Notes 60(6): Resonant Density Functional Methods.

Any Coulombic potential is described in ECE theory by:

$$\underline{\nabla} \cdot \underline{E}^{a} = \rho^{a} / \epsilon_{0} \quad -(1)$$

$$\underline{E}^{a} = -\frac{\partial \underline{A}^{a}}{\partial t} - \underline{\nabla} \phi^{a} - c\omega^{a}{}_{b} \underline{A}^{b} + \underline{\omega}^{a}{}_{b} \phi^{b} \quad -(2)$$

In non-magnetic situations only the scalar potential need be considered, so:

$$\underline{E}^{a} = -\underline{\nabla} \phi^{a} + \underline{\omega}^{a}{}_{b} \phi^{b} \quad -(3)$$

From eqns (1) and (3) we obtain a resonance equation:

$$-\nabla^{2} \phi^{a} + \underline{\nabla} \cdot \left(\phi^{b} \underline{\omega}^{a}{}_{b} \right) = \rho^{a} / \epsilon_{0} \quad -(4)$$

From "Vector Analysis Problem Solver", p. 292, 7-19, eqn. (3):

$$\underline{\nabla} \cdot \left(\phi^{b} \underline{\omega}^{a}{}_{b} \right) = \underline{\nabla} \phi^{b} \cdot \underline{\omega}^{a}{}_{b} + \left(\underline{\nabla} \cdot \underline{\omega}^{a}{}_{b} \right) \phi^{b} \quad -(5)$$

so:

$$\boxed{-\nabla^{2} \phi^{a} + \underline{\omega}^{a}{}_{b} \cdot \underline{\nabla} \phi^{b} + \left(\underline{\nabla} \cdot \underline{\omega}^{a}{}_{b} \right) \phi^{b} = \rho^{a} / \epsilon_{0}} \quad -(6)$$

This equation applies to any Coulombic potential ϕ^{a} in any situation in physics, chemistry, engineering etc.

In density functional or ab initio methods the potential energy in the Schrödinger equation is obtained from ϕ^{a}:

$$V^{a} = -e \phi^{a} \quad -(7)$$

for each electron of charge $-e$. In density functional codes any Coulombic potential obeys eqn (6). The Hartree term is:

2)

$$\bar{V}_H = \int \frac{e^2 n_s(\underline{r}')}{|\underline{r} - \underline{r}'|} d^3 r' \quad -(8)$$

and is used in the effective single particle potential $\bar{V}_s$ of the Kohn-Sham equations of the auxiliary system. The Hartree term $\bar{V}_H$ describes the electron-electron Coulomb repulsion. So the Hartree potential obeys a resonance equation. If for simplicity we omit superscripts in eqn. (6):

$$\nabla^2 \bar{V}_H - \underline{\omega} \cdot \underline{\nabla} \bar{V}_H - \left(\underline{\nabla} \cdot \underline{\omega}^a_b\right) \bar{V}_H = -\frac{\rho}{\epsilon_0} \quad -(9)$$

So at resonance the multi-electron electron repulsion is greatly enhanced, causing ionization and the production of free electrons if the binding energy is exceeded. NEW SOURCE OF POWER.

Code Modification

Code up eqn. (9) in the part of the code following the computation of $\bar{V}_H$, then return to the iteration code.