

During his more than 50 years in chemistry, John really had at least four careers, working in:

- \* Statistical Mechanics
- \* NMR
- \* Semi-Empirical Theory
- \* Ab Initio Electronic Structure Theory.

Moreover, his accomplishments in each area would be remarkable had that been his only area of work.

### *From Statistical Mechanics to NMR to Semi-Empirical Methods*

Although John wrote a few early papers on computational electronic structure theory while a graduate student with Sir John Lennard-Jones [1], his primary interest for his first decade of research was in Statistical Mechanics. The model for liquid water he published in the 1950's [2] remained the standard for many years.

Next, John became interested in the then-emerging field of NMR, publishing important papers on the underlying theory [3] and also coauthoring the then-standard textbook on the subject [4]. As this work progressed, he developed an interest in computing properties such as chemical shifts, which lead him to electronic structure. Since first principles (non-empirical) methods appeared to be far too expensive computationally to apply to typical problems in organic chemistry, John used and developed semi-empirical models. Simultaneously with Pariser and Parr, John developed what became known as the PPP model for  $p$ -excitations [5], one of the earliest successful semi-empirical models. In spite of its simplicity, this model still has its uses 40 years later.

Eventually, John's work with semi-empirical models drew him away from NMR altogether. Along with various students, he developed the widely used CNDO [6] and INDO [7] models. In the course of this work, John articulated and clarified the approximations used both in this generation of models [8] and by other researchers such as Michael Dewar in later models such as MINDO/3 [9], MNDO, and AM1. From the beginning of his semi-empirical electronic structure work, John had the goal of creating computer programs which would be useful to chemists who were not experts in the theory. His CNDO/INDO program was one of the most popular distributed through the Quantum Chemistry Program Exchange.

### *Electronic Structure Theory*

After several years of developing successively more accurate and more computationally costly semi-empirical models, John realized that with improvements to the algorithms, it would be possible to make non-empirical (by then called "ab initio") calculations fast enough to apply to significant problems [10]. This type of theory remained his focus for the final three decades of his work. His work on the STO-3G basis set remains among his most cited papers [11].

After he and his student Warren Hehre had developed a new algorithm which made Hartree-Fock calculations much faster than had previously been thought possible, the resulting program, *Gaussian 70* [12], was made available through QCPE. Earlier programs by other theorists (e.g., PolyAtom) had been distributed to and used by many theoretical research groups, but because of both its speed and ease of use, *Gaussian 70* became the first ab initio program used by significant numbers of non-theorists.

During the 1970's, John and his group worked on more sophisticated ab initio methods, including larger basis sets (6-31G, 6-31G\* [13], etc.) and going beyond Hartree-Fock to include electron correlation, examining several rival methods which had been advocated by different researchers, including Configuration Interaction, Perturbation Theory and Coupled Cluster [14].

Through the 1970's and 1980's John was one of the leaders (along with Bartlett and Schaefer) in the development of models and algorithms for SCF, CI [15], perturbation theory [16], and coupled cluster methods. One of his most notable accomplishments was a 1979 paper with Schlegel, Raghavachari, and Binkley which presented both the first practical algorithm for analytic Hartree-Fock second derivatives and the first gradients for the MP2 correlated method [17].

Work in John's group continued in these areas, as well as on improved algorithms for integral evaluation, Hartree-Fock calculations, resulting in the HGP [18] and PRISM [19] algorithms, and on direct and semi-direct algorithms for large MP2 calculations [20].

In the 1990's, John saw that Becke had applied the Model Chemistry approach (see below) to various density functional models and demonstrated that some of these functionals had sufficient accuracy to be useful for chemical problems, and began to work in this area as well [21]. Work in recent years has focused on the development of the high accuracy Gaussian-1 theory [22] and its follow-ons.

### *Model Chemistries: John Pople's Legacy*

In approaching each of these methods in turn, John was guided by his principle of *Model Chemistries*, an original concept for which he was solely responsible and articulated in a hard-to-find seminal paper [23]. This approach, in which one carefully calibrates the difference between the chemistry predicted by a particular model and that observed in the real world, and then uses the same model for studies of new systems in which the accuracy--and error--of the model is known from the previous calibrations, represented a significant departure from the approach taken in earlier theoretical work.

Traditionally, theorists tried to do the best calculation they could on a particular problem, using different models, basis sets, and so on for each study. As a result, the accuracy of a new calculation was difficult to evaluate even for experts (and impossible for non-expert to even estimate). The consequence so this were two-fold:

- \* It effectively prevented the application of electronic structure calculations to a broad range of problems.
- \* It made it extremely difficult for non-experts to use electronic structure calculations as part of their research.

By articulating the principle of model chemistries and then carefully calibrating particular models, John made it possible for people to apply computational models with confidence because they knew to what extent to trust the results. This fundamental principle has been essential to the success of almost all methods in electronic structure theory, not just those originated or favored by John, and has also been essential to the widespread use of electronic structure computations, regardless of which software package is involved. This is undoubtedly John Pople's most significant contribution, and will still influence the development of the field long after the particular models he developed have become obsolete.

I started as a graduate student of John in 1979, in what turned out to be the middle of his career. Actually, I was one of a succession of graduate students each of whom was widely assumed to be John's last student, but fortunately this turned out to be far from the case. While I learned about many technical aspects of theory from John, I think that the most valuable wisdom he passed on to me and his other students and post-docs consisted of the principles he applied to his research and the approach he advocated:

- \* Theorists should compute what is measured, not just what is easy to calculate
- \* Theorists should study systems people care about, not just what is easy or inexpensive to study.
- \* Models should be calibrated carefully and the results presented with scrupulous honesty about their weaknesses as well as their strengths.
- \* One should recognize the strengths as well as the weaknesses of other people's models and learn from them.
- \* If a model is worth implementing in software, it should be implemented in a way which is both efficient and easy to use. There is no point in creating models which are not useful to other chemists.

These ideas seem as sound to me today as they did when I first learned them from John more than twenty years ago. The goal of making theory a useful tool for all chemists has clearly been adopted by many of his students. As John was very fond of pointing out, his former group members have started a total of five software companies. I would add the note that since all five companies are still in operation after a decade or more, that the people involved have also learned some of John's other lessons about how to do theory in a way that matters to the field as a whole.

As is often the case with great scientists, John demonstrated a keen ability for putting aside the many non-essential details of a complicated problem, and identifying and focusing on the critical issues. I'm sure that all his students try to follow his example in this, but that none of us would claim to have his talent at it. His passing is a loss to everyone in our field.

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### *John Pople Chronology*

1925	Born October 31st, Burnham-on-Sea, Somerset, England to Keith and Mary Pople.
1943-1945	Entered Cambridge University on a Mathematics scholarship.
1945-1947	Wartime employment with Bristol Aeroplane.
1947-51	Resumes studies at Cambridge University. Begins studying Quantum Chemistry among other scientific topics. Receives his Ph.D. in Mathematics in 1951.
1952	Marries Joy Bowers (his piano teacher).
1952	Research Fellow, Trinity College, Cambridge.
1954-1958	Lecturer on Mathematics Faculty.
1958-64	Head of the new Basics Physics Division at the National Physical Laboratory near London.
1961-1962	Spends sabbatical year at Carnegie Institute of Technology in Pittsburgh, PA.
1964-1993	Carnegie Professor of Chemical Physics at Carnegie Mellon University, Pittsburgh and later John Christian Warner Professor of Natural Sciences.
1993-2004	Board of Trustees Professor of Chemistry at Northwestern University.
1998	Winner, Nobel Prize in Chemistry (with Walter Kohn).
2003	Knight Commander of the Order of the British Empire (K.B.E.).
2004	Died, March 15th.