This Week's Citation Classic® CC/NUMBER 7 FEBRUARY 13, 1989

Baerends E J, Ellis D E & Ros P. Self-consistent molecular Hartree-Fock-Slater calculations. I. The computational procedure. *Chem. Phys.* 2:41-51, 1973.
[Scheikundig Laboratorium, Vrije Universiteit, Amsterdam, The Netherlands]

A new method is presented of calculating molecular wavefunctions using a one-particle model. The calculation of two-electron integrals inherent to *ab initio* quantum-chemical methods is avoided through the use of three-dimensional numerical integration and Slater's $\varrho(r)^{1/3}$ exchange potential. A density fitting employing atom-centered Slater-Type Orbital basis functions affords an accurate description of the electronic potentials. [The *SCI®* indicates that this paper has been cited in over 255 publications, making it this journal's most-cited paper.]

Full Potential LCAO Xα Calculations

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July 20, 1988

The work described in this paper is the outgrowth of a visit by D.E. Ellis from Northwestern University, Evanston, to Amsterdam in the summer of 1971. My thesis supervisor, P. Ros, had collaborated with Ellis in 1965-1966 when they were both at MIT in Slater's group. In the years 1967-1970 Ellis had been developing a three-dimensional numerical integration scheme[1] for the Hamiltonian matrix elements and had applied this, with G.S. Painter, in band structure calculations.[2] For molecules also, this technique offers important advantages. In particular, the time-consuming calculation and processing of numerous two-electron integrals, characteristic for the standard *ab initio* quantum-chemical methods, is avoided. For the same reason the multiple scattering Xα technique was causing much excitement at the time. We felt, however, that the ultimate success of these unconventional methods would depend on the accurate solution, for a given density $\varrho(r)$, of the Poisson equation for the electronic Coulomb potential. After some unsuccessful attempts with numerical techniques, a fairly straightforward expansion of the electron density in an auxiliary basis of atom-centered Slater-Type Orbital functions turned out to be both accurate and feasible.

Why has the paper been frequently cited? There are probably two reasons. In the first place, interest was stimulated by the strong controversies over the MSXα method. On the other hand, the reception of the work also suffered from the strong feelings about Xα in the quantum-chemical community. From our work it appeared that, compared to Hartree-Fock, Xα and other density-functional potentials turned out to give superior agreement with experiments over a wide range of molecular properties. Opinions differ even today on whether or not this fact is convincingly explained by density-functional theory. It is remarkable to find in this "hard" science of ours a theory that is applauded and widely applied in solid-state physics and, at the same time, looked upon with skepticism, if not despised, in quantum chemistry (with, however, important and increasing exceptions).

In the second place, there has been since the early 1970s a continuous and steady development of methods in the same spirit. Codes developed independently in Amsterdam and at Northwestern University form one family. Another one is the Gaussian breed. In 1975 H. Sambe and R. Felton[3] took up the idea of a density fitting procedure for Coulomb and exchange potentials and combined it with exact integral evaluations rather than using numerical integration. They therefore used Gaussian basis functions and stayed much closer to *ab initio* methods. Their work has had a follow-up in solid-state physics and in molecular codes.

Most (but not all) of the heat of the early debates has dissipated. Indeed, in this field a lifelong commitment to one method with concomitant strong feelings is the rule rather than the exception. This endangers the acceptance of unconventional methods. Still, new methods should be given the time to prove themselves right (or wrong). Although Paul Feyerabend's "anything goes" may not be the right adage here, it is clear that Popper's falsification does not work smoothly and quickly either in the everyday life of computational physicists and chemists. We may still hope for a blending of new computer architectures (for example, vector and parallel processing) with new mathematical techniques[4] to generate major methodological advances.

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1. **Ellis D E.** Application of diophantine integration to Hartree-Fock and configuration interaction calculations. *Int. J. Quantum Chem.* 2S:35-42, 1968. (Cited 65 times.)
2. **Ellis D E & Painter G S.** Discrete variational method for the energy band problem with general crystal potentials. *Phys. Rev. B—Solid State* 2:2887-98, 1970. (Cited 275 times.)
3. **Sambe H & Felton R.** A new computational approach to Slater's SCF-Xα equation. *J. Chem. Phys.* 62:1122-6, 1975. (Cited 135 times.)
4. **Boerrigter P M, Te Velde G & Baerends E J.** Three-dimensional numerical integration for electronic structure calculations. *Int. J. Quantum Chem.* 33:87-113, 1988.

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