Density Functional Theory Revisited

8/6/03

Hohenberg-Kohn Theorem

[P. Hohenberg & W. Kohn, Phys. Rev. 136, B864 ('64)]

Consider a system of N electrons in an external potential $v(\mathbf{r})$, described by the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} + \hat{U} \tag{1}$$

where (in the atomic unit)

$$\begin{cases} \hat{T} = \frac{1}{2}\int \nabla\hat{\psi}^{\dagger}(\mathbf{r})\cdot\nabla\hat{\psi}(\mathbf{r})\,d\mathbf{r} & (2) \\ \hat{V} = \int v(\mathbf{r})\,\hat{\psi}^{\dagger}(\mathbf{r})\,\hat{\psi}(\mathbf{r})\,d\mathbf{r} & (3) \\ \hat{U} = \frac{1}{2}\int \hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}^{\dagger}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\hat{\psi}(\mathbf{r}')\,\hat{\psi}(\mathbf{r})\,d\mathbf{r}\,d\mathbf{r}' & (4) \end{cases}$$

and $\{\hat{\psi}(\mathbf{r}), \hat{\psi}^{\dagger}(\mathbf{r}')\} = \delta(\mathbf{r}-\mathbf{r}')$. Let $|\Psi\rangle$ be the ground state of this Hamiltonian and the density

$$\rho(\mathbf{r}) = \langle\Psi|\hat{\rho}(\mathbf{r})|\Psi\rangle = \langle\Psi|\hat{\psi}^{\dagger}(\mathbf{r})\hat{\psi}(\mathbf{r})|\Psi\rangle \tag{5}$$

> (Hohenberg-Kohn Theorem) The ground-state density, $\rho(\mathbf{r})$, and the external potential, $\{v(\mathbf{r})+c\}$ (c is a constant), are bijective functional (or one-to-one correspondence).

$\because$ $v(\mathbf{r}) \mapsto |\Psi\rangle \mapsto \rho(\mathbf{r})$ is obviously a unique functional. We now prove that $\rho(\mathbf{r}) \mapsto \{v(\mathbf{r})+c\}$ is a unique functional by proof-by-contradiction.

Assume that $\rho(\mathbf{r}) \mapsto \{v(\mathbf{r})+c\}$ is not unique, thus $\exists v'(\mathbf{r}) \neq v(\mathbf{r})+c$, for which $\rho(\mathbf{r})$ is the ground state. Let

$$E = \langle\Psi|\hat{T}+\hat{V}+\hat{U}|\Psi\rangle = \langle\Psi|\hat{H}|\Psi\rangle \tag{6}$$

is the ground-state energy in the presence of $v(\mathbf{r})$ and

$$E' = \langle \Psi' | \hat{T} + \hat{V}' + \hat{U} | \Psi' \rangle = \langle \Psi' | \hat{H}' | \Psi' \rangle \tag{7}$$

is that with $v'(\mathbf{r})$. From the variational principle on the ground state,

$$E' = \langle \Psi' | \hat{T} + \hat{V}' + \hat{U} | \Psi' \rangle$$

$$< \langle \Psi | \hat{T} + \hat{V}' + \hat{U} | \Psi \rangle \quad (\because |\Psi\rangle \text{ is not the ground state of } \hat{H}')$$

$$= \langle \Psi | \hat{T} + \hat{V} + \hat{U} | \Psi \rangle + \langle \Psi | \hat{V}' - \hat{V} | \Psi \rangle$$

$$= E + \int [v'(\mathbf{r}) - v(\mathbf{r})]\, \rho(\mathbf{r})\, d\mathbf{r} \tag{8}$$

By inverting the role of $v(\mathbf{r})$ and $v'(\mathbf{r})$,

$$E < E' + \int [v(\mathbf{r}) - v'(\mathbf{r})]\, \rho'(\mathbf{r}) \tag{9}$$

$\rho'(\mathbf{r}) \equiv \rho(\mathbf{r})$ ($\because$ by assumption)

Adding Eqs. (8) and (9),

$$E' + E < E + E'$$

which is a contradiction. //

(Corollary 1)

Let

$$F = \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle \tag{10}$$

Then, $F[\rho(\mathbf{r})]$ is a universal functional, independent of $v(\mathbf{r})$ and N.

(Hohenberg-Kohn Variational Theorem)

Let

$$E_v[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} + F[\rho] \tag{11}$$

(note $v(\mathbf{r}) \neq v[\mathbf{r};\rho(\mathbf{r})]$). Then $E_v[\rho]$ takes the minimum value for the correct $\rho[\mathbf{r};v(\mathbf{r})]$ within the variational space satisfying

$$N[\rho] = \int \rho(\mathbf{r})\,d\mathbf{r} = N \tag{12}$$

$\because$ Consider the ground-state energy functional

$$\mathcal{E}_v[\Psi'] = \langle \Psi' | \hat{V} | \Psi' \rangle + \langle \Psi' | \hat{T} + \hat{U} | \Psi' \rangle \tag{13}$$

which takes the minimum at the correct $\Psi[v]$.

$$\therefore \mathcal{E}_v[\Psi'] = \int v(\mathbf{r})\rho'(\mathbf{r})\,d\mathbf{r} + F[\rho']$$

$$> \int v(\mathbf{r})\rho(\mathbf{r})\,d\mathbf{r} + F[\rho] = \mathcal{E}_v[\Psi]$$

which establishes the variational property of $E_v[\rho]$. //

Kohn-Sham Equation

[W. Kohn & L.J. Sham, Phys. Rev. 140, A1133 ('65)]

(Def — Exchange-Correlation Functional)

Let $E_{xc}[\rho]$ be the exchange-correlation functional defined through

$$F[\rho] = \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + T_S[\rho] + E_{xc}[\rho] \tag{14}$$

where the first term is the mean-field (Hartree) estimation of $\langle\Psi|\hat{U}|\Psi\rangle$ and $T_S[\rho]$ is the kinetic energy $\langle\Psi|\hat{T}|\Psi\rangle$ of the ground state of non-interacting electrons with density $\rho(\mathbf{r})$.

(Kohn-Sham Variational Theorem)

$$E_v[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho] + T_S[\rho] \tag{15}$$

takes its minimum at the correct ground-state density $\rho[v]$ in the variational space of N electrons

$$N[\rho] = \int \rho(\mathbf{r})\, d\mathbf{r} = N \tag{16}$$

∵ Eq. (15) is identical to Eq. (11). //

(Euler Equation)

The constrained minimization is achieved by the variation of

$$K_v[\rho] = E_v[\rho] - \mu\,(N[\rho] - N) \tag{17}$$

with respect to both ρ and μ.

$$\begin{cases} \dfrac{\delta K_v}{\delta \rho(\mathbf{r})} = \dfrac{\delta E_v}{\delta \rho(\mathbf{r})} - \mu = 0 & (18) \\[2ex] \dfrac{\delta K_v}{\delta \mu} = -N[\rho] + N = 0 & (19) \end{cases}$$

More specifically, the Euler equation (18) is

$$v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} + \frac{\delta T_s}{\delta \rho(\mathbf{r})} = \mu \tag{20}$$

(Kohn-Sham Equation)

The Euler equation (20) is equivalent to that of non-interacting electrons, for which

$$E_v[\rho] = \int v(\mathbf{r})\,\rho(\mathbf{r})\, d\mathbf{r} + T_s[\rho] \tag{21}$$

i.e.,

$$\frac{\delta K_v}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta T_s}{\delta \rho(\mathbf{r})} - \mu = 0 \tag{22}$$

provided $v(\mathbf{r})$ is replaced by

$$v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \tag{23}$$

※ Then $T_s[\rho] = \sum_i \Theta(\mu-\epsilon_i) \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r})$ (25′)

The non-interacting Euler equation (22) is solved through the solution of single-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \tag{24}$$

as

$$\rho(\mathbf{r}) = \sum_i \Theta(\mu-\epsilon_i) |\psi_i(\mathbf{r})|^2 \tag{25}$$

where $\Theta(t)$ is the step function.

Therefore, the interacting Euler equation is solved through the solution of Kohn-Sham equation.

$$\boxed{\begin{aligned} &\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})}\right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) && (26) \\ &\rho(\mathbf{r}) = \sum_i \Theta(\mu-\epsilon_i) |\psi_i(\mathbf{r})|^2 && (27) \end{aligned}}$$

(Total Energy)

$\sum_i \Theta(\mu-\epsilon_i) \times \int d\mathbf{r}\, \psi_i^*(\mathbf{r}) \times$ Eq. (26)

$$\underbrace{\sum_i \Theta(\mu-\epsilon_i) \int d\mathbf{r}\, \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r})}_{T_s[\rho]} + \underbrace{\int d\mathbf{r}\, v(\mathbf{r}) \rho(\mathbf{r})}_{V[\rho]}$$

$$+ \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int d\mathbf{r} \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) = \sum_i \Theta(\mu-\epsilon_i) \epsilon_i$$

$$\therefore \left\{ \underbrace{T_s[\rho] + V[\rho] + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho]}_{E \ (\because \text{Eq. } (15))} \right\}$$

$$+ \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int d\mathbf{r} \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) - E_{xc}[\rho] = \sum_i \Theta(\mu-\epsilon_i) \epsilon_i$$

$$\boxed{\therefore E = \sum_i \Theta(\mu-\epsilon_i)\,\epsilon_i - \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + \left\{ E_{xc}[\rho] - \int d\mathbf{r}\,\frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}\rho(\mathbf{r}) \right\}} \tag{28}$$

(Local Density Approximation)

$$E_{xc}[\rho] \simeq \int d\mathbf{r}\,\epsilon_{xc}(\rho(\mathbf{r}))\,\rho(\mathbf{r}) \tag{29}$$

$$\delta E_{xc} = \int d\mathbf{r}\,\frac{d}{d\rho}(\epsilon_{xc}\rho)\Big|_{\rho=\rho(\mathbf{r})}\delta\rho(\mathbf{r}) \equiv \int d\mathbf{r}\,\mu_{xc}(\rho(\mathbf{r}))\,\delta\rho(\mathbf{r}) \tag{30}$$

$$\therefore E = \sum_i \Theta(\mu-\epsilon_i)\,\epsilon_i - \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + \int [\epsilon_{xc}(\rho(\mathbf{r})) - \mu_{xc}(\rho(\mathbf{r}))]\,\rho(\mathbf{r})\,d\mathbf{r} \tag{31}$$

where

$$\mu_{xc}(\rho) = \frac{d}{d\rho}[\epsilon_{xc}(\rho)\,\rho] = \frac{d\epsilon_{xc}}{d\rho}\rho + \epsilon_{xc} \tag{32}$$

Substituting Eq. (32) in (31),

$$E = \sum_i \Theta(\mu-\epsilon_i)\,\epsilon_i - \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' - \int \frac{d\epsilon_{xc}}{d\rho}\Big|_{\rho(\mathbf{r})}\rho^2(\mathbf{r})\,d\mathbf{r} \tag{33}$$