Lesson 8 - Density Functional Theory
Unit 8.1 Thomas-Fermi density functional

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Thomas-Fermi functional (I)

In 1927 Thomas and Fermi described the electronic structure of atoms by focusing on the electron local density $\rho(\mathbf{r})$ of N electrons, such that

$$\int d^3\mathbf{r}\ \rho(\mathbf{r}) = N\ . \tag{1}$$

According to Thomas and Fermi, the ground-state energy of the electrons can be captured by the functional

$$E_{TF}[\rho] = T_{TF}[\rho] + E_D[\rho] + \int d^3\mathbf{r}\ U(\mathbf{r})\ \rho(\mathbf{r})\ , \tag{2}$$

where

$$T_{TF}[\rho] = \int d^3\mathbf{r}\ \frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2)^{2/3}\rho(\mathbf{r})^{5/3} \tag{3}$$

is the Thomas-Fermi kinetic energy, i.e. the local approximation to the kinetic energy of the ideal Fermi gas,

$$E_D[\rho] = \frac{1}{2}\int d^3\mathbf{r}\ d^3\mathbf{r}'\ \rho(\mathbf{r})\ V(\mathbf{r}-\mathbf{r}')\ \rho(\mathbf{r}')\ , \tag{4}$$

is the (Hartree-like) direct energy of electron-electron interaction $V(\mathbf{r})$, while $U(\mathbf{r})$ is the nucleus-electron interaction potential.

Thomas-Fermi fuctional (II)

The Thomas-Fermi energy functional of the local electronic density $\rho(\mathbf{r})$ can be minimized with the constraint of the normalization of $\rho(\mathbf{r})$ to N. In this way one finds

$$\frac{\hbar^2}{2m}(3\pi^2)^{2/3}\rho^{2/3} + U(\mathbf{r}) + U_{mf}(\mathbf{r}) = \mu \,, \tag{5}$$

where

$$U_{mf}(\mathbf{r}) = \int d^3\mathbf{r}' \; V(\mathbf{r}-\mathbf{r}') \; \rho(\mathbf{r}') \tag{6}$$

is the Hartree-like mean-field potential acting on the electrons and μ is the Lagrange multiplier fixed by the normalization. The previous equation can be written as

$$\rho(\mathbf{r}) = \frac{(2m)^{3/2}}{3\pi^2\hbar^3}\left(\mu - U(\mathbf{r}) - \int d^3\mathbf{r}' \; V(\mathbf{r}-\mathbf{r}') \; \rho(\mathbf{r}')\right)^{3/2} \tag{7}$$

Eq. (7) is an implicit integral equation for the local electronic density $\rho(\mathbf{r})$ which can be solved numerically by using an iterative procedure.

Thomas-Fermi-Dirac-von Weizsäcker fuctional (I)

The Thomas-Fermi functional does not include the exchange energy of the electrons due to the Pauli principle. A better theoretical description is obtained with the Thomas-Fermi-Dirac-von Weizsäcker model, whose energy functional is given by

$$E_{TFDW}[\rho] = E_{TF}[\rho] + E_X[\rho] + E_W[\rho] \,, \tag{8}$$

where $E_{TF}[\rho]$ is the Thomas-Fermi energy functional of Eq. (2),

$$E_X[\rho] = -\int d^3\mathbf{r}\ \frac{3}{4}\frac{e^2}{4\pi\varepsilon_0}(\frac{3}{\pi})^{1/3}\rho(\mathbf{r})^{4/3} \tag{9}$$

is the functional correction introduced by Paul Dirac in 1930 to take into account the exchange energy which appears in the Hartree-Fock method, and

$$E_W[\rho] = \int d^3\mathbf{r}\ \lambda_W \frac{\hbar^2}{2m}(\nabla\sqrt{\rho(\mathbf{r})})^2 \tag{10}$$

is the functional correction introduced by Carl Friedrich von Weizsäcker in 1953 to improve the accuracy of the kinetic energy with λ_W a phenomnological parameter.