8th. World Congress on Computational Mechanics (WCCM8)
5th. European Congress on Computational Methods in Applied Sciences and Engineering (ECCOMAS 2008)
June 30 – July 5, 2008
Venice, Italy

Adaptive models for electronic structure computations of solids and defects

Denis Aubry and *Ann-Lenaig Hamon

Laboratoire MSS-Ma t UMR CNRS 8579 – Ecole Centrale Paris
Grande Voie des Vignes – 92290 Châtenay-Malabry - France
http://www.mssmat.ecp.fr

Key Words: *First principle, Hartree-Fock, finite element method (FEM)*

ABSTRACT

The first principle approach is mostly used nowadays to evaluate physical and mechanical properties of solids. In fact, the macroscopic behaviour depends on the type of binding through the electronic density, derived from the quantum mechanics Schrödinger equation. It also allows designing new materials with cutting edge performances.

When willing to solve the Schrödinger equation for a global system of N_e electrons, one faces a problem of partial differential equations in $\mathbb{R}^{3Ne}$ and needs to approximate the form of the wave function ψ (or of the equation itself) one looks for. Among them is the density functional theory (DFT) [1]. But it includes a whole set of approximations, from the most basic one known as LDA (local density approximation) where the exchange correlation energy E_{xc} is written as a functional of the electron density ρ, to more elaborated ones such as general gradient approximation (GGA) and other meta-GGA where E_{xc} is a functional of ρ, and also of its gradient, its laplacian… This sequence of more elaborated approximations, referred as "Jacob's ladder", shows that soon one wished to decrease the error due to the approximation as its complexity was increased. Nevertheless, the comparison is based on experimental values and not on error estimation.

Apart from DFT, there exists another model known as the Hartree-Fock approximation (HF) where ψ is written as a single Slater determinant [2]. That model, mostly used for molecular systems, is based on a variational principle, and the global $\mathbb{R}^{3Ne}$ Schrödinger equation is rewritten as a system of N_e $\mathbb{R}^3$ equations.

If we consider N_n nuclei and N_e electrons, without any external electric nor magnetic field, this equation reads for the wave function $\psi(x_i,X_A)$ (in atomic units):

$$-\frac{1}{2}\Delta_i\psi-\frac{1}{2M_A}\Delta_A\psi+\left(V_{en}+V_{ee}+V_{nn}\right)\psi=E\,\psi \qquad (1)$$

with $(x_i)_{1\le i\le Ne}$ the electron positions and $(X_A)_{1\le A\le Nn}$ the nucleus positions,
and where V_{en}, V_{ee} and V_{nn} stands for the Coulomb type potentials.
In the classical Born-Oppenheimer approximation, the nucleus motions and the related laplacians are neglected. The wave function only depends on the electrons:

$$-\frac{1}{2}\Delta_i\psi+\left(V_{en}+V_{ee}\right)\psi=E_e\,\psi \qquad (2)$$

The HF approach uses N_e spin-orbitals φ_i, collected into a column vector

$$\forall\, x \in \mathbb{R}^3, \qquad \Phi(x) = (\varphi_1(x) \ldots \varphi_{Ne}(x))^T. \tag{3}$$

These functions are normalized: $\int_{\mathbb{R}3} \Phi \otimes \Phi^* = \mathbf{I}$

and ψ satisfies the Pauli exclusion principle through a Slater determinant:

$$\psi_{HF}(x_i) = \mathrm{Det}[\Phi(x_1) \ldots \Phi(x_{Ne})] \tag{4}$$

The Schrödinger equation gives the HF system with the unknown diagonal matrix ε:

$$-1/2\ \Delta_x\Phi + [(V_{en} + \mathrm{Tr}\mathbf{G})\ \mathbf{I} - \mathbf{G}]\ \Phi = \varepsilon(\Phi) \quad \text{and} \quad -\Delta_x\mathbf{G} = 4\ \pi\Phi \otimes \Phi^* \tag{5}$$

However simple, it does not take into account the electron correlation correctly. Here again, further approximations have been elaborated known as post-HF, among which stands the configuration interaction (CI). In that case the form of the global wave-function is a linear combination of Slater determinants, where the first one is the HF solution, and where the number of terms shall be discussed as well as the (virtual) spin-orbitals taken into account: $\Phi_m(x) = (\varphi_{m1}(x) \ldots \varphi_{mNe}(x))^T$ (6)

and

$$\psi_{CI}(x_i) = \sum \alpha_m\, \mathrm{Det}\left[\Phi_m(x_1) \ldots \Phi_m\left(x_{N_e}\right)\right] \tag{7}$$

To detail the error estimation regarding HF, there are two models to consider: the Schrödinger equation (1) and the HF model (6). Their weak forms read respectively:

$$\forall\, \psi_t, \text{ a test function, } 1/2 \int_{\mathbb{R}3} \nabla\psi.\nabla\psi_t^* + \int_{\mathbb{R}3} (V_{en} + V_{ee})\ \psi\,\psi_t^* = E_e \int_{\mathbb{R}3}\ \psi\,\psi_t^* \tag{8}$$

and

$$\begin{cases} \frac{1}{2}\int_{R^3} \nabla\Phi.\nabla\Phi_t^* + \int_{R^3}\left[\left(V_{en} + \mathrm{Tr}\mathbf{G}\right)\mathbf{I} - \mathbf{G}\right]\Phi.\Phi_t^* = \int_{R^3} \varepsilon(\Phi).\Phi_t^* \\ \int_{R^3} \nabla\mathbf{G}.\nabla\mathbf{G}_t^* = 4\pi\int_{R^3} \mathrm{Tr}\left(\Phi\otimes\Phi_t^*.\mathbf{G}_t^*\right) \end{cases} \tag{9}$$

Since the HF model has really been computed from it, that last equation is equivalent to:

$$1/2 \int_{\mathbb{R}3} \nabla\psi_{HF}.\nabla\psi_{HFt}^* + \int_{\mathbb{R}3} (V_{en} + V_{ee})\ \psi_{HF}\ \psi_{HFt}^* = E_{eHF} \int_{\mathbb{R}3}\ \psi_{HF}\ \psi_{HFt}^* \tag{10}$$

So:

$$\begin{aligned} (E_e - E_{eHF}) \int_{\mathbb{R}3}\ \psi_{HF}\ \psi_{HFt}^* &= 1/2 \int_{\mathbb{R}3} (\nabla\psi - \nabla\psi_{HF}).\nabla\psi_{HFt}^* \\ &+ \int_{\mathbb{R}3} (V_{en} + V_{ee})\ (\psi - \psi_{HF})\ \psi_{HFt}^* - E_{eHF} \int_{\mathbb{R}3}\ (\psi - \psi_{HFt})\ \psi_{HF}^* \end{aligned} \tag{11}$$

The residual of ψ_{HF} in the exact Schrödinger equation appears in the right hand side, and we get the following final result:

$$\left|E_e - E_{eHF}\right| = \frac{\left\|\psi - \psi_{HFt}\right\|.\left\|\mathrm{Res}\left(\psi_{HFt}\right)\right\|}{\left|\int_{R^3} \psi.\psi_{HF}^*\right|} \tag{12}$$

which means that the exact energy E_e is approximated by the HF energy E_{eHF} to the extent that the residual $\mathrm{Res}(\psi_{HFt})$ is small and that the two wave functions ψ and ψ_{HF} are not orthogonal. Finally it should be pointed out that the term $\|\psi - \psi_{HFt}\|$ is small if it is possible to approximate the exact wave by *any suitable* Slater determinant.

A similar *a posteriori* error estimation can be inferred for ψ itself. It would be possible then to extend the analysis to other quantities of interest such as ρ, the derivative of E with respect to the nucleus positions to get the stresses… Using a conforming finite element method, the discrete trail space for the HF system is embedded in the HF space of Slater determinant so that the preceding analysis can be easily extended.

REFERENCES

[1] P. Hohenberg and W. Kohn, *Phys. Rev.* B, Vol. 136, p. 864, (1964); W. Kohn and L.J. Sham, *Phys. Rev.* A, Vol. 140, p. 1133 (1965).

[2] J.A. Pople and R.K. Nesbet, *J. Chem. Phys.*, Vol. 22, p. 571, (1954).