

Early Experiences with Computational Quantum Chemistry

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ABSTRACT: A description is given of the progress in computational quantum chemistry in the early 1960s, the time of the early mainframe computers. In particular, the first calculation of the barrier to internal rotation in ethane and the first molecular application of perturbed self-consistent-field equations are described with the accompanying developments, trials, and tribulations.

My Ph.D. research began in the summer of 1960 with W. N. (Colonel) Lipscomb, who had moved to Harvard the previous year. Most of his graduate students were doing crystal structures of boron hydrides, but he had told me that he thought it was now almost possible to do a theoretical calculation of the barrier to internal rotation in ethane.

He said that Michael Barnett and co-workers, working in J. C. Slater's group at MIT, were making good progress in evaluating the needed multicenter integrals over Slater orbitals. Presumably, another reason why he suggested this problem was that he had seen how much computers could help in solving X-ray crystal structures and had anticipated their impact on quantum chemistry as well.

The early theoretical discussions of the ethane internal rotation barrier had been made in the context of the perfect-pairing approximation in valence bond theory, which involved the largely unknown effect of the neglect of many integrals.¹ By 1960, it had been established that the molecular orbital approach was much more computationally efficient.² Thus, the goal of this and many other calculations at this time was a self-consistent-field (SCF) calculation with a minimum basis set of Slater orbitals.

Other students in the Lipscomb group doing theoretical work were Bill Kern (magnetic resonance parameters), Larry Lohr (semiempirical theory), and Roald Hoffman, just returning from a year in Russia and developing extended Hückel theory to apply to carboranes. Bill Kern introduced me to the new Fortran II and to Michael Barnett. The advantages of using a high-level programming language were becoming accepted, but some research groups continued to use assembler languages. Bill also showed me around the main computer center available, an IBM 704 at the regional New England facility at MIT. It was a vacuum-tube computer with 32k 36-bit words of memory and many tape drives. Input was by IBM punched cards. We drove to MIT every day or so to submit jobs and pick up output. The programs for molecular integrals were in various stages of development, and there was no SCF program available for use or adaptation. When the crystallography students found out that we went to MIT often, they asked us to get their liquid nitrogen containers filled up there also.

The Barnett–Coulson method (for Slater orbitals) was to expand all functions in the integrand in spherical harmonics about one of the nuclei (centers) involved.³ The simplest example of this expansion is

$$\frac{e^{-\beta r_b}}{r_b} = \beta \sum_{n=0}^{\infty} (2n+1) P_n(\cos \theta_a) i_n(\beta r_<) k_n(\beta r_>)$$

where $r_< = \text{minimum}(r_a, r_b)$, $r_> = \text{maximum}(r_a, r_b)$, and i_n and k_n are spherical Bessel functions, giving an expansion of an exponential function at center b in terms of spherical coordinates at center a . r_b is the distance between centers, and center b is on the z axis of the coordinates. Other powers of r_b can be obtained by differentiation with respect to β .

All one- and two-center integrals except two-center exchange resulted in finite expressions. Two-center exchange and all three-center integrals resulted in singly infinite angular momentum expansions. Four-center integrals resulted in triply infinite expansions with triangle conditions on the angular momentum indices. The expansions almost always converged to the desired 0.000001 accuracy in 50 terms or less, but they all had to be checked.

We were in correspondence with Martin Karplus and Shi Shavitt (at Columbia University and IBM Watson Lab) who were using an entirely different approach (Gaussian transforms) to the integral evaluation.⁴ The basic transform is

$$e^{-\beta r} = (\beta/\sqrt{4\pi}) \int_0^\infty s^{-3/2} e^{-\beta^2/(4s)} e^{-sr^2} ds$$

which, when used for all four orbitals gives a readily evaluated integral over Gaussian functions, which can then be integrated over the transform variables.

I visited them twice to discuss comparisons on test cases, which was quite helpful in debugging the programs. Col. Lipscomb sent me to the 1962 Gordon Conference on Theoretical Chemistry (forerunner of the present ACTC Conferences), which gave me the opportunity to meet a number of people in the field, including people whose papers I had been reading.

Organizing the integrals for the as yet unwritten SCF program was done by making a list of the symmetry-unique integrals using the D_{3h} and D_{3d} molecular symmetries of eclipsed and staggered ethane. The list I generated was 1653-integrals-long in both cases, with some integrals appearing in both lists. Much later, I discovered that one of these integrals was zero by symmetry, but by that time it was easier just to keep the same list and enter the 0.0 value. The integrals came from several different programs and had to have the orientation of their p orbitals rotated to the molecular axes, so the values were entered into a notebook along with their two or four orbital indices and an "occurrence factor" determined by

Received: May 17, 2011

Published: June 30, 2011

their symmetry and permutation properties.⁵ This stage of hand-processing was the most error-prone part of the work and was rechecked extensively. Each integral and its accompanying information was put on its own punch card.

I read enough about supermatrix formulations of SCF calculations^{6,7} to write an SCF program specific to ethane using these ideas. By late 1962, I had complete sets of integrals and was ready to run the SCF program. By this time, the regional MIT center had an IBM 7090 (transistorized) machine and the Slater group had purchased their own (used) IBM 709 machine, which was set up in a large space under one of MIT's domes. The SCF calculations took comparatively little time, and I soon had a rotational barrier value of 3.3 kcal/mol, reasonably close to the then-quoted experimental value of 2.875 ± 0.125 kcal/mol.⁸ The ethane barrier could not be measured by simple straightforward spectroscopic methods because of its lack of a dipole moment, but more sophisticated techniques later gave a value of 2.90 ± 0.03 kcal/mol.⁹

The credibility of such calculations in 1963 was a serious problem. Calculations at this level (SCF, minimum basis set of Slater orbitals) had been published previously on smaller molecules, with the integrals computed using desk calculators, and some of them were known to contain errors due to their overall difficulty. For example, the April 1960 issue of *Reviews of Modern Physics* contains papers from a theoretical chemistry conference. A paper by B. J. Ransil contains similar calculations, including exponent optimization, for a number of diatomic molecules and were done with no hand processing.¹⁰ I think the results were generally considered to be correct, but of different accuracy for different molecules. On the other hand, there were two similar papers on formaldehyde, and their computed dipole moments had opposite signs.^{11,12} In the case of ethane, a number of similar calculations were subsequently performed within a few years, and all gave similar results, reinforcing the validity of my calculations. It took an additional number of years and the establishment of several complete program systems before disagreement of reported experimental and theoretical results was considered a serious matter requiring further examination of both results. By that time, contracted Gaussian basis sets had been shown to be more efficient computationally than Slater basis sets.

The rotational barrier in ethane turned out to have been a quite fortunate choice of computational project because alkanes do not have the complications of multiple bonds or lone pairs of electrons. One aspect of this is that alkanes have a higher ratio of basis functions to number of electrons than other types of molecules. In comparison, the skew structure of hydrogen peroxide is not obtained until larger basis sets are used.¹³ H. F. Schaefer has summarized this result in private and perhaps in public by saying that minimum basis sets give surprisingly good results for structural properties of alkanes.¹⁴

An additional project during this time involved a younger graduate student, Dick Stevens. Oktay Sinanoglu had given a seminar on his ideas about correlation energy and had spoken to Col. Lipscomb about the possible effects of electron correlation on magnetic properties. This was to be Dick's project. On closer examination, we saw the need to get Hartree–Fock values of such properties first. We worked out the equations for perturbed Hartree–Fock theory using a basis set expansion and notation similar to Roothaan's² for the effects of uniform external magnetic and electric fields. These equations are coupled between the occupied MOs. Other workers had spent considerable effort to find ways to make approximations to uncouple the equations. Our view of the problem at the time was that solving the coupled

equations was not as difficult as doing the integrals, so why not go ahead and solve them with no further approximation? Dick set out to do the programming. He had been given an object deck for a diatomic integral program, but not the source deck. Dick's response was to obtain a core dump of the program and then proceed to translate the numerical op codes into an assembler version for his work, which seemed to me to be a rather daunting task. In due time, he had a program to study the electric and magnetic properties of diatomic molecules and first applied it to LiH.¹⁵ His results helped to establish some of the magnetic properties of this molecule.

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