1949**, *17*, 264–268.
97. Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; John Wiley & Sons: New York, 1961, pp. 115-116.
98. Streitwieser, A., Jr.; Nair, P. M. *Tetrahedron* **1959**, *5*, 149–165.
99. Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 4123–4135.
100. Streitwieser, A., Jr. Private communication to E. T. Strom, Mar. 8, 2011.
101. Wheland, G. W.; Matlow, S. L. *Proc. Natl. Acad. Sci. U.S.A.* **1952**, *38*, 364–371.
102. Wheland, G. W. *J. Chem. Phys.* **1955**, *23*, 79–83.
103. Wheland, G. W. *J. Chem. Phys.* **1956**, *24*, 67–70.

Chapter 4

The Free-Electron Model

From Otto Schmidt to John Platt

William B. Jensen[*]

Department of Chemistry, University of Cincinnati,
Cincinnati, Ohio 45221-0172
[*]E-mail: jensenwb@ucmail.uc.edu

This paper outlines the historical development of the free-electron model of chemical bonding and spectra as a representative example of attempts by quantum chemists, in the period 1935-1965, to develop, in lieu of effective computerized computations, approximate "pen and paper" models of both chemical bonding and spectra. Beginning in 1938 with the pioneering work of Otto Schmidt, the history of the free-electron model is traced through the 1960s, with emphasis on the work of Hans Kuhn in Switzerland and John Platt and associates at the University of Chicago. It concludes with a brief evaluation of the continuing pedagogical relvance of the model.

The Lull in Quantum Chemistry

Beginning about 1935, and extending through the mid-1960s, quantum chemistry hit a lull. The reasons for this were vividly outlined in a lecture given at Reed College in July of 1959 by the quantum chemist, George Kimball (Figure 1) of Columbia University (*1*):

> *Quantum mechanics was first invented or discovered in about 1925, and from there until about 1935 the field seemed to open right up. Progress was extremely rapid, all kinds of ideas came tumbling out, many of which very rapidly got into quite elementary books. Then, all of a sudden, about 1935 the whole thing seem to come to a stop. Most of the people who had been working in the field got into something different, and the situation today [i.e., in 1959] is not really very different from what it was in 1935.*

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Figure 1. George Elbert Kimball (1906-1967). (Courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati.)

The reason for this lull, Kimball went on to explain, was quite simple (*1*):

> *Now the reason why progress seemed to stop is the fact that all the easy things were done. In trying to tackle further problems the mathematical difficulties were so great they simply overwhelmed everybody who tried them.*

Noting that even the advent of the early electronic computer had so far failed to solve this problem, Kimball pessimistically concluded that (*1*):

> *When you take a cold-blooded look at the situation it is really discouraging. In the face of all of the problems in atomic and molecular structure, the only ones which have been solved with real precision are: the problem of the hydrogen atom, the problem of the helium atom, the problem of the hydrogen molecule,* H_2 *and that's all. That has been the absolute limit to which really complete calculations have been carried.*

Responses to this situation varied. As already noted by Kimball, many simply left the field for greener intellectual pastures. Thus Heisenberg moved into the field of nuclear physics, whereas Schrödinger and a host of younger physicists and quantum chemists, such as Walter Elsasser, Max Delbrück, and Leslie Orgel, would be attracted to the rising field of molecular biology. Others, such as John Platt, H. Christopher Lonquet-Higgins, and ultimately Kimball himself, would leave physical science altogether, whereas yet others would stick it out by resigning themselves to the laborious working out of ever better approximations for apparently intractable integrals and ever more complex computational algorithms as the computer gradually increased in power and efficiency.

Though we owe the current successes of quantum chemistry to the persistence of this latter group, there was yet a third group, who, hoping for a quicker return, would opt instead for the pursuit of radically simplified approximate bonding models which, while retaining the qualitative essences of quantum mechanical insights, would remain mathematically tractable – if of low quantitative accuracy. Indeed, this third approach was taken by Kimball himself before ultimately deserting the field altogether. As he explained in his lecture (*1*):

> *The other problems have produced an almost ridiculous flow of approximate calculations. It struck me, some time ago, that there was a remarkable feature that all these approximate calculations had in common, and that was that, starting from almost any old assumption, including some that were definitely known to be wrong, one ground a mathematical crank and came out with answers that were within 10% or so of the truth. Almost any assumption would give that degree of accuracy; but even the most sophisticated work, trying to improve that degree of accuracy, got nowhere. Well I beat my head against this business about trying to get better accuracy for a long time, and finally I got tired of it and said, "Let's try a different angle. Instead of trying to make a better calculation, let's try reversing the situation and see how bad a calculation we can make and still come out with the same first approximation." There seemed to be abundant evidence that you could make perfectly terrible first approximations and come out with this 10% sort of accuracy.*

The result of Kimball's discontent was his development, via the Ph.D theses of five graduate students spanning the period 1952-1957, of an approximate localized MO model known as the "charge-cloud model" which became the basis of the 1964 CBA high school chemistry textbook and was further refined, under the rubric of the "tangent-sphere model," in a series of more than a dozen papers and reviews published by Henry Bent during the 1960s (*2*).

Likewise the early semi-quantitative work of Linnett and Mellish on spin correlation was amplified by Nyholm and Gillespie in 1957 and further refined by Gillespie throughout the 1960s into what is now known as the “Valence-Shell Electron Pair Repulsion” or “VSEPR” model of molecular geometry (*3*, *4*), and Linnett, again during the 1960s, also eventually elaborated his earlier work into a refinement of the original Lewis model known as “double-quartet theory” (*5*, *6*).

Though the present author feels that both the charge-cloud and the double-quartet models still have much to recommend them – certainly far more than the circa 1916 Lewis dot structures and memorized random fragments of VB and MO theory which currently dominate the Freshman textbook – of these approximate models, only VSEPR theory has survived as an inherent part of both the introductory and inorganic textbook. However, yet a fourth approximate bonding model developed during this period in response to these pressures has also survived in the textbook literature, albeit not in the Freshman text. This is the free-electron model for π-conjugated electron systems and is the central focus of this paper.

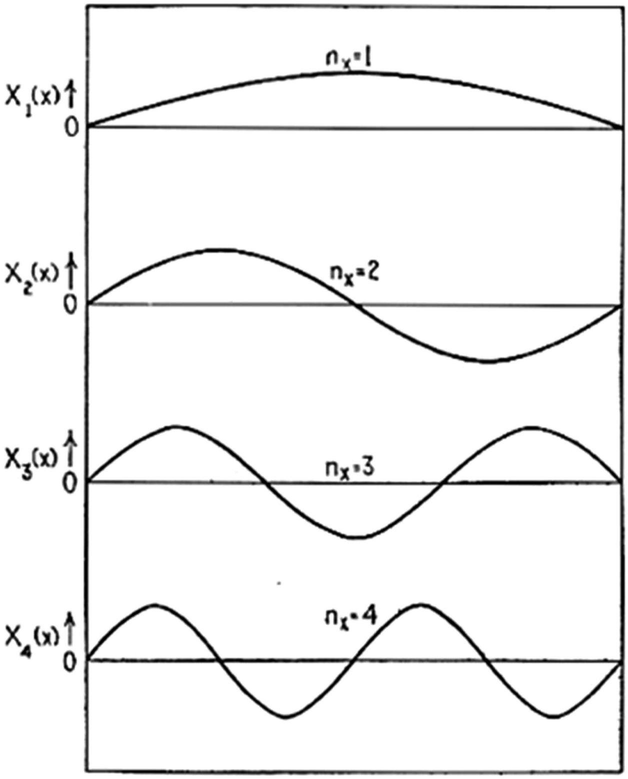


Figure 2. The graphical representation of the results for the simple one-dimensional particle in a box problem as given in the 1935 text by Pauling and Wilson (7).

Otto Schmidt and the Double-Bond Rule

By the mid 1930s the classical problem of a particle in a one-dimensional box with infinite walls had made it into textbooks on quantum mechanics, as illustrated by Figure 2, which is taken from the classic 1935 text by Pauling and Wilson (*7*). Here it was used to illustrate one of the simplest quantitative applications of the Schrödinger equation – a pedagogical role which it continues to play in textbooks on quantum mechanics even to this day.

The first attempt to apply this model, not just as a simple exercise in mathematical computation, but as an actual physical approximation for the π-electron systems of conjugated molecules, was made by the German organic chemist, Otto Schmidt (Figure 3), in a series of papers published between 1938 and 1942 (*8–11*). Born in Cologne in 1874, Schmidt studied chemistry at Bonn and Zürich, receiving a doctorate in chemistry from Bonn in 1900 for work done under Eugen Bamberger. After a stint in academia, Schmidt became an industrial chemist in the employ of the Badische Anilin und Soda Fabrik (BASF), where he remained until his retirement in 1931, after which he maintained an affiliation with the University of Darmstadt until his death in 1943 (*12*).

Schmidt is best remember today for his development of the so-called "double-bond" or "Schmidt rule," which states that the presence of a double bond or of a conjugated system, such as a phenyl group, in an organic molecule tends to stabilize the sigma bonds immediately adjacent to it (i.e. in the α-positions) but weaken and thus activate those once removed (i.e. in the β-positions) (*13*, *14*).

Schmidt's exploration of the free-electron model was ultimately driven by his attempts to find a theoretical rationale for his double-bond rule. Though he spent the period 1931-1932 as a visiting Professor at Caltech and interacted with Linus Pauling, he would reject the standard VB rationale of the rule involving differing degrees of resonance stabilization for the various alternative products formed after sigma bond cleavage. Likewise, though he would distinguish between tightly bound "*A*-electrons" and the loosely bound "*B*-electrons" unique to multiple bond and conjugated systems, he would never adopt the more conventional MO designations of sigma (σ) and pi (π) for these two types of electrons. Rather he assumed that the loosely bound *B*-electrons (i.e. π-electrons) of the multiple bond system could interact with the adjacent sigma bonds in the parent molecule to cause an alternation in bond strengths, making the immediately adjacent sigma bond stronger, the sigma bond once removed weaker, the sigma bond twice removed stronger, etc, with the effect gradually dying out as one moved further from the multiple bond system.

It was this concept of loosely bound *B*-electrons coupled to alternating bond strengths – and hence alternating electron densities – which no doubt attracted Schmidt to the problem of the particle in the box, with its alternating nodal properties, in the hope that it would support his theory of the double-bond rule. In his papers, he applied the free-electron model almost exclusively to benzene and related aromatic systems, modeling their π-electrons (i.e., *B*-electrons) as freely moving particles in a cylindrical box of constant potential (Figure 4). In recognition of this assumption he eventually came to refer to the theory as the *Kastenmodell* or "box model" of the chemical bond.

Figure 3. Franz Otto Schmidt (1874-1943). (Courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati.)

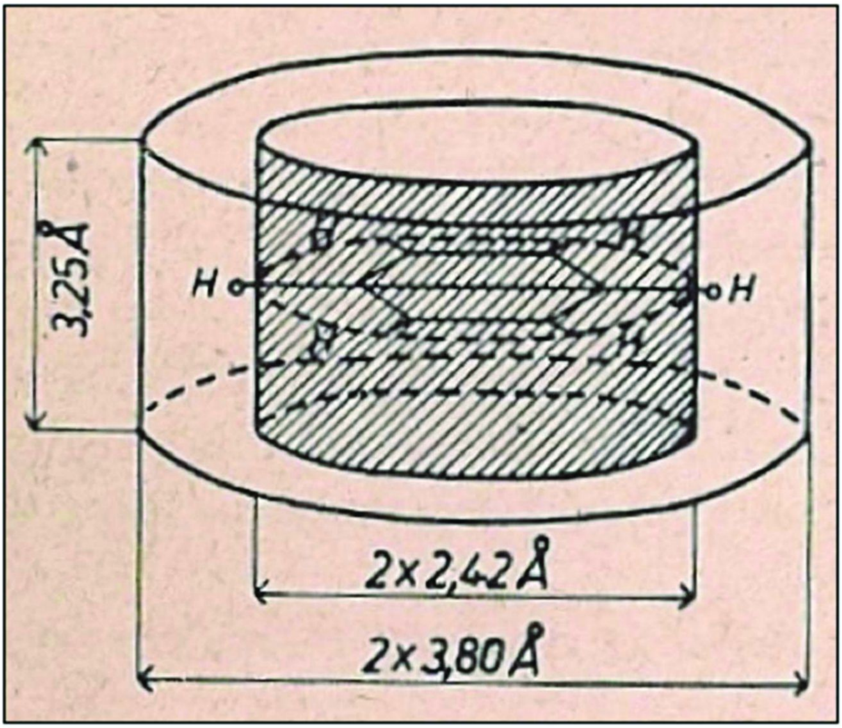


Figure 4. Schmidt's cylindrical box model for the π-electrons of benzene.

The disruptions of the Second World War and the fact that Schmidt chose to publish in journals not widely read by quantum chemists meant that his initial application of the free-electron model to conjugated systems went largely unnoticed. It was not until 1948 that interest in this approach was rekindled when three independent papers dealing with the model appeared in rapid succession – the first by the Australian spectroscopist, Noel Bayliss (*15*), the second by the Swiss chemist, Hans Kuhn (*16*, *17*), and the third by the American chemist, William Simpson (*18*). The next year this trio was joined by yet a fourth author – John R. Platt of the Department of Physics at the University of Chicago (*19*).

None of these four authors seems to have initially been aware of Schmidt's pioneering work, though Kuhn and Platt would eventually come to acknowledge it. Indeed, both Bayliss and Kuhn suggested that they had been inspired instead by Sommerfeld's original 1928 free-electron model of the metallic bond and even Schmidt had made passing comparisons between his so-called *B*-electrons and the conduction electrons in metals (*20*). Though Bayliss would go on to write the first definitive review article on the free-electron model in 1952 for the British journal *Quarterly Reviews* (*21*), it is Kuhn and Platt who would eventually emerge over the next decade as the major advocates of the model and whose contributions thus require closer scrutiny.

Hans Kuhn and Dye Chemistry

Born in 1919 in Berne, Switzerland, Hans Kuhn (Figure 5) studied chemistry at both the ETH in Zürich and the University of Basel, receiving his doctorate in chemistry from the latter institution for work done under the guidance of Werner Kuhn (no relation). From 1946-1947 he was a postdoctoral fellow with Linus Pauling at Caltech. In 1951 he was appointed Professor of Chemistry at the University of Basel, followed in 1953 by his move to the University of Marburg, where he served as Director of the Institute of Physical Chemistry. In 1970 he joined the Max Planck Institute for Biophysical Chemistry in Göttingen, where he served as Director of the Department of Molecular Systems Assembly until his retirement in 1985.

As is well known by those attending this symposium, the standard solution for a particle in a one-dimensional box with infinite walls gives a series of energy levels defined by the equation:

$$E = (h^2/8m)(n^2/L^2)$$

where h is Planck's constant, m is the mass of the particle and L is the length of the box. For a box containing N electrons, the energy of transition, ΔE, between the highest occupied energy level and the lowest unoccupied energy level will correspond to a transition between the quantum levels $n_{HO} = N/2$ and $n_{LU} = N/2 + 1$ and will give the final result:

$$\Delta E = E_{LU} - E_{HO} = (h^2/8m)(N + 1)/L^2$$

or, alternatively, in terms of the corresponding wavelength for the transition:

$$\lambda = hc/\Delta E = (8mc/h)L^2/(N + 1)$$

By expressing both N and L as reasonable functions of the number of carbon atoms (Z) in a conjugated hydrocarbon chain and the average bond length (l) between each atom, this result becomes a simple model for the excitation of the molecule's π-electrons (Figure 6):

$$\lambda = (8ml^2c/h)[Z^2/(Z + 1)]$$

and allows one to establish a correlation between λ and Z for a series of related compounds.

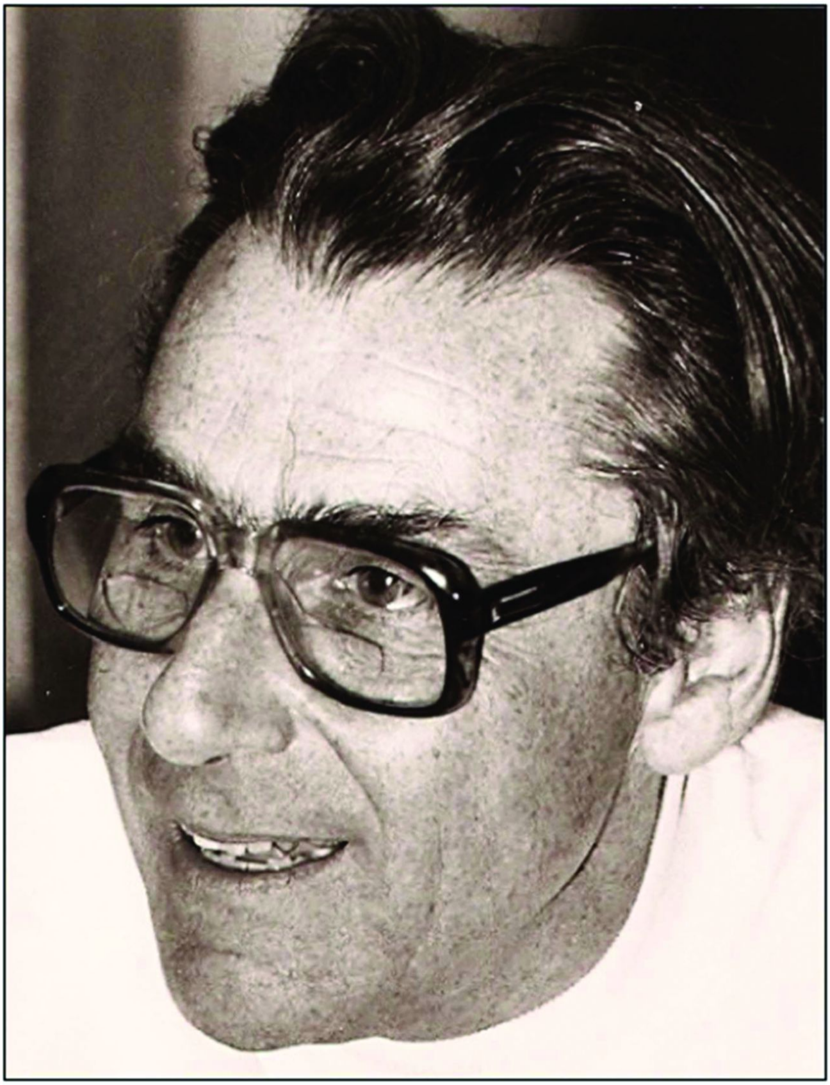


Figure 5. Hans Kuhn (b. 1919). (Courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati.)

In his initial paper, Bayliss had applied these results to the spectra for a series of simple linear polyenes but had obtained only moderate agreement between the calculated and measured values of λ (*15*). In contrast, Kuhn, after a preliminary study of the spectra of various conjugated chain systems, concluded that the symmetrical cyanine dyes, which consisted of conjugated polyene chains with resonance-equivalent auxochrome groups attached at each end, displayed the most regular spectra and was able to obtain excellent agreement between the calculated and measured values of λ for the maximum absorption peak for these systems (*16*).

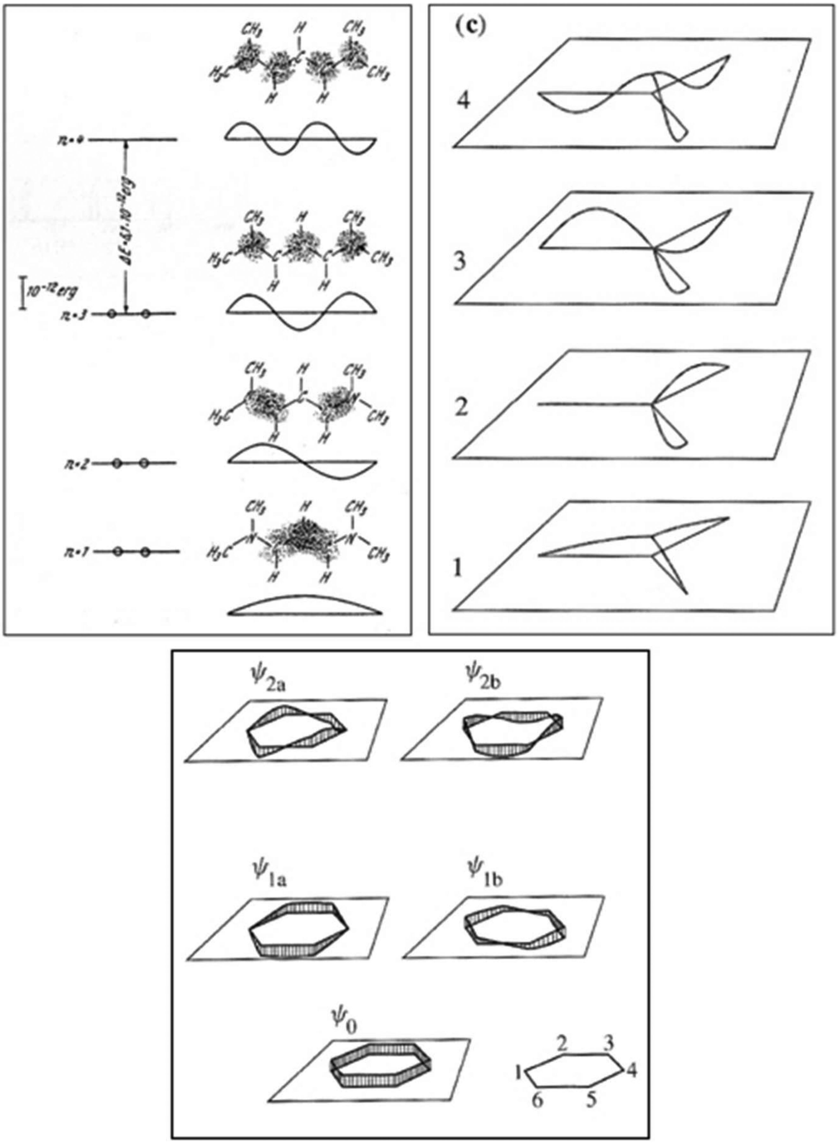


Figure 6. Example applications of the free-electron model to: (upper left) the linear π-system of the $(CH_3)_2N\text{-}CH{=}CH\text{-}CH\text{-}N(CH_3)_2^+$ ion; (upper right) the

branched π-system of the guanidinium cation $C(NH_2)_3^+$; and (bottom) the cyclic π-system of benzene.

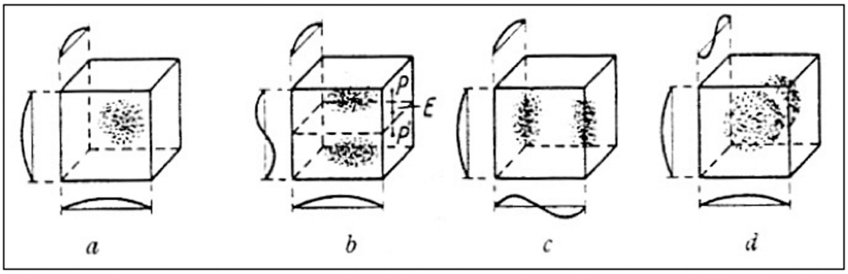


Figure 7. A FE analog of the s- and p-orbitals of a H atom based on an electron in a 3D box.

Between 1948 and 1963 Kuhn and his coworkers would publish more than two dozen papers, reviews and notes dealing with various aspects of the free-electron model (*22*). Though they would also explore the application of the model (Figure 6) to branched and cyclic conjugated systems, as well as free-electron (FE) analogs of both the H atom (Figure 7), and the H_2^+ molecule, the central focus would always remain the linear conjugated dye systems which had prompted the initial work. While some of the papers done in conjunction with his graduate students at Marburg were quite mathematical, Kuhn would repeatedly publish general interest articles in both German and English in a wide variety of chemical journals directed primarily at practicing organic chemists in which results of interest were presented with a minimum of mathematical detail and with striking diagrams and figures designed to effectively summarize the results. As a consequence, by the 1960s and early 1970s brief treatments of the free-electron model of conjugated systems had begun to appear in both books on dye chemistry and in textbooks dealing with physical organic chemistry (*23–25*).

The culmination of Kuhn's work came with the publication of a small monograph in German entitled (in translation), *The Electron-Gas Method*, which was Kuhn's preferred name for the free-electron model. This was based on a series of lectures given in September of 1963 at a conference on the Theory of π-Electron Systems held in Constance Germany and contains a fairly comprehensive bibliography of his publications on this subject (*26*).

John Platt and the Chicago Group

The work of Platt, on the other hand, shows some significant contrasts with that of Kuhn, many of which are traceable to the simple fact that he was trained as a physicist rather than as a chemist. John Rader Platt (Figure 8) was born in 1918 in Jacksonville, Florida, and was educated at Northwestern University and the University of Michigan, from which he received his doctorate in physics in 1941. From 1945-1965 he taught physics at the University of Chicago and was also a member of Robert S. Mulliken's Laboratory for Molecular Structure and Spectra.

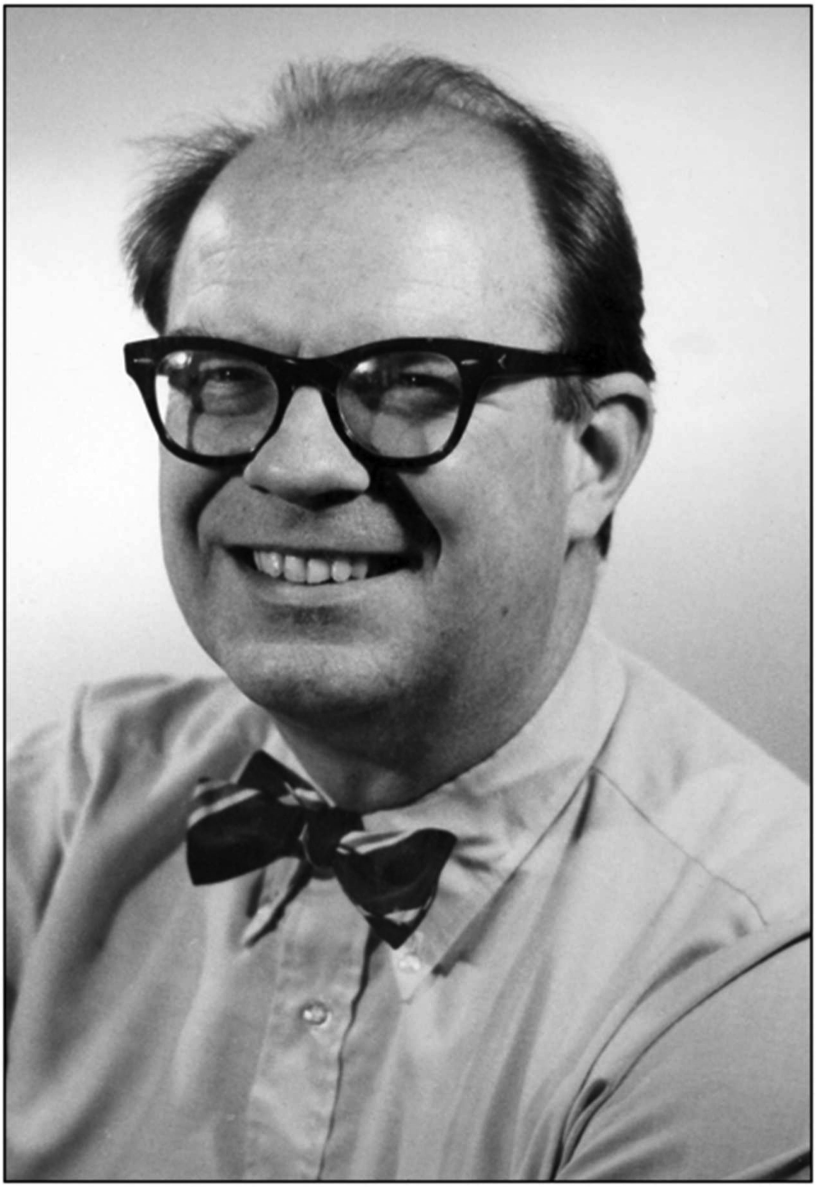


Figure 8. John Rader Platt (1918-1992). (Courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati.)

Between 1949 and 1964 Platt and his students and associates at Chicago would publish roughly 21 papers dealing with the free-electron or FE-model, as they preferred to call it, and another 35 papers dealing with the measurement and systemization of the spectra for conjugated systems. In 1964 these papers where reissued as collected volumes by the laboratory at Chicago, the first set, dealing with FE theory, under the title *Free-Electron Theory of Conjugated Molecules: A Sourcebook* (*27*), and the second set, dealing with spectra, under the title *Systematics of the Electronic Spectra of Conjugated Molecules: A Source Book* (*28*).

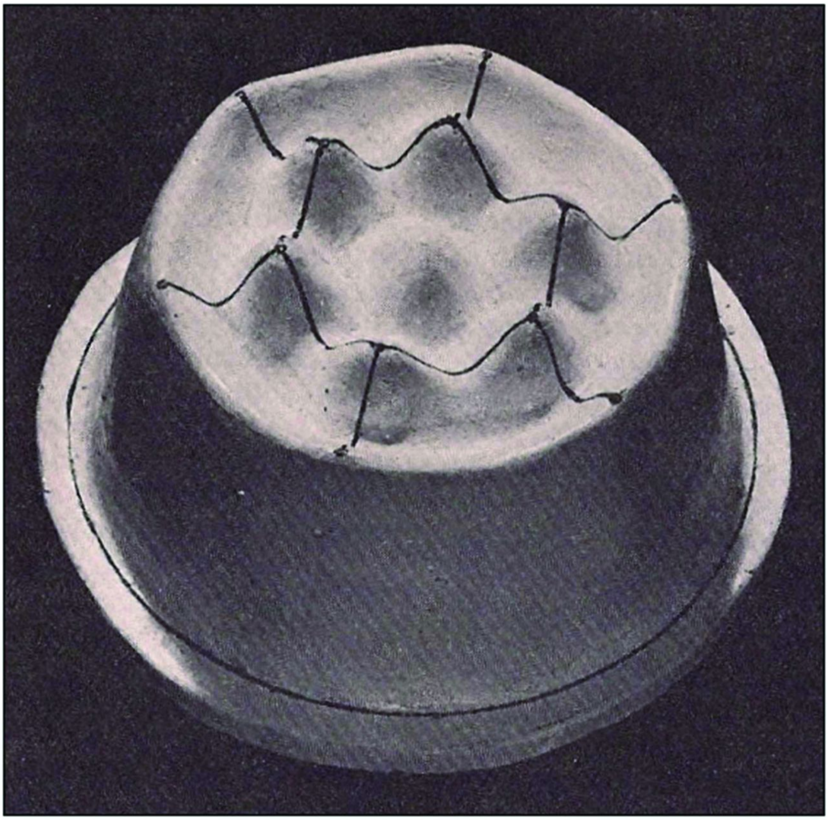


Figure 9. One of Platt's plaster models for electron density distributions. This one is for the sigma densities on benzene.

Whereas Kuhn's work had centered primarily on linear conjugated chain systems, that of Platt and his associates was centered primarily on condensed or polynuclear conjugated ring systems. Likewise, whereas Kuhn made an effort to communicate his results to practicing organic and industrial chemists, the work of the Chicago group was directed almost solely at other theoreticians and was far more mathematical and formal in nature. This is also reflected in the fact that virtually all of it was published in the *Journal of Chemical Physics,* whereas Kuhn, though occasionally publishing in this journal, placed his work in a much broader range of journals and also published in both German and English. Though Platt did publish several papers dealing with the construction of visual models to represent the electron densities predicted by the FE model – one involving wire and wooden pegs and the other plaster casts (Figure 9), for the most part the publications of the Chicago group lacked the abundance of visual aids characteristic of many of Kuhn's more popular reviews (*29*).

While many of these differences, as already suggested, simply reflect a difference in the research styles typical of physicists versus chemists, they are also a partial reflection of a unique emphasis within the Chicago group itself. Though the major attraction of the free-electron model lies in its physical and computational simplicity, Mulliken was fully convinced that what was needed in quantum chemistry was a more rigorous *ab initio* approach to computation. As a result, much of the work at Chicago also involved an effort to both elucidate the nature of the assumptions underlying the FE model and its formal relationship to the more conventional LCAO approach to MO theory. Many years later Mulliken would rather tersely summarize his final take on the entire enterprise in his autobiography (*30*):

> *The free-electron model, a favorite with Platt, is rather artificial and not rigorous, but gives interesting and suggestive results similar to those of MO theory.*

Though Platt was undoubtedly the guiding spirit behind the work of the Chicago group on FE theory and published several papers on the theory himself, the most significant contribution of the group – a sophisticated mathematical version of the theory specifically designed to deal with branching and polycyclic systems known as the "Free-Electron Network Model" – was actually the work of his colleagues, Charles Scherr, Norman Ham, and especially that of a young German-born postdoctoral fellow named Klaus Ruedenberg (Figure 10). In a recent assessment of this work, Ruedenberg has noted that (*31*):

> *The distinctive difference between our work and that of Kuhn and Bayliss was that we were interested in demonstrating and did demonstrate the rigorous equivalence between the free-electron-network model and the Hückel-type LCAO model. This equivalence provided a conceptually instructive visualization of Hückel-type LCAO coefficients as amplitudes of harmonic network waves and entailed for the LCAO resonance integral the order of magnitude. These equivalences were important to John Platt. On the other hand, they also exhibited the limitations of the free-electron model by showing that it gives reasonable results because it abstracts essential features of the LCAO coefficient variations and not because it correctly describes the local shapes of the electron cloud in detail.*

As many in the audience are aware, Ruedenberg would go on to have a highly distinguished career in theoretical chemistry at Iowa State University (*32*). Among his many accomplishments are his definitive analysis of the roles of the kinetic versus the potential energy terms in covalent bond formation and his extensive studies of localized MO distributions, both of which strongly influenced the present author while still a graduate student at the University of Wisconsin.

In 1965 Platt, like Kimball before him, left the field of quantum mechanics to pursue research in the fields of sociology, political science, and biophysics, eventually becoming Associate Director of the Mental Health Research Institute at the University of Michigan, from which he retired in 1977. He died in Boston in 1992 at age 74 (*33*).

Figure 10. Klaus Ruedenberg (b. 1920). Taken about the time he was working on the FE Network Model. (Courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati.)

Other Contributors

In focusing on the work of Schmidt, Kuhn, Platt, and Ruedenberg I do not mean to imply that there were no other contributors to the development of the free-electron model. In a bibliography of papers and books dealing with the model, and spanning the years 1938-2010, I have identified no less than 125 contributions and 220 individual contributors (*22*). Thus, the French physicist, Segré Nikitine, for example, contributed nearly a dozen papers in the early 1950s, as did a number of Japanese investigators, including Gentaro Arkai, Takeshi Nakajima, Kenichi Fukui, Yuzuru Oshika, and Shigeru Huzinaga.

Just as Schmidt preferred the term "box model," Kuhn the term "electron-gas model," and Platt the term "free-electron model," so Nikitine – following the lead of Bayliss – always referred to it as the *modèle métallique* or "metallic model" of the chemical bond (*34*). In addition to the calculation of spectroscopic transition energies, electron densities, bond orders, and bond lengths pioneered by Kuhn and Platt, these other workers also suggested further applications to account for such diverse phenomena as electronegativity effects (*35*), aromatic substituent effects (*36*), and even color changes for acid-base indicators (*37*).

Pedagogical Consequences

In the preface to the 1964 edition of the collected papers of the Chicago group on the FE model, Platt also commented on the potential pedagogical advantages of the model (*27*):

> *These equivalencies have established the free-electron network model as the most fruitful and, in fact, the only natural way of conceptually grasping LCAO wave functions in conjugated systems. It is therefore a useful teaching device and a valuable subject for the beginner and the advanced chemist alike. Moreover, it permits a number of interesting problems to be solved quantitatively even by first-year chemistry students without the help of matrix algebra, which is indispensable for the LCAO approach.*

Just about the time that Platt penned these words, the nature of the literature dealing with the free-electron model began to change in such a fashion as to partially justify these claims. More and more papers began to appear in the chemical education literature rather than in the primary research literature and the focus began to shift from refinements and extensions of the initial model to potential pedagogical applications. Between 1963 and 2010 at least two dozen papers dealing with either the free-electron model or with other applications of the particle-in-a-box model have appeared in the *Journal of Chemical Education*. By creatively invoking a variety of differently shaped potential wells (Figure 11), it has been successfully applied as a useful approximate rationalization for the Bohr atom, the spacing of molecular rotational and vibrational levels, the Jahn-Teller effect, and bond polarity effects, to name but a few (*22*).

Some of these simple applications were actually incorporated into the short, introductory, undergraduate supplements on bonding theory and quantum mechanics that were popular throughout the late 1960s and the 1970s (*38–40*). Though this particular publishing genre seems to have now largely disappeared, many of these simple applications have more recently been included in the superb textbook of physical chemistry coauthored by Hans Kuhn after his retirement and which is now in its second edition (*41*).

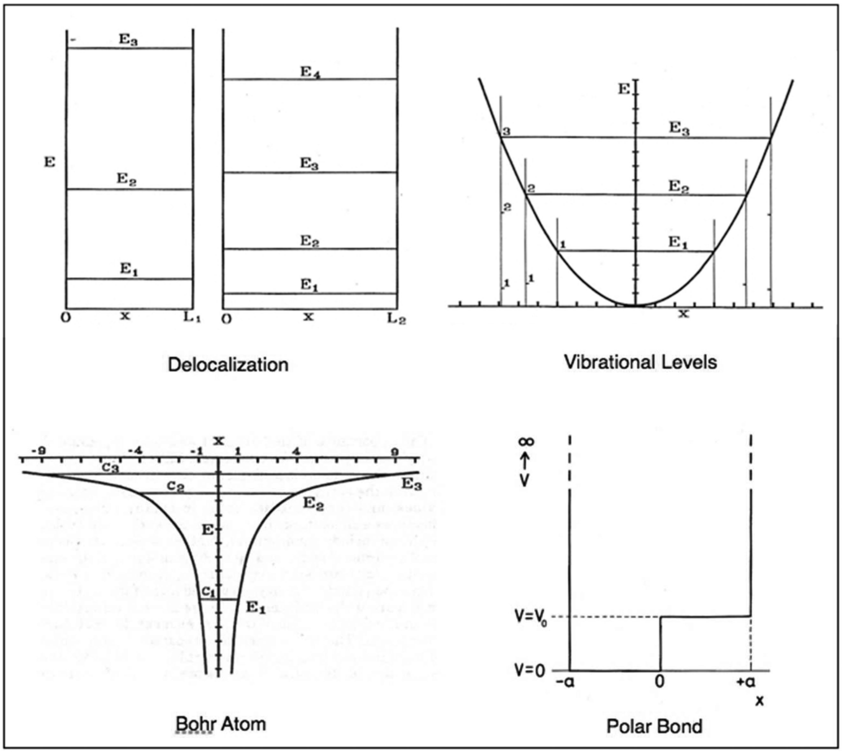


Figure 11. Some of the potential wells that have been used to develop particle-in-a-box analogs for a variety of fundamental chemical concepts.

The only part of Platt's assessment that has not been fulfilled is the application of the FE model to first-year chemistry courses. Given the well-known lack of mathematical competency among American college students, such an application would be possible merely by "physically" fitting the wave function to the allowed path length of the postulated potential well:

$$L = n\lambda/2$$

and invoking the de Broglie relation:

$$\lambda = h/mv = h/(2mE)^{0.5}$$

rather than by solving a simplified Schrödinger equation. Such an application would also require a radical reformation of the current "memorized fragment" approach to both MO and VB theory currently found in the Freshman textbook. Indeed, it would require a recognition of the point made by Mulliken in his

1966 Nobel Prize lecture (*42*) – namely that, while both the total energy and the total electron density of a ground-state atom or molecule are invariant, the dissection of these two parameters into contributions from various component orbitals is to some extent arbitrary. Of these various alternatives, Mulliken singled out two choices for analyzing a given molecule – either in terms of a set of fully delocalized, symmetry-adapted MOs, which he called *spectroscopic orbitals* because of their use in rationalizing spectra, ionization energies and other one-electron properties, or in terms of a set of relatively nonoverlapping localized MOs, which he called *chemical orbitals* because of their use in rationalizing the ground-state structures of molecules. Obviously the free-electron model would be a simple way of illustrating the use of a typical set of spectroscopic orbitals, whereas the Kimball charge-cloud model would be a simple way of illustrating, *a la* the VSEPR rules, the use of a typical set of chemical orbitals (*43*).

Though these quantum mechanical concepts are now well over a half century old, I am not particularly optimistic that such a reformation is still possible. As the American university becomes increasingly dominated by the corporate business mentality, which demands interchangeable educational credits and standardized exams with standardized and memorizable black and white answers and vocabulary, chemistry departments have increasingly lost creative control of their introductory chemistry courses, whose contents are now largely determined by the marketing departments of the book publishers rather than by the actual instructors. The adoption of the spectroscopic/chemical orbital dichotomy would be profoundly at odds with this trend as it would require recognition that theoretical models are not God-given truths to be memorized for exams but rather pragmatic solutions to certain problems and that, as the nature of the problem changes, so must the theoretical model. Part of the skill of a good scientist is knowing how to select the proper model for a given problem and, even more so, how to select the proper level of sophistication for the model through the creative application of Einstein's famous dictum:

> Make it as simple as possible, but no simpler.

Acknowledgments

I would like to thank Bernard Hoogenboom of the Department of Chemistry of Gustavus Adolphus College for sharing his knowledge of the life and work of Otto Schmidt and for donating a high-quality photo of Schmidt to the Oesper Collections many years ago. I would also like to thank the late Hans Jaffe of the Department of Chemistry of the University of Cincinnati for his extensive files of reprints dealing with the free-electron model which provided much of the material for the preparation of this paper, and Dr. Klaus Ruedenberg of the Department of Chemistry of Iowa State University for sharing his memories of the Chicago group and for providing figures 8 and 10 as well as several pertinent references.

References

1. Kimball, G. *The Application of Wave Mechanics to Chemistry. Lecture given to the CBA Writing Conference at Reed College on 20 July 1959*; Typewritten transcript, Oesper Collections, University of Cincinnati.
2. Listed in Jensen, W. B. *Bibliography of the Kimball Charge-Cloud Model*; University of Wisconsin, June 1977. Copies available on request.
3. Gillespie, R. J.; Nyholm, R. S. Inorganic Stereochemistry. *Q. Rev., Chem. Soc.* **1957**, *11*, 339–380.
4. Gillespie, R. J. *Molecular Geometry*; Van Nostrand: New York, 1972.
5. Linnett, J. W. A Modification of the Lewis-Langmuir Octet Rule. *J. Am. Chem. Soc.* **1961**, *83*, 2643–2653.
6. Linnett, J. W.*The Electronic Structure of Molecules: A New Approach*; Methuen: London, 1964.
7. Pauling, L.; Wilson, E. B. *Introduction to Quantum Mechanics with Applications to Chemistry*; McGraw-Hill: New York, 1935; pp 33−34, 95−100.
8. Schmidt, O. Die Beziehungen zwischen Dichteverteilung bestimmter Valenzelektronen (*B*-Elektronen) und Reaktivität bei aromatischen Kohlenwasserstoff. *Z. Phys. Chem.* **1938**, *39B*, 59–82.
9. Schmidt, O. Die Charakterisierung der einfachen und Krebs erzeugenden aromatischen Kohlenwasserstoffe durch die Dichteverteilung bestimmter Valenzelektronen (*B*-Elektronen). *Z. Phys. Chem.* **1939**, *42B*, 83–110.
10. Schmidt, O.; Schmidt, H. Weiter Untersuchen zum Kastenmodell (Zylinderring Kompression der *B*-Elektronen). *Z. Phys. Chem.* **1939**, *44B*, 185–193.
11. Schmidt, O. Verschiebungen in den Absorptionsspektren einkerniger Aromaten. *Berichte* **1941**, *74*, 987–1001.
12. Hecht, O. Otto Schmidt, 1874-1943. *Berichte* **1943**, *76A*, 121–125.
13. Hoogenboom, B. E. A History of the Double-Bond Rule. *J. Chem. Educ.* **1998**, *75*, 596–603.
14. Though reference 13 discusses Schmidt's earlier rationale of the rule based on spin interactions, it does not mention his later use of the free-electron model. After completing the initial draft of this paper, Dr. Klaus Ruedenberg brought an interesting article to my attention by Werner Kutzelnigg which contains a tribute to Schmidt and his work on free-electron theory as well as fascinating information on Hückel's opposition to Schmidt's work. See: Kutzelnigg, W. What I Like About Hückel Theory; *J. Comput. Chem.* **2006**, *28*, 25−34.
15. Bayliss, N. S. A "Metallic" Model for the Spectra of Conjugated Polyenes. *J. Chem. Phys.* **1948**, *16*, 287–292.
16. Kuhn, H. Free-Electron Model for Absorption Spectra of Organic Dyes. *J. Chem. Phys.* **1948**, *16*, 840–841.
17. Kuhn, H. Elektronengasmodell zur quantitativen Deutung der Lichtabsorption von organischen Farbstoffen. *Helv. Chim. Acta* **1948**, *31*, 1441–1455.
18. Simpson, W. T. Electronic States of Organic Molecules. *J. Chem. Phys.* **1948**, *16*, 1124–1136.

19. Platt, J. R. Classification of Spectra of Cata-Condensed Hydrocarbons. *J. Chem. Phys.* **1949**, *17*, 484–495.
20. Bayliss and other early writers on the free-electron model generally reference the treatment of the Sommerfeld free-electron model of metals given in Mott, N. F.; Jones, H. *The Theory of the Properties of Metals and Alloys*; Clarendon: Oxford, 1935; pp 51−56.
21. Bayliss, N. S. The Free-Electron Approximation for Conjugated Compounds. *Q. Rev., Chem. Soc.* **1952**, *6*, 319–339.
22. Jensen, W. B. *Bibliography of the Free-Electron Model*; University of Cincinnati, January, 2011. Copies available upon request.
23. Rys, P. *Fundamentals of the Chemistry and Application of Dyes*; Wiley-Interscience: New York, 1972.
24. Karagounis, G. *Introductory Organic Quantum Chemistry*; Academic Press: New York, 1962; pp 155−164.
25. Sandorfy, C. *Electronic Spectra and Quantum Chemistry*; Prentice Hall: Englewood Cliffs: NJ, 1964; Chapter 14.
26. Kuhn, H. *Die Methode des Elektronengases: Vorträge am Internationalen Ferienkurs über die Theorie der π-Elektronensysteme*; Konstanz, 1963.
27. Platt, J. R., Ed. *Free-Electron Theory of Conjugated Molecules: A Source Book*; Laboratory of Molecular Structure and Spectra, University of Chicago: Chicago, IL, 1964.
28. Platt, J. R., Ed. *Systematics of the Electronic Spectra of Conjugated Molecules: A Source Book*; Laboratory of Molecular Structure and Spectra, University of Chicago: Chicago, IL, 1964.
29. See papers 4, 10, and 11 of reference 27.
30. Mulliken, R. S. *Life of a Scientist*; Springer-Verlag: Berlin, 1989; p 123.
31. Correspondence with K. Ruedenberg, February 22, 2011.
32. Ruedenberg, K. Autobiography. *J. Phys. Chem.* **2010**, *114A*, 8490–8495.
33. Page, E. John R. Platt, 74, Scientific Scholar in Many Disciplines. *The New York Times* **1992** June23.
34. Both Kuhn and Platt would also eventually come to use Schmidt's term "Box Model" for certain applications of the FE approach.
35. Basu, S. Nitrogen Electronegativity Correction in Free-Electron Network Theory. *J. Chem. Phys.* **1954**, *22*, 162.
36. Basu, S. Free-Electron Treatment of the Orientation of Substituents in Aromatic Molecules. *J. Chem. Phys.* **1954**, *22*, 1952.
37. Nikitine, S. Sur le modéle métallique de la thionine et du bleu de méthylène. Essai d'une théorie quantique d'indicateurs colorés. *J. Chim. Phys.* **1951**, *48*, 175–184.
38. Murrell, J. N.; Kettle, S. F. A.; Tedder, J. M. *Valence Theory*; Wiley: New York, 1965; pp 10−13, 291−292.
39. Barrett, J. *Introduction to Atomic and Molecular Structure*; Wiley: London, 1970; pp 52−56, 185−186, 224−228,
40. Orchin, M.; Jaffe, H. *Symmetry, Orbitals and Spectra*; Wiley-Interscience: New York, 1970; Chapter 4.
41. Kuhn, H.; Försterling, H-D.; Waldeck, D. H. *Principles of Physical Chemistry*, 2nd, ed.; Wiley: Hoboken, NJ, 2009.

42. Mulliken, R. Spectroscopy, Molecular Orbitals, and Chemical Bonding. *Science* **1967**, *157*, 13–24.
43. Interestingly, Platt summarized both the free-electron and Kimball charge-cloud models in his last major review on chemical bonding: Platt, J. R. The Chemical Bond and the Distribution of Electrons in Molecules. In *Handbuch der Physik*; Flügge, S., Ed.; Springer: Berlin, 1961; Vol. 37 (II), pp 173−281.

Chapter 5

Michael J. S. Dewar: A Model Iconoclast

Eamonn F. Healy[*]

**Department of Chemistry, St. Edward's University,
Austin, Texas 78704**
[*]E-mail: healy@stedwards.edu. Tel: (512) 448 8467. Fax: (512)448 8492

Nearly all who knew him, and many who knew of him, would agree that Michael Dewar is the memoirist's ideal subject: colorful, opinionated and incorrigibly brilliant. This brilliance took the form of a superbly analytical mind that produced solutions to confounding puzzles, ingenious descriptions of complex processes, and inventive approaches to seemingly intractable problems. While the stories associated with these exploits have served to burnish his maverick reputation, it will be the ideas that will endure as his scientific legacy. And what ideas they were.

In 1949 a book titled "The Electronic Theory of Organic Chemistry" was published by Clarendon Press. The author was Michael J. S. Dewar, an Oxford-educated organic chemist, who at the time was working at the fiber manufacturer Courtaulds in Maidenhead, England. The author's purpose was *"…to give as complete an account as possible of organic chemistry in the light of modern quantum theory"*, while acknowledging at the outset that *"few chemists have a real knowledge of both subjects"* (*1*, *2*). What follows is an ambitious mechanistic reexamination of all major organic reactions in light of "modern theory", culminating in a discussion of light absorption and color in conjugated systems. Featured prominently throughout are mechanistic schemes involving the generation of a novel π-complex species.

The following year Michael was invited to present two lectures on his theoretical framework at an international Colloquium in Montpelier, France. In a compelling account of this presentation of his π-complex theory the author

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

concludes that Dewar's inability to communicate his ideas resulted in a missed opportunity to enlighten an influential audience as to the utility of Molecular Orbital (MO) theory in the analysis of structure and mechanism in physical organic chemistry (*3*). This failure was compounded, as per the account, by apparent errors in the presentation of key experimental details, and further exacerbated by the central character's rather possessive attitude towards his, albeit demonstrable, theoretical knowledge. While acknowledging the challenges posed by both Dewar's near-legendary combativeness and his rather polemical style of presentation, a case can be made that the disparate chemical philosophies of Dewar and his mainly American protagonists was always going to prove an insurmountable impediment to formulating any common structural understanding of the problems under discussion.

Michael Dewar would arrive in France as a self-described unknown and, at least as it related to his theoretical abilities, self-taught chemist, whose day job at Courtaulds was supplemented by his nighttime and weekend labors completing his book and writing papers on the application of MO theory to organic chemistry. It is fair to say that Michael's years in the academic wilderness were about to come to an abrupt end.

Structural Ontology and the π-Complex

At Montpelier Dewar would have been following his compatriot Coulson's admonition that *"..the role of quantum chemistry is to understand [chemical] concepts and show what are the essential features in chemical behavior"* (*4*) by explaining the addition of a halogen to an alkene as proceeding through the π-complex shown in Figure 1(i), a structural assignment *sufficient* to explain the observed specificity of the reaction. The prevailing mechanism of Roberts and Kimbal, which was initially proposed to explain the observed *trans* addition, is shown in Figure 1(ii) (*5*). From a topological perspective the cation in Figure 1(i) is equivalent to the structures in Figure 1(iii), and a bonding interaction between the component atoms could equally well be described by the structure Figure 1(iv). Such was stated explicitly by Winstein when after Dewar's presentation he complained that *" I find troublesome Dewar's statement that our formulation of the ethylene brominium ion involves a ring and his doesn't. All that is meant by a 3-ring is a triangular arrangement of three atoms"* (*3*).While Dewar's failure to include a more detailed description of his new μ-bond did not help his case, the very disparate ontological frameworks of Dewar, a structural agnostic, and Winstein, a researcher whose career was in many ways defined by structural controversies, was always going to make for discussions that would yield more heat than light. The structures in Figure 1(iii) would have been seen by Dewar as an unnecessary obfuscation, and indeed he subsequently described structure Figure 1(iv) as an *"obscure dotted line representation"*. More fundamentally he would have considered these resonance structures as unwarranted by the reaction mechanism and unsupported by any appeal to the nature of the wave function.

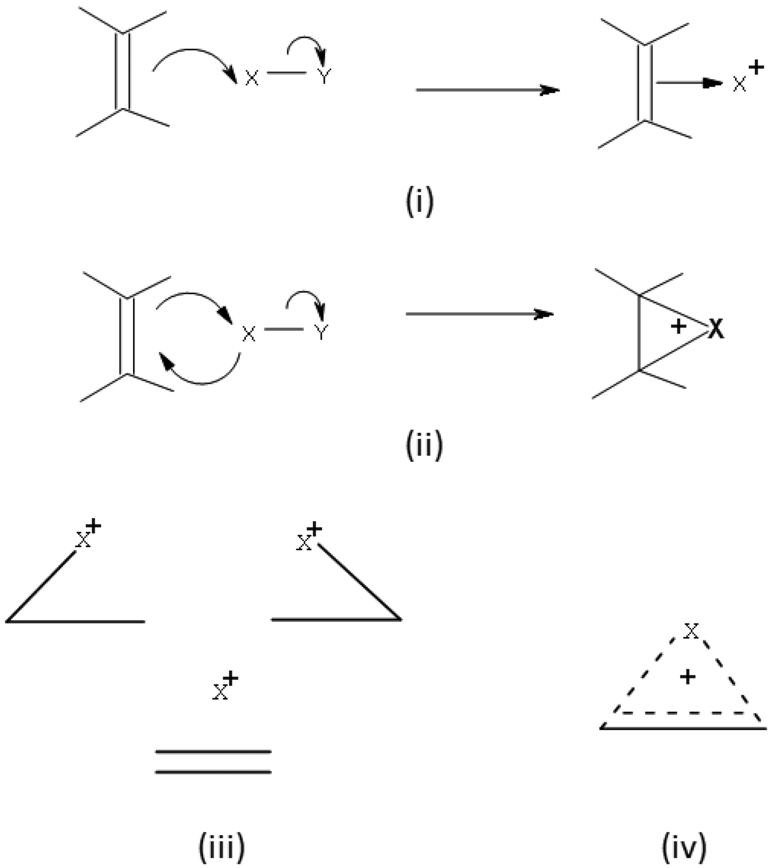


Figure 1. (i) The π-complex; (ii) Roberts and Kimbal mechanism; (iii) resonance notation; (iv) Winstein's dotted line structure.

These competing structural ontologies are still in evidence today. Whether explained by reference to the quantum phenomena of superposition or entanglement, the fact that the 3N-dimensional wave function, $\Psi(x_1,y_1......z_N)$, for any given system cannot be decomposed to N 3-dimensional waves of the form $\sum_N \psi^N(x,y,z)$ is ultimately a consequence of Heisenberg's uncertainty principle. Though the localization of a molecule can readily be achieved by using the center of mass, the wave function in configuration space does not directly provide information about internal molecular structure. This consequence of wave mechanics was realized early on by Schrödinger himself when he stated that *"...the true mechanical process is realized or represented in a fitting way by the wave processes in q-space, and not by the motion of image points in this space"* (*6*), with his concession nearly a decade later that *"I am long past the stage where*

I thought that one can consider the Ψ-function as somehow a direct description of reality” (*7*). Quantum mechanics only becomes quantum chemistry with the adiabatic separation of electronic and nuclear motion, commonly referred to as the Born-Oppenheimer approximation, implying that molecular structure is not an intrinsic quantum mechanical (QM) property. As is to be expected this view is not universally accepted. By characterizing atomic nuclei as attractors in the electron density field of the molecule, ρ(r), the Quantum Theory of Atoms in Molecules (QTAIM) defines the atom as the union of an attractor and its basin of attraction (*8*). The gradient vector of ρ(r), Δρ, can then be used to trace out a unique path, termed a bond path, that passes through a critical point where $\Delta\rho=0$ and connects the atomic termini. The locus of points satisfying the quantum condition $\Delta\rho \cdot \vec{n} = 0$, where the $\vec{n}$ vector is normal to the surface, connected by the unique bond paths defines a molecular graph for the state function Ψ. This definition of molecular structure allows for a rigorous quantum mechanical description of an atom in a molecule, allowing for the recovery of classical structure through topology.

But this encounter in 1950 also highlights a clash of chemical cultures, an experience that was to become a *modus vivendi* for Dewar, especially during his years at the University of Texas. In Dewar’s mechanistic framework a model of the potential energy surface (PES) for the reaction is constructed with the π-complex identified as a local minimum. The observed regio- and stereochemical specificities are then used to refine and extend this model. Such a methodology would have been a radical departure from the more accepted approach at the time of applying the fundamental principles of Robinson and Ingold’s arrow notation to obtain a reaction mechanism consistent with the experimental data. Within the first, or *constructive* theoretical framework, a model of the PES is fashioned by assigning structures for stationary states and saddle points appropriate to their position on the hypersurface. Within the second, or *principled* theoretical framework, the reaction is described by applying the principles underlying the arrow notation to generate structures for appropriate chemical intermediates subject to the limitations imposed by the rules of valence. One characteristic previously noted of the early constructive theorists in quantum chemistry is their inattention to “*consistency and rigor*” (*9*). Such traits were also ascribed to Dewar by Paul Bartlett in his review of Dewar’s book a year earlier, when he classified it as something written by *“...young enthusiasts with fresh viewpoints rather than by mature scholars bent on accuracy”* (*10*). Winstein was even more blunt in his review when he noted that while the content might stimulate further research it also exemplified *“carelessness and even irresponsibility in preparation*”. (*11*).

Dewar’s response to such criticism can be seen by his later recollection that while the book *“..had a whole lot of reviews, each worse than the last, each time another review appeared the sales went up”.* Meanwhile the promiscuity of Dewar’s model was also in evidence at Montpelier where the ensuing discussions of metal-olefin complex formation resulted in Dewar’s seminal publication the following year introducing key elements of what has been come to be be called the Dewar-Chatt-Duncanson theory (*12*). Ever the verbal flamethrower Dewar subsequently characterized the formulation of this model of back-coordination as one where *"…Chatt got credit for the idea by showing that I was right and he was wrong!"* (*13*). Though the intellectual interrelatedness of Dewar's American protagonists (*14*) may have played a role in the events at Montpelier, it has been previously noted that Dewar's pi-complex theory also failed to gain traction among his British colleagues, at least within the organic community (*15*). However metal complexes, with their multiplicity of electron-deficient and hypervalent compounds, provided fertile ground for exemplifying the utility of Dewar's μ−bonding scheme. The synergistic bonding components formed by forward donation from the olefin, through overlap of the filled π bonding orbital and an empty metal s-orbital, and back donation from the metal, formed by overlap of a filled metal d-orbital and the π^* antibonding orbital, Figure 2, represented at once a simple model and a profound insight, a combination that can be rightly called an *"…outstanding leap of imagination"* (*15*). Even before Michael's 1951 paper, experimental confirmation had appeared in the form of asymmetric $Ag(C_6H_6)ClO_4$ complexes where the silver atom was identified as bonding to opposite edges of the rings above and below the plane of the metal, rather than positioned symmetrically over the ring, as might be expected from arguments based on resonance theory (*16*). Tellingly the authors found this result *"…interesting due to possible implications in organic reaction mechanism"* and proceeded to reference Michael's just published book on MO theory. So it would seem that Michael was not as "unknown" as he might have imagined, though one might question to what extent he truly believed in his own self-characterization. Either way it was clear that the inorganic community was much more receptive to his novel bonding model than the organic community, and it would be hard to overstate its impact on the burgeoning field of organometallic chemistry. A small portion of this debt was repaid many years later when the journal Organometallics accepted his manuscript, written in honor of Rowland Pettit, for publication despite the outlandish title of "Why Life Exists" (*17*)!

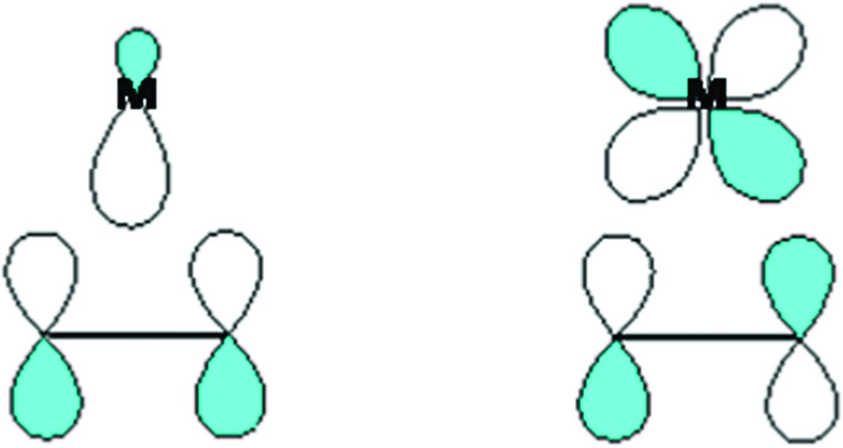


Figure 2. Dewar-Chatt-Duncanson.

While it might be tempting to view the encounter at Montpelier as just another skirmish in what at the time was an ongoing struggle between molecular orbital and valence bond proponents, care must be taken in formulating such a facile characterization. In his review of Dewar's book Bartlett wrote that while *"...no general operational superiority is demonstrated for the rather nebulous notation of molecular orbitals...in comparison to the well developed resonance scheme. It is healthy, nevertheless, to have this substantial reminder that resonance is not a phenomenon of nature."* This comment predates by six years a similar admonition from Wheland who, in clarifying and narrowing the use of the term, stated that *"...we shall never speak of resonance as a phenomenon*". (*18*). And while it is resonance theory that permits Winstein to equivalence the π-complex of Dewar with the classical structures in Figure 1(iii), his championing of the *"obscure"* dotted line representation can hardly mark him as a foe of novel bonding models. Though Michael himself was adamant, some would say strident, in declaiming his opposition to *"...the kind of intuitive arguments on which resonance theory is based"* , he, like Mulliken, accepted VB theory as a *"...valuable and correct method of approximation*" (*19*). In a much more fundamental sense the encounter at Montpelier highlighted a clash of not just chemical perspectives but chemical philosophies. Ensuing battles would regularly feature Michael Dewar presenting the case for MO theory in what Robert Mulliken, in his 1966 Nobel lecture, delicately termed a *"rather forceful"* manner.

Chemical Epistemology and MO Theory

The question of whether quantum mechanics can be imported as a complete construct from physics into chemistry, or whether it needs to be adapted to fit the explanatory demands of its sister science , is a matter of both perspective and philosophy. The case for the former was put rather bluntly by Fritz London when he is reputed to have said that*"...the chemist is made out of hard wood and he needs to have rules even if they are incomprehensible"* (*20*).

While most practicing chemists today are content to flit back and forth between conceptual models according to what is most convenient at the time, the situation was considerably more fraught in the second quarter of the 20th century. Crystallizing the view from the physicist's perspective was the statement by J. C. Slater that *"Physics is the simplest science, and the one which most nearly gets us back to first causes...Next, now hardly distinguishable from it, comes chemistry"* (*21*). Interestingly this parochial view of chemistry was accompanied by a disinclination to discuss varied interpretations of QM. Pauling likewise claimed to *"...have never been bothered by detailed or penetrating discussions about interpretation of quantum mechanics"* (*22*), a not wholly surprising coincidence given Pauling's stated admiration of P.W. Bridgman's operational philosophy and the fact that Slater completed his Ph. D under Bridgman, the 1946 Nobel Laureate in physics, at Harvard. Thus the valence bond (VB) approach, developed in Europe by Heitler and London and elaborated in America by Pauling and Slater, with its superposition of states corresponding to classical chemical structures, is most properly aligned with this parochial view of Chemistry.

While the pre-eminent American champion of the MO approach was Robert Mulliken, in England it was Charles Coulson who filled that role. Michael was to publish his only paper with Coulson in 1947, an outcome prompted by a manuscript sent to Dewar by Coulson *"...ferociously attacking my admittedly rather naïve contribution",* a reference to Michael's first presentation of his π-complex theory at a Faraday discussion. The view of chemistry as an autonomous discipline is exemplified by Coulson's statement that *"...our approximations to an exact solution [of the wave equation for a molecule] ought to reflect the ideas, intuitions and conclusions of the experimental chemist"* (*23*). Fifty years after that lone paper with Coulson Michael would summarize his singular achievements by simply describing himself as *"...the first organic chemist to really find out what quantum theory is about and to use it to interpret chemical behavior"* (*13*). While some earlier papers sounded the call, and whereas his use of the definite article in the title of his book signified it as a manifesto, the battle with the forces of resonance was truly joined by Michael's publication in 1952 of six theoretical papers published back to back in the Journal of the American Chemical Society. Their intent, laid out clearly in the first paragraph of the first paper, was *"...to present a general theory of organic chemistry which seems to offer important advantages over the current resonance theory"* (*24*). What followed was a presentation that has variously been called impenetrable (*25*), inscrutable (*26*), and *"virtually incomprehensible to practicing chemists"* (*27*). Others however found his application of perturbation methods to MO theory to represent *"...a splendid mixture of mathematical rigour, chemical knowledge and insight"* (*28*), and after much back and forth among the reviewers, Mulliken and George Wheland, and the JACS editor at the time, Albert Noyes, it was decided to publish the work after changes to streamline the notation and some condensation of the content (*29*). Michael subsequently attributed much of the difficulty people encountered with the presentation to this abridgement, stating that because *"...they were shortened by 25%...in their final form they were difficult to read"*. In addition the title for these papers, was *"A Molecular Orbital Theory of Organic Chemistry"*, a not-insignificant, if understandable, accommodation on Michael's part. A seventh paper in the series, with Rowland Petit as co-author and Michael now ensconced as Chair of the Chemistry department at Queen Mary College (QMC) in London, subsequently appeared in the Journal of the Chemical Society (*30*). While the 74 theorems presented in these papers does provide a challenge for the reader, the results are impressive and powerful. For example by treating aromatic substitution as a perturbation of the aromatic system (R) by the substituent (S) the Hamiltonian operator for RS is represented as: $H^{RS} = H^{R} + H^{S} + P$, where P represents the bonds formed between R and S. Applying perturbation methods, instead of the more common variation procedure, Dewar's PMO theory allows for the MOs of the Wheland intermediate to be expressed as linear combinations of the MOs of R and S. The coefficients thus calculated for the non-bonding MO (NBMO) of the cationic system allowed for a ready calculation of quantities such as resonance energies, bond orders and charge distributions. All obtained of course by *"...rigorous reasoning....and no appeal made to the kind of intuitive arguments on which resonance theory is based"* (*19*).

This work was expanded, and to a great extent simplified, in his 1975 book, "The PMO Theory of Organic Chemistry", written with Ralph Daugherty.

Michael's assault on resonance theory was theoretically based but philosophically driven. Michael's view that *"...a scientific model must simulate the behavior of the universe, or some part of it, while remaining simple enough for us to understand"* meant that *" the test of such a model is purely operational..."* and more critically *"there is of course no question of a model being true or false. ... The question "Is it true?" is meaningless in science"*. In adopting this ethos he was profoundly influenced by Robin Collingwood, the Oxonian philosopher, who interestingly was a practicing archeologist and, like Michael's wife Mary, a native of Lancashire. Collingwood's view of philosophy is essentially historicist, and his drive to develop a *"metaphysics without ontology"* led to his refusal to grant ontological status to explanations of a causal character. Similar arguments by Mach lead inevitably to a questioning of the ontological status of theoretical entities, and such thinking would place Michael very firmly in the instrumentalist camp. This undoubtedly played a role, not just in how he formulated theories, but also in his future decision to adopt a semi-empirical approach to the construction of the wavefunction.

The resonance theory of the day could be viewed as more realist, whether by attributing ontological status to either the discrete resonance structures, or the resonance hybrid. In a 1952 paper with his good friend Longuet-Higgins, who had obtained his D. Phil with Coulson at Oxford, Dewar writes that the successes of resonance theory are due"..*to its correspondence with MO theory rather than to the validity of its own premises*" (*31*). Ironically Michael was to play a critical role in decoupling of resonance from VB theory and aligning it with MO theory by redefining it as a delocalization concept, thus hastening the demise of VB theory as a practical tool (*32*).

While not from this era Michael's work on pericyclic reactions is also noteworthy, not just for the novelty of the approach but also because it showed Michael to be an equal opportunity antagonist. By identifying the transition states of such reactions as either aromatic or anti-aromatic, depending on the nature of the orbital overlap, Michael, and separately Howard Zimmerman, developed a classification for such reactions not based on orbital symmetry. One advantage of such an interpretation is is that it allows for the characterization of "anti- Hückel" systems, or transition states with an odd number of out-of-phase overlaps, or what today is termed Möbius aromaticity. Displaying a magnanimous idiosyncracy that was his hallmark Michael stated that *"...this explanation required no originality on my part"* since these ideas had, in Michael's view, been fully exposited by M. G. Evans in the late 1930s. While others have questioned Evans role in this exposition, this alternative model did provide Michael with one his most most memorable moments. Following a presentation where Michael again asserted that the Woodward-Hoffmann rules were obviously foreshadowed by work reported by Evans, and as such were basically derivative, he was asked, by none other than Roald Hoffmann himself , why, if the rules were all that obvious, didn't Dewar himself devise them. Michael's simple response: *"I suppose I should have, really"* (*33*).

Semi-Empiricsim and Quantum Chemistry

In the semi-empirical method some of an equation's theoretically-determined parameters are replaced by values either taken directly from, or fitted to, experimental data. Michael was to achieve his greatest impact through the development of a series of semi-empirical quantum chemistry methods parametrized to calculate a wide range of chemical properties to an accuracy that might prove useful to a practicing chemist. The progression from complete neglect of differential overlap (CNDO) to intermediate neglect of differential overlap (INDO), through to neglect of diatomic differential overlap (NDDO) involves the sequential addition of progressively more integrals of the form $< \phi^1_\mu \phi^1_\nu \left| \frac{1}{r_{12}} \right| \phi^2_\lambda \phi^2_o)$ to the Hamiltonian. The methods developed by Dewar, in the years after his appointment to the Robert A. Welch Chair at UT Austin, included parametrized INDO Hamiltonians, most notably MINDO/3 (*34*) where M signifies "modified", the more generally applicable MNDO Hamiltonian (*35*), and a reparametrization, termed Austin Model 1 (AM1), developed to correct the widely noted over-estimation of van der Waals repulsion found in MNDO (*36*). The fact that the original AM1 work still garnered nearly 500 citations in the chemical literature a decade after Michael's death stands as a testament to the widespread utility of these procedures. Michael was always at pains to emphasize that *"...the development of satisfactory parametric procedures…is a far more difficult matter than most people realize"* (*37*), and emboldened by the confidence he felt in their mechanistic predictions he regularly joined battle with those misguided souls who placed their faith in the *ab initio* methodology.

One of his most provocative mechanistic predictions was that multibond reactions cannot normally be synchronous, and that the favored mechanism for such processes involved proceeding in a stepwise, i.e. asynchronous, fashion. Characterizations of reactions such as the Cope and Claisen rearrangements, as well as cycloadditions such as the Diels-Alder reaction, by MINDO/3 and MNDO consistently predicted *biradicaloid* mechanisms,. This led Michael to induce that such a two-step mechanism is to be considered the norm, unless other factors are present that would favor a synchronous process. Michael even bearded the enemy in their own lair by undertaking high level and compute-intensive *ab initio* calculations on UT Austin's newly acquired Cray supercomputer, calculations that to his great amusement supported his hypothesis (*38*). That publications such as Science magazine, in covering this controversy, would characterize him as a *"a maverick theoretician"* with a reputation for *"...taking extreme positions"* only served to embolden him (*39*). Far from being chagrined by their reporting of him as being viewed by some as an *enfant terrible* or as the "*bête noire of theoretical chemistry"* , such commentary caused him no end of merriment. As Michael himself noted *"...my contributions have also not always been expressed too tactfully"*.

Another controversy of note, one that was not instigated by Michael but one nevertheless to which he contributed with, as noted by George Olah, *"..his customary flair"* (*40*), was the saga of 2-norbornyl cation. When Michael's MINDO/3 calculations, used because of it's specific efficacy for calculations on cations, identified an asymmetric π-complex as the favored cationic structure Michael became, in his own words, *"...the only participant in the notorious controversy to change sides"*.

Michael's preference for accuracy and speed, over what some have characterized as consistency and rigor, was yet another manifestation of his underlying philosophy. While approximate solutions to the Schrödinger equation would have been nothing new, Michael's approach was reminiscent of that undertaken by Polanyi and Eyring in 1931 (*41*), and just as controversial. To produce what has been described as *"...the first workable potential energy surfaces for chemical reactions"* (*42*), Polanyi and Eyring subtracted the coulombic energy term, as calculated by London's equations, from the total binding energy,determined by fitting the spectroscopic data to the Morse potential, to generate a plot of the resonance energy as a function of interatomic distance. After suitable correction these resonance plots were combined with the *ab inito* coulombic plots to generate a final reaction energy plot. While methodologically and numerically more complex, Dewar's adjustment of the theoretically derived electronic Hamiltonian fundamentally reflects the same approach. Philosopically it highlights a preference for precision over unitary derivation, and for predictive capability over explanatory function. While Michael was happy to concede that his semi-empirical procedures were not faithful to the underlying physics, a common criticism of Polyani's approach, he was much more vocal in his defence of another of these criticisms: specifically that such approaches merely accommodate the experimental data by interpolation. Michael's ultimate justification that *"...our procedures provide a very good representation of the way molecules behave"* clearly reflects the view that accuracy is the most important criterion for judging the efficacy of a prediction.

The application of this pragmatic philosophy to the problem of electron correlation had an earlier manifestation when Michael proposed that pairs of electrons in p orbitals be "vertically correlated" through the use of separate functions to describe the two lobes of a given p-orbital (*43*). While capable of yielding impressive results this approach did suffer from the fatal flaw that these so-called "split p-orbitals" were non-orthogonal and while correcting the problem, full orthogonalization resulted in a procedure *"...more clumsy than the conventional methods"* (*44*). Michael did note however that his introduction of this concept did cause *"...something of a furor"*, rousing the eminent theoretician S. F. Boys *"...to a passionate outburst"*, and causing him to become so upset *"...that he retired to bed with the 'flu'"*.

A Puzzling Personality

At a 1987 symposium in Austin held in honor of Michael's 70th birthday Nobel laureate and close friend Sir Darek Barton, at the beginning of his keynote, posed a mechanistic problem for Michael to solve before the end of the lecture. Some in the audience felt discomfited by this, more so since Michael failed to provide the correct solution (the problem is shown in Figure 3). Michael however was delighted by the challenge, and laughed uproarisly as Barton commented that

"...too much calculation has had a bad effect on you". Michael's inventive and superbly analytical mind was made for solving puzzles, This was demonstrated early on when as a post-doctoral student he was the first to deduce the correct structure for stipitatic acid, Figure 4. In addition he insightfully characterized the enolized form of the parent structure , tropolone, as aromatic. This was the first such characterization for a seven membered ring, and began a lifelong fascination with aromaticity. In addition to the earlier described theoretical work on aromatic transition states, Michael was the first to synthesize a wide range of borazaromatic molecules, noting that *"...the most interesting thing about borazaromatics is that they are in no way remarkable"* (*28*). The fact that a hospital was just around the corner from Queen Mary College was considered fortunate by the students working on this synthesis. In a forward to a series of books titled "Challenging Problems in Organic Reaction Mechanisms" Michael writes of the attraction for the organic chemist: *"First, his problems are set by Nature, not by man, and we are not told the solutions; it is therefore impossible to cheat. And second, organic chemistry has practical value, so that the organic chemist can enjoy his intellectual pastimes under the justifiable conviction that he is benefitting mankind by doing so"* (*45*).

Figure 3. Barton's problem.

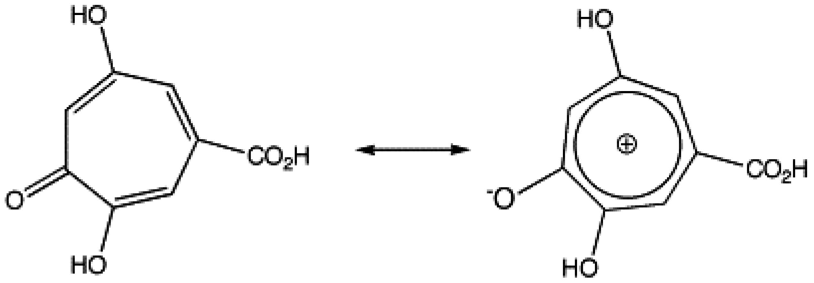


Figure 4. Stipitatic acid.

As noted earlier some reviews of Michael's 1949 book commented on what was perceived as the speculative nature of his theorizing. His presentation in 1950 of his π-complex mechanism for the benzidine rearrangement was likewise marred by a propensity for less than thorough explication of the experimental details. Even those admiring of his work have noted that *"Michael was a great scientist in many respects, but he would one year come along with this marvelous theory, he would explain how terrific it was, and in the next year he would come along with another theory, and it would be a bit more complicated but different..."* (*46*). Such characterizations actually preceeded Michael's arrival in America in 1950 to deliver the O'Reilly lectures at Notre Dame, the work that laid the foundation for his seminal publications on PMO theory. In writing to Robert Mulliken to recommend Michael for a visit, his former tutor at Balliol, R.P. Bell writes that *"In my view some of his work is rather careless"* (*29*). Interestingly "Ronnie" Bell played a central role in Michael's academic odyssey, from Oxford to Courtauld's to QMC to Chicago to UT Austin and finally to UF Gainesville, by being the lone, but key, dissenter in a plan to appoint Michael as the second Chemistry fellow at Balliol, this time in organic. Outraged Michael moved to Courtaulds as a means of *"...shaking the dust of the place off my feet"* (*13*). One advantage to these travels is that they provided Michael with a fund of stories, most of which he was more than willing to relate in most any setting. Of particular note are the various explanations of why he left Chicago for Austin, from the official one (*"to take part in a project...to make the university one of the best in the country"*, or as a colleague explained it *"to build a chemistry department that the football team could be proud of"*), to the reputed one (Chicago was dragging its feet with regard to providing Michael with an air conditioner for his office (*47*)), to the reported one (U. Chicago President: *"Why would you go from a first rate university to a second rate one for just more money?";* Michael:*"President, I have done so once before"* (*28*)), to the oft-told one over drinks (U. Chicago Provost: *"In America one does not just leave Chicago for a place such as Texas, it's a matter of prestige"* ; Michael: *"Provost, if it was a matter of prestige I would not have left England in the first place"*).

The long-running and particularly acrimonious controversy waged between Michael's post-doctoral mentor Robert Robinson and Christopher Ingold may have originated in disagreements regarding details of their respective electronic theories, but ultimately centered around authorship of, and recognition for, many of the pioneering ideas that lie at the heart of modern mechanistic organic chemistry (*48*). Returning to electronic theory from his first love of natural products, Robinson intended to collaborate with Michael on a larger exposition of his earlier work, but in the event, he just authored the foreword to Michael's 1949 text. Michael's close personal, they played much chess together while at Oxford, and professional relationship with Robinson undoubtedly influenced his interactions with Ingold. Additionaly perceived difficulties with what he termed "an Ingold referee" while at Queen Mary further frayed the relationship, and led to very public, and openly antagonistic, interactions between the two. Apart from his interactions with Ingold, Michael was often apt to see himself as a casualty of certain cliques within the chemical establishment, especially as regards the peer review process. This readiness to question the origin of some reviews, and the motivation of some reviewers, was exacerbated by Michael's ferocious loyalty to his friends and students.

In hindsight Michael's perception of himself as an outsider is not altogether surprising. Beginning with his birth in India to expatriate parents Michael often found himself at odds with British norms. While his schooling, first at Winchester, one of the leading English public schools, and later at Oxford, where he eventually obtained his D. Phil. under F. E. King, seems quintessentially establishment in character, the reality for Michael was more nuanced. At Winchester Michael was a scholarship recipient. This being Michael ,of course was he was top of the scholarship list, but by his own reckoning *"...by no means well off"*. In turn Michael's choice of college at Oxford, Balliol, was in large part driven by economy, he himself often noting that with his scientific inclinations *"...he really should have gone to Cambridge"* (*13*). His two scholarships at Balliol allowed him to live independently, and not draw on his Mother's meager resources, his father having died when he was ten. The move to industry in the dreary town of Maidenhead was considered by many as an unfortunate choice, placing him, as it did, firmly on the outside of the academic community. His ability to move from there to a professorship at Queen Mary was, in his own words, *"...almost incredible"* (*13*), a professorship at a major British institution being generally reserved for a much more senior academic. Shocking again , though for different reasons, was his subsequent move to America in 1958. And thus one sees a career path that both reflected, and in turn reinforced, Michael's view of himself as something of a maverick. Styling himself as an organic chemist practicing theory was not a conceit, but a way of distinguishing himself from more traditional chemical theorists, those specifically trained as such, or what he would call the *"true believers"*. Thus unburdened by convention, at least in the intellectual sense, Michael's inveterate and inventive theorizing becomes perhaps a little less surprising, but no less impressive.

Michael's previously noted fealty to students and colleagues was reciprocated, even by some who had the misfortune to have been singled out for some of Michael's more colorful commentary. This affection is witnessed by a collection of reminiscences by former students initiated and collated, tellingly, by just such an unfortunate colleague. Scattered throughout that collection are many wildly funny and wonderfully illuminating stories. Such as the day Michael mixed up his lecture notes and proceeded to give the advanced lecture on electronic theory to the beginning class on organic mechanism. Or the story of the Burgenstock spoof, where Michael had a conference audience convinced he had constructed a detector that would emit audible tones of either a soothing or a screeching quality, depending on whether the process being monitored was either symmetry allowed or symmetry forbidden. Michael's thesis, inspired by collision theory, that by breaking the speed limit, and thus ensuring that one's car spent more time in the garage and at rest, one was actually minimizing the chances of a catastrophic accident, was also recalled fondly by several contributors. What is clear from these anecdotes is that Michael considered science, and in particular chemistry, as *"...something one should enjoy"*. Michael fretted more than once that many practitioners *"...seem to have forgotten that the first motive of any scientist should be curiosity"*. Allied to his conviction that *"...the purpose of argument was to test a proposition, not defend one's ego..."* these indelible elements of his character combined to produce not just *"one of the most colourful characters of modern chemistry"* (*28*), but a man of true brilliance.

Acknowledgments

It is only appropriate that the entire, extended Dewar research group, from the years Michael spent at Queen Mary College, through his stay at the University of Chicago, to his phenomenally prolific period at the University of Texas, to his final sojourn at the University of Florida, be recognized. It is hoped that this perspective on Michael's life and work does justice to our collective memory of his genius.

References

1. Where not specifically referenced all quotations for Michael Dewar are to be found in his autobiography: Dewar, M. J. S. *A Semiempirical Life (Profiles, Pathways and Dreams)*; Seeman, J. I., Ed.; American Chemical Society: Washington, DC, 1992
2. Dewar, M. J. S. *The Electronic Theory of Organic Chemistry*; Clarendon Press: Oxford, 1949; pp ix−x.
3. Berson, J. A. *J. Phys. Org. Chem.* **2005**, *18*, 572–577.
4. Coulson, C. A. *Rev. Mod. Phys.* **1960**, *32*, 170–177.
5. Roberts, I.; Kimball, G. E. *J. Am. Chem. Soc.* **1937**, *59*, 947–948.
6. Schrödinger, E. *Annal. Der Phys.* **1926**, *79*, 13−40; English translation in "Collected Papers on Wave Mechanics" AMS Chelsea, Providence, RI , 1982.
7. Bradley, M. *Philos. Sci.* **2006**, *73*, 778–789.
8. Bader, R. F. W. *J. Phys. Chem. A* **2010**, *114*, 7431–7444.
9. Ramsey, J. *Stud. Hist. Philos. Mod. Phys.* **2000**, *31*, 549–567.
10. Bartlett, P. D. *J. Am. Chem. Soc.* **1949**, *71*, 3859–3860.
11. Winstein, S. *Chem. Eng. News.* **1949**, *27*, 3440.
12. Dewar, M. J. S. *Bull. Soc. Chim.* **1951**, *18*, C71.
13. Hargittai, I. *Candid Science: Conversations with Famous Chemists*; Imperial College Press: London, 2000; pp 165−177.
14. Gortler, L. *J. Chem. Educ.* **1985**, *62*, 753–757.
15. Mingos, D. M. P. J. *Organomet. Chem.* **2001**, *635*, 1–8.
16. Rundle, R. E.; Goring, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 5337.
17. Dewar, M. J. S.; Healy, E. F. *Organometallics* **1982**, *1*, 1705–1708.
18. Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley and Sons: New York, 1955; p 75.
19. Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341–3345.
20. Gavroglu, K. *Fritz London: A Scientific Biography*; Cambridge University Press: Cambridge, 1995; pp 85.
21. Schweber, S. S. *Hist. Stud. Phys. Biol. Sci.* **1990**, *20*, 339–406.
22. AHQP (Archive for the History of Quantum Physics), interview transcript part 2. Interview by John Heilbron. March 27, 1964.

23. Hendry, R. F *Proceedings of the 2002 Biennial Meeting of The Philosophy of Science Association Part II:Vol. 71, No. 5, Symposia Papers*; Mitchell, S. D., Ed.; University of Chicago Press: Chicago, 2004; pp 1048−1059
24. Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341–3363.
25. Gilbert, J. C.;Bard, A. J.; Bauld, N. L. *Documents and Minutes of the General faculty Rport*; Memorial Resolution Committee, 1998; pp 22595−22597.
26. Hargittai, I. *Candid Science: Conversations with Famous Chemists*; Imperial College Press: London, 2000; pp 191−209.
27. Michl, J.; Fox, M. A. *Biographical Memoirs*; National Academy of Sciences: Washington, DC, 1999; Vol. 77, pp 191−209.
28. Murrell, J. N. Michael James Steuart Dewar. 24 September 1918-11 October 1997. *Biogr. Mem. Fellows. R. Soc.* **1998**, *44*, 129−140.
29. Mulliken, R. S. Papers, [Box 18, Folder 15], Special Collections Research Center, University of Chicago Library.
30. Dewar, M. J. S.; Petit, R. *J. Chem. Soc.* **1954**, 1625.
31. Dewar, M. J. S.; Longuet-Higgins, H. C *Proc. R. Soc. London* **1952**, *214*, 482–493.
32. Schaad, L. J.; Hess, B. A., Jr. *Chem. Rev.* **2001**, *101*, 1465–1476.
33. Strom, E. T. *Southwest Retort* **1998**, *51*, 17.
34. Bingham, C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285–1293.
35. Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.
36. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
37. Dewar, M. J. S. The Role of Semi-Empirical SCF MO Methods. In *Wave mechanics: The First Fifty Years*; Price, W., Chissick, S., Ravensdale, T., Eds.; John Wiley and Sons: New York, NY, 1973; pp 239−354.
38. Dewar, M. J. S.; Healy, E. F. *Chem. Phys. Lett.* **1987**, *141*, 521–524.
39. *Science* **1984**, *223*, 1162–63 (DOI 10.1126/science.223.4641.1162).
40. Olah, G. A.; Surya Prakash, G. K. *Acc. Chem. Res.* **1985**, *18*, 292–293.
41. Eyring, H. J.; Polyani, M.; London, F. *Z. Phys. Chem.* **1931**, *B12*, 279–311.
42. Ramsey, J. L *Philos. Sci.* **1977**, *64*, 627–653.
43. Dewar, M. J. S.; Hojvat, N. L. *J. Chem. Phys.* **1961**, *34*, 1232.
44. Coulson, C. A.; Sharma, C. S. *Proc. R. Soc. London* **1961**, *264*, 431–444.
45. Ranganathan, D.; Ranganathan, S. *Challenging Problems in Organic Reaction Mechanisms*; Academic Press: New York, 1972; p ix.
46. Interview with Professor John N. Murrell; Anders, U. (http://www.quantum-chemistry-history.com/Murr7.htm).
47. Gilbert, J. C. Rowland Petit: A biographical Memoir. In *Biographical Memoirs*; National Academies Press: Washington, DC, 1995, vol 77; pp 293−313.
48. Satzman, M. D. *J. Chem. Educ.* **1980**, *57*, 484–488.

Chapter 6

H. C. Longuet-Higgins: The Man and His Science

Weston Thatcher Borden*

Department of Chemistry and the Center for Advanced, Scientific Computing and Modeling, University of North Texas, 1155 Union Circle, #305070, Denton, Texas 76203-5070
***E-mail: borden@unt.edu**

From his publication in 1943, as an Oxford undergraduate, of the correct structure for diborane, to his explanation in 1967 of the anomalous chemical shifts of the protons in [4n]annulenes, H. C. Longuet-Higgins made many important contributions to theoretical chemistry. These contributions include: (a) showing how to find rapidly the non-bonding MOs of odd alternant hydrocarbons and demonstrating that these MOs can be used, in place of resonance structures, to make predictions about the π systems of organic molecules, (b) explaining the observed UV-Vis spectra of unsaturated hydrocarbons in terms of the interactions between transition diploes, (c) predicting that $B_6H_6^{-2}$ and $B_{12}H_{12}^{-2}$ each have a closed shell of electrons and (d) that cyclobutadiene should form stable complexes with transition metals, (e) investigating the intersections between potential energy surfaces, showing the limitations of the non-crossing rule, and discovering the change in the "Berry phase" around points at which two surfaces intersect, (f) predicting bond-length alternation in [4n+2]annulenes (but not in polyacenes) for sufficiently large values of n, (g) showing that the symmetry group for a non-rigid molecule can be generated from a combination of permutations of identical atoms and inversion of the molecule through its center of mass, (h) interpreting the ESR spectra of radical anions in terms of the nodal properties of the singly-occupied MOs, and (i) introducing the use of correlation diagrams for understanding and predicting the outcomes of electrocyclic reactions. This chapter presents a

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

brief biography of Christopher Longuet-Higgins and a detailed discussion of each of the most important contributions that he made to theoretical chemistry, before he left the field in 1967, in order to begin research in artificial intelligence.

Introduction

Hugh Christopher Longuet-Higgins (Figure 1) was a leading member of what could be termed “The British School of Quantum Chemistry". Among the other prominent members of this school were Charles Coulson, who was Longuet-Higgins’ Ph.D. adviser at Oxford, Michael Dewar, who also received his Ph.D. degree at Oxford, but in organic chemistry, and John Pople, who, like Coulson, received his Ph.D. at Cambridge. Since Coulson and Pople both did their graduate research under John Lennard-Jones and since Longuet-Higgins was Lennard-Jones scientific grandson, it seems fair to call Lennard-Jones the "Founder of the British School".

Christopher (as he preferred to be called) Longuet-Higgins succeeded Lennard-Jones as Professor of Theoretical Chemistry at Cambridge University, and during Longuet-Higgins’ tenure, from 1954 to 1967, the theoretical chemistry department at Cambridge was arguably the best in the world. John Pople, Frank Boys, and Leslie Orgel were among the members of the Department while Christopher Longuet-Higgins occupied the John Humphrey Plummer Chair.

Longuet-Higgins was a paper-and-pencil theoretician, and he took a rather dim view of "machine experiments," which is what he called computer calculations (*1*). It is, therefore, ironic that it was Frank Boys’ use of Gaussian expansions that made it possible to do rapidly the integrals necessary for *ab initio* calculations. Additionally, after emigrating to the U.S., Pople did more than anyone else in the world to make performing such calculations easy, even for non-specialists, through his distribution of the *Gaussian* packages of programs. Following Dewar's emigration to the U.S., he too became a computational chemist. Dewar created a succession of semiempirical methods, which he claimed were far superior to the *ab initio* calculations that were popularized by Pople. Boys, Dewar, and Pople is each the subject of a chapter in this book.

Like John Pople and Michael Dewar, Leslie Orgel was also part of the British “brain drain” of the late 1950s and early 1960s. However, when he emigrated to the U.S. from Cambridge, he became a molecular biologist, rather than a computational chemist.

Although Longuet-Higgins did not become a computational chemist or emigrate to the U.S., he too left Cambridge and changed fields. In 1967 he moved to the University of Edinburgh, to begin research on artificial intelligence (AI). In 1968 Longuet-Higgins became a Royal Society Research Professor at Edinburgh; and in 1974 he transferred his Professorship to the University of Sussex, where he remained active in AI research, until he retired in 1988.

Having identified some of the other most important members of the “British School” of theoretical chemistry, the rest of this chapter is devoted to Christopher Longuet-Higgins. Following a section that gives a brief account of his life, most of this chapter provides a description of what the author believes are the most important contributions that Longuet-Higgins made to theoretical chemistry. These descriptions are organized, more or less chronologically, around the papers that Longuet-Higgins published.

Figure 1. Hugh Christopher Longuet-Higgins, April 11, 1923 - March 27, 2004. (Photo courtesy of Professor Michael Longuet-Higgins.)

The names Coulson, Dewar, Pople, and Orgel appear again in the section of this chapter about Longuet-Higgins' contributions to theoretical chemistry, since Longuet-Higgins co-authored important papers with each of these theoretical chemists. Frank Boys' name also reappears in a discussion of one of the rare instances where Longuet-Higgins' pencil-and-paper calculations were proven to be wrong; whereas, *ab initio* calculations by Boys turned out to have been right.

The next section of this chapter, regarding Longuet-Higgins' life, draws heavily from the Royal Society's excellent Biographical Memoir, written by Richard L. Gregory and John N. Murrell (*2*). It was published in 2006, following Longuet-Higgins' death on March 27, 2004.

I am indebted to Christopher's younger brother, Michael Longuet-Higgins, for providing me by email with reminiscences about their family and some information about Christopher's life during the years after Christopher retired. I am also grateful to Professors Michael Longuet-Higgins, John Murrell, Roald Hoffmann, and Lionel Salem, and to Dr. Jeff Seeman for their comments on various drafts of this chapter.

The author's personal fondness and admiration for Christopher Longuet-Higgins will be readily apparent to the reader of this chapter. Both developed during the 1964-65 academic year, when I had the good fortune to have a Fulbright Fellowship to study theoretical chemistry with Professor Longuet-Higgins at Cambridge. I met with him once each week in tutorial; and I lived at Leckhampton, the Graduate hostel of Corpus Christi College, for which Professor Longuet-Higgins was then the Warden (*3*).

I was only 20 when I first met Christopher Longuet-Higgins, and I was much more easily impressed then than I am now. Nevertheless, nearly half a century later, I still believe that Christopher had the best and certainly the quickest mind of any chemist whom I have known. Christopher was, in fact, famous for his ability to penetrate rapidly to the essence of any problem.

However, he was also famous for his lack of patience with chemists who did not think as clearly or as quickly as he did. I frequently tried Christopher's patience, during my weekly tutorial with him, to the point that he would exclaim, at least once each tutorial, "Weston, you are talking nonsense again!" Nevertheless, learning how Christopher thought about scientific problems and how he then used the clarity of his insights to solve them, has, during the past 47 years, been even more valuable to me than the considerable amount of theoretical chemistry that I learned during my year in Cambridge.

A Brief Biography

Hugh Christopher Longuet-Higgins was born on April 11, 1923 in the Vicarage in Lenham, Kent. Christopher was the second of three children. His elder sister, Patricia, excelled in English and won a scholarship to Lady Margaret Hall College in Oxford.

Their younger brother, Michael, is a scientist; and he is arguably as brilliant and successful as Christopher was. Michael Selwyn Longuet-Higgins is a world renowned mathematical oceanographer, who, like Christopher, held a

Professorship at Cambridge and was elected to the Royal Society. Also like Christopher, Michael Longuet-Higgins eventually left Cambridge, moving to the University of California, San Diego in 1989.

As might be inferred from Christopher's birth in a vicarage, his father was a clergyman. From an early age, Christopher was an outspoken atheist; and this apparently led to some major disputes between Christopher and his father. However, according to Michael Longuet-Higgins, the family would frequently gather around the piano to sing, while Christopher played; and the musical harmony presumably served to restore at least a measure of interpersonal harmony between Christopher and his father,

Christopher was not only a gifted scientist; he was also a gifted musician. "In 1932 he was awarded a choral scholarship to the Pilgrims' School at Winchester; and he became a chorister at Winchester Cathedral, where he rose to become the 'solo boy'. At the age of 12 years he composed a choral setting for evensong that was performed in the cathedral (*2*)."

In 1935 Christopher entered Winchester College, one of the oldest and most famous "public" (i.e., private) schools in England. Among Christopher's elder classmates at Winchester were two of Britain's most famous physicists – Freeman Dyson and James Lighthill, both of whom went on to be elected as Fellows of the Royal Society. Michael J. S. Dewar, who was five years older than Christopher, was also a Winchester student; and, as already noted, Dewar too went on to become a world-famous theoretical chemist.

In 1941 Christopher was awarded a Fraser and Domus scholarship to attend Balliol College, Oxford, where Michael Dewar had also studied chemistry. At Balliol, Christopher was awarded an organ scholarship, meaning that he was paid to play the organ in the college chapel during services. Christopher's interest in music also led him to found his own *a cappella* choral group. Although Christopher was primarily studying chemistry at Oxford, he also passed Part 1 of the Tripos exams in Music.

As an undergraduate, Christopher did both theoretical and experimental research in chemistry with his tutor, Ronnie Bell. Christopher graduated from Oxford in 1945, with a first-class honors degree in Chemistry; and, after graduation, he remained at Oxford to pursue a D. Phil degree. Christopher's doctoral research was directed by Charles Coulson, who was actually in the Mathematics Department at Oxford. Christopher's undergraduate and graduate research at Oxford are described in the next section of this chapter.

Following receipt of his D. Phil. degree, Christopher stayed on as a Junior Research Fellow at Balliol College, after which he spent one year as a Post-doctoral Research Associate in the group of Robert S. Mulliken at the University of Chicago. Christopher then returned to England, where he joined the Faculty at the University of Manchester as a Lecturer. Christopher was promoted to Reader in 1951; and, in 1952, when Charles Coulson returned to Oxford as Rouse Ball Professor of Mathematics, Christopher succeeded his scientific father as the Professor of Theoretical Physics at King's College, London.

Christopher spent only two years at Kings College, and he apparently had just one graduate student, whose name was Peter Higgs. Higgs worked with Longuet-Higgins in the area of solid-state structure; but, subsequently, Higgs did research on the theory of fundamental particles. The most sought after fundamental particle in physics, the Higgs boson, is named after him.

In 1954, at the age of only 31, Christopher succeeded his scientific grandfather, John Lennard-Jones, as John Humphrey Plummer Professor of Theoretical Chemistry at Cambridge University. In Cambridge, Christopher was elected a Fellow of Corpus Christi College, where he enthusiastically participated in the College's musical activities, both as a performer and as a conductor. Christopher also became the inaugural Warden of Leckhampton, the first communal residence for graduate students at Cambridge.

Christopher's scientific activities won him a Fellowship in the Royal Society in 1958, election as a Foreign Associate of the US National Academy of Sciences in 1968, and honorary doctorates from the universities of York, Essex, Bristol, and Sussex. His activities, not just in performing but also in analyzing music, won him election Fellow of the Royal Society of Arts in 1970 and an honorary doctorate in music from the University of Sheffield.

I have mentioned in the Introduction that, when I knew Christopher in 1964-65, he was impatient and did not suffer fools gladly. In his reminiscences about Christopher, John Murrell writes, "Most people are kind to their [guest] lecturers, but if Longuet-Higgins thought the work wasn't of the highest quality …, he would interrupt and he would say, 'Look, I think, you got it wrong,' or 'This is not good enough,' etc (*4*)."

However, except for those moments in weekly tutorial, when Christopher would suddenly pounce on me, I found him to be extremely approachable and affable. He was capable of unselfconsciously displaying a charming and almost childlike enthusiasm for many things, but, most notably, chemistry and music.

For example, one day in the spring of 1965, I was playing croquet on the lawn in front of the old house at Leckhampton, where Christopher had his rooms on the second floor. Suddenly, Christopher flung open one of his windows and shouted down to me in great excitement, "Weston, listen to this." He then leaned out of his window and performed a first-rate rendition of the "Star Spangled Banner" on the French horn, which he was learning to play at the time.

I sometimes saw the same type of boyish enthusiasm in tutorial, when Christopher would show me how to use molecular orbital (MO) theory to answer a question about organic chemistry that I asked him. However, I never saw Christopher quite as excited as the day in tutorial that he showed me a letter from R. B. Woodward that Christopher had just received. R. B. Woodward was generally regarded as the greatest organic chemist of his time, an opinion that I believe Christopher shared.

Christopher told me that "Bob" Woodward had sent him a copy of a paper about the stereochemistry of several thermal and photochemical ring opening and ring closing reactions (*5*). Christopher laid out the experimental facts for me; and then he told me about Woodward's explanation of these observations, which had been created in collaboration with "someone named Hoffmann". The Woodward-Hoffmann explanation was based on the symmetry of the highest occupied MO in the reactant; but Christopher said, "Even you, Weston, should know that the right way to tackle this problem is through the use of correlation diagrams."

I had, in fact, learned how to construct correlation diagrams for the electronic states of transition metal ions; but I would never have thought to use correlation diagrams to explain the experimental results that Woodward had sent to Longuet-Higgins. In addition to being thrilled that Christopher had been willing to take the time to show his explanation to me, I was delighted to have born witness to the boyish excitement that Christopher felt about his own discovery.

I believe that part of his excitement came from Christopher's knowing that his explanation was more rigorous than that proposed by Woodward and Hoffmann. In fact, Christopher ended my tutorial that day by saying, “I am going to write this up as a *JACS* Communication (*6*) and send a copy to Bob Woodward.” Christopher must have been very pleased and flattered when Hoffmann and Woodward immediately applied correlation diagrams to cycloaddition reactions (*7*).

During the 1964-65 academic year that I was in Cambridge, Christopher seemed to be very interested in the work of Richard L. Gregory, who was another Fellow of Corpus Christi College. Gregory was using analogies from computer science to try to understand how the brain functions, and he was also using neural analogies to try to design new machines. In 1967 Longuet-Higgins and Gregory both left Cambridge, to join Donald Michie in founding the Department of Machine Intelligence and Perception at the University of Edinburgh.

Why did Christopher leave chemistry? Some people have speculated that he foresaw theoretical chemistry was going to become increasingly dominated by “machine experiments (*1*),” for which Christopher had little respect (*2*, *4*). However, it was not until 1970, three years after Christopher had decided to leave chemistry and Cambridge, that it first began to become apparent that *ab initio* calculations, carried out on computers, might prove superior to the qualitative theoretical arguments and pencil and paper calculations that Christopher favored.

Instead, I think that Christopher left chemistry because he had a tremendous intellectual curiosity. I believe that, after more than twenty years of doing research in theoretical chemistry, Christopher was ready to challenge himself by beginning research in a new area of science and potentially one of much more central importance than theoretical chemistry.

Additionally, according to Michael Longuet-Higgins, Christopher's younger brother, Christopher had long been interested in the field of perception and thought deeply about it. In fact, Christopher had "written an original essay on color vision, while he was still at school at Winchester College. This [essay] impressed his teachers."

Since the subject of this chapter is Christopher Longuet-Higgins' work in electronic structure theory, I will not attempt even to give a brief summary of his research in artificial intelligence. The interested reader is referred to the excellent Biographical Memoir of Longuet-Higgins by Murrell and Gregory (*2*).

However, over the years, I had, like many chemists, wondered whether Christopher's contributions to artificial intelligence came close to equaling the importance of those that he made to theoretical chemistry. On this question, Murrell and Gregory wrote, “Christopher’s impact on cognitive science did not reach the height of his impact on chemistry (*2*).” I have good reason to believe that Christopher would have agreed with this assessment.

A few years before Christopher's death on March 27, 2004, I was given Christopher's email address at the nursing home where he was then living. I sent him an email message, thanking him for all that I had learned from him; and I boldly inquired as to whether his research in artificial intelligence had been as important to that field as his research in theoretical chemistry had been to chemistry. Christopher's forthright reply was, "No. The only important thing I did was to provide the name 'cognitive science' to this field."

Christopher's reply was certainly much too modest. An award named after Christopher is given annually by the journal *Computer Vision and Pattern Recognition*. Another award, named after Christopher, is given annually by *Molecular Physics*, the journal that Christopher founded. Thus, Christopher is probably one of the few scientists ever to have an award named after him in two, completely different fields.

Christopher's answer to my question about his impact on the field of AI might not have been a case of false modesty. Instead, it might have reflected his actual feelings about his research in cognitive science at the time that I wrote to him. According to an email message I received in December of 2011 from Michael Longuet-Higgins, after Christopher retired in 1988 from the University of Sussex, "He suffered from a clinical depression, and he was confined to two nursing homes. At the first of these he was very unhappy; but owing to the help of his colleague [at Sussex] and former research student John Murrell, … [Christopher] was accepted at an excellent nursing home in Brighton, where he partially recovered. According to John Murrell, Christopher retained in detail all of his previous grasp of physical chemistry."

Michael Longuet-Higgins continued, "He [Christopher] never lost his deep interest in music, as I know since he played the recordings that I gave him, and shared them with the nursing-home staff. After his depression, however, he was barely able to perform [again]."

It is probably superfluous for me to add anything to what Michael Longuet-Higgins wrote. However, having known Christopher in his prime as both a chemist and a musician, and having grown fond of him during the year that I studied theoretical chemistry with him, I cannot keep from adding, "How sad!"

Contributions to Chemistry

In this section I discuss what I believe to be Christopher's most important contributions to chemistry, by describing the contents of what I think are his most significant publications. Clearly, this choice is highly subjective; and I expect that another theoretical chemist would have left out some of the papers that I have included and included others that I have left out. Nevertheless, I believe that the selection of papers in this section will at least afford the interested reader a good idea of the breadth and depth of Longuet-Higgins' many contributions to chemistry.

The Structure of Diborane

Christopher made his first major contribution to chemistry when he was still an undergraduate at Balliol College. In an essay, written for his chemistry tutorial (*8*), Christopher proposed that the structure of $(BH_3)_2$ contains four terminal hydrogens (connected to the two boron atoms by the wedged and hashed bonds in Fig, 2) and two bridging hydrogens, which lie in a plane perpendicular to that containing the terminal hydrogens.

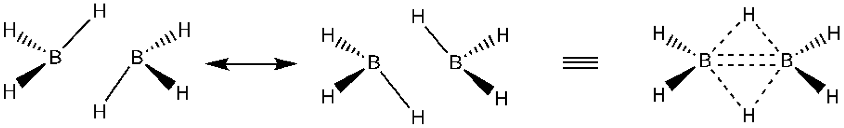


Figure 2. The two resonance structures, drawn by Longuet-Higgins, for $(BH_3)_2$. The dotted lines connecting the borons and bridging hydrogens in the third structure represent a pair of two-electron, three-center bonds.

Christopher postulated that resonance between the two structures, shown in Figure 2, is responsible for the bonding of the bridging hydrogens to boron. In fact, Christopher gave this type of bonding the name "resonance link". In more modern terminology, the two resonance structures, when taken together, describe a two-electron, three-center bond between the two borons and each of the bridging hydrogens.

Christopher's essay became a paper, published in 1943 by Christopher and his tutor at Oxford, Ronnie Bell (*9*, *10*). They were not the first to postulate a doubly bridged structure for $(BH_3)_2$; but they were the first to provide a credible explanation for the bonding in such a structure. They also argued that the doubly bridged structure explained: (a) the known chemistry of $(BH_3)_2$, including its reaction with Lewis bases, such as CO and ammonia and (b) the existence of dimers of CH_3BH_2 and $(CH_3)_2BH$, but not $(CH_3)_3B$.

Electronic Structures of Conjugated Systems

Christopher's D. Phil. research was published as a series of five papers (*13–17*), coauthored by Charles Coulson, Christopher's doctoral adviser. These papers explored some of the mathematical relationships that can be derived from Hückel theory. These relationships were then applied to the π systems of specific, conjugated molecules.

For example, Longuet-Higgins and Coulson showed that, in Hückel theory, the derivative of the energy with respect to the Coulomb integral (α_r) at atom r is the Hückel charge (q_r) on that atom (*13*). Therefore, the most favorable atom at which to substitute a more electronegative element (one with a more negative α) is the atom with the largest Hückel charge. Similarly, Longuet-Higgins and Coulson showed that the derivative of the energy with respect to the resonance integral (β_{rs}) between two atoms, r and s, is the Hückel bond order (p_{rs}) between those atoms (*13*). Therefore, the most favorable bond to shorten (thus making β more negative) is the one with the highest bond order.

Computing and Using the Hückel Nonbonding (NB)MOs of Alternant Hydrocarbons

Alternant hydrocarbons (AHs) are conjugated molecules in which the carbons can be divided into two sets, traditionally called starred and unstarred, in which no two atoms belonging to the same set are nearest neighbors. Examples of such molecules are shown in Figure 3.

Coulson and Rushbrooke showed that in Hückel theory, the energies of the π MOs of an AH come in pairs, symmetrically substituted around the non-bonding energy, E = α (*18*). Coulson and Rushbrooke also showed that, in MOs that are paired, the coefficients of each of the atomic orbitals (AOs) have the same magnitude in both MOs, but differ in sign at either the starred or unstarred atoms.

A non-Kekulé AH is an AH that has no Kekulé structures in which all of the carbons are doubly bonded. Examples of non-Kekulé AHs in Figure 3 are allyl and trimethylenemethane (TMM). In three sole-authored papers, which Longuet-Higgins wrote while he was a post-doc at the University of Chicago and published back-to-back-to-back in 1950, he showed how to rapidly find and make use of the nonbonding (NB)MOs of non-Kekulé AHs (*19–21*).

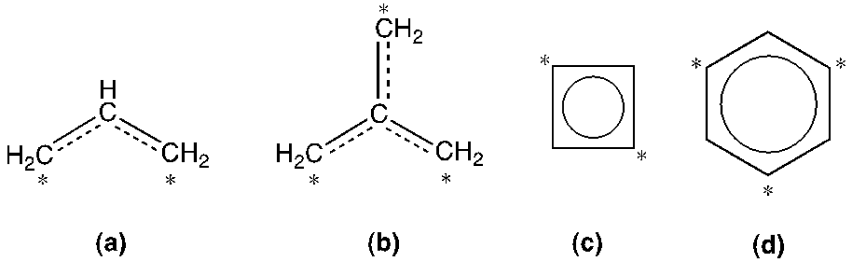


Figure 3. Four alternant hydrocarbons (AHs): (a) allyl, (b) trimethylene-methane (TMM), (c) cyclobutadiene (CBD), and (d) benzene. Starred and unstarred carbons are shown.

Longuet-Higgins used the Coulson-Rushbrooke pairing theorem (*18*) to prove that the number of non-bonding (NB)MOs in a non-Kekulé AHs is at least as great as the number of carbons that are not doubly bonded in any Kekulé structures (*19*). Thus allyl has one π NBMO, and TMM has two π NBMOs. AHs, such as square cyclobutadiene, which contain 4n-membered rings, also have a pair of NBMOs, despite the existence of resonance structures in which all of the carbons are doubly bonded. That is why counting the number of carbons that are not bonded in any resonance structure provides only a lower limit to the number of NBMOs.

Longuet-Higgins went on to show that finding the NBMOs in any AH is trivial (*19*). He proved that the coefficients of the starred atoms in an NBMO must sum to zero about each unstarred atom and *vice-versa*. In an odd AH, if the more numerous set of carbons is chosen to be the starred set, the coefficients of the unstarred atoms in the NBMO are all zero; so the NBMO has non-zero coefficients at only the starred atoms. The coefficients at the starred atoms in the NBMO can be easily found from the zero-sum rule; i.e., their coefficients must sum to zero about each unstarred atom.

Exactly how the zero-sum rule works can be seen in Figure 4, which shows the process for finding the NBMO of benzyl. Since the two *meta* carbons and the *ipso* carbon are unstarred, their coefficients must be 0 in the NBMO of this odd AH. If the coefficient a is assigned to the *para* carbon, coefficients of $-a$ must be assigned to each of the *ortho* carbons. Then, in order to satisfy the zero- sum rule for the substituted ring carbon, the CH_2 group must be assigned a coefficient of $2a$. Normalization of the NBMO then requires that the sum of the squares of the coefficients of the 2p-π AOs in it be equal to one, giving $a^2 + 2(-a)^2 + (2a)^2 = 7a^2 = 1$; so $a = 1/\sqrt{7}$.

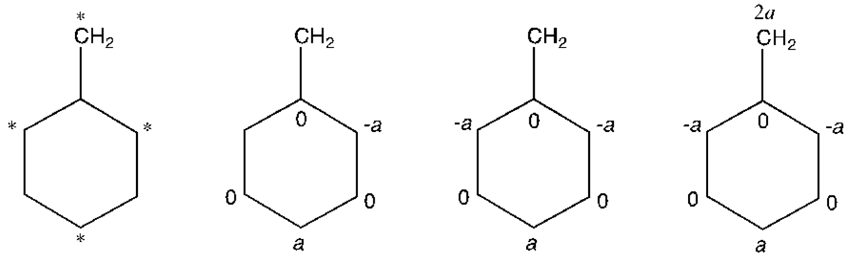


Figure 4. Starred and unstarred carbons in benzyl, and how the zero-sum rule can be used to find the coefficients of the carbons in the π NBMO of this odd AH. Normalization gives a = 1/√7.

In the benzyl radical, one electron occupies the NBMO. Thus, having found the NBMO, it is easy to see, without actually doing a Hückel calculation, what Hückel theory predicts for the distribution of unpaired spin in benzyl radical. 3/7 of the unpaired spin density should be found equally distributed between the *ortho* and *para* carbons, and 4/7 of the unpaired spin density should found on the exocyclic CH_2 group.

In a neutral AH, all of the carbons are uncharged (*18*). Therefore, as Longuet-Higgins pointed out, the distribution of charge in the benzyl anion and benzyl cation can easily be calculated from the coefficients in the NBMO (*19*). In the anion one electron is added to the NBMO of benzyl radical, and in the cation the electron in the NBMO of the radical is removed. Consequently, Hückel theory predicts that 4/7 of the negative charge in benzyl anion and 4/7 of the positive charge in benzyl cation is localized on the exocyclic CH_2 group.

In the two subsequent papers in this series, Longuet-Higgins used the NBMOs of AHs to investigate the effects of heteroatom substitution on basicity

(*20*) and reactivity (*21*). For example. using Longuet-Higgins' finding with Charles Coulson, that the best position at which to substitute an electronegative atom is at the carbon of highest charge (*13*), it is easy to predict that, in benzyl anion, substitution of N^+ for C would best be made at the CH_2 group, to afford aniline (Ph-NH_2).

One can further predict that in aniline, the nitrogen will have a partial positive charge, because only 4/7 of the negative charge in benzyl anion appears at the CH_2 group. In addition, some of the negative charge in benzyl anion will remain at the *ortho* and *para* carbons of the ring in aniline. Consequently, aromatic substitution reactions at the *ortho* and *para*, but not the *meta* positions, should be accelerated by the amino group in aniline.

Of course, the same types of predictions can be made qualitatively by drawing resonance structures. However, unlike Hückel theory, resonance theory does not make a quantitative prediction of the distribution of spin in benzyl radical or charge in benzyl cation and anion. Resonance theory also fails to predict that square cyclobutadiene has two electrons in non-bonding MOs and is not stabilized by resonance. Therefore, to the extent that Hückel theory is superior to resonance theory, it is desirable to make predictions based on the former, rather than the latter theory. In fact, Longuet-Higgins subsequently co-authored a paper with Michael Dewar in which they claimed that the successes of resonance theory are due to the correspondences between it and the much more satisfactory MO theory (*22*).

Longuet-Higgins' demonstrations that (a) the Hückel NBMOs of AHs can be found by using the zero-sum rule (*19*), without actually performing Hückel calculations; and (b) the NBMOs of odd AHs can be used to make many useful predictions (*19–21*) proved to be very useful contributions to theoretical-organic chemistry. Indeed, Christopher's three 1950 papers provided the foundation for the subsequent development by Michael Dewar of "Perturbation Molecular Orbital (PMO) Theory (*23–25*)." As Dewar wrote in the first of the series of six consecutive papers on PMO theory that Dewar published in *JACS* in 1952 (*22*), "It should be emphasized at the outset that the general plan behind this treatment is not new, and that perturbation methods have been applied to the MO theory in this connection by Coulson and Longuet-Higgins (*13–17*) and by Longuet-Higgins (*19–21*)."

Statistical Mechanics

In 1951 Longuet-Higgins published two papers in the area of statistical mechanics – one on a general treatment of the statistical thermodynamics of multicomponent systems (*26*) and the other on an application of the general theory to a mixture of carbon dioxide and ethylene (*27*). Since this chapter is concerned with Christopher's contributions to electronic structure theory, these and his subsequent papers on statistical mechanics will not be discussed here. However, it is worth noting that, in publishing papers on both electronic structure theory and statistical mechanics, Christopher was following in the tradition of John Lennard-Jones, whom Christopher succeeded as Professor of Theoretical Chemistry at Cambridge.

According to an email message that I received from John Murrell in December of 2011, one of the hallmarks of the "English School" of theoretical chemistry, founded by Lennard-Jones, "was to be broad in outlook…. This is why people like L-H and Orgel switched fields so easily, and why others moved on [so readily] across the paper/computer divide when technology advanced."

Electronic Spectra of Conjugated Molecules

In a series of four papers, published in 1954 and 1955, Longuet-Higgins discussed various aspects of the electronic spectra of conjugated molecules. (*28–32*). The first paper in the series, which Christopher coauthored with Michael Dewar (*28*), began by pointing out that Hückel theory cannot account, even qualitatively, for the UV spectra of aromatic hydrocarbons, such as benzene, naphthalene, and anthracene. However, Dewar and Longuet-Higgins showed that electron repulsion results in strong mixing between excited electronic configurations that are degenerate in Hückel theory; and inclusion of this mixing gives a good account of the UV absorption spectra of these hydrocarbons.

For example, in the case of naphthalene, Hückel theory would lead to the prediction of two strong absorptions. As shown in Figure 5, the lowest energy absorption should correspond to the excitation of an electron from the highest occupied (HO)MO (ψ_5) to the lowest-unoccupied (LU)MO (ψ_6). The transition dipole, corresponding to this excitation, is given by the product of these two MOs, multiplied by the charge of an electron. The product, ψ_5 x ψ_6, shows that the transition dipole is polarized along the short molecular axis of naphthalene, as indicated by the red arrow in Figure 5.

Since naphthalene is an AH, the pairing theorem (*18*) shows ψ_5 and ψ_6 are paired with each other, as are ψ_4 and ψ_7. Therefore, the Hückel energies for $\psi_4 \rightarrow \psi_6$ and $\psi_5 \rightarrow \psi_7$ must be the same. In addition, the transition dipoles for these two excitations, which involve the products, ψ_4 x ψ_6 and ψ_5 x ψ_7, are both polarized along the long molecular axis; and the two transition dipoles must also be the same size.

A simple physical model for explaining why the zeroth-order, energetic degeneracy between $\psi_4 \rightarrow \psi_6$ and $\psi_5 \rightarrow \psi_7$ is lifted is that the transition dipoles that are associated with these two excitations interact electrostatically (*34*). As shown in Figure 5, if the transition dipoles interact in-phase, they add; so the resulting transition is strongly allowed. However, it is high in energy, because the parallel transition dipoles repel each other electrostatically.

On the other hand, if the transition dipoles interact out-of-phase, the resulting transition dipole vanishes; so the resulting transition is, to a first approximation, forbidden. Although vibrational borrowing can make the transition slightly allowed, it should be weak in intensity. However, this transition should be low in energy, because the anti-aligned dipoles attract each other electrostatically.

Assuming that, as shown in Figure 5, the electrostatic attraction between the transition dipoles in the out-of-phase combination of $\psi_4 \rightarrow \psi_6$ and $\psi_5 \rightarrow \psi_7$ is strong enough to overcome the lower Hückel energy of the $\psi_5 \rightarrow \psi_6$ excitation, the UV spectrum of naphthalene should consist of a weak absorption at longest wavelength, followed by an absorption of moderate intensity at a shorter wavelength and a very strong absorption at an even shorter wavelength. In addition, Figure 5 shows that the energy difference between the weakest and the medium intensity band in the naphthalene spectrum should be much smaller than the energy difference between the medium and strongest intensity absorptions.

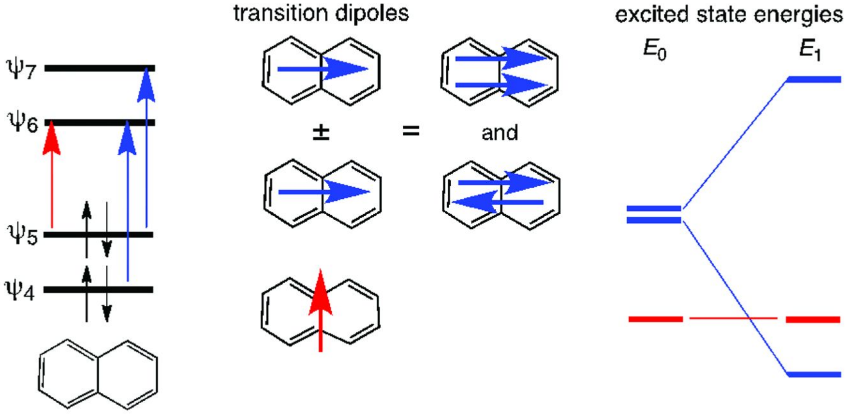


Figure 5. Excitations, transition dipoles, and excited state energies in naphthalene. Although the pairing theorem (18) shows that the energies of $\psi_4 \rightarrow \psi_6$ *and* $\psi_5 \rightarrow \psi_7$ *excitations are the same in zeroth-order (i.e., in Hückel theory), Coulombic repulsion mixes the two excitations and gives rise, in first-order, to a total of three naphthalene excited state energies. (see color insert)*

Not only were Dewar and Longuet-Higgins thus able to account for the UV spectrum of naphthalene, they were also able to account for the UV spectra of benzene and anthracene (*28*). In addition, they pointed out that the pairing theorem, when applied to odd-AH radicals, predicts that the HOMO → singly occupied (SO)MO and SOMO → LUMO excitations have the same Hückel energies and same sized transition dipoles, since the HOMO and LUMO are paired. This is illustrated in Figure 6 for allyl radical.

Therefore, rather than the single absorption, predicted by Hückel theory, radicals like allyl should have two UV-Vis bands. The weak band should appear at longer wavelengths than the strong band, since the former absorption corresponds to the out-of-phase combination of the HOMO → SOMO and SOMO → LUMO transition dipoles; whereas, the latter absorption corresponds to the in-phase combination of these transition dipoles.

The consequences of the pairing theorem in odd AHs were further explored in a paper by Longuet-Higgins and Pople (*30*). They began by pointing out that the pairing theorem applies to the restricted, open-shell, Hartree-Fock (ROHF) MOs for an odd-AH radical. Therefore, the conclusions of Dewar and Longuet-Higgins about odd-AH radicals (*28*), which were derived from Hückel theory, should apply when electron repulsion is explicitly included in the Hamiltonian, as it is in ROHF calculations.

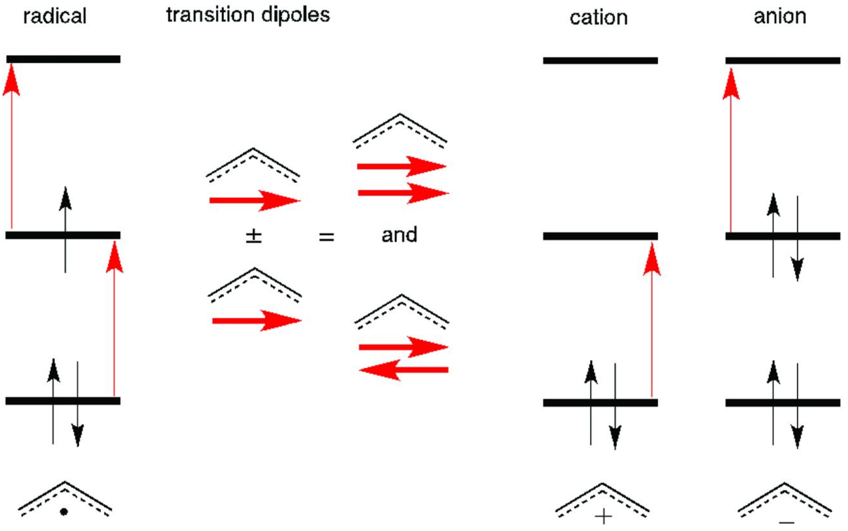


Figure 6. Hückel excitation energies and transition dipoles in allyl radical, and Hückel excitation energies in allyl cation, and allyl anion. (see color insert)

Longuet-Higgins and Pople pointed out that the pairing theorem also makes a prediction about odd-AH ions. As shown in Figure 6 for allyl, the cation and the anion should have low-lying excited states (both singlets and triplets) with the same energies. Longuet-Higgins and Pople also demonstrated that the energy differences between the excited triplet and singlet states of the anion and of the cation should be the same and roughly equal to the energy difference between the two, low-lying, excited states of the radical.

In the final paper in this series on UV-Vis spectra, Longuet-Higgins and Murrell showed that the spectra of molecules, such as butadiene and biphenyl, can be treated as linear combinations of the largely local, π excitations of, respectively, two ethylenes and two benzenes (*31*). The dominant interaction is between the transition dipoles that arise from the local excitation of each of the two fragments.

In fact, the theme of this series of four papers by Longuet-Higgins (*28–31*) is that the electronic spectra of many AHs can be understood, at least semiquantitatively, on the basis of a simple model. It considers the electrostatic interactions between the transition dipoles in the in-phase and out-of-phase combinations of two excitations that are predicted by Hückel theory to have the same energy.

The Electronic Structures of CaB_6 and of $B_{12}H_{12}$

In 1954 and 1955, in collaboration with M. de V. Roberts, Christopher worked out the MOs for the octahedron of boron atoms in CaB_6 (*35*) and for the icosahedron of boron atoms in, the then unknown, $B_{12}H_{12}$ (*36*). Having worked out the MOs for these highly symmetrical cages of boron atoms, assignment of the three valence electrons on each B to these MOs allowed Longuet-Higgins and Roberts to make predictions about the electronic structures of both molecules.

The boron octahedra in crystalline CaB_6 are each linked by six B-B bonds to the adjoining boron octahedra. The interoctahedral B-B bonds account for one orbital and one electron on each boron. The remaining three valence AOs on each B consist of a hybrid AO, pointing 180° away from the AO used for bonding to a boron atom of the adjacent octahedron, and a pair of degenerate 2p AOs that are oriented at 90° to the two hybridized AOs. The question then becomes, "Which of the MOs that are formed from symmetry combinations of these $6(4 – 1) =18$ AOs are occupied by the total of $6(3 – 1) = 12$ remaining valence electrons of boron?"

Longuet-Higgins and Roberts used group theory to show that the six inward-pointing hybrid AOs on the six boron atoms span the a_{1g}, e_{2g}, and t_{1u} representations of the O_h point group. The 2p AOs span the t_{1g}, t_{1u}, t_{2g}, and t_{2u} representations of this point group. The radially oriented t_{1u} combinations of hybrid AOs can mix with the t_{1u} combinations of 2p AOs to form triply degenerate, bonding and antibonding t_{1u} MOs. The triply degenerate set of t_{2g} MOs, which are formed entirely from 2p AOs, are also bonding. The bonding a_{1g} MO, one of the three, degenerate, bonding t_{1u} MOs and one of the bonding t_{2g} MOs are depicted in Figure 7.

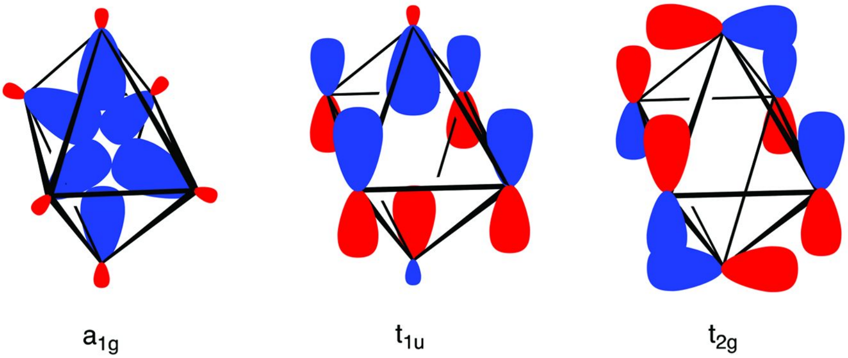


Figure 7. The a_{1g} MO, one of the triply degenerate t_{1u} bonding MOs, and one of the t_{2g} MOs in octahedral B_6. (see color insert)

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

There are seven bonding MOs within an octahedron of six boron atoms, but only twelve electrons to occupy these MOs. However, in CaB_6 the calcium contributes another pair of electrons, so that each B_6 octahedron has a closed shell of fourteen electrons. Similarly, although neutral, octahedral B_6H_6 would be two electrons short of having a closed-shell electronic structure, the $B_6H_6^{-2}$ dianion should have a closed-shell of electrons.

This dianion has, in fact, been prepared (*37*). Since carbon has one more valence electron than boron, replacing two borons in $B_6H_6^{-2}$ with two carbons should confer a closed-shell electronic structure on $B_4C_2H_6$. In fact, both isomers of this carborane, one with the carbons *cis* and the other with the carbons *trans*, are known compounds (*38*).

Constructing the MOs for the icosahedron of boron atoms in $B_{12}H_{12}$ (*36*) proved a much more formidable challenge than finding the MOs for the octahedron of boron atoms in B_6H_6 (*35*). Longuet-Higgins and Roberts met this challenge by inscribing the boron icosahedron on a cube; so that, as shown in Figure 8, one bond between a pair of borons passes through the center of a face of the cube and is parallel to an edge. The 2p AOs on the borons could then be divided into three sets – a radial set, pointing toward the center of the cube, and two tangential sets.

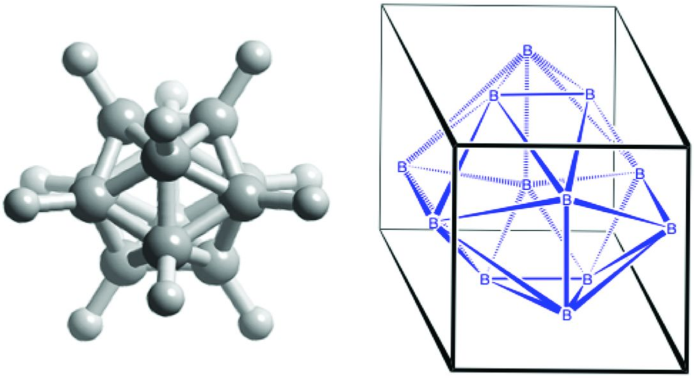


Figure 8. $B_{12}H_{12}$ and an icosahedron of boron atoms, inscribed onto a cube, so that one B-B bond passes through the center of each face and is parallel to an edge of the cube.

Group theory enabled Longuet-Higgins and Roberts to determine which representations of the icosahedral point group were spanned by the three different types of 2p AOs and the 2s AO on each B and what combinations of the AOs belonged to each representation. Hückel theory was then used to compute the interactions between AO combinations of the same symmetry and to find the MOs derived from them.

Longuet-Higgins and Roberts found that, in addition to 12 B-H bonding MOs, in $B_{12}H_{12}$ there are one non-degenerate, one triply degenerate, one quadruply degenerate and one quintuply degenerate sets of B-B bonding MOs. These B-B bonding MOs can accommodate a total of 2 + 6 + 8 + 10 = 26 electrons; but, after forming 12 B-H bonds, the 12 borons of the icosohedron have a total of only 12(3 – 1) = 24 valence electrons. Therefore, Longuet-Higgins and Roberts predicted that $B_{12}H_{12}$ would not be a closed-shell molecule, but that $B_{12}H_{12}^{-2}$ would be (*36*, *39*).

This prediction was confirmed by the subsequent preparation of $B_{12}H_{12}^{-2}$ (*42*) and by the preparation of the isoelectronic carboranes $B_{11}CH_{12}^-$ (*43*) and $B_{10}C_2H_{12}$ (*44*). The $B_{11}CH_{12}^-$ anion has proven particularly useful. With the negative charge delocalized over 11 borons and a carbon, $B_{11}CH_{12}^-$ and its derivatives are anions that coordinate only very weakly to cations (*45*).

Stabilization of Cyclobutadiene in Transition Metal Complexes

In 1956 Longuet-Higgins and Leslie Orgel speculated that cyclobutadiene (CBD) might be stabilized by complexation with a suitable transition metal (*46*). Looking back 55 years, it does not seem much of an intellectual stretch to imagine that complexes of CBD might exist. However, in 1956, at the time that Longuet-Higgins and Orgel published their paper, there were no examples of the stabilization of highly reactive molecules, such as cyclobutadiene, by transition metal complexation. Therefore, the prediction that CBD might be stabilized by bonding to a transition metal really was ground breaking.

Longuet-Higgins and Orgel considered a hypothetical $(C_4H_4)ML_2$ complex, in which L is a two-electron donor ligand to transition metal atom, M, which is also complexed to the π system of cyclobutadiene. Longuet-Higgins and Orgel assumed the ligands both lie in the xz plane, and they then constructed a table which classified the orbitals of the metal, the orbitals of L_2, and the π MOs of CBD with respect to xy and xz planes of symmetry. Longuet-Higgins and Orgel noted that the table showed symmetry matches between each of the four π MOs of CBD and certain AOs of the metal, M; and Longuet-Higgins and Orgel then deduced how many electrons could be accommodated in bonding MOs, formed from each of the four sets of orbitals of different symmetry.

For example, Longuet-Higgins and Orgel observed that eight electrons can be accommodated in low-energy orbitals that arise from the in-phase combination of donor orbitals on the L ligands, the lowest π MO, ψ_1, of CBD, and the s, p_x, d_{z^2}, and $d_{x^2-y^2}$ AOs on M. The metal orbitals d_{z^2}, and $d_{x^2-y^2}$ are largely nonbonding and so can each be doubly occupied; and the empty s and p_z AOs on M can each accept a pair of electrons from the in-phase combination of donor orbitals on the L ligands and from the lowest π MO of CBD.

The out-of-phase combination of ligand MOs and ψ_2, the degenerate CBD non-bonding MO with the same symmetry, can both mix with the p_z and d_{xz} AOs of M. Only two more, low-energy MOs result from these orbital interactions. Therefore, if d_{xz} is filled, ψ_2 must be left empty.

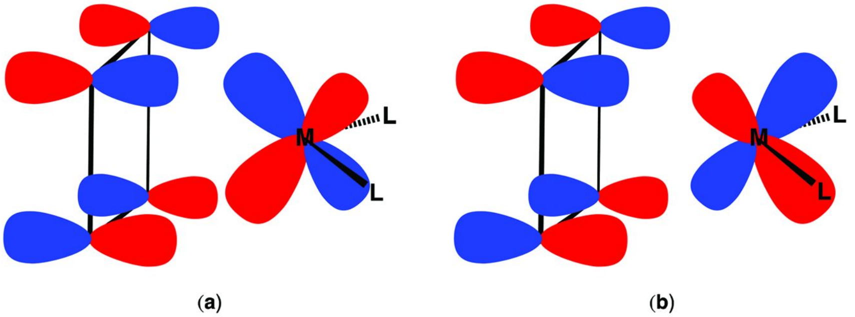


Figure 9. Schematic depiction of the two lowest energy MOs that result from mixing of the d_{xy} and p_y AOs of a metal, M, with ψ_3, one of the two nonbonding π orbitals of CBD. (see color insert)

Another pair of electrons can be accommodated in the d_{yz} orbital on the metal, which forms a weak δ bond with the antibonding ψ_4 MO of CBD. This brings to 14 the total number of electrons that can be accommodated in low-energy MOs in an $(C_4H_4)ML_2$ complex.

Still to be considered are the interactions between the other, degenerate CBD MO, ψ_3, and the d_{xy} and p_y AOs of the metal, M. The two lowest-energy MOs that result from these interactions are depicted schematically in Figure 9. In the lower energy of these two MOs, shown in Figure 9(a), ψ_3 and d_{xy} are in-phase, and d_{xy} is polarized toward the CBD ring by mixing of p_y, also in-phase, with ψ_3. The resulting MO is strongly bonding between the metal and the CBD ring. If d_{xy} on the metal is empty, the remaining pair of CBD π electrons can be accommodated in this MO. Thus, Longuet-Higgins and Orgel predicted that d^8 $(C_4H_4)ML_2$ complexes, with a total of 16 electrons, should be stable.

Longuet-Higgins and Orgel also considered the circumstances under which d^{10} $(C_4H_4)ML_2$ complexes, with a total of 18 electrons, might be stable. Longuet-Higgins and Orgel noted that the smaller the energy separation is between d_{xy} and p_y, the more strongly the empty p_y AO will be mixed into the MO in Figure 9(b). This MO is antibonding between the CBD ring and the metal, but mixing between d_{xy} and p_y results in polarization of d_{xy} away from ψ_3. Therefore, strong mixing of p_y into this MO might make it possible for this metal-CBD anti-bonding MO to hold a pair of electrons.

Longuet-Higgins and Orgel argued that zero-valent transition metals have smaller energy separations between d_{xy} and p_y than positively charged transition metals do; so they speculated that a d^{10} complex, such as $(C_4H_4)Ni(CO)_2$, in which the metal is zero-valent, might prove stable. However, had Longuet-Higgins and Orgel actually drawn the MOs that arise from the mixing between ψ_3 of CBD, and the d_{xy} and p_y AOs of M, they would have seen another reason why the 18-electron complex $(C_4H_4)Ni(CO)_2$ might prove stable.

As shown in Figure 9(b), mixing of p_y into d_{xy} polarizes the resulting metal AO toward the ligands. Therefore, if the ligands have low-lying, unfilled, π* MOs, a pair of electrons in the MO in Figure 9(b) can be stabilized by back-donation from the metal to the ligands. Back donation from Ni^0 into the low-lying, π* MOs of the CO ligands in $(C_4H_4)Ni(CO)_2$ should be especially favorable, and this provides anther reason why $(C_4H_4)Ni(CO)_2$ might prove to be a stable complex of CBD.

Although $(C_4H_4)Ni(CO)_2$ might be a stable complex of CBD, this molecule has apparently not been prepared. However, another 18-electron complex, $(C_4H_4)Fe(CO)_3$, is well known, and was thoroughly studied experimentally by Roland Pettit and his coworkers (*47*, *48*). It is a very stable molecule; in, fact, the CBD ring of the complex actually undergoes aromatic substitution reactions.

$(C_4H_4)Fe(CO)_3$ differs from $(C_4H_4)Ni(CO)_2$ by having one more CO ligand and two less electrons in 3d orbitals on the metal. However, there is also a more subtle difference. In an $Fe(CO)_3$ fragment, the $3d_{xz}$ and $3d_{xy}$ orbitals of Fe are degenerate by symmetry, as are the ψ_2 and ψ_3 orbitals of CBD. Therefore, the question of which of the two degenerate 3d AOs on the metal and which of the degenerate nonbonding orbitals of CBD is filled and which is empty in forming $(C_4H_4)Fe(CO)_3$ is not meaningful.

In fact, the reason why $(C_4H_4)Fe(CO)_3$ is a very stable, closed-shell, molecule; whereas, both CBD and $Fe(CO)_3$ are very reactive, open-shell, molecules, is that in $(C_4H_4)Fe(CO)_3$ there is a strong interaction between the pairs of half-filled, degenerate MOs on each of the two fragments. The resulting pair of (nearly) degenerate bonding MOs in $(C_4H_4)Fe(CO)_3$ can accommodate the total of four electrons that occupy degenerate pairs of orbitals in CBD and in the $Fe(CO)_3$ fragment.

Intersections between Potential Energy Surfaces

In 1958 Longuet-Higgins published the first of three papers on the intersections between potential energy surfaces (PESs) and on the vibrations that lift the energetic degeneracies between the PESs at the points where they intersect. In this first paper, Longuet-Higgins collaborated with Opik, Pryce, and Sack on a quantitative study of the coupling between electronic and vibrational wave functions in a non-linear radical with a doubly degenerate electronic state (*49*). This paper used as a model an electron on a ring. The lowest energy wave function for an electron on a ring is non-degenerate; but higher energy wave functions come in degenerate pairs, starting with a pair of wave functions that, like $2p_x$ and $2p_y$ AOs, each have one node.

Longuet-Higgins and his coauthors considered two, orthogonal, elliptical deformations of the ring, that might be caused by vibrations. For example, one deformation might shorten the radius of the ring along the x axis, while lengthening it along the z axis. The other phase of the same deformation would have the opposite effect on the lengths of the radii along these two axes. A second deformation, orthogonal to the first, would alternately shorten and lengthen the radii of the ring along axes at 45° to the x and z axes.

The model used by Longuet-Higgins and his coauthors did not correspond to a real physical system. However, they noted that the equations "obtained by arguments based on [this] simple model, may be regarded as the mathematical starting-point for a general discussion of the Jahn-Teller coupling between a doubly degenerate electronic state and a doubly degenerate vibration (*49*)."

As shown in Figure 10, under the influence of a Jahn-Teller effect (*50*), in which the degeneracy between two components of a degenerate electronic state is lifted by a degenerate pair of vibrations, a pair of conical potential energy surfaces is obtained. The energy difference between the higher and lower energy surfaces is $2k'r$, where r is the magnitude of the vibrational distortion and ±k' are the energies of destabilization/stabilization per unit of distortion. The energies of the two surfaces both also contain a quadratic term, $kr^2/2$, where k is the quadratic force constant for the pair of vibrations that are Jahn-Teller active.

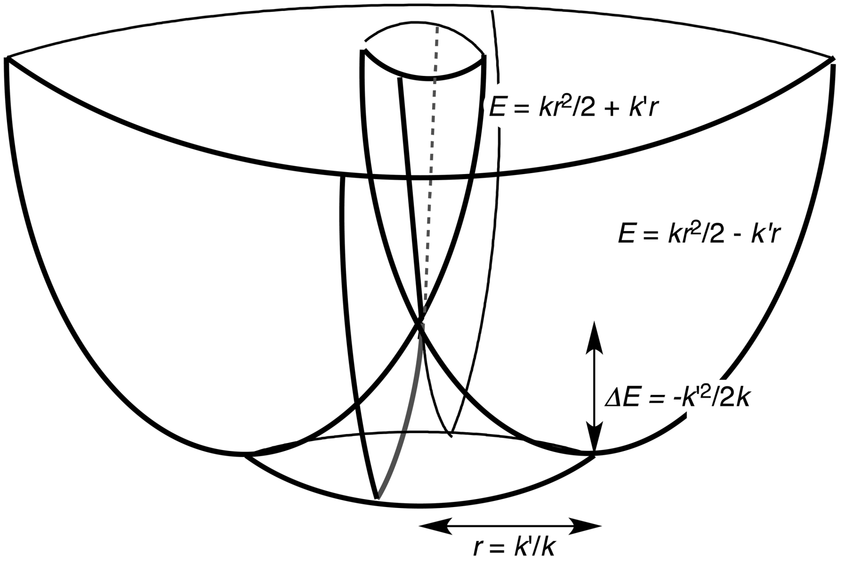


Figure 10. The two potential energy surfaces that result from the effect of a degenerate pair of vibrations on the two components of a degenerate electronic state. The upper of the two potential energy surfaces is an inverted cone, with its vertex at the undistorted geometry (r = 0). The lower energy surface is also a cone, with its vertex at r = 0 and its circular base at r = k'/k, where –k'r is the energy lowering due to molecular distortion of magnitude r; and k is the quadratic force constant for molecular distortion. The energy around the circular base of the lower cone is $\Delta E = -k'^2/2k$ *lower than the energy at the vertex. Both the upper and lower cones can be generated by parabolas with the formula* $E = kr^2/2 - k'r$, *provided it is understood that r is negative on the higher energy surface, above E = 0, the energy at which the parabolas intersect.*

If one of the pair of orthogonal vibrations that lifts the degeneracy of the two electronic states is assumed to lie along the x axis (in the plane of the paper) of Figure 10, the other vibration lies along the z axis (out of the plane of the paper). It should be noted that both vibrations and any linear combination of them have the same effect on the potential energy of both surfaces; and that is why the minima on the lower surface all occur at a distortion of $r = k'/k$ and at an energy of $\Delta E = -k'^2/2k$ lower than that of the undistorted molecule. Therefore, in this simple model, a molecule can pass from one distorted geometry to another, around the circular base of the lower cone, with no change in energy.

Longuet-Higgins and his coworkers made an interesting observation (*49*). They were able to show that, on making a 360° circuit around this circle, the electronic wave function changes sign. They pointed out that, since the total wave function, which is a product of the electronic and vibrational wave functions, must be single-valued, the vibrational wave function must also change sign. The sign change in the electronic wave function is now known as the "Berry geometric phase", named after Michael Berry, who subsequently generalized the finding published by Longuet-Higgins and his coauthors (*51*).

Longuet-Higgins returned to the subject of this phase change in a second paper, published in 1963, and coauthored by Gerhard Herzberg (*52*). The paper investigated the intersections of potential energy surfaces in polyatomic molecules, in which the intersections between the surfaces are not mandated by symmetry. Such intersections differ from those encountered in molecules that undergo Jahn-Teller distortions (*50*), where the intersections occur between two components of an electronic state that is degenerate by symmetry and where the electronic degeneracy is lifted by a pair of degenerate vibrations.

Longuet-Higgins and Herzberg argued that, in order for two electronic states to have exactly the same energy at some point in space, two conditions must be satisfied. Not only must the two states have the same energy at that point, but also, they must not mix with each other.

In a diatomic molecule, the X-Y bond length is the only degree of freedom. This makes it highly unlikely that both conditions for two states having the same electronic energy will be satisfied simultaneously, unless a difference between the symmetries of the states prevents them from mixing with each other at all X-Y bond lengths. However, if two electronic states have the same symmetry, then there is no reason to suppose that they will not mix. This gives rise to the "non-crossing rule" – states of the same symmetry do not cross in a diatomic molecule, because their mixing will lift their zeroth-order degeneracy.

However, in non-linear, polyatomic molecules, there are $3n - 6$ internal coordinates. Thus, even in a triatomic molecule ($n = 3$), there are three degrees of freedom. Therefore, it is possible, at least in principle, that in a polyatomic molecule two states of the same symmetry will have the same energy at one or more geometries and will not mix with each other. Consequently, Herzberg and Longuet-Higgins claimed that the non-crossing rule may be violated in polyatomic molecules.

Herzberg and Longuet-Higgins then explored what happens at a point where a crossing between two electronic states occurs. Assuming that the state crossing occurs along one coordinate and that the two states mix along a second coordinate, Herzberg and Longuet-Higgins showed that a double cone, similar to that in Figure 10, is obtained.

However, there is a difference between a Jahn-Teller effect (*50*), involving the two components of an electronic state that are degenerate by symmetry, and the "accidental" crossing of two non-degenerate electronic states. In a Jahn-Teller effect, the energy decrease from the point of intersection of the upper and lower cones is the same in the coordinates for both degenerate vibrations and for any linear combination of them. This is illustrated in Figure 10.

In contrast, when an intersection occurs between two states that are not degenerate by symmetry, the vibrations that lift the "accidental" energetic degeneracy are not degenerate by symmetry either. Consequently, unlike the case in Figure 10, the energy changes are different along the two vibrational coordinates.

Suppose the energy of each of the two, unmixed, non-degenerate, states changes along the x axis (in the plane of Figure 10), with the energy of one state increasing and the other decreasing on a distortion along +x. The energies of the two states change in opposite directions along –x, the opposite phase of the same distortion. Since the states are not degenerate by symmetry, the energy change along +x, where one state is lower in energy, and along –x, where the other state is lower in energy, are different. If the wave functions for the two states mix along the z axis (out-of the-plane of Figure 10). the energy changes along the ±z axis are the same, but different from those along the +x and –x axes.

The equations for the type of state crossing that gives a double-cone potential energy surface had been previously derived by Teller (*53*). However, Herzberg and Longuet-Higgins pointed out something that had apparently been missed by Teller -- the wave function on the lower surface changes sign on a passage of 360° about an adiabatic (constant energy) loop around the conical intersection. As discussed above, this had, been proven previously by Longuet-Higgins and coworkers for a Jahn-Teller effect, involving the two components of an electronic state that is degenerate by symmetry (*49*). However, Herzberg and Longuet-Higgins generalized this argument to a conical intersection between two states that are not degenerate by symmetry (*52*).

The sign change that accompanies passage around a conical intersection was illustrated by Herzberg and Longuet-Higgins, using the valence-bond wave function for three hydrogen-like atoms that form a ring. Figure 11 illustrates the sign change, using, instead, the MO that is singly occupied in the ground electronic state for the Jahn-Teller pseudorotation of cyclic H_3 around a D_{3h} geometry.

At a D_{3h} geometry the ground state of H_3 is a doubly-degenerate $^2E'$ state, in which the unpaired electron can occupy a linear combination of two degenerate, e' MOs, ψ_x and ψ_y. These MOs are shown in Figure 11. Which linear combination is occupied is dictated by the type of Jahn-Teller, e', distortion that the molecule undergoes. For example, a geometry distortion that lengthens one bond and shortens two bonds puts the unpaired electron in ψ_x. The opposite phase of the same geometry distortion, which shortens one bond and lengthens two, puts the unpaired electron in ψ_y.

A distortion which shortens one bond and lengthens another destroys the plane that confers different symmetry on ψ_x and ψ_y. Therefore, ψ_x and ψ_y are mixed by such a distortion. Distortions that take the H_3 molecule to geometries in which a symmetry plane passes through one of the two other H atoms, mix ψ_x and ψ_y in such a way that another of the possible ψ_x type MOs (ψ_x' or ψ_x'') or ψ_y type MOs (ψ_y' or ψ_y') in Figure 11 is occupied. The H_3 molecule can pseudorotate from one distorted geometry to another, around the circular base of the lower cone in Figure 10, with no energetic cost.

Pseudorotation about this circle can be described by an angle, θ, which changes from θ=0° to θ=360°. The geometry with one long bond and two short bonds, at which the odd electron occupies ψ_x, can be arbitrarily chosen as corresponding to θ = 0°. Then the MO that is occupied by the unpaired electron is given by $\psi = \psi_x(\cos\theta/2) + \psi_y(\sin\theta/2)$, so that the unpaired electron, which starts off in ψ_x at θ = 0°, occupies ψ_y at θ = 180°. Continuing on to θ = 360°, the wave function becomes not ψ_x, but $-\psi_x$. This is the sign change that Longuet-Higgins discovered (*49*, *52*) and which is now known as the Berry geometric phase (*51*).

Herzberg and Longuet-Higgins conjectured that the observation of this type of sign change in the wave function for a molecule, on passage around an adiabatic loop, indicates that, somewhere within the loop there must be a conical intersection. They also conjectured that conical intersections are possible when a molecule has no elements of symmetry. Both of these hypotheses were subsequently proven by Longuet-Higgins in a third paper on intersecting potential energy surfaces (*54*).

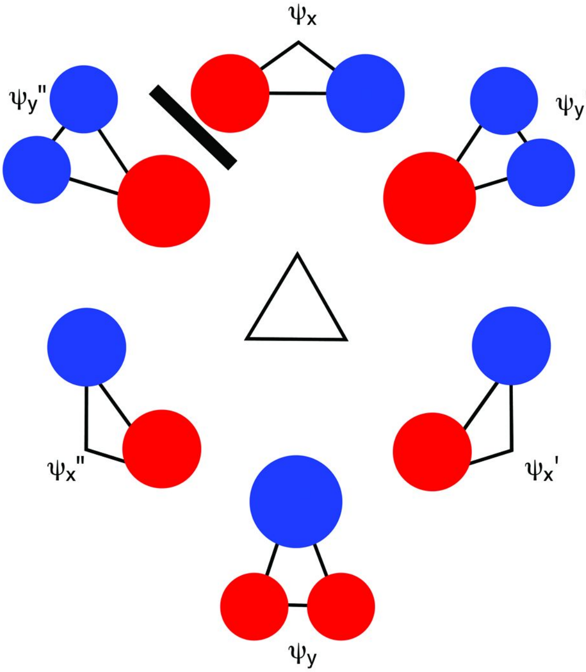


Figure 11. Effect of the molecular geometry on the MO that is singly occupied in the two Jahn-Teller distortions of cyclic H_3. The heavy line drawn between ψ_y'' and ψ_x indicates that pseudorotation around a D_{3h} geometry does not take ψ_y'' into ψ_x, but into $-\psi_x$. (see color insert)

Longuet-Higgins published this paper in 1975, eight years after he had left chermistry. The paper was published in response to a criticism of the 1963 paper that Longuet-Higgins had coauthored with Herzberg (*52*). As well as refuting this criticism, Longuet-Higgins also proved the following pair of theorems.

First, if the wave function for an electronic state changes sign upon adiabatic passage around a loop in the space of the nuclear configurations, a conical intersection occurs somewhere inside the loop. Second, the occurrence of such conical intersections is not limited to those cases where the intersection is mandated by symmetry (i.e., to molecules, such as D_{3h} H_3, that have a degenerate ground state and which are predicted to undergo Jahn-Teller distortions). Nor are conical intersections even limited to the potential energy surfaces for molecules, like LiH_2, where symmetry allows two states of different symmetry to cross, by preventing them from mixing.

Instead, Longuet-Higgins showed that a conical intersection between two electronic states may occur in a molecule, such as NaLiH, which has no element of symmetry, apart from the molecular plane. In NaLiH one electronic state can be thought of as being derived from Na + LiH with two long bonds and one short bond. The other electronic state would then correspond to Li-Na-H and have a more nearly linear geometry. The latter geometry can be transformed by a vibration that lengthens one bond and shortens the other to either LiNa + H or Li + NaH.

The situation for NaLiH is analogous to that depicted in Figure 11 for cyclic H_3. Pseudorotation of cyclic H_3 around a D_{3h} geometry results in the existence of three different, but equivalent, distorted geometries, each having two long bonds and one short bond. The difference between NaLiH and H_3 is, of course, that the three geometries of NaLiH which have two long bonds and one short bond correspond to three different species -- Na + LiH, LiNa + H, and Li + NaH -- all of which have different energies.

Despite the absence of symmetry in NaLiH, Longuet-Higgins proof showed that at some point on the potential energy surface two different electronic states must "accidentally" have the same energy, since the wave function for cyclic NaLiH changes sign on pseudorotation of 360° around a cyclic geometry.

The Geometries of the Lowest Excited State of NH_2 and of the Ground States of CH_2 and BH_2 – Even Longuet-Higgins Was Sometimes Wrong

In 1958, the same year that Longuet-Higgins published his paper on the dynamic Jahn-Teller Effect (*49*), he also published a paper with John Pople on the Renner effect in NH_2 (*55*). A Renner effect occurs at linear geometries of a radical like NH_2, in which bending in any plane results in two different electronic states (*56*). The two states have the same energy at a linear geometry, but bending occurs, not as the result of mixing of the two degenerate states with each other, but as a result of mixing of each of the states with a different excited state. Therefore, bending is a so-called second-order Jahn-Teller effect, because the states that are mixed by bending are non-degenerate; so the energy lowering that occurs on bending is quadratic, rather than linear, in the bending coordinate.

The ground state ($^2B_1$) of NH_2 is bent, with two electrons occupying a σMO(a_1) and the unpaired electron occupying a 2p-π AO (b_1) on nitrogen. In the first excited state the orbital occupancy is reversed. With only one electron in the a_1 orbital that is stabilized by bending, the $^2A_1$ excited state of NH_2 should be much less bent than the $^2B_1$ ground state, but the excited state should be bent.

Pople and Longuet-Higgins calculated the vibrational features in the electronic spectrum of NH_2 radical, which had been obtained by Dressler and Ramsay (*57*). Dressler and Ramsay had concluded that their spectrum showed that the $^2A_1$ excited state of NH_2 is linear; and Pople and Longuet-Higgins incorporated this assumption into their computational modeling of the spectrum. Their calculated spectrum provided a satisfactory fit to the experimental spectrum that had been obtained by Dressler and Ramsay; so Pople and Longuet-Higgins concluded that the $^2A_1$ excited state of NH_2 is, indeed, linear, as posited Dressler and Ramsay.

Subsequently, Jordan and Longuet-Higgins performed semiempirical calculations on NH_2 and other triatomic molecules (*1*). The calculations confirmed the assumption that the $^2A_1$ excited state of NH_2 is linear. However, later semiempirical (*58*) and *ab initio* (*59*) calculations found that this state of NH_2 is bent. Prior to the publication of these later computational results, Dixon had reinterpreted the NH_2 spectrum in terms of bent equilibrium geometry for the $^2A_1$ state (*60*). Thus, although Pople and Longuet-Higgins succeeded in fitting the spectrum, observed by Dressler and Ramsay (*57*), their calculations were based on the incorrect assumption that the $^2A_1$ excited state of NH_2 is linear (*61*).

Among the other triatomic species whose geometries were computed by Jordan and Longuet-Higgins were BH_2 and the triplet ground state of CH_2 (*1*). Like the $^2A_1$ excited state of NH_2, each of these molecules has one electron in an a_1 σ MO. BH_2, triplet CH_2, and excited NH_2 differ by having the b_1, 2p-π, AO on the central atom occupied by, respectively, 0, 1, and 2 electrons. Since differences in the occupancy of this MO have little effect on the geometries of AH_2 molecules (*62*), if Jordan and Longuet-Higgins' calculations were incorrect in predicting a linear geometry for the $^2A_1$ excited state of NH_2, their calculations must also have erred in predicting linear geometries for the ground states of BH_2 and CH_2.

The paper by Jordan and Longuet-Higgins' was published in 1961, but it was not until 1965 that it became clear that the $^2A_1$ excited state of NH_2 has a bent geometry (*60*). It took another five years until the experiments of Wasserman and Bernheim showed conclusively that Jordan and Longuet-Higgins (*1*) (and, before them, Herzberg) had been wrong about the geometry of triplet CH_2 being linear (*63*). However, by then Christopher was doing research in cognitive science; so perhaps he was less upset about having been wrong about the geometries of the $^2A_1$ state of NH_2 and the triplet ground state of CH_2 than he might have been, had he still been doing research in chemistry.

The discovery that triplet CH_2 is bent, with an H-C-H angle of about 140° (*63*), vindicated the pioneering *ab initio* calculations of Foster and Boys, which had predicted this to be the case a decade earlier (*64*). S. F. (Frank) Boys was also a member of the Theoretical Chemistry Department, but his personality was very different from Christopher's. John Murrell stated, "Boys was always a bit diffident, and he didn't have experiments at his finger tips, and [his research in developing the methodology necessary to perform *ab initio* calculations] looked like a branch of mathematics [to Longuet-Higgins] (*4*)." Murrell goes on to say, "Longuet-Higgins…hated the work, simply couldn't abide it (*4*)."

Longuet-Higgins' disdain for Boys' research is evident in the somewhat condescending tone of what Jordan and Longuet-Higgins wrote about Boys' paper on CH_2. "It may be that future theoretical progress will require elaborate variational calculations, such as those of Foster and Boys on CH_2, but until the results of such machine experiments can be interpreted physically, there would seem to be a place for more empirical theories such as that which we now describe (*1*)."

As noted above, at the time that Jordan and Longuet-Higgins published their paper (*1*), the geometry of triplet CH_2 was believed to be linear (*63*). Therefore, it must have been tempting for Christopher to end the last sentence in the previous paragraph with, "…but until the results of such machine experiments can correctly predict the geometries of simple triatomic molecules, such as triplet CH_2, there would seem to be a place for more empirical theories such as that which we now describe." Since it was Christopher's calculations that turned out to get the geometry of triplet CH_2 wrong, it is fortunate that he did not embarrass himself by gloating over the apparent failure of Boys' calculations (*64*) to predict correctly the geometry of triplet CH_2 (*65*).

Bond Alternation in [4n+2]Annulenes and Polyacenes

In 1959 and 1960 Longuet-Higgins and his graduate student, Lionel Salem, published a series of three papers, which used Hückel theory to investigate bond alternation in several types of conjugated molecules (*66–68*). Perhaps the most important conclusion of this work is, even in monocyclic, conjugated molecules (annulenes) that satisfy the Hückel 4n+2 rule for aromaticity, the C-C bonds must alternate in length for sufficiently large values of n (*66*, *69*).

Indirectly, the paper on bond alternation in [4n+2]annulenes answered the question of why there is a major difference between allyl radical and benzene on one hand and H_3 and cyclic H_6 on the other. Allyl radical and benzene both have equal C-C bond lengths; but the bond lengths in linear H_3 and cyclic H_6 alternate so strongly that H_3 is a transition structure, connecting $H\bullet + H_2$ to $H_2 + H\bullet$; and H_6 is unstable with respect to distortion to three H_2 molecules.

If the Hückel bonding parameter, β, is assumed to decrease exponentially with distance, Hückel theory correctly predicts that H_3 is a transition structure and that cyclic H_6 is unstable with respect to dissociation to three molecules of H_2. Why, then, do allyl radical and benzene have equal bond lengths, when Hückel theory, applied to π electrons of these two molecules, gives exactly the same types of equations as Hückel theory applied to, respectively, H_3 and H_6?

Longuet-Higgins and Salem showed that the π systems of conjugated molecules, such as allyl radical and benzene, actually do prefer geometries with unequal bond lengths; but the σ bonds prefer to have the same length (*66*). Thus, Longuet-Higgins and Salem were the first to demonstrate that the six π electrons of benzene (like the six electrons of H_6) favor alternating long and short bonds, and that the equal bond lengths in benzene are due to the preference of the σ bond lengths for equality (*70*).

Longuet-Higgins and Salem went on to show that the bond lengths of [4n+2]annulenes must, for sufficiently large n, alternate, because the preference of the π system for alternating bond lengths eventually will overcome the preference of the σsystem for equal bond lengths (*66*). The, parameterized, semiempirical, Hückel calculations, performed by Longuet-Higgins and Salem, gave n ≈ 8 as the value at which bond length alternation should begin to occur, with an associated stabilization energy of only about 0.02 kcal/mol. More recent DFT calculations suggest that bond length alternation first appears for n = 7 in [30]annulene (*71*).

Why, for large values of n, does the preference of the π system for alternating bond lengths eventually overcome the preference of the σ system for equal bond lengths? A simple way to understand why this is so involves the variation with n of the size of the second-order Jahn-Teller effect that mixes filled with unfilled π MOs upon bond length alternation (*66*). The effect of this mixing is larger, the smaller the size of the energy gap between the highest occupied (HO)MO and lowest unoccupied (LU)MO.

The Hückel expression for the HOMO-LUMO energy gap in a [4n+2]annulene is

$$\Delta E = 4|\beta|\cos(2\pi n/4n{+}2) = 4|\beta|\cos(\pi n/2n{+}1)$$

In the limit of n >> 1, this becomes

$$\Delta E = 4|\beta|\cos(\pi/2) \approx 0$$

Thus, for sufficiently large n, the HOMO-LUMO gap in a [4n+2]annulene approaches zero.

The approach to zero of the HOMO-LUMO gap in a [4n+2]annulene means that, for very large n, the stabilization energy, associated with HOMO-LUMO mixing, becomes first-order in the distortion coordinate that causes the mixing. Bond length alternation allows the HOMO and LUMO to mix. Therefore, the stabilization energy, associated with bond length alternation, will, for very large n, dominate any quadratic terms (e.g. the energies of the σ bonds) that resist bond length alternation. Therefore, bond length alternation must occur in [4n+2]annulenes for values of n that are sufficiently large.

The importance of the energy gap between filled and empty orbitals that are mixed by bond length alternation is the origin of the surprising finding by Longuet-Higgins and Salem that bond length alternation is *not* expected to occur around the 4n+2 carbon perimeter of the polyacenes, no matter how large the value of n (*67*). As in the [4n+2]annulenes, the energy gap between the HOMO and the LUMO in polyacenes goes to zero as n increases, but it is not the HOMO and the LUMO that are mixed by bond length alternation in polyacenes. Instead, as shown in Figure 12, bond length alternation mixes the HOMO-1 with the LUMO and the HOMO with the LUMO + 1. The energy gaps between these pairs of MOs do not go to zero but remain finite.

The reason why there is an energy gap between these pairs of MOs, even though the HOMO-LUMO gap goes to zero, is that the cross-link bonds lift the degeneracy that exists in a [4n+2]annulene between the HOMO and the HOMO - 1 and between the LUMO and the LUMO + 1. The HOMO and the LUMO of polyacenes have nodes at the carbons that are joined by the crosslink bonds. Therefore, the energies of the HOMO and LUMO in a polyacenes are the same as those in the corresponding [4n+2]annulene, in which the cross-link bonds are absent.

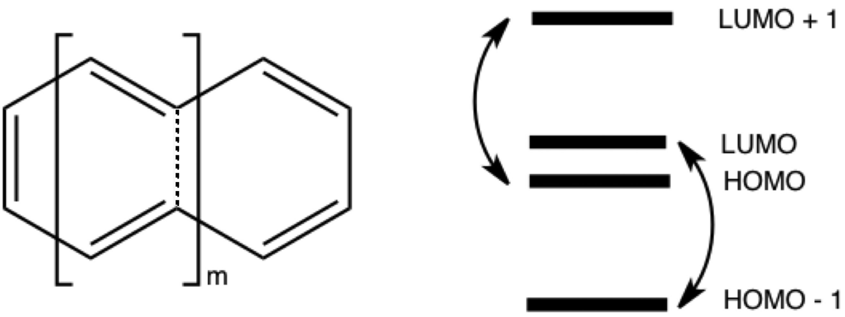


Figure 12. Polyacenes (e.g. m = 1 is naphthalene, m = 2 is anthracene). The cross-link bonds between the carbons of the 4n+2 carbon periphery are indicated by the dotted line. The relative energies of the two, highest-lying, filled π MOs and the two, lowest-lying empty π MOs are depicted schematically. The arrows indicate that bond length alternation mixes the HOMO - 1 with the LUMO and the HOMO with the LUMO + 1.

However, the HOMO-1 and LUMO+1 of polyacenes do not have nodes at these carbons. The HOMO-1 is stabilized by π bonding interactions between the pairs of carbons that are joined by the cross-links, and the LUMO+1 is destabilized by π antibonding interactions between these pairs of carbons. Therefore, as shown schematically in Figure 12, there is always a finite energy gap between the HOMO and the LUMO + 1 and between the HOMO-1 and the LUMO in a polyacene.

The paper by Longuet-Higgins and Salem has sparked many additional calculations on polyacenes at various levels of theory. A review of the research in this area has been published by Bettinger (*72*).

Symmetry Groups of Non-Rigid Molecules

Perhaps Longuet-Higgins most important contribution to molecular spectroscopy and, without doubt, his most original, was his paper on the symmetry groups of non-rigid molecules (*73*)(*74*). It showed how permutation groups can be used to classify the wave functions of non-rigid molecules in the same way that point groups are used to classify the wave functions of rigid molecules. In fact, as Longuet-Higgins pointed out, permutation groups can be used for this purpose in rigid molecules,

The Hamiltonian operator is invariant, not only to permutations of identical nuclei, but also to inversion of the coordinates of all of the atoms through the center of mass. The latter invariance holds because the energy of a molecule is independent of the choice of whether a left-handed or right-handed coordinate system is used. Since the permutation and inversion operators commute with the Hamiltonian, the eigenfunctions of the Hamiltonian are also eigenfunctions of these operators. Therefore, the permutation and inversion operators can be used to classify the wave functions of a molecule, according to the behavior of each wave function with respect to effects of permutation of identical nuclei and molecular inversion.

However, some of these operations may not be achievable without breaking bonds; and the operations of interest are only those that are feasible, without having to pass over an insuperable energy barrier. This point can be illustrated by considering H_3C-BF_2, the molecule to which Longuet-Higgins devoted the most space in his paper (*73*).

Figure 13 shows a projection of this molecule, looking down the C-B bond. The molecule could have been drawn in one of two different conformations that have a plane of symmetry, but the conformation depicted in Figure 13 has no elements of symmetry. The three equivalent hydrogens are numbered 1 – 3, and the two equivalent borons are numbered 4 and 5.

The permutation 1→2→3→1 is easily accomplished by rotating the methyl group through a dihedral angle of 120° about the C-B bond. Longuet-Higgins denoted this permutation as (123). Rotation of the methyl group by -120° is denoted as (132). Another possible permutation is accomplished by rotating the BF2 group through a dihedral angle of 180° about the C-B, and this permutation was denoted by Longuet-Higgins as (45). (123)(45) and (132)(45) denote simultaneous permutations of the hydrogens and of the fluorines.

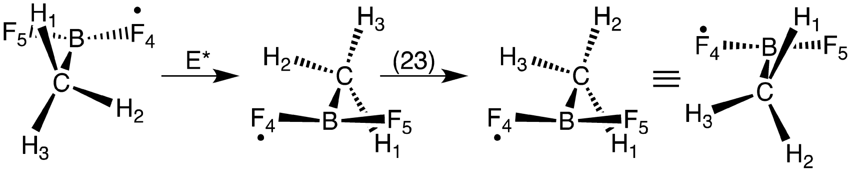


Figure 13. The effect of (23) on an asymmetric conformation of CH_3BF_2. This operation consists of inversion through the center of mass, E*, followed by the permutation of H_2 and H_3, (23). The • represents an electron on F_4, above the F-B-F plane on the left and right sides of the diagram.*

Three permutations (12), (23), and (13) need not be considered, because they could only be accomplished by C-H bond breaking. As shown in Figure 13, inversion through the center of mass, which was denoted by Longuet-Higgins as E*, need not be considered either, because it also would require C-H bond breaking. However, inversion through the center of mass, followed by permutation of hydrogens 2 and 3, is possible. Longuet-Higgins denoted this combined permutation and inversion as (23)*. (12)* and (13)* also are possible, because, like (23)*, these inversion-permutation operations do not require C-H bond breaking.

The operation (23)*, looks at first as though it has the same effect as the permutation (45). But consider the electron on fluorine 4, shown as being above the F-B-F plane on the left side of Figure 13. This figure shows that inversion of the molecule through its center of mass places the electron below the F-B-F plane. Although the electron is unaffected by the permutation (23), Figure 13 shows that, following this operation, redrawing the molecule puts the electron above the F-C-F plane. In contrast, the operation (45), which is accomplished by rotating the BF_2 group by 180°, places the electron on F_4 below the F-C-F plane Therefore, (23)* and (45) really are different operations.

The distinct classes of operations in the permutation-inversion group to which CH_3-BF_2 belongs are thus the identity operation (E), the two, three-fold permutations of the hydrogens [(123) and (132)], the three, inversion-two-fold permutations of the hydrogens [(12)*, (13)*, and (23)*], the two-fold permutation of the fluorines [(45)], the two simultaneous permutations of the hydrogens and of the fluorines [(123)(45) and (132)(45)] and the three, inversion-two-fold permutations of the hydrogens, accompanied by the two-fold permutation of the fluorines [(12)*(45), (13)*(45), and (23)*(45)].

As Longuet-Higgins pointed out, the permutation-inversion group for CH_3-BF_2 is isomorphous with the both the D_{3h} and C_{6v} point groups. The former point group contains, in addition to the identity operation, 2 C_3 axes, 3 C_2 axes, a C_s plane perpendicular to the three-fold axis, 2 improper S_3 axes, and 3 C_v planes. The latter point group contains, in addition to the identity operation, 2 C_6 axes, 3 C_v planes, a C_2 axis, 2 C_3 axes, and 3 C_d planes.

It is to be emphasized that CH_3BF_2 can have, at most, C_s symmetry; and, in fact, the conformation drawn in Figure 13 has no symmetry. However, because CH_3BF_2 has a permutation-inversion group that is isomorphous with both the D_{3h} and C_{6v} point groups, the characters of either point group should be capable of being used to characterize the possible rotational and torsional wave functions of the molecule. In fact, in 1955 Wilson and coworkers had found that it was possible to use a group isomrphous with C_{6v} to do just this (*75*). Longuet-Higgins' paper on the symmetry groups for non-rigid molecules showed why this was possible (*73*).

In this paper Longuet-Higgins also discussed the permutation-inversion groups for trimethylboron, ethane, and hydrazine. In a subsequent paper with Phil Bunker, Longuet-Higgins used permutation groups to analyze the IR spectrum of dimethylacetylene, a molecule in which the barriers to methyl torsions are much lower than in ethane (*76*).

ESR Spectroscopy

Starting in 1960, Longuet-Higgins began publishing papers with Alan Carrington, an ESR spectroscopist at Cambridge. My personal favorite (for reasons that will become apparent) is a paper on why one deuterium perturbs the ESR spectrum of benzene radical anion, but not that of cyclooctatetraene radical anion ($COT^{\bullet -}$) (*77*).

In the case of the benzene radical anion-d_1 a non-uniform spin distribution is observed, with more spin found at the carbons that are *ortho* and *meta* to the carbon to which the deuterium is attached (*78*). The degenerate pair of benzene antibonding MOs, between which the unpaired electron must be distributed, are shown in Figure 14(a).

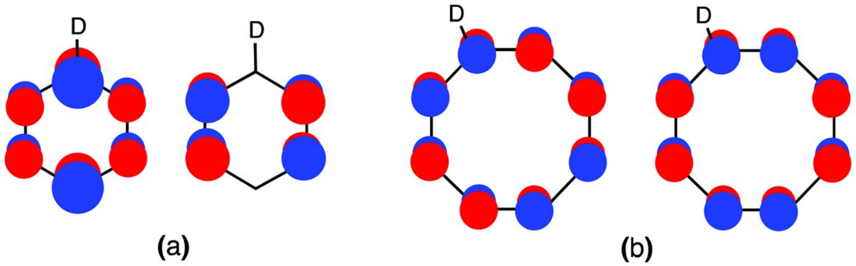


Figure 14. Degenerate pairs of MOs between which one electron must be distributed in the radical anions of (a) benzene and (b) cyclooctateraene. (see color insert)

A substituent attached to one carbon will lift the degeneracy of the two MOs in Figure 14(a), since in one MO it will be attached to a carbon with a large coefficient, and in the other MO it will be attached to a nodal carbon. However, a deuterium cannot lift the degeneracy of the MOs in the same way that a methyl or a fluoro substituent can, because the substitution of a deuterium nucleus for the proton in a hydrogen atom cannot directly affect the electronic wave function. Nevertheless, a deuterium can lower the zero-point energy (ZPE) for an out-of-plane vibration at the benzene carbon to which it is attached, since deuterium has twice the mass of hydrogen. The greatest ZPE lowering will be achieved when deuterium replaces hydrogen at a carbon that has the highest possible frequency for an out-of-plane vibration.

The odd electron in the benzene radical anion occupies an antibonding MO; so the odd electron will lower the frequencies for out-of-plane bending at the carbons that have large coefficients in the MO that is occupied. The out-of-plane bending frequencies of the hydrogens that are attached to a nodal carbon in an antibonding MO will be least affected. Therefore, substitution of deuterium for hydrogen at such a carbon will supply the largest possible reduction in ZPE for an out-of-plane vibration. This analysis predicts that deuterium will favor the odd electron occupying the benzene MO that has a node at the carbon to which the deuterium is attached, and that is exactly what was found experimentally by Lawler and coworkers (*78*).

As shown in Figure 14(b), the pair of degenerate MOs that are occupied by the odd electron in COT radical anion differ from the pair of MOs that are occupied by the odd electron in the benzene radical anion in an important way. The degenerate COT MOs in Figure 14(b) have equal coefficients at all the carbons, so that deuterium will not be able to affect which MO is occupied by the odd electron. This was the rationalization that Carrington and Longuet-Higgins used to explain the experimental observation that, unlike the case in benzene radical anion, the ESR spectrum of the COT radical anion is unaffected by deuterium substitution (*77*).

However there is a complication. Unlike the case in the benzene radical anion, in $COT^{\bullet -}$ the pair of vibrations that result in the first-order Jahn-Teller effect are not degenerate. One of them shortens half of the C-C bond lengths and lengthens the other half, and it is that vibration that selectively stabilizes one of the two degenerate MOs in Figure 14(b). The other Jahn-Teller active vibration in $COT^{\bullet -}$ affects the bond angles, increasing four of them and decreasing the other four. However, that vibration does not lift the degeneracy of the MOs in Figure 14(b). Instead, it mixes these MOs, to give two new MOs, each of which has coefficients at four of the carbons and nodes at the other four.

Shouldn't deuteration lift the degeneracy of those MOs, since one will have a node at the carbon to which the deuterium is attached and the other will not have a node at this carbon? The ESR spectrum of $COT^{\bullet -}$ indicates that the answer to this question must be no, but not why that is the answer. There are actually two reasons.

First, the Jahn-Teller distortion that lengthens and shortens alternate C-C bond lengths has a much larger effect on lowering the energy than the Jahn-Teller distortion that increases and decreases alternate C-C-C bond angles. In fact, *ab initio* calculations find that geometries with alternating bond angles are transition states connecting geometries with alternating bond lengths (*79*).

In other words, the circle in Figure 10 that represents the pathway for pseudorotation in a Jahn-Teller-distorted D_{6h} molecule, such as benzene radical anion, is actually an oval for the Jahn-Teller distortions in $COT^{\bullet -}$. The short axis of the oval corresponds to the two possible bond angle alternations in D_{8h} $COT^{\bullet -}$, and the long axis corresponds to the two possible bond length alternations. More importantly, the energy around the pseudorotation pathway is not constant in $COT^{\bullet -}$. The energy minima occur along the long axis of the oval, which corresponds to bond length alternation; and the maxima occur along the short axis, which correspond to bond angle alternation.

Should substitution of D for H have some effect on the relative energies of the two maxima along the pseudorotation pathway in $COT\text{-}d_1^{\bullet -}$? The reason that the answer to this question is no is that, unlike the degenerate benzene MOs in Figure 14(a), which are C-C antibonding, the degenerate COT MOs in Figure 14(b) are nonbonding. Therefore, although occupation of the degenerate, antibonding benzene MOs in Figure 14(a) lowers the frequency for out-of-plane bending vibrations of the hydrogens in benzene radical anion, occupation of the nonbonding COT MOs in Figure 14(b) (or a linear combination of them) has little effect on the frequencies for the out-of plane bending vibrations of the hydrogens in $COT^{\bullet -}$.

Use of Correlation Diagrams for Electrocyclic Reactions

In the biographical section of this chapter I have recounted Christopher's excitement at his discovery that correlation diagrams could be used to understand the preference for conrotation or disrotation in electrocyclic reactions. Christopher's approach involved classifying the MOs in the reactant and product of an electrocyclic ring opening reaction with respect to the C_2 axis of symmetry that is maintained in a conrotatory mode of ring opening, or the plane of symmetry that is maintained in a disrotatory mode. If the filled MOs of the reactant correlate with the filled MOs of the product, the reaction is allowed by orbital symmetry (*6*).

On the other hand, if a filled MO of the reactant correlates with an empty MO of the product and *vice versa*, the reaction is forbidden by orbital symmetry. Longuet-Higgins showed that the ground state of the reactant, nevertheless, correlates with the ground state of the product, because the doubly excited state of the reactant (which is orbitally correlated with the ground state of the product) and the ground state of the reactant have the same symmetry. Therefore, assuming the validity of the non-crossing rule along the reaction coordinate, the crossing of these two states is avoided. Nevertheless, the "intended" state crossing that is avoided creates a barrier on the ground state potential energy surface, but this barrier is absent when only filled MOs of the reactant and product correlate with each other (*6*).

An interesting observation about Christopher's paper (*6*) is that, although it was concerned with orbital symmetry, no pictures of MOs appeared in it. [This was also the case in Christopher's paper with Leslie Orgel on orbital interactions in transition-metal complexes of cyclobutadiene] (*46*). Instead, tables were provided to show which orbitals of the reactants and products are correlated.

In contrast, in the Communication that appeared in *JACS* immediately after Christopher's, in which Hoffmann and Woodward used correlation diagrams to analyze cycloaddition reactions (*7*), orbital pictures did appear; and they were featured prominently (colored blue and green, the former being Woodward's favorite color) in the Woodward-Hoffmann *magnum opus* on the "Conservation of Orbital Symmetry" (*80*).

What caused this difference between Longuet-Higgins on one hand and Woodward and Hoffmann on the other? I believe that it was a matter of cultures. Most physical chemists think in terms of mathematics, and Longuet-Higgins was certainly a physical chemist. In contrast, most organic chemists think in terms of pictures, and Woodward was certainly an organic chemist Although Roald Hoffmann was trained as a physical chemist, he has always thought like an organic chemist; and, throughout his career as an independent researcher, pictures have featured prominently in all his publications.

Paramagnetic Ring Currents

Following publication in 1965 of the paper by Longuet-Higgins and Abrahamson on electrocyclic reactions, Christopher authored or coauthored several more very interesting papers in chemistry. Two of them have already been discussed. One is the paper with Carrington on the difference between the effects of deuterium on the ESR spectra of the radial anions of benzene and COT (*77*). The other is the paper on the intersection of potential energy surfaces in polyatomic molecules (*54*), published in 1975, eight years after Christopher had left chemistry.

A third very interesting paper was published by Longuet-Higgins in 1968. It was coauthored by David Buckingham, who was Longuet-Higgins successor as Professor of Theoretical Chemistry at Cambridge. The paper was concerned with the quadrupole moments of dipolar molecules (*81*). It was the last paper that Longuet-Higgins published in *Molecular Physics*, the journal that he founded.

The final contribution of Longuet-Higgins to chemistry that will be discussed in this chapter was not actually a paper, but part of the proceedings of an international symposium on Aromaticity, held in Sheffield in July of 1966 (*82*). Longuet-Higgins contribution was short, only three pages; and it followed a 33 page paper by Franz Sondheimer, a synthetic organic chemist, who was also a Professor at Cambridge (*83*).

In his paper Sondheimer described his research group's syntheses of [4n]- and [4n+2]annulenes and the ^{1}H NMR spectra of these compounds. Most of the annulenes were large enough to have protons both inside and outside the annulene ring. As expected from previous work, in the [4n+2]annulenes the outer protons appeared at low field (high δ); whereas the inner protons appeared at very high field (low and even negative δ values). In contrast, in the [4n]annulenes the outer protons were found at significantly higher fields (lower δ) than in the [4n+2]annulenes, but the inner protons were found at very low fields (high δ values). It was this difference that Longuet-Higgins explained in his short presentation at the symposium in Sheffield (*82*).

Longuet-Higgins noted that, when a cyclically conjugated molecule is placed in a magnetic field, a diamagnetic ring current is induced by Larmor precession of the π electrons around the ring. The field due to this induced ring current opposes the applied magnetic field. It is this type of field that shields the inner protons and deshields the outer protons in [4n+2]annulenes.

In [4n]annulenes there is also an induced diamagnetic ring current, but it is opposed and overwhelmed by the induced paramagnetic ring current that comes from mixing of the ground state with an excited electronic state. The closer in energy that these two states are, the stronger their mixing, and the larger the induced paramagnetic ring current that results from it.

Longuet-Higgins pointed out that in [4n]annulenes there is a pair of nearly degenerate MOs, one of which is filled and the other empty. Consequently, [4n]annulenes should have low-lying, excited, electronic states. This situation contrasts, of course, with that in [4n+2]annulenes, which have closed-shells of π electrons and, except for [4n+2]annulenes with very large values of n, large HOMO-LUMO gaps.

Finally, Longuet-Higgins showed that the nearly degenerate HOMO and LUMO of a [4n]annulene can be mixed under the influence of an applied magnetic field. The mixing of the HOMO with the LUMO produces an induced paramagnetic ring current, which gives a magnetic field that adds to the applied field. It is this field in a [4n]annulene that deshields the inner protons and shields the outer protons (*84*).

Summary

Starting with his publication of the correct structure of diborane in 1943 (*9*) Christopher Longuet-Higgins' career as a theoretical chemist lasted only about a quarter of a century. His Ph.D. research at Oxford with Charles Coulson led to a deeper understanding of some aspects of Hückel theory (*13–17*). On his own, Longuet-Higgins showed how the NBMOs of odd AHs can be easily found and used to deduce many facts about conjugated organic molecules, (*19–21*), wholly within the context of Hückel theory (*22*), and often with less work than it takes to draw resonance structures (*86*).

Longuet-Higgins and Dewar were apparently the first to understand why it is necessary to include electron repulsion in order to account successfully for the UV-Vis spectra of conjugated molecules (*28*); and Christopher continued to work in this area of research in Cambridge, in collaborations with Murrell (*29*, *31*) and Pople (*30*).

During his career in chemistry, Longuet-Higgins also advanced the understanding of other types of spectroscopy. His ground breaking work on the symmetries of non-rigid molecules (*73*) led to insights into the rotational (*75*) and vibrational spectra (*76*) of such molecules. His collaboration with Alan Carrington contributed to ESR spectroscopy (*77*), and Longuet-Higgins provided the correct explanation for the anomalous chemical shifts of the protons inβ the ^{1}H NMR spectra of [4n]annulenes (*82*).

Longuet-Higgins predicted the existence and properties of a number of unusual and surprisingly stable molecules. These included $B_6H_6^{-2}$ (*35*) and $B_{12}H_{12}^{-2}$ (*36*). Both dianions were subsequently prepared (*37*, *42*), as were the isoelectronic carboranes (*38*, *43*, *44*), related to these two borane dianions.

In addition to contributing to inorganic chemistry through his predictions about the stability of $B_6H_6^{-2}$ and $B_{12}H_{12}^{-2}$, Longuet-Higgins also contributed to organometallic chemistry by predicting the existence of transition metal complexes of cyclobutadiene (*46*). Less well known is the fact that, as an undergraduate, Longuet-Higgins also made contributions to organic chemistry through his *experimental* studies of enolate halogenations (*11*, *12*)

Much better known to most organic chemists are Longuet-Higgins' theoretical contributions. His predictions, made with Lionel Salem -- that the bonds in [4n+2]annulenes should, for sufficiently large values of n, alternate in length (*66*), but that the bonds in polyacenes should not (*67*), -- have both stimulated a great deal of subsequent research. (*70–72*).

However, Christopher's most important contribution to organic chemistry was his demonstration that correlation diagrams can be used, in place of frontier orbital theory (*5*), in order to provide a more rigorous treatment of electrocyclic reactions (*6*). Correlation diagrams were then immediately applied by Hoffmann and Woodward to the analysis of cycloaddition reactions (*7*). Consequently, Christopher's introduction of correlation diagrams for the analysis of pericyclic reactions was a very important contribution to what became known as the conservation of orbital symmetry (*80*), for which Roald Hoffmann was awarded the Nobel Prize in Chemistry in 1981 (*87*).

Had Christopher Longuet-Higgins not left chemistry in 1967, what else might he have contributed to this discipline? We will, of course, never know. However, we do know that, for the quarter of a century that Christopher was actively doing research in theoretical chemistry, he made fundamental and important contributions to spectroscopy, inorganic, organic and organometallic chemistry; and he was arguably one of the most original and insightful theoretical chemists in the world. A book on *The Pioneers of Quantum Chemistry* would not be complete without a chapter on H. C. Longuet-Higgins.

References

1. Jordan, P. C. H.; Longuet-Higgins, H. C. *Mol. Phys.* **1962**, *2*, 121.
2. Gregory, R. L.; Murrell, J. N. *Biogr. Mem. Fellows R. Soc.* **2006**, *52*, 149.
3. For the benefit of American readers of this chapter, Leckhampton was not a prison, and Longuet-Higgins was not a “warden”. Had Leckhampton been an independent Cambridge College, rather than the graduate hostel of Corpus Christi College, Professor Longuet-Higgins might have been called the “Master” of Leckhampton College.
4. Anders, U. “Interview with Professor John Murrell,” http://www.quantum-chemistry-history.com.
5. Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395.
6. Longuet-Higgins, H. C.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1965**, *87*, 2045.
7. Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 2046.
8. This essay is apparently still preserved in the archives of Balliol College in Oxford.*(2)*
9. Longuet-Higgins, H. C.; Bell, R. P. *J. Chem. Soc.* **1943**, 250.
10. It is interesting that Christopher also published two *experimental* papers with Ronnie Bell, one on the halogenation of acetone in alkaline solutions *(11)* and the other on based-catalyzed bromination of diethyl malonate *(12)*. Under the experimental conditions used, base-catalyzed enolate formation was shown to be the rate determining step in both reactions.
11. Bell, R. P.; Longuet-Higgins, H. C. *J. Chem. Soc.* **1946**, 636.
12. Bell, R. P.; Everett, D. H.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1946**, *186*, 443.
13. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1947**, *191*, 39.
14. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1947**, *192*, 16.

15. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1948**, *193*, 447.
16. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1948**, *193*, 456.
17. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1948**, *195*, 188.
18. Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 193.
19. Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.
20. Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 275.
21. Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 283.
22. Dewar, M. J. S.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1952**, *214*, 482.
23. Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; pp. 191−247.
24. Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975.
25. Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341.
26. Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1951**, *205*, 247.
27. Cook, D.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1951**, *209*, 28.
28. Dewar, M. J. S.; Longuet-Higgins, H. C. *Proc. Phys. Soc. London, Sect A* **1954**, *67*, 795.
29. Murrell, J. N.; Longuet-Higgins, H. C. *Proc. Phys Soc. London, Sect. A* **1955**, *68*, 329.
30. Longuet-Higgins, H. C.; Pople, J. A. *Proc. Phys Soc. London, Sect. A* **1955**, *68*, 591.
31. Longuet-Higgins, H. C.; Murrell, J. N. *Proc. Phys Soc. London, Sect. A* **1955**, *68*, 601.
32. This was actually a five part series of papers on the "Electronic Spectra of Aromatic Molecules". However, Part II is a paper by John Pople, on which Longuet-Higgins' name does not appear.*(33)*
33. Pople, J. A. *Proc. Phys. Soc, London, Sect. A* **1955**, *68*, 81.
34. In addition to the Coulombic interaction between the transition dipoles, there is also a second type of term that can be interpreted as an exchange interaction between them. This term involves a charge distribution that is given by the product of the MOs from which the excitations occur (ψ_4 and ψ_5 in naphthalene) interacting electrostatically with a charge distribution that is given by the product of the MOs into which the excitations occur (ψ_6 and ψ_7 in naphthalene). To the extent that the two excitations are localized in different regions of space, the overlap between these pairs of MOs of the two chromophores will be small. Therefore, although the energy that is associated with the Coulombic interaction between the transition dipoles of chromophores that are localized in different regions of space may be large, the energy associated with the exchange interaction between the transition dipoles of such chromophores will be very small.

35. Longuet-Higgins, H. C.; Roberts, M. de V. *Proc. R. Soc. London, Ser. A* **1954**, *224*, 336.
36. Longuet-Higgins, H. C.; Roberts, M. de V. *Proc. R. Soc. London, Ser. A* **1955**, *230*, 110.
37. Boone, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5036.
38. Shapiro, I.; Keilin, B.; Williams, R. E.; Good, C. D. *J. Am. Chem. Soc.* **1963**, *85*, 3167.
39. At about the same time that Longuet-Higgins and Roberts worked out the electronic structure of B_6H_6 and $B_{12}H_{12}$, William N. Lipscomb, who would go on to win a Nobel Prize for his theoretical and experimental studies of the boron hydrides, also worked out the MOs for these two molecules *(40)*. Lipscomb and coworkers came to the same conclusion as Longuet-Higgins and Roberts about the electronic structure of B_6H_6. However, Lipscomb and coworkers were apparently unable to do the "moderately difficult" Hückel calculations that were necessary, in order to establish which MOs of $B_{12}H_{12}$ were filled; so they were unable to predict unequivocally whether neutral $B_{12}H_{12}$ would have an open or closed shell of electrons. About five years later Lipscomb assigned a graduate student, named Roald Hoffmann, the task of remedying this problem by writing an extended Hückel computer program [based, in part, on approximations that Longuet-Higgins and Roberts had used *(36)*], to carry out calculations on caged molecules, such as $B_{12}H_{12}$. The program that was developed *(41)* confirmed the results that Longuet-Higgins and Roberts had obtained on this molecule. The same computer program was subsequently used in the first collaboration between Woodward and Hoffmann on electrocyclic reactions *(5)*. Thus, it can be argued that there is at least a tenuous connection between the papers on $B_{12}H_{12}$, by Longuet-Higgins *(36)* and by Lipscomb *(40)* and the beginning of the collaboration, ten years later, between Woodward and Hoffmann *(5)*.
40. Eberhardt, W. H.; Crawford, B.; Lipscomb, W. N. *J. Chem. Phys.* **1954**, *22*, 989.
41. Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179.
42. Hawthorne, M. F.; Pitochelli, A. R. *J. Am. Chem. Soc.* **1960**, *82*, 3228.
43. Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1274.
44. Heying, T. L.; Ager, J. W., Jr.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szymanski *Inorg. Chem.* **1963**, *2*, 1089.
45. Review: Reid, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.
46. Longuet-Higgins, H. C.; Orgel, L. E. *J. Chem. Soc.* **1956**, 1969.
47. Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131.
48. Roland Pettit actually received two Ph.D. degrees, one from the University of Adelaide in Australia and the other from Queen Mary College in London, where his adviser was M. J. S. Dewar. There is a rather amusing account, written by Dewar, of Pettit's second Ph.D. oral exam, in which Dewar and H. C. Longuet-Higgins conspired to ask Pettit questions that he could not answer. Dewar admits that he and Longuet-Higgins could not have answered most of the questions they asked Pettit either. This story can be found at http://www.nap.edu/readingroom/books/biomems/rpettit.html.

49. Longuet-Higgins, H. C.; Opik, U.; Pryce, M. L.; Sack, R. A. *Proc. R. Soc. London, Ser. A* **1958**, *244*, 1.
50. Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A* **1937**, *161*, 220.
51. Berry, M. V. *Proc. R. Soc. London, Ser. A* **1984**, *392*, 45.
52. Herzberg, G.; Longuet-Higgins, H. C. *Discuss. Faraday Soc.* **1963**, *35*, 77.
53. Teller, E. *J. Phys. Chem.* **1937**, *41*, 109.
54. Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1975**, *344*, 147.
55. Pople, J. A.; Longuet-Higgins, H. C. *Mol. Phys.* **1958**, *1*, 372.
56. Renner, R. *Z. Phys.* **1934**, *92*, 172.
57. Dressler, K.; Ramsay, D. A. *Philos. Trans. R. Soc. London, Ser. A* **1959**, *251*, 533.
58. Pople, J. A.; Segal, J. A. *J. Chem. Phys.* **1966**, *44*, 3289.
59. See, for example, Bender, C. F.; Schaefer, H. F. III, *J. Chem. Phys.* **1971**, *53*, 4798.
60. Dixon, R. N. *Mol. Phys.* **1965**, *9*, 1965.
61. The reason that Pople and Longuet-Higgins were, nevertheless, able to fit the portion of the NH_2 spectrum, observed by Dressler and Ramsay *(57)*, is that, although the $^2A_1$ excited state of NH_2 is non-linear, the energy minimum for the bent radical is so shallow that the first excited vibration is higher in energy than the barrier to linearity *(60)*.
62. Walsh, A. D. *J. Chem. Soc.* **1953**, 2260.
63. Review: Shavitt, I. *Tetrahedron*, 1985, *41*, 1531.
64. Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 305.
65. Nevertheless, more than one computational chemist has opined that Christopher's disdain for "machine experiments" *(1)*, in general, and for the research of Frank Boys *(64)*, in particular, set back the development and use of *ab initio* calculations by many years. Although no one seems to question the quality of Christopher's contributions to theoretical chemistry, some computational chemists do question whether Christopher's effect on the field was, overall, beneficial.
66. Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1959**, *251*, 172.
67. Salem, L; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1960**, *255*, 435.
68. Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1960**, *257*, 445.
69. In an email message to me in January 2012, Lionel Salem wrote that Christopher once said to him, "Think of molecules as they are, not as you would like them to be." For example, one might wish that something as fundamental as the Hückel 4n+2 rule would be inviolate, but Longuet-Higgins and Salem showed that the validity of the 4n+2 rule also has limits.
70. Review: Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *Chem. Rev.* **2001**, *101*, 1501.
71. Annulene review: Spitler, E. L.; Johnson, C. A. II; Haley, M. M. *Chem. Rev.* **2006**, *106*, 5344.
72. Polyacene review: Bettinger, H. F. *Pure Appl. Chem.* **2010**, *82*, 905.

73. Longuet-Higgins, H. C. *Mol. Phys.* **1963**, *6*, 445.
74. This is also Christopher's most frequently cited paper. His next most cited papers are two of those on the intersections of potential energy surfaces *(49,54)*.
75. Wilson, E. B.; Lin, C. C.; Lide, D. R. *J. Chem. Phys.* **1955**, *23*, 136.
76. Bunker, P. R.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1964**, *280*, 340.
77. Carrington, A.; Longuet-Higgins, H. C.; Moss, R. E.; Todd, P. F. *Mol. Phys.* **1965**, *9*, 187.
78. Lawler, R. G.; Bolton, J. R.; Fraenkel, G. K.; Brown, T. H. *J. Am. Chem. Soc.* **1964**, *86*, 520.
79. Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.
80. Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
81. Buckingham, A. D.; Longuet-Higgins, C. H. *Mol. Phys.* **1968**, *14*, 63.
82. Longuet-Higgins, C. H. In *Aromaticity*, Special Publication No. 21; The Chemical Society: London, 1967; pp 109−111.
83. Sondheimer, F.; Calder, I. C.; Elix, J. A.; Gaoni, Y.; Garrat, P. J.; Grohmann, K.; di Maio, G.; Mayer, J., Sargent, M. V.; Wolovsky, R. In *Aromaticity*, Special Publication No. 21; The Chemical Society: London, 1967; pp 76−108.
84. In a footnote, Longuet-Higgins noted that the same explanation had been independently provided by Untch and Pople *(85)*.
85. Untch, K. G.; Pople, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 4811.
86. Although Michael Dewar certainly gave birth to PMO theory *(23-25)*, it can certainly be argued that Christopher was its father.
87. If Woodward had still been alive in 1981, there is no doubt that he would have added to his Nobel Prize for his contributions to organic synthesis, a second Nobel Prize for his co-discovery with Hoffmann of the importance of orbital symmetry in pericyclic reactions. Kenichi Fukui shared the 1981 Nobel Prize in Chemistry with Roald Hoffmann for Fukui's contributions to frontier molecular orbital theory, which Woodward and Hoffmann used in their first paper on orbital symmetry *(5)*. Had Christopher still been a chemist in 1981, one can certainly wonder whether he might have been considered more carefully for a share of the Nobel Prize with Hoffmann and Fukui, either for Christopher’s introduction of the use of correlation diagrams for the understanding of pericyclic reactions *(6)*, or for his many other contributions to theoretical chemistry.

Chapter 7

The Golden Years at LMSS and IBM San Jose

Paul S. Bagus*

Department of Chemistry, University of North Texas,
1155 Union Circle, #305070, Denton, Texas 76203-5017
***E-mail: bagus@unt.edu**

This chapter describes some of the research efforts in Quantum Chemistry at two centers: one was the the Laboratory of Molecular Structure and Spectra, LMSS, at the University of Chicago and the other was the Large Scale Scientific Computations Department at the IBM Research Laboratory in San Jose, California. The description of the work at IBM San Jose is focused on the ALCHEMY project, which was devoted to advances in Quantum Chemistry. The efforts at LMSS and IBM San Jose are closely related since there was a close association between these two centers and since several students from LMSS joined the group at IBM San Jose. These two centers made important contributions to the development of theoretical and computational chemistry. The topics that are reviewed have been selected because of their relevance for our present day activities in Quantum Chemistry. The research and computing environment at LMSS and IBM San Jose will be contrasted to the resources and environment that is available today.

Introduction

The decades of the 1950's, 1960's, and 1970's were exciting times for the fledgling discipline that we now know as Quantum Chemistry. It was a period when three key factors came together. First, the theoretical foundations for Quantum Chemistry were formalized. Second, the first programs were being written to perform calculations of the wavefunctions and properties of atoms and molecules. And third, the computers that could be used to carry out these calculations were becoming more powerful and more easily available to the

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

chemists and physicists who needed calculations for their research. One of the centers that made important contributions to the development of Quantum Chemistry was the Laboratory of Molecular Structure and Spectra, LMSS, within the Physics Department at the University of Chicago. LMSS was a large center for research in computational and theoretical chemistry directed by Professors R. S. Mulliken and C. C. J. Roothaan. At LMSS, there were visitors and post-docs from several foreign countries including England, Italy, Germany, and Japan, as well as from the U.S. There were also many graduate students; one of them was the author, who received his Ph.D. in 1966. Several of the LMSS students joined the IBM Research Division laboratory at San Jose California, the author among them, in a department directed by Dr. Enrico Clementi where much of the work that was initiated at LMSS was continued and enhanced.

This chapter will present selected reviews of major advances carried out at LMSS and IBM San Jose. An important criterion for the selection of the projects to be discussed is the relevance of these efforts to present day research efforts. In a real sense, there are things that we can learn today from the pioneers at LMSS and IBM San Jose about how we should use computational theory to understand scientific problems. Another way to describe this is that the pioneers can help us understand how to design the right computations to resolve important questions and the kind of answers that one should expect. Still another thing that can be learned is how to organize calculations to insure they give reliable answers and to understand how to evaluate the reliability of the computational and theoretical results. There is no question that today's computations are performed in a very different environment than they were in these early days. This chapter will also review the environment for computing then and contrast it to our present environment. Photographs of members of the staffs at LMSS and IBM San Jose will be included in this chapter to show the human side of the pioneers.

In the early days, it was not generally accepted that theory based on rigorous computational methods was, or would be, a viable approach to understanding the electronic properties of atoms and molecules. It was not clear that theoretical and computational chemistry could be used to understand and predict chemical properties or chemical processes. An important turning point in the realization of the role that Quantum Chemistry could play was the Conference on Molecular Quantum Mechanics held in Boulder in 1959 and known by the short name of the Boulder conference. The conference was sponsored by the U.S. National Science Foundation and the organizing committee included R. S. Mulliken, J. C. Slater, and J. O. Hirschfelder; all of whom are known today for their pioneering contributions. The committee was chaired by R. G. Parr, who is still active in Quantum Chemistry. The proceedings of the Boulder conference were edited by Parr and published in 1960 as an issue of the Reviews of Modern Physics (*1*). The proceedings contained 42 original research articles describing new methodology and presenting quantum chemical computations for atoms and molecules using what was then called *ab initio* theory. At this time, the phrase *ab initio* meant that the integrals over the operators in the Schrödinger equation were not approximated, as compared to semi-empirical theories where these integrals are approximated; see for example an early paper on benzene by Roothaan and Mulliken (*2*). Of the 42 technical papers in this issue, 11 of the contributions were from LMSS. These included Roothaan's first paper on rigorous Hartree-Fock theory for open shell systems (*3*), an early paper by Kolos and Roothaan on accurate solutions for the H_2 molecule (*4*), and a paper by Mulliken on using linear combinations of "Slater type orbitals", STO's, to describe molecular orbitals (*5*). These papers, especially Kolos' H_2 work, will be discussed more later in this chapter. These proceedings gave a path and a vision for a future where theory and computation would have a leading role in chemical research. They were read carefully, and in great detail by the graduate students at LMSS and helped shape our research paths. The picture in Figure 1 shows two graduate students at LMSS. The journal circled on the desk of the student on the right is his dog eared copy of the Reviews of Modern Physics proceedings issue. The picture was taken around 1960; the author is the student on the left and A. D. McLean is the student on the right.

Figure 1. Two LMSS graduate students, circa 1960. The student on the left is the author and on the right is Doug McLean. The photograph was taken in Ryerson Hall of the University of Chicago. (Courtesy of Hidemi Suzuki.)

Accurate Calculations For H_2

The first example of research at LMSS to be discussed is a series of papers by Kolos and his collaborators on the calculation of accurate potential energy curves for the ground and electronic excited states of H_2 (*4*, *6–10*). In the late 1950's and early 1960's, Wlodzimierz Kolos was a frequent visitor to LMSS from his permanent positions in Warsaw. Considering the strong mutual distrust at that time between the Soviet Union and its Eastern European satellites with the United

States and its allies in Western Europe, it is impressive that the governments of both Poland and the United States were willing to allow Kolos to make these repeated trips. It indicates that, in this period, science and individual scientists were able to help diffuse this distrust. The pioneering, very accurate work on H_2 was reported in a series of three papers in the Journal of Chemical Physics by Kolos and Wolniewicz (*6*, *7*, *9*). A measure of the impact of these three papers is that they have been cited over 1,300 times (*11*). The 1968 paper (*9*) reported a disagreement between the accurate theoretical value for the dissociation energy, D_0, of the H_2 ground state and experiment. The theoretical result was 3.8 cm^{-1} larger than experiment. Furthermore, non-adiabatic corrections to the Born-Openheimer potential curve that was used would actually increase the disagreement between theory and experiment. The disagreement meant that the calculated energy of H_2 is lower than the energy obtained from experiment while, from the variational principle, the calculated energy should be an upper bound to the exact energy. In a measured remark, Kolos and Wolniewicz stated (*9*) that "…… therefore the theoretical and experimental results are inconsistent." The inconsistency was resolved when Herzberg (*12*), in 1970, repeated his earlier measurements of the H_2 absorption spectra and from these new measurements concluded that the experimental dissociation energy had to be revised and increased by approximately 4.5 cm^{-1} from the previously accepted value. Herzberg wrote that: "In other words, there is essential agreement between theory and experiment ……" (*12*). Herzberg's new results brought experiment into agreement with the accurate theoretical calculations.

Important lessons to be learned from the work of Kolos and Wolniewicz are that: (1) The quantum theory embodied in the Schrödinger equation is correct to a very high level of precision for many electron systems. And, (2) that results obtained from this theory may be more accurate than experimental results. We should also bear in mind that these very accurate calculations were performed on the IBM 7094 computer available at the University of Chicago. Although, the 7094 was a powerful computer for the 1960's, the power of present day PC's and MAC's is orders of magnitude greater than that of the 7094.

There is, however, an even more important lesson for scientists on how to proceed when there is a disagreement between theory and experiment. When there are such disagreements, it is common for theorists to assume that the theoretical computations are in error and to shift or to scale computational results to bring them into agreement with experiment. As an example, consider the scaling factors provided for use with vibrational frequencies calculated with several different theoretical methods to bring the calculated frequencies closer to experiment (*13*). Kolos' work showed that one of the major advantages of using rigorous theory is that errors in experiment can be detected and corrected. Moreover, Kolos demonstrated how rigorous theory can be used to obtain internal validation of the theory by improving the level of the theory to higher accuracy to determine whether the disagreement persists. Kolos steadily increased the number of terms that were used in the expansion of the H_2 wavefunction until he could be confident that his results had converged to a desired accuracy and that it was the experiment which was in error.

The Dipole Moment of CO

An important use of theory is to obtain other molecular properties besides energy. These properties may give insight into the character of the chemical bonds and the chemical bonding. Thus, it was a surprise, and a disappointment, when early self-consistent field, SCF, and correlated configuration interaction, CI, calculations gave the wrong sign for the dipole moment, μ, of the CO molecule (*14*). The experimental μ(CO) is + 0.12 Debye at the equilibrium C-O bond distance (*15*), where the sign indicates a charge distribution that is C^+O^-. On the other hand, the theoretical results of Fraga and Ransil at LMSS, published in 1962 (*14*), gave $\mu(SCF)=-0.06$ D and a $\mu(CI)=-0.09$ D. Although these results were discouraging, they were obtained with a very small basis set to describe the molecular orbitals, MO's, of the CO molecule. It was hoped that, if larger basis sets would be used to describe the MO's, then Hartree-Fock, HF, and, if necessary, better CI wavefunctions, WF's, would give the correct sign for μ(CO). A part of this hope was proven correct. Starting in the late 1960's, more powerful computers became available to chemists and physicists and calculations of the CO WF were performed with larger basis sets for the MO's so that the wavefunctions were reasonably accurate (*16*, *17*). The HF value of the dipole moment (*16*), $\mu(HF)=-0.27$ D, was in even poorer agreement with experiment but the correlated CI WF's gave $\mu(CI)=+0.12$ D (*17*), in good agreement with experiment.

In the second half of the 60's, news reached LMSS of preliminary SCF and CI results for μ(CO) using extended basis sets for the MO's, where the correct sign of μ had been obtained with CI wavefunctions. Students and post-docs gathered in the LMSS conference area to discuss these exciting new results and because we were enthusiastic and excited, we were a bit boisterous. The conference area was just outside of Mulliken's office; he heard and was distracted by our celebration. Mulliken came out of his office to ask us what we were celebrating. We explained that the serious error of HF calculations, which gave the wrong sign for the dipole moment of CO, had been corrected by new calculations that took electron correlation effects into account. Mulliken disagreed with us and explained why the HF value of the dipole moment of CO was useful and gave chemical insight. He reminded us that $\mu(CO)=+0.12$ D is unusually small. For example, the dipole moment of H_2O is 1.85 D (*18*); i.e., almost an order of magnitude larger than μ(CO). Mulliken concluded that HF correctly showed that u(CO) is unusually small and furthermore, he pointed out to us that the difference between the experimental result of $\mu=+0$ and the HF result of $\mu=-0$ was not very important.

Mulliken gave us a very important lesson at this impromptu meeting. We should focus on the chemical information from calculations and not be distracted by "small" errors. The chemical information is that the dipole moment of CO is unusually small. Once this is recognized, the important question becomes why is $\mu(CO)\approx 0$ and the answer is immediately obvious. It comes from the fact that the charge densities in molecules are not spherical and μ is not a good guide to the atomic charges in a molecule and this departure from spherical behavior is particularly large in CO. The 5σ highest occupied MO, HOMO, of CO is a lone pair that is directed away from the C-O bond; see Refs. [(*19*) and (*20*)] for the properties of the 5σ MO. If one looks at the derivative of the dipole moment, $d\mu/dz$, a quantity directly related to the intensity of vibrational excitations (*21*), instead of the absolute value of the dipole moment, one gets a very different view. Both for HF WF's and for experimental measurements, $d\mu/dz \approx -1$, in units of electrons (*22*), and thus the atomic charges are roughly C^+ and O^-, exactly as expected. The absolute value of μ is almost zero at the equilibrium because the contributions to μ of opposite sign from the 5σ lone pair of the polarization of charge from C to O, primarily in the 1π MO, almost exactly cancel each other at this distance.

Population Analysis

The discussion of the dipole moment in the section above raises the question of how to determine the effective charges of atoms in molecules. The formation of polarized bonds, the transfer of charge between atoms, and the effective charges of atoms in molecules and in solids are important aspects of chemical bonding and are vital to our understanding of chemical interactions and chemical bonding. Thus, it is important to have methods for extracting information about effective charges and related quantities from rigorous wavefunctions. In a series of 4 papers published in the Journal of Chemical Physics in 1955, Mulliken proposed a population analysis, now called a Mulliken population analysis, MPA, as a way of assigning charges to atoms using quantities that are called Net, Overlap, and Gross atomic charges (*23–26*). These MPA charges are still widely used as a way to identify the character of chemical bonds. It is not uncommon that papers in the scientific literature will report populations, especially gross populations to a precision of 0.001 electrons; see, for example, Ref. (*27*). However, the values of the MPA populations may depend strongly on the choice of the basis set used to describe the MO's in the calculation of the WF's (*28*, *29*). Chang *et al.* (*29*) showed that with the large basis sets for the Ni and O atoms, that they used to obtain accurate WF's for bulk NiO, the charge on Ni was negative. A negative charge on Ni is in strong contrast to the Ni charge of +2 expected from crystal and ligand field theories for this ionic insulator (*30*); thus, the negative charge on Ni was attributed to artifacts of the MPA when large basis sets are used (*29*). At a meeting held in 1997 on Quantum Chemical methods and applications, see the proceedings in Ref. (*31*), there was an animated discussion about the accuracy of MPA's. Arguments were made that because the absolute value of a population might be uncertain, then the value of MPA's was very limited. Roothaan was present at this meeting and he made an important comment about how Mulliken had intended his MPA's to be used. Roothaan was in a position to know this since he worked, for many years, closely with Mulliken, first as a graduate student and then as a colleague in LMSS and on the faculty of the Physics Department at the University of Chicago. A close paraphrase of Roothaan's comment is: Robert (*32*) didn't believe populations had quantitative value. He meant them to be a guide to the chemistry and the bonding.

This is a very telling observation and it applies to the MPA (*23–26*) as well as to other methods of determining effective charges of atoms from WF's; see, for example, Refs. (*33–35*). The immediate lesson is that, in a molecule or a solid, electrons are shared between atoms and it is not meaningful to claim that electrons belong to atoms to a precision of 0.001 or even 0.01 electrons.

This is an essential feature of chemical bonding. Another important lesson is that one should consider different methods of estimating charges and to look for conclusions consistent with the atomic charges obtained with the different methods. Overlap populations, also introduced by Mulliken (*24*), are much less used than the single number for the effective charge of an atom obtained from the gross populations. However, overlap populations provide a way of estimating the possible uncertainty that should be associated with the effective charges. They also give information about the bonding character of an orbital; i.e., whether it is bonding, anti-bonding, weakly bonding, or non-bonding. Clementi, who, in the late 1950's and early 1960's, was a frequent visitor to LMSS from the IBM Research Laboratories in San Jose, made a detailed study of the electron distributions in several small molecules and used MPA overlap populations as well as gross atomic charges (*36*). This work combines gross and overlap populations to characterize the charge distributions and the chemical bonding from accurate HF WF's. Clementi's work on populations (*36*) is an example of how important it is to go beyond a single method for determining the effective charge on an atom. In more recent work by the author and his collaborators (*35, 37*), several different methods, including orbital projections and dipole moment curves, have been compared to characterize the charge distribution and bonding.

Atomic charges are important quantities for characterizing and understanding chemistry and chemical bonding. This is the reason that Mulliken developed and formulated the method of Mulliken Population analyses (*23–26*). However, he did not mean for people to report populations to a higher numerical precision than has chemical meaning. We need to view populations and atomic charges as qualitative properties, where we need to think about their meaning and to correlate this meaning with other quantities and properties. This is how Mulliken would have told us to proceed.

An Early Study of a Chemical Reaction

In one of the first rigorous, non-empirical studies, perhaps even the first such study, of a chemical reaction, Clementi (*38*) published, in 1967, WF's and a potential energy surface for the reaction of NH_3 + HCl to form NH_4Cl. The abstract of this paper begins: "*Ab Initio* computations are presented for the reaction $NH_3+HCl \rightarrow NH_4Cl$. The two reactants are studied at a large number of positions and for each point an SCF LCAO MO wavefunction and the corresponding total energy are obtained. These results are in an energy surface diagram. All the electrons of the system are considered ……". Since a considerable portion of the work was carried out while Clementi was a visitor at LMSS, the paper lists his affiliations at both LMSS and IBM. This work is another of the early successes of Quantum Chemistry. It is an early proof that the expectations and the vision formulated at the 1950 Boulder conference were indeed coming about. The work of Kolos and Wolniewicz, discussed above in the section on "Accurate Calculations for H_2', showed that rigorous theory could prove that an accepted value obtained from experiment was wrong and could lead experimentalists to reconsider and repeat their measurements. The work of

Clementi showed us that a chemical reaction could be carried out on a computer. This was heady stuff. It allowed Clementi to attract several of the LMSS students to take positions at IBM.

The Environment and Infrastructure at LMSS

The way in which we work today and our overall environment have changed dramatically from the conditions we worked under in the 1950's and 1960's. The picture in Figure 2 shows Mulliken, on the left, Roothaan, on the right, and, between them, a Research Associate, B. J. Ransil, whose work on the dipole moment of CO was described above. They are in the LMSS discussion area, which was also used to store journals, reports, and computer output. Our present day offices are air-conditioned; in those days, fans, see the upper left hand corner of the picture, provided cooling in the summer. We now work in smoke free buildings; Mulliken is smoking a cigarette; he regularly smoked Chesterfields. We now have powerful desktop and laptop PC's with high-speed connections to the internet and to high performance workstations and supercomputers; we are accustomed to using interactive editors to store and display our results. In those days, we looked at paper to examine our results. We also made extensive use of electric desk calculators to do elementary arithmetic calculations.

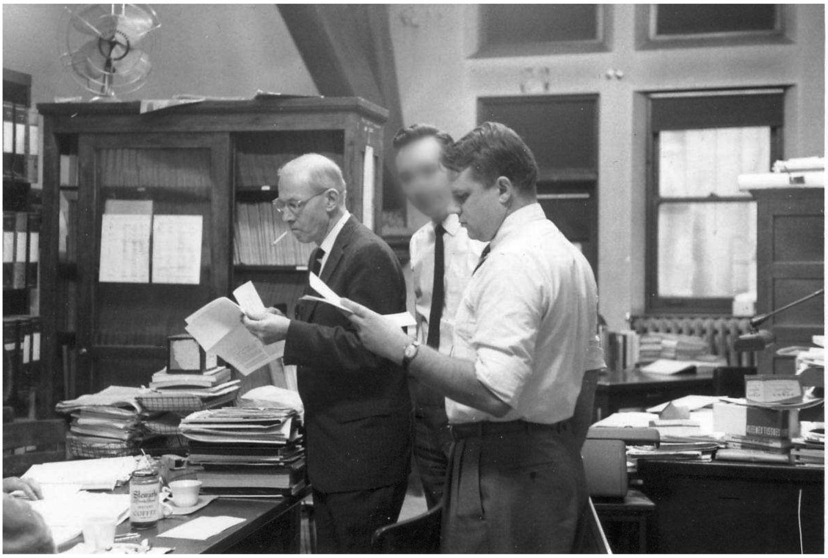


Figure 2. Mulliken, B. J. Ransil, an LMSS Research Associate, and Roothaan meeting in the LMSS discussion area. Note the journals and technical material in the bookcases. (Courtesy of Hidemi Suzuki.)

Figure 3. (a) A general view of an IBM 704 computer of the type at Argonne National Laboratory used by members of LMSS. At the center of the figure is the operators console, to the left is a card reader used to input programs and data; just to the right of the card reader is an impact printer. At the far left is a portion of the CPU where some of the vacuum tube logical units are shown. (b) A close-up of the CPU showing, on the right, in more detail the vacuum tube logical units. (Courtesy of IBM Archives.)

The mechanics of computing and the computers available for calculation in these early days are a contrast to our present day computing. In those days, for efficient calculations, one had to be physically present at the center where the computer was located. Before about 1960, LMSS used computers at the Wright-Patterson Air Force base in Dayton, Ohio, which was about 300 miles from Chicago. The computers at Wright-Patterson were a Remington Rand 1103 and the improved 1103A. The LMSS post-docs and graduate students normally flew to Dayton and spent a week or so doing calculations before returning to the University of Chicago. Remote computing, if one had to use it, was accomplished using mail. The program and the input for a calculation were mailed to the computer center staff who would have your job run on the computer and who would then return the input and the printed output listing by mail. This sort of turnaround is hardly suitable for debugging a new program. Another difficulty for writing and debugging code was that the input to the Remington Rand computers was on paper tape and not even on punched cards, which were used with IBM computers. We did not use a compiler or an assembler; instead we wrote out the program instructions in octal, a base eight number system, and typed them onto the paper tape. In the early 1960's, I was able to get permission to use the IBM 704 computer at Argonne National Laboratory. This was a dramatic improvement for me since Argonne is less than 30 miles from the University and the drive to Argonne took less than an hour. One did have to be careful driving since the route that we took in those days took us through the town of Justice, which we felt was a speed trap. The IBM 704 was a fairly powerful computer for its time. A picture of one of the 4000 logic units that made up what we now call the Central Processing Unit, CPU, is shown in Figure 3; the 704 used vacuum tubes rather than transistors. One of the things that the IBM customer engineer who maintained the 704 had to do was to check that the vacuum tubes were working correctly. A standard problem was that the filaments would burn out. They were checked with what looked to be a dentist's mirror that was moved along the rack of tubes shown in Figure 3 to see whether the filaments were glowing.

An important aspect of debugging a new computer program is to check the results of a sample calculation. This is done today by checking the calculation against the results obtained with other programs or by designing test problems with additional output obtained either by using interactive debuggers or by adding print statements to the program. It was more difficult to use these methods in the early days since fewer programs were available for comparing results, changing codes to add extra statements was not routine, interactive debuggers were not available, and travel to remote computer sites was required. LMSS had a technician, Tracy Kinyon, whose official title was Mathematics Assistant. His tasks involved doing arithmetic calculations on an electric calculator, see Figure 4 where the calculator used, probably a Marchand, is circled in the lower left hand of the picture. Before computers became available, Kinyon's responsibility was to carry out the calculations for the work reported in papers. In the footnote to one of his paper (*39*), Mulliken described his assistance as "indispensable". Once computers were used, Kinyon's main responsibility became checking the results of the computer calculations to see that they were correct. A significant difficulty for these hand calculations was the evaluation of elementary functions such as logarithms, exponentials and trigonometric functions that were required for the calculation of 4 index, 2 electron, Coulomb and exchange integrals over the basis functions used to describe the MO's (*40–43*). While today, middle range hand calculators can calculate these elementary functions, this was not the case, especially in the 1950's and the early 1960's, when even the calculation of a square root was not routine.

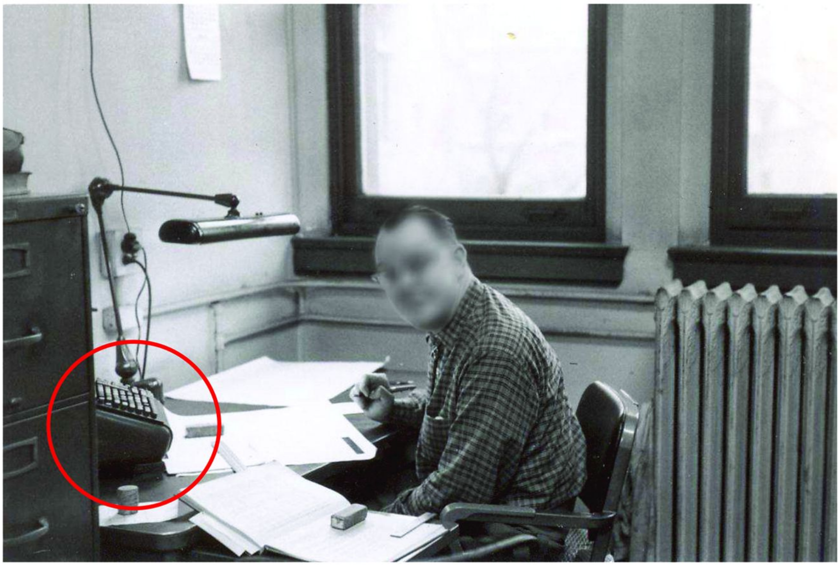
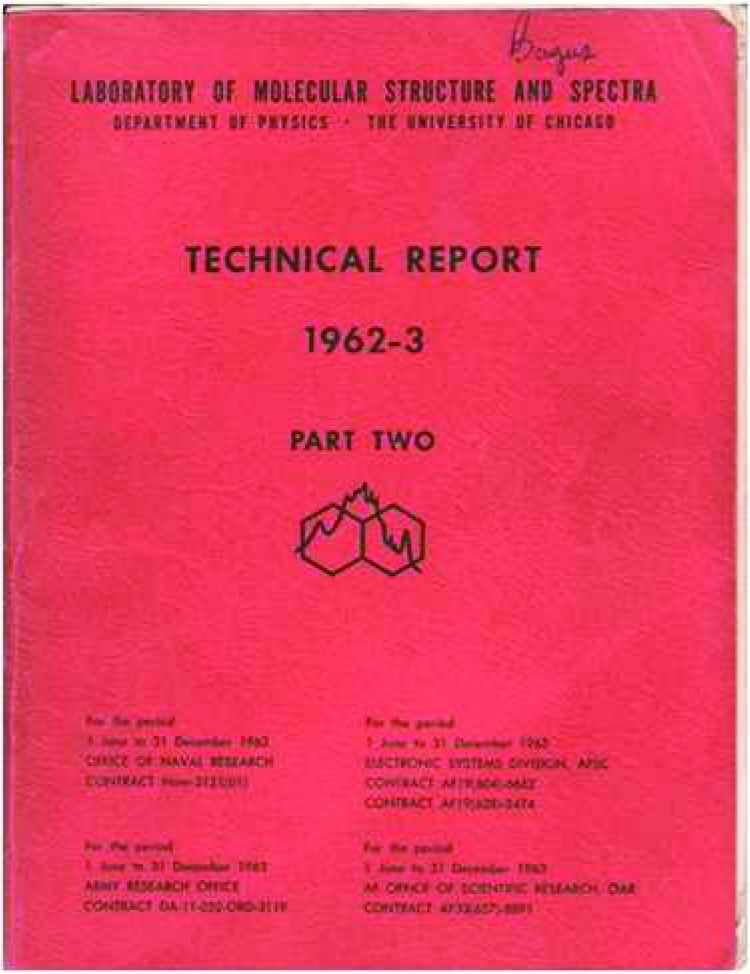


Figure 4. A Mathematical Assistant at LMSS, using an electric calculator to check results obtained with computer programs. (Courtesy of Hidemi Suzuki.)

In the early 1960's major steps were taken to provide an enhanced computational environment. An IBM 7090 computer, which was the top of the line of computers available at this time and which used transistor technology, was installed at the University of Chicago. Roothaan was the first director of the computer center and his goal was to allow users at the University, including users from LMSS, maximum access and good support for technical questions. Prof. Sigrid Peyerimhoff, now emeritus at the University of Bonn, was a post-doc at LMSS in 1963. Of her time at LMSS, she wrote (*44*); "In Chicago, I realized for the first time how important it was to have access to a reasonably sized computer (IBM 7090) on campus, even if runs could be performed only during the night." Clearly, Roothaan succeeded in making the 7090 available for scientific use. His efforts were the first step toward the 24/7 access to computation that we have today. With the fast turnaround that we now have, it is possible for scientists to literally interact with their calculations and to modify theoretical models and methods based on results of the current calculation; this type of responsiveness is something that we only dreamed of in the early days.



Boggs

LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA
DEPARTMENT OF PHYSICS · THE UNIVERSITY OF CHICAGO

TECHNICAL REPORT

1962-3

PART TWO

Figure 5. The cover of Part Two of the LMSS Technical Report for the period 1962-1963.

One other feature of the environment at LMSS that merits attention is the LMSS Technical Reports that were bound and printed with red covers; an example is shown in Figure 5. These reports were prepared as descriptions of the work at LMSS supported by U.S. Funding agencies. The LMSS technical reports were widely distributed. They were read and retained because the reports contained detailed information, important for specialists, which were not included in published papers. The reports also contained copies of the journal articles that were published by members of LMSS. Thus, the LMSS advances were all conveniently documented in the technical reports. The importance of these technical reports is in strong contrast to the progress reports that are submitted today to satisfy requirements of grants but have little scientific impact. There are two other mechanisms currently used that provide some of the role of the LMSS Technical Reports. The first is supplemental material now accepted by some journals so that specialized material, of interest only to a fraction of the readers is available for present and future readers of a paper. The other mechanism is that Ph.D. theses are available on-line at the web sites of certain research groups.

In the discussions in this section about the environment for research and computing at LMSS, the differences between the way that Quantum Chemical research was carried out 50 years ago and the way that it is carried out today have been stressed. It is fitting to close this section with a demonstration that there is one thing that has not changed; this is the dedication that scientists and their students bring to their work. Figure 6 shows Mulliken in his office working late at his desk, which is crowded with papers, books, and notes. The horizontal silver bar in the center foreground of the picture is the top of the chair that could be used by visitors to Prof. Mulliken. The picture was taken around 1960, six years before Mulliken received the Nobel Prize in Chemistry. He continued his work schedule even after he received the prize.

Figure 6. Mulliken working in his office at LMSS. (Courtesy of Hidemi Suzuki.)

Quantum Chemistry at IBM San Jose

There was close contact between Enrico Clementi, who was permanently at the IBM San Jose Research Laboratory, and LMSS. Clementi had, and still has, a vision to unify theoretical methods used to study different time and size scales in order to obtain a complete determination of the properties of materials and of chemical processes. In order to reach this vision, Clementi created the Large Scale Scientific Computations, LSSC, Department within the IBM Research Laboratory at San Jose. The LSSC was home to people working on a broad range of subjects including: Quantum Chemistry, Thermodynamics, Statistical Mechanics, Solid State Physics, and Hydrodynamics. Clementi's dream and vision for the multi-scale use and application of theory is still being pursued at the present time. The Material and Process Simulation Center (*45*) at the California Institute of Technology, directed by W. A. Goddard, is an excellent example. The Center for Advanced Scientific Computing and Modeling (*46*), CASCaM, at the University of North Texas, that combines theoretical efforts in the Chemistry and the Materials Science and Engineering Departments, is also rapidly developing capabilities for multi-scale modeling. The focus of the descriptions of LSSC will be on only one of the many areas of research, the ALCHEMY project within LSSC, which was primarily concerned with Quantum Chemistry and which carried out pioneering efforts in what can properly be regarded as modern Quantum Chemistry. Clementi attracted several students from LMSS to form the heart of the Quantum Chemistry efforts; the author was one of these students..

From my point of view, working at IBM was a golden opportunity. I had access to outstanding computational facilities that were great improvements over those that I had been able to use previously. Furthermore, the computer resources were regularly upgraded as IBM improved its mainframe computers. I was free to pursue research with only limited administrative duties and without the need to write grant proposals. I also felt that the starting salary I received in 1968, about $15,000, was excellent. Furthermore, and perhaps most important of all, there was a great team of people to work with, many from LMSS. Because of these advantages, being at IBM Research was in many ways preferable to being at a University. We pursued only academic scientific research and we did not have responsibility for the development of commercial products. In our later years at IBM, I, and other members of the ALCHEMY project, did become involved in activities of potential commercial value to IBM. However during our time in LSSC, we did not have such responsibilities.

The LMSS "veterans" who joined IBM San Jose are shown in Figure 7, a photograph taken in about 1970. They are, from left to right, A. D. McLean, Megumu Yoshimine, Bowen Liu, Bill Lester, and the author. Bill Lester began his LMSS association as a high school senior when he was hired as a clerk typist. After being admitted to the University of Chicago, he majored in Chemistry and continued working at LMSS. He gained much of his enthusiasm for Quantum Chemistry at LMSS, before he went on to receive his Ph.D. at the Catholic University in Washington. On this basis, he can properly be counted as an LMSS veteran. Figure 8 shows Clementi, who brought us together and who is still active in Quantum Chemistry, in a picture taken in 2010 at the 50th Sanibel meeting, an annual meeting on Quantum Theory that was first held in 1961.

Figure 7. LMSS "veterans", from left to right Doug McLean, Megumu Yoshimine, Bowen Liu, Bill Lester and the author, taken circa 1970. (Courtesy of Hidemi Suzuki.)

Figure 8. Enrico Clementi, who created and headed the LSSC Department at IBM San Jose; taken at the 50th Sanibel meeting in 2010.

In the sections below, two aspects of the contributions from the LSSC Alchemy project will be discussed. The first concerns the linear molecule project for the calculation of accurate molecular wavefunctions using Slater Type Orbitals, STO's, for the expansion of the MO's. The second topic concerns the general purpose program system, ALCHEMY, developed at IBM and which contained features for the calculation of accurate HF and correlated wavefunctions and their properties.

The Linear Molecule Project at IBM San Jose

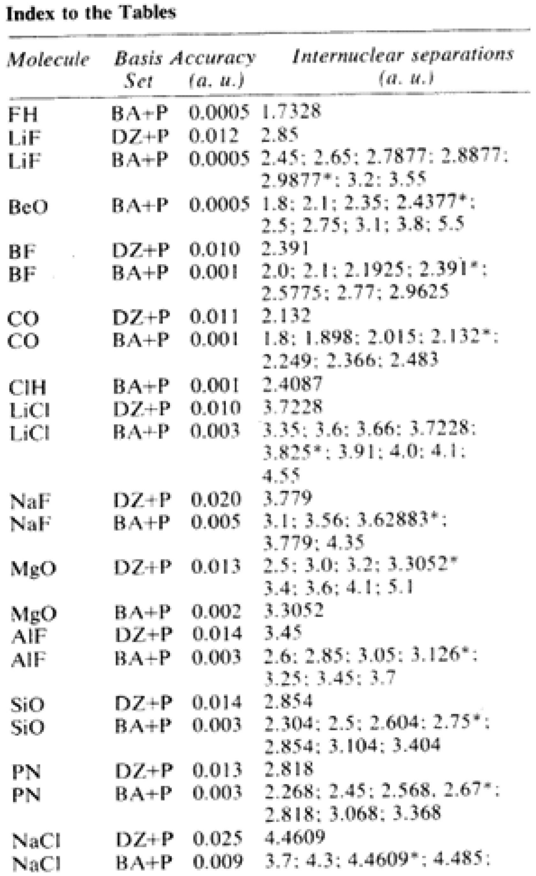
Integrals Over Basis Functions

It is a standard mathematical technique for solving partial differential equations to convert them to matrix equations, which can be solved, or diagonalized, with relative computational ease. Applications of the conversion of the coupled Hartree-Fock differential equations to matrix equations can be found in the papers of Roothaan (*3*, *47*, *48*). In order to make this conversion, it is necessary to expand the MO's, φ_i in terms of basis functions, χ_j with

$$\varphi_i = \Sigma_j C_{i,j}\chi_j.$$

It is natural to use for the χ's, the so-called Slater Type Orbitals (*5*, *49*), STO's, where the radial portion of the function is $R(r) \infty r^{n-1}\exp(-\zeta r)$, normally expanded about one or another of the atomic centers in the molecule. The advantages of STO's include that they have, for suitable choices of ζ, the correct asymptotic behavior for the MO's at small and large r. This led Mulliken (*5*) to write that efforts should be "...... devoted mainly to approximating SCF AO's and MO's as linear combinations of ...... STO's ......". Thus, there was a large effort at LMSS devoted to the calculation of accurate Coulomb and exchange electron repulsion integrals for molecules (*40–43*). The difficulty is that the calculation of these integrals is numerically very intensive. This led Clementi and Davis (*50*) and many others, see references cited in Ref. (*51*), to use Gaussian Type Orbitals, GTO's, where the radial part of the basis function is $R(r) \infty r^{nl}\exp(-\alpha r^2)$. While GTO's cannot give the correct asymptotic forms of the MO's, the immense reduction of computer time lead to their general use for calculations of molecular electronic structure from the late 1960's to the present. However, McLean and Yoshimine at IBM San Jose extended the work that they had begun while students at LMSS and prepared a general program for the calculation of integrals over STO's for linear molecules. This program was used for a major study of potential curves and surfaces for linear molecules, to be discussed in the following sub-section.

Despite the wide use of GTO's as basis functions, there remained a certain level of interest in and calculations with STO's from the 1960's to the present time. The use of STO's for the study of the photoionization of diatomic molecules at Orsay was reviewed in a paper by Lefebvre-Brion and Raşeev (*52*) published in 2003. The authors wrote: "To represent a Rydberg orbital, the diffuse atomic Slater orbitals are particularly well adapted ......" and "Many authors are now returning to the use of Slater basis sets ......". In large part, the resurgence of interest in the use of STO's has come about because the present computing power makes possible the calculation of the integrals over STO's in a time reasonable enough to allow calculations on large systems. One measure of the renewed interest in STO's is the workshop in Canakkale, Turkey, September, 2012, on "Molecular Electronic Structure at Troy" (*53*). One of the main topics at this workshop will be "molecular integration over exponentially decaying orbitals and the supporting mathematics"; in other words, the calculation of integrals over STO's. Furthermore, it is intended to establish a software repository for the programs that perform these calculations. In a very real sense, this effort is a natural extension of the computational efforts pioneered at LMSS and then continued at IBM San Jose. The planned repository reflects the effort that will be required for the development of programs for the calculation of integrals over STO's. It is almost certain that Mulliken and Roothaan would give strong recommendations that this effort should be supported.



Index to the Tables

Molecule	*Basis Set*	*Accuracy (a. u.)*	*Internuclear separations (a. u.)*
FH	BA+P	0.0005	1.7328
LiF	DZ+P	0.012	2.85
LiF	BA+P	0.0005	2.45: 2.65: 2.7877: 2.8877: 2.9877*: 3.2: 3.55
BeO	BA+P	0.0005	1.8; 2.1; 2.35; 2.4377*: 2.5; 2.75; 3.1; 3.8; 5.5
BF	DZ+P	0.010	2.391
BF	BA+P	0.001	2.0; 2.1; 2.1925; 2.391*: 2.5775; 2.77; 2.9625
CO	DZ+P	0.011	2.132
CO	BA+P	0.001	1.8; 1.898; 2.015: 2.132*: 2.249; 2.366: 2.483
ClH	BA+P	0.001	2.4087
LiCl	DZ+P	0.010	3.7228
LiCl	BA+P	0.003	3.35; 3.6: 3.66: 3.7228: 3.825*: 3.91; 4.0: 4.1: 4.55
NaF	DZ+P	0.020	3.779
NaF	BA+P	0.005	3.1: 3.56: 3.62883*: 3.779; 4.35
MgO	DZ+P	0.013	2.5: 3.0: 3.2; 3.3052* 3.4: 3.6; 4.1; 5.1
MgO	BA+P	0.002	3.3052
AlF	DZ+P	0.014	3.45
AlF	BA+P	0.003	2.6: 2.85: 3.05: 3.126*: 3.25: 3.45: 3.7
SiO	DZ+P	0.014	2.854
SiO	BA+P	0.003	2.304; 2.5; 2.604: 2.75*: 2.854; 3.104; 3.404
PN	DZ+P	0.013	2.818
PN	BA+P	0.003	2.268: 2.45: 2.568. 2.67*: 2.818; 3.068; 3.368
NaCl	DZ+P	0.025	4.4609
NaCl	BA+P	0.009	3.7: 4.3: 4.4609*; 4.485:

Figure 9. A portion of the index to the table of Linear Molecule wavefunctions published in 1967 as a supplement to the IBM Journal of Research and Development.

Linear Molecule Project

Using their programs for the calculation of integrals over STO's, McLean and Yoshimine computed accurate HF potential curves and surfaces for the ground states of 35 closed shell linear molecules: 20 diatomic molecules, 9 triatomic molecules, and 6 molecules with 4 or 5 atoms. The results of these calculations were published in 1967 and 1968 (*54–56*), where Ref. (*55*) contains the total and orbital energies as well as the basis sets and the MO expansions for each molecule and each geometry. These calculations were carried out with a level of care and concern for accuracy that set the stage for later work as illustrated in Figure 9, which is a portion of the index to the tables of the calculations in Ref. (*55*).

The table, Figure 9, lists the quality of the basis sets used as either DZ+P or BA+P, where DZ indicates a double-zeta basis set, BA indicates "best atom" basis set, and P indicates that polarization functions have been added to the DZ and BA basis sets that were optimized for the atoms. Then estimates of the accuracy of the calculations, defined as the difference between the calculated total energy and the "Hartree-Fock limit", are made. This accuracy is now the described as the difference with respect to the complete basis set, CBS, limit; see, for example, the discussion in Ref. (*57*) and references therein. Now, with much greater computing power, it is standard to determine the CBS limits by extrapolation from calculations with increasingly larger basis sets (*57*, *58*). In their work, McLean and Yoshimine (*55*) had to depend on making estimates based on a careful analysis of the atomic and molecular calculations. However, they showed that one needed to estimate errors in work aimed at accurate calculations. Finally, under the heading "Internuclear separations", the table shows the portions of the potential surfaces calculated. While the work of McLean and Yoshimine was limited to linear molecules, it was perfect for people interested in the spectroscopy of diatomic molecules (*52*).

The ALCHEMY Program System

The programs and methods originally developed at LMSS for the calculation of molecular wavefunctions were extended at IBM San Jose into the ALCHEMY program system, an integrated package for the calculation of molecular wavefunctions and properties. The original version of ALCHEMY was developed by Bagus, Liu, McLean, and Yoshimine in the early 1970's and it contained several important features that were novel for the time, with some still being novel today, 40 years later. A later version, ALCHEMY II, which was developed in the 1990's, included new features and other contributors (*59*); here the focus will be on the original package.

The integrated ALCHEMY suite of programs included features for the calculation of SCF-HF and CI WF's and for the calculation of properties of these WF's. It was possible to use STO basis sets, for linear molecules only, and GTO basis sets for molecules of all geometries. The program for integrals over GTO basis functions was adapted from a program written by J. Almlof (*60*); it was added to ALCHEMY in the mid-1970's when Almlof was a visitor at IBM San Jose. The SCF WF's could be calculated for configurations with several open shells and it was possible to calculate SCF MO's variationally optimized for a particular multiplet or for an average of configurations. The CI wavefunctions were determined for a basis of configuration state functions (*59*, *61*), CSF's, rather than determinants. The CSF's are combinations of determinants that have the desired spatial and spin symmetries. The use of CSF's leads to a modest reduction in the size of the CI expansion and allows the use of symmetry in the calculation of excited states and in the interpretation of the CI WF. The calculation of the matrix elements between CSF's was achieved by the calculation of a formula file for the matrix elements in terms of interaction integrals over the molecular orbitals. Novel and very efficient sorting algorithms were developed by Yoshimine (*62*, *63*) to transform the integrals over the basis functions into integrals over the MO's and to merge the transformed integrals and the matrix element formulas to determine the CI H-matrix. The CSF's could be chosen with a very flexible selection of active orbital and configurational spaces with a flexibility comparable to the General Active Space, GAS, algorithms in use today (*64*). For the analysis of the CI WF's, a natural orbital analysis was possible (*65*). The calculation of one-electron transition matrix elements between different states represented with relatively long CI expansions, as is required for the determination of the intensities of emission and adsorption of light with dipole matrix elements, was also available. The important feature of these transition moments was that different sets of orbitals could be used for the initial and final states of the transition. While the orbitals were orthogonal within an individual set, the sets were not mutually orthogonal. The expression for the calculation of the many-electron matrix elements in terms of the one-electron matrix elements and the orbital overlap matrix elements was given by Lowdin (*65*). The difficulty is that these expressions are relatively complex. The matrix elements can be determined either by a cofactor analysis (*66*) or by the use of a corresponding orbital transformation (*67*, *68*). Yoshimine implemented a program based on cofactors that can compute a transition matrix element between WF's described by relatively large CI expansions. This capability is quite important and is not, to the author's knowledge, generally available. The ALCHEMY program was widely, and freely, distributed and the ALCHEMY II version developed in the 1990's is available through MOTECC (*59*).

Concluding Remarks

LMSS is no longer a part of the Physics Department at the University of Chicago. In the second half of the 1970's, the LSSC department at IBM was disbanded and the ALCHEMY project members continued their research in other groups. Work on the ALCHEMY program system continued into the 1990's but is no longer being pursued. However, these two institutions made fundamental and important contributions to theoretical and computational chemistry. They also provided guidance and lessons about directions of research in Quantum Chemistry that are relevant for people who are active in this field today.

In a sense, the wide distribution of program systems to calculate electronic structure can be viewed as the realization of the dreams and visions of the people at LMSS and IBM San Jose. Today scientists are able to use Quantum Chemistry programs as a part of their research and many do use computation in this way. However, we must understand that computation, as with any of the other tools used in scientific research, is not turnkey. We must understand the physical and mathematical approximations that are used in the calculations in order to understand the meaning of the results.

The author would like to express his gratitude to Clemens Roothaan, his PhD thesis advisor, to Robert Mulliken, and to Enrico Clementi for different but very important lessons that he learned from them. He learned from Clemens Roothaan the mathematical and programming skills that have served him well since his days as a graduate student at the University of Chicago. He learned from Robert Mulliken how to think about and how to understand the results of Quantum Chemical calculations. He learned from Enrico Clementi how to combine these two talents into research programs directed toward using theory to understand the physical and chemical significance of measurements of different chemical properties. He would also like to thank the many experimentalists that he has collaborated with over the years who have helped and guided his efforts to find answers for the right questions. In particular, he would like to acknowledge his long term and on-going collaboration with Hajo Freund, director of the Chemical Physics department at the Fritz-Haber Institute in Berlin.

The photographs of Figures 1, 2, 4, and 6 were taken, circa 1960, by Megumu Yoshimine, then a graduate student at LMSS, and provided to the author by Ms. Hidemi Suzuki, Megumu's niece. The photograph in Figure 7 was given to the author by Megumu Yoshimine and the photograph in Figure 8 was taken by the author. Figure 9 was copied from Ref. (*55*).

References

1. *Rev. Mod. Phys.* **1960**, *32*.
2. Roothaan, C. C. J.; Mulliken, R. S. Molecular Orbital Treatment of the Ultraviolet Spectra of Benzene and Borazole. *J. Chem. Phys.* **1948**, *16*, 118.
3. Roothaan, C. C. J. Self-Consistent Field Theory for Open Shells of Electronic Systems. *Rev. Mod. Phys.* **1960**, *32*, 179.
4. Kolos, W.; Roothaan, C. C. J. Accurate Electronic Wave Functions for the H_{2} Molecule. *Rev. Mod. Phys.* **1960**, *32*, 219.
5. Mulliken, R. S. Self-Consistent Field Atomic and Molecular Orbitals and Their Approximations as Linear Combinations of Slater-Type Orbitals. *Rev. Mod. Phys.* **1960**, *32*, 232.
6. Kolos, W.; Wolniewicz, L. Accurate Adiabatic Treatment of the Ground State of the Hydrogen Molecule. *J. Chem. Phys.* **1964**, *41*, 3663.
7. Kolos, W.; Wolniewicz, L. Potential-Energy Curves for the X $^1\Sigma_g^+$, b $^3\Sigma_u^+$, and C $^1\Pi_u$ States of the Hydrogen Molecule. *J. Chem. Phys.* **1965**, *43*, 2429.

8. Kolos, W.; Wolniewicz, L. Vibrational and Rotational Energies for the B $^1\Sigma_u^+$, and C $^1\Pi_u$, and a $^3\Sigma_g^+$ States of the Hydrogen Molecule. *J. Chem. Phys.* **1968**, *48*, 3672.
9. Kolos, W.; Wolniewicz, L. Improved Theoretical Ground-State Energy of the Hydrogen Molecule. *J. Chem. Phys.* **1968**, *49*, 404.
10. Kolos, W.; Wolniewicz, L. Lower Bound for the Dissociation Energy of the Hydrogen Molecule. *J. Chem. Phys.* **1969**, *51*, 1417.
11. See the AIP site for the *Journal of Chemical Physics*. http://jcp.aip.org.
12. Herzberg, G. The dissociation energy of the hydrogen molecule. *J. Mol. Spectrosc.* **1970**, *33*, 147.
13. Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency Scale Factors. *J. Phys. Chem. A* **2007**, *111*, 11683.
14. Fraga, S.; Ransil, B. J. Studies in Molecular Structure. VII. Limited Configuration Interaction for Selected First-Row Diatomics. *J. Chem. Phys.* **1962**, *36*, 1127.
15. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand: Reinhold: New York, 1979.
16. Grimaldi, F.; Lecourt, A.; Moser, C. The calculation of the electric dipole moment of CO. *Int. J. Quantum Chem.* **1967**, *1*, 153.
17. Green, S. Electric Dipole Moment of Diatomic Molecules by Configuration Interaction. I. Closed-Shell Molecules. *J. Chem. Phys.* **1971**, *54*, 827.
18. Clough, S. A.; Beers, Y.; Klein, G. P.; Rothman, L. S. Dipole moment of water from Stark measurements of H_2O, HDO, and D_2O. *J. Chem. Phys.* **1973**, *59*, 2254.
19. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1973.
20. Bagus, P. S.; Hermann, K.; Bauschlicher, C. W., Jr. A new analysis of charge transfer and polarization for ligand-metal bonding: model studies of Al_4CO and Al_4NH_3. *J. Chem. Phys.* **1984**, *80*, 4378.
21. Ibach, H.; Mills, D. L. *Electron energy Loss Spectroscopy and Surface Vibrations*; Academic: New York, 1982.
22. Hermann, K.; Bagus, P. S.; Bauschlicher, C. W., Jr. Enhancement of dynamical dipole moment in adsorbed molecules: theoretical studies for CO/Cu(100). *Phys. Rev. B* **1984**, *30*, 7313.
23. Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. *J. Chem. Phys.* **1955**, *23*, 1833.
24. Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. II. Overlap Populations, Bond Orders, and Covalent Bond Energies. *J. Chem. Phys.* **1955**, *23*, 1841.
25. Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. III. Effects of Hybridization on Overlap and Gross AO Populations. *J. Chem. Phys.* **1955**, *23*, 2338.
26. Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. IV. Bonding and Antibonding in LCAO and Valence-Bond Theories. *J. Chem. Phys.* **1955**, *23*, 2343.

27. Lu, Q. L.; Jalbout, A. F.; Luo, Q. Q.; Wan, J. G.; Wang, G. H. Theoretical study of hydrogenated Mg, Ca@Al$_{12}$ clusters. *J. Chem. Phys.* **2008**, *128*, 224707.
28. Bauschlicher, C. W., Jr.; Bagus, P. S. The metal-carbonyl bond in Ni(CO)$_4$ and Fe(CO)$_5$: a clear-cut analysis. *J. Chem. Phys.* **1985**, *81*, 5889.
29. Chang, H.; Harrison, J. F.; Kaplan, T. A.; Mahanti, S. D. Cluster study of the neutron-scattering form factor for antiferromagnetic KNiF3 and NiO. *Phys. Rev. B* **1994**, *49*, 15753.
30. Griffith, J. S. *The Theory of Transition-Metal Ions*; Cambridge Press: Cambridge, 1971.
31. *THEOCHEM* **1999**, *458*.
32. Roothaan was the only person at LMSS who called Mulliken by his first name. Although, it was common for us to address each other by our first names, an exception was for Mulliken because we held him in very high regard.
33. Davidson, E. R. Electronic Population Analysis of Molecular Wavefunctions. *J. Chem. Phys.* **1967**, *46*, 3320.
34. Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural population analysis@f^{a}@f$^{)}$. *J. Chem. Phys.* **1985**, *83*, 735.
35. Nelin, C. J.; Bagus, P. S.; Philpott, M. R. The nature of the bonding of CN to metals and organic molecules. *J. Chem. Phys.* **1987**, *87*, 2170.
36. Clementi, E.; Clementi, H. Electron Distributions in Small Molecules. *J. Chem. Phys.* **1962**, *36*, 2824.
37. Bagus, P. S.; Clotet, A.; Curulla, D.; Illas, F.; Ricart, J. M. Charge displacement analysis: A new general method to estimate atomic charges in molecules and clusters. *J. Mol. Catal. A* **1997**, *119*, 3.
38. Clementi, E. Study of the Electronic Structure of Molecules. II. Wavefunctions for the NH$_3$+HCl --> NH$_4$Cl Reaction. *J. Chem. Phys.* **1967**, *46*, 3851.
39. Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. Formulas and Numerical Tables for Overlap Integrals. *J. Chem. Phys.* **1949**, *17*, 1248.
40. Roothaan, C. C. J. A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. I. *J. Chem. Phys.* **1951**, *19*, 1445.
41. Rudenberg, K. A Study of Two-Center Integrals Useful in Calculations on Molecular Structure. II. The Two-Center Exchange Integrals. *J. Chem. Phys.* **1951**, *19*, 1459.
42. Ruedenberg, K.; Roothaan, C. C. J.; Jaunzemis, W. Study of Two-Center Integrals Useful in Calculations on Molecular Structure. III. A Unified Treatment of the Hybrid, Coulomb, and One-Electron Integrals. *J. Chem. Phys.* **1956**, *24*, 201.
43. Roothaan, C. C. J. Study of Two-Center Integrals Useful in Calculations on Molecular Structure. IV. The Auxiliary Functions $C_{\alpha\beta}^{\gamma\delta\varepsilon}(\rho_a,\rho_b)$ for $\alpha \geq 0$. *J. Chem. Phys.* **1956**, *24*, 947.
44. Peyerimhoff, S. D. The Development of Computational Chemistry in Germany. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2002; Vol. 18, p 257.
45. Materials and Process Simulation Center. http://www.wag.caltech.edu/.

46. Center for Advanced Scientific Computing and Modeling. http://cascam.unt.edu/.
47. Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.
48. Roothaan, C. C. J.; Bagus, P. S., Atomic Self-Consistent Field Calculations by the Expansion Method. In *Methods in Computational Physics*; Alder, B., Fernbach, S., Rotenberg, M., Eds.; Academic Press: New York, 1963; Vol. 2, p 47.
49. Slater, J. C. *Phys. Rev.* **1930**, *36*, 57.
50. Clementi, E.; Davis, D. R. Electronic structure of large molecular systems. *J. Comput. Phys.* **1966**, *1*, 223.
51. Guseinov, I. I.; Mamedov, B. A. Evaluation of incomplete gamma functions using downward recursion and analytical relations. *J. Math. Chem.* **2004**, *36*, 341.
52. Lefebvre-Brion, H.; Raseev, G. Ab initio calculations of the photoionization of diatomic molecules. *Mol. Phys.* **2003**, *101*, 151.
53. Canakkale Workshop. http://sites.google.com/site/troymolelecstruct/home
54. Yoshimine, M.; McLean, A. D. Ground states of linear molecules: Dissociation energies and dipole moments in the hartree–fock approximation. *Int. J. Quantum Chem.* **1967**, *1*, 313.
55. McLean, A. D.; Yoshimine, M. Tables of Linear Molecules Wave Functions. *IBM J. Res. Develop.* **1967**, *12* (Supplement).
56. McLean, A. D.; Yoshimine, M. Computation of molecular properties and structure. *IBM J. Res. Develop.* **1968**, *12*, 206.
57. Van Mourik, T.; Wilson, A. K.; Peterson, K. A.; Woon, D. E.; Dunning, T. H. The Effect of Basis Set Superposition Error (BSSE) on the Convergence of Molecular Properties Calculated with the Correlation Consistent Basis Sets. *Adv. Quantum Chem.* **1999**, *31*, 105.
58. Feller, D. Application of systematic sequences of wave functions to the water dimer. *J. Chem. Phys.* **1992**, *96*, 6104.
59. McLean, A. D.; Yoshimine, M.; Lengsfield, B. H.; Bagus, P. S.; Liu, B. ALCHEMY II: A Research Tool for Molecular Electronic Structure and Interactions. In *Modern Techniques in Computational Chemistry: MOTECC-90*; Clementi, E., Ed.; ESCOM: London, 1990.
60. Almlof, J. *MOLECULE - A Program System for the Non-empirical Calculation of the Electronic Structure of Molecules II. Integral Section*; USIP Report 74 - 29; Institue of Theoretical Physics, University of Stockholm: Stockholm, 1974.
61. Bagus, P. S.; Liu, B.; McLean, A. D.; Yoshimine, M. Application of Wave Mechanics to the Electronic Structure of Molecules through Configuration Interaction. In *Wave Mechanics: The first 50 Years*; Price, W. C., Chissick, S. S., Ravensdale, T., Eds.; Butterworth & Co: London, 1973; p 99.
62. Yoshimine, M. IBM Research Report RJ555: 1969.
63. Yoshimine, M. Construction of the hamiltonian matrix in large configuration interaction calculations. *J. Comput. Phys.* **1973**, *11*, 449.
64. Knecht, S.; Jensen, H. J. A.; Fleig, T. Large-scale parallel configuration interaction. I. Nonrelativistic and scalar-relativistic general active space

implementation with application to $(Rb\text{--}Ba)^+$. *J. Chem. Phys.* **2008**, *128*, 014108.

65. Löwdin, P. O. Quantum Theory of Many-Particle Systems. I. Physical Interpertations by Means of Density Matrices, Natural Spin-Orbitals, and Convergence Problems in the Method of Configurational Interaction. *Phys. Rev.* **1955**, *97*, 1474.
66. Prosser, F.; Hagstrom, S. Corresponding Orbitals and Cofactors. *J. Chem. Phys.* **1968**, *48*, 4807.
67. King, H. F.; Stanton, R. E.; Kim, H.; Wyatt, R. E.; Parr, R. G. Corresponding Orbitals and the Nonorthogonality Problem in Molecular Quantum Mechanics. *J. Chem. Phys.* **1967**, *47*, 1936.
68. King, H. F.; Stanton, R. E. Reply to Comments by Prosser and Hagstrom Concerning Corresponding Orbitals and Cofactors. *J. Chem. Phys.* **1968**, *48*, 4808.

Chapter 8

Quantum Chemistry Program Exchange, Facilitator of Theoretical and Computational Chemistry in Pre-Internet History

Donald B. Boyd*

Department of Chemistry and Chemical Biology, School of Science,
Indiana University – Purdue University Indianapolis (IUPUI),
402 North Blackford Street, Indianapolis, Indiana 46202-3274
***E-mail: dboyd@iupui.edu**

The Quantum Chemistry Program Exchange (QCPE) was a service conceived in 1962 and that started operating in 1963. Its purpose was to provide an inexpensive mechanism for theoretical chemists and other scientists to exchange software. Most of the computer programs were distributed as source code, so scientists, if they wanted to, could learn from or improve upon the inner workings of the algorithms. QCPE reached its zenith in the 1980s when computational chemistry was growing rapidly and becoming widely recognized by the scientific community. The service was convenient and much used by experts, students, and experimentalists who wanted to perform research calculations in the study of molecules. QCPE also played an educational role by conducting workshops and providing on-call help to countless beginners. QCPE was based at Indiana University in Bloomington, Indiana, and serviced a worldwide clientele. Introduction of the Internet in the 1990s diminished the role of QCPE.

Introduction

As the name implies, the Quantum Chemistry Program Exchange (QCPE) started with the purpose of being a distribution hub for software tools used by quantum chemists. QCPE was a great boon to theoretical and other chemists as the field of computational chemistry developed in the 1970s and 1980s. QCPE

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

started operations in 1963 and served a vital function during its lifetime. Most of the leading names in theoretical chemistry – and later computational chemistry – joined QCPE because it provided a service in high demand. Unlike most commercial software companies, QCPE expedited science by distributing source code at nominal cost and providing free guidance to users. But by the first decade of the 21st century, the service had done its duty and most of its functions had ceased or were winding down. Most of the individuals involved with QCPE's creation and operation are unfortunately getting to the point where the patina of maturity is turning to the rust of old age. This situation increases the urgency of writing this chapter now.

Much of the original documentation related to QCPE has been digitized or discarded or is in private collections. This historical account is based partly on personal recollections (however faulty they may be) and partly on records and old QCPE publications. These resources have been substantially supplemented with recent e-mail correspondence and interviews with some of the key players. In one or two cases, different people had differing recollections, so the author tried to steer toward a middle ground of what may have happened. The author has tried to be as accurate as possible, given the circumstances. This is a story that has an abundance of heroes and no "bad guys". The author also presents previously unpublished photographs of historical interest. QCPE is a case that illustrates that if individuals with initiative set out to perform a needed function, there are many rewards.

The author published a *Reader's Digest*-version of the history of QCPE in 2000 (*1*). The important role of QCPE was also discussed in a 2007 book (*2*).

A Stellar Idea

The older readers of this chapter will remember QCPE and may have used its services, but some of our younger readers may never have heard of this service. So our narrative begins at the beginning. QCPE was founded at the inspiration of Professor Harrison G. ("Harry") Shull, a quantum theoretician and research professor at Indiana University, Bloomington (IUB) in the years1955-1979 (Figure 1). He had obtained his baccalaureate degree from Princeton in 1943 and earned his doctorate in physical chemistry at the University of California, Berkeley in 1948. Shull has been described as the sort of person from whom ideas bubbled forth. He was good at team building. He had a knack for inspiring people around him to gladly work on his ideas. Shull did not mind letting his associates get credit for the achievements they accomplished.

Shull chaired a Gordon Conference on Theoretical Chemistry in the summer of 1962. This gathering was attended by two future winners of the Nobel Prize in Chemistry: Robert Sanderson Mulliken (University of Chicago), who won in 1966, and John Anthony Pople (National Physical Laboratory, Teddington, England), who won in 1998. As expected, most of the theoreticians at the conference were from academia, but even back in 1962, a few of them were from industry. American companies, even back in the 1960s, recognized the value of theoretically and computationally trained chemists (*3*).

Figure 1. Professor Harrison G. Shull in the late 1950s or early 1960s. The photograph is courtesy of Judi Roberts and Roger Beckman of the Indiana University staff.

Shull's vision was to have a central, international, sharable repository of software available to quantum chemists. At the conference, Professor Stanley A. Hagstrom (Figure 2) chaired a session on software sharing. Hagstrom was an IUB assistant professor of chemistry who had obtained two bachelor degrees from the University of Omaha and in 1957 a Ph.D. degree in theoretical chemistry under Shull at what is now called Iowa State University. Already, Professor Clemens C. J. Roothaan at the University of Chicago had set up a registry and exchange for two-electron integrals. So, there was precedence for avoiding tedious duplication of effort. Many theoreticians could see the advantage of exchanging computer programs. It was inefficient for graduate students at one university to have to write a program to do the same quantum mechanical calculations that had already been programmed elsewhere. It made sense to have these widely needed programs available in order to avoid "reinvention of the wheel", as it were. A second motivation for setting up a library of shared software was to create a more or less permanent repository. So, if a graduate student finished a thesis and left a university, or if a professor changed research interests, the fruits of their labors - in terms of software written - would not be lost or lie unused on some dusty shelf or in a forgotten cabinet.

Figure 2. Professor Stanley A. Hagstrom in the late 1950s or early 1960s. The photograph is courtesy of Judi Roberts and Roger Beckman of the Indiana University staff.

A third motivation for a central repository was to create an intermediary between the code writers/owners and users. Quantum chemistry professors whose students had created useful programs could directly share copies with other research groups. However, the users in the other groups might not understand all the requirements of operation or the limitations for getting useful results. The new program might be minimally or unclearly documented. Hence these users would frequently be asking the developers for help. For widely used programs, such requests could consume time and distract the original developers from other work. So, someone at a central depository could field at least some of these routine questions from the users, thereby freeing the developers from being badgered for technical support.

There was a fourth motivation. Depositing programs with QCPE could be regarded as a form of "publishing" the code. Recall that back in the 1960s, there were few or no means of publishing codes in the vetted scientific literature. In this regard, academic traditionalists were just beginning to think about the fact that creating a significant computer code was, in effect, a form of intellectual writing.

At the Gordon Conference, there was sufficient interest in having a central repository for exchanging programs, so when Shull returned to Bloomington, Indiana, he recruited his postdoctoral associate from England, Dr. Keith M. Howell (Figure 3), to set up the exchange. Howell had graduated from Bristol University (England) in 1952 and crossed the Atlantic to work with Hagstrom at

IUB in 1956, first on a card-programmed calculator and then on an IBM 650 with magnetic drum storage. After gaining his Ph.D. at Southampton University in 1960, he worked in industry before sailing back to the United States in October 1962 with his bride. Shull gave Howell *carte blanche* to set up QCPE.

The initial effort was partially supported by the Air Force Office of Aerospace Research (ARAC) and Indiana University. Howell developed the initial mechanics for submitting, testing, and distributing software in collaboration with Hagstrom and Dr. Franklin (Frank) Prosser, another member of Shull's group. Prosser had obtained two degrees at Georgia Institute of Technology and then a Ph.D. at The Pennsylvania State University. The fact that Hagstrom and Prosser had part-time appointments in the IUB Computing Center greatly facilitated this activity.

QCPE's first newsletter in April 1963 contained an editorial by Shull. His objective was to make it as easy as possible for donors to send their programs to QCPE and for users to obtain copies of the programs. The success of the endeavor would "depend in good part on the willingness of others to contribute, to help, and above all, to be reasonable, good-natured, and understanding". The first newsletter offered 23 pieces of software ready for distribution. Most of the programs were written by Prosser and a couple of the programs were written by Hagstrom. These QCPE initial offerings were routines for matrix diagonalization, matrix multiplication, and determination of integrals over elliptical orbitals. The programs were written in FORTRAN Assembly Program (FAP) and FORTRAN II. The QCPE newsletters were edited by Howell for the next two years. A group in Germany volunteered to assist Howell with distribution of QCPE material in Europe.

Figure 3. Dr. Keith M. Howell at IUB when he was in charge of QCPE 1963-1965. The photograph is courtesy of Dr. Howell.

When Howell and his wife returned to England in 1965, Shull asked Prosser to assume responsibility for running QCPE. QCPE's initial membership of 55 individuals had grown to 425 representing 179 research groups. The QCPE library had grown from 23 to 71 programs. Five hundred copies of the programs had been distributed. QCPE was off to a good start. Dr. Roald Hoffmann (a future Nobel Prize winner in 1981) deposited his extended Hückel theory (EHT) program (QCPE 30) in July 1966. The most frequently requested programs were for running EHT molecular orbital (MO) calculations and for calculating two-electron integrals as needed for what we now call ab initio calculations. Back in the 1960s, these latter calculations were commonly called self-consistent field (SCF) calculations, or sometimes non-empirical calculations. The integrals were also needed for configuration interaction (CI) calculations.

The author of this historical piece became involved with QCPE when he was a graduate student at Harvard University with Professor William N. Lipscomb (a Nobel Prize winner in chemistry in 1976 and nicknamed "The Colonel" because of his Kentucky upbringing). One of the nice features of the QCPE newsletters was that members could make brief announcements about what each group was working on. Lipscomb, who was an early subscriber to QCPE, assigned me the task to write a report on his group in 1966 (*4*).

Putting Programs in the Hands of Users

QCPE thus served as a conduit through which individual researchers could donate their programs. The programs were checked by the QCPE staff or volunteers to make sure that the software compiled, performed as claimed, and contained at least a minimal amount of documentation in the form of "comment cards" in the program itself or in a written description. Then the availability of the programs was announced through QCPE's newsletters and catalog. The software was sent to subscribers who paid the modest distribution and handling costs. A distinctive service that QCPE provided was to ship not only the source code and documentation, but also a sample input data set and a printout of the corresponding output. Thus, the user could verify that the program yielded numerical results on the user's computer that were identical to the expected results.

One of the main reasons for the popularity of QCPE, besides the low costs to subscribers, was that most of the programs distributed were in the form of source code. Theoreticians liked to publish elegant equations, the more elegant and simple looking, the better. But sometimes it is not obvious or unambiguous how a piece of theory should be implemented. Source code lets others see exactly how a concept was accomplished as an algorithm. By obtaining source code, other researchers could easily extend, improve, cannibalize, or otherwise modify a piece of software. Subroutines could be borrowed for use in other programs.

In the 1960s, the software was distributed on computer cards or magnetic tape. Computer ("IBM") cards were heavy and expensive to ship by mail. Machines for reading those cards and magnetic tapes have almost entirely disappeared today, thus rendering the original media of the software totally obsolete. Generally the programs were written in whatever was the current version of FORTRAN, and they ran on mainframe computers, such as the behemoths of International Business Machines (IBM) and Control Data Corporation (CDC). A few of the programs ran on the machines of other manufacturers such as Burroughs, Honeywell, Univac, Floating Points Systems (FPS), and a sprinkling of smaller companies that have long since disappeared from the scene.

The quarterly QCPE Newsletters contained announcements of new programs, upcoming meetings, new books, bug fixes, results of surveys taken of QCPE members, and other news. The newsletters contained progress reports from individual theoretical chemistry research groups around the world. These reports increased awareness of what each group was currently working on. Such reports could help avoid duplication of effort and may also have spurred competitive races.

In the 1960s, QCPE regularly published a list of its members. The list kept growing in length until finally it became too long to include in the newsletters. By February 1970, membership was around 1200. We do not have room for a full list obviously, but some of the names besides Mulliken, Pople, Lipscomb, Hoffmann, and the IU people include Leland Allen, Gordon Amidon, Richard Bader, Paul Bagus, Carl Ballhausen, Stephen Berry, David Beveridge, David Bishop, John Bloor, George Blyholder, James Boggs, Ronald Breslow, Paul Cade, Jean-Louis Calais, Vernon Cheney, Donald Chesnut, Ralph Christoffersen, Alice Chung, Jon Clardy, Enrico Clementi, Charles Coulson, Durward Cruickshank, Imre Csizmadia, Louis Cusachs, Ernest Davidson, Janet Del Bene, Raymond Dessy, Delos DeTar, Russell Drago, Thomas Dunning, Frank Ellison, Inga Fischer-Hjalmars, Marshall Fixman, Arthur Frost, Kenichi Fukui (who was co-recipient with Hoffmann of the Nobel Prize in Chemistry in 1981), Benjamin Gimarc, William Goddard, Jerry Goodisman, Mark Gordon, Gary Grunewald, Peter Gund, Lowell Hall, Hendrik Hameka, James Harrison, Hermann Hartmann, Edgar Heilbronner, Robert Hermann, William Herndon, Ian Hillier, Alan Hinchliffe, Joseph Hirschfelder, Sigeru Huzinaga, Hans Jaffe, Karl Jug, Martin Karplus, Joyce Kaufman, William Kern, Lemont Kier, Harry King, Morris Krauss, Werner Kutzelnigg, William Laidlaw, Jean-Marie Lehn, Arthur Lesk, William Lester, Joel Liebman, John Light, J. W. Linnett, Lawrence Lohr, Per-Olov Löwdin, John Lowe, Peter Lykos, Gerald Maggiora, John McKelvey, Roy McWeeny, William Meath, Richard Messmer, Harvey Michels, Frank Momany, Keiji Morokuma, Jules Moskowitz, Robert Nesbet, Yngve Ohrn, W. J. Orville-Thomas, Neil Ostlund, Robert Parr, Ruben Pauncz, Lee Pedersen, Frank Pilar, Russell Pitzer, Peter Politzer, Heinzwerner Preuss, Bernard Pullman, Pekka Pyykko, Herschel Rabitz, Milan Randic, Bernard Ransil, Mark Ratner, Robert Rein, Graham Richards, Björn Roos, Klaus Ruedenberg, John Sabin, Dennis Salahub, Lionel Salem, Lawrence Schaad, Fritz Schaefer, Harold Scheraga, Don Secrest, Gerald Segal, Harris Silverstone, Massimo Simonetta, William Simpson, Lawrence Snyder, Richard Stevens, Andrew Streitwieser, Thomas Strom, Brian Sutcliffe, Ignacio Tinoco, Carl Trindle, Donald Truhlar, John Van Wazer, Alain Veillard, Arnold Wahl, Anthony Whitehead, Kenneth Wiberg, Bright Wilson, Megumu Yoshimine, Richard Zare, Daniel Zeroka, and Howard Zimmerman.

In 1967 Prosser and Hagstrom both left for temporary assignments in the Theoretical Physics Group at the Lockheed Research Laboratory in Palo Alto, California. Richard W. Counts (Figure 4), with a physics background and a Master's degree, was hired from the National Aeronautics and Space Administration (NASA) office at IUB to run QCPE. Counts' title was Project Supervisor. Under his leadership, QCPE continued growing and provided exemplary service to the community of theoretical chemists with an ever-expanding library of programs. Some of the deposited programs ran without problem, but others were written specifically for one machine or one operating system. Hagstrom and other colleagues at IUB provided assistance to QCPE by getting such programs operational on other machines.

Figure 4. Mr. Richard W. Counts at a computer terminal in the QCPE office, probably in the late 1970s or early 1980s. The photograph is courtesy of Judi Roberts and Roger Beckman of the Indiana University staff.

When Air Force support of QCPE ceased due to the Mansfield Amendment of 1969, QCPE was able to obtain a grant from the National Science Foundation (NSF) in 1971. The grant carried the operation along until QPCE became self-supporting in 1973. A modest annual membership fee was charged to members. Users purchasing software at QCPE's low distribution fee was another source of revenue.

There is not enough space here to list all the programs in the library, but one of the more popular ones *circa* 1970 was the semi-empirical CNDO/INDO program (QCPE 141) from Paul Dobosh in Pople's group at Carnegie-Mellon University. Professor N. L. Allinger (University of Georgia) deposited his MMI/MMPI molecular mechanics program (QCPE 318) in November 1976. Pople's group released their ab initio MO program called Gaussian 70 through QCPE in

November 1973. Gaussian 76 (QCPE 368) was available from QCPE in 1978. Human nature being what it is, it was not uncommon for research groups to release an older version after they had developed a newer version for themselves. (When Professor Pople decided to form Gaussian, Inc. in 1987 to sell the newest, best version of the program his group had produced, he withdrew the QCPE versions. QCPE regarded ownership of its programs as residing with the original donors, so withdrawal was allowed.)

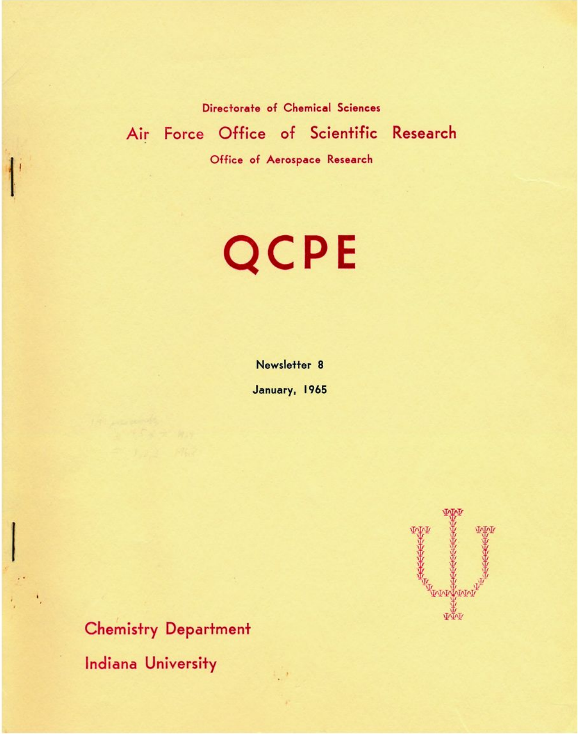
As business at QCPE increased, Counts hired temporary graduate student assistants, work-study students, and part-timers to assist him. Such a beneficent policy created jobs and helped students who needed to work their way through college. In 1973, he hired Margaret (Peggy) Edwards (Figure 5) initially on a part-time basis while she worked toward a Ph.D. in English at IUB and later full-time. She grew up in Indianapolis and had gone to Butler University. She taught English at the college level in Wyoming, Vermont, and Montana and had worked at Eli Lilly & Company in Indianapolis in a department that handled communications to physicians and pharmacists. By working in Bloomington, she could help her elderly mother in Indianapolis.

Figure 5. Margaret (Peggy) Edwards at the QCPE workshop in Oxford, England in 1986. Her parents were originally from the United Kingdom, so it was an extra great pleasure to be there. Dr. Edwards supplied the photograph.

A standardized format for citing QCPE software was published in the QCPE Newletter in February 1978, and indeed QCPE programs were becoming more and more cited in the scientific literature. (We return to this subject later.)

In 1979, up to ten individuals at one institution could be members at QCPE for only $100 per year. This was very reasonable considering access to the growing library of programs and information being published in the quarterlies.

In 1979, Hagstrom had a temporary appointment as software manager at the National Resource for Computational Chemistry (NRCC) at the Lawrence Berkeley National Laboratory in Berkeley, California. NRCC had started operating in 1977. Hagstrom heard talk at NRCC that it might be advantageous for NRCC to "take over" QCPE as a way to gain greater "exposure" for the government-funded center. Since Counts did not have the academic credentials to oppose such a move, Hagstrom advised Counts that he might want to create an advisory board that could speak on QCPE's behalf. Hagstrom's view was that taking over QCPE was not important to NRCC's mission. Counts proceeded to appoint a General Advisory Board. (One wonders if someone was trying to insert a little humor in creating an entity with the acronym GAB; the word General was later dropped.) The purpose of the board was to ensure QCPE's role inside and outside the university was proceeding in the proper direction and had the gravitas to maintain its independence.



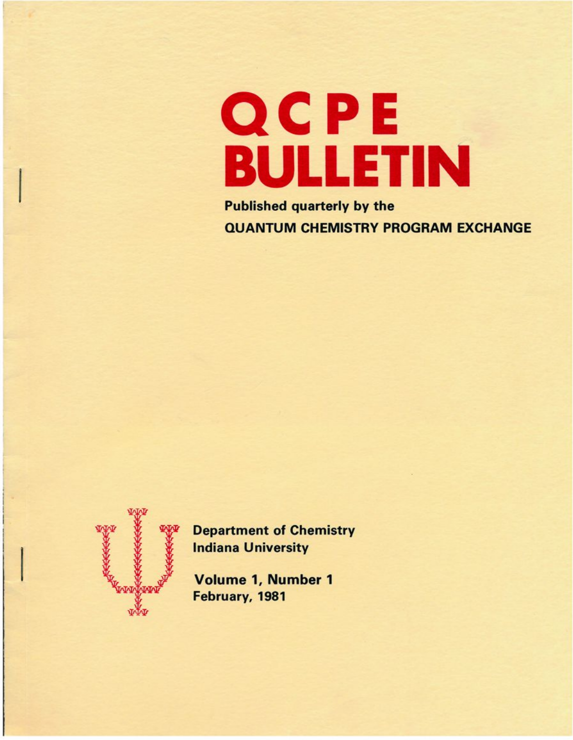
Directorate of Chemical Sciences
Air Force Office of Scientific Research
Office of Aerospace Research

QCPE

Newsletter 8
January, 1965

Chemistry Department
Indiana University

Figure 6. Cover of an early (1965) QCPE Newsletter. Note that the Greek Psi is meaningful to both IU as its logo and to quantum chemists through its use as a symbol for a wave function in the Schrödinger equation. The Air Force Office of Scientific Research was providing support to QCPE in 1965.



QCPE
BULLETIN
Published quarterly by the
QUANTUM CHEMISTRY PROGRAM EXCHANGE

Department of Chemistry
Indiana University

Volume 1, Number 1
February, 1981

Figure 7. Cover of the first (February 1981) QCPE Bulletin. The original covers were a corn yellow, although this reproduction is not exactly the right shade.

The board that Counts assembled consisted of Shull (then at Rensselaer Polytechnic Institute), who was made chairman, Norman L. (Lou) Allinger (University of Georgia), Harry F. King (State University of New York, Buffalo), Max M. Marsh (Eli Lilly and Company), Horace Martin (Rhode Island Hospital of Brown University), David Pensak (E. I. du Pont de Nemours), and Michael Zerner (University of Guelph, Canada). The only prominent quantum chemists among these were King, who helped develop the HONDO ab initio program, and Zerner, who was known for the semi-empirical molecular orbital program ZINDO. Allinger was a world expert on the structure of organic molecules, which he studied by quantum mechanics and later molecular mechanics (force field calculations). One of the industrial representatives was Mr. Marsh, a Research Advisor at Lilly Research Laboratories in Indianapolis. He was one of the first people to foresee the possibility of computer-aided drug design. (At the time, Research Advisor was the highest rank on the scientific ladder at Lilly, although now after three decades of title inflation, that title is only a mid-level rank.) The other industrial representative was Dr. Pensak, a group leader of the computational chemists at DuPont's Experimental Research Station in Wilmington, Delaware. The chairman of the IUB chemistry department was not exactly happy that his stamp of approval had not been obtained for the board appointments, but nevertheless the arrangement was allowed to go forward.

One of the changes emanating from the first board meeting on January 7, 1980 was formalizing the QCPE Newsletter (Figure 6) as the *QCPE Bulletin* (Figure 7) starting in 1981. An objective of the change was to make published items citable in the scientific literature. At the same time, Counts and the board did not want to infringe on existing journals such as Professor Dr. Hermann Hartmann's *Theoretica Chimica Acta*, Professor Per-Olov Löwdin's *International Journal of Quantum Chemistry*, Professor DeLos F. DeTar's *Computers and Chemistry*, and Allinger's *Journal of Computational Chemistry*. These journals published peer-reviewed articles. The bulletin was published quarterly and included short citable communications, as well as editorials, announcements of newly deposited software, a list of programs released earlier in the year, and other news of interest to the community. The bulletins occasionally had advertising inserts as a courtesy to authors of books and organizers of scientific meetings. Counts was Editor and Edwards was Assistant Editor.

Hands-on Workshops

Another topic the Advisory Board addressed in January 1980 was a proposal by Counts to organize workshops on applications of quantum chemistry. Counts and the board anticipated that a workshop would be a new revenue stream for QCPE. Because the university was theoretically and legally a nonprofit organization, the new revenues would have to be handled appropriately within the bureaucratic framework of the university. The chairman of the IUB chemistry department suggested that income from holding a workshop go into a special account held by the Indiana University Foundation for use by the chemistry department. This arrangement was standard on campus and was accepted.

With a green light from the chemistry department and the advisory board, Counts organized annual summer workshops starting in 1980. The idea for workshops came from a successful NRCC-QCPE workshop that had been held in Bloomington in 1979 when Hagstrom was temporarily working for NRCC. The QCPE workshops exposed about 20-45 individuals each year to the computational chemistry tools of that era. Many of the workshops were fully subscribed. Attendance was limited based on the computer facilities available. Not all of the individuals taking the courses were newcomers to the field; many were experienced users who came to learn about the latest programs and the advantages and limitations of each method. Most of these intense courses were held at IUB, but one was held on the West Coast in La Jolla, California, and another on the East Coast in Marlboro, Massachusetts. Professor Henry Rzepa (Imperial College London) helped organize the QCPE workshop held at Oxford University in 1986. In 1987, Counts handed over the "UK franchise" to Rzepa, who continued to manage them until they were taken over by one of the spinout companies of Professor Graham Richards (Oxford University).

The QCPE workshops were taught by practicing computational chemists including ones from industry. Computational chemists in industry had experience dealing with research questions that may not be ideally suited to any of the available methods, but nevertheless required the best possible answers, immediately if not sooner. In contrast, academic users could be more selective in choosing problems where available methods can be expected to give something publishable at some point down the road. The author of this chapter served on the faculty of four of these workshops. For a registration fee of $400, participants in the workshops would get to hear the lectures describing the methods and, even more importantly, warning about the pitfalls of the methods. The attendees were given hands-on experience running important programs in QCPE's holdings. Back in the early 1980s input data was still prepared on IBM punch cards, and the jobs were run as batch jobs overnight on the mainframes at IUB. At the end of the workshop, each attendee received a magnetic tape with copies of all the programs covered.

The joint NRCC-QCPE workshop in 1979 gave instruction on the following programs and methods: GAUSSIAN 76, HONDO, GVB, ACIS, AMES/CI, ATOM/CI, MNDO, CNINDO, PCILO, and MMI/MMPI. In 1980, QCPE's first stand-alone summer workshop covered then popular methods: extended Hückel theory (EHT), neglect-of-differential-overlap (NDO) semi-empirical MO methods, and Allinger's molecular mechanics method MMI. As the methods of computational chemistry advanced, so did the material covered by the QCPE workshops. The program in 1982 was on Practical Applications of Ab Initio Techniques. It covered HONDO 76 and GAUSSIAN 76. The instructors were Professor Harry F. King (one of the developers of HONDO along with Dr. Michel Dupuis) and Dr. Sidney Topiol (one of the contributors to Pople's GAUSSIAN 80 and a researcher in what was called quantum biology at the Department of Pharmacology, Mount Sinai School of Medicine in New York City). In addition, Hagstrom lectured on post-Hartree-Fock techniques at the 1982 workshop.

At the QCPE Workshop on Practical Applications of Semi-Empirical Techniques, June 19-22, 1983, the instructors were Boyd, Dr. John McKelvey (Eastman Kodak), and Allinger. In addition, Dr. James J. P. Stewart was present to elaborate on his new semi-empirical MO program MOPAC. In 1987, the workshop was held at the San Diego Supercomputer Center (SDSC) in La Jolla, California. The instructors Allinger, Dr. Richard Hilderbrandt (SDSC), McKelvey, and Topiol covered semi-empirical and ab initio techniques. Later workshops held in the UK covered topics such as density functional theory, the COSMO solvation method, and the CAChe molecular modeling system running on an interactive, stereoscopic workstation. In conjunction with IBM Corporation and QCPE, Professor Ernest R. Davidson organized and taught the First Workshop on Vectorization of QCPE Software, held at Indiana University February 9-10, 1988.

The QCPE workshops turned out to be great successes financially and in training more scientists in the techniques of computational chemistry, as well as in bringing new people to Bloomington and increasing awareness of Indiana University and its chemistry department. The workshops were so effective at training users and generating revenues that other universities and organizations emulated them and eventually captured much of the market for such courses after the late 1980s.

Figure 8. The first quantum chemistry workshop at Indiana University was organized by QCPE and the National Resource for Computation in Chemistry (NRCC) August 12-24, 1979. It was called the Joint Workshop on Computation Methods for Molecular Structure Determination: Theory and Techniques. Participants included Dr. Chung Wong (front row, left) and Dr. Herschel Weintraub (front row, third from right). Counts and McKelvey are second and third from the right in the second row. Hagstrom (left, fourth row) was working as Software Manager at the NRCC during this period. Also in the fourth row, fourth from left, is Professor Ernest Davidson (University of Washington, Seattle); he is standing behind the hirsute Professor Steve Scheiner (Southern Illinois University). In the fourth row, Zerner is second from right and Dr. John Wendoloski is second from left in the fifth row. Photograph courtesy of Dr. Edwards, who is at the right end of the front row.

Figure 9. Instructors and students at the weeklong QCPE Workshop on Practical Applications of Quantum Chemistry, June 22-27, 1980. Edwards, Professor Kenneth B. (Kenny) Lipkowitz (IUPUI), Counts, and Boyd (Lilly Research Laboratories) are among those in the first row. Dr. David Herron (an organic chemist at Lilly) is at the right end of the front row, and Dr. Harold (Hal) Almond (McNeil Pharmaceutical) is at the right end of the second row. McKelvey is second from left in the last row. The photograph is courtesy of Dr. Edwards, who is at the left of the front row.

Figure 10. Instructors and students at the weeklong QCPE Workshop on Practical Applications of Quantum Chemistry in Bloomington, June 21-26, 1981. Dr. Yvonne Martin (Abbott Laboratories) is third from left in the first row. Counts is in the center of the second row. He is standing behind Edwards and Lipkowitz; next to Lipkowitz is Boyd. The photograph is courtesy of Dr. Edwards, who is in the front row center.

Figure 11. The QCPE Workshop on Practical Applications of Computational Chemistry: Ab Initio Techniques held at Indiana University, June 20-23, 1982. Counts, Topiol, and Lipkowitz are among those on the left in the first row. Professor King is in the last row, second from left. The photograph is courtesy of Dr. Edwards, who is in the second row.

Figure 12. The QCPE Workshop on Practical Applications of Semi-Empirical Techniques at Indiana University, June 19-22, 1983. Instructors in the front row include Boyd (third from left). Lipkowitz (third from right), and Allinger (second from right). Dr. Robert C. (Bobby) Glen (Wellcome Laboratories, UK) is at the right end of the front row. In the back row are Drs. Stewart (fourth from the left) and McKelvey (goatee). Hagstrom is third from the right in the second row. The photograph is courtesy of Dr. Stewart (back row, fourth from right.

Figure 13. The QCPE workshop at the University of Oxford, England in 1987. Stewart is in the second row (third from right), and Dr. George Purvis (CAChe) is in the tie and business suit. The third row includes Counts (left end) and Dr. Nigel Richards (third from left; from the group of Professor Clark Still; hence the MacroModel t-shirt). Professor Henry Rzepa is in the back row (second from left). Edwards (second from left) is in the front row. The photograph is courtesy of Dr. Stewart (second row, third from right).

Figure 14. QPCE workshop held in Äspenäs, Sweden the week of July 1-6, 1991. Some of the instructors in the front row are Dr. Phillip Bowen (light tie), Allinger (third from left), Counts, and Stewart (dark tie). Professor Tommy Liljefors (light pants) and Dr. Ingrid Pettersson are second and third from the left end of the second row. The photograph is courtesy of Dr. Stewart.

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Figures 8-14 show group photographs of scientists participating in the workshops. To the author's knowledge, these have not been published before. The author apologizes for being unable to name all the scientists in each photograph. If individuals can identify themselves to the author, the names could be added to a website.

The Golden Years

Having covered the QCPE workshops, our narrative now returns to the timeline of QCPE's history. To give an idea of how QCPE had grown, we can cite the following data: from April 1980 to April 1981, 451 programs were distributed to the United States, 212 to West Germany, 138 to Great Britain, 106 to Japan, and 77 to Switzerland. Also in 1981, the short-lived U.S. National Resource for Computation in Chemistry (NRCC) ceased operations at the recommendation of a review committee representing a broad range of chemical interests (*5*). A theoretician, Professor William Goddard (California Institute of Technology), headed the committee, but more than half the committee members were experimentalists. Some had concerns that a centralized computational center would divert government handouts away from principal investigators. The committee also recommended that NRCC turn its software collection over to QCPE. Incidentally, the idea for an organization like NRCC came from Shull in 1965, but chemists did not embrace it as well as they did his idea for QCPE.

In the early 1980s, Chemical Abstract Service (CAS) of the American Chemical Society started offering a literature alerting service to help chemists keep up with the burgeoning scientific literature. (At the time, there were no free e-mail alerts from publishers or CAS like there are today.) Subscribers to the CAS service could create a profile with keywords that pertained to their specific field of interest. As a service to its members, QCPE created a profile pertaining to quantum chemistry. The semimonthly reports from CAS were redistributed to QCPE members who chose to subscribe.

Many popular programs such as the molecular mechanics program MM2 from Allinger's group and the semi-empirical molecular orbital programs (MINDO and MNDO) from Professor Michael J. S. Dewar's group (University of Texas) appeared in QCPE's catalog. Allinger's MM2 (QCPE 395) became available through QCPE in August 1980. Another significant milestone occurred in May 1983 when Stewart deposited his MOPAC program, a general MOlecular orbital PACkage. He was a talented, generous Scotsman on extended leave from the University of Strathclyde, Scotland, working as a postdoctoral associate in Dewar's group in Austin, Texas. MOPAC (QCPE 455) became by far the most popular and influential program in QCPE's offerings. A distinctive advantage of the program over what was previously available was that it could automatically do "geometry optimizations" (finding equilibrium bond lengths and bond angles in a three-dimensional molecular structure). This ability was a "quantum leap" from the tedious manual optimizations that had been necessary up until that time.

The appearance of MOPAC coincided with the manufacture of the hugely successful VAX 11/780 superminicomputers from Digital Equipment Corporation (DEC). Because the operating system was so much better and easier to use than those of the mainframes of that era (and earlier times), the VAXes significantly changed the way computational chemistry was being done. The price of these machines was low enough that many chemistry departments and even research groups could afford their own dedicated computer. The late 1980s thus saw an increasing number of QCPE holdings that ran on departmental computers. Many programs that had been developed for large mainframes were ported to these less expensive machines and eventually to personal computers.

In the 1980s, QCPE charged only about $45 for a small program and about $125 for a large program. This was a real bargain compared to what commercial computational chemistry software was going for (*ca.* two orders of magnitude more expensive). QCPE's cash flow in 1981 was $112,000. At its zenith around 1986, QCPE had annual income of about $400,000. This is remarkable considering the small charges for the software and the modest annual membership fee that was between $200 and $300. It is worth remembering that QCPE was designed and operated entirely to be a benefit to other scientists. Except for a brief period of government support, the operation stood on its own feet and was self-sufficient. QCPE was primarily a service to the community; it was not designed to become a big revenue generator.

Many on the IUB chemistry faculty, particularly those who did no calculations, had no interest in or were indifferent to the QCPE operation. Although QCPE members knew mailings from QCPE came with a return address of "Department of Chemistry, Indiana University", most members probably had only a fuzzy notion of how QCPE fit in the departmental framework. For a number of years, Counts had operated essentially independently of the chemistry department hierarchy, even to the extent of being able to set his own salary. However, a few IUB faculty members and especially the chairmen of the department viewed QCPE strictly as departmental "property". QCPE benefitted and supported the department as a magnet for government research grants and as a stimulus for donations of computer hardware to be used by the department and university.

In 1981, the chairman of the chemistry department, Professor Adam Allerhand, named Hagstrom to be Director of QCPE. In effect, Hagstrom served as faculty advisor. Counts continued to run the day-to-day operations. Given Hagstrom's long association with QCPE and his deep knowledge of both theoretical chemistry and computers, he was a logical person for the appointment. His assignment was to make sure QCPE was serving the interests of the department. The name QCPE carried quite a bit of weight and helped secure research funding for the chemistry department. For example, in 1983, Hagstrom and IUB Professor Peter Langhoff submitted a proposal to the National Science Foundation (NSF) for purchasing a VAX 11/780 to be used by QCPE for program testing and distribution as well as for non-QCPE research. The proposal won approval because of the QCPE component. Moreover, in 1984, NSF agreed to upgrade the VAX and let Hagstrom and Langhoff obtain a floating-point processor. Incidentally, Counts never did move the QCPE operation over to the VAX.

In late June 1984, the author telephoned Counts to express concern about "the survivability of QCPE in the face of increased and intense commercialization of molecular modeling software". Counts was aware of the situation but seemed less concerned than the author was. Counts was certain that companies that did not release source code would be self-limiting in increasing their share of the market. (Most software companies that entrepreneurs were starting in the 1980s to serve the growing computational chemistry market rarely distributed their source code. Commercial source codes were generally viewed as proprietary.)

Shortly after the telephone conversation, the author wrote a memo to Marsh, an advisor to QCPE and respected colleague at Lilly, stating the following: "Richard seems to feel that people are still submitting plenty of software to QCPE. However, my impression from reading the listings of new programs in the *QCPE Bulletin* is that donation of software is drying up. I do not think this is a transient problem. It will get worse. More molecular modeling software companies are cropping up: Molecular Design, Tripos Associates, Chemical Design Ltd., etc."

Part of the author's proposal was that if QCPE were to remain viable, it should offer a financial incentive to donors of software. The financial incentive could be fairly modest, such as what authors typically get paid for writing a book chapter. The incentive could encourage an increased number of donations of software for QCPE to distribute, which in turn would have the effect of increasing QCPE's revenues. A further part of the author's 1984 proposal was that QCPE could use some of its revenues to hire one or two programmers who, with permission of the original programmers, could add interfaces or other enhancements to popular holdings in the QCPE library. Although the author had no inside knowledge at the time, we now know that QCPE revenues were sufficient for a little profit sharing.

On July 2, 1984, Marsh forwarded the author's memo to Counts and Hagstrom for consideration at an upcoming advisory board meeting. The author was not privy to the deliberations of Counts and the advisory board, but the proposal was not accepted. There could have been opposition to the suggestions because of concerns about whether QCPE's revenues should be shared outside the chemistry department, concerns about potential liabilities if use of a computer program were alleged to be associated with a harmful decision in a research project, or concerns about whether ownership of the programs might be considered not purely with the original programmers.

The year 1984 also marked another step in QCPE's history when Professor Ernest R. Davidson (Figure 15) was enticed to move his group from the University of Washington in Seattle to IUB. Davidson did his undergraduate training as a chemical engineer at what is now called Rose-Hulman Institute of Technology in Terre Haute, Indiana. With light guidance from Shull and occasional mentoring from Hagstrom, he had obtained his Ph.D. at IUB in just three years. In addition to his faculty position at IUB, the chairman of the department at the time, Professor Paul Grieco, named Davidson to replace Hagstrom as director of QCPE. The appointment helped win approval for Davidson's pending proposal for purchasing his own large IBM computer. The strategy worked. In its heyday, the QCPE "brand", as we say nowadays, carried with it prestige and the aura of a worthwhile service to the community.

Some observers had the impression that Davidson had only a limited investment in QCPE's future. Perhaps because of this, efforts by Davidson to become more familiar with QCPE's operation were not always met with cooperation. He even had trouble getting his name put on the mailing list for the *QCPE Bulletins*. Nevertheless, Davidson did contribute his ab initio program MELD to the QCPE catalog, and he performed the annual function of reviewing and approving salary increases for the QCPE staff. Davidson obtained a grant from IBM Corporation to hire programmers who could get some QCPE programs running on the new IBM computers. In the following years, Davidson's leadership resulted in money from QCPE being used to create an endowed lectureship in theoretical chemistry. Prominent theoreticians were invited to Bloomington to give a seminar as a result.

Figure 15. Professor Ernest R. Davidson in the mid-1980s when he joined the faculty of IUB. . The photograph is courtesy of Judi Roberts and Roger Beckman of the Indiana University staff.

Counts and Edwards continued to manage the day-to-day operations of QCPE. They were assisted by Mildred Perkins and Judy Chatten, who had been hired on a full-time basis in the late 1970s or early 1980s to handle the growing business.

Perkins reproduced the programs for shipment and helped arrange the workshops. Chatten shipped tapes and other material to the customers and literally put the quarterlies together in terms of assembling the pages and stapling them.

To provide new viewpoints, Counts started rotating the membership of the QCPE Advisory Board. Drs. Enrico Clementi (IBM) and Isaiah Shavitt (Ohio State University) were enlisted in 1986. In 1987, the board consisted of the author Dr. Donald B. Boyd (Lilly), Clementi, Davidson, Dr. Gilda H. Loew (Molecular Research Institute, Palo Alto, Calif.), and Shavitt. In 1989, Dr. Charles Bender (Ohio State University where he was first director of the Ohio Supercomputer Center) and Dr. Herschel J. R. Weintraub (then at Merrell Dow in Cincinnati) were enlisted. Dr. Harel Weinstein (Mt. Sinai School of Medicine) was enlisted in 1991, and Dr. James J. P. Stewart (at the time a consultant to Fujitsu, which sponsored the development of MOPAC for a few years) was enlisted in 1992. However, Counts eventually quit convening the Advisory Board.

In its heyday (1980s), QCPE distributed about 2500 programs per year. The software catalog, which was distributed annually in hard copy, became so thick that it was broken into categories. Computer programs contributed to QCPE were grouped into ten sections listed below. Although there is no category for force field (molecular mechanics) programs, these were arbitrarily thrown in with programs for Approximate MO Methods and Chemical Reactions for some reason.

I. Numerical Methods
II. Integrals
III. Ab Initio Systems
IV. Semi-Empirical MO-SCF Systems
V. Approximate MO Methods
VI. Scattering & Crystallography
VII. Spectroscopy
VIII. NMR/ESR/EPR Systems
IX. Chemical Reactions
X. Systems for Education, General Utility and Computer Graphics

It is evident from the above categories that QCPE had indeed branched out from its original concept of being about quantum chemistry. QCPE truly served the whole breadth of computational chemistry. The name of the operation was shortened from Quantum Chemistry Program Exchange to simply the acronym QCPE. This change was intended to convey the fact that the software library had broadened from quantum chemistry to all of computational chemistry. In the first two-thirds of the 20th century, theoreticians thought quantum mechanics would be like a sun lighting up the universe, speaking metaphorically. As the field of computational chemistry developed, an increasing number of observers came to understand that quantum chemistry was just one planet circling the solar system of computational chemistry.

Home in Indiana

During its lifetime, QCPE occupied several different offices. The spaces allotted to QCPE were characterized by being filled with a variety of computers so that programs could be tested on machines prevalent in the user community at the time. Also, the offices had many piles of mimeographed and later photocopied documentation corresponding to each program in the catalog. This paperwork was needed because a copy of the documentation was shipped with the computer cards or magnetic tape to each requestor.

After the QCPE office vacated the Chemistry Building at Indiana University, it was located in a temporary structure called the Quonset hut (Figures 16), which stood in a nearby parking lot. Such structures with corrugated metal roofs were popular during and after World War II because of their low cost and quick construction. QCPE's next move was upward: it "moved up" to the top floor of one of the towers of the nearby Indiana Memorial Union (IMU). The top floor was once occupied by an IU president who enjoyed the view (Figures 17). Still later, QCPE moved to a university building on Indiana Route 46 Bypass, which circled part of the perimeter of the campus. This building has since been torn down to make way for a large new information technology building. In October 1999, QCPE operations were moved back to the Chemistry Building where they were spread over four rooms. In the period 2001-2011, QCPE operations were conducted in the small-molecule X-ray crystallography laboratory on the fourth floor of the chemistry department annex, which is a large laboratory building behind the older chemistry building.

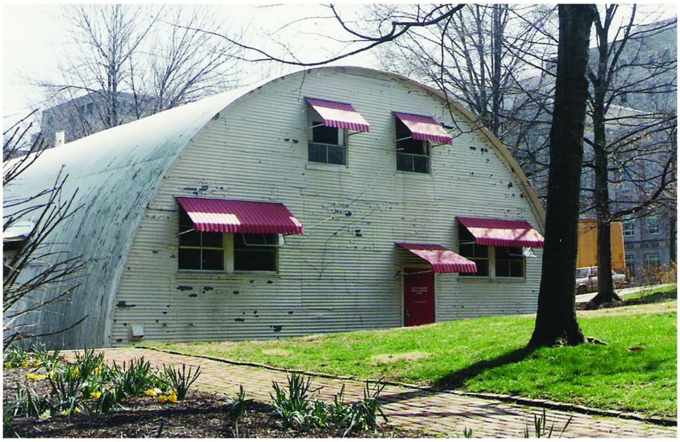


Figure 16. The QCPE office was on the second floor of the Quonset hut on the Indiana University campus. For many years, this temporary structure was the home of Dr. John C. Huffman's highly productive small-molecule X-ray crystallography laboratory. The photograph was supplied by Mrs. Carolyn Huffman.

Figure 17. The top floor of the central tower of the Indiana Memorial Union (IMU) was occupied by Counts and coworkers in the 1980s. Another part of the large IMU building provided hotel accommodations for particpants at the QCPE workshops. The building is constructed with Indiana limestone, the same material as used on the Empire State Building in New York City. The photograph is by the author.

Clouds of the Horizon

Despite the positive impact of QCPE, not all theoreticians, quantum chemists, force field practitioners, and other computational chemists bought in to the concept of exchanging software through QCPE. Reasons for people not depositing programs in QCPE can be hypothesized. Again considering human nature, some people are competitive and did not want to share the fruits of their labor with rivals or less capable individuals. Others saw the potential to make money by selling their software themselves or through one of the existing computational chemistry software companies. Some principal investigators preferred to keep their programs under strict personal control; in effect, these researchers wanted to be gatekeepers to decide who could and could not have access to their programs. Perhaps some scientists felt their source code had things in it that they did not want others to see or check. Certainly it is difficult to remove all bugs from a long program consisting of thousands, even tens of thousands, of lines of code, and these bugs may have affected published data. Many others never shared their software through QCPE because they did not want to take the time to get their programs documented and ready for others to use. As time passes, programmers may have forgotten details, making it difficult to document a program that had been written for an earlier project. For whatever reason, many researchers elected not to deposit their programs in QCPE.

A number of factors undermined the important role QCPE was playing. The 1980s and 1990s witnessed the commercialization of software by relatively large companies in the computational chemistry business. In order to obtain the latest versions with the most features and with the most recently fixed bugs, customers had to buy commercial versions of MOPAC, AMPAC, MM3, Gaussian, and other popular programs. The software companies often had large staffs of Ph.D. computational chemists who could both continually improve their products and respond to queries from their customers.

The commercial programs tended to be written (or rewritten) in current program languages according to what were the current standards. In contrast, some of the QCPE holdings had been hastily written in older languages and lacked sufficient comment cards to explain the detailed thinking of the programmers.

The older QCPE software holdings became less relevant as the expectation of user-friendly input to software became more and more popular. By 1990, the QCPE library had started to acquire some programs with graphical user interfaces (GUIs). The library also had some elaborate programs qualifying for the name "system" or "package".

Another significant trend in the 1990s was the emergence of the Internet that gave individuals an independent way to distribute software they produced. The healthy flow of new programs being deposited in QCPE gradually diminished as some had predicted. The number of programs being requested also slowed in the 1990s. Software had been deposited by American chemists as well as by researchers in other advanced countries. However, distribution of programs in the 1990s was largely to places outside the United States. Interestingly, the Japanese remained some of the main customers of QCPE's holdings.

Another trend impacting QCPE was the fact that users wanted and expected technically supported software, i.e., they wanted to be able to call up a toll-free telephone number or send an email to ask questions about the operations of a program. Mr. Counts provided support to QCPE "customers" on an ad hoc basis. His efforts at keeping QCPE running are to be applauded, but it was hard to compete with large software companies. These changes in attitudes and expectations, as well as other factors, slowly undermined the important role QCPE had been playing.

The relationship of QCPE and the IUB faculty has already been touched upon. In some respects, QCPE was in the chemistry department but in other respects QCPE was out of the mainstream of faculty awareness. This second aspect is illustrated by a book written by Professor Harry G. Day. He was one of the chemists behind the stannous fluoride in Procter & Gamble's popular Crest toothpaste for strengthening enamel and preventing caries. He was also notable because he had served as a chairman of the department. In his retirement, Day wrote a monumental history of chemistry at Indiana University covering the period 1829 to 1991 (*6*). The tome covered almost everything and was 668 pages long. However, Day forgot to mention QCPE at all. When this was brought to his attention by Max Marsh in his usual gentle fashion, Day formatted a one-page description of QCPE to fit within the book, which had already been published.

Honoring Years of Service of Richard W. Counts and QCPE

The last and only major tribute to QCPE was at a symposium organized in honor of Counts for his service to the field of computational chemistry. That service had extended more than a quarter century. The symposium was held by the Division of Computers in Chemistry (COMP) of the American Chemical Society (ACS) at their spring meeting of 1994. These meetings typically draw thousands of chemists from across the United States and the world to partake of a rich assortment of concurrent symposia. Here is a reproduction of the program for the half-day session (*7*).

207th American Chemical Society
National Meeting & Exposition Program
San Diego, California
March 13-17, 1994
COMP
Division of Computers in Chemistry
A. R. Rossi, Program Chairman
WEDNESDAY MORNING
Section A
Marriott
Columbia 1&2, North Tower, Lobby Level

Special Symposium on Computers in Chemistry in Honor of Richard W. Counts for Service to the Field of Computational Chemistry

J. McKelvey, R. L. Hilderbrandt, J. J. P. Stewart, Organizers
J. McKelvey, Presiding
8:30 - Introductory Remarks. J. McKelvey
8:40 - 134. The QCPE experiment. H. Shull
9:20 - 135. Funding computational chemistry in the 1980s and 1990s. N. L. Allinger
10:00 - Intermission.
10:20 - 136. Whys and why-nots of commercially distributed software. M. C. Zerner
11:00 - 137. Thirty years of the software support problem. R. W. Counts

Here is a reproduction of the abstracts for the half-day session (*8*).

134. THE QCPE EXPERIMENT. Harrison Shull, Provost, Naval Postgraduate School, Monterey, CA 93943

The history of perhaps the only continuously successful voluntary computer program exchange is described from the time of the Shelter Island Conference of 1951 until 1979. The key roles of Keith M. Howell and Richard Counts are reviewed. The general principles which [sic] have been essential to QCPE success are summarized.

135. FUNDING COMPUTATIONAL CHEMISTRY IN THE 80'S AND 90'S

Dr. Norman L. Allinger, Chemistry Department, University of Georgia, Athens GA 30602

Funding available in chemistry has changed markedly in the last twenty-five years or so. While the overall funding is supposedly similar, or even greater, in real dollars, much of it is earmarked for speacial [sic] projects, and the tendency has been towards fewer and larger grants. The average university chemist sees this in the fashion that the rich get richer, and the poor get poorer. These changes have prompted reactions on the part of those who do university science, and some of these changes will be discussed.

136. WHYS AND WHY-NOTS OF COMMERCIALLY DISTRIBUTED SOFTWARE

Michael C. Zerner, Quantum Theory Project, University of Florida, Gainesville, Florida 32606

There is little question that computational chemistry has become an important tool in chemistry, now reaching out and effecting [sic] nearly all of chemistry's subdisciplines. It is rare today to see forefront science performed without an attempt at understanding aided through computation. With this popularity has come a problem: complex software and advanced concepts in molecular electronic structure, statistical mechanics and molecular dynamics have left the realm of those who designed this software and have become the everyday tools of scientists not trained to necessarily use this software to greatest advantage, or even correctly. Some problems lend themselves to easy interpretation, others do not. Mistakes are made, some embarrassing to the user, others embarrassing to an innocent software developer. Out of these time requirements on the part of the developer has arisen, therefore, the trend to seek assistance through commercial distribution and support. These issues are discussed.

137. THIRTY YEARS OF THE SOFTWARE SUPPORT PROBLEM

R. W. Counts, QCPE, Indiana University, Bloomington, IN 47405

If computational chemistry as a field is going to develop into the broadly useful tool, which it currently is for a relatively small number of people, the problem of software backup and support is going to have to be separated into its component parts and seriously addressed. From the earliest days, QCPE recognized that it is virtually meaningless to distribute software unless a modicum of support can be provided. We have made efforts to provide such support as is within our resources. We now have a fairly accurate understanding of the magnitude of the problem.

The author of this review had the pleasure of being among the many attending the symposium. We devote some space here to convey some of the content and flavor of the talks. Presiding at the session, Dr. John McKelvey (Eastman Kodak) opined in his introduction that the annual QCPE workshops in the early 1980s were the most exhilarating experience in computational chemistry he had ever encountered. He acknowledged the following companies for financially supporting the symposium: Digital Equipment Corporation (DEC, maker of the VAXes), Eastman Kodak (McKelvey's employer), Fujitsu (associated with J. J. P. Stewart and MOPAC), Sterling-Winthrop Pharmaceuticals, and Stewart Computational Chemistry (Jimmy Stewart's business).

Shull's Talk

Appropriately, the first speaker was the founder of QCPE, Harry Shull. He noted that even though he was a 50-year member of the American Chemical Society, it was the first national meeting he had attended in a long time because of his administrative duties. Shull expounded on his background. He obtained his B.S. from Princeton University in 1943. Toward the end of World War II, he worked two years at the Naval Research Laboratory. He considered this experience working in a non-academic environment to be valuable and recommended it to scientists in training. He earned his Ph.D. in spectroscopy at the University of California Berkeley in 1948. *Quantum Chemistry* by Eyring, Walters, and Kimball was his favorite quantum mechanics textbook, but he noted that it was full of typographical errors. Shull received a postdoctoral appointment with the famous Robert Mulliken at the University of Chicago.

Shull was a faculty member at what is now called Iowa State University in 1951 when he was invited to fill in at the first Shelter Island Conference on Quantum Mechanics in Valence Theory. (Shelter Island is in the Atlantic Ocean near Long Island.) Twenty-five people attended this conference. In 1954 and again in 1958, Shull spent a leave studying with the famous Swedish quantum physicist Per-Olov Löwdin in Uppsala, Sweden (*9*). Shull moved to IU in 1955. He organized the first Gordon Conference on Theoretical Chemistry in 1962. Keith Howell was his postdoctoral associate from Southampton, UK in 1962, and was given the task to set up the operational details for QCPE. After the Shelter Island meeting and prior to QCPE, Roothaan at the University of Chicago had set up a registry for exchange of two-electron integrals.

QCPE's early experience was that half of the programs submitted failed to reproduce the output from the supplied input. [This fact implies that more than a few inaccurate results could have been published with faulty programs.] Such programs had to be sent back to the programmers to be fixed. As computational chemistry evolved, Shull was surprised to see non-quantum mechanical programs such as those for conformational analysis being submitted to QCPE, but he had placed no restrictions on what could be accepted. In explaining why QCPE had to become self-supporting, Shull stated that the "Delaney Amendment" shut off funding from the Air Force to QCPE. [This was a misstatement; it was the Mansfield Amendment that limited funding from the Department of Defense to strictly military missions; Mike Mansfield was a Democrat U.S. Senator from Montana.]

Shull, in speaking of the honoree of the symposium, noted that "Dick" Counts had an M.S. in Physics from Washington University. Prior to Counts being hired to manage QCPE, he worked for the Air Force technology transfer office in Bloomington. [This was a misstatement. Counts worked at the NASA office in Bloomington.] Shull quipped that before QCPE brought fame to Indiana University, people outside of Indiana knew IU principally as the home of the Kinsey Institute where research was done on human sexual behaviors! Shull recalled that back in the 1960s, theoretician Robert Parr [then at Johns Hopkins University] observed that each major university in the United States had a theoretician. Proudly, Shull noted that IU had hired three theoreticians the same year. After QCPE got started, Shull admitted that he devoted only a few minutes per year to checking on its operation.

Allinger's Talk

Allinger began by stating that in 1994 it was costing $150 million on average for a pharmaceutical company to bring one new drug to market. [The cost is nearing an order of magnitude higher now.] Without mentioning the Democrats in the White House and in the Congress by name, he pointed out that if politicians tried to reform healthcare by price controls on pharmaceuticals, it would be killing the goose that laid the golden egg. Pharmaceutical companies depended on their sales to support large, vigorous research programs that provided many excellent jobs for scientists.

In the early days, universities charged only 10% overhead on grants, but as bureaucracies grew, the universities skimmed off more and more money from the research grants that the professors were obtaining. When Allinger started his faculty career, he won a grant from the NSF to buy an NMR spectrometer. However, his university bureaucrats never got around to supplying the required matching funds, and NSF took their money back. That is what prompted Allinger to refocus his research on a computational approach to conformational analysis. Back in those days, he and a few others referred to it as "calculational chemistry."

NSF funded his molecular mechanics work during the years 1969-1975, but after that he never got another proposal approved. Other government agencies also turned down his research proposals. Even one bad review would kill any chance of getting a proposal funded. There was always some [uninformed] reviewer who alleged that molecular mechanics should not work. Fortunately, grants from Eli Lilly, DuPont, and the American Petroleum Institute (API) kept his research going. He started marketing his molecular mechanics programs (MM2 etc.) through Tripos, a computational chemistry software company in St. Louis. It was necessary for him to take this step in order to obtain funding for his research group.

Allinger prophesied [correctly] that theoretical chemistry would always be important. Computational chemistry is like experimental chemistry in that the chemist is trying to solve a problem.

Zerner's Talk

Zerner was of the school that went into science because it was beautiful, not because it was useful. Referring back to his graduate school days at Harvard when he and his contemporaries lugged around heavy boxes of computer cards, he jokingly defined “one Clementi” as one box of 2000 computer cards! [Enrico Clementi was a respected quantum chemist who worked for IBM Corporation.] Zerner reminded the audience that some of the greatest figures in theoretical chemistry did not do many calculations. Instead they made advances in mathematical equations and concepts.

Zerner lectured the audience on the issue of whether developers of computer programs created using the public’s money should make the programs available free to the public. ZINDO, his famous semi-empirical molecular orbital method for predicting UV/vis spectra, was a product of his grants from the NSF. Zerner’s policy for many years had been to give his program freely to people who requested it. For years he and his group handled distribution of his program. However, he found that it took more and more of his time and that of his research group to respond to questions from the users. There were annoyances such as people not returning the magnetic tapes that he sent the program out on. Although ftp (file transfer protocol) was more convenient than shipping a tape in the mail, it was relatively slow.

Zerner showed examples of emails from people requesting or even demanding a copy of the ZINDO program. One shameless email was from someone with an illegal copy of his program who had gotten a grant to convert it to the Cray supercomputer. Zerner was getting 5-10 emails per day complaining or asking about ZINDO. [Many of these aggravations would have been alleviated if he had deposited his program in QCPE]. People would ask him annoyingly simplistic questions such as how to convert between bohrs and angstroms. He also saw a lot of requests for help because of convergence problems. Further vexation came when colleagues, even prominent ones, would use his program and not give him credit. By 1984, Zerner had quit distributing ZINDO himself. He arranged for ZINDO to be sold through two companies, BIOSYM and CAChe. He felt justified in taking this course of action but regretted that a costly program would impede science.

In the question and answer period following Zerner’s talk, Shull made the point that a computer program ought to be regarded like an experimental apparatus: it can be used repeatedly to generate data, and there is no expectation that the developer gives away copies. Dr. Richard L. Hilderbrandt (NSF) affirmed that recipients of NSF grants were no longer obligated to give software away free even if it was developed with taxpayers’ money. Having had experience working for a commercial software vendor, Hilderbrandt also defended these businesses because they added value by fielding questions from users who refused to read program manuals.

In anticipation of Counts’ scheduled time to talk, the audience grew from about 40 people to about 60. There could have been some prominent IUB authority figures in the audience at the San Diego symposium for Counts, but none were noticed. It was almost as if the leaders at IUB were unaware of the important role that QCPE had played in broadening the use of computational chemistry from just theoreticians to mainstream chemical research. The following recounting of Counts’ talk at the ACS meeting runs long, but we would like to leave a record because he and QCPE’s history were so long intertwined. Also, his talk gives insight into his service and mindset. He had firsthand familiarity with the evolution of scientific computing. The version below is not verbatim, but rather is a paraphrase based on the author's notes and a preview copy of Counts' prepared remarks that he had given the author.

Counts' Talk

Counts began by asserting that *Computer Physics Communications* (published in Belfast, Northern Ireland) was a library. According to Counts, physicists buried their code there, and no one ever saw it again. In contrast, QCPE's service to chemistry was much more.

Ever since its launch in 1962, QCPE's mission has been to collect and distribute computer software in source form. [The idea of having a quantum chemistry program exchange was first aired in 1962, but operation began in 1963.] Counts said this straightforward description was correct but did not convey the scope of the organization's true usefulness. QCPE provided continuity on potentially important pieces of software. By this he meant that QCPE could be a stable repository even when professors changed their area of research or when graduate students and postdoctoral associates came and went.

It was around 1960 that people began to write scientific "codes" in FORTRAN. Much software for science and engineering was written in FORTRAN II. This version of FORTRAN could be moved from computer to computer with a minimum of difficulty. The programming language was a significant advance in the computing world.

According to Counts, continuity in this period meant a person who looked after the program. A piece of software was useful as long as the person who wrote the software was available to talk to. When the person disappeared for any reason, the software was often abandoned. In large laboratories such as Lawrence Livermore Laboratory in California, all the major codes had someone whose sole responsibility was to maintain the continuity of that code.

When continuity was broken on a piece of software, it was to a large extent lost to posterity. The cost of developing and debugging this software was lost, and this sort of thing happened in laboratories around the world. It was impossible to estimate the amount of money wasted when there was a breakdown of continuity of computer software. Counts came to see that one of the vital services of QCPE was to maintain an accurate version of any program in its catalog. It was a responsibility to keep programs workable on each new generation of computers.

Another role QCPE played was to be a mechanism of communication. While operating under rules different from those of a formal journal, the QCPE quarterlies allowed ideas and information to be aired that might not qualify for publication in a peer-reviewed journal.

In Counts' opinion, QCPE also brought the creation of an important computer code to some level of respectability in the academic world. Many institutions started to accept the contribution of a successful computer code as similar to having publications. In some cases, the publicity that came to a programmer could be the determining factor in a tenure decision.

An advantage for QCPE was that it dealt only in source code. From a scientific point of view executable code, which was all that most software companies provided, was not especially useful because the user must regard it as a black box. One had no idea what the science in the code actually was. Counts found it amazing that such codes sold in great numbers and sometimes without adequate documentation. Sometimes people who had bought a commercial code would have to come to QCPE seeking help on what the commercial product could and could not do. Sometimes the commercial firms even referred their customers to QCPE to obtain documentation for a specific program.

Having enumerated the main contributions of QCPE, Counts turned to the evolution of computer architecture. At the time of QCPE's establishment, computing was a homogenous business. There was essentially IBM, and scientific computing was carried out on one of their 36-bit computers. This greatly simplified user support. There were no questions about tape formats. There were no problems of compilers because there was really only one, although slightly different release numbers might be found on different machines.

In the early days, QCPE distributed software as printed listings, punched cards, or on magnetic tape. The tapes were 7-track with very low recording densities such as 200 bits per inch [a quaint unit from the early days of computing] or 556 bpi. IBM made most of the computers and associated equipment, so the tapes were generally readable at the computer center of each university.

QCPE's job was easier back when there was only one computer architecture and one version of FORTRAN. In 1964-65, a new computer design by Control Data Corporation (CDC) and Seymour Cray came on the scene. No longer was there just FORTRAN II, but now there was FORTRAN 66 and word lengths increased to 48-bit and eventually 60-bit words in their architectures. To meet the needs of QCPE subscribers, it was necessary to match the version of the program with the requirements of the computer to be used. The main user support problem became separating IBM users from CDC users. Once a few rules for guidance were developed, programmers undertook the task of porting needed codes between the different computers. This user support environment remained steady into the early 1970s.

The next major change came with new operating systems and the capability for virtual memory. With new operating systems came a proliferation of magnetic tape formats and the former 6-bit character gave way to the 8-bit byte prevalent in the 1990s. Tape densities changed, their recording technology changed, and the number of formats grew. The problem of transferring source code to clients throughout the world became more complicated.

QCPE had the advantage of possessing source code, so the programs could be ported to different computers by knowledgeable volunteers. It became necessary for QCPE to distribute operating system programming along with the programs. By having the necessary equipment at IUB, QCPE could interconvert tape formats. All the early computers had available freestanding, open-reel, half-inch magnetic tape drives. But this was about to change. As long as everyone was using FORTRAN and everyone had the standard magnetic tape drive available, the distribution of computer software remained a relatively straightforward business. In the early days, the average length of computer codes was about 2000 lines of code (one standard cardboard box of punched IBM cards).

In the 1960s and early 1970s, the number of users of computational chemistry was still quite small, and these users tended to be capable of taking care of things themselves. The number of computer programs involved was small. QCPE's clientele were usually knowledgeable about what operating system they were using. User support was not a big issue.

In the late 1970s and the early 1980s, two events shook the computing landscape and also changed the nature of user support. In 1978 the VAX superminicomputer came onto the scene and that was followed a few years later by the IBM desktop minicomputer. Up to that time, computers had been confined to one isolated computer center on each campus. Each center was controlled and maintained by a powerful bureaucracy and its staff. The users carried their computer cards to the centers and picked up their printouts a day or two later. The VAX broke the monopoly that the administrators of central computer centers had on computational resources. The IBM personal computer (PC) moved the resource to the desktop of each user.

During this period when changes in major hardware and operating systems were taking place, QCPE's holdings were constantly growing. QCPE began to receive and distribute software for the PC in 1984 and a few years later began the same activity for the newly arrived Apple Macintosh. As of 1994, QCPE was maintaining and distributing software from its holdings of some 650 mainframe and workstation programs, 130 PC programs, and 20 Macintosh programs. Whereas the typical commercial firm had a few software products to deal with, QCPE had almost 800 programs in its inventory. Counts also operated with the added constraint of a staff of just a few people.

As the software holdings and versions proliferated, it became rare to simply pick up something from the shelf and mail it. It was advisable to interview customers to determine what they might be able to use.

By the 1980s, semi-empirical methodology and computer programs were improving and becoming fairly useful. These approximate calculations depended upon parameters. Each different atom needed to be described by a set of experimentally or theoretically determined parameters. While this may sound innocent, it was a major difficulty for the average user who needed to treat a molecule with an uncommon element or atom type. [Theoreticians had not extended their methodologies to the less frequently encountered elements and bonding situations.] If the program did not have parameters for certain atom types that theoreticians had included or published, the aspiring user faced a daunting task. [The user had to derive or guess the values of needed parameters and have some confidence that they would lead to valid results.]

There were several different semi-empirical approximations in use in 1994. One type of approximation was especially useful for predicting ultra-violet spectra [i.e., ZINDO] and another type was especially useful for predicting heats of formation [i.e., MOPAC]. The typical novice user of the 1980s was simply not knowledgeable enough about the many approximations in use and the implications of their use.

Counts felt his duty to QCPE clients was to make available a version of a given program that was most appropriate to their specific computing environment. He often had to help users who might know the name of the program but were unfamiliar with QCPE's program numbering system. Other users might be uncertain of the name of the program but had the developer's name or perhaps a description of the program's functionality. The person doing the ordering sometimes had only imprecise information for a situation that required highly specific information. To deal with this, Counts developed an informal questionnaire that could be administered by telephone, fax, or e-mail to extract the exact information required. Depending on the information level of the individual he was dealing with, the series of standard questions that he needed to ask could be started at different points. A challenge for QCPE was to know enough to differentiate among the various versions of a given program. The clientele of QCPE operated in diverse computing environments.

From the user's viewpoint, the main questions were: can the program treat my molecules and provide useful answers? Many people who were not intimately familiar with semi-empirical calculations did not question whether a program such as MOPAC was capable of doing calculations with every element that one might want to treat. It was necessary to find out exactly what sort of chemistry the user was working on and then assess whether MOPAC could be used at all. Inorganic chemists or researchers who were working on molecules containing transition metals were often unaware of how scarce parameters were for such atoms or that the then current version of MOPAC would be unable to assist them if the chemistry they happened to be looking at required d orbitals. Counts endeavored to ensure that clients obtained programs that had some hope of providing needed information.

This problem of appropriateness of a given program for the research question being addressed pertained not just to MOPAC versions, but also to ab initio programs and molecular mechanics programs as well. There was no point in the user wasting time using a program for a question that it was not designed to answer. The message that had to be conveyed was that there was no single solution to everyone's problems. There was a range of computational tools that could be brought to bear, and the user had to be made aware of what the tools could and could not do. Sometimes the users had to be told there were currently no programs in existence that could answer their questions. This assessing of the computability of a given situation was perhaps one of the most complex user support problems that QCPE confronted.

When a first-time user ventured into conducting computational experiments it could be disconcerting if the program halted abruptly without providing the answers hoped for. The user quickly learned to dread the appearance of the warning message about missing parameters. Problems could arise in computational experiments whether the hurdle was finding new required parameters for semi-empirical or molecular mechanics programs or finding an appropriate basis set and level of theory for ab initio programs. Such unanticipated questions may confront the first-time user. There seemed to be little awareness that the ab initio programs were solving a set of differential equations by means of a technique in which one estimates a solution by means of a supposedly closed set of functions that spanned the mathematical space in which the solution was to be found. The important point often missed was that the closed set needs to be infinite to guarantee a correct solution.

Counts attempted to educate and inform QCPE's clientele of these and other common difficulties. For instance, naive users sometimes looked only at one piece of information in the output from a computer run. They might need the dipole moment, for example. Over the years he urged users to examine the whole output to make sure the calculation properly completed and produced no warning messages or internal inconsistencies in the output. As part of the software support effort, QCPE provided a continuing education program to any user who would listen to advice. QCPE endeavored to make sure the user received a program that contained the science to solve his problem, that ran on the user's computer, and that the program performed as it should.

Considering the large number of programs in the QCPE catalog and its worldwide audience, Counts set a high goal for his operation. He acknowledged that he could not have achieved his goals without the help of others, particularly those who submitted their software for distribution.

At the time of this symposium (1994), QCPE was distributing software for Intel-based PCs, UNIX workstations, VMS (VAX) systems, Apple computers, and several others. Whereas Counts did not need to be an expert on all these computers and operating systems, he did need to be able to recognize when a computing problem was system related. He also needed to be able to isolate a problem on a computer that was remote from his location in Bloomington. Over the years he had developed simple-minded consistency schemes that permitted him to do this. It was usually possible to understand a problem a user was having and figure some way around it. Counts developed experience dealing with a diverse clientele spanning different levels of expertise.

QCPE's business was focused by its order stream, so Counts became fairly knowledgeable with the 15 or so programs that were distributed most frequently. He became familiar with the users' computing habits and the computational approaches in use. He was hearing from different users the same questions about a given piece of software over and over. He developed a repertoire of answers for the usual questions.

It was sometimes the case that he was an intermediary between the developers of the software and the users. These cases tended to be on the more technical issues. However, once a given problem was solved, the solution became part of Counts' repertoire of solutions. He could save the software developer from being pestered with repetitive questions from other users. For system related questions, he could usually deal with them without recourse to the program developer.

Another responsibility Counts undertook was to keep the users running the versions of the programs current with the latest bug fixes. Any correction to QCPE's master files was made immediately to avoid any further propagation of the error. Counts took two approaches to handling communications with the customer base. If he had delivered only a few copies of a program, he could contact each recipient individually about the correction. In the case of computer programs that QCPE had distributed to hundreds of users, Counts would publish a notice of the error in the next available issue of the QCPE quarterly. He would be on alert when anyone called regarding the system that had just been corrected. In addition to users who had obtained a program directly from QCPE, there were many users who had received a QCPE program second-hand from a colleague. Such users would have to depend on their friends to learn about bugs.

Error correction was viewed as one of the most critical parts of the software support effort. As error corrections accumulated, they were filed by program number in chronological order. Counts often received requests asking if there had been any corrections since a certain date. Thanks to his system of tracking corrections to programs in the catalog, Counts could supply the requested information. When a series of bug corrections became too complicated or too extensive, Counts simply replaced the program with the current version. Both customers and often developers of systems could depend on QCPE to maintain the definitive, correct version of a given piece of source code.

With the less frequently ordered programs, QCPE might not have had the benefit of accumulated information. In this case, Counts would begin by trying to replicate the problem that was being experienced by a user. Hence, Counts required access to appropriate computers, operating systems, and compilers to do this. He made a point to cover all the popular hardware. By being able to replicate an error and having access to the original developers, he could usually respond to a major question in a timely manner. The usefulness of software clearly depends on users being able to get help when they encountered a problem. QCPE viewed its obligation to not only ship out copies of programs, but also to assist users in using them.

As computer manufacturers changed their operating systems and their architectures, QCPE attempted to assess how much trouble such change would introduce for both the process of distributing the software and supporting it. Working primarily with FORTRAN and a limited amount of C programming language, there had been no changes that could not be dealt with. Unfortunately, computer companies paid little or no attention to the inconvenience or cost they may impose on the customer base with each new generation of product.

The science of computational chemistry was changing more slowly than the computer systems. It was not uncommon for many man-years of effort to be invested in bringing a piece of software into existence. The MOPAC system with which everyone in this field was familiar in 1994 was in its thirteenth year of development. The MM3(92) system of Allinger may reflect many more man-years than thirteen as it has been worked on by multiple individuals over the last 20 years.

Whereas a scientific manuscript may have achieved its purpose once it is published, scientific programs must be continually maintained in a state of readiness so that papers may continue to be generated from new results produced by the program. Going back to the theme of continuity, maintaining software in this state of readiness means making modifications to the code so that it compiled and ran on each new generation of hardware, compilers, or operating system. Sometimes the code had to be completely rewritten in a newer computer language. The person making the updates needed examples of input data sets for problems that the program was supposedly capable of solving and examples of results that were thought to be correct. Access to detailed documentation for the software might also be vital.

QCPE had served as a source from which this software could be reliably obtained. Counts had also been able to help users by being familiar with the history of a program. Documentation alone might not suffice.

Counts concluded his talk by noting that QCPE came into existence in 1962 [sic, 1963] with the primary purpose of distributing existing pieces of software so that the small number of workers in the field of quantum chemistry would not have to duplicate each other's efforts. As the field of computational chemistry emerged, QCPE's role was augmented by concern for the continuity of the software in its care. Other fields of science have not addressed problems related to the preservation and development of its software resources to the same extent that had been achieved in chemistry.

Many individuals have played important roles in bringing QCPE into an effective organization. The name Harrison Shull certainly comes to mind. He saw more clearly than most other theoreticians that something needed to be done. Building on his foundation were all the chemists who contributed their programs to QCPE for distribution. Key points of Counts' philosophy were that ownership of these programs remained with the original developers and that the role of QCPE was to faithfully distribute and support source code.

In the question and answer period, someone in the audience, not visible from where the author was sitting, reminded the rest of the audience of the contributions of Drs. Howell and Prosser. The ACS symposium ended with a warm round of applause for Counts and the other speakers. Although Edwards was not able to attend the symposium, McKelvey was instrumental in getting a recognition award sent to her.

Measuring QCPE's Impact

It is not easy to quantify the positive effect that QCPE had on the growth of computational chemistry. In an attempt to obtain such a quantitation, we used a cheminformatics approach to search Google Scholar to find the number of mentions of "QCPE" that have been made each year. We also did an Advanced Search of publications of the American Chemical Society (ACS) on their website (*10*). Their database covers only ACS journal articles and books. Again, we looked for the term "QCPE" and determined the number of hits per year. The results are shown in Figure 18.

We see that occurrences of the term QCPE are more frequent in the Google Scholar search than in the ACS advanced search. The former covers publications by many science-technology-engineering-mathematics (STEM) publishers, whereas the latter covers journals and books of only one publisher, the ACS. A recent study found that by 2010, Google Scholar had been improved to the point of covering 98-100% of scholarly journals from both publicly accessible web contents and from subscription databases that were allowed to be "crawled" by Google (*11*). Another recent evaluation found that Google Scholar supplies 70-90% of the articles found by searching traditional databases of the scientific literature. At the same time, Google Scholar gives more hits than the other databases when looking for specific words (*12*).

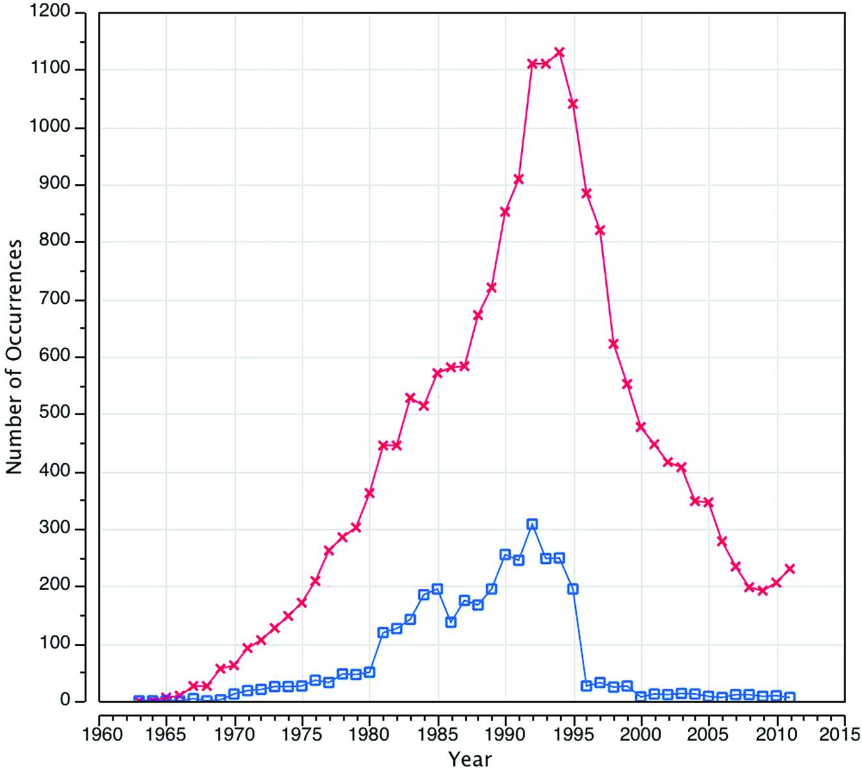


Figure 18. Annual number of times QCPE is found in searches of Google Scholar (red curve with data points marked by x's) and ACS Publications (blue curve with data points marked by squares). The upturn at the right end of the red curve is curious.

The author of this chapter had no preconceived notions about how much QCPE would be cited, but the numbers found from our approach are impressive. Both curves in Figure 18 show a growing impact of QCPE in the 1970s and 1980s. Both sets of data show a peak of citation in the early 1990s. The ACS-only curve shows a peak of about 300 occurrences of the term QCPE per year, whereas Google Scholar peaks at over 1100 mentions per year. Presumably many, if not most, of the mentions of QCPE occurred when researchers credited QCPE as the source of some program(s) they used in research being published. It is not uncommon for there to be a lag of several years between when some research is done and when it gets published. Even after QCPE ceased formal operations in the early 2000s, it continues to be cited in the scientific literature.

Winding Down

In 1994 when Hagstrom was retiring from Indiana University, some of the principal figures of QCPE returned to Bloomington for a happy reunion. Photographs from that reunion are shown in Figures 19-21.

Figure 19. Counts receives a visit from Hagstrom and Howell in the QCPE office. The photograph is courtesy of Drs. Howell and Hagstrom.

Figure 20. Howell, Prosser, and Hagstrom enjoy a reunion in Bloomington, Indiana. The photograph is courtesy of Drs. Howell and Hagstrom.

A theme sounded by the QCPE Advisory Board and others was that QCPE needed to adapt to new technologies and to bolster itself against two trends: the free, independent exchange of software between scientists and the commercialization of computational chemistry software. From an academic point of view, the development of convenient peer-to-peer (PTP) communication spelled the impending doom of a service like QCPE. PTP was made possible by the creation of the Internet and secure file transfer protocols. From an industrial point of view, information technology managers at companies (particularly pharmaceutical companies where many computational chemists were employed) felt safer obtaining software from commercial vendors with good salesmen and promises of complete technical support (at a high price).

Figure 21. Shirley Howell and Harrison Shull at Hagstrom's retirement party at IUB in 1994. When departmental secretaries were unavailable (back in the days of secretaries), Mrs. Howell assisted her husband Keith with one of the QCPE newsletters in the early 1960s. The photograph is courtesy of Drs. Howell and Hagstrom.

One of the reasons QCPE responded slowly to changes in technology was because Counts wanted to tailor QCPE's services to accommodate clientele in parts of the world that did not have e-mail and/or web browsers in the 1990s. He did adopt some advances in technology. In 1989, QCPE became reachable via e-mail over BITNET. Starting in 1993, QCPE made its catalog available by file transfer protocol (ftp) and began distributing software that way. Also in 1993, QCPE acquired an e-mail address on the Internet.

Density functional theory (DFT) calculations were increasingly used by chemists in the late 1990s and 2000s. DFT algorithms were being incorporated in well-known quantum mechanical and molecular modeling programs, but QCPE did not have many of the current ones with this functionality. Likewise the well-known molecular dynamics programs such as AMBER, CHARMM, etc., never were within the realm of QCPE. Although the consequences on QCPE are impossible to measure, the effect of not having these programs was surely not positive.

Whereas at one time 2000 members were receiving the *QCPE Bulletin*, the membership had slipped toward 1000 in the 1990s. These membership numbers do not fully reflect the number of people who saw the quarterlies, etc. Oftentimes one or two people at a university or company would be members of QCPE, and they would circulate the QCPE material to their colleagues or students. The issues of the *QCPE Bulletin* became thinner. Fewer programs were being deposited.

One may wonder if the people with power to control QCPE's destiny in the 1990s could have made more changes to adapt to the new technological and market environments. Were the policies at Indiana University conducive for QCPE to adapt? Was there benign neglect? Was there resistance to change? Was there unwillingness to take advice? Were bridges burned instead of built as individuals involved tended to protect their little empires? Was the culture within the IUB chemistry department sustaining? A few prominent faculty members left or had left IUB to find happier places to work. More than one departmental chairman, after his term of service, felt he had been, at best, unappreciated.

On the other hand, there is a consensus that the Internet was the primary factor undermining QCPE's role, and this wonderful technological advance came along regardless of any other factors affecting QCPE. Many people thought that QCPE had fulfilled its role (very admirably) and was simply no longer needed. One of the sad things about the pending demise of QCPE was that there would no longer a stable repository of computational chemistry software to serve worldwide users. This collection represented hundreds of thousands of line of source code, much hard work, and immense creativity and skill.

There were discussions between the people at IUB and Dr. Jan K. Labanowski, the creator and owner of the well-known Computational Chemistry List (CCL), which is based in Columbus, Ohio. The purpose of the discussions was to see whether the programs being held by QCPE could be made available to users through CCL. When university lawyers in Bloomington examined QCPE's operation, they were surprised that the ownership of the programs being distributed had always resided with the original programmers. This was a philosophy that Counts and the other project supervisors of QCPE had faithfully adhered to. The lawyers at IUB were worried that since the program ownership remained with the original authors, QCPE was not authorized to transfer most of its holdings to another entity. Only if the original author approved or had died might QCPE be able to turn over a program to another entity. Labanowski already had gained a well-known web presence and would have welcomed software from QCPE. However, no QCPE software was forthcoming.

In the late 1990s, the chair of the IUB chemistry department asked Dr. John Huffman, to be the faculty supervisor over QCPE. Huffman's official title was Director of Technical Services, which included responsibility for the machine shop, glass shop, mass spectrometry, duplicating, etc. Even in 1999 when Counts retired, software continued to be deposited in – and distributed by – QCPE, but at a slow and declining pace. The QCPE library was approaching 775 programs for mainframes and workstations, plus about 200 additional programs for desktop computing.

QCPE's budget was made a part of the chemistry department's budget. QCPE had been taking up much office space to store all the computers, copies of paper manuals, copies of catalogs, and so forth. QCPE's expenses for personnel, office space, and infrastructure were taken from QCPE's revenue. Another issue facing QCPE was the way Counts had organized the programs. Each program that was ported to a different machine was given a new QCPE number. Hence the same program had many different numbers. Counts could keep all of the different QCPE numbers and versions straight, but others had difficulty.

Dr. Marty Pagel, already Director of Information Technology and NMR for the chemistry department, volunteered to assist Huffman by handling QCPE's operations. In May 1999, Pagel and Ken DeHart joined the QCPE staff on an unofficial basis to become familiar with operating procedures and to assist with getting QCPE's infrastructure organized. When Counts retired from Indiana University on August 1, 1999, Pagel became Director of QCPE and DeHart became Systems Administrator of QCPE. Edwards continued working on an hourly basis until October 15, 1999 to assist with continuity. In mid-November, Kristine Schleede, an IUB business student, was hired on an hourly basis as Manager of Business Operations. She was good at getting things organized in a more business-like manner. Pagel assumed responsibility for maintaining the QCPE website, managing the archives, manuals, and catalogs, editing the *QCPE Bulletin*, validating new programs, and providing advice to QCPE clientele. DeHart and Schleede handled correspondence. Unfortunately, Pagel left IUB for another position in 2000. Schleede continued working for QCPE through 2001.

Before he left, Pagel produced an excellent status report on QCPE for the year 1999. The unpublished report is probably the last complete record of QCPE's operation. The report is very informative. QCPE operations were based on two Silicon Graphics Indigo (SGI) workstations, four IBM desktop machines, and two DEC computers. QCPE had received and distributed 963 different programs or program versions since its inception. Most, but not all, were in the form of source code. But due to changes in technology, only 276 programs were still operational and available for distribution. Two hundred of these programs were for UNIX workstations, 38 were for personal computers, 21 were for Macintoshes, and 17 were for Linux platforms. Seven new programs were deposited in QCPE in 1999.

On average, programs were being ordered at a rate of only about 12 per month. There were no statistics in Pagel's report about which were the most requested programs. Distribution of the programs was by ftp 72% of the time, 20% by mailing a floppy disk, 3% by mailing a tape, 3% via the QCPE website, 1% by email, and 1% by mailing a CDROM. In 1999, 48% of the QCPE customers were located in the United States (consisting of 38% academic and 10% commercial), 30% were located in Europe (22% academic, 8% commercial) and 22% were located elsewhere in the world (16% academic, 6% commercial). Fifty nine percent of the customers were paying by credit card, 34% were paying by purchase order, and 7% by check or wire transfer.

The last QCPE workshop was the one held in Sweden in 1991. The last printed issue of the *QCPE Bulletin* was dated May 1999. The catalog and a document about general information about QCPE procedures were made available on the website. The last QCPE Current Awareness Profile on Quantum Chemistry was distributed in June 1999. Declining revenues and high operating costs were problems. Back in the first quarter of 1996, revenues had been nearly $20,000. Over the next three years, revenues declined to less than $2000 per quarter. Thanks to Pagel's efforts at reducing expenses, QCPE's operating finances improved from a budget deficit of $4323 per month in January 1999 to a monthly profit of $1292 in December 1999. This was quite an achievement.

After Pagel departed, Dr. John C. Bollinger, a crystallographer at IUB, was recruited to assume the role of director of QCPE. He continued the operation and hired Mrs. Carolyn Huffman to replace Kristine Schleede who graduated in 2001. Bollinger was an expert in FORTRAN programming and did remedial work to get UNIX-based programs usable with LINUX. Bollinger eventually left IUB in 2007. Mrs. Huffman carried on QCPE activities. But due to university requirements, normal distribution of programs ceased with loss of a secure office to conduct QCPE business. Mrs. Huffman has been converting historical paper files, such as program listings, bulletins, and catalogs, to electronic Portable Document File (PDFs). Her goal is to deposit the remaining programs and the PDFs in the Indiana University Archives if permission can be obtained from the original authors or to return the files electronically to the authors, if possible.

In the early 2000s, programs were requested and distributed at a rate of about 15 per month. The molecular surface program (QCPE 429) was often requested in this period (at a rate of about 17 copies per year). Several inquiries about various QCPE programs still come in per month. Most of these inquiries come from Asia. Carolyn Huffman has carried on the operations of QCPE toward a responsible conclusion.

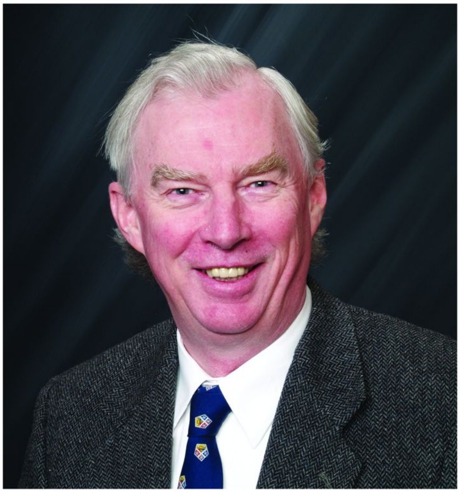


Figure 22. James J. P. Stewart, developer of MOPAC, the famous semi-empirical molecular orbital program. MOPAC was QCPE's most popular offering. The photograph is courtesy of Dr. Stewart.

We will miss the frequent interactions with Richard Counts, Peggy Edwards, and the others who have retired. These individuals as well as Howell, Prosser, and Pagel served with dedication and integrity. They cared about the mission of QCPE and tried to assist QCPE's clients to pursue their research goals. All the others, too numerous to mention, who were involved in QCPE, and especially all the individuals who generously deposited programs, deserve profound thanks. As we have seen from the citation data in Figure 18, their impact on science has been significant. The programmers and others associated with QCPE are to be lauded for their altruism. They and QCPE helped bring about the birth and development of computational chemistry. Dr. James J. P. Stewart (Figure 22) has rightly described QCPE as the "midwife of modern computational chemistry".

The Last Stanza

In this final section, we review the current status of some of the key players involved with QCPE.

Figure 23. Dr. Keith Howell and his wife reside in Norwich, England. The photograph is courtesy of Dr. Howell.

Dr. Harrison Shull went on to a successful career as an administrator in higher education. He was provost and vice president for academic affairs at Rensselaer Polytechnic Institute in Troy, New York from 1979 to 1982. He was chancellor of the University of Colorado at Boulder from 1982-1985. His final career move was to become Provost at the Naval Postgraduate School in Monterey, Calif. Shull retired in 1995. He died in July 2003 at the age of 79. His obituary mentions that he spent 24 years at IUB (*13*). Besides being a professor of chemistry during this time, he was dean of the Graduate School, one of the university's vice presidents, and head of the university's Research Computing Center. His idea for QCPE is listed as one of his major accomplishments.

The men who played a key role in getting QCPE's operations off the ground were Drs. Howell (Figure 23), Prosser (Figure 24), and Hagstrom (Figure 24). All are retired now. After Howell returned to England in 1965, he joined Imperial Chemical Industries (ICI), where he carried out operational research, which involved looking systematically at business operations as diverse as marketing budgets and warehouse layouts to optimize performance. Later he designed management information systems at ICI.

Prosser (Figure 24) had a successful career as a faculty member in the computer science department at IUB. Hagstrom (Figure 24) served full-time on the faculty in the chemistry department 1958-1972, became Associate Director of the computer center 1962-1972, and was a founding member of the IUB computer science department. In 1973-1994, he held a half-time appointment in computer science and half-time in chemistry. Although retired, Hagstrom continues to think about quantum chemistry and computers when he is not piloting a glider plane. He also thinks about what should be done about legacy software. Nothing has filled the void left by NRCC and QCPE.

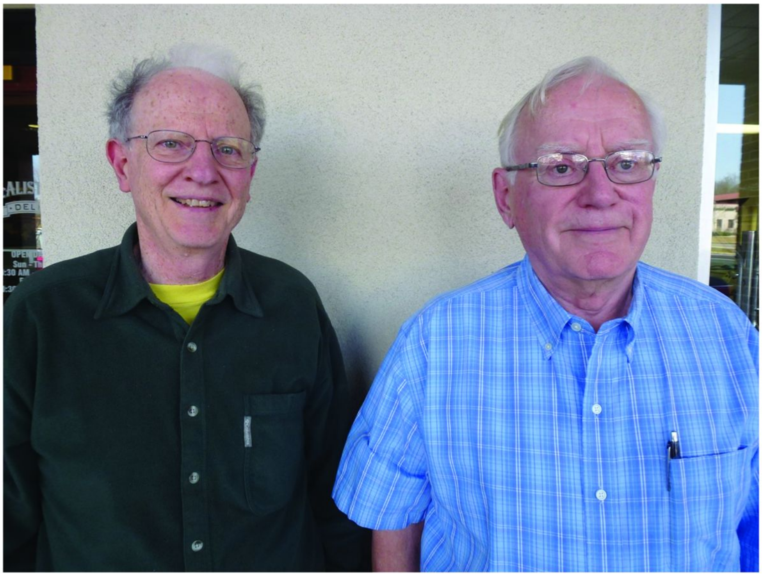


Figure 24. Dr. Franklin Prosser (left) is Professor Emeritus of Computer Science at IUB. Dr. Stanley Hagstrom (right) is Professor Emeritus of Chemistry and of Computer Science at IUB. Photograph taken by the author in Bloomington, Indiana in February 2012.

Figure 25. Mr. Richard W. Counts in the Indiana Memorial Union taken by Dr. Vera Mainz in February 2011 and reproduced here thanks to her kindness.

Figure 26. Dr. Margaret Edwards in her home in Bloomington. Photograph taken by the author in February 2012.

Theoretical and computational chemists throughout the world are indebted to Counts (Figure 25), who ran QCPE for 32 years. He retired at the end of July 1999. He was, understandably, less than pleased with the way things turned out. His longtime coworker, Edwards (Figure 26) officially retired from Indiana University at the end of 1998, but continued working for QCPE on an hourly basis until Dr. Pagel and coworkers were up to speed in 1999. It is a sad, lonely moment when someone turns out the light and exits the door to one's workplace a final time. Regrettably, no one had arranged a celebratory event or came to say thank you or give a little pat on the back. Counts and Edwards each continue to reside in Bloomington, a comfortable college town with many trees, low rumpled hills, and landscaped yards. Counts and Edwards and a host of others made QCPE successful at a time of critical need for such a service.

Besides his term as Director of QCPE in the 1980s, Professor Ernest Davidson (Figure 27) served as chair of the IUB chemistry department from 1999 until his retirement at age 65 in June 2002. His research activities continued at the University of North Carolina and the University of Washington. He is Professor Emeritus at both Indiana University and the University of Washington. He and his wife reside in Seattle. He is still an associate editor of the *Journal of Chemical Physics* and works out of his home office.

Figure 27. Professor Ernest R. Davidson receiving the National Medal of Science from President George W. Bush in the White House in 2002. Davidson's alma mater, Rose-Hulman, has pointed out that he was the first quantum chemist to receive the nation's highest award for lifetime achievement in the field of scientific research. The photograph is from Google Images and is available on the www.nsf.gov and www.rose-hulman.edu websites.

In 2007, Dr. John Huffman (Figure 28) retired from a highly prolific career as cystallographer. He still attends the annual staff dinners that IUB arranges. Like many chemists in his age bracket, he feels very fortunate to have had his career during a period when opportunities in chemistry were so great. Beyond being the last employee of QCPE, Carolyn Huffman continues to do QCPE-related work, mostly at their home. The purest and noblest form of service is working not for recognition, riches, or requirement, but doing it because it needs to be done.

Figure 28. Dr. and Mrs. John C. Huffman in their home in Bloomington. Carolyn still does QCPE related work. The photograph was taken by the author in February 2012.

Acknowledgments

The author acknowledges Dr. E. Thomas Strom (Department of Chemistry and Biochemistry, University of Texas at Arlington), who is Chair of the ACS Division of the History of Chemistry (HIST), and Dr. Vera V. Mainz (University of Illinois, Urbana), who is Secretary-Treasurer of HIST, for their encouragement to undertake this writing task. The author is also deeply appreciative to those who shared files and took time to respond to questions and correspondence. Mainz generously supplied material she collected for her talk at the 241st American Chemical Society National Meeting in Anaheim, Calif., March 27-31, 2011. The author is grateful to friends and colleagues at Indiana University: Roger E. Beckman (Head Librarian of the Chemistry and Life Sciences Libraries), Peggy Edwards, Stan Hagstrom, Carolyn Huffman, John Huffman, Dina Kellams (Associate Archivist), Max Marsh (retired from Lilly and IU), Frank Prosser, and Judi Roberts (Assistant to the Chair of the Chemistry Department) for their kind help. Keith Howell foresightedly preserved copies of the early QCPE Newsletters and shared those with the author. In addition, he saved and shared snapshots dating from his times at Indiana University including those for the retirement parties for Professors Hagstrom (1994) and Prosser (1999). Edwards, Carolyn Huffman, and Stewart generously shared photographs they had saved. The author appreciates the typescript of the 1994 talk from Richard Counts. The author also acknowledges Eric Snajdr (Assistant Librarian at the IUPUI University Library). Henry S. Rzepa kindly filled the author in on the QCPE workshops in the U.K. Ernest Davidson shared helpful insight. Many of the imperfections in earlier drafts of this chapter were fixed thanks to valuable input from Hagstrom, Counts, Edwards, Howell, Marsh, Stewart, Mainz, Strom, Davidson, Carolyn Huffman, and Susanne Boyd Esquivel.

References

1. Boyd, D. B. A tribute to the halcyon days of QCPE. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2000; Vol. 15, pp v−xi.
2. Boyd, D. B. How computational chemistry became important in the pharmaceutical industry. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Cundari, T. R., Eds.; Wiley-VCH: Hoboken, NJ, 2007; Vol. 23, pp 401−451.
3. Boyd, D. B. Prospects for career opportunities in computational chemistry. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Ed.; Wiley-VCH: Hoboken, NJ, 2011; Vol. 27, pp 369−394.
4. Boyd, D.; Switkes, E.; Newton, M.; Gerratt, J.; Palke, W.; Hegstrom, R.; Lipscomb, W. N. *QCPE Newsletter 15*; Chemistry Department: Indiana University, October, 1966; p 13.
5. Robinson, A. L. Plug pulled on chemistry computer center: After an unusually brief trial, NSF and DOE decide to phase out chemists' first try at big science, the National Resource for Computation in Chemistry. *Science (Washington, D.C.)* **1980**, *209*, 1504–1506.
6. Day, H. G. *The Development of Chemistry at Indiana University 1836-1991*; Published privately in Bloomington, IN, *ca.* 1991−1992 (no date or copyright in book).
7. *207th American Chemical Society National Meeting & Exposition Program*; American Chemical Society: Washington, DC, 1994.
8. *207th American Chemical Society National Meeting Book of Abstracts*; American Chemical Society: Washington, DC, 1994.
9. Shull, H. Ernest Roy Davidson as a student. *Mol. Phys.* **2002**, *100* (3), 331–333.
10. http://pubs.acs.org/search/advanced.

11. Chen, X. Google Scholar's dramatic coverage improvement five years after debut. *Ser. Rev.* **2010**, *36* (4), 221–226.
12. Walters, W. H. Comparative recall and precision of simple and expert searches in Google Scholar and eight other databases. *Libraries Academy* **2011**, *11* (4), 971–1006.
13. During the course of writing this chapter, the University of Colorado website with Harrison Shull's obituary changed from http://dirwww.colorado.edu/news/r/3b202799a7cac6804d964c8929abae10.html to https://www.cu.edu/sg/messages/2256.html.

Chapter 9

Molecular Orbital Theory for Organic Chemists

Andrew Streitwieser*

Department of Chemistry, University of California, Berkeley, CA 94720-1460
***E-mail: astreit@berkeley.edu**

In 1931 Erich Hückel published his treatment of benzene with a method now generally referred to as the Hückel MO (HMO) method. He showed how cyclic arrays of 2, 6 and 10 π-electrons form closed shells that provide enhanced stability. By the middle thirties he had applied his approach to other aspects of organic chemistry but thereafter did no further original work. Extensive theoretical and experimental work on his concepts was done by others. "Molecular Orbital Theory for Organic Chemists" was written a quarter century later and documented brilliant syntheses of new "4*n*+2" molecules as well as numerous applications of HMO theory to redox processes, aromatic substitution, carbocation and carbanion reactions, rearrangements, as well as "Frontier Orbital" perturbation approaches. The period reviewed developed predominantly the chemistry of π-electrons but was followed shortly after by various treatments of σ-electrons in what can now be recognized as the next era of quantum chemistry.

Erich Hückel

This chapter concerns the first few decades of quantum organic chemistry. The father of quantum organic chemistry is undoubtedly Erich Hückel (Fig. 1) who gave us the Hückel molecular orbital theory. Erich Hückel was an enigmatic personality and even though we now have several bibliographical studies about his life and work, some key parts of this life are still mysterious. His autobiography (*1*) written five years before his death, is available only in German; however, in 1977 he was elected as a foreign member of the Royal Society and on his death three

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

years later, Hartman and Longuet-Higgins, recognizing that his autobiography is in German, presented salient features of his life in their English memoir (*2*). Several years ago, Jerry Berson wrote a marvelous and perceptive article (*3*) about him. This article has since been expanded as a chapter in his book on chemical creativity (*4*). Gernot Frenking provided a review in German on the occasion of what would have been Hückel's birth centennial (*5*). Recently, a new biography appeared by Andreas Kalachalios (*6*) that reflects not only on his life but details his discoveries in the context of the chemistry and physics of his time.

Figure 1. Erich Hückel in 1938, age 42. (Reprinted with permission from ref. (1). Copyright 1975 Wiley-VCH Verlag GmbH & Co.)

A look at Hückel's earliest papers (*7–10*) shows that in the course of less than a decade he was involved in two of the important theories in modern chemistry. It is relevant that these are not so much theories as they are approximations or models; that is, both use severe approximations, some of which are difficult to justify, but give results in agreement with experiment and also lead to important insights.

His work on molecular orbital theory starts with his development of a quantum theory of double bonding published in 1930 (*9*). The late 1920s was a period of rapid and remarkable developments in quantum chemistry starting with the Heitler-London theory of bonding in 1927 (*11*). Hückel made effective use of many of these developments by others in his own work. His model for ethylene actually starts with Lennard-Jones' 1929 model (*12*) of oxygen with its two different types of O-O bonds, a σ bond and two orthogonal π and π* bonds. Lennard-Jones had shown how the application of Hund's Rule, which had previously been used only with atoms, to the degenerate π*-orbitals can explain the paramagnetism of oxygen. The two electrons available would singly occupy each of the degenerate π*-orbitals with the same spin.

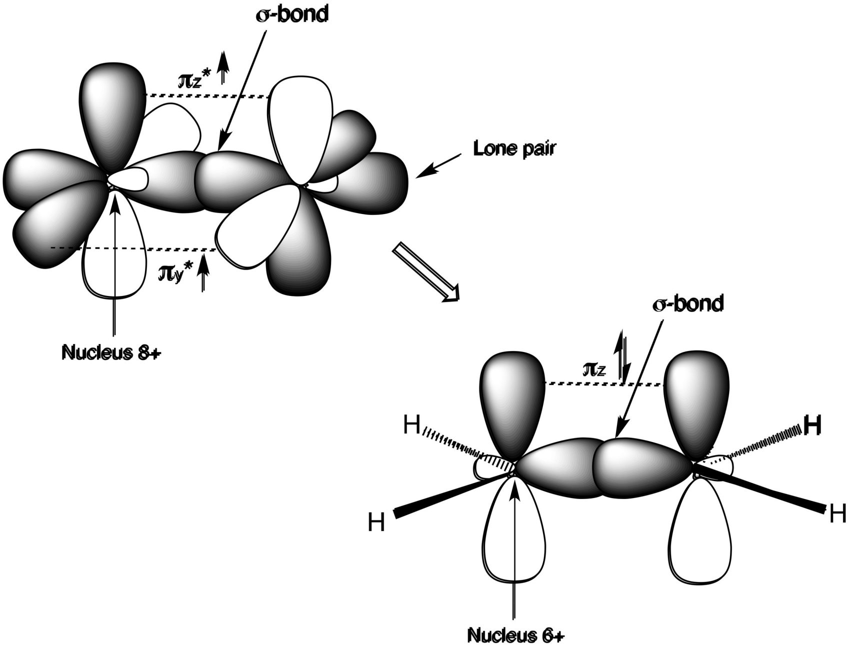


Figure 2. Hückel's derivation of ethylene from oxygen. The doubly occupied πy and πz orbitals are not shown for clarity.

Hückel applied a clever *gedanken* experiment (*13*) to this model of oxygen. As shown in Figure 2 he removed two protons from the nucleus of each oxygen (thus converting each to carbon) and using lone pair and π-orbitals converted them into C-H bonds. Doing this with one oxygen produces formaldehyde and with the second gives ethylene. That leads to two bonds between the carbons, one σ and one π. The two oxygen π*-electrons, no longer confined singly to a degenerate pair of orbitals, can now be put with opposite spin into the single ethylene π-orbital. The existence of the π bond rationalizes the known barrier to cis-trans isomerism in double bonds. Hückel was well aware of this feature and was intrigued by these two different types of bonds with their different symmetries with respect to the molecular plane. He sometimes called them electrons of type one and type two although the σ–π nomenclature had already been used by others (*14*) as well as by Hückel himself in his double bonding paper.

This work provided an important introduction to developing his model for benzene (*10*). He started with a planar hexagonal structure of benzene and treated the C-H and C-C σ electrons as localized and did not consider them further. The remaining π-electrons (x's in Figure 3) are *mobile* electrons that were then treated quantum-mechanically.

He used two methods. One derived from the Heitler-London approach and is now called Valence-Bond Theory. This method has important limitations and he preferred his second method, which we now refer to as the Hückel MO or HMO method. This method resulted in molecular states characterized by quantum numbers associated with nodes in the wave function. For quantum number zero there is a single state that can be occupied by two electrons and thereafter the quantum states are doubly degenerate.

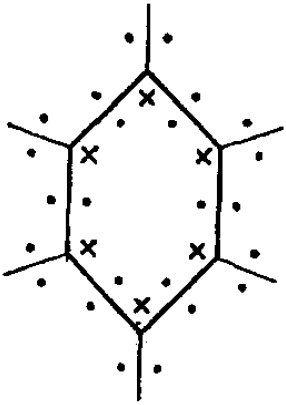


Figure 3. σ (dots) and π (crosses) electrons in benzene.

Thus, for quantum numbers higher than zero the states could be occupied by four electrons. He considered these states as shells and likened these 2+4=6e molecular states to the 2+6=8e shells in atomic structure. He recognized the important generality of this result, namely, that it provides not only an understanding of the stability of benzene but explains the importance of the aromatic sextet (*15*). The importance of a sextet of electrons, rather than the number of atoms in a ring, was already well known to organic chemists but no one understood what was unique about a sextet of electrons until the work of Hückel. In this way he explained the known relatively high acidity of cyclopentadiene. The corresponding seven-member cycloheptatriene is relatively non-acidic because its anion has a cycle of eight electrons and an unfilled shell. Cyclooctatetraene, which had been prepared by Willstäter (*16*, *17*) and shown to be a polyolefin, is also consistent with a non-aromatic cyclic octet of electrons. Hückel noted that Willstäter had tried and failed to prepare cyclobutadiene and he took this as further evidence that six electrons have unique aromatic character. He predicted that cycloheptatrienyl cation, with six π-electrons, would have relative stability and that cyclodecatetraene, with its 10 π electrons and filled shell, would be aromatic.

None of this distinctive chemistry came out of his first method, the Valence-Bond approach and, understandably, he much preferred his second method.

He put his work together summarizing many of his results in an important review article in 1937 (*18*). The following year his article was reprinted as a book (*19*). Although this work is available only in German, a look at the table of contents at the beginning shows that it covers a wide range of topics all the way from olefins and benzene and the applications of valence bond theory with its “mesomerie” or resonance to applications of his molecular orbital approach to benzene, heterocycles, poly-benzenoid hydrocarbons and even free radicals. The relative stability of triphenylmethyl radical was known and could be accounted for by Hückel. This amount of organic chemistry would be surprising for a physical chemist, much less a physicist! Erich Hückel, however, had an older brother, Walter (1895-1973), who became an important organic chemist in Germany; as early as 1927 he had accepted a call as extraordinary professor of organic chemistry at Freiburg (Breisgau). The brothers collaborated extensively at that time. Erich contributed to and helped write sections of Walter Hückel’s first edition of his two-volume work, “Theoretical Foundations of Organic Chemistry”, published in 1931 (*20*).

Up to this time, Erich Hückel himself had only temporary positions of various types but in 1938 he was appointed to the lifetime position of extraordinary professor of theoretical physics at the University of Marburg. Remarkably, following a decade and a half of astonishing creativity, after this 1937 work there is virtually nothing for the rest of his life - only a few publications and those mostly reviews. This is the Hückel enigma and is only partially explained in his autobiography and by others who have looked into his life. Contributing factors were probably a heavy teaching load, feelings about having to join the Nazi party and perhaps an intellectual isolation. His molecular orbital theory, however, was quickly taken up by others and many advances were made in the following years. Lennard-Jones used his method the same year in a study of bond distances compared to calculations (*21*). This work was also continued by Charles Coulson, who was a student of Lennard-Jones and by Longuet-Higgins, who was a student of Charles Coulson. Many developments of the theory and its applications subsequently came from England and other parts of the world, notably France and the US, but interestingly, not until much later in Germany. Hückel himself thought part of the problem was the German academic culture.

He was a physicist and therefore chemists paid no attention to him but he was a physicist who did chemistry so physicists were not interested. In other parts of the world the new area of chemical physics was coming into vogue but this did not happen in Germany until much later.

Charles A. Coulson

Charles Coulson is arguably the single most important person responsible for the development of Hückel molecular orbital theory during the 1940's. Two thorough biographies of Coulson are available. One is his memoir as a Fellow of the Royal Society (*22*) and the other is a more recent chemical history review (*23*). Both discuss his personal life as well as his scientific contributions so only a few highlights will be mentioned here.

Charles Alfred Coulson was born in Dudley, England on December 13, 1910. In 1928, he entered Trinity College, Cambridge, in mathematics but took courses also in chemistry, physics, and quantum mechanics. This combination of interests was to persist his entire life; that is, he was really a mathematician, or more accurately, an applied mathematician, but his research interests were in physics and chemistry. His important scientific contributions thus involved the application of applied mathematics to quantum mechanics and quantum chemistry. To Coulson, chemistry was a part of physics.

He remained at Cambridge for his Ph.D., working first with the physicist Ralph H. Fowler and then with John E. Lennard-Jones, who occupied the first chair of theoretical chemistry in England. Coulson's dissertation on molecular orbital theory and electronic structure already shows the direction of his subsequent scientific career.

After Cambridge, Coulson spent several years as Senior Lecturer in Mathematics at Dundee, Scotland. He carried a heavy teaching load because many of his colleagues were away at war. He became a conscientious objector; he was active in the Methodist Church and religion was an important part of his life. He spoke and wrote extensively on science and religion over the rest of his life. The Dundee period was also difficult because of the virtual absence of research students. Nevertheless, with a graduate student, C. S. Rushbrooke, he did publish a significant paper (*24*) on the special properties of molecular orbitals of what were later called *alternant hydrocarbons*, those having no odd-membered rings.

In 1944, Coulson left Dundee for Oxford where he started a research group of chemists and physicists. It was here with Longuet-Higgins that he produced a series of five papers in 1947-8 on the general theory of molecular orbitals (*25–29*). These are probably the most important papers on the HMO method published since the work of Hückel himself. After five highly productive years as Professor of Theoretical Physics at King's College, London, he returned to Oxford in 1952 as the Rouse Ball Professor of Mathematics. He played an important role in developing the new Mathematical Institute and its new building that opened in 1966.

I had met Charles Coulson briefly in 1966 and in 1969 spent a sabbatical month in Oxford with him. He was a kind and gentle man and very considerate of others. He was a Fellow of Wadham College and I remember his taking me on a tour of the college and telling me proudly about its history and the many famous people who were previous Fellows.

In 1972, Coulson was appointed to the newly created chair of Theoretical Chemistry at Oxford, sadly just two years before his premature death from cancer in 1974.

Molecular Orbital Theory for Organic Chemists

In 1961, Jack Roberts and I both published books on molecular theory for organic chemists (*30*, *31*). Although there were some earlier books by others on quantum organic chemistry, our books had an enormous impact and probably helped to train an entire generation of organic chemists in molecular orbital theory. The two books came out at a propitious time, a quarter century after Hückel's work. This was also a critical point in the history of quantum organic chemistry. Up until then this chemistry had dealt almost entirely with π-electronic systems. Extensive work with σ-electrons only came afterwards, in the decade of the 60's, with the Extended Hückel Theory as developed by Roald Hoffmann (*32*) and the all-electronic semiempirical methods CNDO, INDO, etc., introduced by John Pople (*33*, *34*). Equally important, of course, was the development of *ab initio* methods with the increasing power of computers that started in the late 1960s.

Both of our books have a common origin. My introduction to Hückel first came from my Ph.D. work with William von Eggers Doering during my last year at Columbia in 1950-1951. In one of our group meetings, Doering presented some results of Hückel Theory, in particular the $4n+2$ rule and its implications that he in turn had learned from George Kimball, a physical chemist at Columbia at the time. Although Doering understood the degenerate energy pattern that led to $4n+2$, he did not know its theoretical origins. He complained that his own mathematical background was not sufficient to allow him to really understand the theory (*35*). I was no help because when I was supposed to have learned about molecular orbital theory from Kimball's course, the year I took his course he talked instead about a semi-classical model he was working on for the hydrogen molecule. That model went nowhere and this part of his course was a total waste of time.

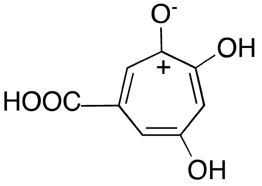
This changed, however, when I went the following academic year to John D. Roberts for my postdoctoral year at MIT. Jack Roberts was also interested in MO theory and was particularly intrigued by a book that Dewar had recently published on the electronic theory of organic chemistry (*36*). It was frustrating for Jack that, although in his book Dewar promotes MO theory with many applications to chemistry, he gave no information about how one actually does these calculations. Available sources in 1951 were also not useful. The English translation (*37*) of Syrkin and Dyatkia's "Structure of Molecules and the Chemical Bond" was published in 1950 and would have been useful, but we were not aware of it at the time. Later, in 1952, the Pullmans' book (*38*) "Les théories électronique de la chimie organique," gave a complete account of both the Valence Bond and HMO methods. Coulson's popular book on "Valence" also appeared in 1952 (*39*), a few months too late to be helpful to us. Fortunately for us, as Roberts points out in his chemical autobiography (*40*), he was able to get personal instruction from his physical chemistry friend Bill McMillan. Then, knowing that the best way to learn something is to teach it, Jack in turn taught the theory to several coworkers who formed a seminar group. I was an eager member of this group and learned by doing a number of calculations using a Marchant electric calculator available to us. Jack and I together with Clare Regan, who was also part of the group, published an article with a number of calculations of compounds with small-membered rings that have intriguing properties (*41*).

Jack moved back to Caltech in 1953. He taught the HMO method in his course to seniors and graduate students and then converted his notes to a book. In the summer of 1952 I had moved to Berkeley and several years later I was invited to give a short course on the molecular orbital method at the Shell Development Company in the nearby town of Emeryville, California. I prepared an extensive set of notes for this course and it was suggested that I convert them to a book. I did so during a Sabbatical in Residence during 1959-60. And so we ended up with two books, but two quite different books, more complementary than competitive.

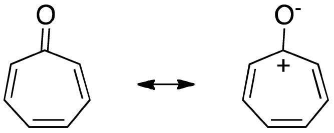
Jack's book (*30*) "Notes on Molecular Orbital Calculations," is a "practical introduction" explaining how to do Hückel calculations with several worked-out examples and applications. My book (*31*) "Molecular Orbital Theory for Organic Chemists," is a more complete monograph that includes a review of the results of many others with extensive literature references. By 1960 a great deal had been done experimentally and theoretically by many contributors. It is useful to divide these developments into four topics: the $4n+2$ rule, the properties of molecular orbitals, the properties of single MO's and the use of total π-energies.

4*n*+2 Rule

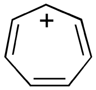
The mid-twentieth century marks the beginning of a spectacular era of synthetic organic chemistry related to what is now generally referred to as the Hückel $4n+2$ rule. The several examples of this rule known to Hückel expanded to a wealth of chemistry by the time of Roberts' and my books. I like to start this era with Dewar's brilliant derivation of the structure of stipitatic acid **1** just from data reported in the literature (*42*). Dewar did not note the presence of the tropylium cation ring system but did recognize that this system appears to have aromatic character. The parent molecule tropone **2** was synthesized independently by Dauben and Ringold (*43*) and by Doering and Detert (*44*). Both groups recognized that the polarized resonance structure **2b** contains a tropylium cation **3**, a $4n+2$ cycle, that contributes more importantly to the resonance hybrid than normal ketones. In fact this is an interesting use of the $4n+2$ rule; that is, the implication is that those structures that conform to the rule have higher weight in the resonance structures of qualitative valence-bond theory. In accord with this principle, tropone has an enhanced dipole moment compared to normal ketones.



1

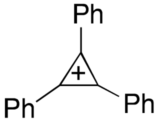


2a **2b**



3

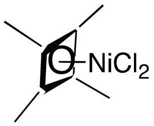
Three years later Doering and Knox (*45*) synthesized the tropylium cation **3** itself and showed that it has remarkable stability; it could be isolated and characterized as crystalline salts. The decade of the 50's also brought the synthesis of the first cyclopropenyl cation (a 4*n*+2 cycle with *n* = 0) derivative, triphenylcyclopropenyl cation **4**, by Breslow and Yuan (*46*). They also were able to obtain it as stable crystalline salts. Several years later the Breslow group was able to isolate salts of the parent cyclopropenyl cation **5** itself (*47*, *48*).



4

5

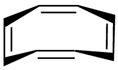
6



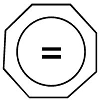
7

Cyclobutadiene **6** was known for some time to be an unstable molecule that readily dimerizes. It could, however, constitute a ligand in organometallic structures as shown by the compound **7** synthesized by Criegee and Schröder in 1959 (*49*, *50*). Cyclobutadiene itself was prepared in 1965 by the Pettit group but not isolated (*51*). Isolation by photolysis in an argon matrix at low temperature was achieved independently by the Krantz (*52*, *53*) and Chapman (*54*) groups in 1972-3. The polyolefinic character of Willstätter's cyclooctatetraene was so different from benzene that his synthesis was questioned. The synthesis, however, was confirmed by Cope and Overberger (*55*) and cyclooctatetraene also became available in quantity from acetylene with Reppe's catalytic process (*56*).

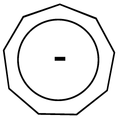
Although cyclooctatetraene **8** itself is a typical polyolefin, it adds two electrons at the dropping mercury electrode at a relatively low potential. Katz (*57*) was able to prepare cyclooctatetraene dianion **9** as alkali metal salts and showed it to be planar despite the angle strain involved. Somewhat later Katz and Garratt (*58*) synthesized the corresponding cyclononatetraenyl anion **10**, another 10-electron π-system that's also remarkable stable.



8

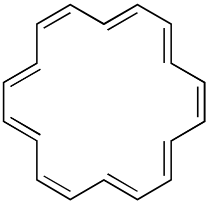


9



10

During the 1950's, Sondheimer (*59*) began his classic work on the higher annulenes, monocyclic C_nH_n compounds with formal alternating single and double bonds. [18]-Annulene, **11**, for example, was shown later to have aromatic character.



11

Cyclodecapentaene was predicted by Hückel to be a 10-π electron aromatic system but this prediction would only apply to a planar molecule. Two stereoisomers of such [10]-annulenes were prepared by the Masamune group (*60*) in the early 1970's and were found to be highly unstable and non-aromatic in character and also nonplanar. A planar [10]-annulene apparently incorporates too much ring strain to compete with nonplanar conformations.

These various brilliant and prolific studies renewed interest in the whole subject of aromaticity and led to further work on so-called pseudo-aromatic compounds and non-benzenoid aromatics. An example is the subsequent use of ring currents as measured by NMR chemical shifts as a measure of aromaticity. Aromatic compounds can sustain a magnetically induced ring current that has measurable effects on chemical shifts (*61*). By this means, [14]- and [18]-annulenes were shown to be aromatic, whereas [16]-annulene, a 4*n* system, is not (*62*). These studies also led to interesting concepts, such as the symmetrical hexagonal structure of benzene stemming primarily from σ−electrons rather than π (*63*, *64*). Within a few years of our books there were two international conferences, in 1966 (*65*) and 1970 (*66*) devoted to aromaticity as well as several books on the subject (*67*, *68*). Interest in this topic continues: at the start of the present century, in 2001, a whole issue of *Chemical Reviews* was devoted to the subject (*69*).

Properties of MOs

A number of applications of Hückel molecular orbital theory relate to properties derived from the wave function. Many of these are now of only historical significance such as Free Valence, atom-atom, atom-bond and bond-bond polarizabilities, the so-called Superdelocalizability, etc. An example is the early work done with the bond order defined by Coulson (*70*) in 1939 as a product of the coefficients of bonded atoms in occupied molecular orbitals. It was thought that there should be a correlation between the bond order and bond distance and one could see that there should be some sort of relationship of this sort; for example, if there is a node between two atoms, this would be an anti-bonding situation. The two coefficients have opposite sign and would subtract from the bond order. Even in 1960 there were a number of X-ray crystal structures of a variety of polycyclic aromatic hydrocarbons and accordingly many bond distances were known experimentally that could be compared with the calculated bond orders to give a correlation such as that shown in Figure 4. One can see that there is a general trend that the higher the bond order the shorter the bond distance but it's a pretty rough correlation with a low correlation coefficient of $R^2 = 0.79$.

It's furthermore interesting that modern *ab initio* methods are hardly any better. Using the same data as in Figure 4, Hartree-Fock calculations with the 6-31G* basis set gives the results in Figure 5, which have no better quantitative predictive value. It should be emphasized, however, that the total range of bond distances involved is barely more than 0.1 Å.

None of these methods has turned out to be of particular importance.

Total π-Energies

In the early history of Hückel molecular theory there was much qualitative chemistry that gave good agreement between experiment and theory but what was lacking were quantitative data suitable to provide numerical tests of the theory. In the 1950s a number of groups were developing such experimental quantitative measurements of aromatic compounds. The general idea was that if we divide their electronic structures into σ and π systems and if the σ-energy changes in a given reaction or process are relatively constant then the differences would be entirely due to the π-electrons which could in principle be computed. One of the first of these quantitative tests was published by me in 1952 while I was at MIT. Jack Roberts would frequently attend the seminars of Paul Bartlett's group at Harvard and would take his postdocs with him. At one of these seminars Norman Lichtin, who had recently joined the faculty at Boston University, told about his work on the ionization dissociation of triarylmethyl chlorides in liquid sulfur dioxide (*71*, *72*).

$$\mathrm{Ar_3CCl} \xrightleftharpoons{\mathrm{SO_2}} \mathrm{Ar_3C^+} + \mathrm{Cl^-}$$

I recognized that this work provides the quantitative type of experiment needed to test MO theory because one could calculate the change in π-energy going from the individual aromatic rings to the triarylmethyl cation. These are big molecules and all of the calculations were done by hand using just an electric calculator but I got the results shown in Figure 6 (*73*). There is a smooth correlation for most of the compounds but the correlation is not linear. One could argue that this is not the best example to use because the triarylmethyl cations are not fully coplanar and no correction was included for this factor. Nevertheless, the result was promising.

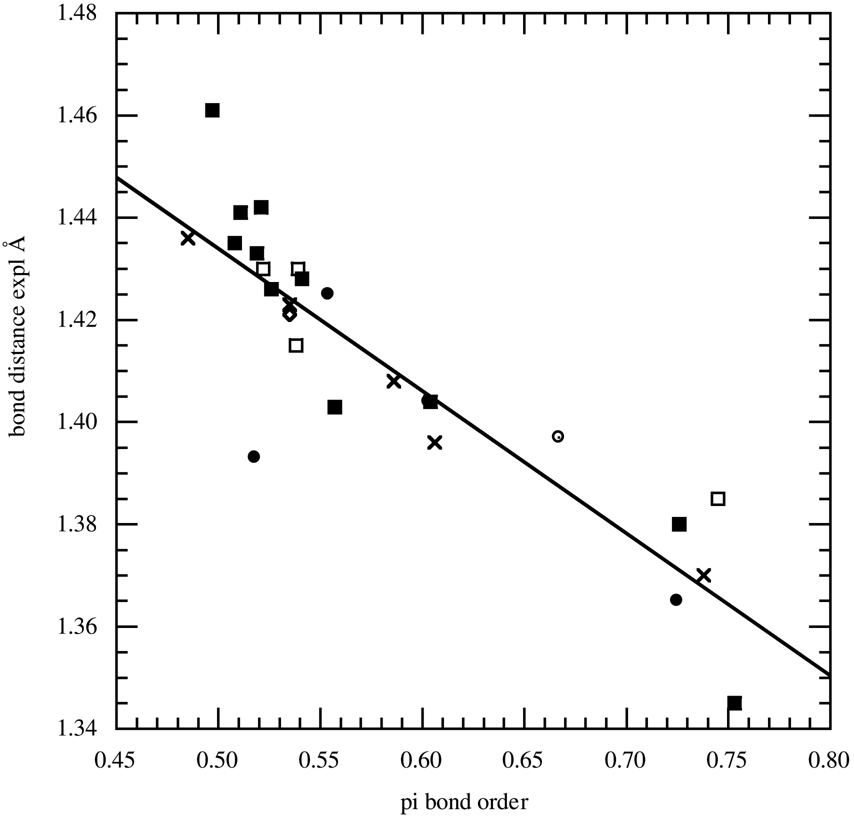


Figure 4. Experimental bond distances of aromatic hydrocarbons compared to the HMO pi-bond order. Points are: open circle, benzene; filled circles, naphthalene; x, anthracene; open squares, coronene; filled squares, ovalene; triangle, graphite. The correlation line shown is: 1.573 ± 0.017 - (0.278 ± 0.029)x; R^2 = 0.79.

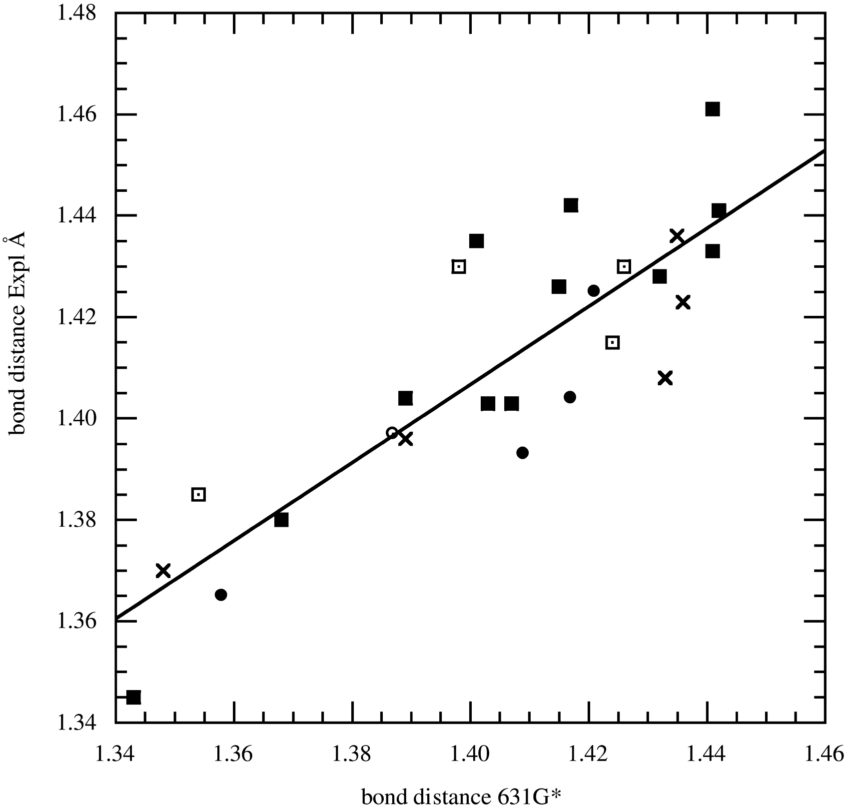
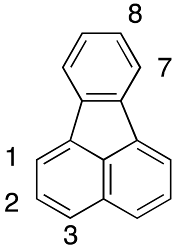
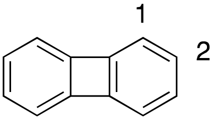


Figure 5. Experimental bond distances of aromatic hydrocarbons compared to 6-31G computed values. Points have the same meaning as in Figure 4. The regression line shown is: 0.328 ± 0.131 + (0.771 ± 0.093)x; R^2 = 0.74.*

Electrophilic aromatic substitution was a popular topic at the time looking at orientation effects, for example, in nitration or chlorination. The formation of a new σ-bond between the electrophilic reagent and the aromatic ring disrupts the conjugation of the π-system. The corresponding change in π-energy was recognized by Wheland (*74*) in 1942 to be a model for aromatic substitution and was later named the *localization energy* by Brown (*75*). For example, the localization energy of benzene is the difference in π-energy between benzene and pentadienyl cation. Localization energies accounted *qualitatively* for orientation effects in aromatic substitutions but for *quantitative* tests we and others looked at reaction rates. Dewar, for example, determined relative rates of nitration for a number of polycyclic aromatic hydrocarbons (naphthalene, phenanthrene, triphenylene, etc) and compared the results with HMO theory (*76*). We added nitration rates for fluoranthene (*77*) to give the correlation shown in Figure 7. The correlation shows a general trend but is at best only fair. Fluoranthene **12** has an odd-membered ring and is a so-called *non-alternant hydrocarbon,* but fits in just as well with the other *alternant systems*.



12



13

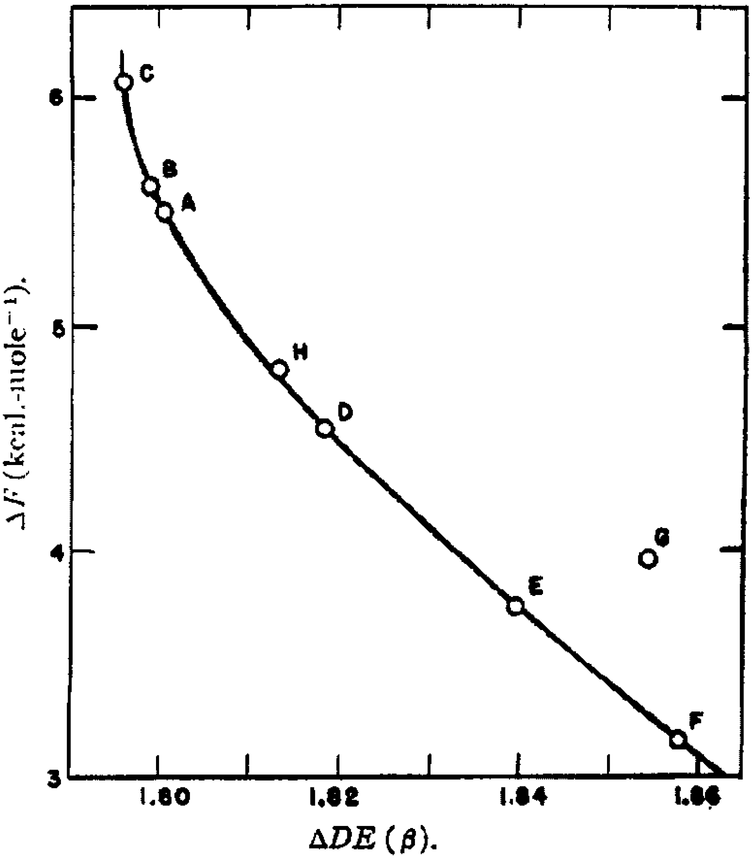


Figure 6. Correlation of ionization equilibria of triarylmethyl chlorides in liquid sulfur dioxide with difference in calculated Hückel π−energies. Letters refer to different compounds in which the Ar groups are phenyl, biphenylyl and naphthyl. (Reprinted with permission from ref. (73). Copyright 1952 American Chemical Society.)

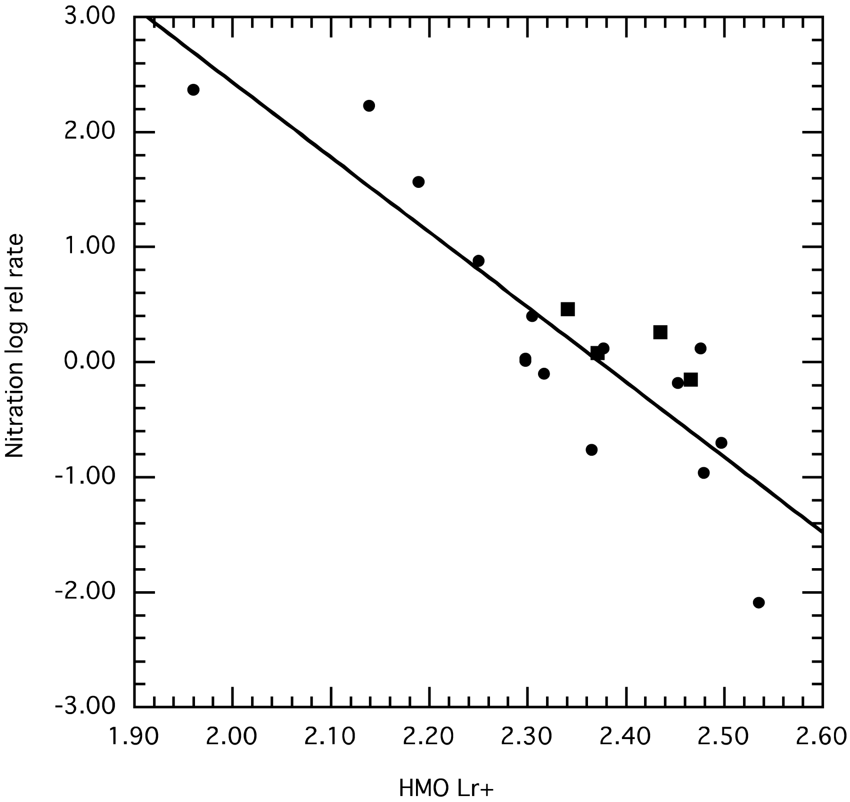


Figure 7. Nitration in acetic anhydride at 0°C compared to HMO localization energies, Lr+. The regression line shown is: 15.47 ± 2.06 - (6.52 ± 0.88)x; R^2 = 0.77 . The squares are fluoranthene positions.

Later, we used rates of the acid-catalyzed protodetritiation of tritium-labeled aromatic compounds (*78*). This method allows more accurate partial rate factors and extension to a wider range of reactivities, but just emphasized the limitations of the HMO method for such quantitative correlations (*79*). Qualitatively, however, it has some notable successes. For example, it successfully predicts that the 2-position of biphenylene **13** is more reactive than the 1-position, in contrast to naphthalene (*80*).

Other attempted quantitative applications fare no better. For example, the study of solvolysis reactions was also quite popular in the 50's. A number of groups studied the use of polycyclic arylmethyl halides and their solvolysis reactions that would give transition structures resembling carbocations that could then be compared to a HMO model. For benzyl itself, the corresponding π-energy change would be that of benzene going to benzyl cation. Dewar, for example, studied solvolysis in formic acid. He was able to interpret effects of structure and solvent with HMO theory but quantitative correlations were not good (*81*).

Successful qualitative interpretations but poor quantitative correlations were not uncommon with HMO theory and demonstrate that the whole approach of using total π-energy differences is too simplistic. These methods are now just of historical interest because such correlations are now done entirely by ab initio methods. Nevertheless, the π–approach can sometimes lead to interesting insights. For example, while rereading parts of my book for the first time in years in preparation for this symposium, I came across a footnote I had completely forgotten about (*82*). Consider the orbital picture of an S_N2 reaction at the bottom of Figure 8.

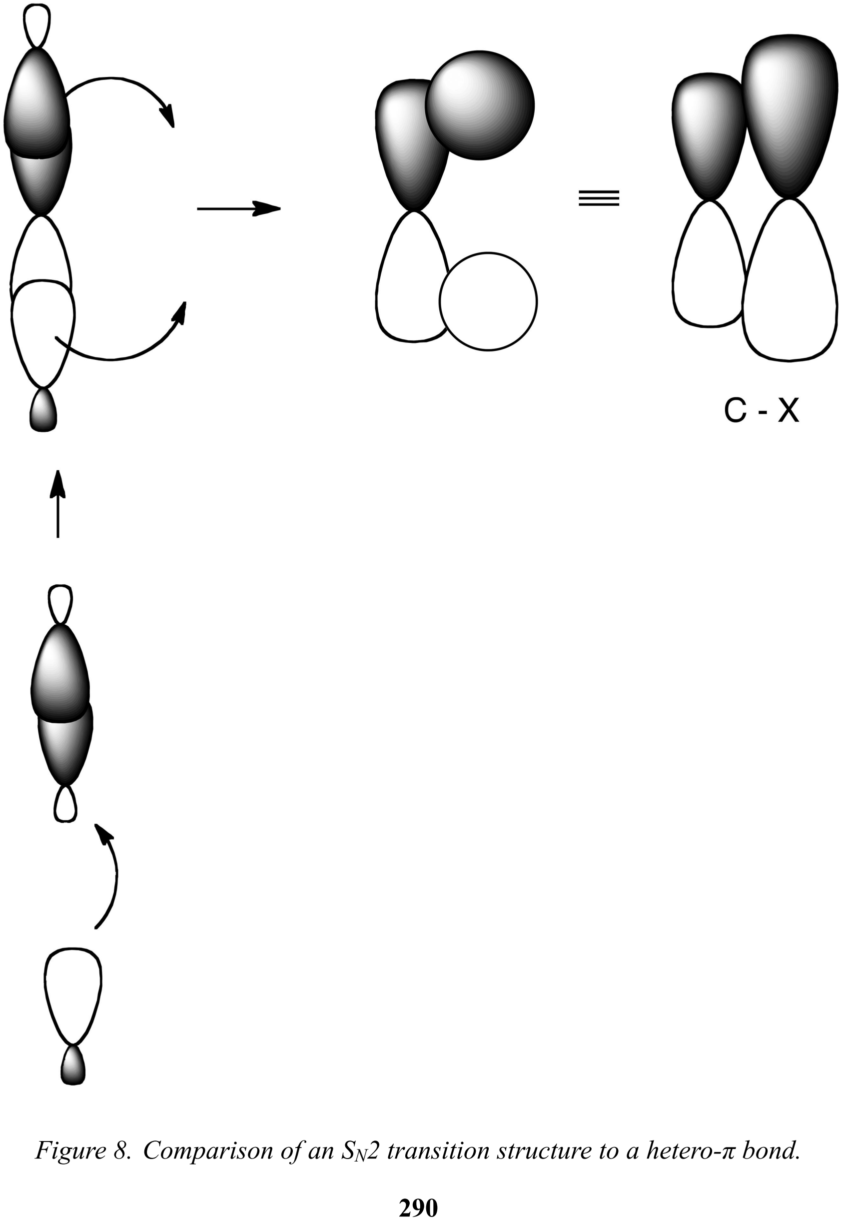


Figure 8. Comparison of an S_N2 transition structure to a hetero-π bond.

An incoming nucleophile gives rise to the three-center transition state shown. If we move the orbitals from the incoming and leaving groups to the side, the result has the symmetry of a p-orbital and the picture is that of a C-X π-bond. We might then expect a relationship between the formation of the S_N2 TS and the energy of a C-X π-bond. Data in my book were given for the reaction of arylmethyl chlorides with KI and the reduction potentials of aromatic aldehydes. Comparing the two in Figure 9, we find an excellent correlation, one that might not be expected in the absence of this type of analysis.

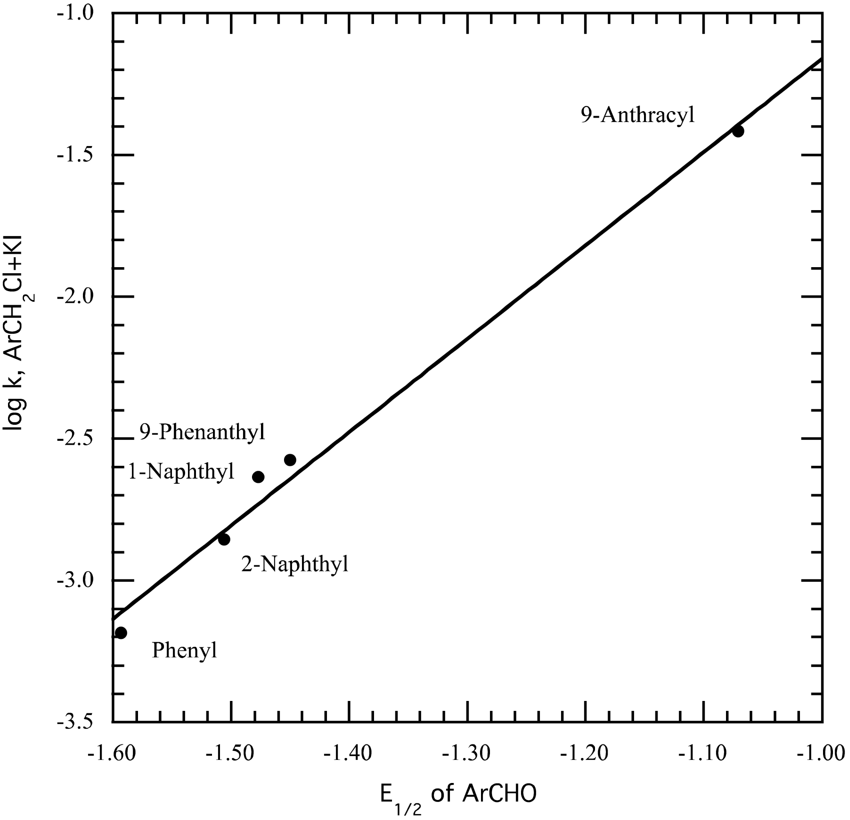


Figure 9. S_N2 reactivity of arylmethyl chlorides compared to the reduction potentials of the aryl aldehydes.

Individual MOs: HOMO and LUMO

This point is further emphasized by the applications of individual MOs, and, in particular, the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO). In 1949, Maccoll (*83*) showed that the polarographic reduction

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

potentials of several conjugated hydrocarbons are linearly related to the energy of the HMO LUMO; the lower this energy, the easier it is to add a electron to give the reduced compound. This work was rapidly confirmed by others, and in my book the linear correlation had been expanded to 50 compounds. Maccoll had also suggested that the theory could be applied to dissolving metal reductions. Indeed, in the Birch reduction (*84*) “the positions occupied by the two incoming hydrogens can be predicted to a remarkable degree by HMO theory.” Many examples were cited in my book.

The energy required to remove an electron from the HOMO by Koopmans’ theorem (*85*) is the ionization or oxidation potential. In 1958, Hoijtink (*86*) showed that there is an excellent correlation of the polarographic oxidation half-wave potentials of a number of polycyclic aromatic hydrocarbons with the energies of their HOMO as shown in Figure 10.

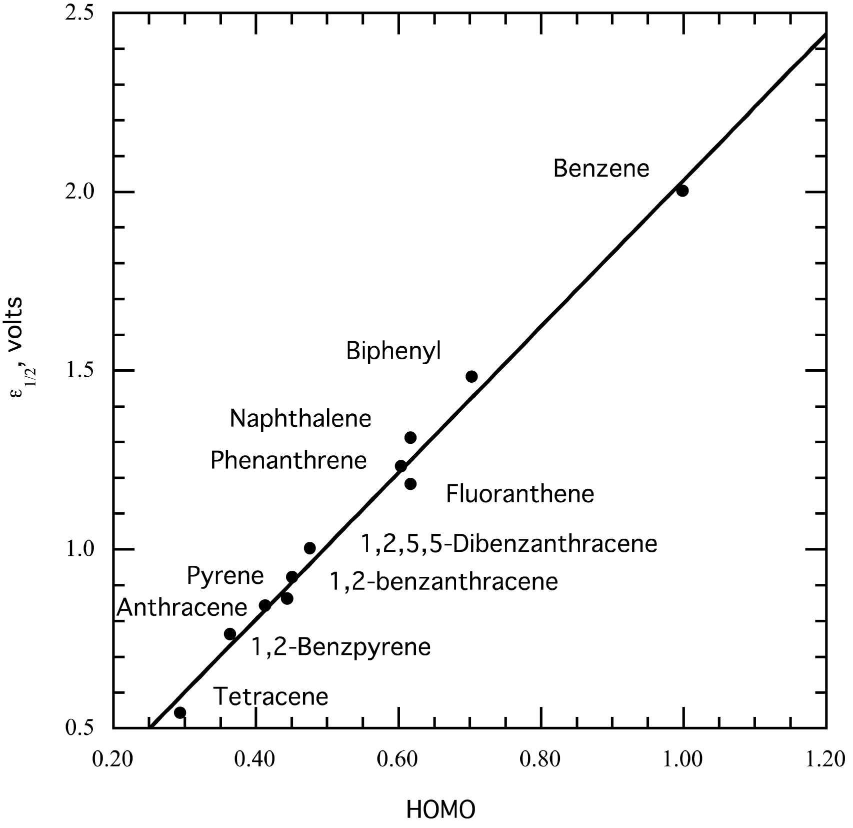


Figure 10. Polarographic half-wave potentials vs HMO HOMO. Regression equation is: -0.013 ± 0.042 + (2.047 ± 0.073)x; $R^2 = 0.99$.

Excited states are normally not well represented by single electronic configurations. Nevertheless, many electronic transitions in polyenes, unsaturated carbonyl compounds, polycyclic aromatic hydrocarbons and various carbocations and anions can be approximated as transitions of an electron from the HOMO to the LUMO and give excellent correlations of absorption frequency with the HMO HOMO-LUMO energy differences.

These are energy levels within the same molecule. In 1948, Benesi and Hildebrand (*87*, *88*) reported the formation of a complex between aromatic hydrocarbons and iodine that give rise to new absorption bands. Shortly thereafter, Mulliken (*89–91*) recognized these complexes as examples of a general class of Donor-Acceptor or Charge-Transfer complexes that he described in terms of the two resonance structures **14A** and **14B** in which 14B is a structure with some electron transfer from the donor D to the acceptor A. An absorption band is then associated with the excitation from a ground state dominated by **14A** to an excited state in which **14B** dominates.

$$\mathrm{D{:}\ \ A} \quad \longleftrightarrow \quad \mathrm{D^{\cdot +}\,A^{\cdot -}}$$

14A **14B**

McConnell, Ham and Platt (*92*) then showed that the ease of charge transfer and therefore of the frequency of the C-T absorption band depends on the ionization potential of the donor and electron affinity of the acceptor. A few years later Bhattacharyu and Basu (*93*) showed that the absorption frequency of the complexes of polycyclic hydrocarbons with iodine correlate well with the HOMO of the hydrocarbons.

By the early 1960's a number of such D-A complexes were recognized, often with acceptors containing several electron-attracting groups; e.g., trinitrofluorenone and tetracyanoethylene (*94*). Other results have turned out to be quite general, namely, that the stability of the D-A complexes and their absorption bands depend on the HOMO of the donor and the LUMO of the acceptor. Note the comparison with the absorption spectra of the hydrocarbons themselves – with the complexes the HOMO and LUMO pertain to different molecules albeit in close association.

A question that this discussion raises is: "Why is the use of the HOMO and LUMO so much better than the total π-energy?" The answer is probably that the important attributes used in the HOMO and LUMO are the nature, character, and symmetry of the nodes and therefore on the bonding, anti-bonding and non-bonding relations among the orbital centers and that these attributes are given correctly even by simple theory. This aspect subsequently achieved great importance in such applications as the Woodward-Hoffmann rules and frontier orbital treatments of reactions.

Aftermath

The development in the early 1960's of an Extended Hückel Theory (EHT) by Hoffmann (*32*) and of the CNDO, INDO and NNDO semi-empirical SCF methods of Pople, et al (*33*, *34*, *95*) extended MO theory to σ−electrons. Computers had reached the development that even *ab initio* calculations were being undertaken (*96*).

Pericyclic reactions are a special class of reactions whose transition states involve the interation of orbitals in a cycle that resemble the types of system to which the 4*n*+2 rule applies. Stereochemical aspects of such cyclic arrays are dependent on the presence of 4*n* or 4*n*+2 electrons and form the basis of the Woodward-Hoffmann rules that were first published in 1965 (*97–99*). The rules can also be derived from the principle that orbital symmetry is preserved during the course of a concerted reaction (*100*, *101*).

Included in this class of reactions are some that are important in organic synthesis such as Diels-Alder and 1,3-dipolar (*102*) cycloadditions, Cope and Claisen rearrangements and some ring-opening and closing reactions. All of a sudden, synthetic organic chemists needed to know some organic quantum chemistry in order to understand the stereochemistry of such reactions.

More incentives followed in short order. Many reactions can be considered as having donor-acceptor character. Examples are any reaction of a nucleophile (donor) with an electrophile (acceptor) (e.g. S_N2 reactions, aromatic substitution, carbonyl additions, etc.) as well as some Diels-Alder reactions. Reactivity, regiochemistry and stereochemistry can often be correlated with the properties of the appropriate HOMO and LUMO. These are also the *Frontier Orbitals* of Fukui (*103–105*) and their importance can be rationalized by simple perturbation theory as follows (*106*, *107*):.

The transition state for the reaction of atom *r* in R with *s* in S is treated as a perturbation, H_{rs}. The energy change for each MO in R is then given by equation 1.

$$\Delta\varepsilon_{\iota} = \sum_{\kappa}^{\substack{\text{unoccupied}\\ \text{MO of S}}} \frac{(c_{ir}\, c_{ks}\, H_{rs})^2}{\varepsilon_{\iota} - \varepsilon_{\kappa}} \qquad \text{eq. 1}$$

A similar expression is given for the MO's in S. The summation is taken over the unoccupied MO's of S because for each such term between *r* and an occupied MO in S there is a comparable term between *s* and an occupied MO in R with a reversed sign in the denominator. These terms cancel as shown in Figure 11. Only the interactions between occupied and unoccupied MO's lead to a net reduction in energy. If R is a donor and S is an acceptor the denominator in equation 1 is smallest between the HOMO of R and the LUMO of S and is the strongest stabilizing interaction.

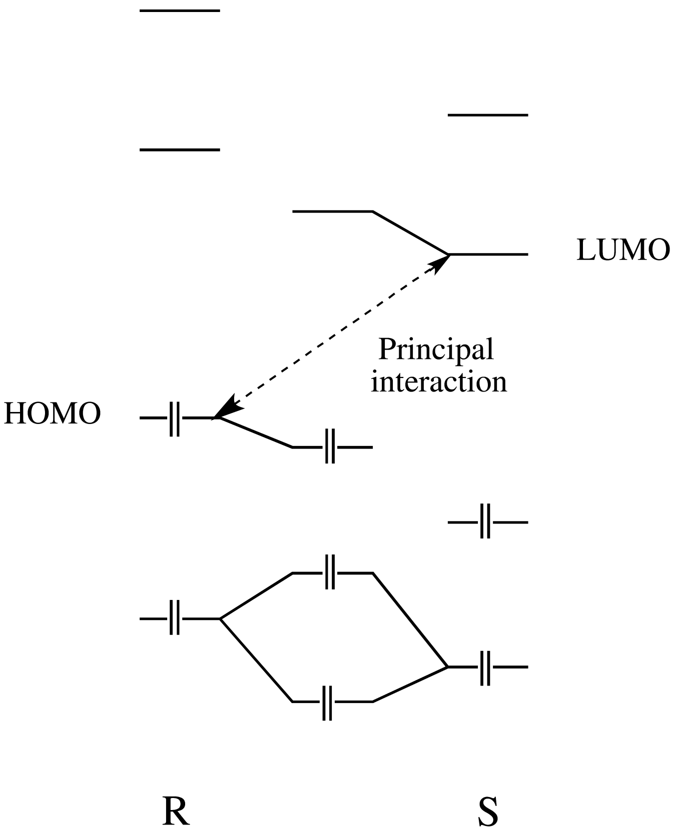


Figure 11. Showing the effect on MO's of the interaction of R and S. Only a single filled MO – filled MO is shown for simplicity. The largest stabilizing interaction is between the HOMO of a donor and the LUMO of an acceptor.

The importance for organic chemists was that these principles have wide generality and can be applied even without computations. Even when σ-orbitals are involved, the HOMO and/or LUMO are frequently π-MOs whose nodal properties are usually apparent from simple principles and are frequently sufficient for determining the relative magnitudes of HOMO-LUMO interactions. This important aspect of the use of Hückel MOs in perturbation theory for stereochemistry, the Woodward-Hoffmann rules and other applications of Frontier Orbital theory so important in the chemistry of the past half-century came mostly after our 1961 books and the theory they reviewed but perhaps they can claim to have set the stage. For example, one result of this growth of interest in applications of theory was a plethora of books. In the two decades following the publication of Roberts and Streitwieser more than two dozen books were published dealing with some aspects of quantum organic chemistry. Some are of the lecture note or problems type with limited bibliography (*108–110*), while others deal mostly with HMO theory and some applications (*111–117*). Some provide extensive treatments of theory beyond HMO (*118–125*), whereas still others are primarily textbooks or edited volumes in the applications to organic chemistry of orbital symmetry and perturbation methods (*101*, *126–131*). With the development of computer programs that became increasingly easier to use, *ab initio* computations played a growing role in understanding organic chemistry. Before WWII many organic chemists had little knowledge of or interest in chemical theory. At the present time, quantum chemistry, even at a rather sophisticated level, is important to the modern organic chemist and this situation is unlikely to change in the foreseeable future. Nevertheless, even in these days of widespread use of powerful computer programs, concepts and interpretations based on HMO are so useful and important that, in the words of Werner Kutzelnigg (*132*) “the HMO model is indispensable.”

References

1. Hückel, E. *Ein Gelehrtenleben*; Verlag Chemie: Weinheim, 1975.
2. Hartmann, H.; Longuet-Higgins, H. C. *Biogr. Mem. Fellows R. Soc.* **1982**, *28*, 153–162.
3. Berson, J. A. *Angew. Chem., Int. Ed.* **1996**, *35*, 2750–2764.
4. Berson, J. A. *Chemical Creativity*; Wiley-VCH: Weinheim, 1999.
5. Frenking, G. *Chem. Unserer Zeit* **1997**, *31*, 27–31.
6. Karachalios, A. *Erich Hückel (1896-1980)*; Springer: Dordrecht, 2010.
7. Debye, P.; Huckel, E. *Z. Phys.* **1923**, *24*, 305–325.
8. Debye, P.; Huckel, E. *Phys. Z.* **1923**, *24*, 185–206.
9. Huckel, E. *Z. Phys.* **1930**, *60*, 423–456.
10. Huckel, E. *Z. Phys.* **1931**, *70*, 204–286.
11. Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 455–472.
12. Lennard-Jones, J. E. *Trans. Faraday Soc.* **1929**, *25*, 668–686.
13. Hückel’s analysis is given in greater detail by Berson (see ref 3).
14. For a review with history of σ and π electrons in organic chemistry, see Kutzelnigg, W.; Re, G. D.; Berthier, G. *σ and π electrons in Theoretical Organic Chemistry*; Springer-Verlag: Berlin, 1971.
15. For a history of the aromatic sextet, see Kikuchi, S. *J. Chem. Ed.* **1997**, *74*, 194−201.
16. Willstätter, R.; Heidelberger, M. *Ber.* **1913**, *46*, 517–527.
17. Willstätter, R.; Waser, E. *Ber.* **1911**, *44*, 3423–3445.
18. Huckel, E. *Z. Elektrochem. Angew. Phys. Chem.* **1937**, *43*, 752−788, 827−849.
19. Hückel, E. *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*; Verlag Chemie: Berlin, 1938.
20. Hückel, W. *Theoretishe Grundlagen der Organischen Chemie*; Akademische Verlagsgesellschaft: Leipzig, 1931.
21. Lennard-Jones, J. E. *Proc. R. Soc. London, Ser. A* **1937**, *158*, 280–296.
22. Altmann, S. L.; Bowen, E. J. *Biogr. Mem. Fellows R. Soc.* **1974**, *20*, 74–134.
23. Simoes, A.; Gavroglu, K. *Hist. Stud. Phys. Biol. Sci.* **1999**, *29*, 363–406.

24. Coulson, C. A.; Rushbrooke, G. S. *Math. Proc. Cambridge Philos. Soc.* **1940**, *36*, 193–200.
25. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1947**, *191*, 39–60.
26. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1947**, *192*, 16–32.
27. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1948**, *195*, 188–197.
28. Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1948**, *193*, 447–456.
29. Coulson, C. A.; Longuet-Hiiggins, H. C. *Proc. R. Soc. London, Ser. A* **1948**, *193*, 456–464.
30. Roberts, J. D. *Notes on Moleular Orbital Calculations*; W. A. Benjamin, Inc.: New York, 1961.
31. Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; John Wiley & Sons, Inc.: New York, 1961.
32. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412.
33. Pople, J. A.; Santry, D. P.; Segal, G. A. *J. Chem. Phys.* **1965**, *43*, S129–S135.
34. Pople, J. A.; Segal, G. A. *J. Chem. Phys.* **1965**, *43*, S136–S149.
35. William von Eggers Doering, interview by James J. Bohning at Philadelphia, PA and Cambridge, MA, 9 November 1990 and 29 May 1991 (Philadelphia: Chemical Heritage Foundation, Oral History Transcript # 0085).
36. Dewar, M. J. S. *The Electronic Theory of Organic Chemistry*; Oxford University Press: London, 1949.
37. Syrkin, Y. K.; Dyatkina., M. E. *Structure of molecules and the chemical bond*; Butterworths Scientific Publications London, 1950.
38. Pullman, B.; Pullman, A. *Les théories électronique de la chimie organique*; Masson et Cie: Paris, 1952. This book, in French, gives worked out examples of the Hückel method. Although the book emphasizes the valence-bond approach it includes discussions of Hückel MO theory.
39. Coulson, C. A. *Valence*; Oxford University Press: London, 1952.
40. Roberts, J. D. *The Right Place at the Right Time*; American Chemical Society: Washington D.C., 1990.
41. Roberts, J. D.; Streitwieser, A., Jr.; Regan, C. M. *J. Am. Chem. Soc.* **1952**, *74*, 4579–4582.
42. Dewar, M. J. S. *Nature* **1945**, *155*, 50–51.
43. Dauben, H. J., Jr.; Ringold, H. J. *J. Am. Chem. Soc.* **1951**, *73*, 876.
44. Doering, W. v. E.; Detert, F. L. *J. Am. Chem. Soc.* **1951**, *73*, 876–877.
45. Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203–3206.
46. Breslow, R.; Yuan, C. *J. Am. Chem. Soc.* **1958**, *80*, 5991–5994.
47. Breslow, R.; Groves, J. T.; Ryan, G. *J. Am. Chem. Soc.* **1967**, *89*, 5048.
48. Breslow, R.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 984–987.
49. Criegee, R.; Schröder, G. *Angew. Chem.* **1959**, *71*, 70–71.
50. Criegee, R.; Schröder, G. *Liebigs Ann.* **1959**, *623*, 1–8.
51. Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *67*, 3253–3254.

52. Krantz, A.; Lin, C. Y.; Newton, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 2744–2746.
53. Lin, C. Y.; Krantz, A. *J. Chem. Soc., Chem. Commun.* **1972**, 1111–1112.
54. Chapman, L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614–617.
55. Cope, A. C.; Overberger, C. G. *J. Am. Chem. Soc.* **1948**, *70*, 1433–1437.
56. Reppe, W.; Sehliehting, O.; Khger, K.; Toepel, T. *Liebigs Ann. Chem.* **1948**, *460*, 1–92.
57. Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3784–3785.
58. Katz, T. J.; Garratt, P. J. *J. Am. Chem. Soc.* **1963**, *85*, 2852–2853.
59. Sondheimer, F. *Acc Chem. Res.* **1972**, *5*, 81–91.
60. Masamune, S.; Darby, N. *Acc. Chem. Res.* **1972**, *5*, 272–281.
61. Jackman, L. M.; Sondheimer, F.; Amiel, Y.; Ben-Efraim, D. A.; Gaoni, Y.; Wolovsky, R.; Bothner-By, A. A. *J. Am. Chem. Soc.* **1962**, *84*, 4307–4312.
62. Oth, J. F. M.; Gilles, J.-M. *Tetrahedron Lett.* **1968**, *60*, 6259–6264.
63. Hiberty, P. C. *Top. Curr. Chem.* **1990**, *153*, 27–39.
64. Gobbi, A.; Yamaguchi, Y.; Frenking, G.; Schaefer, H. F., III *Chem. Phys. Lett.* **1995**, *244*, 27–31.
65. The Chemical Society; 1967; Vol. Special Publication No. 21, p 249.
66. Bergmann, E. D., Pullman, B., Eds.; Israel Academy of Sciences and Humanities, 1970.
67. Snyder, J. P., Ed.; *Nonbenzenoid Aromatics*; Academic Press: New York, 1969.
68. Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; *Topics in Nonbenzenoid Aromatic Chemistry*; Hirokawa Publishing Company, Inc.: Tokyo, 1977.
69. Schleyer, P. v. R. *Chem. Rev.* **2001**, *101*, 1115–1117.
70. Coulson, C. A. *Proc. R. Soc. London, Ser. A* **1939**, *169*, 413–428.
71. Lichtin, N. N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1951**, *73*, 5530–5536.
72. Lichtin, N. N.; Glazer, H. *J. Am. Chem. Soc.* **1951**, *73*, 5537–5541.
73. Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 5288–5290.
74. Wheland, G. W. *J. Am. Chem. Soc.* **1942**, *64*, 900–908.
75. Brown, R. D. *Q. Rev.* **1952**, *6*, 63–99.
76. Dewar, M. J. S.; Warford, E. W. T. *J. Chem. Soc.* **1956**, 3581–3585.
77. Streitwieser, A., Jr.; Fahey, R. C. *J. Org. Chem.* **1962**, *27*, 2352–2355.
78. Streitwieser, A., Jr.; Lewis, A.; Schwager, I.; Fish, R. W.; Labana, S. *J. Am. Chem. Soc.* **1970**, *92*, 6525–6529.
79. Streitwieser, A., Jr.; Mowery, P. C.; Jesaitis, R. G.; Lewis, A. *J. Am. Chem. Soc.* **1970**, *92*, 6529–6533.
80. Streitwieser, A., Jr.; Schwager, I. *J. Am. Chem. Soc.* **1963**, *85*, 2855.
81. Dewar, M. J. S.; Sampson, R. J. *J. Chem. Soc.* **1957**, 2946–2952.
82. Footnote 26 on page 368 of ref 31.
83. Maccoll, A. *Nature* **1949**, *163*, 178–179.
84. Birch, A. J. *Q. Rev.* **1950**, *4*, 69–93.
85. For SCF wavefunctions, Koopmans, T. *Physica* **1934**, *1*, 104−113.
86. Hoijtink, G. J. *Recl. Trav. Chim.* **1958**, *77*, 555.
87. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1948**, *70*, 2832–2833.

88. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.
89. Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600–608.
90. Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801–822.
91. Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811–824.
92. McConnell, H.; Ham, J. S.; Platt, J. R. *J. Chem. Phys.* **1953**, *21*, 66–70.
93. Bhattacharya, R.; Basu, S. *Trans. Faraday Soc.* **1958**, *54*, 1286–1290.
94. Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden-Day, Inc.: San Francisco, 1964.
95. Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026–2033.
96. For one personal account of this period, see Pitzer, R. M. *J. Chem. Theory Comput.* **2011**, *7*, 2346−2347.
97. Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 4388–4389.
98. Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 4389–4390.
99. Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395–397.
100. Longuet-Higgins, H. C.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1965**, *87*, 2045–2046.
101. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie, GmbH: Weinheim, 1970.
102. Huisgen, R. *Angew. Chem., Int. Ed.* **1963**, *2*, 565–632.
103. Fukui, K.; Fujimoto, H.; Eds. *Frontier Orbitals and Reaction Paths: Selected Papers of Kenichi Fukui*, 1997.
104. Fukui, K.; Yonezawa, T.; Nagata, C. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 423–427.
105. Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, *20*, 722–725.
106. Dewar, M. J. S. *J. Am. Chem. Soc.* **1952**, *74*, 3341–3345.
107. This is a simplified version in which overlap integrals are neglected and the orbitals in R and S are nondegenerate; that is, all $\varepsilon i \neq \varepsilon k$.
108. Coulson, C. A.; O'Leary, B.; Mallion, R. B. *Hückel Theory for Organic Chemists*: Academic Press: London, 1978.
109. Wagniere, G. H. *Introduction to Elementary Molecular Orbital Theory and to Semiempirical Methods*; Springer-Verlag: Berlin, 1976.
110. Zahradnik, R.; Carsky, P. *Organic Quantum Chemistry Problems*; Plenum: New York, 1973.
111. Heilbronner, E.; Bock, H. *Das HMO-Modell und seine Anwendung*; Verlag Chemie: Weinheim, 1968.
112. Higasi, K.; Baba, H.; Rembaum, A. *Quantum organic chemistry*; Interscience Publishers: New York, 1965.
113. Liberles, A. *Introduction to molecular-orbital theory*; Holt, Rinehart and Winston: New York, 1966.
114. Flurry, R. L., Jr. *Molecular Orbital Theories of Bonding in Organic Molecules*; Marcel Dekker, Inc.: New York, 1968.
115. Salem, L. *The molecular orbital theory of conjugated systems*; Benjamin: New York, 1966.
116. Yates, K. *Hückel Molecular Orbital Theory*; Academic Press: New York, 1978.

117. Zimmerman, H. E. *Quantum Mechanics for Organic Chemists*; Academic Press: New York, 1975.
118. Borden, W. T. *Modern Molecular Orbital Theory for Organic Chemists*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1975.
119. Csizmadia, I. G. *Theory and practice of MO calculations on organic molecules*; Elsevier Scientific Pub. Co.: Amsterdam, 1976.
120. Dewar, M. J. S. *The molecular orbital theory of organic chemistry*; McGraw-Hill: New York, 1969.
121. Murrell, J. N.; Harget, A. J. *Semi-empirical self-consistent-field molecular orbital theory of molecules*; Wiley-Interscience: London, 1972.
122. Orchin, M.; Jaffé, H. H. *Symmetry, orbitals, and spectra*; Wiley-Interscience: New York, 1971.
123. Segal, G. A. *Semiempirical methods of electronic structure calculation*; Plenum Press: New York, 1977.
124. Sinanoğlu, O.; Wiberg, K. B. *Sigma molecular orbital theory*; Yale University Press: New Haven, 1970.
125. Turner, A. G. *Methods in molecular orbital theory*; Prentice-Hall: Englewood Cliffs, NJ, 1974.
126. Anh, N. T. *Les Regles de Woodward-Hoffmann*; Ediscience: Paris, 1970.
127. Dewar, M. J. S.; Dougherty, R. C. *The PMO theory of organic chemistry*; Plenum Press: New York, 1975.
128. Fleming, I. *Frontier orbitals and organic chemical reactions*; Wiley: Chichester, 1976.
129. Gilchrist, T. L.; Storr, R. C. *Organic reactions and orbital symmetry*; Cambridge University Press: Cambridge, 1979.
130. Orchin, M.; Jaffé, H. H. *The importance of antibonding orbitals*; Houghton Mifflin: Boston, 1967.
131. Pearson, R. G. *Symmetry rules for chemical reactions : orbital topology and elementary processes*; Wiley: New York, 1976.
132. Kutzelnigg, W. *J. Comput. Chem.* **2007**, *28*, 25–34.

Chapter 10

John Pople: The Man and His Science

Janet E. Del Bene[*]

Department of Chemistry, Youngstown State University,
Youngstown, Ohio 44555
[*]E-mail: jedelbene@ysu.edu

John A. Pople was the dominant theoretical chemist of the second-half of the twentieth century and the recipient of the Nobel Prize in Chemistry in 1998. More than anyone, John brought theoretical and computational chemistry from a discipline for the few who were computer and mathematically oriented, to a tool for the many and a partner with experiment in chemical research.

Introduction

When I was asked to give a talk on “John Pople, the Man and His Science” at the Symposium on the Pioneers of Quantum Chemistry, I was both honored and overwhelmed. How would it be possible to describe in 25 minutes the many contributions of Sir John A. Pople, Nobel Laureate in Chemistry in 1998? I began by contacting some of my friends who were also Pople students, and asking them for their input. Their response was overwhelming, and gave me much more material than I could possibly use in a 25-minute presentation. These individuals are acknowledged at the end of this chapter. Some of the information not used in the oral presentation because of time constraints will be included in this chapter.

As I read through the mountains of material that I had received, I decided that the best I could possibly do was to give an overview of some of the areas in which John had made seminal contributions, but emphasize the area in which he had made his most important contributions in terms of their impact on the field of theoretical and computational chemistry. Of course, this is my personal selection, so others may have chosen differently. While I will mention all areas, I will focus on ab initio molecular orbital theory.

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Early Years

John Pople was born in Burnham-on-Sea, Somerset, England, in 1925. John's father was a merchant, and each night he would bring home with him the receipts of the day. At age three, John would tally them in pounds, shillings, and pence. This was the first sign that there was a mathematical genius in the making! A detailed account of John Pople's early years can be found in his autobiography at Nobelprize.org (*1*).

Cambridge and the National Physical Laboratory

Fast-forward now to John Pople at Cambridge University (Figure 1). John received his Bachelor of Arts (1946), Master of Arts (1950), and Doctoral (1951) degrees, all in Mathematics, from Cambridge University. However, his research at Cambridge was not in mathematics, but in chemistry. Having finished his degree work, he began planning for the future. The following passage is taken from John's autobiography (*1*).

> "The highly competitive stage accomplished [referring to his Ph.D.], I was able to relax a bit and formulate a more general philosophy for future research in chemistry. The general plan of developing mathematical models for simulating a whole chemistry was formulated, at least in principle, some time late in 1952."

This statement is even more impressive when placed in context. It was made in 1952, a time when computers were just beginning to enter the world of science, and only a few people were even thinking about using computers in what would become computational chemistry.

After receiving his Ph.D., John Pople remained at Cambridge as a Research Fellow from 1951-1954, and a Lecturer in Mathematics from 1954-1958. During the Cambridge years his research spanned several areas. John's initial work at Cambridge began with Sir John Leonard-Jones and was in two areas, molecular orbital theory of chemical valency (*2–4*) and statistical mechanics (*5*, *6*). During this time he produced an early model of liquid water which influenced the thinking about the structure of water for many years (*7*). He investigated the electrical and magnetic properties of small molecules, some of this work with A. David Buckingham, John's first Ph.D. student (*8*, *9*). Perhaps John's best-known work from this time was on π electron theory. He independently developed a theory of π electrons (*10*) at about the same time that Pariser and Parr (*11*) were developing their π electron theory. These three theorists joined their efforts to produce Pariser-Parr-Pople π electron theory, or PPP. This work had an immediate impact, and was used to investigate ground and excited states of molecules containing π electrons, particularly aromatic systems. A more detailed description of John's early work at Cambridge can be found in an article written by A. David Buckingham (*12*).

Figure 1. John as a Cambridge student. Photo courtesy of Hilary Pople.

John often said that his years at Cambridge were the most intellectually stimulating of his life. Nevertheless, the following statement appears in his autobiography (*1*).

> "By 1958, I had become dissatisfied with my mathematics teaching position at Cambridge. I had clearly changed from being a mathematician to a practicing scientist."

John then resigned his position in the Mathematics Department at Cambridge, and accepted the position of Superintendent, Basic Physics Division, National Physical Laboratory, in Teddington, England. His most significant work from that time was his book "High-Resolution Nuclear Magnetic Resonance", coauthored with W. G. Schneider and R. J. Bernstein (*13*). This book was the first of its kind, and was the Bible of NMR for many years.

Work from the 1960s to 2004

At the urging of Bob Parr, John spent a sabbatical year (1960-1961) at Carnegie Institute of Technology (Carnegie Tech) in Pittsburgh, Pennsylvania, and then returned to the National Physical Laboratory. Although John was very successful in his position at this Laboratory, he was an academician at heart. Thus, in 1964 John Pople resigned from this position and came to the United States. His leaving was front-page news in the British papers, as he was an eminent member of the "British Brain Drain"!

John accepted a position at Carnegie Tech as Carnegie Professor of Chemical Physics. In 1974 he was named John Christian Warner University Professor of Natural Sciences, a position he held until 1993. From 1986 to 2004 he was also an Adjunct Professor of Chemistry at Northwestern University.

During his academic years, John made seminal contributions to three areas of theoretical chemistry: semi-empirical methods (1960's), ab initio molecular orbital theory (late 1960's – 2004), and density functional theory (1990's – 2004). Trying to describe all of this work in an entire book, let alone a single chapter, is like trying to pour an ocean into a drinking cup. I will briefly mention John's work in semi-empirical methods and density functional theory, but focus on ab initio molecular orbital theory. John's contributions in this area are those which I and most theorists consider John's most significant work. These will be presented in chronological order.

Semiempirical Methods

John's early work at Carnegie Tech was in the development of the first all-valence electron theories, CNDO (*14*) and INDO (*15*). These semi-empirical methods represented a major breakthrough which enabled theory to take a quantum leap forward from treating only π electrons, to carrying out calculations on all valence electrons of a molecule. Since these electrons are those primarily involved in chemical reactions, CNDO and INDO opened up new horizons for computing molecular geometries, energies, and a host of other molecular properties. These methods were immediately followed by others such as MINDO (*16*), a method presented by Dewar for the prediction of heats of formation. Del Bene and Jaffé reparameterized CNDO to produce CNDO/S (*17*), a method for investigating electronic excited states of molecules. All of these methods are still in use today.

Ab Initio Molecular Orbital Theory

The second area, the area in which John made his most significant contributions and which will be the subject of the bulk of this chapter, is ab initio molecular orbital theory. In this area he developed new methods, and then applied them to problems of chemical interest.

What are ab initio calculations? Ab initio means "from the beginning" or "from scratch". This implies that these calculations are carried out on a molecular system without any experimental data or adjustable parameters such as those found in semi-empirical methods. Rather, the results of ab initio calculations arise from the fundamental constants, the identity of each nucleus, the number of electrons present, the spin state, and the molecular geometry. These calculations are based on the laws of quantum mechanics using the Schrödinger equation. However, in order to perform an ab initio molecular orbital calculation on a particular chemical system, two choices must be made: basis set and wavefunction model. Basis sets are no more than sets of mathematical functions which are used to describe electrons in *atoms*, that is, they are mathematical atomic orbitals. There are many different sets of atomic orbitals from which to choose, and some of these will be identified below. The second choice is the wavefunction model. A wavefunction is a function which describes electrons in *molecules*. In ab initio theory in its simplest form, the wavefunction consists of a single Slater determinant (*18*) constructed from molecular orbitals which are formed as linear combinations of the atomic orbitals which were selected as the basis set for the calculation. The wavefunction is used to compute from first-principles various properties of molecules. John Pople made seminal contributions to both basis sets and wavefunctions. But before detailing these, it is important to put John's contributions into perspective.

What was the state of ab initio calculations in the late 1960's? There were a few ab initio programs in existence at that time, including IBMOL (*19*) and POLYATOM (*20*). However, these programs were slow and difficult to use. The bottleneck of ab initio calculations was the evaluation of two-electron integrals. In 1968 John visited the University of Florida, and while there, he was said to have disappeared for a few days. When he emerged, he brought with him new algorithms that would revolutionize ab intio calculations. Two features were innovative and of extreme importance.

- He grouped together s and p orbitals in the same shell and constrained these orbitals to have the same exponents. That is, s, p_x, p_y, and p_z orbitals were grouped together into one sp shell. Thus, for integral evaluation the orbitals were treated efficiently as an sp shell rather than as four individual s and p orbitals.
- He designed a unique and computationally efficient method for evaluating and processing two-electron integrals. These new algorithms reduced the time required for these processes by about a factor of 100 (*21*).

At the same time, John and the members of his group were working on a new ab initio computer code, and built into this code the new integral algorithms. In collaboration with Bob Stewart, John and his group developed a new series of basis sets, STO-NG (*22*, *23*). STO stands for Slater-type orbital, and NG represents the number of Gaussian functions (N = 2-6) used to fit each Slater-type orbital. The Pople group showed convergence of this set as the number of Gaussians (N) increased, and chose STO-3G as a reasonable compromise between computational cost and performance. The new ab initio program with the new integral algorithms and STO-NG basis sets eventually became Gaussian 70 (*24*), the first of many releases of this extremely popular and still widely-used ab initio program.

John Pople (Figure 2) always believed that methodological breakthroughs should be accompanied by applications. There was no problem finding applications, since the advent of what was the pre-Gaussian 70 code spurred a flurry of activity among John's students and postdocs. There was not a time when the CDC 1604-A computer was left idle. Warren Hehre, a group member at the time, remarked that the entire group, including John, were like "kids in a candy store". There were a multitude of problems to be investigated, only a sampling of which are listed here. They included studies of

- charge distributions;
- structures and energies of small water polymers;
- equilibrium geometries;
- internal rotational barriers;
- bond separation energies;
- heats of formation of small organic molecules;
- substituent effects.

To say that the computer was singing at this time is literally true. One of the computer operators at Mellon Institute had attached an acoustical device to the computer. So, as Gaussian jobs were running, those of us waiting for output could walk down the hall in the basement of Mellon Institute and hear Gaussian running. There were distinctive cadences for various parts of the program. There was a unique and wonderful cadence at the end of a calculation which signaled that output would soon be at hand! A detailed account of John's work at this time can be found in an article written by Leo Radom (*25*).

Figure 2. John Pople in 1970. Photo courtesy of Warren Hehre.

In retrospect, I have often asked myself how we learned so much at this time, when the methods that we used (Hartree-Fock with the STO-NG basis sets) were so inadequate, certainly as judged by today's standards. I think that the answer to this question lies in John's systematic approach to chemical problems. In general, John's group examined systematically a series of related molecules and/or complexes rather than a single one. This meant that while the absolute values of the numbers that we obtained may not have been quantitatively accurate, the trends observed were real.

John's philosophy concerning computer programs was evident from the very beginning. He believed that computer programs should be easy to use, even by non-experts. He was also a firm believer that if a method was worth coding, it must be coded efficiently so that it executes as fast as possible. One experience I had illustrates the latter. Bob Ditchfield, who was also a postdoc in Pople's group at this time, and I decided that we would like to add to the Gaussian program the capability of doing truncated CI singles calculations to obtain energies of excited states. We wrote the code, and carried out a test calculation on ketene. We managed to get a reasonable answer, but it took about 20 minutes for the computer to finish the calculation. We knew that if we told John about our successful run, he would ask how long it took, and 20 minutes was far too much time for the small test case that we had used. So, we made another pass through the code, using all of the techniques that we knew to make the code execute more efficiently. Our next run took only 10 minutes, but unfortunately, we no longer had the correct answer. We then went back to work, and eventually reduced the running time to about 4 or 5 minutes, and obtained a good result. It was at this point that we told John that we had successfully implemented truncated CI singles.

At this time I was finishing up my work in the Pople group, which had focused primarily on the structures and binding energies of small water polymers (*26*) and polymers of HF (*27*). At that time an announcement was made by the Russian chemist Deryagin that an anomalous form of water existed, called polywater (*28*). There was a lot of excitement about polywater, and I discussed this subject with John. He looked at the calculations that I had done, which showed no support for the proposed stable form of water polymers with symmetric hydrogen bonds, and unlike many others, we did not jump onto the polywater bandwagon. The experimental evidence for polywater was later found to be the result of an impurity in the solution.

When I left John's lab in 1970, he was kind enough to give me a copy of the pre-release version of Gaussian 70. Gaussian 70 was copied for me onto about 25,000 computer cards. I vividly remember making the card copy with the help of three members of the group. One carried cards to the card reader, one boxed the newly punched cards, and one stood at the card reader/punch with his finger on the STOP button to prevent major jams. I then ported this program to Youngstown State University. However, porting prior to the internet was not an easy task, as illustrated in Figure 3.

John certainly did not rest on his laurels, but continued to play a leading role in the development of new methods and their applications. Following the STO-NG basis sets and a few other, lesser-known minimal basis sets, John's group introduced the valence double- and triple-split basis sets, 6-31G (*29*) and 6-311G (*30*). To better describe the anisotropic nature of chemical bonds, they added polarization functions to give 6-31G(d,p) (*31*) and 6-311G(d,p) (*32*) or 6-31G** and 6-311G** as they were named originally. These sets were further extended with the addition of diffuse functions by Schleyer and his group (*33*, *34*).

In addition to basis set development, John explored wavefunction models beyond single-determinant Hartree-Fock so as to account for electron correlation effects. These models included Møller-Plesset perturbation theory at second-, third-, fourth-, and even fifth-order (MP2, MP3, MP4, MP5) (*35–38*). He introduced quadratic configuration interaction (QCI) and QCI with noniterative triple excitations [QCISD(T)] (*39*), and examined how these methods compared with other methods such as coupled cluster CCSD and CCSD(T), Bruckner Doubles (BD), and configuration interaction (CI).

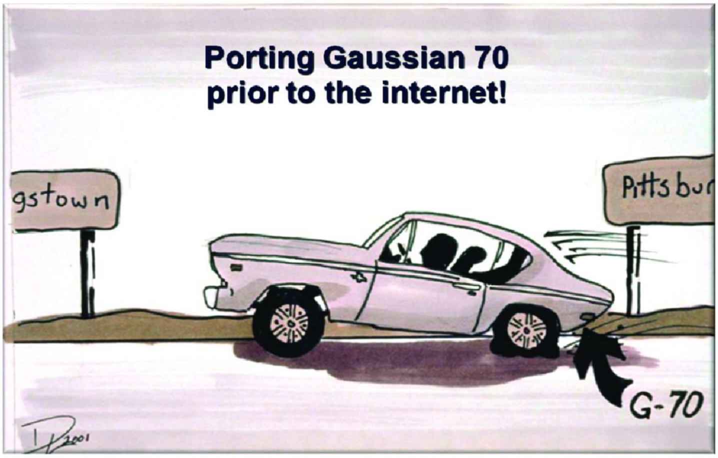


Figure 3. Cartoon courtesy of the Youngstown State University Media Center.

John constantly worked to improve integral evaluation (*40*, *41*). Moreover, he and his students developed and implemented in the Gaussian program the first practical algorithms for computing analytical first and second derivatives (*42*). These allowed for the efficient exploration of potential energy surfaces to find optimized geometries for molecules and complexes, and to determine whether these correspond to equilibrium structures (local minima on the potential surface) or transition structures connecting two minima. The calculation of vibrational frequencies and thus the IR spectra of molecules became routine.

The work on methodology and applications pursued by John Pople and his students led to the asking and answering of some important, fundamental questions, such as the following.

- How do the basis set and wavefunction influence computed optimized geometries?
- To what extent does the choice of basis set and wavefunction influence the relative energies of local minima and transition structures?
- How are specific computed molecular properties influenced by the basis set and wavefunction choice?
- How do the structures, binding energies, and other properties of molecular complexes depend on basis set and wavefunction?

The answers to these and many other related questions led to what most theorists consider John's greatest contribution to computational chemistry. However, to put this contribution into perspective, the state of ab initio theory prior to this work needs to be considered.

For many years, ab initio molecular orbital calculations remained a field restricted to experts. There were many reasons for this, but most important was the difficulty of assessing the reliability of the results of a given calculation. This assessment was an impossible task for nonexperts, and a very difficult one even for experts. What often happened was that a researcher chose what was judged to be the biggest basis set and the best wavefunction model which could be used for a calculation within the limitations of the computer resources available, and then hoped for the best. However, it was difficult if not impossible to judge the reliability of the computed results. While comparison with experimental data was often used as a test of reliability, it became apparent that it was possible for deficiencies in basis set and wavefunction model to cancel, and give a result in agreement with experimental data for a particular molecule. However, when the same basis set and wavefunction were used for a similar molecule, there could be significant differences between computed and experimental results. John then moved to resolve this problem.

During the course of his work, John developed what he termed Model Chemistries, a concept for which John is solely responsible, and which has been widely adopted by many research groups. John first enumerated the requirements of a model in an early 1973 paper (*43*). John and his students, now knowing how basis set and wavefunction influence computed reaction energies, formulated an innovative new model called G1 theory (*44*), the aim of which was to obtain reliable high-level computational results. These are defined as results that would be obtained by using a large, well-balanced basis set and a high-level correlated electronic wavefunction, a combination that might well be computationally unfeasible. However, instead of attempting to perform this calculation, John proposed that a few lower-level calculations which are feasible be performed instead. Some of these calculations are done with large basis sets but lower-level wavefunctions, others with smaller basis sets but higher-level wavefunctions. John presented a formula for combining the results of these calculations, and carefully calibrated the difference between computed properties using this method and corresponding reliable experimental data. G1 theory was followed by improved schemes for selecting basis set and wavefunction models for the lower-level calculations, known as G2 (*45*) and G3 (*46*) theories. With G3, the average difference between computed and reliable experimental energies for a set of test molecules was found to be 1.02 kcal/mol. Since experimental accuracy is about 1 kcal/mol, this approach could be used to evaluate properties of other molecules, now with known error-bars on the computed data, and confidence in the computed results.

There are several advantages to this approach. First and most important, the reliability of computed properties is known. Second, this approach is independent of software package, although it was automated and coded into the Gaussian series of programs. Third, it led to the widespread use of electronic structure calculations across the many subdisciplines of chemistry. With all of these developments, electronic structure calculations could now be used with confidence to

- resolve discrepancies between two different experimental measurements;
- provide new insights into the “why” of chemical reactions or properties;
- suggest new experiments;
- predict properties that had not yet been measured experimentally.

John thus took the leading role in making quantum chemistry an equal partner with experiment in chemical research.

John’s philosophy of science has been summarized succinctly in a tribute to John posted on the web (*47*). John believed that theorists should

- compute what is measured, not just what is inexpensive;
- investigate chemically interesting systems, not just easy ones;
- calibrate models carefully and present them honestly;
- recognize the strengths and weaknesses of other people’s models, and learn from them;
- program worthwhile methods efficiently and make them easy to use.

Density Functional Theory (DFT)

It is not surprising that John Pople brought the same systematic approach to density functional theory that he had used so successfully in his work in ab initio molecular orbital theory. Prior to John’s entrance into density functional theory, DFT papers often failed to describe basis sets and quadrature grids, which made reproducibility difficult if not impossible. And once again, there was little information available by which to judge the quality and consistency of DFT results.

John began by first writing down the Kohn-Sham equations in a finite basis set (*48*). He and his group then embarked on a study to assess the reliability of DFT calculations. To do this, they used six well-defined functionals with the 6-31G(d) basis set and a well-defined grid, to predict the structures, dipole moments, vibrational frequencies, and atomization energies of 32 small molecules. Based on these data and comparisons with ab initio molecular orbital calculations, they were able to assess the strengths and weaknesses of these functionals (*49*). John and his group were also the first to construct and introduce density functionals to correct the long-range deficiencies in DFT calculations (*50*). John’s contributions played a major role in the wide-spread use of DFT calculations in chemisty.

Major Awards

John received many awards for his work, far too many to mention in this chapter. Among his major awards are the American Chemical Society Award in Theoretical Chemistry, the Humphrey Davy Medal of the Royal Society, and the Wolfe Prize, a prize which is generally viewed as a pre-Nobel Prize. Then, in 1998 John A. Pople was awarded the Nobel Prize in Chemistry (Figure 4).

His citation reads “for his development of computational methods in quantum chemistry”. John received an Honorary Doctorate from Cambridge University in 2003. John’s own view of quantum chemical model chemistries can be found in his Nobel Lecture (*51*).

Figure 4. John A. Pople at the Nobel ceremony. Photo courtesy of Leo Radom.

It was a most fortunate circumstance that a group of former Pople students were together at the Sanibel Symposium in Florida in the early months of 1998. We decided that it would be fitting to have a mini-symposium before the end of the century, celebrating John’s position as the dominant theoretical chemist of the second-half of the twentieth century. We planned a celebration which would be limited to John’s students and research collaborators (The Pople People as we call ourselves), and scheduled it for Amelia Island, immediately following the 1999 Sanibel meeting. Although we expected that eventually John would win a Nobel Prize, little did we know that our pre-planned meeting would be the Pople People’s celebration of John’s Nobel Prize! In 2003, John was further honored for his work as Queen Elizabeth II knighted him and bestowed upon him the title of Sir John A. Pople, Commander (KBE) of the Order of the British Empire (Figure 5).

Figure 5. Sir John A. Pople, Commander (KBE) of the Order of the British Empire. Photo courtesy of British Ceremonial Arts Limited.

John A. Pople died in 2004, having bequeathed his Nobel Medal to Carnegie-Mellon University (CMU). The ceremony at which CMU received this gift and inaugurated the John A. Pople Lectures in Theoretical and Computational Chemistry occurred on October 5, 2009.

Concluding Remarks

It is appropriate to ask what made John Pople such an extraordinary scientist. While many qualities could be listed, perhaps among the most important are the following. John Pople

- had a solid background in mathematics, and thought as a mathematician;
- had an early vision of what could be, as evidenced by his 1952 statement;
- worked tirelessly for fifty years to make that vision a reality;
- was well-versed in computers and computer programming;
- employed a systematic approach to chemical problems;
- was scrupulously honest about his science;
- had a keen ability to focus on the essence of a problem, and not get bogged down in details.

The legacy of John A. Pople is not limited to his methodological developments and their applications, as important and revolutionary as they are. His legacy also lives on in his students, many of whom have adopted the Pople Model of approaching chemical problems, and are themselves making important contributions to our discipline. I know that I speak for all when I say that we were indeed fortunate to have had John Pople as a mentor and a friend (Figure 6).

Figure 6. Sir John A. Pople (1925 – 2004).

Acknowledgments

I would like to take this opportunity to thank David Buckingham, Peter Gill, Mark Gordon, Martin Head-Gordon, Warren Hehre, Marshall Newton, Otilia Mó, Neil Ostlund, Leo Radom, Berny Schlegel, and Manuel Yáñez, all students of John Pople, who provided me with some of the information and pictures used in this chapter. Special thanks go to Angela Wilson and Tom Strom for organizing the “Pioneers of Quantum Chemistry Symposium” and inviting me to give a lecture about John Pople, and to John’s daughter, Hilary Pople. Finally, I thank the National Institutes of Health for a postdoctoral fellowship and Youngstown State University for a sabbatical, which enabled me to work with John Pople on two separate occasions.

References

1. Pople, J. A. Autobiography, Nobelprize.org.
2. Lennard-Jones, J.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1950**, *202*, 166.
3. Lennard-Jones, J.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1951**, *210*, 190.
4. Hurley, A. C.; Lennard-Jones, J.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1953**, *220*, 446.
5. Lennard-Jones, J.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1951**, *205*, 155.
6. Pople, J. A. *Proc. R. Soc. London, Ser. A* **1954**, *221*, 508.
7. Pople, J. A. *Proc. R. Soc. London, Ser. A* **1954**, *221*, 498.
8. Pople, J. A.; Buckingham, A. D. *Trans. Faraday Soc.* **1955**, *51*, 1029.
9. Pople, J. A.; Buckingham, A. D. *J. Chem. Phys.* **1957**, *27*, 820.
10. Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375.
11. Pariser, R.; Parr, R. *J. Chem. Phys.* **1953**, *21* (466), 767.
12. Buckingham, A. D. *J. Phys. Chem.* **1990**, *94*, 5421.
13. Pople, J. A.; Schneider, W. G.; Bernstein, H. J. High-Resolution Nuclear Magnetic Resonance; McGraw-Hill Book Co., Inc.: New York, 1959.
14. Pople, J. A.; Santry, D. P.; Segal, G. A. *J. Chem. Phys.* **1965**, *43*, S129.
15. Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.
16. Baird, N. C.; Dewar, M. J. S. *J. Chem. Phys.* **1968**, *50*, 1262.
17. Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807.
18. Slater, J.; Verma, H. C. The Theory of Complex Spectra. *Phys. Rev.* **1929**, *34*, 1293.
19. Davis, D. R.; Clementi, E. IBMOL: Computation of Wave Functions for Molecules of General Geometry. An IBM 7090 Program Using the LCAO-MO-SCF Method; IBM Research Report, December, 1965.
20. Csizmadia, L. G.; Harrison, M. C.; Moskowitz, J. W.; Seung, S.; Sutcliffe, B. T.; Barnett, M. P. *QCPE* **1964**, *11*, 47.
21. Pople, J. A.; Hehre, W. J. *J. Comput. Phys.* **1978**, *27*, 161.
22. Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
23. Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769.
24. Hehre, W. J.; Lathan, W. A.; Newton, M. D.; Ditchfield, R.; Pople, J. A. *QCPE* **1973**, 236.
25. Radom, L. *J. Phys. Chem.* **1990**, *94*, 5439.
26. Del Bene, J.; Pople, J. A. *Chem. Phys. Lett.* **1969**, *4*, 426.
27. Del Bene, J. E.; Pople, J. A. *J. Chem. Phys.* **1971**, *55*, 2296.
28. Deryagin, B. V.; Churayev, N. V. *Priroda (Moskow)* **1968**, *4*, 16.
29. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
30. Ragavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
31. Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **1971**, *28*, 213.
32. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
33. Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 3633.

34. Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.
35. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1.
36. Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.
37. Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244.
38. Raghavachari, K.; Pople, J. A.; Replogle, E. S.; Head-Gordon, M. *J. Chem. Phys.* **1990**, *94*, 5579.
39. Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.
40. Head-Gordon, M.; Pople, J. A. *J. Chem. Phys.* **1988**, *89*, 5777.
41. Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *Int. J. Quantum Chem.* **1989**, *S23*, 269.
42. Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 225.
43. Pople, J. A. Theoretical Models for Chemistry. In *Proceedings of the Summer Research Conference on Theoretical Chemistry, Energy Structure and Reactivity*; Smith, D. W., Ed.; John Wiley & Sons: New York, 1973.
44. Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537.
45. Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.
46. Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
47. Frisch, M. J. Reflections on John Pople's Career and Legacy, Gaussian.com, 2004.
48. Pople, J. A.; Gill, P. M. W.; Johnson, B. G. *Chem. Phys. Lett.* **1992**, *99*, 557.
49. Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.
50. Gill, P. M. W.; Adamson, R. D.; Pople, J. A. *Mol. Phys.* **1996**, *88*, 1005.
51. Pople, J. A. *Rev. Mod. Phys.* **1999**, *71*, 1267.

Editors' Biographies

E. Thomas Strom

Dr. E. Thomas (Tom) Strom is an Adjunct Professor at the University of Texas at Arlington (UTA), where he teaches organic and polymer chemistry. He came to UTA after retiring from Mobil, where he worked 32 years as a research chemist studying oil field chemistry. He was Chair of the ACS Division of the History of Chemistry in 2011-2012. His research interests are in the history of chemistry and the study of anion radicals by electron spin resonance spectroscopy. He was one of the initial ACS Fellows and is a past winner of the Dallas-Fort Worth ACS Section's Doherty Award. He received his B.S.Chem degree from the University of Iowa, his M.S.Chem degree in nuclear chemistry from UC-Berkeley, and his Ph.D. in physical organic chemistry from Iowa State working under mentor Glen A. Russell.

Angela K. Wilson

Angela K. Wilson is a Regents Professor of Chemistry and Director of the Center for Advanced Scientific Computing and Modeling (CASCaM) at the University of North Texas. She received a B.S. in chemistry from Eastern Washington University, and a Ph.D. in chemical physics from the University of Minnesota, under the direction of the quantum chemist, Jan Erik Almlöf, where she worked on the development of *ab initio* local correlation approaches. Her postdoctoral work was with Thom H. Dunning, Jr., at Pacific Northwest National Laboratory, where she was involved in the development of the *ab initio* correlation consistent basis sets. Angela is a Fellow of the American Chemical Society and National Associate of the National Academies, and is a member of the Editorial Advisory Board of the *Journal of Physical Chemistry* and Editorial Boards of the *International Journal of Quantum Chemistry and Computational and Theoretical Chemistry*. Her honors include an NSF CAREER Award, Quantum Systems in Chemistry and Physics Promising Scientist Award of Centre de Mécanique Ondulatoire Appliquée, and Wiley International Journal of Quantum Chemistry Young Investigator Award.

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.

Subject Index

In Pioneers of Quantum Chemistry; Strom, E., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2013.