

# Predictive Methods of Pople

*Swapan K Ghosh*

Professor John A Pople of Northwestern University, Illinois, USA and Professor Walter Kohn of the University of California, Santa Barbara, USA have been awarded the 1998 Nobel Prize in Chemistry for their pioneering contributions to the development of computational methods in quantum chemistry and density functional theory respectively. In the previous issue of *Resonance*, the work of Kohn was highlighted. The contributions of Pople are described in this article.

John A Pople was born in Somerset, UK in 1925. He received the PhD Degree in Mathematics from the University of Cambridge, UK, in 1951 (thesis advisor: Lennard Jones). In 1964, he became Professor of Chemical Physics at Carnegie-Mellon University, Pittsburgh, USA and subsequently has been Professor of Chemistry at Northwestern University, Evanston, USA.

## What is it all About?

Quantum mechanics (QM) provides the framework for theoretical studies of the behaviour of electrons in atoms, molecules and solids and has in principle opened the way to a complete understanding of chemistry and physics. But "... the difficulty is only that the exact application of these laws lead to equations much too complicated to be solvable" was the opinion expressed in 1929 by P A M Dirac, one of the founders of QM. Today, doing computational quantum chemistry and physics is no longer a dream and the independent works of Walter Kohn and John Pople on the development of theoretical and computational methods have been crucial for enabling the chemists to utilise the immense power of QM to understand and also predict the behaviour and properties of atoms, molecules and the materials formed by them. Pople, originally trained as a mathematician, has focused on the electronic structure of molecules.



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The basic approach in QM involves solution of the Schrödinger equation  $H\Psi = E\Psi$  to obtain the many-particle wave function  $\Psi(r_1, r_2, \dots, r_N)$ , which is unfortunately a difficult task even with the help of computers due to the large number of variables (coordinates of all the  $N$ -electrons) for a many-electron system.

Pople contributed towards the development of an approximate but practical method to obtain the wave function  $\Psi$ . He realised that in order to have proper significance and impact in chemistry, a theoretical or computational method has to be simple enough to be accessible by a general chemist, but at the same time sufficiently accurate to yield meaningful results. Besides developing a number of approximate semiempirical quantum chemical methods such as PPP, CNDO, INDO etc, he has used the improved theoretical methodologies of the 50's and 60's to design a computational chemistry package GAUSSIAN-70 that has provided the general chemist a tool to study individual molecules. The package has continued to evolve and the latest version is GAUSSIAN-98.

### How did it Begin?

Quantum chemistry was still in a primitive stage of development when Pople thought of formulating a long term strategy for making QM a useful research tool in (organic) chemistry. His degree was in mathematics and one of Trinity's distinguished organic chemists challenged him with the remark "You should not call yourself a theoretical chemist until you have discovered something about chemistry that other chemists do not already know!" In Pople's own words: "While I am sure I defended my status, this provoked some soul-searching and led me to pose to myself the question: How can QM, as we know it (1952), be turned into a practical procedure which can be applied to current organic chemistry problems in the immediate future? This was no doubt, an ambitious target but the formulation of difficult objectives is always a healthy exercise in any research career."

After contributing to the Pariser-Parr-Pople (PPP) method in

1953–54, Pople however diverted to other fields but came back with new enthusiasm later in 60's to develop many versions of semiempirical theories. As he recollects in 1990.... "In retrospect, I regret some missed opportunities. In particular, the objective of a general theory was abandoned too soon. I eventually returned to this after my move to Pittsburgh in 1964 and developed the CNDO (Complete Neglect of Differential Overlap) theory with Segal and Santry. The general concept of such a theory existed as early as 1952, ...but I failed to recognise this as the true research frontier and to press on it vigorously."

### **The Wave Function Approach of Pople**

An approximate QM procedure makes use of the variational principle to calculate the energy by first evaluating the expectation value of the Hamiltonian operator using a trial function and then minimising it with respect to the parameters in the trial function. The simplest way to form a trial function is to express it as an antisymmetric (for Fermions) product (a Slater determinant) of molecular orbitals (MO), which are one-electron functions spread over the entire molecule. The MO's in turn can be constructed by using a so-called linear combination of Atomic Orbitals (AO) approach, with the coefficients and parameters in the AO's as variational parameters. The corresponding formalism based on Hartree–Fock theory was worked out by C C J Roothan in 1951 and also independently by G G Hall. The AO's are more close to exponential or hydrogen atom wavefunction like functions but analytical evaluation of the multicenter integrals with these functions is difficult. S F Boys in 1950 suggested the use of Gaussian functions as the AO's for which the integral evaluations are easy since the product of two Gaussians centred at two different locations can be written as a single centred Gaussian at a new location. Gaussians, however, are less realistic AO's and hence a compromise was made by representing each exponential or Slater type orbital (STO) as a sum of few (say, 3) Gaussians, known as contraction, leading to orbitals of the kind STO-3G etc. The accuracy increases with choice of more Gaussians at the cost of more computer time. This forms the basis of GAUSSIAN



program of Pople for ab-initio electronic structure calculation of molecules.

This ab-initio MO approach was preceded by the semiempirical electronic structure theory, an alternative simpler approach developed in the 50's and 60's, where one neglects many integrals and assigns empirical values to the rest of the integrals based on either strong physical intuition of the chemists or using suitable experimental data. The well-known Huckel (1931) theory retained integrals involving nearest neighbour atoms and neglected electron repulsion completely, while the PPP theory (1953) incorporated repulsion integrals through empirical parameters. A similar approach was rediscovered in solid state physics in 1963 by Hubbard and has been known as Hubbard model. After the PPP work in 1953–54, Pople however worked in other fields but came back only in 60's to develop more modern versions of semiempirical electronic structure theories known as CNDO, INDO and so on. These semiempirical methods as well as the GAUSSIAN program developed by Pople have played an important role in the electronic structure calculation of molecules.

### Related Work Being Done in India

With the advances in methodologies as well as computational packages available, quantum chemistry can now be used for predicting properties of molecules, nanoparticles, bulk solids etc. to chemical accuracy. Extensive work has been done in India in quantum chemistry using both the wave function approach pioneered by Pople and the density functional theory of Kohn. The GAUSSIAN package is now extensively used by many groups in the country to calculate results of direct relevance to experimental observations.

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### Suggested Reading

- [1] W J Hehre, L Radom, P v R Schleyer and J A Pople, *Ab-initio Molecular Orbital Theory*, Wiley, New York, 1986.
- [2] J A Pople and D A Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1968.