

### Levy-Lieb constrained minimization

It is important to understand that, according to the Hohenberg Kohn theorem, the minimization of  $\Psi$  can be separated into two steps, i.e., density minimization following the wave function minimization under the constraint of reproducing the density as

$$\begin{aligned} E_0 &= \min_{\Psi} \langle \Psi | \hat{T} + \hat{W}_{ee} + \hat{V}_{en} | \Psi \rangle = \min_n \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}_{ee} + \hat{V}_{en} | \Psi \rangle \\ &= \min_n \left\{ \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W}_{ee} | \Psi \rangle + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right\} \\ &= \min_n \{ F[n] + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} \} \end{aligned} \quad (1.18)$$

### Method of Kohn-Sham

Basic idea of KS is to take

$$F[n] = T_s[n] + V_H[n] + V_{xc}[n],$$

where the kinetic energy functional has been replaced by that of a single Slater determinant wave function  $\Phi$ , assuming that the density can be reproduced by  $\Phi$ , as

$$T_s[n] = \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle. \quad (1.21)$$

Then, the minimization can be done as

$$\begin{aligned} E_0 &= \min_n \{ F[n] + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} \} \Rightarrow \min_n \left\{ \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} | \Phi \rangle + E_{Hxc}[n] + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} \right\} \\ &= \min_n \left\{ \min_{\Phi \rightarrow n} \langle \Phi | \hat{T} + \hat{V}_{ne} | \Phi \rangle + E_{Hxc}[n_{\Phi}] \right\} \\ &= \min_{\Phi} \{ \langle \Phi | \hat{T} + \hat{V}_{ne} | \Phi \rangle + E_{Hxc}[n_{\Phi}] \}. \end{aligned} \quad (1.22)$$

Note that the Hartree-exchange-correlation functional can be decomposed into

$$E_{Hxc}[n] = E_H[n] + E_x[n] + E_c[n]$$

where

$$E_x[n] \equiv \langle \Phi[n] | \hat{W}_{ee} | \Phi[n] \rangle - E_H[n], \quad (1.26)$$

and

$$E_c[n] \equiv \langle \Psi[n] | \hat{T} + \hat{W}_{ee} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} + \hat{W}_{ee} | \Phi[n] \rangle. \quad (1.27)$$

As I pointed out last week, there are kinetic energy contribution in addition to the interaction energy contribution as

$$E_c[n] = T_c[n] + U_c[n], \quad (1.27)$$

where

$$\begin{aligned} T_c[n] &\equiv \langle \Psi[n] | \hat{T} | \Psi[n] \rangle - \langle \Phi[n] | \hat{T} | \Phi[n] \rangle \\ U_c[n] &\equiv \langle \Psi[n] | \hat{W}_{ee} | \Psi[n] \rangle - \langle \Phi[n] | \hat{W}_{ee} | \Phi[n] \rangle. \end{aligned}$$

### Kohn-Sham equation

In deriving the Kohn-Sham equation, one should be careful about the minimization of the

Kohn-Sham orbitals  $\phi_i$  that constitute the Slater determinant. For the energy functional

$$E[n] = \langle \Phi[n] | \hat{T} + \hat{W}_{ee} | \Phi[n] \rangle + V_c[n] + V_{ne}[n]$$

where the correlation functional is given locally, we get a Hartree-Fock type equation

$$\left( -\frac{1}{2}\nabla^2 + v_{ne}(\mathbf{r}) + v_H(\mathbf{r}) + v_x(\mathbf{r}) + v_c(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}).$$

Here the exchange potential is described as

$$\begin{aligned} v_x(\mathbf{r})\phi_i(\mathbf{r}) &= -\sum_j^N \int \frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \phi_j(\mathbf{r}) = -\int \frac{\sum_j \phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \phi_i(\mathbf{r}') d\mathbf{r}' \\ &\equiv \int v_x(\mathbf{r},\mathbf{r}')\phi_i(\mathbf{r}') d\mathbf{r}'. \end{aligned}$$

In the conventional formulation, however, the energy functional is given as

$$E[n] = \langle \Phi[n] | \hat{T} | \Phi[n] \rangle + V_H[n] + V_{xc}[n] + V_{ne}[n]$$

where the exchange-correlation functional is described locally in the spirit of the local density approximation (LDA).