DENSITY FUNCTIONAL THEORY

- In a real solid one needs to account for <u>both</u> periodic lattice potential $U(\vec{r})$ and Coulomb interaction between electrons $V(\vec{r}_1 - \vec{r}_2)$.
- This is an intractable problem due to the enormous size of the Hilbert space describing $N \simeq 10^{23}$ particles.
- The only practical way to do these calculations is based on density functional theory (DFT) developed by Walter Kohn in 1960's.

DFT is grounded in the Hohenberg-Kohn theorem, which applies to the family of electron Hamiltonians

$$\hat{H} = \underbrace{\sum_{k,\sigma} \frac{\hbar^2 k^2}{2m} c^+_{k\sigma} c_{k\sigma}}_{\hat{T}} + \underbrace{\sum_{k,q,\sigma} U(\vec{q})\, c^+_{k+q\sigma} c_k}_{\hat{U}} + \underbrace{\frac{1}{2} \sum_{\substack{k,p,q \\ \sigma\sigma'}} V_q\, c^+_{k-q\sigma} c^+_{p+q\sigma'} c_{p\sigma'} c_{k\sigma}}_{\hat{V}} \qquad (1)$$

$\hat{U}$: periodic lattice potential

$\hat{V}$: Coulomb interaction

> <u>HK theorem:</u> The expectation value $\langle \hat{O} \rangle$ of any operator is a UNIQUE FUNCTIONAL $O[n_0(\vec{r})]$ of the ground-state electron density $n_0(\vec{r})$.

- this implies great simplification: In principle, to calculate ANY physical observable, we require only electron density $n_0(\vec{r})$ – a function of 3 variables $\vec{r} = (x, y, z)$ – and not the full many-body wave-function $\Psi(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N)$.

Some remarks: - In Hamiltonian (1) the $\hat{T}$ and $\hat{V}$ pieces are UNIVERSAL (the same for any solid), only $\hat{U}$ differs.

- The HK theorem states that the mapping from $U(\vec{r}) \longrightarrow n_0(\vec{r})$ is REVERSIBLE.

That is, the periodic potential and $n_0(\vec{r})$ are in one-to-one correspondence:

$$\boxed{U(\vec{r}) \longleftrightarrow n_0(\vec{r})} \qquad (2)$$

Because from $U(\vec{r})$ we can in principle obtain $\Psi(\vec{r}_1, .. \vec{r}_N)$ (and thus any expectation value $\langle \hat{O} \rangle$), this implies that we can obtain $\langle \hat{O} \rangle$ from $n_0(\vec{r})$ directly.

PROOF: We show that two potentials $U(\vec{r})$ and $U'(\vec{r})$ that differ by more than a trivial constant, necessarily lead to different ground states $\Psi_0 \neq \Psi_0'$.

$$(\hat{T} + \hat{V} + \hat{U})\Psi_0 = \varepsilon_0 \Psi_0$$
$$(\hat{T} + \hat{V} + \hat{U}')\Psi_0' = \varepsilon_0' \Psi_0' \qquad (3)$$

Proof by contradiction: assume $\Psi_0 = \Psi_0'$, subtract

$$\rightarrow (\hat{U} - \hat{U}')\Psi_0 = (\varepsilon_0 - \varepsilon_0')\Psi_0 \qquad (4)$$

But this would imply that $\hat{U}$ and $\hat{U}'$ differ by a constant, therefore $\Psi_0 \neq \Psi_0'$.

- It is also clear that two different densities, $n_0(\vec{r}) \neq n_0'(\vec{r})$ imply different potentials $U(\vec{r}) \neq U'(\vec{r})$. This follows from the uniqueness of solutions to Schr. equations.

It therefore follows that the ground-state wf is uniquely specified by the electron density*. One can also show that $\Psi_0 \neq \Psi_0'$ implies different densities $n_0(\vec{r}) \neq n_0'(\vec{r})$ which completes the proof. (*For non-degenerate ground states)

- Important variational principle associated with HK:
  - the ground state energy is a functional of $n(\vec{r})$

$$\mathcal{E}[n] = \langle \Psi_0[n] | \hat{T} + \hat{V} + \hat{U} | \Psi_0[n] \rangle \tag{5}$$

such that $\mathcal{E}_0 = \mathcal{E}[n_0]$, the true g.s. energy associated with $U(\vec{r})$. It then holds

$$\boxed{\mathcal{E}_0 < \mathcal{E}[n] \quad \text{for} \quad n \neq n_0} \tag{6}$$

which follows from usual variational principle.

$\Rightarrow$ The g.s. energy can be found by varying the density $n(\vec{r})$ provided we know the form of $\mathcal{E}[n]$.

- $\mathcal{E}[n]$ can usefully be written as

$$\left[\mathcal{E}[n] = F_{HK}[n] + \int d^3r\, n(\vec{r})\, U(\vec{r}) \right] \tag{7}$$

where $F_{HK}[n] = \langle \Psi[n] | \hat{T} + \hat{V} | \Psi[n] \rangle$ is the SAME for all systems $\longrightarrow$ it has to be determined only once!

The second term:

$$n(\vec{r}) = \int \{d^3r\}\, \Psi^*(\vec{r}_1 \ldots r_N) \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)\, \Psi(\vec{r}_1 \ldots \vec{r}_N)$$

$$\langle \Psi_0 | \hat{U} | \Psi_0 \rangle = \int \{d^3r\}\, \Psi^*(\vec{r}_1 \ldots) \sum_{i=1}^{N} U(\vec{r}_i)\, \Psi(\vec{r}_1 \ldots) \tag{8}$$

$$= \int \{d^3r\} d^3r_p\, \Psi^*(\vec{r}_1 \ldots) \sum_i \delta(\vec{r}_p - \vec{r}_i)\, U(\vec{r}_p)\, \Psi(\vec{r}_1 \ldots) = \int d^3r\, n(\vec{r})\, U(\vec{r})$$

The Kohn-Sham formulation

- allows performing practical computations

- The idea is to use a NONINTERACTING reference system $\hat{H}_s = \hat{T} + \hat{U}_s$ with U_s that gives the <u>SAME g.s. density as the interacting system</u> $\hat{H} = \hat{T} + \hat{V} + \hat{U}$.

  (Note that computation of Ψ_0 and n_0 is easy for $\hat{H}_s$.)

- <u>DFT for the reference system:</u>

$$\mathcal{E}_s[n] = T_s[n] + \int d^3r\, U_s(\vec{r})\, n(\vec{r}) \tag{9}$$

$$n_s(\vec{r}) = \sum_{i=1}^{N} |\phi_i(\vec{r})|^2 \tag{10}$$

$$\left[-\frac{\hbar^2\nabla^2}{2m} + U_s(\vec{r})\right]\phi_i(\vec{r}) = \varepsilon_i\,\phi_i(\vec{r}) \tag{11}$$

- Now we want to find the form of $U_s(\vec{r})$:

$$\begin{aligned}\mathcal{E}[n] &= T[n] + V[n] + \int d^3r\, U(\vec{r})\, n(\vec{r}) \\ &= T_s[n] + \underbrace{\left\{T[n] - T_s[n] - \frac{e^2}{2}\int d^3r\, d^3r'\, \frac{n(\vec{r})\,n(\vec{r}')}{|\vec{r}-\vec{r}'|}\right\}}_{\mathcal{E}_{xc}[n]} \\ &\quad + \frac{e^2}{2}\int d^3r\, d^3r'\, \frac{n(\vec{r})\,n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \int d^3r\, U(\vec{r})\, n(\vec{r})\end{aligned} \tag{12}$$

"exchange-correlation functional"

$$\mathcal{E}_{xc}[n] = F_{HK}[n] - \frac{e^2}{2}\int d^3r\, d^3r'\, \frac{n(\vec{r})\,n(\vec{r}')}{|\vec{r}-\vec{r}'|} - T_s[n] \tag{13}$$

- Minimize $\mathcal{E}[n]$ with respect to $n(\vec{r})$

$$0 = \frac{\delta\mathcal{E}[n]}{\delta n(\vec{r})} = \frac{\delta T_s[n]}{\delta n(\vec{r})} + e^2\int d^3r'\, \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + U(\vec{r}) + v_{xc}[n(\vec{r})] \tag{14}$$

where $v_{xc}[n(\vec{r})] = \dfrac{\delta\mathcal{E}_{xc}[n]}{\delta n(\vec{r})}$ "exchange-correlation potential"

- Minimize similarly the ref. system:

$$0 = \frac{\delta \mathcal{E}_s[n]}{\delta n(\vec{r})} = \frac{\delta T_s[n]}{\delta n(\vec{r})} + U_s(\vec{r}) \qquad (15)$$

- Subtract from Eq. (15) to find:

$$\boxed{U_s(\vec{r}) = U(\vec{r}) + e^2 \int d^2r' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}(\vec{r}) \qquad (16)}$$

- The Kohn-Sham formulation is implemented by

① Choose an initial "trial" form of $n(\vec{r})$, substitute to (16) and calculate $U_s(\vec{r})$

② Solve Schr. eq. (11) for $\phi_i(\vec{r})$ and find new density $n(\vec{r})$ using Eq. (10).

③ Iterate the procedure until $n(\vec{r})$ stops changing.

- <u>Remarks</u>: (i) The above procedure is implemented in various software packages (Wien2K, Quantum Espresso, ...)

(ii) These differ mainly in the form of $v_{xc}(\vec{r})$ that is used

(iii) Packagase provide "band structures" i.e. energy eigenvalues $\varepsilon_i(\vec{k})$ of Eq. (11).

- <u>The exchange correlation functional</u>

  - many sophisticated approximation for $\mathcal{E}_{xc}[n]$ have been developed and implemented over the years

  - the simplest such is the LOCAL DENSITY APPROXIMATION (LDA) It assumes that $\mathcal{E}_{xc}$ only depends on LOCAL density:

$$\mathcal{E}_{xc}[n] = \int d^3r \, n(\vec{r}) \, \epsilon_{xc}(n(\vec{r})) \qquad (17)$$

  where $\epsilon_{xc}(n)$ is the exchange-correlation energy (per particle) of a homogeneous electron gas of density n (Jellium),

$$\epsilon_{xc}(n) = \frac{e^2}{a_0 r_s^2}\left(b r_s + c r_s^2 \ln r_s + \dots\right) \qquad (18)$$

  - other popular approximations include LSDA (spin), and GGA: "generalized gradient approximation"

$$\mathcal{E}_{xc}[n] = \int d^3r \left[g_{00}(n) + g_{22}(n)(\vec{\nabla} n)^2 + g_{42}(n)(\nabla^2 n)^2 + \dots \right] \qquad (19)$$

  - many useful generalizations of DFT exist:

    TD-DFT - adds time dependence

    CDFT - "current DFT" includes ext. mag. field

    EDFT - "ensemble DFT" deals with degeneracies