Kwan-Woo Lee

HK: “electron density contains in principle all the information contained in a many-electron wave function.”
Hohenberg-Kohn Theorem

1. \( V=V[n] \)

\( V \) is a functional of ground state density \( n(r) \).

**Proof**

Suppose for two systems with the same \# of particles,

and \( V'(r) \neq V(r) + \text{const.} \) (but that \( n'(r) = n(r) \)).

\[ \Rightarrow \quad \text{if} \quad H|\Psi> = (H_0 + V)|\Psi> = \varepsilon|\Psi> \]

\[ \Rightarrow \quad \text{if} \quad H'|\Psi'> = (H_0 + V')|\Psi'> = \varepsilon'|\Psi'>, \quad \text{where} \quad |\Psi'> \neq |\Psi>. \]
Then,
\[ \varepsilon = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle \quad (\because \ \Psi' \text{ is not the g.s. wave function of } H. ) \]

\[
\text{RHS} = \langle \Psi' | H_0 + V' + (V - V') | \Psi' \rangle \\
= \varepsilon' + \langle \Psi' | V - V' | \Psi' \rangle \\
= \varepsilon' + \int d^3r \ n(r)[v(r) - v'(r)]
\]

So, \[ \varepsilon = \varepsilon' + \int d^3r \ n(r)[v(r) - v'(r)] \]

Exchange (primed ↔ unprimed)
\[ \varepsilon' = \varepsilon + \int d^3r \ n(r)[v'(r) - v(r)] \]
Adding two equations,

\[ \varepsilon' + \varepsilon < \varepsilon + \varepsilon' \]

∴ Contradiction \( \Rightarrow n'(r) \neq n(r)! \)

Therefore, two different potentials cannot give the same ground state density. I.e., given \( n(r) \),

\[ \Rightarrow \text{Some particular } v(r), \text{ or } v \text{ is a functional of } n: V=V[n] \]

Of course, also \( n \) is a finial of \( v \), so \( v \leftrightarrow n \) is 1-to-1.
2. In principle, any property of the system is a finial of \( n! \)
(Each is its own functional.)

In particular, the total energy of the system;

\[
\varepsilon = <\Psi_{g.s.}|H|\Psi_{g.s.}>
\]

\[
= T[n] + U[n] + V[n] = \varepsilon[n] : \text{ground state energy}
\]

\[
\downarrow \quad \downarrow \quad \downarrow
\]

K.E.   P.E.   interaction with external potential
Also, the density that minimizes $\varepsilon[n]$ for a fixed number of electrons is the ground state density:

$$\frac{\delta}{\delta n(r)}[\varepsilon[n] - \mu N[n]]\bigg|_{n_{g.s.}} = 0$$

$$\frac{\delta \varepsilon[n]}{\delta n(r)} = \mu = \text{const.}$$

$$\frac{\delta T}{\delta n(r)} + \frac{\delta U}{\delta n(r)} + v(r) - \mu = 0$$
Kohn-Sham procedure

Separate $\varepsilon[n]$ in a different way

$$\varepsilon[n] = T_0[n] + U_H[n] + \int d^3 r \; \nu n(r) + E_{xc}[n]$$

Here,

$$U_H[n] = 1/2 \iint d^3 r d^3 r' \; n(r) \nu_c(r-r') n(r') : \text{Hartree energy}, \quad \nu_c(r) = \frac{e^2}{|r|}$$

$$T_0[n] = \text{K.E. of non-interacting system with density } n, \text{ i.e., with}$$

$$n(r) = \sum_{i=1}^N |\phi_i(r)|^2,$$

$$T_0[n] \equiv \sum_{i=1}^N \int d^3 r \; \phi_i^* \left( -\frac{\hbar^2 \nabla^2}{2m} \right) \phi_i = \sum_{i=1}^N \int d^3 r \left( -\frac{\hbar^2}{2m} \right) |\nabla \phi_i|^2$$
Now, minimize $\varepsilon[n]$ w.r.t. orbitals,

\[
\left\{ \begin{aligned}
\frac{\delta}{\delta \phi_j^*} &= \frac{\delta n}{\delta \phi_j^*} \frac{\delta}{\delta n} = \phi_j \frac{\delta}{\delta n} \\
&= \text{if } \phi_j \text{ is occupied.}
\end{aligned} \right.
\]

Constraining to normalized orbitals

\[
\frac{\delta}{\delta \phi_i^*(r)} \left[ \varepsilon[n] - \sum_{j=1}^{N} \varepsilon_j \left( \int d^3r \, |\phi_j|^2 - 1 \right) \right] = 0
\]

\[
\Rightarrow -\frac{\hbar^2 \nabla^2}{2m} \phi_i + v_h(r)\phi_i + v(r)\phi_i + \frac{\delta E_{XC}}{\delta n(r)} \phi_i = \varepsilon_i \phi_i
\]

$v_h(r;n)$  \hspace{1cm} $v_{XC}(r;n)$
If the resulting density is the same as the density, then the final is minimized. \( \Rightarrow n_{gs} \) and \( \varepsilon_{gs} \)

Thus, the problem is reduced to a self-consistent field problem.

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(r, n) \right) \phi_i = \varepsilon_i \phi_i : \text{Kohn-Sham equation}
\]

\[ \Rightarrow n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 \]

But,

(i) this looks like a system of non-interacting particles in an effective potential.
(ii) it is really a many-body theory for $\varepsilon_{gs}$ and $n_{gs}$.

(iii) $\varepsilon_i \rightarrow \varepsilon_{kn}$ is the band structure. (come back to this later.)

**Self-consistent Kohn-Sham equations**

1. Initial guess: $n^{\sigma}(r)$

2. Calculate effective potential: $V_{\text{eff}}^{\sigma}(r)$

3. Solve KS equation

4. Calculate electron density: $n^{\sigma}(r) = \sum_i f_i |\Psi^{\sigma}_i(r)|^2$

5. Self-Consistent? *(No, go to 1; Yes, output.)*
The Exchange-Correlation Energy Functional

“Adiabatic Connection”: Coupling constant integration

Introduce \( \lambda \) in \( v_{c,\lambda} = \lambda \frac{e^2}{|r-r'|} \), scaling of Coulomb repulsion.

In DFT, functionals depend only on \( n \) and \( e^2, \hbar, m \).

With \( \lambda \), DFT holds again, but functionals depends on \( \lambda \).

Thus, for a given \( n \), there exists an external potential \( v_{\lambda} \) that gives \( n \) as the ground state density.

Then, let \( n(r) \) be the ground state density corresponding to \( \lambda=1 \),
i.e., to \( v = v_{\lambda = 1} = v_1 \) and full Coulomb repulsion.

Denote \( H_\lambda = T + V_\lambda + \lambda U \).

Here, \( V_\lambda = \int d^3 r \, v_\lambda(r) \, n(r) \),

where at each \( \lambda \), \( v_\lambda \) is that potential which gives \( n \), i.e., \( n(r) \) is fixed as \( \lambda \) varies between 0 and 1.

Also, \( H_\lambda \Psi_\lambda = \varepsilon_\lambda \Psi_\lambda \)
Hellman-Feynman theorem gives
\[ \frac{d\varepsilon_\lambda}{d\lambda} = \left\langle \psi_\lambda \left| \frac{\partial H_\lambda}{\partial \lambda} \right| \psi_\lambda \right\rangle \]
and
\[ \frac{\partial H_\lambda}{\partial \lambda} = \frac{\partial V_\lambda}{\partial \lambda} + U. \]

Also,
\[ \int_0^1 d\lambda \frac{\partial \varepsilon_\lambda}{\partial \lambda} = \varepsilon_1 - \varepsilon_0. \]

\(\lambda=0:\) \quad \varepsilon_0 = T[n] + \int d^3 r v_0 n(r)

\[= T_s[n] + \int d^3 r v_0 n(r): \text{non-interacting system} \]

\(\lambda=1:\) \quad \varepsilon_1 = T_s[n] + \int d^3 r v_1 n(r) + U_H[n] + E_{XC}[n]

(By definition, \(E_{XC}\) contains \(T-T_s\) and \(U-U_H\). \(E_{XC}\) can be decomposed as \(E_X+E_C\), where \(E_X\) is due to Pauli principles and \(E_C\) is due to correlations.)
Then,

- $\varepsilon_1 - \varepsilon_0 = \int d^3 r \ v_1 \ n(r) - \int d^3 r \ v_0 \ n(r) + U_H[n] + E_{XC}[n]$ 

Now, other term is

- $\varepsilon_1 - \varepsilon_0 = \int_0^1 d\lambda \frac{\partial \varepsilon_\lambda}{\partial \lambda} = \int_0^1 d\lambda \left\langle \psi_\lambda \left| \frac{\partial V_\lambda}{\partial \lambda} + U \right| \psi_\lambda \right\rangle$

\[
= \int_0^1 d\lambda \left( \int d^3 r \frac{dv_\lambda}{d\lambda} \ n(r) + \left\langle \psi_\lambda \left| \frac{1}{2} \iint d^3 rd^3 r' n(r) v_C(r-r') n(r') \right| \psi_\lambda \right\rangle \right)
\]

\[
= \int d^3 r \left\{ v_1(r) - v_0(r) \right\} n(r) + \frac{1}{2} \int_0^1 d\lambda \iint d^3 rd^3 r' v_C(r-r') \left\langle \psi_\lambda \left| n(r) n(r') \right| \psi_\lambda \right\rangle 
\]

\[
\equiv n(r)n(r')g_\lambda(r,r')
\]

$g_\lambda(r,r')$ is pair correlation function.
Putting two equations together,

\[ E_{\text{XC}}[n] = \frac{1}{2} \iint d^3r d^3r' \nu(r - r') n(r)n(r') \int_0^1 d\lambda g_\lambda(r,r') - U_H[n] \]

\[ \equiv \frac{e^2}{2} \iint d^3r d^3r' n(r) \frac{\bar{g}(r,r') - 1}{|r - r'|} n(r') \]

(Since \( \bar{g}(r,r') = \int_0^1 d\lambda g_\lambda(r,r') \): Coupling-Constant averaged pair correlation function.)

\[ \equiv \int d^3r n(r) \varepsilon_{\text{XC}}(r;n), \quad \{ \bar{g} = \bar{g}(r,r';n) \} \]
In the local density approximation (LDA),

\[ E_{XC}[n] \equiv \int d^3 r \, n(r) \varepsilon_{XC}(r;n) \]

where \( \varepsilon_{XC}(r;n) = \int d^3 r' \frac{g(r,r') - 1}{|r - r'|} n(r') \)

\( \varepsilon_{XC}(r,n) \rightarrow \varepsilon^{h}_{XC}(n(r)) : \text{homogenous system} \)

Simple!

Surprisingly good!
Meaning of eigen values $\varepsilon_i$, etc.

KS equation:  \[ \{-\nabla^2 + V + V_H + V_{XC}\} \Phi_i = \varepsilon_i \Phi_i \]

Corresponding Green's function

\[ G^{DFT}(r,r';\varepsilon) = \sum_j \frac{\phi_j(r)\phi_j^*(r')}{\varepsilon - \varepsilon_j + i\delta} \]

• Then,

\[ -\frac{1}{\pi} \text{Im} \int_{\varepsilon_F}^\varepsilon d\varepsilon G^{DFT}(r,r';\varepsilon) \bigg|_{r=r'} = -\frac{1}{\pi} \text{Im} \left\{ -i\pi \sum_i \int_{\varepsilon_F}^{\varepsilon} d\varepsilon \delta(\varepsilon - \varepsilon_i) \vert \phi_i(r) \vert^2 \right\} \]

\[ \therefore \frac{1}{x + i\delta} = P \frac{1}{x} - i\pi\delta(x), \quad x = 0^+ \]
or, \[ -\frac{1}{\pi} \text{Im} \int_{\varepsilon_F}^{\varepsilon} d\varepsilon \, G^{DFT}(r, r'; \varepsilon) \bigg|_{r=r'} = \sum_{\varepsilon_i < \varepsilon_F} |\phi_i(r)|^2 = n(r) \]

From many-body theory, the exact single particle Green’s function satisfies

\[ -\frac{1}{\pi} \text{Im} \int_{\varepsilon_F}^{\varepsilon} d\varepsilon \, G(r, r'; \varepsilon) \bigg|_{r=r'} = n(r) \text{ almost from its definition} \]

\[ \Rightarrow \text{ Thus, } G^{DFT} \text{ contains a great deal of } G! \]

- Equations the Green’s functions satisfy: (complex energy \( z \))

Full:

\[ \left\{ -z - \nabla^2_r + v(r) + v_H(r) \right\} G(r, r'; z) + \int dr'' \sum(r, r''; z) G(r'', r'; z) = \delta(r - r') \]
DFT:
\[
\left\{-z - \nabla_r^2 + v(r) + v_H(r)\right\} G^{DFT}(r, r'; z) + v_{XC}(r)G^{DFT}(r, r'; z) = \delta(r - r')
\]

Thus,

- \( v_{XC} \) can be viewed as a local (\( r=r' \)), real, static approximation to self-energy \( \Sigma(r, r'; z) \).

- \( \varepsilon_i \) are approximation to the single particle excitations, a good mean field approximation to excitation energies.

- Both \( \Sigma(r, r'; z) \) and \( v_{XC} \) give rise to the same density.
DFT & the Many Body Problem

The Hamiltonian can be written

\[ H = T + V + U_H \]

\[ = T + V + V_{\text{hxc}} + (U_H - V_{\text{hxc}}) \]

\[ = H_0 + \Delta V \]

where, of course, \( V_{\text{hxc}} \) could be anything.

However, if we choose

\[ V_{\text{hxc}} = \int d^3r \left[ v_H(r) + v_{XC}(r) \right] n(r) \]

\[ = \sum_{i=1}^N \left[ v_H(r_i) + v_{XC}(r_i) \right], \quad \text{where} \quad v_H = \frac{\delta U_H}{\delta n(r)} \]
then

\[ H_0 = \sum_{i=1}^{N} \left[-\frac{\hbar^2 \nabla_i^2}{2m} + v(r_i) + v_H(r_i) + v_{XC}(r_i) \right] \]

Kohn-Sham Hamiltonian for each particle

\[ \sum_{i=1}^{N} h(r_i), \text{ where } h\phi_i = \varepsilon_i \phi_i. \]

Now, \( \Delta V = U_H - V_{\text{hxc}} \) is the full, bare, long-range Coulomb repulsion between pairs, minus a one-body potential \( v_H + v_{XC} \).

\( \Delta V \) does not change the charge density from \( H_0 \)!

However, it gives a big change in the energy: \( \langle \psi_0 | H_0 | \psi_0 \rangle = \sum_{i=1}^{N} \varepsilon_i \),

while \( \varepsilon = \langle \Psi | H | \Psi \rangle \) is much different.
**DFT: Progression/Generalization**

- Non-relativistic, non magnetic: $\varepsilon[n], n(r)$
- Non-relativistic, magnetic: $\varepsilon[n_{\alpha\beta}], \frac{1}{2}n(r)\vec{l} + m\vec{\sigma}$
- Relativistic, magnetic: $\varepsilon[j_{\mu}], 4$-current $j_{\mu\sigma}(r)$
- Non-relativistic, B field: $\varepsilon[j_{\mu}], \text{charge density, current density}$
- $t$-dependent $v_{\text{ext}}(r,t): \varepsilon[n(t'), t'<t]$
- Superconducting states: $\varepsilon[n,\Delta], \text{charge density, pair density}$
• DFT for excited states (orthogonal to ground state)
• DFT for other properties: momentum distribution function, Compton profile
• DFT for ferroelectrics (density-polarization functional theory)
• Temperature-dependent (finite T) DFT
• DFT for the Hubbard model or practically any other model, exists.
Properties Calculated Using DFT

$\epsilon\{\{R_i\}\}, \{R_i\} =$ atom positions in solid (or molecule); “relaxation of structure”

- ground state structure: bcc, fcc, hcp, Pnma, etc.
  (but with many independent coordinates there are many local minima)

- pressure: $P=-\partial \epsilon / \partial V$ ($V=$volume)

- pressure-driven structure transformations

- phonons: $\partial^2 \epsilon / \partial R_i \partial R_j$
- elastic constants
- defect energies

Slope: 
$P = -\frac{\partial \varepsilon}{\partial V}$

Slope gives pressure at which transformation occurs
\( \varepsilon (\{ R_i^0 \}) \): ground state density

- elastic field gradients
- ionization potential/work function
- Fermi surfaces: usually very good! (although not exact)

**Magnetic properties from Spin DFT**

- magnetic order of ground states: magnetic impurities
- hyperfine fields at nuclei
- exchange coupling

**Electric polarization**

**Forces on atom \( \Rightarrow \) ab initio molecular dynamics ("Car-Parrinello")**
Effects of constraints: “constrained DFT”

- example: energy vs. f electron occupation number in ions/atoms

Excitation energies?:

beginning to, from t-dependent DFT, for finite systems.
Functional Derivatives and Differentiation

Functional $F[n]$: function $n(r) \rightarrow$ number $F$

**Definition of functional derivatives**

\[
\frac{\delta F[n]}{\delta n(r)} = \lim_{\varepsilon \to 0} \left\{ \frac{F\left[ n(r') + \varepsilon \delta (r - r') \right] - F[n(r')]}{\varepsilon} \right\}
\]

change $n(r)$ at one point by $\varepsilon \delta(r-r')$
\[ N[n] = \int d^3r' n(r') : \text{particle number} \]

\[
\frac{\delta N}{\delta n(r)} = \lim_{\varepsilon \to 0} \left[ \int d^3r' \left\{ n(r') + \varepsilon \delta(r - r') \right\} - \int d^3r' n(r') \right] \varepsilon
\]

\[
= \lim_{\varepsilon \to 0} \frac{1}{\varepsilon} \int d^3r' \varepsilon \delta(r - r') = 1 \quad \therefore \text{independent of } r
\]

\[ Q[n] = \int d^3r' P(r'; n(r')), \quad P \equiv P(r; n(r)) \]

\[
\frac{\delta Q}{\delta n(r)} = \lim_{\varepsilon \to 0} \int d^3r' \frac{P(r'; n(r')) + \varepsilon \delta(r - r') - P(r'; n(r'))}{\varepsilon}
\]

\[
\approx \lim_{\varepsilon \to 0} \int d^3r' \frac{\left\{ P(r'; n(r')) + \varepsilon \delta(r' - r) \frac{\partial P}{\partial n} + \Box \right\} - P(r'; n(r'))}{\varepsilon}
\]

\[
\Box \int d^3r' \delta(r' - r) \frac{\partial P(r'; n(r'))}{\partial n} = \frac{\partial P(r; n(r))}{\partial n(r)}
\]
• **Differentiation:**

\[ n(r) = \sum_{i=1}^{N} |\phi_i(r)|^2, \quad N: \text{particle} \]

\[
\frac{\delta N[n]}{\delta \phi_i^*(r)} = \frac{\delta}{\delta \phi_i^*(r)} \int d^3r' \sum_{i=1}^{N} \phi_i^*(r')\phi(r')
\]

\[
= \begin{cases} 
\phi(r), & \text{if } i \leq N \text{ (occupied)} \\
0, & \text{otherwise}
\end{cases}
\]