

## A History of Ab Initio Computational Quantum Chemistry: 1950 - 1960

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**Abstract:** Although *ab initio* computational quantum chemistry produced virtually no predictions of chemical interest during the 1950's, an important foundation for future work was laid during this decade. Much of this fundamental computational research was carried out in the laboratories of Frank Boys in Cambridge (England) and Clemens Roothaan and Robert Mulliken in Chicago. Other senior contributors to *ab initio* chemical theory during this period include Klaus Ruedenberg, Robert Parr, John Pople, Robert Nesbet, Harrison Shull, Per-Olov Löwdin, Isaiah Shavitt, Albert Matsen, Douglas McLean, and Bernard Ransil.

In presenting this material, I immediately think in terms of American Graffiti because I am reviewing things that happened in the 1950's. That's a good thing to do, because computational quantum chemistry may be coming down the home stretch on the Nobel Prize, and by talking about what happened in the '50's, I won't very much bring in many of the candidates and should keep myself out of a lot of trouble that way. You could also call this a "Tale of Two Cities" because I'm going to conclude that there were two dominant research groups that were most influential in terms of the way we do quantum chemistry today.

I think that the reason I was invited is that I wrote a book on this subject published by Oxford University press.<sup>1</sup> To begin, I would like to cite the 1979 news article written for *Nature* by Graham Richards<sup>2</sup> called "The Third Age of Quantum Chemistry". "The Third Age of Quantum Chemistry" describes the constructive interplay between theory and experiment in the identification of the electronic spectrum of triplet acetylene. Richards' article shows that the field has become quite useful, as does my review<sup>3</sup> in the March 1986 issue of *Science*.

Where does the story of the 1950's begin? It begins in one of the two cities, namely Cambridge, England. And the story I'm going to tell you is dominated by two persons, the first of whom was Frank Boys. The first landmark paper I cite here may mark the beginning of modern computational quantum chemistry--this is the Frank Boys paper<sup>4</sup> published in 1950 in the *Proceedings of the Royal Society*. It is one of the first papers in which he uses Gaussian basis functions. At the time, this may have seemed like a pretty frivolous thing to do for the simple reason that everyone knew already that Gaussian basis functions were not really very good for describing electronic wave functions. And in fact, it was another 15 years before the

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ideas presented here in Boys' paper really caught hold and people started to do this on a large scale. But the advantage of using Gaussian basis functions was that all the electron repulsion integrals could be done analytically and Boys gave all the formulas right in that paper. The next paper<sup>5</sup> that Boys published in this series was a calculation on the beryllium atom, and this was a configuration interaction wave function. As you'll see, Boys was the person who shaped the modern configuration interaction method, and we all know that all these other newer methods like couple cluster are related to CI. So, this is an important paper, and it is the first paper to really make a significant stab at getting some fraction of the correlation energy for a system bigger than lithium.

The next significant paper is one by Klaus Ruedenberg.<sup>6</sup> In the 15 years, 1950 - 1965, nearly all the work in quantum chemistry was done in terms of exponential or Slater-type orbitals. This is the first paper that talks about a completely organized way of evaluating these integrals to any desired accuracy. Those of you who do this sort of work know that exchange integrals were the hardest ones to evaluate and that's exactly what this paper is aimed at. In fact, a lot of the things in this paper are still used. For example, the best existing codes in the world to compute integrals for linear molecules are those developed by McLean and Yoshimine at IBM San Jose and they use a great deal of the information that was conveyed in this paper by Klaus Ruedenberg.

Next we come to a very well known paper. I said before that this would be a tale of two cities and here is the other city--Chicago, and specifically the University of Chicago. The paper by Roothaan<sup>7</sup> is probably the most widely cited paper in the history of quantum chemistry. What Roothaan did in this paper was to attack the molecular Hartree-Fock problem a little bit differently. All the people who had been doing quantitative atomic calculations followed in Hartree's footsteps and did things numerically. That is, they just evaluated the orbitals for a grid of functions in one dimension; when you even go to two dimensions as is necessary for diatomic molecules, it gets a lot harder. So Roothaan said, let's do this in terms of an analytic basis set. This method has been alternately known as the analytic Hartree-Fock method, the Roothaan Hartree-Fock method, the matrix Hartree-Fock method, because in the ultimate step here, as anyone knows who has ever run Gaussian 82, you have to diagonalize a Fock matrix and that matrix comes out of this paper. George Hall at Nottingham published a related paper<sup>8</sup> at about the same time but I don't want to try to adjudicate the priority dispute between those papers.

Some strongly futuristic aspects were given in a 1952 paper by Bob Parr,<sup>9</sup> entitled "The Superposition of Configurations for the Helium Atom". Parr says here that people have been calculating the helium atom to plenty of precision for many years, but we know that those methods will never work, because they all have interelectronic coordinates explicitly in the wave functions. We know that this "historic" approach will never work for larger systems, says Parr, so let's take a method that will not be as accurate for the helium atom, but is completely general. He says here, there is a systematic practical procedure for obtaining an accurate wave function for any atom or molecule. I think that this is the paper in which the correlation energy was first defined: it would be the difference between the Hartree-Fock energy and the exact result. Next appears a second paper by Parr and Bryce Crawford.<sup>10</sup> They quote this wonderful statement by Dirac<sup>11</sup> from 1929, "The underlying physical laws necessary for the mathematical theory of a large part 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." If you take the time to read this paper at length, they actually talk about computing, and there are references to IBM. They talked in some detail about how to compute integrals. Prior to the Shelter Island Conference Ken Pitzer received a letter from Mulliken inviting him to the meeting. The interesting thing about this exchange was that Pitzer said he wanted to come, but was not sure if he could present anything, because by the time he got the invitation he was Director of Research at the Atomic Energy Commission (for two years after World War II).

The next key paper is by John Pople and Bob Nesbet<sup>12</sup> - again from Cambridge, England - called "Self-Consistent Orbitals for Radicals." They invented in this paper something we now know as the unrestricted Hartree-Fock method. Harry Shull and Per Olov Löwdin<sup>13</sup> then published "Natural Spin Orbitals for Helium." Now we are about five years past Parr's paper<sup>9</sup> on configuration interaction, and people

know you can do it, and they are starting to think very hard about how to do it better. And to do it better, obviously the thing you want to do is get the lowest possible energy, get the biggest fraction of the correlation energy, get the best wave function with the fewest number of configurations. And the way to do that we all recognize now (at least for some systems) is by using natural orbitals. That was done for the very first time in this paper.<sup>13</sup> In succession we see a paper<sup>14</sup> by Per Löwdin as well in which he laid out some of the general principles in using natural orbitals. There is no computer in this paper, but it is a great paper for generations of theorists to read and appreciate.

The next landmark paper cited here is by Bob Nesbet,<sup>15</sup> entitled "Configuration Interaction in Orbital Theory." There's a certain tragedy in what went on in the '50's. Nesbet was a student of Boys, and one of the things he wrote about here was how to evaluate Hamiltonian matrix elements between configurations. The thing that Nesbet pointed out here was that you don't have to explicitly consider all the electrons, at least in a simple formulation. If you just isolate the electrons that are displaced from the occupied orbitals in the Hartree-Fock picture, the formalism becomes a lot simpler. Many people have used this concept - for example, the important direct CI method that Bjorn Roos<sup>16</sup> introduced in 1972 borrows very strongly on this idea.

The next paper<sup>17</sup> is in my estimation perhaps the most significant of all. It comes from the Cambridge group, Boys, *et al.* Many of you know that the Cambridge tradition, that way of thinking about electronic structure, is carried on to this day in Shavitt's laboratory at Ohio State in a brilliant manner. What did they do here? They obtained the biggest CI wave functions that had been known — up to about 33 configurations for H<sub>3</sub>. They also did BH and the water molecule as well. This comes after the famous Ellison and Shull paper,<sup>18</sup> so it is not the first calculation on water, but certainly an amazing piece of work. In addition, Boys and coworkers calculated the quadratic force field and located the transition state for H<sub>3</sub> in this remarkable paper.

Next I would like to turn to a paper<sup>19</sup> by Al Matsen's group in Texas: they used an IBM 650 computer for these calculations on four-electron systems. Until the famous 1966 paper by Bender and Davidson on the iterative natural orbital method, Matsen had the best wave functions for these simple diatomics. Matsen and coworkers used valence bond wave functions in their important work. The next paper cited is a philosophical article:<sup>20</sup> "Broken Bottlenecks in the Future of Molecular Quantum Mechanics" by Mulliken and Roothaan, read before the U. S. National Academy of Sciences. It was really an announcement that they had a completely automatic series of programs to determine self-consistent field wave functions for diatomic molecules, and the capabilities of these programs was quite remarkable. They say here that there will be a whole generation of computing chemists. This is followed by a paper<sup>21</sup> — again the Chicago school — by Doug McLean. This is the first paper I know to report *ab initio* computations on linear polyatomic molecules with Slater-type orbitals. Acetylene and carbon dioxide were the first examples done by McLean and Megumu Yoshimine, now together at IBM Research Laboratory in San Jose. This was the first fruits of their renowned work on self-consistent field wave functions for linear molecules.

Now we're up to 1960 and the next paper is by Ernest Davidson,<sup>22</sup> who did his Ph.D. research with Professor Harry Shull. This is perhaps the first time that a theorist took some spectroscopic data that was genuinely puzzling and made sense out of it. There were spectroscopic observations for the E and F states of H<sub>2</sub> and what Davidson showed is that these two states actually lie upon the same potential energy curve and are connected by a barrier. This was a significant revelation to the spectroscopists at the time and is an important paper. Perhaps one can take this as the forerunner of the many other successes of theory which have occurred since then.

Now I would like to point to a paper by Dick Watson.<sup>23</sup> John Slater had a big operation at this time at M.I.T. and there were a fair number of them interested in molecular wave functions - Lee Allen, Arnold Karo, *etc.* But by and large the ideas coming out of that group have not had quite the penetrating effect as those from Chicago and Cambridge. But this paper by Watson did. He obtained a 37 configuration wave function for beryllium and he recovered about 90% of the correlation energy. This is one of the first papers in which scientists started to talk about calculating a preponderant fraction of the correlation energy. Watson was the

first one to get a variational handle on this business of unlinked clusters that we now recognize as so important.

This brings us to my last landmark paper by Roothaan,<sup>24</sup> the one in which he did open-shell Hartree-Fock theory, *i.e.*, open-shell matrix or analytic Hartree-Fock theory. This paper is referred to abundantly and has been very influential. This is the paper in which open shells were first treated precisely correctly. In Roothaan's restricted Hartree-Fock theory, you obtain wave functions which are proper eigenfunctions of the  $S^2$  operator and this is, in my mind at least, the way that one should proceed with open-shell problems.

Our next paper is an interesting one by Bernie Ransil.<sup>25</sup> This paper is the predecessor to one that many of you are familiar with and that's a paper by John Pople and his group<sup>26</sup> (Marshall Newton was the first author) in 1970 on the structures of a plethora of molecules. They surveyed the structures of a large group of molecules just using minimum basis set self-consistent field theory. For diatomics, Ransil did exactly the same thing in 1960 — he basically took all the diatomic molecules you can make by combining the atoms from hydrogen to fluorine, calculated the potential energy curves, compared dissociation energies with experiment, *etc.*. This is, then, the first paper of the systematizing type that John Pople has become so properly known for in the intervening years.

Next I present in this group the last paper by Nesbet,<sup>27</sup> "Diatomic Molecule Project at RIAS". Nesbet was a professor of physics at Boston University before he went on to IBM in San Jose. He fused what the Chicago and Cambridge groups had to offer, but around 1968, he went off to work in atomic physics. His contributions were monumental, but they would have been staggering if he had stayed in the field.

Next we see one of the last classic papers by Frank Boys. This is a fairly philosophical paper<sup>28</sup> entitled "Mathematical Problems in the Complete Quantum Prediction of Chemical Phenomena." Boys discusses the configuration interaction method, particularly the evaluation of Hamiltonian matrix elements, which he used to call "projective reduction." He says that most of the great intellectual challenges come in this area of projective reduction and I think that what he says is true if you look at some of the newer methods like direct CI<sup>16</sup> and the graphical unitary group approach.<sup>29</sup> Finally we come to the last Boys paper<sup>30</sup> that I'm going to emphasize here. You may know about Boys' work on the structure of  $\text{CH}_2$  and the vindication<sup>3</sup> of that work shortly before his death in 1972. All of Boys' most important work was published in a 10 year period — *i.e.*, all of the work that had monumental impact was published between 1950 and 1960. He of course published things before and after that period, but none of them had the same lasting impact. Boys was in some respects a tragic figure. He was an underperson in the department where Christopher Longuet-Higgins was head and Longuet-Higgins did not appreciate him, but these ten years were remarkable. I'm going to stop now except to say something about Roothaan.

Roothaan was a perfectionist. He would meet with his graduate students and make certain that their computer programs were not only bug-free but efficient to the nth degree. If it weren't for that perfectionism, the field would in no way be in the orderly state it is approaching today. Well, the story of Roothaan is that he became director of the computer center at the University of Chicago, and that was a job that he just wasn't ideally suited to. Eventually he was replaced, and he really never came back to dominate the field in the manner described in this review. And of course Boys really left the mainstream more than five years before Roothaan departed. It is an interesting story with some bittersweet aspects, but that's my view of the history of computational quantum chemistry.

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