Density functional theory: the basics

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Overview

Basic concepts

Wave function is a complex-value entity that describes the quantum state of one or more particles. Example: free electron $\Psi(\mathbf{r}, \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}}$

Expected value in quantum mechanics is the act of performing a measurement on a observable. Example: $E = \langle\Psi|\hat{H}|\Psi\rangle$. Explicitly

$$\langle\Psi|\hat{H}|\Psi\rangle = \int \cdots \int \Psi^*(\vec{x}_1, ..., \vec{x}_N, \vec{R}_1, ..., \vec{R}_M)\hat{H}\Psi(\vec{x}_1, ..., \vec{x}_N, \vec{R}_1, ..., \vec{R}_M)dV \tag{1}$$

Coordinate system In this lecture, $\vec{x}_N$ reffers to the coordinate system of an electron N, whereas $\vec{R}_M$ to a nucleus M

Goal

The goal of the Density Functional Theory is to find the ground state energy E_0 for a given system and its ground state electronic structure, from which one could calculate further material properties such as
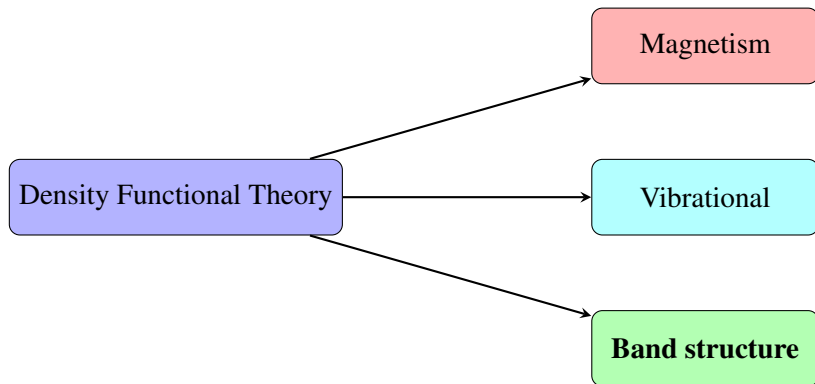
The problem

One can start to solve the following problem

$$\hat{H}\Psi(\vec{x}_1,...,\vec{x}_N,\vec{R}_1,...,\vec{R}_M) = E\Psi(\vec{x}_1,...,\vec{x}_N,\vec{R}_1,...,\vec{R}_M), \qquad (2)$$

where

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>1}^{M}\frac{Z_A Z_B}{R_{AB}} \qquad (3)$$

Too many dimensions! Impossible to solve, but one can attempt to make is simpler. Adiabatic or Born Oppenheimer approximation:

$$\Psi(\vec{x}_1,...,\vec{x}_N,\vec{R}_1,...,\vec{R}_M) = \Psi_{tot} = \Psi_{ele}(\vec{x}_1,..,\vec{x}_N) * \Psi_{nuc}(\vec{R}_1,...,\vec{R}_M) \qquad (4)$$

Born Oppenheimer approximation

Then, the new Hamiltonian will be

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} = \hat{T} + \hat{V}_{Nc} + \hat{V}_{ee} \qquad (5)$$

Example: Water molecule H_2O. 10 electrons. Problem has 30 dimensions!!

Variational principle

The variational principle simply states that any other trial wave function will always give a upper bound energy than the true ground state one

$$\langle \Psi_{trial}|\hat{H}|\Psi_{trial}\rangle = E_{trial} \geq E_0 = \langle \Psi_0|\hat{H}|\Psi_0\rangle \tag{6}$$

Therefore, the strategy is to minimize the functional $E[\Psi]$

$$E_0 = \min_{\Psi \to N} E[\Psi] = \min_{\Psi \to N} \langle \Psi|\hat{T} + \hat{V}_{nc} + \hat{V}_{ee}|\Psi\rangle \tag{7}$$

Our summary so far

$$\{N, Z_A, R_A\} \Rightarrow \hat{H} \Rightarrow \Psi_0 \Rightarrow E_0 \tag{8}$$

Hartree-Fock

One attempt to minimize the energy functional is to use the Slater determinants

$$\Psi_0 = \Phi_{SD} = \frac{1}{\sqrt{N!}} \det \{\chi_1(\vec{x}_1), .., \chi_2(\vec{x}_N)\}, \tag{9}$$

then one has to

$$E_{HF} = \min_{\Phi_{SD} \to N} E[\Phi_{SD}] \tag{10}$$

$$\langle \Phi_{SD} | \hat{H} | \Phi_{SD} \rangle = \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \langle ii | jj \rangle - \langle ij | ji \rangle. \tag{11}$$

Using the variational principle

$$\frac{\delta F}{\delta \chi_j^*} = \langle \Phi_{SD} | \hat{H} | \Phi_{SD} \rangle - \sum_i \epsilon_i \left(\int |\chi_i(\vec{x}_i)|^2 - 1 \right) \tag{12}$$

Hartree-Fock

It will give the Hartree-Fock equation

$$\hat{f}\chi_i = \epsilon_i\chi_i; \; i = 1, 2, 3, .., N \tag{13}$$

with

$$\hat{f} = -\frac{1}{2}\nabla^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i) \tag{14}$$

and

$$V_{HF}(i) = \sum_j^N \left(\hat{J}_j(\vec{x}_1) - \hat{K}_j(\vec{x}_1) \right) \tag{15}$$

$$\hat{J}_j(\vec{x}_1) = \int |\chi_j(\vec{x}_2)|^2 \frac{1}{r_{12}} d\vec{x}_2 \tag{16}$$

$$\hat{K}_j(\vec{x}_1)\chi_i(\vec{x}_1) = \int \chi_j^*(\vec{x}_2) \frac{1}{r_{12}} \chi_i(\vec{x}_2)\chi_j(\vec{x}_1) d\vec{x}_2 \tag{17}$$

Electronic density

Instead of using the wave function with 3N dimensions, one could use the electron density

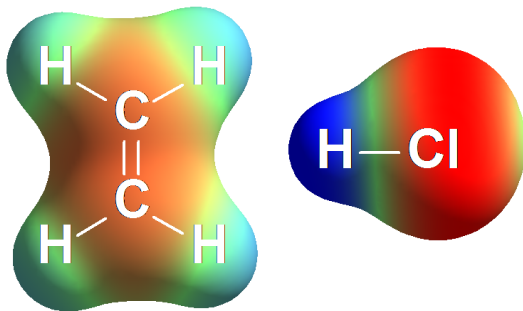$$\rho(\vec{r}) = N \int |\Psi(\vec{x}_1, ..., \vec{x}_N)|^2 d\vec{x}_1...\vec{x}_N \tag{18}$$

Figure 1: Electronic density

HK Theorems

First HK theorem: The external potential, V_{ext}, where the electrons are immersed is a unique functional of the electronic density $\rho(\vec{r})$

Second HK theorem: The energy functional $E[\rho]$ is minimized by the electronic ground state density $\rho_0(\vec{r})$.

Kohn-Sham approach

Starting from the HK theorems

$$E_0 = \min_{\rho \to N} \left(F[\rho] + \int \rho(\vec{r}) V_{Ne} d\vec{r} \right) \tag{19}$$

where $F[\rho]$ is an universal functional

$$F[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho]. \tag{20}$$

In Eq. 20, only $J[\rho]$ is known, while the explicit forms of the other two are unknown. Let us now consider a system with non-interacting electrons.

$$F[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho] \tag{21}$$

where $T_S[\rho]$ is the kinetic energy of the non-interacting electrons, such as $T_S \neq T_C$

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_C[\rho] + E_{ncl}[\rho] \tag{22}$$

Kohn-Sham approach

Then, one has to minimize

$$
\begin{aligned}
E[\rho] = {} & T_S[\rho] + J[\rho] + E_{Ne}[\rho] + E_{xc}[\rho] \\
= {} & -\frac{1}{2}\sum_i^N \int \phi_i(\vec{r}_1)^* \nabla^2 \phi_i(\vec{r}_1) d\vec{r}_1 \\
& + \frac{1}{2}\sum_i^N \sum_j^N \int \int |\phi_i(\vec{r}_1)|^2 \frac{1}{r_{12}} |\phi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \\
& - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{iA}} |\phi_i(\vec{r}_1)|^2 d\vec{r}_1 + E_{ex}[\rho]
\end{aligned}
\tag{23}
$$

Kohn-Sham equation

Finally, if one can use the variational principle to get

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}\right)\phi_i = \epsilon_i\phi_i, \tag{24}$$

with

$$V_{\text{eff}}(\vec{r}) = \int \frac{\rho(\vec{r_2})}{r_{12}}d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{iA}} \tag{25}$$

Notes aobut the exchange-correlation potential

The problem is solved correctly if V_{xc} is known! The whole complexity of the problem boils down to that potential.
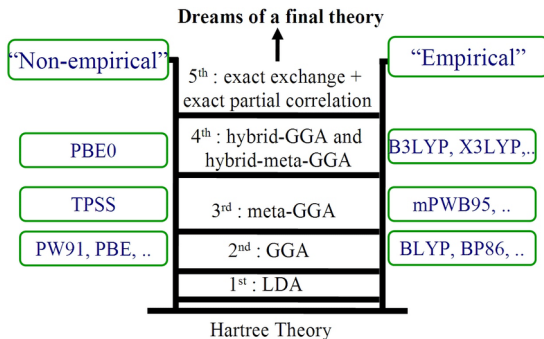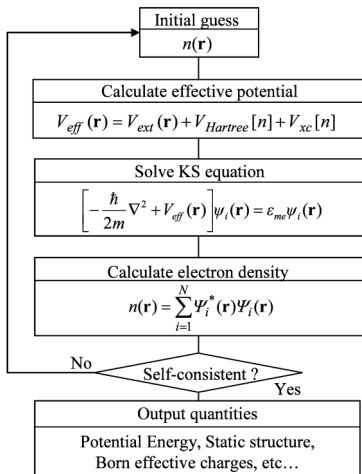

Figure 2: Jacob's ladder

Kohn-Sham scheme

Figure 3: Kohn-Sham scheme