LECTURE #26

Note Title 3/24/2010

INTRO TO DENSITY FUNCTIONAL THEORY

HARTREE-FOCK

$$E^{HF}\left[\{ \psi_i^*(r), \psi_i(r) \} \right]$$ FUNCTIONAL DEPENDENCE

$$\frac{\delta E^{HF}}{\delta \psi_i^*} = \mu \psi_i \rightarrow$$ EFFECTIVE SCHROEDINGER EQ.

DFT

$$E[n(r)]$$

$$\boxed{\frac{\delta E[n(r)]}{\delta n(r)} = \mu}$$

N ELECTRONS

$$H^{TOT} = \underbrace{T}_{\sum_i \frac{p_i^2}{2m}} + V^{ION} + \underbrace{H^{(2)}}_{\frac{1}{2}\sum_{ij} \frac{e^2}{|r_i - r_j|}}$$

UNIVERSAL
SAME FOR
ATOMS, MOLECULES
SOLIDS

- PROPERTIES OF N-ELECTRON SYSTEMS ARE UNIQUELY DETERMINED BY $V^{ION} = v(r)$

- ANY OBSERVABLE IS A FUNCTIONAL OF $v(r)$ $\quad O[v(r)]$

- TOTAL DENSITY $n(r)$ FUNCTIONAL OF $v(r)$

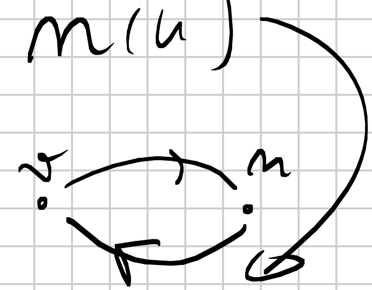
$$n[v(r)]$$

$$v \to n$$
$$v \to n'$$

I HOHENBERG - KOHN THEOREM

$v(r)$ IS UNIQUELY DETERMINED BY $n(r)$

$$v[n(r)]$$



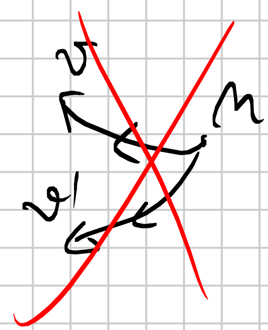
REDUCTIO AD ABSURDUM

IF I NOT TRUE $\Rightarrow$

$v(r)$ $\qquad$ $v'(r)$ $\qquad$ WITH SAME $n(r)$

$\downarrow$ $\qquad$ $\downarrow$

ψ, E_0 $\qquad$ ψ', E_0'



$+v' - v'$

$$E_0 = \langle \psi | T + v + H^{(2)} | \psi \rangle < \langle \psi' | T + v + H^{(2)} | \psi' \rangle =$$

$$\langle \psi' | T + v' + H^{(2)} + v - v' | \psi' \rangle = E_0' + \int dr\, n(r)\left(v(r) - v'(r)\right)$$

$$E_0 - E_0' < \int dr\, n(r) \left(v(r) - v'(r) \right)$$

$$\hphantom{E_0' = \langle \Psi' | T + v' + H^{(2)} | \Psi' \rangle < \langle \Psi | T + v' + H^{(2)} | \Psi \rangle} +v - v$$

$$E_0' = \langle \Psi' | T + v' + H^{(2)} | \Psi' \rangle < \langle \Psi | T + v' + H^{(2)} | \Psi \rangle =$$

$$E_0 + \int dr\, n(r) \left(v(r) - v'(r) \right)$$

$$E_0 - E_0' > \int dr\, n(r) \left(v(r) - v'(r) \right)$$

$$\begin{tikzcd} v \arrow[r, bend left] & n \arrow[l, bend left] \end{tikzcd}$$

$$\begin{tikzcd} v' \arrow[r, bend left] & n' \arrow[l, bend left] \end{tikzcd}$$

ONLY POSSIBLE IF $v(r) = v'(r)$

$$E[v(r)] \longrightarrow E[v[n]] \longrightarrow E[n(r)]$$

$$E[n(r)] = \int dr\, v(r)\, n(r) + F[n]$$

UNIVERSAL FUNCTIONAL

KINETIC + COULOMB

VARIATIONAL METHOD

N

$$\delta\Big(E[n] - \mu \overbrace{\int dr\, n(r)}^{=N}\Big) = 0$$

$$\frac{\delta E[n]}{\delta n} = \mu \quad ; \quad \frac{\delta F[n]}{\delta n} + v(r) = \mu$$

$F[n]$?

NON INTERACTING ELECTRONS

$$H^{(2)} = 0$$

$$E_s[n] = \int dr\, v(r)\, n(r) + T_s[n]$$

$s \downarrow$ NON INTERACTING

DFT EQUATION

$$\frac{\delta T_s[n]}{\delta n} + v(r) = \mu$$

(A) DFT

EQUIVALENT TO:

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v(r) \right] \phi_j = \varepsilon_j \phi_j$$

(B) SCHR EQ

$$n(r) = \sum_j \vartheta(\mu - \varepsilon_j) \, |\phi_j(r)|^2$$

II KOHN – SHAM EQUATIONS

$H^{(2)} \neq 0$

$$E[n] = \overset{(A)}{T_s[n]} + \int dr\, v(r)\, n(r) + \frac{1}{2}\int dr\, dr' \overset{(B)}{\frac{n(r)\, n(r')}{|r-r'|}} + \underbrace{\overset{(C)}{E_{xc}[n]}}$$

(A) KINETIC ENERGY OF NON-INTERACTING SYSTEM WITH DENSITY n

(B) HARTREE

(C) EXCHANGE-CORRELATION (EXCHANGE SCREENING $T \neq T_s$)

$$\frac{\delta E}{\delta n} = \mu$$

$$\boxed{\frac{\delta T_s}{\delta n} + v(r) + \overbrace{\int dr' \, \frac{n(r')}{|r-r'|}}^{v^H(r)} + \overbrace{\frac{\delta E_{xc}[n]}{\delta n}}^{v^{xc}(r)} = \mu}$$

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + v^{EFF}(r) \right] \phi_j = \varepsilon_j \phi_j$$

KOHN SHAM ORBITALS

$$v^{EFF} = v + v^H + v^{xc}(r)$$

$$n(r) = \sum_j \theta(\mu - \varepsilon_j) \, |\phi_j(r)|^2$$

$E_{xc}[n]$ CALCULATED FROM HOMOGENEOUS ELECTRON GAS

$$\boxed{\begin{array}{l}\text{GREEN'S FUNCTIONS} \\ \text{QUANTUM MONTE CARLO}\end{array}} \longrightarrow E_{xc}[n]$$

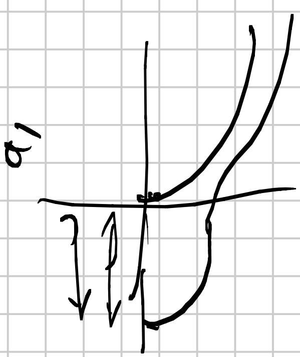
LOCAL DENSITY APPROXIMATION

$$E_{xc}[n] = \int dr\; n(r)\, \varepsilon_{xc}(n(r))$$

KINETIC

EXCHANGE

$$\varepsilon_{xc}(n(r)) = \frac{E_x}{N} = \left(\frac{2.21}{(r_s/a_B)^2} - \frac{0.9}{(r_s/a_B)} \right)$$



$$\frac{4\pi}{3} r_s^3 = \frac{1}{n}$$

$$\varepsilon_{xc} \sim -\alpha \frac{1}{r_s}$$

$$\varepsilon_x \sim -\alpha\, n^{1/3}$$

$$E_{xc}[n] = -\alpha \int dr\, n(r) \left(n(r)\right)^{1/3}$$

$$v_{xc}(r) \sim -\alpha \frac{4}{3} n^{1/3} = \frac{\delta E_{xc}[n]}{\delta n}$$