

Properties and solutions of Kohn-Sham Equations

Lecture 30

CHM 652 / PHY 626

Electronic Structure of Materials

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Lecture Plan

- Implications of the Kohn-Sham scheme
- The local density approximation
- Other exchange correlation functionals

Kohn-Sham Approach to DFT

$$\left(-\frac{\nabla^2}{2} + v_{eff}[n](\mathbf{r}) \right) \psi_i(x) = \epsilon_i \psi_i(x)$$

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r})$$

$$n(\mathbf{r}) = \int d\sigma \sum_{j=1}^N \psi^*(x) \psi(x)$$

Since the potential depends on the density, these equations have to be solved self-consistently like the Hartree-Fock equations.

Implications of the KS scheme

What did we achieve?

- The kinetic energy can be calculated with better accuracy due to the use of orbitals.
- The effective potential is space-local. So solution is less expensive than H-F equations.
- Note that the mapping to the 1-electron system is, in principle, exact. This means that we have a shot at getting the exact ground-state energy, density and other properties unlike the H-F equations.
- The KS equations given here only involve spatial operators. Hence, we expect a spin-degeneracy in the solutions (double-occupancy of orbitals). This appears more naturally here than in HF theory.

Implications of the KS scheme

What we don't have.

While we approximated the kinetic energy and the interaction energies capturing most of their magnitude, we hid away the errors in the XC functional. Unfortunately, we do not know an exact form for this functional.

However, several good approximations exist and are constantly being invented. This allows us to use the KS equations to solve electronic structure of materials in practice to a much greater degree of accuracy than previously possible!

Implications of the KS scheme

Is the KS system real?

$$\hat{h}_{KS} = -\frac{\nabla^2}{2} + v_s(\mathbf{r}) \quad \text{Kohn-Sham Hamiltonian}$$

$$E_0 = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] - \int d^3r v_{xc}(\mathbf{r})n(\mathbf{r}) \neq \sum_{i=1}^N \epsilon_i$$

Orbitals have some pictorial benefits but nothing else.

What about orbital energies?

$$\epsilon_{max} = -I \quad \text{Lowest ionisation energy}$$

$$\frac{\partial E[\{f_i, \psi_i\}]}{\partial f_i} = \epsilon_i \quad \text{Janak's theorem (1978)}$$

Local Density Approximation to XC

We can develop an approximation to E_{xc} based on the uniform electron gas.

$$E_{xc}^{LDA}[n] \equiv \int d^3r n(\mathbf{r}) \epsilon_{xc}^{LDA}(n(\mathbf{r}))$$

XC energy per particle

$$v_{xc}^{LDA}(\mathbf{r}) = \frac{\delta E_{xc}^{LDA}}{\delta n}$$
$$= \epsilon_{xc}^{LDA}(n) + n(\mathbf{r}) \frac{\partial \epsilon_{xc}^{LDA}}{\partial n}$$

Note that the XC energy per particle is assumed to be a function of density instead of a functional.

Local Density Approximation to XC

We can develop an approximation to E_{xc} based on the uniform electron gas.

$$\epsilon_{xc}^{LDA}(n(\mathbf{r})) = \epsilon_x + \epsilon_c$$

$$\epsilon_x^{LDA}(n) = -C_x n(\mathbf{r})^{\frac{1}{3}}$$

The correlation energy is obtained by fitting numerically exact calculations on the homogenous electron gas. (Ceperley, Alder; Vosko, Wilk, and Nusair)

Sometimes the Slater X_α method is also used.