Total Energy and its Calculation in DFT

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As a many-electron problem

With Born-Oppenheimer approximation, the wave function for the N electrons in a solid satisfies the following Schrödinger equation (in the atomic units: $\hbar = 1$, $m_e = 1/2$, $e^2 = 2$):

$$\left[-\sum_{\alpha=1}^{N}\nabla_\alpha^2 + \sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}}\frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \sum_{\alpha=1}^{N} V_{\text{ext}}(\mathbf{r}_\alpha)\right]\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N) = E\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N)$$

where $V_{\text{ext}}(\mathbf{r}_\alpha) = -\sum_n \frac{2Z_n}{|\mathbf{r}_\alpha - \mathbf{R}_n|}$

The electron density with spin s is given by

$$\rho_s(\mathbf{r}) = N\sum_{s_2\ldots s_N}\int_\infty |\Psi(\mathbf{r}, s; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N)|^2 \, d^3\mathbf{r}_2 d^3\mathbf{r}_3 \ldots d^3\mathbf{r}_N .$$

$$\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})$$

and the electronic total energy is

Total energy of the solid: $E_{\text{T}} = E + \sum_n \sum_{m\neq n} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|}$

$$E = \sum_{s_1, s_2, \ldots s_N}\int_\infty \Psi^*(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N)\left[-\sum_{\alpha=1}^{N}\nabla_\alpha^2 + \sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}}\frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \sum_{\alpha=1}^{N} V_{\text{ext}}(\mathbf{r}_\alpha)\right]\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2; \ldots; \mathbf{r}_N, s_N) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N .$$

As a one-electron problem in DFT

At the ground state, the electronic total energy E is a functional of the electron density ρ

$$E = T_0[\rho] + U[\rho] + E_{\mathrm{XC}}[\rho]$$

$$\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r})$$

The electron density ρ can be calculated by $\rho_s(\mathbf{r}) = \sum_{\alpha} f_T(\varepsilon_{\alpha,s} - \varepsilon_F)\psi^*_{\alpha,s}(\mathbf{r})\psi_{\alpha,s}(\mathbf{r})$

where the Kohn-Sham orbital $\psi_{\alpha,s}(\mathbf{r})$ is the self-consistent solution of the following one-electron Schrödinger equation, known as the Kohn-Sham equation,

$$\left[-\nabla^2 + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{ext}}(\mathbf{r}) + V^s_{\mathrm{XC}}[\rho(\mathbf{r})]\right]\psi_{\alpha,s}(\mathbf{r}) = \varepsilon_{\alpha,s}\psi_{\alpha,s}(\mathbf{r})$$

$$V_{\mathrm{ext}}(\mathbf{r}) = -\sum_n \frac{2Z_n}{|\mathbf{r} - \mathbf{R}_n|}$$

and α is the orbital index. For periodic system, $\alpha = \{n, \mathbf{k}\}$, with n the band index, and $\mathbf{k}$ the Bloch wave **k**-vector. The Hartree potential is

$$V_{\mathrm{H}}(\mathbf{r}) = \int_{\infty} \frac{2\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

$$f_T(\varepsilon_{\alpha,s} - \varepsilon_F) = \frac{1}{1 + e^{(\varepsilon_{\alpha,s} - \varepsilon_F)/k_B T}}$$

The many-body problem becomes a one-electron problem with effective potential given by

$$V^s_{\mathrm{eff}}(\mathbf{r}) = V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{ext}}(\mathbf{r}) + V^s_{\mathrm{XC}}[\rho(\mathbf{r})]$$

Decomposition of the electronic total energy

$$E = T_0[\rho] + U[\rho] + E_{\mathrm{XC}}[\rho]$$

The kinetic energy term

$$T_0[\rho] = \sum_{s=\uparrow,\downarrow} \sum_{\alpha} f_T(\varepsilon_{\alpha,s} - \varepsilon_F) \int_\infty \psi^*_{\alpha,s}(\mathbf{r}) \left[-\nabla^2\right] \psi_{\alpha,s}(\mathbf{r}) d^3\mathbf{r}$$

$$= \sum_{s=\uparrow,\downarrow} \sum_{\alpha} f_T(\varepsilon_{\alpha,s} - \varepsilon_F) \int_\infty \psi^*_{\alpha,s}(\mathbf{r}) \left[\varepsilon_{\alpha,s} - V^s_{\mathrm{eff}}(\mathbf{r})\right] \psi_{\alpha,s}(\mathbf{r}) d^3\mathbf{r}$$

$$= \sum_{s=\uparrow,\downarrow} \sum_{\alpha} \left(\int_\infty \varepsilon\, f_T(\varepsilon - \varepsilon_F) \delta(\varepsilon - \varepsilon_{\alpha,s}) d\varepsilon \right) \int_\infty \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 d^3\mathbf{r} - \sum_{s=\uparrow,\downarrow} \int_\infty V^s_{\mathrm{eff}}(\mathbf{r}) \sum_{\alpha} f_T(\varepsilon_{\alpha,s} - \varepsilon_F) \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 d^3\mathbf{r}$$

$$= \sum_{s=\uparrow,\downarrow} \left[\int_\infty \varepsilon\, f_T(\varepsilon - \varepsilon_F) \rho_s(\varepsilon) d\varepsilon - \int_\infty V^s_{\mathrm{eff}}(\mathbf{r}) \rho_s(\mathbf{r}) d^3\mathbf{r} \right]$$

where the spin-resolved density of states $\rho_s(\varepsilon)$ is given by

$$\rho_s(\varepsilon) = \sum_{\alpha} \delta(\varepsilon - \varepsilon_{\alpha,s}) \int_\infty \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 d^3\mathbf{r}$$

The Coulomb energy term

$$U[\rho] = \int_\infty d^3\mathbf{r} \int_\infty \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

$$+ \int_\infty \rho(\mathbf{r}) V_{\mathrm{ext}}(\mathbf{r}) d^3\mathbf{r}$$

$$\rho_s(\mathbf{r}) = \sum_{\alpha} f_T(\varepsilon_{\alpha,s} - \varepsilon_F) \left|\psi_{\alpha,s}(\mathbf{r})\right|^2$$

Exchange-correlation energy

$$E_{\mathrm{XC}}[\rho] \approx \int_\infty \varepsilon_{\mathrm{XC}}[\rho(\mathbf{r})] \rho(\mathbf{r}) d^3\mathbf{r}$$

Electrostatic Potential and Band Energy

For the effective potential: $V_{\text{eff}}^{s}(\mathbf{r}) = V_{\text{H}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) + V_{\text{XC}}^{s}[\rho(\mathbf{r})]$

the sum of the first two terms is the electrostatic potential

$$V_{\text{eff}}^{s}(\mathbf{r}) = V_{\text{Coul}}(\mathbf{r}) + V_{\text{XC}}^{s}[\rho(\mathbf{r})]$$

$$V_{\text{Coul}}(\mathbf{r}) = V_{\text{H}}(\mathbf{r}) + V_{\text{ext}}(\mathbf{r}) = \int_{\infty} \frac{2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' - \sum_n \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|}$$

whose calculation will be discussed in a separate lecture.

At $T = 0$, the first electronic total energy term becomes

$$\int_{\infty} \varepsilon f_T(\varepsilon - \varepsilon_F)\rho(\varepsilon)d\varepsilon = \int_{-\infty}^{\varepsilon_F} \varepsilon\rho(\varepsilon)d\varepsilon = \sum_c \varepsilon_c + \int_{\varepsilon_b}^{\varepsilon_F} \varepsilon\rho_v(\varepsilon)d\varepsilon$$

ε_c is the energy eigenvalue of a core state, whose density of states is just $\delta(\varepsilon - \varepsilon_c)$.

ε_b is the bottom of valence band energy.

$\rho_v(\varepsilon)$ is the density of the valence states.

$\int_{\varepsilon_b}^{\varepsilon_F} \varepsilon\rho_v(\varepsilon)d\varepsilon$ is recognized as band energy

Total Electrostatic Energy of the Solid

The electrostatic energy of the electron system is:

$$U[\rho] = \int_\infty d^3\mathbf{r} \int_\infty \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' + \int_\infty \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3\mathbf{r}$$

$$V_{\text{ext}}(\mathbf{r}) = -\sum_n \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|}$$

$$V_{\text{Coul}}(\mathbf{r}) = \int_\infty \frac{2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' - \sum_n \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|}$$

The electrostatic energy of the solid is given by:

$$U[\rho] + \sum_n \sum_{m\neq n} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|} = \int_\infty d^3\mathbf{r} \int_\infty \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' - \sum_n \int_\infty \rho(\mathbf{r}) \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|} d^3\mathbf{r} + \sum_n \sum_{m\neq n} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|}$$

$$= \int_\infty \rho(\mathbf{r}) \left[\int_\infty \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' - \sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|} \right] d^3\mathbf{r} + \sum_n Z_n \left[-\int_\infty \frac{\rho(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_n|} d^3\mathbf{r} + \sum_{m\neq n} \frac{Z_m}{|\mathbf{R}_n - \mathbf{R}_m|} \right]$$

$$= \frac{1}{2} \int_\infty \rho(\mathbf{r}) V_{\text{Coul}}(\mathbf{r}) d^3\mathbf{r} - \frac{1}{2} \sum_n Z_n V_{\text{Coul}}(\mathbf{R}_n)$$

Total Energy of the Solid

Recognizing the results:

$$V_{\text{eff}}^{s}(\mathbf{r}) = V_{\text{Coul}}(\mathbf{r}) + V_{\text{XC}}^{s}[\rho(\mathbf{r})]$$

$$V_{\text{Coul}}(\mathbf{r}) = \int_{\infty} \frac{2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' - \sum_n \frac{2Z_n}{|\mathbf{r}-\mathbf{R}_n|}$$

$$T_0[\rho] = \int_{-\infty}^{\varepsilon_F} \varepsilon\rho(\varepsilon) d\varepsilon - \int_{\infty} V_{\text{Coul}}(\mathbf{r})\rho(\mathbf{r}) d^3\mathbf{r} - \sum_{s=\uparrow,\downarrow} \int_{\infty} V_{\text{XC}}^{s}(\mathbf{r})\rho_s(\mathbf{r}) d^3\mathbf{r}$$

$$U[\rho] + \sum_n \sum_{m\neq n} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|} = \frac{1}{2}\left[\int_{\infty} \rho(\mathbf{r}) V_{\text{Coul}}(\mathbf{r}) d^3\mathbf{r} - \sum_n Z_n V_{\text{Coul}}(\mathbf{R}_n)\right]$$

The total energy of the solid is therefore given by

$$E_T = T_0[\rho] + U[\rho] + E_{\text{XC}}[\rho] + \sum_n \sum_{m\neq n} \frac{Z_n Z_m}{|\mathbf{R}_n - \mathbf{R}_m|}$$

$$= \int_{-\infty}^{\varepsilon_F} \varepsilon\rho(\varepsilon) d\varepsilon - \frac{1}{2}\left[\int_{\infty} \rho(\mathbf{r}) V_{\text{Coul}}(\mathbf{r}) d^3\mathbf{r} + \sum_n Z_n V_{\text{Coul}}(\mathbf{R}_n)\right] - \sum_{s=\uparrow,\downarrow} \int_{\infty} V_{\text{XC}}^{s}(\mathbf{r})\rho_s(\mathbf{r}) d^3\mathbf{r} + E_{\text{XC}}[\rho]$$

$$\int_{-\infty}^{\varepsilon_F} \varepsilon\rho(\varepsilon) d\varepsilon = \sum_c \varepsilon_c + \int_{\varepsilon_b}^{\varepsilon_F} \varepsilon\rho_v(\varepsilon) d\varepsilon$$

Electron density and Green function

Consider the electron density which is given by

$$\rho_s(\mathbf{r}) = \sum_\alpha f_T(\varepsilon_{\alpha,s} - \varepsilon_F)\left|\psi_{\alpha,s}(\mathbf{r})\right|^2 = \sum_\alpha \left[\int_{-\infty}^{\infty} f_T(\varepsilon - \varepsilon_F)\delta(\varepsilon - \varepsilon_{\alpha,s})d\varepsilon\right]\left|\psi_{\alpha,s}(\mathbf{r})\right|^2$$

$$= \int_{-\infty}^{\infty} f_T(\varepsilon - \varepsilon_F)\left[\sum_\alpha \delta(\varepsilon - \varepsilon_{\alpha,s})\left|\psi_{\alpha,s}(\mathbf{r})\right|^2\right]d\varepsilon$$

Using relation: $\mathrm{Im}\lim_{\eta\to 0}\frac{1}{z+i\eta} = -\pi\delta(z)$, we have

$$\lim_{\eta\to 0}\frac{1}{z+i\eta} = \mathrm{P.V.}\left(\frac{1}{z}\right) - i\pi\delta(z),$$

$$\sum_\alpha \delta(\varepsilon - \varepsilon_{\alpha,s})\left|\psi_{\alpha,s}(\mathbf{r})\right|^2 = -\frac{1}{\pi}\mathrm{Im}\lim_{\eta\to 0}\sum_\alpha \frac{\left|\psi_{\alpha,s}(\mathbf{r})\right|^2}{\varepsilon - \varepsilon_{\alpha,s} + i\eta} = -\frac{1}{\pi}\mathrm{Im}\,G_s(\mathbf{r},\mathbf{r};\varepsilon)$$

Therefore, in terms of the Green function, the electron density is given by

$$G_s(\mathbf{r},\mathbf{r}';\varepsilon) = \lim_{\eta\to 0}\sum_\alpha \frac{\psi^*_{\alpha,s}(\mathbf{r})\psi_{\alpha,s}(\mathbf{r}')}{\varepsilon - \varepsilon_{\alpha,s} + i\eta}$$

$$\rho_s(\mathbf{r}) = -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\infty} f_T(\varepsilon - \varepsilon_F)G(\mathbf{r},\mathbf{r};\varepsilon)d\varepsilon. \quad \text{At } T = 0, \text{ we have: } \rho_s(\mathbf{r}) = -\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};\varepsilon)d\varepsilon$$

Electronic density of state and Green function

The density of states is given by

$$\rho_s(\varepsilon) = \sum_\alpha \delta(\varepsilon - \varepsilon_{\alpha,s}) \int_\infty \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 d^3\mathbf{r} = \int_\infty \left[\sum_\alpha \delta(\varepsilon - \varepsilon_{\alpha,s}) \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 \right] d^3\mathbf{r}$$

Applying the relation shown from the previous slide

$$\sum_\alpha \delta(\varepsilon - \varepsilon_{\alpha,s}) \left|\psi_{\alpha,s}(\mathbf{r})\right|^2 = -\frac{1}{\pi} \operatorname{Im} G_s(\mathbf{r},\mathbf{r};\varepsilon)$$

we have

$$\rho_s(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} \int_\infty G_s(\mathbf{r},\mathbf{r};\varepsilon) d^3\mathbf{r} = -\frac{1}{\pi} \operatorname{Im} \sum_n \int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon) d^3\mathbf{r}$$

The density of states in space domain Ω_n is given by

$$\rho_s^n(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} \int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon) d^3\mathbf{r}$$

Contour integration

The electron density calculation can be carried out along a contour in the complex plane

$$\rho_s(\mathbf{r}) = -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d\varepsilon$$

$$= \sum_c \rho_{c,s}(\mathbf{r}) - \frac{1}{\pi}\,\mathrm{Im}\int_{\varepsilon_b}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d\varepsilon$$

$$= \sum_c \rho_{c,s}(\mathbf{r}) - \frac{1}{\pi}\,\mathrm{Im}\oint_{\varepsilon_b}^{\varepsilon_F} G_s(\mathbf{r},\mathbf{r};z)\,dz$$

$\rho_{c,s}(\mathbf{r})$ is the electron density of core state c with spin s.

$$\rho_v(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\sum_{s=\uparrow,\downarrow}\sum_n \int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d^3\mathbf{r}$$

with $\varepsilon_b \le \varepsilon \le \varepsilon_F$.

So is the band energy calculation,

$$\int_{\varepsilon_b}^{\varepsilon_F} \varepsilon\rho_v(\varepsilon)\,d\varepsilon = -\frac{1}{\pi}\,\mathrm{Im}\sum_{s=\uparrow,\downarrow}\sum_n \int_{\varepsilon_b}^{\varepsilon_F} \varepsilon\left(\int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};\varepsilon)\,d^3\mathbf{r}\right)d\varepsilon$$

$$= -\frac{1}{\pi}\,\mathrm{Im}\sum_{s=\uparrow,\downarrow}\sum_n \oint_{\varepsilon_b}^{\varepsilon_F} z\left(\int_{\Omega_n} G_s(\mathbf{r},\mathbf{r};z)\,d^3\mathbf{r}\right)dz$$