Density Functional Theory - The Hohenberg-Kohn Theorems

Lecture 27

CHM 652 / PHY 626
Electronic Structure of Materials

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Lecture Plan

- Statements and proofs of the Hohenberg-Kohn theorems
- Euler-Lagrange equations of DFT

Quantum Mechanics the DFT way

Conventionally, many-electron problems are solved by solving the Schrodinger equation for a given external potential.

$$\hat{H}\Psi_n(x_1, x_2, \ldots, x_N) = E_n \Psi_n(x_1, x_2, \ldots, x_N)$$

$$v(\vec{r}), N \implies \hat{H} \implies \{E_n, \Psi_n\} \implies \text{All electronic properties}$$

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{W} \qquad (1)$$

$$\left.\begin{array}{ll} \hat{T} = \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} & \text{Kinetic energy} \\ \hat{V}_{ext} = \sum_{i=1}^{N} v_{ext}(\hat{\vec{r}}_i) & \text{external potential} \\ \hat{W} = \sum_{i<j} \frac{1}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|} & \text{e-e repulsion} \end{array}\right\} \quad (2)$$

However, as we saw, this procedure is complicated by the large dimensionality of the wave function.

Quantum Mechanics the DFT way

A simpler object is the 1-electron density given by

$$n(x) = \left\langle \Psi \left| \sum_{j=1}^{N} \delta(\vec{r} - \hat{\vec{r}}_i) \right| \Psi \right\rangle = N \int dx_2 dx_3 \dots dx_N \, |\Psi(x, x_2, x_3, \dots, x_N)|^2 \qquad x = (\vec{r}, \sigma)$$

$$\left. \begin{array}{r} n(x) \geq 0 \\ \int n(x) dx = N \end{array} \right\} \text{For a valid density}$$

Spinless density

$$\int n(x) d\sigma = n(\vec{r})$$

Density Functional Theory is based on the assertion that all properties of the many-electron system are determined once the ground-state 1-electron density of the system is known.

This is a tremendous simplification as handling the 4N-dimensional wave function is now obviated for a simpler (3+1)-dimensional density.

Hohenberg Theorem 1

Statement:

*The external potential v(**r**) is determined, within a trivial additive constant, by the ground-state 1-electron density n(**r**).*

Consequence:

Since *n(**r**)* determines the number of electrons (*N*), *it also determines* $\hat{T}, \hat{W}$

Therefore, it follows that *n(**r**)* determines the ground-state wave function of the system and all other electronic properties.

$$n(\vec{r}) \implies v(\vec{r}), N \implies \hat{H} \implies \{E_n, \Psi_n\} \implies \text{All electronic properties}$$

Hohenberg Theorem 1

Proof: *Reduction ad absurdum*

Consider a system of *N* electrons with a non-degenerate ground-state and with a (valid) 1-electron density $n(\mathbf{r})$.

Let us assume that there exist two external potentials, $v(\mathbf{r})$ and $v'(\mathbf{r})$, differing by more than a trivial constant, that yield the same ground-state density $n(\mathbf{r})$.

The corresponding Hamiltonians will be H and H' with the ground-state wave functions Ψ and Ψ', and energies E_0 and E_0'.

Hohenberg Theorem 1

Proof: (*ctd.*)

By the variational principle we have

$$E_0 < \left\langle \Psi' \middle| \hat{H} \middle| \Psi' \right\rangle = \left\langle \Psi' \middle| \hat{H}' \middle| \Psi' \right\rangle + \left\langle \Psi' \middle| \hat{H} - \hat{H}' \middle| \Psi' \right\rangle = E_0' + \int \left(v(\vec{r}) - v'(\vec{r})\right) n(\vec{r}) d^3r \quad \textbf{(1)}$$

$$E_0' < \left\langle \Psi \middle| \hat{H}' \middle| \Psi \right\rangle = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle + \left\langle \Psi \middle| \hat{H}' - \hat{H} \middle| \Psi \right\rangle = E_0 + \int \left(v'(\vec{r}) - v(\vec{r})\right) n(\vec{r}) d^3r \quad \textbf{(2)}$$

(1) + (2)

$$E_0 + E_0' < E_0' + E_0$$

This is not possible!

Hence, two distinct potentials cannot yield the same ground-state density. Theorem is thus proved.

Hohenberg Theorem 1

Corollary: *The ground-state energy, wave function and all other electronic properties are functionals of the 1-electron density. In particular, there exists a universal functional of density that yields the intrinsic energies of the system.*

$$n(\vec{r}) \implies v(\vec{r}), N \implies \hat{H} \implies \{E_n, \Psi_n\} \implies \text{All electronic properties}$$

$$\Psi_0 = \Psi_0[n]$$

$$E_v[n] = \left\langle \Psi[n] \middle| \hat{T} + \hat{W} + \hat{V}_{ext} \middle| \Psi[n] \right\rangle$$

$$= F_{HK}[n] + \int d^3 r v(\vec{r}) n(\vec{r})$$

$$F_{HK}[n] = \left\langle \Psi[n] \middle| \hat{T} + \hat{W} \middle| \Psi[n] \right\rangle$$ Hohenberg-Kohn universal functional

Hohenberg Theorem 2

Statement:
For a valid trial density $\tilde{n}(\mathbf{r})$, $E_0 \leq E_v[\tilde{n}]$.

That is, an arbitrary (valid) density will yield an upper bound to the exact ground-state energy. This is a variational principle for the density.

Proof: For a system with $\tilde{n}(\mathbf{r})$ as the valid ground state density, from the first theorem, we have

$$\tilde{n}(\mathbf{r}) \implies \hat{\tilde{H}} \implies \tilde{E}_0 = E_v[\tilde{n}], \tilde{\Psi}_0 = \Psi[\tilde{n}]$$

This means for the system with Hamiltonian *H* we have

$$\begin{aligned} E_0 &\leq \left\langle \tilde{\Psi}_0 \middle| \hat{H} \middle| \tilde{\Psi}_0 \right\rangle \\ &= \left\langle \Psi[\tilde{n}] \middle| \hat{H} \middle| \Psi[\tilde{n}] \right\rangle \\ &= E_v[\tilde{n}] \end{aligned}$$

$$\implies E_0 \leq E_v[\tilde{n}]$$

Hence proved.

DFT Euler-Lagrange Equations

The second HK theorem establishes a variational principle for DFT. This means that, given the universal functional, we can seek the ground state energy of an *N*-electron system by minimising the total energy functional with respect to the density.

$$\frac{\delta E_v[n]}{\delta n(\mathbf{r})} = 0$$

Subject to the condition $\int n(\mathbf{r}) d^3r = N$

The constraint can be incorporated using the method of undetermined multipliers and the equations become

$$\boxed{\frac{\delta F_{HK}[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu}$$