

Perspective

Perspective on “Self-consistent molecular Hartree–Fock–Slater calculations”

Baerends EJ, Ellis DE, Ros P (1973) *Chem Phys* 2:41

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Abstract. This paper discusses the title paper by Baerends, Ellis, and Ros. We show the role it has played in the development of density functional theory and the further work it has initiated.

Key words: Density functional theory – Discrete variational quantum chemistry – Hartree–Fock–Slater method

A remarkable development of the past decade has been the general acceptance by the chemical community of ab initio computer codes as modeling tools in a wide variety of applications. While it has been possible to predict molecular spectroscopic and geometric properties for a long time, the accurate prediction of bond energies of large systems has only become possible quite recently. As shown by the 1998 Nobel award to Kohn (shared with Pople), the contribution of density functional theory (DFT) to practical ab-initio calculations is now widely recognized. Rosén has recently highlighted the crucial role of the discrete variational $X\alpha$ method (DVM) in the process that has led to the current state of affairs [1]. The use of the DVM using an expansion of molecular eigenfunctions atomic orbitals was described first in the title paper.

Slater’s multiple scattering $X\alpha$ (MS- $X\alpha$) around 1970 was a promising quantum chemical method [2], although studies of diatomic molecules and the water molecule clearly showed that the method had shortcomings [3]. These were mainly due to the Muffin–Tin approximation that was used for the molecular potential; in particular, the assumption that the molecular potential is constant in the interatomic region.

Baerends et al. were the first to show how to do accurate $X\alpha$ calculations without scattered waves and

without Muffin–Tin potentials. This was accomplished in the time-honoured fashion of quantum chemistry with a basis-set expansion in localized functions; in particular, Slater-type orbitals. This was not only used for the Kohn–Sham orbitals, but also to fit the electronic density. This allowed the accurate calculation of the molecular potential. The other important point of the paper was that numerical methods were used to calculate integrals. These methods were based on previous work by Ellis and Painter [4–6], and have since been known as the DVM. The use of a numerical method solved the problem of the complicated integrals involving the density functional; not just the one of $X\alpha$, but also later ones such as those of the local density approximation and the generalized gradient approximation [7–11].

Initial applications focused on the electronic structure of carbonyl complexes [12] and clusters [13] as models of surfaces. A special feature of the method developed by the groups of Baerends and Ziegler [14–16] is the analysis of the bond energy, which allows decomposition in terms of the σ and π bonding between the free fragment orbitals. This enables a quantitative assessment of donating and backdonating energy contributions.

The methods described in the paper by Baerends et al. were implemented in the Amsterdam density functional program (ADF) [17]. This program has played an important role in the acceptance of DFT as an alternative method to wavefunction-based methods for doing quantum chemical calculations. It was later extended, amongst other, by Ziegler’s transition-state method [15] that allowed a direct calculation of the bond energy on the basis of the change in the electron density when the bond is formed. The numerical integration methods were made more user-friendly. Nowadays only the desired accuracy has to be specified. Various improved density functionals were also incorporated. Since about 1990 there has also been a version to do DFT calculations on systems with translational symmetry (ADF-BAND) [17]. The first application was to solve the problem of the adsorption site of CO on Cu [18], which cluster models of metals incorrectly predict to be

a high-coordination site, whereas slab calculations yield the atop site as the preferred one. A more recent application is the calculation of the six-dimensional potential-energy surface for H_2 dissociation on Cu(100) [19]. ADF-BAND can be considered the counterpart of DFT codes using plane-wave basis sets.

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