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

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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 $\boldsymbol{\Psi}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$, the associated one-body local density $\rho(\mathbf{r})$ reads

$$\rho(\mathbf{r}) = N \int d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N \; |\boldsymbol{\Psi}(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N)|^2 \; . \tag{1}$$

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

$$\hat{H} = \hat{T} + \hat{U} + \hat{V} \tag{2}$$

where $\hat{T} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2$ is the many-body kinetic energy operator, $\hat{U} = \sum_{i=1}^{N} U(\mathbf{r}_i)$ is the many-body external potential operator, and $\hat{V} = \frac{1}{2}\sum_{\substack{i,j=1 \\ i \neq j}}^{N} V(\mathbf{r}_i, \mathbf{r}_j)$ is the many-body interaction potential operator.

Hohenberg-Kohn theorem (II)

Lemma: Given the many-body wavefunction $\mathbf{\Psi}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$, for the the external energy one gets

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

where $\rho(\mathbf{r})$ is the one-body local density associated to $\mathbf{\Psi}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$.

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

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

where

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

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

The functional $F[\rho]$ is universal: it does not depend on the external potential $U(\mathbf{r})$ but only on the inter-particle potential $V(\mathbf{r} - \mathbf{r}')$, which is the familiar Coulomb potential in the case of electrons.

Kohn-Sham functional (I)

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

$$F_{KS}[\rho] = T_{KS}[\rho] + E_D[\rho] + E_{XC}[\rho] \tag{3}$$

where

$$T_{KS}[\rho] = \sum_{i=1}^{N} \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\mathbf{r}) \tag{4}$$

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

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \ , \tag{5}$$

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.

Kohn-Sham functional (II)

The minimization of the Kohn-Sham density functional gives

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) + \int d^3\mathbf{r}'\, V(\mathbf{r}-\mathbf{r}')\, \rho(\mathbf{r}') + \frac{\delta E_{XC}[\rho]}{\delta\rho(\mathbf{r})} \right] \phi_i(\mathbf{r}) = \epsilon_i\, \phi_i(\mathbf{r}) \tag{6}$$

which are the local Kohn-Sham equations for the orbitals $\phi_i(\mathbf{r})$, with ϵ_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

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

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

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

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

$$U(\mathbf{r};\{\mathbf{R}_\alpha\}) = -\sum_{\alpha}^{N_n} \frac{Z_\alpha e^2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{R}_\alpha - \mathbf{r}|} \ , \tag{9}$$

with $\mathbf{r}$ the position of the electron and $\mathbf{R}_\alpha$ the position of the α-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

$$E[\rho,\{\mathbf{R}_\alpha\}] = F_{KS}[\rho] + \int d^3\mathbf{r}\ U(\mathbf{r};\{\mathbf{R}_\alpha\})\ \rho(\mathbf{r}) \ , \tag{10}$$

where $\rho(\mathbf{r})$ is the local density of the electrons and $\mathbf{R}_\alpha$ the position of the α-th nucleus.

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