Nobel Prize Honors Kohn and Pople for Methods of Quantum Chemistry

The Royal Swedish Academy of Sciences has chosen Walter Kohn and John Pople as the recipients of the 1998 Nobel Prize in Chemistry. Kohn, a research professor of physics at the University of California, Santa Barbara, is being honored for "his development of density functional theory," and Pople, a professor of chemistry at Northwestern University, is being cited for "his development of computational methods in quantum chemistry." Through their separate contributions, according to the academy, Kohn and Pople were "the two most prominent figures" in the "enormous theoretical and computational development" leading to the emergence of quantum chemistry.

Kohn and Pople have followed very different career paths, the common denominator being their mutual interest in systems with many electrons. Kohn, a theoretical physicist, has focused primarily on condensed-matter systems. His density functional theory has been the method of choice for condensed-matter physicists interested in electronic structures ever since he and his colleagues formulated it in the mid-1960s. In recent years, it has taken hold in the chemistry community as well. Pople, trained as a mathematician, has concentrated on the electronic structure of molecules. Starting in the 1960s, Pople and his students, with great innovation and foresight, began to create and continually improve computer programs based on the Hartree–Fock approach to facilitate the complex calculation of molecular structures. By early in the 1990s, most of those programs had incorporated the density functional approach as well. Roughly half of the electronic structure calculations in chemistry today are done with the density functional approach.

Quantum mechanics tells you how to solve molecular structure, in principle. Kohn and Pople, in different ways, made it possible in practice.

Starting with Schrödinger

The basic starting point for any calculation of multi-electron systems is the Schrödinger equation. It's straightforward enough to write down, but nearly impossible to solve exactly: The motion of each electron depends on that of the other electrons, and accurate numerical solution of the many-electron wavefunction for systems of more than a few electrons is beyond even today's computing capabilities. Approximations are needed to make any headway.

A simple way to start is to assume that the electrons move in independent orbitals, determined by the field of the nucleus and the mean field of all the other electrons. The total wavefunction is then written as an antisymmetric product of the independent-particle orbitals, and the Schrödinger equation separates into as many equations as one has electrons. With these independent-particle wavefunctions, one can calculate the effective Coulomb interaction term and solve for a new set of wavefunctions in an iterative procedure. That is the method developed in the 1930s by such individuals as Douglas Hartree, Vladimir Fock and John Slater; it is the heart of the now-familiar Hartree–Fock method.

Significant improvements have been made to the original formulation of the Hartree–Fock method. The electronic orbitals are now written as linear combinations of basis functions, using the formalism introduced in influential 1951 papers by Clemens Roothaan and by George Hall. Using basis functions changes the problem from a set of differential equations to a matrix formulation, which lends itself well to treatment by computer. The first basis functions used—ones suggested by Slater—were accurate but difficult to use. S. Frank Boys suggested that one could facilitate the calculations by choosing, as a basis set, Gaussian functions having essentially the form $e^{-\alpha r^2}$. That's where the Hartree–Fock method stood in the 1960s.

The density functional theory

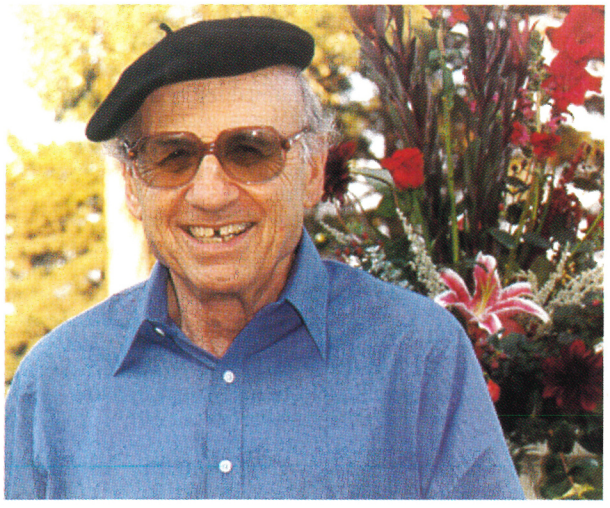
In 1964, Kohn and Pierre Hohenberg were sharing office space as visitors to the Ecole Normale Supérieure in Paris. Together they formulated a startling theorem, that the effect of an external potential (such as the nuclear potential) on the ground state energy of an interacting electron system can be expressed entirely in terms of the electron density.[1] In principle, you can get all the information about the electronic structure from this one function; you don't need to worry about the full many-body wavefunction. That's a great simplification: You can focus on three spatial variables rather than the enormous set needed to describe a host of electrons. Furthermore, the electron density can be found by using a variational principle, thanks to the existence of a functional (a function of a function) of the density whose minimum is the exact ground-state energy.

Years before, Llewellyn Thomas and Enrico Fermi had developed a similar idea of representing the atomic problem in terms of electron densities. Kohn's work with Hohenberg placed this earlier model on a more rigorous footing.

When Kohn returned to his home base, which at the time was the University of California, San Diego, he involved his postdoc, Lu Sham, in the same problem. Together they set forth a computational scheme, known as the Kohn–Sham equations, for solving the problem formulated in terms of density functionals.[2] In the process, they showed that the density functional approach is equivalent to the Hartree procedure, but with a significant improvement: The electron exchange and correlation interactions, which are ignored by Hartree, are included in the Kohn–Sham equations as an additional, additive potential in the single-particle Schrödinger equations.

These two papers of Kohn's—the one with Hohenberg and the one with Sham—pointed to a new direction.[3] But the hard work of specifying the functional remained. As Hohenberg puts it, they had replaced one unsolvable problem with another. However, by focusing on the electron density, the density functional approach has had a deep impact on the way people think about chemical and physical problems. It has led not only to computational simplifications but also to conceptual insights.

One such insight was the local density approximation introduced by Kohn and Sham, according to which the correlations and exchange interactions are treated as if the density were constant within each small, local region. This approximation has served condensed-matter physicists well for over 30 years, playing a role, for example, in the energetics determining the crystal structures of different phases of solids. In the 1980s, Michele Parrinello (Max Planck Institute for Solid-State Research in Stuttgart) and Roberto Car (University of Geneva) further extended the scope of the theory by using it to perform *ab-initio* molecular dynamics calculations. Today, the approach is used for evaluating static, thermodynamic and dynamical properties not only of crystals but also of many other classes of materials, such as amorphous solids, liquids and biomolecules.



WALTER KOHN

JOHN POPLE

Kohn himself has played a role in extending the density functional theory, contributing to its application to surfaces (in work he did in the early 1970s with Norton Lang, his postdoc at the time) and to the development of time-dependent density functional analysis. Kohn's colleagues in condensed matter point to the many effects that bear his name: the Kohn anomaly, a kink in the phonon dispersion relation; the Kohn–Korringa–Rostoker method for band structure calculations; and the Luttinger–Kohn picture of impurity states in semiconductors. When asked to name those contributions besides the density functional theory of which he was most proud, Kohn mentioned his exploration of the nature of the insulating state and his work with Joaquin Luttinger on semiconductors and on superconductivity with purely repulsive interactions.

The promise of computers

During the 1950s and early 1960s, Pople pursued theoretical studies of molecules with many electrons, especially hydrocarbons, in which one can essentially reduce the problem to only one electron per atom. In 1952, he formulated a model similar to the extended Hubbard model in solid-state physics, featuring interactions of electrons both with nearest and next-nearest neighbors. This model became the PPP model—named for Pople and for the team of Robert Parr and Rudolph Pariser, who developed it independently.

As computers came on the scene, Pople was among the first to realize their potential for enabling useful predictions of molecular properties. Mark Ratner, a colleague at Northwestern, said Pople appreciated early the value of minicomputers (akin to today's workstations) rather than the mainframes that reigned in the 1960s; in fact, Pople purchased the third minicomputer made by the Digital Equipment Corp. Pople admits, however, being surprised at how quickly computers evolved into an essential tool: Not only did powerful computers come along at an unexpectedly rapid pace, but he and others were successful in finding efficient ways to use them.[4]

One of Pople's contributions was to streamline computation of the many (on the order of 10^6 to 10^9) integrals involved in solving the Hartree–Fock equations. According to the Nobel committee, Pople's integration techniques reduced the computing costs by factors of 10 to 100.

Starting in the 1960s, Pople developed a standard set of basis functions to describe the electron wavefunctions. Before then, everyone had used a different set, and each set produced different results. Pople systematically tested his chosen basis set against a large collection of experimental results to assess and refine its accuracy. As an example of how closely Pople has kept in touch with both the computational and chemical worlds, Ratner mentioned that Pople has published papers both on the physics of his methodology and on the application of the methodology. Pople told us that his students also must be well grounded in the same two aspects of the work: computer development and chemistry.

By the 1970s, chemists were requiring greater accuracy than the 1% afforded by the Hartree–Fock approach so that they could determine relative energies such as bond energies or heats of reaction. To go further required incorporating the detailed effects of electron–electron correlations, which are treated only in an average way in the Hartree–Fock assumption of independent electron motions. Pople and his students developed a series of perturbation expansions (up to fourth order). With the fourth-order expansion, one can improve the accuracy to roughly 0.1%.

Together with his students, Pople designed a computer program called GAUSSIAN. Besides improving the efficiency and accuracy of the calculations, they provided what is now called a user-friendly interface. Although Pople initially distributed the program free of charge, he later founded a company called GAUSSIAN to sell it commercially, starting in 1970. Today, a number of commercial firms market various types of programs for computational chemistry, four headed by former students of Pople's. Such programs are used not only by chemists but by geologists, astronomers, biomedical researchers, materials scientists and biologists.

Density functionals in chemistry

Computer programs such as Pople's did not incorporate the density functional approach until the early 1990s, although some researchers before then did use that approach in treating molecules and clusters. Parr, who is now at the University of North Carolina, was one of the few chemists who took an early interest in the density functional theory. Kohn credits him with using it to gain conceptual insights and also with bringing the technique to the attention of chemists through a book he wrote with Weitao Yang (Duke University),[5] and the students and postdocs Parr trained. Parr told us that density functional theory was not attractive to large numbers of chemists until its accuracy was improved and it

was incorporated into accessible computer programs.

Chemists demand a high level of accuracy because of the very small energy differences needed to understand chemical phenomena. To gain the desired accuracy in the density functional theory required a more sophisticated treatment of electron–electron correlations than is employed by the local density approximation. These correlations were introduced by the use of generalized gradients of the density, thanks to successive contributions by David Langreth, John Perdew and Axel Becke.

Currently, the accuracy of the density functional approach varies with the application. Kohn suspects that this approach, by its nature, may never be a theory for achieving great accuracy. Its unique advantage is its ability to deal with larger molecules, in which there is increasing interest. By contrast, the Hartree–Fock or other, more conventional calculations become much more difficult as the number of electrons in the problem increases.

By the early 1990s, the improved accuracy in the density functional theory and increased interest in large molecules had motivated Pople and others to incorporate the density functional theory into their computer programs.

Full careers

Kohn describes his early life as "turbulent". Born of Jewish parents in Vienna in 1923, he was just young enough to qualify for the last *Kindertransport* out of Nazi-occupied Austria when he was 16. After two years with a family in England, he was just old enough to be sent for detention in Canada as an "enemy alien." There, he eventually served in the Canadian armed forces during World War II. After the war, he attended the University of Toronto, earning a BA (1945) and an MA (1946) in applied mathematics. He got his PhD in physics under Julian Schwinger at Harvard University in 1948, staying on for two years as an instructor. From 1950 to 1960, Kohn was a professor of physics at the Carnegie Institute of Technology (today, Carnegie Mellon University) from 1950 to 1960 and at the University of California, San Diego, from 1960 to 1979. In 1979, he became the first director of the newly created Institute of Theoretical Physics at the University of California, Santa Barbara, guiding that institute through its first five years. In 1984, he became a professor of physics at UCSB and continues to be active as a research professor there.

Pople was born in the UK in 1925. He earned his PhD in mathematics at the University of Cambridge in 1951, working under John Lennard-Jones. Pople remained at Cambridge until 1958, first as a research fellow and then as a lecturer in mathematics, all the while doing semiempirical studies of molecules. In 1964, after six years as superintendent of the basic physics division of the National Physical Laboratory in Teddington, England, Pople went to Carnegie Tech as a professor of chemical physics. In 1974, he became the John Christian Warner University Professor of Natural Sciences. He has been at Northwestern since 1986, where he continues to pursue his interests in molecular structure.

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Two-Dimensional Electron Gases Continue to Exhibit Intriguing Behavior

The startling discoveries of the integral and fractional quantum Hall effects were made in two-dimensional electron gases subjected to very high magnetic fields (see the story on page 17). Now, it appears, other surprises await us at lower fields. In a recent study, the longitudinal resistivity exhibited a strong anisotropy in a certain range of temperature and magnetic field: When plotted as a function of the magnetic field, the resistivity has a dip when the current flows in one direction and a strong peak when it flows in an orthogonal direction.[1] There's no *a priori* reason to think that these two directions are different.

When researchers from Caltech and Bell Laboratories, Lucent Technologies, reported these results last August at a conference on quantum Hall and mesoscopic systems held at the Institute for Theoretical Physics in Santa Barbara, California, the audience suggested ways to check for this or that possible confounding factor. Having survived further experimental scrutiny, the anisotropy is now attracting increasing interest from the theorists.

Researchers have taken a closer look at some funny structure noted years ago in the resistivity of a quantum Hall sample at low magnetic fields. The prevailing explanation for what they see is that the electrons are forming charge density waves.

The leading speculation is that the anisotropy reflects the formation of theoretically predicted charge-density waves, with the electrons all lined up in rows.

Shades of the past

The work reported in Santa Barbara began last May, when Jim Eisenstein of Caltech set out to explore in more depth an effect that he and Robert Willett had seen in quantum Hall samples back in 1988 when both were working at Bell Labs. Similar anomalies were subsequently reported at the March 1993 meeting of the American Physical Society by Horst Stormer, who had been working with Daniel Tsui and Rui Du. Other groups also had evidence of anisotropic behavior, but no one explored it further at the time.

For his second look, Eisenstein was joined by Michael Lilly and Kenneth Cooper of Caltech; they enlisted Loren Pfeiffer and Kenneth West of Bell Labs to prepare very clean, high-mobility samples. The samples were gallium arsenide/aluminum gallium arsenide heterojunctions, in which an electron gas forms at the interface.

The researchers zeroed in on the regions around filling factors of $^9/_2$ and $^{11}/_2$. By contrast, strong fractional quantum Hall states usually show up at filling factors less than 2, such as $^1/_3$ or $^2/_5$. The filling factor, ν, indicates the number of electrons for each flux quantum. Thus, one gets a filling factor of $^1/_3$ at a high value of the magnetic field, where there are three flux quanta for each electron. At these fields, even the very lowest Landau level ($N = 0$) is not filled (it is filled when there is one electron of each spin for each flux quantum). One gets higher filling factors of $^9/_2$ and $^{11}/_2$ by decreasing the field.

The behavior of the two-dimensional gas at these higher filling factors