Quantum Chemistry Comes of Age

George B. Kauffman* **and Laurie M. Kauffman**

Department of Chemistry, California State University–Fresno, Fresno, CA 93740-8034, george_kauffman@csufresno.edu

Abstract: On December 10, 1998, the 102nd anniversary of Alfred Nobel's death, in Stockholm's Konserthus (Concert Hall), Sweden's King Carl XVI Gustav awarded one half of the 1998 Nobel Prize in Chemistry (3,800,000 kronor, about $489,000) to Professor John A. Pople, 73, of Northwestern University, Evanston, Illinois "for his development of computational methods in quantum chemistry." The remaining half of the prize, the *ne plus ultra* of chemistry, was awarded to Professor Walter Kohn, 75, of the University of California, Santa Barbara "for his development of the density-functional theory" [1–9]. Because of health problems in his family, Kohn was unable to attend the ceremony but presented his Nobel lecture in Stockholm on January 28, 1999. According to the Royal Swedish Academy of Sciences: "The laureates have each made pioneering contributions in developing methods that can be used for theoretical studies of the properties of molecules and the chemical processes in which they are involved" [7].

The Emergence of Quantum Chemistry

For many years scientists have tried to understand how the bonds between atoms in molecules function as well as how to calculate the properties of molecules and the interactions between them. At the beginning of the twentieth century the advent of quantum mechanics offered some possibilities for solving these problems, but applications in the field of chemistry were not forthcoming, for it was not possible in practice to apply the complicated mathematical equations to such complex systems as molecules inasmuch as the number of variables is enormous (Each atom affects every other electron, and each atom affects the quantum condition of each of its neighbors.). As one of the founders of quantum physics, Paul Adrien Maurice Dirac, the English theoretical physicist who shared the 1933 Nobel Prize in Physics with Erwin Schrödinger, expressed it in 1929: "The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are...fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved" [7]. During the 1960s, however, as computers began to find use for solving these complex equations, the application of quantum mechanics to chemical problems emerged as a new field called quantum chemistry [1, 10, 11].

Pople and Kohn, neither of whom, strictly speaking, was a chemist (Their degrees were in mathematics and physics, respectively.), working independently, have been the two most prominent pioneers in this field that has revolutionized the entire science of chemistry. Kohn, whose theory greatly simplified the mathematics, was interested mainly in understanding the properties of solids, while Pople, who developed the computer programs powerful enough to deal with the equations, was interested mostly in the chemical applications. Their recent recognition by their colleagues and the Royal Swedish Academy of Sciences marks the coming of age of quantum chemistry.

John Anthony Pople

Pople (Figure 1) was born on October 31, 1925 in Burnham-on-Sea, a small resort town in Somerset County on England's west coast (He has retained his British citizenship.) [12]. He was the son of Herbert Keith Pople, the owner of a men's clothing store, and Mary Frances Pople (née Jones), who had been a tutor to children in a rich family and, during World War I, a librarian in the British Army. Although no one in his family was involved in science or technology (He was the first to attend a university.), both his parents considered education as a way of advancement in life. In the spring of 1936 at the age of ten, he began to attend the Bristol Grammar School (BGS) in the nearest big city, at first boarding at the school and returning home by train every weekend. He later commuted daily—two miles by bicycle, 25 miles by train, and one mile on foot, a difficult trip during the early days of World War II when Bristol was subjected to frequent air bombardment. Many classes were held in damp concrete shelters, but he considered the education that he received to be superb.

When Pople was 12, he became greatly interested in mathematics and even began several mathematical research projects, which he found were either unsuccessful or not original. As an example of the latter, he formulated the theory of permutations in response to a challenge about the number of possible orders of the 11 members of a cricket team. Nevertheless, these early experiences helped him to develop an attitude of persistence in research.

Pople kept his mathematical activity secret, and in class, in order to avoid giving the impression of being too clever, he often deliberately introduced errors in his exercises. Except for science and mathematics, his grades were undistinguished. However, in his third year at BGS, when R. C. Lyness, the new Senior Mathematics Teacher, gave the class an unusually difficult test, Pople accepted the challenge and turned in a perfect paper. The Headmaster decided that for his remaining two years at BGS Pople should receive intense personal coaching from Lyness and Senior Physics Master T. A. Morris

Figure 1. John A. Pople, News Release, The Royal Swedish Academy of Sciences, 1998.

in preparation for a mathematics scholarship at Cambridge University. Ironically, Pople abandoned chemistry, the discipline for which he was to receive the Nobel Prize 57 years later, to concentrate on mathematics and physics. He was awarded a scholarship and entered Cambridge in October 1943.

Although most young men were inducted into the armed forces at age 17, a small group of students in mathematics, science, and medicine, including Pople, were allowed to attend the university after which they were obligated to participate in wartime research projects. In May 1945, just as the European war was ending, Pople completed Part II of the mathematical tripos (final honors examination). Because the government no longer needed his services and the university had to make room for returning servicemen, he was forced to leave Cambridge and take industrial employment at the Bristol Aeroplane Company. He received his B.A. degree in mathematics in 1946.

In October 1947 Pople was allowed to return to Cambridge as a mathematics student, but he spent courses in as many branches of theoretical science that he could manage, such as quantum mechanics (taught in part by Dirac), fluid dynamics, cosmology, and statistical mechanics. That year he tried to learn to play the piano in the attic in which he lived in Trinity College. The philosopher Ludwig Wittgenstein, who had retired to live undisturbed, occupied the neighboring room, and Pople relates, “There is some evidence that my musical efforts distracted him so much that he left Cambridge shortly thereafter” [12]. In 1948 Pople was awarded the Mayhew Prize, and, with almost no chemistry background (He had only taken a chemistry course at BGS at the age of 15.), he began his career in theoretical chemistry as a research student with Sir John Lennard-Jones (LJ) working on the theory of liquids.

That same year Pople sought a professional teacher and decided on Joy Cynthia Bowers, who, after a long courtship, became his wife on September 22, 1952. The couple eventually had a daughter, Hilary Jane; three sons, Adrian John, Mark Stephen, and Andrew Keith; and eleven grandchildren. In his Nobel biography he paid tribute to her and his family:

> I have benefited immeasurably from the love and support of my wife and children. Life with a scientist who is often changing jobs and is frequently away at meetings and on lecture tours is not easy; without a secure home base, I could not have made much progress [12].

Pople’s research on the nature of the lone pair of electrons on the water molecule, an initial step toward a theory of hydrogen bonding between these molecules and a preliminary study of the structure of liquid water, earned him his M.A. (1950) and Ph.D. (1951) degrees and a research fellowship in mathematics at Trinity College, Cambridge (1951–1954). He was awarded the Smith Prize in 1950. He dates his general plan for “developing mathematical models for simulating a whole chemistry” from late 1952, when computational resources were limited to hand calculators and extremely limited access to “motorized electric machines.” In Pople’s modest words,

> I see myself as a chemist although I have no professional qualifications in chemistry. I went into quantum chemistry because I was looking for a direction. There's a big tradition of mathematicians going on to theoretical physics, especially in England and particularly in Cambridge [3].

Pople’s attempts to simplify molecular orbital theories enough to make them practical [13] paralleled the studies of Rudolph Pariser [14] and Robert G. Parr [15], and their combined work became known as PPP theory, on which he began to lecture at international meetings beginning in 1955. Parr spent a year at Cambridge to work with Frank Boys, the Lecturer in Theoretical Chemistry, and he shared an office and had many valuable discussions with Pople, who acknowledged, “He was to have a major influence on my career.”

In addition to his PPP work, Pople commenced other theoretical studies in physical chemistry such as that of the properties of compressed gases. In 1952 he began to supervise David Buckingham, the first of his numerous dedicated and able research students. In 1954 LJ was succeeded as Professor of Theoretical Chemistry by H. Christopher Longuet-Higgins, who was soon joined by Leslie E. Orgel, and Pople, although he had undertaken new teaching responsibilities as Lecturer in Mathematics (1954–1958), continued to spend more time in the very active Chemistry Department, whose visitors included such luminaries as Linus Pauling, Robert S. Mulliken, John G. Kirkwood, Clemens C. J. Roothaan, and William G. Schneider.

In late 1955 Pople developed an interest in nuclear magnetic resonance, which was then emerging as a powerful technique for studying molecular structure and which became the main area of his research during his final years at Cambridge. Consequently, he spent two summers (1956 and 1957) at the National Research Council in Ottawa, Canada with Schneider and Harold J. Bernstein working on the theoretical background of NMR. They measured NMR spectra, interpreted the nuclear spin behavior of many common compounds for the first time, and wrote a well-received book on the subject [16].

By 1958, having recognized that he had changed from a mathematician to a practicing scientist and dissatisfied with his mathematics teaching position, Pople became superintendent of the new Basic Physics Division at the National Physical Laboratory in Teddington near London (1958–1961; 1962–1964), a post whose administrative responsibilities left him with little time for his own research. In the spring of 1961, together with Charles A. Coulson and Longuet-Higgins, he organized an international conference at Oxford where Parr, an invited speaker, urged Pople to join him at the Carnegie Institute of Technology in Pittsburgh for a sabbatical year (1961–1962) as Ford Visiting Professor, an invitation that Pople accepted.

During this year, Pople decided to leave his administrative post to seek an opportunity to devote as much time as possible to chemical research, for although he was almost 40 years old with a substantial list of publications, he had never held a position in a chemistry department. Coincidentally, Kohn was just leaving Pittsburgh at about the time that Pople arrived. According to Kohn, “I was in the Physics Department, and he was in Chemistry so we just barely knew each other” [9]. Pople returned to Carnegie Tech (which in 1967 merged with the Mellon Institute to form Carnegie–Mellon University (CMU)), where he served as Professor of Chemical Physics (1964–1974) and John Christian Warner Professor of Natural Sciences (1974–1993) as well as Adjunct Fellow in Chemistry at the Mellon Institute (1964–1976). Although leaving England was a painful and difficult decision, Pople recognized that the environment for research in theoretical chemistry was clearly better in the United States. His departure from England helped initiate a political furor there about a scientific “brain drain,” and he estimated that at the time as many as 10% of British scientists with doctorates were emigrating because of low salaries and poor opportunities. He told the Pittsburgh Post-Gazette,

> Scientific research receives much better backing in the United States, and the scientists themselves tend to get paid more. But the main reason I came over and settled in Pittsburgh is the dynamic environment resulting from the presence of so many people in my field [5].

At CMU Pople again took up the fundamental problems of electronic structure that he had contemplated only abstractly many years earlier. Now, however, with the emergence of high-speed computers (Pople admits that “I was late in recognizing the role that computers would play in the field” [12].), he realized that “the development of an efficient computer code was one of the major tasks facing a practical theoretician and [he] learned the trade with enthusiasm” [12]. Over the years Pople and his group kept up with the rapid developments in computer technology, using more sophisticated models as they became available, for example, Univac 1108 in 1971 and Digital Equipment Corporation VAX/780 in 1978. They began to distribute programs to the general chemical community, and more recently their techniques became available on small workstations and personal computers. During the early 1990s they were able to include Kohn’s density functional theory in their methodologies.

By 1979, all the Poples’ children had left home, and he and his wife decided to move to Illinois, where their daughter Hilary had settled. In 1981 they moved to Chicago and in 1988 to Wilmette. From 1981 to 1993 he continued to supervise his CMU research group by frequent commuting and telephone and e-mail communications. In 1986 Northwestern University in nearby Evanston offered him an Adjunct Professorship, and he became Professor of Chemistry in 1993.

Pople’s numerous honors include the Marlow Medal, Faraday Society (1958); Morley Award (1976); Senior Scientist Award, Alexander von Humboldt Foundation (1981); G. Willard Wheland Award, University of Chicago (1981); Evans Award, Ohio State University (1982); Oesper Award, University of Cincinnati (1984); Davy Medal, Royal Society (1988); Wolf Foundation Prize in Chemistry, Jerusalem (1992); and Joseph O. Hirschfelder Prize, University of Wisconsin (1993). His American Chemical Society honors include the Irving (1970), Harrison Howe (1971), Gilbert Newton Lewis (1972), Pittsburgh (1975), Pauling (1977), and Computers in Chemistry (1991) awards and the Kirkwood Medal (1994). The author of more than 400 scientific articles, some of which are among the most frequently cited of chemical papers [17], a Foreign Associate of the U. S. National Academy of Sciences and the American Physical Society, a member or fellow of numerous scientific societies, and a member of the Editorial and Advisory Boards of *Molecular Physics*, *Chemical Physics*, and *Computers in Chemistry*, he was awarded an honorary D. Sc. degree from the University of Toronto in 1990.

In his Nobel biography, Pople graciously states,

> Almost all of the work honoured by the Nobel Foundation was done at CMU. That institution deserves much of the credit for their continuing support and encouragement over many years.... I must emphasize that my contribution to quantum chemistry has depended hugely on work by others. The international community in our field is a close one, meeting frequently and exchanging ideas freely. I am delighted to have had students, friends and colleagues in so many nations and to have learned so much of what I know from them. This Nobel Award honours them all [12].

Walter Kohn

Kohn (Figure 2) was born on March 9, 1923 in Vienna, Austria into a middle class Jewish family that was part of the secular and artistic life of the capital [18–20]. His father, Salomon Kohn, owned a business, Postkartenverlag Brüder Kohn Wien I, whose main product was high-quality-art postcards, mostly based on paintings by contemporary artists. Although the business had flourished during the first two decades of the century, because of the death of his father’s brother Adolf, an Austrian soldier, during World War I, the dismantling of the Austrian monarchy, and the postwar economic depression, it gradually fell upon hard times during the 1920s and 1930s, and Kohn’s father struggled from crisis to crisis to maintain his business and support his family. Kohn and his mother and sister spent their summer vacations at their property, a holdover from more prosperous times, in Heringsdorf, Germany, on the Baltic Sea until Hitler came to power in 1933. His father joined them for occasional visits (The family business had a branch in Berlin).

Kohn’s mother, Gittel Kohn (née Rappoport), was the daughter of Orthodox Jews who lived a simple life in retirement and through whom the Kohn family maintained contact with traditional Judaism. Her father spent much time in study and prayer at the local *Schul* (synagogue). She was a highly educated woman with a good knowledge of German, Latin, Polish, and French and some acquaintance with Greek, Hebrew, and English. After Kohn had completed his public

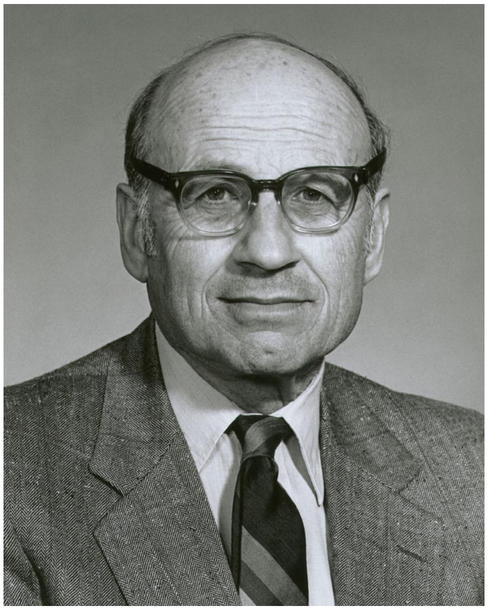

Figure 2. Walter Kohn, Department of Physics, University of California, The Royal Swedish Academy of Sciences, 1998.

elementary school studies, she enrolled him in the Akademisches Gymnasium (Academic High School), where for almost five years he received an excellent classical education, strongly oriented toward Latin and Greek. His favorite subject was Latin, and, ironically, at that time he had no interest in, or apparent talent for, mathematics, the subject in which he received his only grade of C. It was then tacitly understood that he would eventually head the family business, "a prospect which [he] faced with resignation and without the least enthusiasm" [19].

After the Nazi *Anschluss* (annexation) of Austria in 1938, the family business was confiscated, Kohn's father was forced to continue to manage it without compensation, his older sister Minna managed to emigrate to England, and he was expelled from school. He then spent a year and a half in the Chajes Gymnasium, a special high school for Jewish children, where Drs. Emil Nohel and Victor Sabbath, both later killed by the Nazis, taught him physics and mathematics, respectively. He recently told the Austrian daily newspaper, *Kurier*, "There were two teachers there who got me interested in the natural sciences for the first time. Before then I had only paid attention to Latin" [21].

In 1939, only three weeks before the outbreak of World War II, he managed to flee to England, but his parents, who had helped him and his sister escape the Holocaust but were unable to leave Austria, were deported to the concentration camps at Theresienstadt and then Auschwitz, where they perished.

Kohn's feelings toward his native land are still painful, especially since the *Anschluss* was supported by the great majority of the Austrian population with an enthusiasm that surprised even the Germans themselves, whom the Austrians exceeded in brutality. On receiving the news of Kohn's award, Austrian Chancellor Viktor Klima stated, "I am deeply delighted that a Nobel prize goes to someone born in Austria, " but his pride was mixed with "the pain that many of our best sons and daughters were driven out of the country. All these fates commit us to confront the dark chapters of our history in an honest and open manner" [21].

Arriving in England in August 1939, Kohn worked in a training farm in Kent, intending to become a farmer, for he had seen many unemployed intellectuals during the 1930s. He contracted a serious case of meningitis, and his "acting parents," Charles and Eva Hauff, with whom he lived in Sussex with his sister, arranged for him to attend the East Grinstead County School there, where he concentrated on mathematics, physics, and chemistry. Of the Hauffs and of the Mendels (Dr. Bruno and his wife Hertha, with whom he was to live several years later in Toronto, Canada and who also encouraged him in his studies), Kohn said, "I cannot imagine how I might have become a scientist without their help" [19].

In May 1940, shortly after he had turned 17, Kohn was interned as an male "enemy alien" (He held an enemy passport.) for about two months in several British camps, including one on the Isle of Man, where his school sent him the books that he needed to study and where he audited "with little comprehension" lectures on mathematics and physics by interned scientists. In July he was shipped across the U-boat-infested Atlantic as part of a British convoy to Québec City, Canada, and thence by train to a camp in Trois Rivières, where he again attended internee-taught courses, including one on set theory, conducted by Dr. Fritz Rothberger, also from Vienna. Later he was moved to other camps in Québec and New Brunswick, where, as elsewhere, camp educational programs were supported by the Canadian Red Cross and Jewish Canadian philanthropic sources.

In a camp school organized by art historian and fellow internee, Dr. A. Heckscher, Kohn prepared to take the official Canadian High School examinations, and he passed the McGill University Junior Matriculation examination and those in mathematics, physics, and chemistry on the Senior Matriculation level. At age 18, looking forward to a career in physics with a strong secondary interest in mathematics, he used the 20 cents per day that he earned as a lumberjack at the camps to purchase copies of Hardy's *Pure Mathematics* and John C. Slater's *Chemical Physics*, which still reside on his bookshelves today.

In January 1942, "having been cleared by Scotland Yard of being a potential spy" [19], Kohn was released from internment and joined the Mendel family in Toronto, Ontario. He intended to take up engineering rather than physics to be able to support his parents better after the war, but Professor Leopold Infeld of the University of Toronto convinced him that his true love was physics and that majoring in the university's excellent but difficult Mathematics and Physics program would prepare him to earn as decent a living as would engineering. Because of his German nationality, he was not permitted to enter the chemistry building, where war work was in progress, so he was unable to enroll in any chemistry courses. Because chemistry was required, Samuel Beatty, Dean and Head of the Mathematics Department, helped him and several others to enter the program as special students whose status was regularized one or two years later.

During summers and part-time during the school year Kohn became an industrial physicist for the Sutton Horsley Company, a small firm that developed electric instruments for military planes (1941–1943), and he spent two summers working for a geophysicist searching for gold deposits at Koulomzine in Québec (1944–1946). Although his father had been a pacifist, after his junior year he joined the infantry of the Canadian Army as a volunteer (1944–1945), during which time he developed strict bounds on the precession of heavy, symmetrical tops, resulting in a publication [22]. Having completed only two-and-a-half years of a four-year program, he received a war-time B.A. degree "on active service" in mathematics and physics (1945). After his army discharge, he enrolled in an excellent crash program and received his M.A. degree in applied mathematics (1946) with a thesis consisting of his article on tops and a paper on scaling of atomic wave functions.

A Lehman Fellowship (1946–1948) provided financial support for Kohn's graduate studies at Harvard University, where, under young Professor Julian Schwinger, later (1965) Nobel physics laureate, he received his Ph.D. degree in physics in 1948 for developing what was later known as Kohn's variational principle for scattering, useful for nuclear, atomic, and molecular problems. He then served as Instructor in Physics (1948–1950), working under Schwinger's supervision on quantum electrodynamics and the emerging field theory of strong interactions between nucleons and mesons. During the summer of 1949, he worked at the Polaroid laboratory in Cambridge, Massachusetts. Needing to learn about solid state physics for this work, he consulted Professor John H. Van Vleck, the Physics Department Chairman and later (1977) Nobel physics laureate. About to take a leave of absence, Van Vleck asked him if he could teach a course on this subject which he had planned to offer. Frustrated by his work in quantum field theory, Kohn agreed and taught one of the first courses on solid state physics in the United States. Kohn's first wife, Lois, gave him great support during the early phases of his scientific career. The couple had three daughters—J. Marilyn Kohn, Ingrid E. Kohn Katz, and E. Rosalind Kohn Dimenstein.

During a visit to the new Westinghouse nuclear reactor laboratory in Pittsburgh, PA, looking for a position, Kohn found that United States citizenship was required. His Canadian friend Alfred Schild remarked that because Frederick Seitz and several of his colleagues had just left the Physics Department of the Carnegie Institute of Technology, there might be an open position. In 1950 Kohn became Assistant Professor of Physics at Carnegie Tech, where he rose through the ranks, becoming successively Associate Professor (1953–1957) and Professor (1957–1960). He was a National Research Council Fellow (1950–1951) and Ørsted Fellow (1951–1952), both at Niels Bohr's institute in Copenhagen during a two-year leave of absence; Senior National Science Foundation (NSF) Fellow at Imperial College, London (1958); and Guggenheim Fellow (1963) and NSF Senior Postdoctoral Fellow (1967), both in Paris.

He became Professor of Physics (1960–1979) at the University of California, San Diego, where he also served as Department Chairman (1961–1963). In 1978 he married Mara Schiff, daughter of the famous biologist and photographer Roman Vishniac, who documented Jewish life in eastern Europe before the Holocaust.

Kohn moved to the University of California, Santa Barbara, where he was the founding Director of the National Science Foundation's Institute of Theoretical Physics (1979–1984), which brings together leading scientists from throughout the world to work on major problems in theoretical physics and related fields. Under his leadership it quickly developed into one of the leading physics research centers and has served as a model for similar other institutes. Kohn remained at UCSB as Professor of Physics (1984–1991) and retired in 1991, but he remains active as Professor Emeritus and Research Professor. Since 1991 he has also been Research Physicist at UCSB's Center for Quantized Electronic Structures.

The author of more than 200 scientific articles and reviews, consultant to several laboratories, visiting scholar at various domestic and foreign universities, member of the U.S. National Academy of Sciences (since 1969) and other domestic and foreign scientific societies, Kohn holds honorary doctorates from the University of Toronto (L.L.D, 1967), University of Paris (D.Sc., 1980), Brandeis University and Hebrew University of Jerusalem (Ph.D., 1981), Queens University, Kingston (D.Sc., 1986), Eidgenössische Technische Hochschule (ETH), Zürich (D. nat. sci., 1994), Universität Würzburg (D. rer. nat., 1995), Technical University of Vienna (D.Sc., 1996), and Weizmann Institute of Science, Rehovot (Ph.D., 1997). His awards include the Oliver E. Buckley Prize (1960), Davisson–Germer Prize (1977), National Medal of Science (1988), Feenberg Medal (1991), and Niels Bohr/UNESCO Gold Medal (1998).

In addition to his Nobel-winning work on density functional theory (notes, see Figure 3), Kohn is a condensed matter theorist who has made major contributions to the theory of solids, surface physics, collision theory, semiconductors, superconductivity, catalysis, and other areas of physics. His outspoken opposition to nuclear weapons research at the University of California's Lawrence Livermore and Los Alamos laboratories and his unsuccessful faculty initiatives to terminate the university's role in this research have made him a thorn in the side of the UC Board of Regents.

Kohn has been actively involved in Jewish life and affairs, being instrumental in the founding of the UC, San Diego's Jewish Studies Department and maintaining close ties with colleagues and universities and institutes in Israel. At UCSB he is a member of the Advisory Board of the Hillel Foundation, which provides religious, cultural, communal, and counseling services to Jewish students, and he regularly participates in faculty Torah study sessions. He is also involved in the life of the Santa Barbara community and in broader political and social issues.

Kohn enjoys listening to classical music, reading (including French literature), cooking (He is "unjustifiably proud of" his ratatouille.), walking with his wife, and roller blading, a throwback to the ice skating of his Viennese childhood. Although he became a naturalized American citizen in 1957, like many scientists, he has a strong sense of global citizenship, with strong affinities to Canada, Denmark, England, France, and Israel, where he worked and lived with his family for considerable periods of time. He offered early support to Jeffrey Leiffer, the founder of the student Pugwash movement, concerned with global issues with a strong scientific component and in which scientists can play useful roles, and he remains committed to a humane and peaceful world. Convinced that early stabilization of the world's population is important for the attainment of these objectives, he recently joined the Board of the Population Institute.

Pople's Gaussian Program

In his presentation speech for the 1998 Nobel Prize in Chemistry Professor Björn Roos, a member of the Swedish

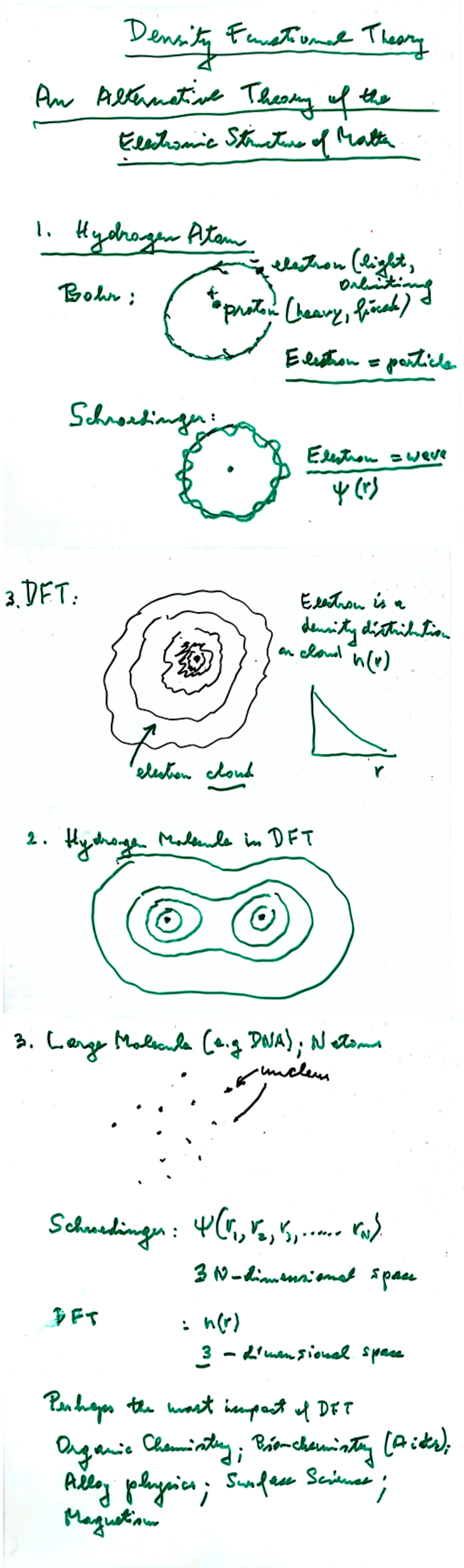

Figure 3. Walter Kohn's notes on density functional theory, Institute of Theoretical Physics, University of California, Santa Barbara Web Site, 1998.

Academy of Sciences and the Nobel Committee for Chemistry, proclaimed,

> With the aid of computer simulations, we can make weather forecasts, calculate the structural integrity of bridges, the aerodynamical characteristics of airplanes, etc. Today, we celebrate the fact that mathematics has invaded chemistry, that by means of theoretical calculations we can predict a large variety of chemical phenomena. Professors Walter Kohn and John Pople have individually made fundamental contributions to this development [23].

Pople himself agreed with this statement when he wrote, "The science of chemistry as we know it today is in the throes of revolution. Its extension from an experimental science to a mathematical science is well under way" [6]. One of the first to apply computers to quantum chemistry during the 1960s, Pople had made valuable contributions to so-called semiempirical methods, which approximated the more difficult integrals and parameters in place of other methods, such as the PPP method, for studying electronic spectra of unsaturated organic molecules [24–26]. Like Dirac, he thought that so-called nonempirical or *ab initio* (Latin, from the beginning) methods such as the Hartree–Fock (HF) approximation of the famous Schrödinger wave equation could not compete with semiempirical methods because the necessary computational power was much too large [6, 27, 28].

The HF procedure consists of two steps: (1) conversion of the Schrödinger-type molecular orbitals to a so-called "basis set" of atom-centered Gaussian functions that replace the complicated differential equations with a simpler matrix amenable to solution by a computer; and (2) integration of the different energy components, for example, kinetic energy and electron-electron repulsion. In spite of his earlier skepticism about the nonempirical approach, Pople managed to develop relatively easy-to-use methods of computation giving reasonably accurate results and yet not requiring excessive computer time. He created an approach that reduced the computational cost of determining the electron-electron and nuclear repulsion integrals by several orders of magnitude by constructing sets of basis functions and testing them in large calculations. He also developed methods to extend these calculations from merely describing equilibrium structures to following reaction paths and transition states, thus making them useful for practical, real-life chemistry [6, 29].

In 1968 Pople initiated *ab initio* work, and by 1969 he published the general theoretical model HF/STO-3G [30]. It was made generally available the following year as Gaussian-70, his first commercial software program, which allowed chemists to analyze the structure, properties, and interactions of complex molecules by simply inputting data into a computer. In the words of Nicholas C. Handy, Professor of Chemistry at Cambridge University and a former colleague of Pople's, "He distributed his program widely. At a stroke, computational quantum chemistry became available to anyone who had a computer" [3].

Pople's software could be used to simulate the biochemical effects of potential drug molecules such as those to fight the AIDS virus; to predict the effect of chemical pollutants such as Freons on the ozone layer, atmosphere, and environment; and to analyze the composition of interstellar matter in distant galaxies. During the 1970s and 1980s Pople continued to improve the program so that now it has become a standard

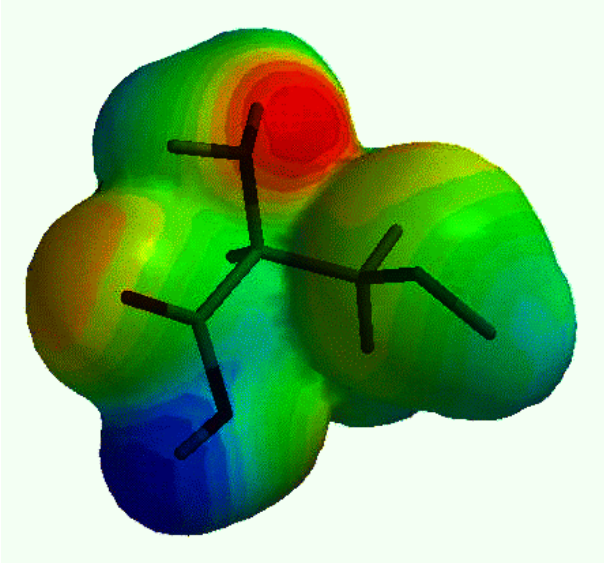

Figure 4. Electron density in the amino acid cysteine, $HSCH_2CH(NH_2)COOH$, calculated using a quantum chemistry computer program, news release, the royal swedish academy of sciences, 1998. The picture shows the surface where the electron density is 0.002 electrons/ $å^{-3}$ (meaning that nearly all electrons are inside the surface). The gray scale shows the electrostatic potential at this surface, darker portions representing negative potential.

tool—an all-purpose workhorse—that can be used to study proteins and other complex systems. New versions of Gaussian programs, managed and marketed by Gaussian, Inc. of Pittsburgh, continue to be released and are used by thousands of universities and companies worldwide. More than 10,000 scientists now use the latest version, Gaussian-98. Today four *ab initio* quantum software program packages (Gaussian, Jaguar, Spartan, and Q-Chem) by four software companies (Gaussian, Schrödinger, Wavefunction, and Q-Chem, respectively), all headed by former Pople students, specialize in quantum chemistry software packages, single copies of which cost about $10,000.

Recently a furor has arisen involving software packages [31]. On March 19, 1999 Northwestern University received a letter from Gaussian, Inc., with which Pople was no longer associated (He is now a member of the Board of Directors of Gaussian's competitor Q-Chem.), stating that Professor Mark A. Ratner's group's failure to notify Gaussian of the previous association of Ratner's postdoctoral fellow Vitaly Rassolov with Pople violated their license agreement and that consequently the entire university's license to use Gaussian was revoked. The license agreement that Northwestern signed with Gaussian forbade access to their software by competitors. Pople has refused to become involved in the imbroglio, which he characterizes as "regrettable," but Professor William A. Goddard III of the California Institute of Technology, one of his defenders, has stated that the "extremely shabby treatment of John Pople by Gaussian is inexcusable and unacceptable" [31].

Kohn's Density Functional Theory

In quantum mechanics an approach known as the Thomas–Fermi (TF) approximation deals not with wave functions, like the HF method, but rather with the simpler electron densities [6]. Dirac had incorporated electron densities into the HF approach to produce the so-called Hartree–Fock–Dirac (HFD) approach, but, nevertheless, the TF approach did not meet with much interest or success. In 1964, however, Kohn and Pierre Hohenberg, an American who shared an office with him at the École Normale Supérieure in Paris where Kohn was spending a sabbatical semester, published a theoretical "exactification" for the TF approximation, now known as the Hohenberg–Kohn (HK) variational principle, which demonstrated that the ground-state electron density was in principle sufficient to characterize completely an electronic system [32]. In Kohn's words, "It is astonishing that such a simple quantity like density can take the place of a wave function, which might be a function of a million variables" [1]. The following year Kohn, now back in San Diego, and his postdoctoral fellow Lu J. Sham derived a series of equations for calculating the ground-state energy, now known as the Kohn–Sham (KS) equations, thus leading to the successful application of the HK theory [33]. Kohn's new approach, density functional theory (DFT) [34], was successful with solid-state applications, but it did not work well with molecules. Another quarter century of work by many physicists and chemists was required before the remaining obstacles were overcome. In 1992 and 1993 the computational work of Pople [35] and Nicholas C. Handy [36] permitted the incorporation of DFT into the latest versions of the Gaussian program. Because DFT is simpler than the alternative methods based on wave functions, its use allowed the application of quantum chemistry to larger molecules such as enzymes. It is now used to make predictions in molecular structure; transition states and reaction paths in chemistry and biochemistry; electrical, optical, and magnetic properties of molecules; X-ray, NMR, and other types of spectroscopy; and intermolecular interactions in macromolecules, crystals, and solvents.

Quantum Chemistry Computer Applications

Quantum theory not only gives quantitative information on molecules and their interactions but also permits a deeper understanding of molecules that cannot be obtained from laboratory experiments alone [7]. For example, to produce a computer image of the amino acid cysteine, $HSCH_2CH(NH_2)COOH$, using the quantum chemistry program, from the menu one would select a molecule in which a carbon atom (C) is bonded to a hydrogen atom (H), an amino group (NH_2), a thiolatomethyl group (CH_2SH), and a carboxyl group (COOH) and ask the computer to use a quantum chemical calculation to determine the geometry of the molecule. The picture on the screen gradually changes toward greater accuracy up to a predetermined level (the greater the accuracy desired, the longer the time required). The computer can then be asked to calculate different properties for the system. Figure 4 depicts a surface with constant electron density with the surface colored according to the value of the electrostatic potential. These data can be used, for example, to predict how the molecule interacts with other molecules and changes in its environment and to study how proteins, which are composed of amino acids, interact with other substrates, such as in pharmaceuticals.

In another example (Figure 5), atmospheric scientists can use quantum chemical computations to study the destructive reactions occurring when Freon molecules (CF_2CCl_2) released

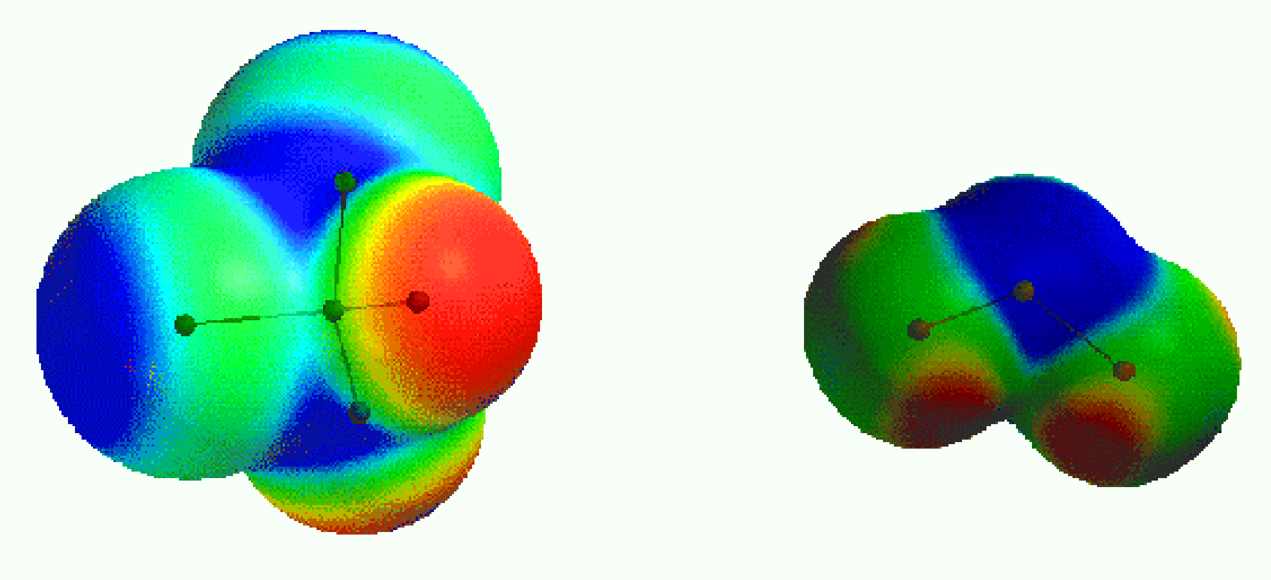

Figure 5. Simulation of freon and ozone using a quantum chemistry computer program, news release, the royal swedish academy of sciences, 1998. High up in the atmosphere, CF_2Cl_2 (freon) molecules (left) are destroyed by ultraviolet light. Free chlorine atoms are formed, which react with ozone (O_3) molecules (right) and destroy them. The process can be studied using quantum chemical calculations.

into the atmosphere from aerosols or air conditioners encounter the thin layer of ozone (O_3) molecules that protects life on Earth from solar ultraviolet radiation. The calculations can be used to describe and understand the reactions in detail with the goal of ameliorating or preventing atmospheric pollution.

In another example, astrophysicists can study from the Earth the great quantities of interstellar matter in the universe, which are often collected in huge clouds, through the radiation that the molecules emit because of their rotation. The composition and appearance of the molecules can be determined from the frequency spectrum of this radiation, but this is a very difficult task, for these molecules cannot always be produced in the laboratory to obtain material for comparative studies. Such limitations, however, do not plague quantum chemistry calculations, which, based on assumed structures, can yield information on radiation emission frequencies that can be compared directly with data collected from radio telescopes and thus determine the composition of interstellar matter that may consist of exotic molecules that do not exist on Earth.

The Laureates' Legacy

Thanks to Kohn and Pople's groundwork, now the formerly scorned theoretical chemist has access to a new tool that actually provides information about molecules that cannot be gleaned from "practical" experiments alone. Quantum chemistry already impinges on so many areas of the research of today's chemists, biochemists, and other scientists that they may take some time to come to terms with the philosophical implications of this revolution, which brings a theoretical description of all of chemistry within reach.

A Cautionary Tale

The World War II diaspora of many European scientists to avoid persecution by the Nazis has created an American domination of the Nobel prizes, a position formerly held by Great Britain and Germany. Since the inception of the Nobel prizes in 1901, the United States has won 186 prizes to Great Britain's 67 and Germany's 64 in the categories of chemistry, physics, and physiology or medicine [37]. An additional reason for the emigration has been the opportunities and funding for unrestricted basic research not generally available in other countries. As we have seen, both Pople and Kohn emigrated to the United States—from England and Austria, respectively. In Kohn's words, "We have all taken advantage of the excellent climate for scientific research that has long existed in the United States" [37]. Also, in contrast to the situation abroad, the United States itself was relatively unscathed by the worldwide conflict. As Jerome Singer, Professor Emeritus of Engineering and Biophysics at the University of California, Berkeley, recently stated,

> While Europe, Japan, and the Soviet Union were rebuilding devastated countries...America was putting huge amounts of emphasis on the kinds of science that helped win the war. The amount of money we have put into the research has attracted the very best and brightest in the world [37].

However, Steven G. Brush, Professor of the History of Science at the University of Maryland, is worried that Congressional cuts to funding for basic research may soon cause the United States to lose its dominance:

> For the last decade, the proportion of money the United States spends on science as a proportion of [gross national product] is smaller than [that of] Europe or Japan. It is a puzzle that we aren't yet beginning to feel the effects of such decreased funding [37].

Let us hope that his words will reach and have an effect on Congress before it is too late.

Acknowledgment. We gratefully acknowledge the assistance of Diane Majors of CSUF's H. M. Madden Library Reference Department, of Nobel laureates Walter Kohn and John A. Pople, and of Kristina Fallenius of the Nobel

Foundation, Stockholm, Sweden for providing valuable source materials used in the preparation of this article.

References

1. Amato, I. "Quantum Chemistry for the Masses" *Science* **1998,** *282*, 611.
2. Bradley, D. "Nobel awards theoretical chemists" *Educ. Chem.* **1999**, *36*, 7.
3. Lawton, G. "Clean sweep for quantum researchers" *Chem. & Ind.* **Nov. 2, 1998**, *No. 21*, 873.
4. Miller, J. "1998 Nobel Prizes: Chemistry" *J. Chem. Educ.* **1999**, *76*, 12.
5. Spice, B. "Nobel winner's work at CMU paved the way to the prize" *Pittsburgh Post-Gazette*, Oct. 14, 1998; http://www.post-gazette.com/healthscience/19981014pople1.asp.
6. Stevenson, R. "Nobel rewards for quantum steps" *Chem. Br.* **1998**, *34*(11), 29.
7. "The Nobel Prize in Chemistry 1998"; http://www.nobel.se/announcement-98/chemistry98.html.
8. "The 1998 Nobel Prizes in Science: Chemistry: Reactions on a Computer" *Scientific American* **1999**, *280*(1), 17.
9. Wilson, E. "Chemistry Nobel goes virtual" *Chem. Eng. News* **Oct. 19, 1998**, *76*(42), 12.
10. Matthews, P. *Quantum Chemistry of Atoms and Molecules*; Cambridge University Press: Cambridge, England and New York, 1986.
11. Wilson, E. K. "Theoretical Chemistry Expands and Diversifies Across Chemical Disciplines" *Chem. Eng. News* **Aug. 19, 1996**, *74*(34), 35.
12. Pople, J. A. "Quantum Chemical Models" Nobel Lecture, December 8, 1998; biographical sketch, typewritten copies; to be published by the Nobel Foundation in *Les Prix Nobel 1998*, © Nobel Foundation, 1999.
13. Pople, J. A. "Electron Interaction in Unsaturated Hydrocarbons" *Trans. Faraday Soc.* **1953**, *49*, 1375.
14. Pariser, R.; Parr, R. G. "A Semi-Empirical Theory of the Electronic Spectra and Electronic Structure of Complex Unsaturated Molecules. I" *J. Chem. Phys.* **1953**, *21*, 466, 767.
15. Parr, R. G. "A Method for Estimating Electronic Repulsion Integrals over Linear-Combination-of-Atomic Orbitals Molecular Orbitals in Complex Unsaturated Molecules" *J. Chem. Phys.* **1952**, *20*, 1499.
16. Pople, J. A.; Schneider, W. G.; Bernstein, J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959.
17. Jeffrey, G. A.; Pople, J. A.; Radom, L. "The application of *ab initio* molecular orbital theory to the anomeric effect. A comparison of theoretical predictions and experimental data on conformations and bond lengths in some pyranoses and methyl pyranosides" *Carbohyd. Res*. **1972**, *25*, 117; Jeffrey, G. A. "This Week's Citation Classic" *Curr. Contents* **June 23, 1980**, *25*; also In *Citation Classics in Physical, Chemical, and Earth Sciences*; Thackray, A., Ed.; ISI Press: Philadelphia, PA, 1986; p 34.
18. Kohn, W. "Personal Biographical Details" http://www.physics.ucsb.edu/~kohn.
19. Kohn, W. "Electronic Structure of Matter—Wave Functions and Density Functionals" Nobel Lecture, January 28, 1999; biographical sketch, typewritten copies; to be published by the Nobel Foundation in *Les Prix Nobel 1998*, © Nobel Foundation, 1999.
20. "Press Conference on the Award of the 1998 Nobel Prize in Chemistry to Dr. Walter Kohn" http://www.itp.ucsb.edu/online/nobel/kohn.
21. Nobel Prize Awakens Shame Over Nazi Past. *Israel Wire*, Oct. 14, 1998; http://www.israelwire.com/New/981014/98101419.html.
22. Kohn, W. "Contour Integrations in the Theory of the Spherical Pendulum and the Heavy Symmetrical Top," *Trans. Amer. Math. Soc*. **1946**, *59*, 107.
23. Roos, B. "Presentation Speech, 1998 Nobel Prize in Chemistry" Nobel Foundation web site, 1998; http://www.us.nobel.se/festivities/98/speeches/chemistry-presentation.html.
24. Martin, D. "John Pople and the search for chemical truth" *Chem. Br.* **1992**, *28*(2), 138.
25. Burton, W. "Pople applies math to chemical problems" *Northwestern Observer*, Nov. 22, 1998; http://www.nwu.edu/univ-relations/media/observer/category/university-news/poplesci-uwn.html.
26. Schleyer, P. v. R., Ed. *Encyclopædia of Computational Chemistry*; John Wiley & Sons: New York, 1998.
27. Pople, J. A.; Beveridge D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.
28. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.
29. Krieger, J. H. "Computational Chemistry Impact" *Chem. Eng. News*, **May 12, 1997**, *75*(19), 30.
30. Hehre, W. J.; Stewart, R. F.; Pople, J. A. "Self-Consistent Molecular-Orbital Methods. I. Use of Gaussian Expansions of Slater-Type Atomic Orbitals" *J. Chem. Phys.* **1969**, *51*, 2657.
31. Wilson, E. K. "Quantum Chemistry Software Uproar: Gaussian says license policies are needed to protect code, but some chemists say restrictions go too far" *Chem. Eng. News* **July 12, 1999**, *77*(28), 27.
32. Kohn, W.; Hohenberg, P. "Inhomogeneous Electric Gas" *Phys. Rev*. **1964**, *136*, B864.
33. Kohn, W.; Sham, L. J. "Quantum Density Oscillations in an Inhomogeneous Gas" *Phys. Rev*. **1965**, *137*, A1697.
34. Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York; Oxford, England, 1989.
35. Pople, J. A.; Gill, P. M. W.; Johnson, B. G. "Kohn-Sham Density-Functional Theory within a Finite Basis Set" *Chem. Phys. Lett.* **1992**, *199*, 557.
36. Handy, N. C.; Murray, C. W.; Amos, R. D. "Study of Methane, Acetylene, Ethene, and Benzene Using Kohn–Sham Theory" *J. Phys. Chem*. **1993**, *97*, 4392.
37. Wood, D. B. "Why U.S. Dominates Science: Holocaust Drove Many to United States" *Christian Science Monitor*, Oct. 16, 1998; http://abcnews.go.com/sections/science/DailyNews/nobel_us981016.html.