Additional background material on the Nobel Prize in Chemistry 1998

The Royal Swedish Academy of Sciences has decided to award the 1998 Nobel Prize in Chemistry with one half to

Professor **WALTER KOHN**, University of California at Santa Barbara, California, USA

for his development of density functional theory

and the second half to

Professor **JOHN A. POPLE**, Northwestern University, Evanston, Illinois, USA

for his development of computational methods in quantum chemistry

This additional background material is written mainly for scientists working in chemistry or physics.

Walter Kohn and John Pople have both given pioneering contributions to the development of computational methods for studying the properties of molecules and their interactions. In 1964 Walter Kohn (together with Pierre Hohenberg) proved a theorem, which states that it is enough to know the ground state density to determine all observable quantities of a stationary quantum system. One year later he derived (together with Lu Sham) a set of equations, which can be used to determine the ground state density. The Hohenberg-Kohn theorem and the Kohn-Sham equations forms the basis of modern density functional theory (DFT), which has for a long time been extensively used to determine the electronic structure of solids and is today also becoming a very important basis for theoretical studies of molecular systems.
John Pople has developed quantum chemistry into a tool that can be used by the general chemist and has thereby brought chemistry into a new era where experiment and theory can work together in the exploration of the properties of molecular systems. Chemistry is no longer a purely experimental science.

1. Historical background
The theoretical foundation for modern physics (and chemistry) was laid more than 70 years ago with the formulation of quantum mechanics. It then became possible, in principle, to understand how the electrons and atomic nuclei interact and form the chemical bonds that tie the nuclei into molecules and solids. However, as Paul Dirac stated in 1929:

The underlying laws necessary for the mathematical theory of large parts of physics and 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 soluble.

This statement was certainly correct in 1929 and the application of the new quantum mechanics in chemistry was in the early days mainly of a qualitative nature (the most prominent exception was the careful study of the helium atom performed by Hylleraas in 1928-30). This work soon gave a good understanding of the nature of the chemical bond and the new science *quantum chemistry* was born. It was, however, not until the early 60-ies that the scientists seriously started to challenge the pessimistic view of Dirac on the possibilities to solve the quantum mechanical equations for molecules. The advent of computers made it possible to look upon the complex equations from new angles.

The first attempts were based upon the so called independent particle model, where the many-body problem is resolved into a set of one-particle problems, by assuming that each electron is moving independently of the others in the field created by the fixed nuclei and the mean-field of the other electrons. The term orbitals (atomic or molecular) was created for these one-electron wave functions. This method had been developed already in the 30-ies (Hartree, Fock, Slater and others) and had been applied successfully in studies of atoms by Hartree and co-workers. It is called the Hartree-Fock (HF) method. An important early contribution was a paper by C. C. Roothaan in 1951, where he suggested that the orbitals should be expanded into a basis set, thereby transforming the differential equations into a matrix problem, which as it turned out, is well suited to solve using computers. Another important early contribution was given by the late S. F. Boys, who suggested that these basis functions could be in the form of Gaussian type functions, which would lead to considerable simplifications in the calculation of the necessary integrals. Armed with this knowledge, a number of scientists started in the early 60-ies to develop the Hartree-Fock method for molecular systems.

The HF method is an approximation to the Schrödinger equation, where the wave function is written as an (anti-symmetrized) product of one-electron functions, the orbitals. It is the starting point for a hierarchy of models, where the aim is to obtain as accurate solutions to the Schrödinger equation as possible.

A drastic but very attractive approximation to quantum mechanics was suggested by Thomas and Fermi already in 1927, the Thomas-Fermi (TF) approximation. Here one does not consider the wave function, but tries instead to work with the much simpler electron density, $\rho(r)$, only and to express the energy E from ρ alone, symbolically written as $E[\rho]$. The TF approximation was not very successful and did not play any crucial role in the early developments of quantum chemistry. In line with the idea of basing the treatment on the electron density alone, Dirac sug-

gested to replace the cumbersome exchange term in the HF equations with an expression depending on the density only. This led to the Hartree-Fock-Dirac approximation, which is a step in the direction of the TF model, since now only the kinetic energy depends explicitly on the wave function, all other terms are obtained from the density. Slater refined this approach and developed programs for general applications. He introduced an adjustable parameter α to improve agreement with experiment and the method was given the acronym X_α. The method had, however, serious deficiencies and the whole idea of using density-based methods in quantum chemistry (but not in solid state) was abandoned. This was the situation at the time when Walter Kohn made his contributions.

2. The contributions of John Pople

30 years ago the efforts of quantum chemistry was ridiculed by many if not most chemists as a rather futile undertaking with little effect on chemistry. This is completely different today: there is an unquestioned recognition of the usefulness and the great potential of quantum chemistry. There is also a broad consensus that this breakthrough is one of the most important developments in chemistry over the last one or two decades. Of the many scientists that have contributed to this breakthrough, John Pople stands out as the one that has given the most important and decisive contributions. Pople has been the master builder, who has made it possible for chemists to use quantum chemical methods as day-to-day laboratory tools along with their experimental equipment.
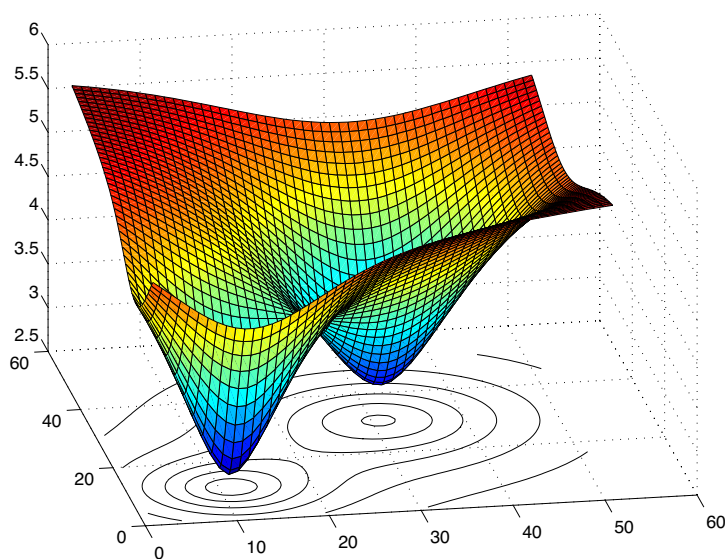
During the 50-ies, Pople made important contributions to the development of semi-empirical methods in quantum chemistry. He was one of the inventors of the so-called Pariser-Parr-Pople method for studies of electronic spectra of unsaturated organic molecules. Later he extended this $\pi-$electron theory to an all valence-electron theory called CNDO, which became very popular in the chemistry community. In the beginning Pople did not believe that the non-empirical methods could compete with the semi-empirical, since the computer resources needed would be much too large. He was himself going to change this situation.

The Hartree-Fock method consists computationally of two major steps. The molecular orbitals are expanded in a basis set composed of atomic centered Gaussian functions (according to the recipe originally suggested by Boys). In this representation, the one-electron "Schrödinger equation" is replaced by a matrix eigenvalue problem, which determines the orbital energies and the expansion coefficients. The matrix elements are composed of integrals over the basis functions describing the different energy components, such as the kinetic energy, the nuclear attraction energy and the electron-electron repulsion energy. It is the calculation of these integrals that is the most demanding in terms of computer resources. The second step consists in the diagonalization of the HF matrix. This is an iterative procedure, which has to be carried to self-consistency, since the matrix elements

depend on the molecular orbitals themselves.

The major bottleneck was the calculation of the integrals, in particular the electron repulsion integrals. They are many (of the order of $10^6 - 10^9$) and they are six-dimensional. Pople invented an approach which reduced the computational costs with one to two orders of magnitude. This was a decisive achievement, since with this improvement it became possible to use the HF method in real chemical applications. Pople realized that if the method was to be used on a large scale it had to be carefully designed and calibrated. He constructed sets of basis functions with gradually improved quality and tested them in large sets of calculations. This was the beginning of what he would later call a *theoretical model chemistry*. Pople also realized that the calculation of the energy alone is not enough to make the theoretical tool of general interest in chemistry.

The energy surface (in two dimensions) for a hypothetical chemical reaction from one equilibrium over a barrier (transition state) to the second equilibrium.

The most important characteristic of a molecule is its structure, that is, the bond distances and bond angles. Quantum chemistry has to be able to determine this structure if it is going to have any influence in chemistry. The equilibrium structure for a molecule is the geometrical arrangement of the atoms, which yields the lowest energy (see the figure above for a simple illustration of how the energy of a molecule may vary with the geometrical parameters). Theoretically, it must thus

be possible to minimize the energy of the system with respect to variations in the geometrical parameters. In order to do that, one needs not only the energy itself for a given geometry, but also the energy derivatives, at least the gradient, but preferably also the second derivatives, the Hessian. Pople realized this and developed methods for effective calculation of these derivatives, based on an earlier development by P. Pulay. These methods can not only be used to determine equilibrium structures, but also to follow the path for chemical reactions, and to determine the energy barrier for the reaction, the transition state. Thereby it becomes possible to use theoretical methods to investigate and explain reaction paths for chemical reactions, a development, which has been of utmost importance for the application of quantum chemical tools in chemistry. Pople collected all this development into a computer program, GAUSSIAN, which was distributed freely to the chemical community for a number of years (today it is a commercial product). The first version was released in 1970.

The HF model is surprisingly accurate, considering the fact that the electrons are treated as if they move independently of each other. The error in the total energy is less than one percent. It is called the correlation energy, since it describes the correlation of the electronic motion that is not included in the independent particle model. Pople realized that it was necessary to include methods to compute the correlation energy if the theory should be able to reach "chemical accuracy" in its prediction of relative energies (bond energies, activation energies, heats of reaction, etc). This area was a matter of intense studies in the early 70-ies. Pople again realized that it was necessary to develop methods that were simple to use and that scaled with the size of the system. Not all methods had this property. He decided to use perturbation theory and developed efficient methods to compute the perturbation energy up to fourth order. Of special importance for large scale applications was the simple second order approach for which energy derivatives were also developed. All this was introduced into later versions of GAUSSIAN. During the 80-ies he made important contributions in even more accurate correlation treatments, based on the cluster expansion of the wave function.
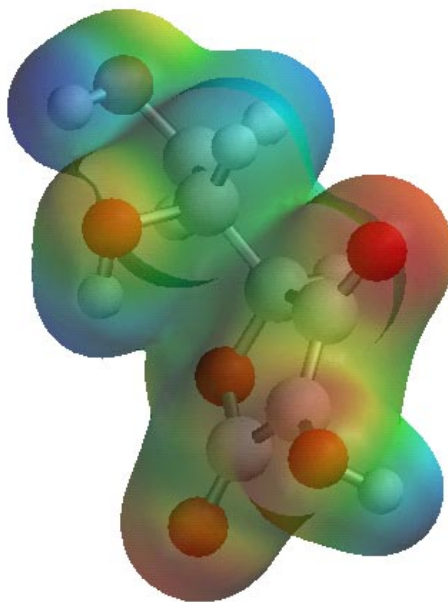
The creation, constant improvement, and the extension of the functionality of GAUSSIAN is an outstanding achievement. It is **the** example for the success of the field and its impact on chemistry and neighboring fields like physics, astrophysics, biochemistry, material sciences, etc. GAUSSIAN is today used by thousands of scientists all over the world.

3. Density functional theory and the contributions of Walter Kohn

The methods that John Pople has developed are based on the Schrödinger equation and are all attempts to solve this equation with approximate methods that are accurate enough to yield results that can be used to make reliable predictions about the properties of molecular systems. It has been the dominating approach up until

about ten years ago. In order to understand the changes that the field has under-gone during the last ten years we have to go back 35 years. In 1964 Hohenberg and Kohn (P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964)) proved a very important theorem, which gave the theoretical foundation for the Thomas-Fermi approach in quantum mechanics. They proved that the exact ground state electron density uniquely specifies the acting one-electron potential $v(r)$. Since the kinetic energy of the electrons and their Coulomb interaction cannot be modified, it was concluded that the ground state density specifies the Hamiltonian of the system and thereby all properties of the ground state. Or stated in the usual way: They proved the existence of a functional $E[\rho]$, which gives the exact ground state energy for the exact ground state density. They further showed that the minimum of E is reached for the exact density thus giving a variation principle to determine ρ and the ground state energy exactly. Thus they proved the existence of an exact Thomas-Fermi theory.

The electron density around the vitamin C molecule. The colors show the electrostatic potential with the negative areas shaded in red and the positive in blue.

In a second paper 1965 (W. Kohn and L. J. Sham, *Phys. Rev. A* **140**, 1133 (1965)) Kohn and Sham extended the results and proved the existence of an exact HFD-

type method together with a corresponding variational procedure helpful to solve the resulting equations. Thus a computational scheme was set up for an, in principle, exact calculation of the ground state energy and the density. Only one problem remained to be solved: the form of the functional. The original formulation of Kohn and his co-workers was based on analogies with the homogeneous electron gas. It worked well in solid state theory (a field where the approach was immediately successful), but was less successful in applications to molecules. It was going to take 20-25 years before the form of the functional had been refined so much that it became meaningful to develop computational techniques for large scale applications in chemistry. It was work of many scientists (Becke, Langreth, Parr, Perdew, and others) that led to this development. On the computational side important contributions were given by N. Handy and J. Pople, and in 1992 the density functional approach was implemented in the GAUSSIAN program. DFT is today one of the most frequently used methods in quantum chemistry. It is simpler than the more advanced wave function based methods and can therefore be applied to larger molecules. Today it is possible to treat systems with several hundred atoms. The accuracy is in most cases sufficiently high, even if exceptions are known where the DFT approach works less well. The functional is by nature approximative (the exact functional would be the Schrödinger equation itself) and different forms of the functional can yield slightly different results. This has led to the development of empirical functionals were parameters are adjusted to give as good results as possible for a given set of observable quantities (normally binding energies). DFT has resulted in a second revolution in quantum chemistry, which would not have been possible without the pioneering work of Walter Kohn.

4. The applications of quantum chemistry

Quantum chemistry is today used to study a large variety of phenomena in chemistry and molecular physics. Here is a list of some examples where theory is today used to make predictions:

- The equilibrium structures of molecules; transition states and reaction paths.

- Molecular properties: Electrical, Magnetic, Optical, etc.

- Spectroscopy, from NMR to X-ray.

- Reaction mechanisms in chemistry and biochemistry.

- Intermolecular interactions giving potentials which may be used to study macromolecules, solvent effects, crystal packing, etc.

Some detailed examples were given in the press release. Quantum chemistry is today a mature science, which penetrates all of chemistry. This is an extraordinary achievement, where the work of the two laureates, Walter Kohn and John Pople has been of profound importance. Who could believe 10 years ago that quantum chemistry would play an important role in biochemistry, for example, in the understanding of mechanisms for enzymatic reactions, or explain the relation between structure and spectroscopic properties in transition metal containing proteins. Theory works today hand in hand with experimental chemistry in the exploration of the properties of matter.

4. Further reading

Inhomogeneous Electron Gas, P. Hohenberg and W. Kohn, *Phys. Rev. B*, **136**, 864 (1964).
Self-Consistent Equations Including Exchange and Correlation Effects, W. Kohn and L. J. Sham, *Phys. Rev. A*, **140**, 1133 (1965).
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