CHEMICAL REVIEWS

EDITORIAL

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Introduction to the *Quantum Chemistry 2012* Issue

1. BACKGROUND

Quantum chemistry started when Heitler and London[1] treated the covalent bonding in the hydrogen molecule. Six early books were those by Haas,[2] Pauling and Wilson,[3] Hellmann,[4] Pauling,[5] Eyring et al.,[6] and Pitzer.[7] In addition to books devoted entirely to the subject, the field of quantum chemistry worked its way into the classic physical chemistry textbooks of the era.

An early goal that emerged soon after WW II were what are now known as ab initio[8] calculations, where chemical conclusions are obtained from the general principles of quantum mechanics. Naturally, a level of approximation, such as Hartree−Fock, and technical details, such as a basis set, had to be chosen first, with each choice yielding what later came to be known as a "model chemistry". Some well-crystallized approaches have been different truncations of configuration interaction, various orders of many-body (Møller−Plesset) perturbation theory, the coupled-cluster approach that involves summing certain perturbation theory terms to infinite order, and the complete active space (CAS) method. The electron correlation problem for strongly multiconfigurational systems still cannot be regarded as solved in a satisfactory manner.

Traditionally, quantum chemistry has been based on the nonrelativistic Schrödinger equation and the Born−Oppenheimer (clamped-nuclei) approximation. For almost a half-century, it has been appreciated that relativistic effects (included via the Dirac equation or its various approximations) are important for heavier atoms and molecules. If high accuracy is needed, they are necessary for all molecules. There had been, of course, earlier relativistic studies in atomic and solid-state physics, but how the relativistic effects impacted anything associated with chemistry, or periodic trends, was very seldom considered. More recently, a new scientific frontline in quantum chemistry has considered the effects of quantum electrodynamics (QED). In addition to relativistic effects, the other major approximation of quantum chemistry—the Born−Oppenheimer picture—sometimes needs to be addressed when high accuracy is the goal or when certain classes of problems are considered. Finally, parity nonconservation is a fascinating phenomenon, although it is an extremely small effect that has not yet been observed experimentally in molecules.

Beyond teaching us a great deal about how molecules behave and interact with their environment, quantum chemistry has yielded a very important product: software packages, some of them representing commercial enterprise and others given away freely to help others further the cause of science. In either case, these programs are being used by an ever-growing base of users. Although the very many capabilities of some of the better packages are such that their use by the inexperienced is a bit like putting a beginning driver behind the wheel of a Ferrari, it is undeniable that many branches of chemistry utilize the efforts of the quantum chemists through the software that they have produced.

Concerning their inner organization, the quantum chemists have benefitted from an unusually strong, worldwide, social cohesion. Early on there were international meetings, such as the 1959 Boulder Molecular Quantum Mechanics[9] and 1963 Sanibel[10] meetings, the schools in Sweden and Florida that were organized by Löwdin, the Coulson schools at Oxford, and many others. The International Congresses of Quantum Chemistry (ICQC) have been organized every third year since 1973 by the International Academy of Quantum Molecular Sciences (IAQMS), the next one being held at Boulder, CO, in 2012. A dynamic forum for quantum chemistry, albeit with a different emphasis, has been that provided by the WATOC meetings; the first of these was in 1987, and the latest was at Santiago de Compostela, Spain, in 2011. The current MQM (Molecular Quantum Mechanics) meetings form a third triannual series, geared toward audiences comprising those traditionally associated with both ICQC and WATOC. The American, Asia-Pacific, Canadian, Central European CESTC, European ECCC, German STC, Spanish ESPA, etc. regional meetings have been more international than their names might suggest. Beyond these, there are a vast number of other meetings ranging from large sessions devoted to quantum chemistry in the massive events known as ACS meetings, the annual Sanibel Symposia that have been held for more than a half century, and the PACIFICHEM series to the Quitel series that presents theoretical chemistry in the Latin languages (French, Spanish, and others). Indeed, the visibility of, and support for, quantum chemistry is widespread; those that work in this field definitely do not toil in solitude. An idea of the state of progresss of quantum molecular science in various parts of the world is given in the IAQMS survey, which is available online: www.iaqms.org/survey.php.

Quantum chemistry has also been recognized by major prizes. Nobel Prizes given for the quantum-mechanical treatment of molecules were given to Pauling (1954), Mulliken (1966), Fukui and Hoffmann (1981), and Kohn and Pople (1998); other major awards won by quantum chemists include the Wolf Prize (Pople, in 1992) and the Nobel Peace Prize (Pauling, 1966). Like any other group of able academics, the quantum chemists have also seen some of their former colleagues make an impact in quite disparate fields, ranging from economics (Koopmans) and neuroscience (Longuet-Higgins) to leading a major European country.

2. THE PRESENT ISSUE

The present issue offers a wide array of articles dealing with the current state of quantum chemistry. They comprise work devoted to new approaches that are different in spirit than (but retain the same goal as) those traditionally applied to the solution of the nonrelativistic Schrödinger equation in the Born−Oppenheimer approximation; contributions detailing and reviewing methods that go beyond the limitations of this "workhorse" treatment of electrons in molecules—relativistic and nonadiabatic effects; and applications of quantum chemistry toward systems much larger than those to which it was once effectively restricted.

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Fundamental to achieving high accuracy in quantum chemistry is the selection (and development) of basis sets that serve to describe the electrons in atoms and molecules. One of the most problematic issues associated with basis sets is that it can be shown that the exact electronic wave function of any atom or molecule must have a "cusp" (a nondifferentiable point) when the coordinates of two electrons with opposite spin become coincident. This condition is not met at the Hartree–Fock level but rather is, in essence, a "correlation effect". A direct consequence of this is that results tend to converge more quickly to the "basis set limit" at the Hartree–Fock level than do results using a correlated method like configuration interaction, perturbation theory, coupled-cluster approximation, etc. Although the traditional route to this problem was brute force—use larger and larger basis sets until the results display acceptable convergence—other approaches have found use. One of these is to simply extrapolate the results given by a well-defined hierarchy of basis sets, but another is to use basis sets that contain the interelectronic distance (and with it, the cusp behavior) explicitly within them. Such methods, known as "explicitly correlated" approaches, are reviewed here by Hättig, Klopper, Köhn, and Tew (DOI: 10.1021/cr00168z) as well as by Kong, Bischoff, and Valeev (DOI: 10.1021/cr200204r). Approaches for dealing with the correlation problem reviewed here are the traditional multireference methods with additional treatments of correlation—some well-tried and others quite new—by Szalay, Müller, Gidofalvi, Lischka, and Shepard (DOI: 10.1021/cr200137a) as well as the formidably difficult issue of how best to use coupled-cluster theory in a multireference framework [Lyakh, Musiał, Lotrich, and Bartlett (DOI: 10.1021/cr2001417)]. Less traditional methods that are designed to approach the limit of the nonrelativistic Schrödinger equation within the Born–Oppenheimer picture include the density matrix methods that arise from what is known as Nakatsuji's theorem—that the exact wave function can be written in a form considerably simpler than the so-called full CI expansion—and have evolved to various treatments of the "contracted Schrödinger equation" and "reduced density matrix" theories, which are reviewed herein by Mazziotti (DOI: 10.1021/cr2000493). Other nontraditional approaches include quantum Monte Carlo approaches that are reviewed here by Austin, Zubarev, and Lester (DOI: 10.1021/cr2001564). An entirely different approach to the nonrelativistic Born–Oppenheimer limit is, of course, that taken by density functional theory (DFT, which is completely distinct from "density matrix" theories), which is founded on the premise that the exact energy can be expressed as an (unknown to date and probably not universal) functional of the reduced one-electron density of a molecular or atomic system. The current state of this field, which is undergoing development and transformation at a rather furious pace, is assessed by Cohen, Mori-Sánchez, and Yang (DOI: 10.1021/cr200107z) in this issue, with an emphasis on remaining challenges for the field. In our view, a quite interesting recent development in DFT is the constrained DFT approach [reviewed here by Kaduk, Kowalczyk, and Van Voorhis (DOI: 10.1021/cr200148b)] that works in a framework that is akin to the quasiadiabatic picture that is often so chemically appealing as well as being computationally useful.

Quantum chemistry, as emphasized at the beginning of this piece, neither begins nor ends with the nonrelativistic Born–Oppenheimer picture. Indeed, many of the real frontiers of the field lay in the fertile fields beyond these boundaries. And here, our issue has much to offer. Starting from the physical fundamentals, Pyykkö (DOI: 10.1021/cr200042e) discusses the size of the aforementioned QED corrections. For the heavier elements, they are of the order of 1% of the Dirac-level relativistic effects. Qualitatively, the Dirac–Coulomb Hamiltonian hence is "101% right". A small collection of recent examples of relativistic effects on chemical properties is given in the accompanying applications review.[11] Concerning the ways of implementing the Dirac Hamiltonian in quantum chemical calculations, the Douglas–Kroll–Hess transformation represents one of the more common approaches. The current situation is discussed by Nakajima and Hirao (DOI: 10.1021/cr200040s). Outside our own box (this issue), one can mention the possibility of going to infinite-order or "exact 2-component (X2C)" Hamiltonians.[12] An even more common way of easily incorporating relativistic effects in a quantum mechanical, wave-function theory (WFT) or density functional theory (DFT) calculation is the use of pseudopotentials (effective core potentials). The latest developments are described by Dolg and Cao (DOI: 10.1021/cr2001383), who represent the "Stuttgart" pseudopotential school, which has long been very visible in this area and whose work is perhaps currently of best accuracy. In the pseudopotential approach, the valence-space orbitals are the lowest states in that "pseudopotential". The three advantages are that one thereby omits both the innermost electrons, the basis functions needed to describe them, and can moreover introduce the relativistic effects, with or without spin–orbit coupling (SOC). The limitations of the Born–Oppenheimer approximation and the rich class of "nonadiabatic" phenomena in chemistry are reviewed in detail by Yarkony (DOI: 10.1021/cr2001299) in this issue, as well as a number of recent developments in which quasidiabatic pictures (useful in solving problems that feature Born–Oppenheimer breakdown) are constructed using traditional methods of quantum chemistry. Another erudite review on this subject is also included in which Yonehara, Hanasaki, and Takatsuka (DOI: 10.1021/cr200096s) discuss non-adiabatic effects in chemistry.

Nor does quantum chemistry begin and end with the development and implementation of new and improved theories in the program packages mentioned earlier. The field, which is ultimately a practical endeavor, is also used to understand chemical problems—spectroscopy, reactivity, solvation, conformations, etc. The calculation of molecular "properties" (a term generally used in the field to refer to anything that is not based on the energy itself, but rather its derivatives, which includes dipole and higher-order moments, vibrational frequencies, magnetic properties including NMR parameters, and a vast array of other important phenomena) is reviewed by Helgaker, Coriani, Jørgensen, Kristensen, Olsen, and Ruud (DOI: 10.1021/cr2002239); the treatment of very large systems and solvation effects within a class of quite promising new approaches are reviewed by Gordon, Fedorov, Pruitt, and Slipchenko (DOI: 10.1021/cr200093j). And, as said, one of us (P.P.) presents a treatment of the fundamental physics that sits (hiding, but not very well) behind the periodic table that is a part of every child's education.

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BIOGRAPHIES

Photo 2009 by Jussi Aalto.

Pekka Pyykkö was born in Hinnerjoki, Finland, in 1941 and received his education in the nearby city of Turku with a Ph.D. in 1967. His two latest employers were Åbo Akademi University in 1974−1984 and the University of Helsinki in 1984−2009. Since November 2009, he continues research in Helsinki as Professor Emeritus. He now has about 300 papers. He led in 1993−1998 the program "Relativistic Effects in Heavy-Element Chemistry and Physics (REHE)" of the European Science Foundation (ESF) and in 2006−2008 the Finnish Centre of Excellence in Computational Molecular Science (CMS). In addition to his own research, he currently chairs two Academies and one Editorial Board.

John F. Stanton is the Watt Centennial Professor of Chemistry at the University of Texas at Austin, where he has been on the faculty since 1993. He was raised in the Philadelphia area, attended the University of Michigan (B.G.S, 1984), and received a Ph.D. in Chemical Physics at Harvard University in 1988. After postdocs at the University of Chicago and the University of Florida, he took a position in Austin. His research has dealt with various aspects of theoretical chemical physics, particularly quantum chemistry and its application to molecular spectroscopy. He is director of the Institute for Theoretical Chemistry and is active in undergraduate education.

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REFERENCES

(1) Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 455.

(2) Haas, A. *Die Grundlagen der Quantenchemie. Eine Einleitung in vier Vorträgen*; Akademische Verlagsgesellschaft: Leipzig and Wien, Germany, 1929.

(3) Pauling, L.; Wilson, E. B., Jr. *Introduction to Quantum Mechanics with Applications to Chemistry*; McGraw-Hill: New York, 1935.

(4) Hellmann, H. *Kvantovaya Khimiya*; ONTI: Moscow and Leningrad, 1937; German version: *Einführung in die Quantenchemie*; Deuticke: Leipzig and Wien, Germany, 1937.

(5) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939.

(6) Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry*; Wiley: New York, 1944.

(7) Pitzer, K. S. *Quantum Chemistry*; Prentice-Hall: New York, 1953.

(8) An interesting detail is who introduced the term ab initio in the sense *from first principles*? The earliest journal reference we find is by Chen,[13] who quotes an unpublished MIT report by Allen and Nesbet.[14] The next journal article is by Roothaan.[15] Allen and Karo[16] use the term in their title and also strictly define it. The expression ab initio was used earlier by Parr and co-workers, but in the meaning of several workers performing the same calculation "from scratch", as recognized by Parr himself.[17]

(9) Parr, R. G. *Revs. Mod. Phys.* **1960**, *32*, 169. Issue no. 2 of the journal (pp. 169−476) contains the Proceedings of the Boulder 1959 Symposium.

(10) Löwdin, P. O. *Revs. Mod. Phys.* **1963**, *35*, 415. This issue contains lectures from the Sanibel Symposium, January 14−19, 1963.

(11) Pyykkö, P. *Annu. Rev. Phys. Chem.* **2012**, *63*, DOI: 10.1146/annurev-physchem-032511-143755.

(12) Liu, W.-J. *Mol. Phys.* **2010**, *108*, 1679.

(13) Chen, T. C. *J. Chem. Phys.* **1955**, *23*, 2200. See ref 7.

(14) Allen, L. C.; Nesbet, R. K. *Quarterly Progress Report, Solid-State and Molecular Theory Group, MIT* **1955**, *July 15*, 27.

(15) Roothaan, C. C. J. *J. Chem. Phys.* **1958**, *28*, 982.

(16) Allen, L. C.; Karo, A. M. *Rev. Mod. Phys.* **1960**, *32*, 275.

(17) Parr, R. G. *Int. J. Quantum Chem.* **1990**, *37*, 327. See page 331 for the copy of a letter of May 17, 1950, from D. P. Craig.