

The variational principle and Density Functional Theory

Let us start from the many-body Hamiltonian of electrons interacting with a set of fixed ions (external potential)

$$H = -\frac{\hbar^2}{2m} \sum_{l=1}^N \nabla_l^2 + \underbrace{\sum_{l=1}^N U_{\text{ion}}(\vec{r}_l)}_{V_{\text{ext}}} + \frac{1}{2} \sum_{l \neq l'} \frac{e^2}{|\vec{r}_l - \vec{r}_{l'}|}$$

The density of the many-electron system in GS at position \vec{r} is

$$\begin{aligned} n(\vec{r}) &= \langle \Psi_{GS} | \sum_{e=1}^N \delta(\vec{r} - \vec{r}_e) | \Psi_{GS} \rangle = \\ &= N \int d\vec{r}_1 \dots d\vec{r}_N \Psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \delta(\vec{r} - \vec{r}_1) \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \end{aligned}$$

Theorem:

V_{ext} is a unique functional of $n(\vec{r})$, apart from a trivial additive constant.

If $n(\vec{r})$ is associated to a ground state Ψ_{GS} in the external potential V_{ext} and $n'(\vec{r})$ is associated to V'_{ext} , then if $n'(\vec{r}) = n(\vec{r}) \Rightarrow V'_{\text{ext}} = V_{\text{ext}} + \text{const}$

Proof by reductio ad absurdum

$V_{\text{ext}} \neq V'_{\text{ext}}$ but give rise to same $n(\vec{r})$

$$H = T + U_{\text{ee}} + V_{\text{ext}} \rightarrow H \psi_{\text{gs}} = E \psi_{\text{gs}} \quad \psi \neq \psi'$$

$$H' = T + U_{\text{ee}} + V'_{\text{ext}} \rightarrow H' \psi'_{\text{gs}} = E' \psi'_{\text{gs}}$$

variational principle

$$E = \langle \psi_{\text{gs}} | H | \psi_{\text{gs}} \rangle < \langle \psi'_{\text{gs}} | H | \psi'_{\text{gs}} \rangle = \langle \psi_{\text{gs}} | (H' + V_{\text{ext}} - V'_{\text{ext}}) | \psi'_{\text{gs}} \rangle \\ = E' + \int d\vec{r} n(\vec{r}) [V_{\text{ext}} - V'_{\text{ext}}]$$

$$\psi' \text{ is also a gs wf} \Rightarrow E' < E + \int d\vec{r} n(\vec{r}) [V'_{\text{ext}} - V_{\text{ext}}]$$

Adding the two results

$$E + E' < E + E' \quad \text{a contradiction} \Rightarrow$$

$$V'_{\text{ext}} = V_{\text{ext}}$$

V_{ext} is therefore a unique functional of $n \Rightarrow$

$$E[n] = \langle \psi_{\text{gs}} | H | \psi_{\text{gs}} \rangle$$

If we know the functional $E[n]$ then the

true ground-state density $n(\vec{r})$ minimizes it

subject to $\int d\vec{r} n(\vec{r}) = N = \text{total number of electrons}$

$n(\vec{r})$ determines V_{ext} and $\#$ and hence all

the system properties [the density is clearly a functional of V_{ext}]

$$E[n] = T[n] + U_{\text{ee}}[n] + V_{\text{ext}}[n]$$

$E[n]$ does not depend on $V_{\text{ext}} \Rightarrow$ is a universal functional for all systems of N electrons

If $E[n]$ is known \Rightarrow we solve all many-body problems for all V_{ext}