

# Density Functional Theory

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**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  $n(\mathbf{r})$ .

## Proof]

Suppose for two systems with the same # of particles,

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

$$\Rightarrow \bullet H|\Psi\rangle = (H_0 + V)|\Psi\rangle = \epsilon|\Psi\rangle$$

$$\bullet H'|\Psi'\rangle = (H_0 + V')|\Psi'\rangle = \epsilon'|\Psi'\rangle, \quad \text{where } |\Psi'\rangle \neq |\Psi\rangle.$$

**Then,**

$$\varepsilon = \langle \Psi | \mathbf{H} | \Psi \rangle < \langle \Psi' | \mathbf{H} | \Psi' \rangle \quad (\because \Psi' \text{ is not the g.s. wave function of H.})$$

$$\begin{aligned} \text{RHS} &= \langle \Psi' | \mathbf{H}_0 + \mathbf{V}' + (\mathbf{V} - \mathbf{V}') | \Psi' \rangle \\ &= \varepsilon' + \langle \Psi' | \mathbf{V} - \mathbf{V}' | \Psi' \rangle \\ &= \varepsilon' + \int d^3\mathbf{r} \, n(\mathbf{r}) [\mathbf{v}(\mathbf{r}) - \mathbf{v}'(\mathbf{r})] \end{aligned}$$

$$\text{So, } \varepsilon = \varepsilon' + \int d^3\mathbf{r} \, n(\mathbf{r}) [\mathbf{v}(\mathbf{r}) - \mathbf{v}'(\mathbf{r})]$$

**Exchange (primed  $\leftrightarrow$  unprimed)**

$$\varepsilon' = \varepsilon + \int d^3\mathbf{r} \, n(\mathbf{r}) [\mathbf{v}'(\mathbf{r}) - \mathbf{v}(\mathbf{r})]$$

**Adding two equations,**

$$\varepsilon' + \varepsilon < \varepsilon + \varepsilon'$$

**$\therefore$  Contradiction  $\Rightarrow n'(r) \neq n(r)$  !**

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

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

**Of course, also  $n$  is a functional of  $v$ , so  $v \leftrightarrow n$  is 1-to-1.**

2. In principle, **any property of the system is a functional of  $n$ !**  
(Each is its own functional.)

In particular, the total energy of the system;

$$\varepsilon = \langle \Psi_{\text{g.s.}} | H | \Psi_{\text{g.s.}} \rangle$$

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



**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:**

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

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

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

# Kohn-Sham procedure

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

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

Here,

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

$T_0[n] =$  K.E. of **non-interacting** system with density  $n$ , i.e., with

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

$$T_0[n] = \sum_{i=1}^N \int d^3r \phi_i^* \left( -\frac{\hbar^2 \nabla^2}{2m} \right) \phi_i = \sum_{i=1}^N \int d^3r \left( -\frac{\hbar^2}{2m} \right) |\nabla \phi_i|^2$$

Now, minimize  $\varepsilon[\mathbf{n}]$  w.r.t. orbitals,

$$\left( \begin{array}{l} \text{Using, where necessary,} \\ \frac{\delta}{\delta\phi_j^*} = \frac{\delta n}{\delta\phi_j^*} \frac{\delta}{\delta n} = \phi_j \frac{\delta}{\delta n} \quad \text{if } \phi_j \text{ is occupied.} \end{array} \right)$$

Constraining to normalized orbitals

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

$$\Rightarrow -\frac{\hbar^2 \nabla^2}{2m} \phi_i + \underbrace{v_h(r)}_{\mathbf{v}_h(\mathbf{r};\mathbf{n})} \phi_i + v(r) \phi_i + \underbrace{\frac{\delta E_{XC}}{\delta n(r)}}_{\mathbf{v}_{XC}(\mathbf{r};\mathbf{n})} \phi_i = \varepsilon_i \phi_i$$



**If the resulting density is the same as the density, then the final energy is minimized.  $\Rightarrow n_{gs}$  and  $\epsilon_{gs}$**

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

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

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

**But,**

**(i) this looks like a system of non-interacting particles in an effective potential.**

(ii) it is really a many-body theory for  $\epsilon_{gs}$  and  $n_{gs}$ .

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

## Self-consistent Kohn-Sham equations

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

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

3. Solve KS equation

4. Calculate electron density:  $n^\sigma(\mathbf{r}) = \sum_i f_{\sigma_i} |\Psi_{\sigma_i}^\sigma(\mathbf{r})|^2$

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  $v \equiv v_{\lambda=1} \equiv v_1$  and full Coulomb repulsion.**

**Denote  $H_\lambda = T + V_\lambda + \lambda U$ .**

**Here,  $V_\lambda \equiv \int d^3r v_\lambda(r) n(r)$ ,**

**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,  $H_\lambda \Psi_\lambda = \epsilon_\lambda \Psi_\lambda$**

**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,**  $\int_0^1 d\lambda \frac{\partial \varepsilon_\lambda}{\partial \lambda} = \varepsilon_1 - \varepsilon_0$ .

**$\lambda=0$ :**  $\varepsilon_0 = T[\mathbf{n}] + \int d^3\mathbf{r} v_0 \mathbf{n}(\mathbf{r})$   
 $= T_s[\mathbf{n}] + \int d^3\mathbf{r} v_0 \mathbf{n}(\mathbf{r})$ : **non-interacting system**

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

**(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,

- $\epsilon_1 - \epsilon_0 = \int d^3r v_1 n(r) - \int d^3r v_0 n(r) + U_H[n] + E_{XC}[n]$

Now, other term is

- $\epsilon_1 - \epsilon_0 = \int_0^1 d\lambda \frac{\partial \epsilon_\lambda}{\partial \lambda} = \int_0^1 d\lambda \left\langle \psi_\lambda \left| \frac{\partial V_\lambda}{\partial \lambda} + U \right| \psi_\lambda \right\rangle$

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

$$= \int d^3r \{v_1(r) - v_0(r)\} n(r) + \frac{1}{2} \int_0^1 d\lambda \iint d^3r d^3r' v_C(r-r') \underbrace{\langle \psi_\lambda | n(r)n(r') | \psi_\lambda \rangle}_{\equiv n(r)n(r')g_\lambda(r,r')}$$

$g_\lambda(r,r')$  is pair correlation function.

**Putting two equations together,**

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

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

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

$$\equiv \int d^3r n(r) \varepsilon_{XC}(r; n), \quad \left\{ \bar{g} = \bar{g}(r, r'; n) \right\}$$

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

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

## In the local density approximation (LDA),

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

**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,

$$-\frac{1}{\pi} \text{Im} \int^{\varepsilon_F} d\varepsilon G^{DFT}(r, r'; \varepsilon) \Big|_{r=r'} = -\frac{1}{\pi} \text{Im} \left\{ -i\pi \sum_i \int^{\varepsilon_F} d\varepsilon \delta(\varepsilon - \varepsilon_i) |\phi_i(r)|^2 \right\}$$
$$\left( \because \frac{1}{x+i\delta} = P \frac{1}{x} - i\pi\delta(x), \quad x=0^+ \right)$$

$$\text{or, } -\frac{1}{\pi} \text{Im} \int^{\varepsilon_F} d\varepsilon G^{DFT}(r, r'; \varepsilon) \Big|_{r=r'} = \sum_{\varepsilon_i < \varepsilon_F} |\phi_i(r)|^2 = n(r)$$

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

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

**⇒ Thus,  $G^{DFT}$  contains a great deal of  $G$ !**

**• Equations the Green's functions satisfy: (complex energy  $z$ )**

**Full:**

$$\left\{ -z - \nabla_r^2 + v(r) + v_H(r) \right\} G(r, r'; z) + \int dr'' \Sigma(r, r''; z) G(r'', r'; z) = \delta(r - r')$$

## 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  $\Sigma(r, r'; z)$ .
- $\epsilon_i$  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

$$\begin{aligned}\mathbf{H} &= \mathbf{T} + \mathbf{V} + \mathbf{U}_H \\ &= \mathbf{T} + \mathbf{V} + \mathbf{V}_{hxc} + (\mathbf{U}_H - \mathbf{V}_{hxc}) \\ &= \mathbf{H}_0 + \Delta\mathbf{V}\end{aligned}$$

where, of course,  $\mathbf{V}_{hxc}$  could be anything.

However, if we choose

$$\begin{aligned}V_{hxc} &= \int d^3r [v_H(r) + v_{XC}(r)] n(r) \\ &= \sum_{i=1}^N [v_H(r_i) + v_{XC}(r_i)], \quad \text{where } v_H = \frac{\delta U_H}{\delta n(r)}\end{aligned}$$

**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

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

**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:  $\epsilon[n], n(\mathbf{r})$
- Non-relativistic, magnetic:  $\epsilon[\mathbf{n}_{\alpha\beta}], \frac{1}{2}n(r)\vec{1} + m \bullet \vec{\sigma}$
- Relativistic, magnetic:  $\epsilon[\mathbf{j}_{\mu}], 4\text{-current } \mathbf{j}_{\mu\sigma}(\mathbf{r})$
- Non-relativistic, B field:  $\epsilon[\mathbf{j}_{\mu}], \text{ charge density, current density}$
- t-dependent  $v_{\text{ext}}(\mathbf{r}, t)$ :  $\epsilon[n(t'), t' < t]$
- Superconducting states:  $\epsilon[n, \Delta], \text{ charge density, pair density}$

- **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

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

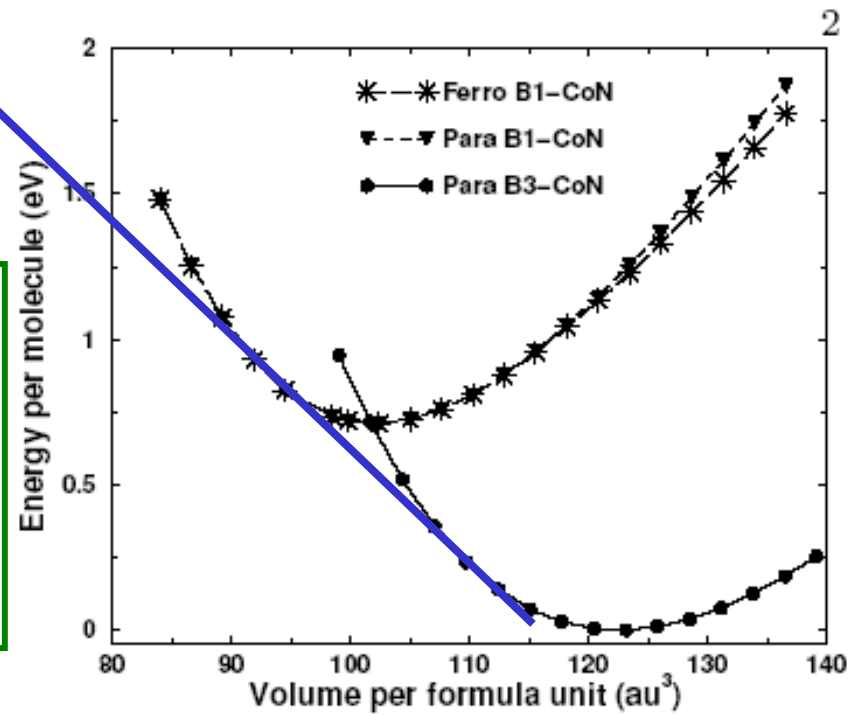
- ground state structure: bcc, fcc, hcp, Pnma, etc.  
(but with many independent coordinates there are many local minima)
- pressure:  $P = -\partial\epsilon/\partial V$  ( $V$ =volume)
- pressure-driven structure transformations
- phonons:  $\partial^2\epsilon/\partial\mathbf{R}_i\partial\mathbf{R}_j$



- elastic constants
- defect energies

**Slope:**  
 $P = -\partial \epsilon / \partial V$

**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  $n(r)$   $\implies$  number  $F$

## Definition of functional derivatives

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

change  $n(r)$  at one point by  $\varepsilon \delta(r - r')$

- **[Example]**  $N[n] = \int d^3 r' n(r')$ : particle number

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

$$= \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} \int d^3 r' \varepsilon \delta(r - r') = 1$$

$\therefore$  independent of  $\mathbf{r}$

- **[Example]**  $Q[n] = \int d^3 r' P(r'; n(r'))$ ,  $P \equiv P(r; n(r))$

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

$$\approx \lim_{\varepsilon \rightarrow 0} \int d^3 r' \frac{\left\{ P(r'; n(r')) + \varepsilon \delta(r' - r) \frac{\partial P}{\partial n} + \square \right\} - P(r'; n(r'))}{\varepsilon}$$

$$\square \int d^3 r' \delta(r' - r) \frac{\partial P(r'; n(r'))}{\partial n} = \frac{\partial P(r; n(r))}{\partial n(r)}$$

- **Differentiation**:  $n(r) = \sum_{i=1}^N |\phi_i(r)|^2$ ,  $N$ : particle

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

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