

Chapter 8. Density Functional Theory

Hohenberg-Kohn theorem (1964): ground state E only depends on the electron density $\rho(\vec{r})$.

Energy is a functional (function of a function) of $\rho(\vec{r})$:

$$E = E[\rho(\vec{r})]$$

but in what form?

Kohn-Sham theorem (1965):

$$\begin{aligned} E = & -\frac{1}{2} \sum_i \int \psi_i^*(1) \nabla_1^2 \psi_i(1) d\tau_1 & T \\ & - \sum_a \int \frac{Z_a \rho(1)}{r_{1a}} d\tau_1 & V_{ne} \\ & + \frac{1}{2} \iint \frac{\rho(1)\rho(2)}{r_{12}} d\tau_1 d\tau_2 & V_{ee} \\ & + E_{XC}[\rho] & \text{exchange-} \\ & & \text{correlation energy} \end{aligned}$$

The major problem with DFT is the exchange-correlation functional!

The density is expressed in terms of the Kohn-Sham orbitals:

$$\rho = \sum_i |\psi_i\rangle\langle\psi_i| = \sum_i |\psi_i|^2$$

These orbitals have no physical significance, and are obtained by solving the one-electron equation:

$$\hat{F}_{KS}|\psi_i\rangle = \varepsilon_i|\psi_i\rangle$$

where the Kohn-Sham operator is

$$\hat{F}_{KS} = -\frac{1}{2}\nabla_1^2 - \sum_a \frac{Z_a}{r_{1a}} + \sum_j \hat{J}_j(1) + V_{XC}(1)$$

with the Coulomb operator

$$\hat{J}_j(1) = \int \rho(j)/r_{1j} d\tau_j$$

and the exchange-correlation functional

$$V_{XC}(1) = \delta E_{XC}[\rho(1)] / \delta \rho(1). \quad \text{(functional derivative)}$$

The equation is often solved using SCF method.

Approximation of $E_{XC}[\rho]$

- local density approximation (LDA)

$$E_{XC}^{LDA}[\rho] = \int \rho \varepsilon_{XC}(\rho) d\tau$$

where $\varepsilon_{XC}(\rho)$ is the known exchange-correlation energy per electron in homogeneous electron gas with the density ρ .

Often the energy density $\varepsilon_{XC}(\rho)$ is given in analytical forms.

For example, in the X α method (correlation ignored):

$$E_{X\alpha}[\rho] = C\alpha \int \rho^{4/3} d\tau$$

with α as an adjustable parameter.

Extension: local spin density approximation (LSDA), treating α and β electrons separately.

Simple, reasonably good.

- non-local gradient-corrected functionals

Include the contribution of the density gradients.

Often separated into exchange and correlation parts.

Exchange functional of Becke:

$$E_x[\rho] = E_x^{LSDA}[\rho] - b \sum_{\sigma=\alpha,\beta} \int \frac{\rho_\sigma^{4/3} x_\sigma^2 d\tau}{1 + 6bx_\sigma \sinh^{-1} x_\sigma}$$

with b fitted to HF exchange energy and

$$x_\sigma = \frac{|\nabla\rho_\sigma|}{\rho_\sigma^{4/3}}$$

Correlation functional of Lee-Yang-Parr:

$$E_C[\rho] = -a \int \frac{r + b\rho^{-2/3} \left[C_F \rho^{5/3} - 2t_W + \left(\frac{t_W}{9} + \frac{\nabla^2 \rho}{18} \right) e^{-cr^{-1/3}} \right] d\tau}{1 + d\rho^{-1/3}}$$

where a , b , c , d , and C_F are constants and

$$t_W = \sum_i \frac{|\nabla\rho_i|^2}{\rho_i} - \frac{\nabla^2 \rho}{8}$$

The BLYP (B3LYP for more updated version) functional.

SCF solution of Kohn-Sham equation

Expansion of Kohn-Sham orbitals

$$|\psi_i\rangle = \sum_{\nu} c_{\nu i} |\phi_{\nu}\rangle$$

where $|\phi_{\nu}\rangle$ are atomic basis such as STO and GTO.

Substituting back to the K-S eq, we have

$$\mathbf{HC} = \mathbf{SCE}$$

Where \mathbf{H} and \mathbf{S} are Hamiltonian and overlap matrices, respectively.

As \mathbf{H} contains ρ , the equation has to be solved self-consistently under a given set of functionals:

- initial guess of ρ
- construct \mathbf{H} and \mathbf{S}
- diagonalize \mathbf{S} and \mathbf{H} for K-S orbitals ψ_i and energies ε_i
- construct new ρ
- iterate until convergence

Pros and cons of DFT:

- include correlation energy, at least partially.
- simple and fast, comparable to HF.
- particularly suitable for transition metals.
- not variational, difficult to improve.
- because of empirical functional forms, results can be unpredictable.
- no excited states (TD-DFT can handle some excited states).