Lesson 8 - Density Functional Theory
Unit 8.2 Hohenberg-Kohn theorem and Kohn-Sham density functional

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Structure of Matter - MSc in Physics
Hohenberg-Kohn theorem (I)

The density functional approach was put on a solid theoretical basis by Pierre Hohenberg and Walter Kohn in 1964.

First, they observed that, given a many-body wavefunction of \( N \) identical particles \( \Psi(r_1, r_2, \ldots, r_N) \), the associated one-body local density \( \rho(r) \) reads

\[
\rho(r) = N \int d^3r_2 \ldots d^3r_N |\Psi(r, r_2, \ldots, r_N)|^2.
\]  

(1)

Then, they formulated a rigorous theorem for a system of identical particles (bosons or fermions) described by the many-body Hamiltonian

\[
\hat{H} = \hat{T} + \hat{U} + \hat{V}
\]

(2)

where \( \hat{T} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m} \nabla_i^2 \) is the many-body kinetic energy operator, \( \hat{U} = \sum_{i=1}^{N} U(r_i) \) is the many-body external potential operator, and \( \hat{V} = \frac{1}{2} \sum_{\substack{i,j=1 \atop i \neq j}}^{N} V(r_i, r_j) \) is the many-body interaction potential operator.
**Lemma:** Given the many-body wavefunction $\Psi(r_1, r_2, ..., r_N)$, for the the external energy one gets

$$\langle \Psi | \hat{U} | \Psi \rangle = \int d^3r \ U(r) \ \rho(r) ,$$

where $\rho(r)$ is the one-body local density associated to $\Psi(r_1, r_2, ..., r_N)$.

**Theorem:** For a system of $N$ identical interacting particles in an external potential $U(r)$ the density functional

$$E[\rho] = F[\rho] + \int d^3r \ U(r) \ \rho(r) ,$$

where

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V} | \Psi \rangle ,$$

is such that $E[\rho] \geq E[\rho_{gs}] = E_{gs}$ for any trial density $\rho(r)$, and the equality holds only for $\rho(r) = \rho_{gs}(r)$ the ground-state density profile.

The functional $F[\rho]$ is universal: it does not depend on the external potential $U(r)$ but only on the inter-particle potential $V(r - r')$, which is the familiar Coulomb potential in the case of electrons.
Nowadays the most used density functional for electrons is the one proposed by Walter Kohn and Lu Jeu Sham in 1965. In the Kohn-Sham density functional approach the universal functional $F[\rho]$ is given by

$$F_{KS}[\rho] = T_{KS}[\rho] + E_D[\rho] + E_{XC}[\rho]$$

where

$$T_{KS}[\rho] = \sum_{i=1}^{N} \phi_i^*(r) \left(-\frac{\hbar^2}{2m} \nabla^2\right) \phi_i(r)$$

is the Kohn-Sham kinetic energy, where the orbitals $\phi_i(r)$ determine the local density, namely

$$\rho(r) = \sum_{i=1}^{N} |\phi_i(r)|^2,$$

the direct (or Hartree-like) energy of interaction $E_D[\rho]$ has the familiar form, and $E_{XC}[\rho]$ is the so-called exchange-correlation energy, which simply takes into account the missing energy with respect to the exact result.
The minimization of the Kohn-Sham density functional gives

\[
-\frac{\hbar^2}{2m} \nabla^2 + U(r) + \int d^3 r' \ V(r - r') \ \rho(r') + \frac{\delta E_{XC}[\rho]}{\delta \rho(r)} \]

\[= \phi_i(r) = \epsilon_i \phi_i(r) \tag{6} \]

which are the local Kohn-Sham equations for the orbitals \( \phi_i(r) \), with \( \epsilon_i \) the Lagrange multipliers fixed by the normalization to one of the orbitals. Notice that the third term on the left side of the previous equation is obtained by using

\[
\frac{\delta E_{XC}[\rho]}{\delta \phi^*_i(r)} = \frac{\delta E_{XC}[\rho]}{\delta \rho(r)} \frac{\delta \rho(r)}{\delta \phi^*_i(r)} = \frac{\delta E_{XC}[\rho]}{\delta \rho(r)} \phi_i(r). \tag{7} \]

In many applications the (usually unknown) exchange-correlation energy is written as

\[E_{XC}[\rho] = Ex[\rho] + E_C[\rho], \tag{8} \]

where the correlation energy \( E_C[\rho] \) is fitted from Monte Carlo calculations and sometimes it is set to zero.
Born-Oppenheimer approximation (I)

In the case of a molecule made of \( N_n \) atomic nuclei with electric charges \( Z_\alpha e \), the external potential acting on one electron is given by

\[
U(r; \{ R_\alpha \}) = -\sum_{\alpha}^{N_n} \frac{Z_\alpha e^2}{4\pi\varepsilon_0} \frac{1}{|R_\alpha - r|},
\]

(9)

with \( r \) the position of the electron and \( R_\alpha \) the position of the \( \alpha \)-th nucleus.

Within the so-called Born-Oppenheimer approximation, which treats the atomic nuclei as classical objects also neglecting their kinetic energy, and adopting the Kohn-Sham approach, the total energy of the molecule can be written as

\[
E[\rho, \{ R_\alpha \}] = F_{KS}[\rho] + \int d^3r \ U(r; \{ R_\alpha \}) \rho(r),
\]

(10)

where \( \rho(r) \) is the local density of the electrons and \( R_\alpha \) the position of the \( \alpha \)-th nucleus.

Minimizing \( E[\rho, \{ R_\alpha \}] \) with respect to \( \rho(r) \) and \( R_\alpha \), one finds for the molecule the ground-state local density and the ground-state positions of all nuclei.