FYS4480/9480, lecture October 23, 2025

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Energy functional

$$E_{HK}[n] = T[n] + E_{int}[n]$$

$$+ \int d\vec{r}\, V_{ext}(\vec{r})\, n(\vec{r}) + \underbrace{E_{II}}_{\text{atomic nuclei}}$$

$$n(\vec{r}) = n(\vec{r}_1) = \int d\vec{r}_2 \cdots \int d\vec{r}_N \times |\Psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N)|^2$$

$$E_{HK}[n] = F_{HK}[n] + \int d\vec{r}\, V_{ext}(\vec{r})\, n(\vec{r})$$

$$F_{HK}[n] = T[n] + \frac{1}{2}\int d\vec{r} \int d\vec{r}\,' \times \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \underbrace{E_{xc}[n]}_{\text{exchange-correlation part.}}$$

Example: Thomas-Fermi-Dirac functional

$$E_{TF} = \underbrace{C_1 \int d\vec{r}\, n(\vec{r})^{5/3}}_{\text{kinetic energy of electron gas}} \qquad \left(C_1 = \frac{3}{10}(3\pi)^{2/3}\right)$$

$$+ \int d\vec{r}\, V_{ext}(\vec{r})\, n(\vec{r})$$

$$+ \underbrace{C_2 \int d\vec{r}\, n(\vec{r})^{4/3}}_{\text{Exchange from electron gas}}$$

$$C_2 = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

$+$

$$+ \frac{1}{2} \int d\vec{r} \int d\vec{r}' \, \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$\int d\vec{r}\, n(\vec{r}) = N$$

Lagrange multiplier

$$\Omega_{TF}[n] = E_{TF}[n]$$

$$- \mu \left\{ \int d\vec{r}\, n(\vec{r}) - N \right\}$$

small

small variations $\delta n(\vec{r})$

$$\int d\vec{r} \left\{ \Omega_{TF}[n(\vec{r}) + \delta n(\vec{r})] - \Omega_{TF}[n] \right\}$$

$$= 0$$

$$\int d\vec{r} \left\{ c_1 \frac{5}{3} n^{2/3}(\vec{r}) + V(\vec{r}) - \mu \right\} \delta n(\vec{r}) = 0$$

$$V(\vec{r}) = V_{ext} + V_{Hartree} + V_X$$

$$c_2 \, 4/3 \, n^{1/3}$$

$$\underbrace{\frac{1}{2}\left(3\pi^2\right)^{2/3} n(\vec{r})^{2/3}}_{\text{kinetic}} + \underbrace{V(\vec{r})}_{\text{pot}} = \underbrace{\mu}_{\text{energy}}$$

Equation of motion

Hohenberg-Kohn theorems

Theorem 1

For any system of interacting particles in an external potential Vext, the external potential is uniquely determined except for a constant, by the ground state density $n_0(\vec{r})$ (single-particle density)

Corollary I

since the Hamiltonian is fully determined, except for a constant shift of the energy, it follows that the many-body wave functions for all states are determined.

HK 1

$$\begin{tikzcd} n_0(\vec{r}) \arrow[r, Rightarrow] & V_{ext}(\vec{r}) \arrow[d, Rightarrow] \\ \Psi_0(\vec{r}) \arrow[u, Rightarrow] & \Psi_1(\vec{r}) \arrow[l, Rightarrow] \end{tikzcd}$$

Theorem II

A universal functional for the energy $E[n]$ ($F_{HK}[n]$) in terms of $n(\vec{r})$ can be defined, valid for any external potential V_{ext}.

For a particular V_{ext}, the exact ground state energy of the system is the global minimum of the functional. And the density $n(\vec{r})$ that minimizes $E[n]$ is the ground state density $n_0(\vec{r})$

Corollary II

The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density.

Proof of theorem 1

$n(\vec{r})$ is a basic variable

Suppose we have $V_{ext}^{(1)}$ and $V_{ext}^{(2)}$, and they differ by more than a constant.

and they lead to the same ground state density $n_0(\vec{r})$

$$H^{(1)} = T + V_{int} + V_{ext}^{(1)} \xrightarrow{GS} \psi^{(1)}$$

$$H^{(2)} = T + V_{int} + V_{ext}^{(2)} \xrightarrow{GS} \psi^{(2)}$$

But we assume that $\psi^{(1)}$ and $\psi^{(2)}$ have the same $n_0(\vec{r})$

Since

$$E^{(1)} = \langle \psi^{(1)} | H^{(1)} | \psi^{(1)} \rangle$$

$$< \langle \psi^{(2)} | H^{(1)} | \psi^{(2)} \rangle$$

(GS is non-degenerate)

$$\langle \psi^{(2)} | H^{(1)} | \psi^{(2)} \rangle =$$

$$\underbrace{\langle \psi^{(2)} | H^{(2)} | \psi^{(2)} \rangle}_{E^{(2)}}$$

$$+ \langle \psi^{(2)} | H^{(1)} - H^{(2)} | \psi^{(2)} \rangle$$

$$= E^{(2)} + \int d\vec{r} \left[V_{ext}^{(1)} - V_{ext}^{(2)} \right] n_0(\vec{r}) \quad (*) \quad > E^{(1)}$$

On the other hand, if we consider $E^{(2)}$ in exactly the same way, we find

$$E^{(2)} < E^{(1)} + \int d\vec{r}\,\left[V_{ext}^{(2)} - V_{ext}^{(1)}\right] \times n_0(\vec{r}) \qquad (**)$$

Adding $(*)$ and $(**)$ leads to

$$E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)}$$

contradiction

$n(\vec{r})$ uniquely determines the external potential to within a constant

Proof of theorem 2

Since all properties such as kinetic, potential energy etc are uniquely defined if $n(\vec{r})$ is specified, each property can be viewed as a functional of $n(\vec{r})$

$$E_{HK}[n] = T[n] + E_{int}[n] \quad (***)$$
$$+ \int d\vec{r}\, V_{ext}(\vec{r})\, n(\vec{r}) \; (+E_{II})$$

$n^{(1)}(\vec{r})$ and $v_{ext}^{(1)}(\vec{r})$

$$E^{(1)} = \langle \psi^{(1)} | H^{(1)} | \psi^{(1)} \rangle$$

consider $n^{(2)}$ and $\psi^{(2)}$

$$E^{(1)} = \langle \psi^{(1)} | H^{(1)} | \psi^{(1)} \rangle$$

$$< \langle \psi^{(2)} | H^{(1)} | \psi^{(2)} \rangle$$

The energy given by (***) of the HK functional evaluated for the correct GS density $n_0(\vec{r})$ is indeed lower than the value for any other density $n(\vec{r})$

Kohn-Sham equations

They rest on two assumptions

(i) The exact ground state can be represented by the ground state density of an auxiliary system of non-interacting particles

Example

$$\Phi(x_1, x_2, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \cdots & \varphi_1(x_N) \\ \varphi_2(x_1) & & \vdots \\ \vdots & & \vdots \\ \varphi_N(x_1) & & \varphi_N(x_N) \end{vmatrix}$$

$$n(x) = \sum_{i=1}^{n} |\varphi_i(x)|^2$$

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

(ii) The auxiliary $\mathcal{H}$ is chosen to have the usual kinetic energy and effective local potential $V_{eff}(x)$

Parallel: HF potential

$$\hat{h}^{HF} = \underbrace{\hat{t} + \hat{u}_{ext}}_{\hat{h}_0} + \hat{u}^{HF}$$

$$\langle p | \hat{h}^{HF} | q \rangle = \langle p | \hat{h}_0 | q \rangle + \sum_{j \le F} \langle pj | v | qj \rangle_{AS}$$

$|\Phi_0^{HF}\rangle$