LECTURE #25

Note Title 3/23/2009

$$\left(\underbrace{-\frac{\hbar^2 \nabla^2}{2m} + V^{ION}(\vec{r})}_{H_i}\right)\psi(\vec{r}) = E_i\,\psi_i(\vec{r})$$

ψ_i BLOCH ELECTRONS

$i \in \{k, m\}$ → BAND INDEX

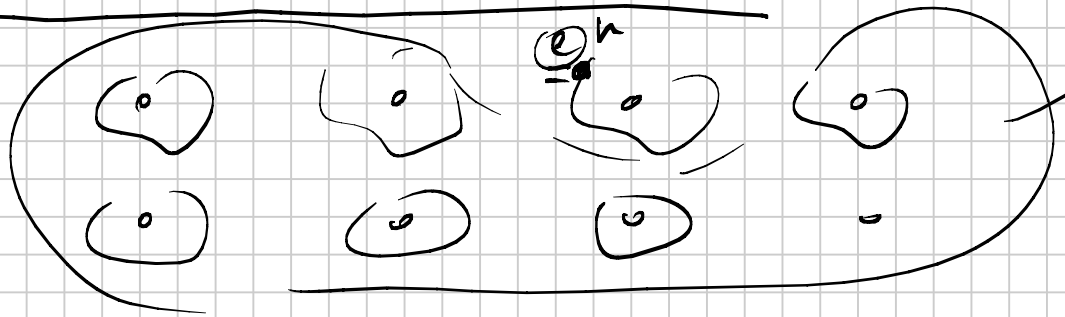
N ELECTRONS:

$$\Psi(r_1 s_1, r_2 s_2, r_3 s_3 \ldots r_N s_N)$$

$$H^{TOT} = \sum_i -\frac{\hbar^2 \nabla_i^2}{2m} + V^{ION}(r_i) + \frac{1}{2}\sum_{j \neq i} \frac{e^2}{|r_i - r_j|}$$

$$H^{TOT}\Psi(r_1 s_1, \ldots r_N s_N) = E\,\Psi(r_1 s_1, \ldots r_N s_N)$$

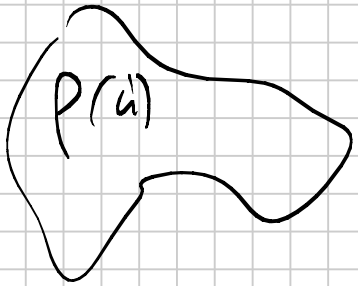
MEAN FIELD APPROACH



ALL OTHER ELECTRONS CREATE A CHARGE DENSITY $\rho(r)$

HARTREE APPROXIMATION

$$\left[-\frac{\hbar^2\nabla^2}{2m} + V^{ION}(r) - e\left[\int dr' \frac{\rho(r')}{|r-r'|}\right]\right]\psi(r) = E\,\psi(r) \qquad (1)$$



$V(r)$

$$V(r) = \int \frac{\rho(r')}{|r-r'|}\,dr'$$

ψ_i SET OF BLOCH STATES FROM SINGLE PARTICLE SE

$$\rho(r) = -e \sum_{i\,\in} |\psi_i(\vec{r})|^2 \qquad (2)$$

ALL OCCUPIED STATES

(1) + (2) → HARTREE APPROXIMATION

SOLVED BY ITERATION OR SELF-CONSISTENCY

FIRST LOOP

NO e-e INTERACTION

$$\left(-\frac{\hbar}{2m}\nabla^2 + V^{ION}\right)\psi(r) = E\psi(r) \;\Rightarrow\; \psi^{(0)}_{i\in(k,m)},\ \varepsilon^{(0)}_i$$

$$\rho^{(0)}(r) = -e \sum_{i\ \text{OCCUPIED}} |\psi^{(0)}(r)|$$

SECOND LOOP

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V^{ION}_{(r)} - e\int \frac{\rho^{(0)}(r')\,dr'}{r-r'}\right)\psi(r) = E\psi(r) \;\Rightarrow\; \psi^{(1)}_i,\ \varepsilon^{(1)}_i$$

ITERATION

IF $\rho^{(m+1)} \sim \rho^{(m)}$ STOP

$\psi^{(m)}_i(r)$

HARTREE!

$$\Psi_H(r_1 s_1 \dots r_N s_N) = \psi_1(r_1 s_1) \cdot \dots \cdot \psi_N(r_N s_N)$$

$e^{-\alpha|r_1 - r_2|}$ $\Rightarrow$ CANNOT BE REPRESENTED AS A PRODUCT STATE

NO CORRELATIONS

$\psi(r_1) \cdot \psi(r_2)$ ←

ELECTRONS ARE FERMIONS:

$$\Psi(r_1 s_1, r_2 s_2 \dots r_N s_N) = -\Psi(r_2 s_2, r_1 s_1, \dots r_N s_N)$$

$\Rightarrow$ HARTREE – FOCK APPROXIMATION

$$\Psi_{HF}(r_1 s_1, r_2 s_2 \dots r_N s_N) =$$

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1 s_1) & \psi_1(r_2 s_2) & \psi_1(r_3 s_3) & \cdots \\ \psi_2(r_1 s_1) & \psi_2(r_2 s_2) & \psi_2(r_3 s_3) & \cdots \\ \psi_3(r_1 s_1) & \psi_3(r_2 s_2) & \psi_3(r_3 s_3) & \cdots \\ \vdots & \vdots & \vdots & \end{vmatrix}$$

SLATER DETERMINANT

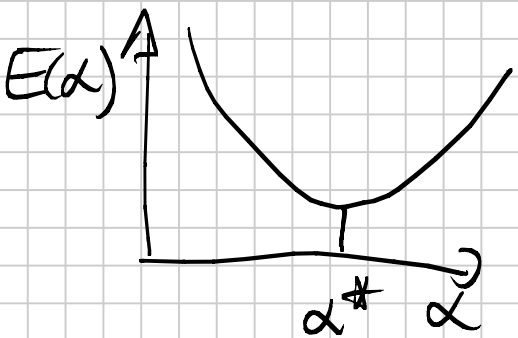
$= 0$

ANSATZ $\Longleftrightarrow$ VARIATIONAL PRINCIPLE

$$\underbrace{\left(-\frac{\hbar^2\nabla^2}{2m} - \frac{e^2}{r}\right)}_{H} \psi(r) = E\,\psi(r)$$

ANSATZ

$$\psi_\alpha = e^{-\alpha r^2} \Rightarrow \langle \psi_\alpha | H | \psi_\alpha \rangle = E(\alpha)$$



$$\frac{dE(\alpha)}{d\alpha} = 0$$

MANY BODY ANSATZ

VARIATIONAL APPROACH IS WITH RESPECT TO FUNCTIONS, NOT PARAMETERS

$$\Psi_H(r_1 s_1, \dots r_N s_N) = \psi_1(r_1 s_1) \dots \psi_N(r_N s_N)$$

$$\langle \Psi_H | H_{TOT} | \Psi_H \rangle = E_{TOT}[\{\psi_i(r_i, s_i)\}] \rightarrow \text{FUNCTIONAL DEPENDENCE}$$

$$E^{TOT}[\{\psi_i^*, \psi_i\}] = \sum_i \int dr\, \psi_i^*(r) \left(-\frac{\hbar^2 \nabla^2}{2m} + V^{ION}(r) \right) \psi_i(r) +$$

$$+ \frac{e^2}{2} \sum_{i \neq j} \int dr \int dr' \frac{|\psi_i(r)|^2 |\psi_j(r')|^2}{|r - r'|}$$

FIX TOTAL # ELECTRONS

$$N = \sum_i \int |\psi_i(u)|^2 du$$

I MINIMIZE THE FUNCTIONAL

LAGRANGE MULTIPLIER

$$F = E_{TOT}[\{\psi_i^* \psi_i\}] - \mu N$$

$$\frac{\delta F}{\delta \psi_i^*} = 0 \Rightarrow \frac{\delta E_{TOT}[\{\psi_i^* \psi_i\}]}{\delta \psi_i^*} = \mu \psi_i(u)$$

$$N = \sum_j \int du \; \psi_j^*(u) \psi_j(u) = \int (\psi_i^* \psi_i)$$

$$\frac{\delta \int}{\delta \psi_i^*} = \psi_i$$

$$\frac{\delta E_H^{TOT}[\{\psi_i^* \psi_i\}]}{\delta \psi_j^*} = \left(-\frac{\hbar^2 \nabla^2}{2m} + V_{(r)}^{ION}\right)\psi_j(r) \quad +$$

$$+ e^2 \int dr' \sum_i \frac{|\psi_i(r')|^2}{|r-r'|}\, \psi_j(r) = \mu\, \psi_j(r)$$

$$= 0$$

USE SLATER DETERMINANT AS ANSATZ (HARTREE-FOCK)

$$E_{HF}^{TOT}[\{\psi_i^* \psi_i\}] \qquad \frac{\delta[E_{HF}^{TOT} - \mu N]}{\delta \psi_j^*} = 0$$

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V^{ION}\right)\psi_j(r) + e^2\int dr' \frac{\sum_{i\neq j}|\psi_i(r')|^2}{|r-r'|}\psi_j(r)$$

$$- e^2\int dr' \sum_{i\neq j}\frac{\psi_i^*(r')\psi_j(r')\psi_i(r)}{|r-r'|}\delta_{s_i,s_j} = \mu\,\psi_j(r)$$

$$\int dr' \; V_x(r,r')\,\psi_j(r')$$

NON-LOCAL POTENTIAL

EXCHANGE INTERACTION IS SPIN-DEPENDENT