LECTURE #19

Note Title 2/24/2010

CHAPT 17 NEXT WED MARCH 2

MIDTERM

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

BLOCH ELECTRONS

$i \in \{K, \underset{\downarrow}{n}\}$

BAND INDEX

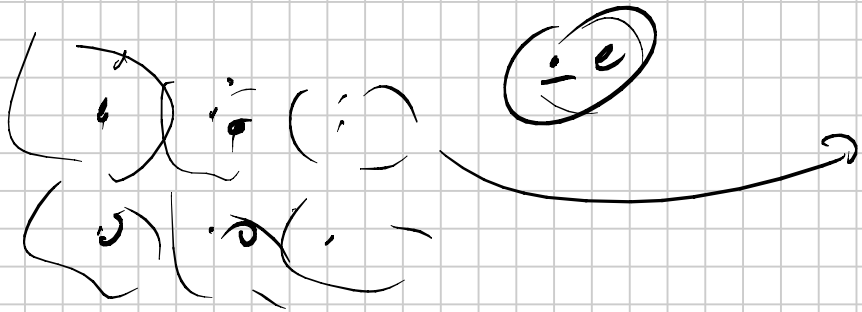
N ELECTRONS

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

$$H^{TOT} = \sum_{i=1}^{N}\left(-\frac{\hbar^2\nabla_i^2}{2m} + V^{ION}(\vec{r}_i)\right) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$H^{TOT}\Psi = E^{TOT}\Psi$$

MEAN FIELD APPROX



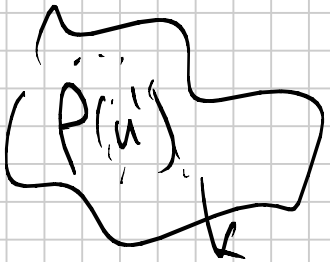
FOCUS ON ELECTRON 1

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

HARTREE APPROXIMATION

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

$V(r)$



CHARGE DISTRIBUTION

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

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

(1) + (2) HARTREE EQS. SOLVED BY ITERATION

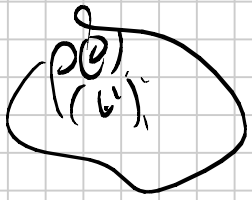
(OR SELF CONSISTENT METHODS)

STEP 1

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

$$\rho^{(0)}(\vec{r}) = -e \sum_{i \in \text{OCCUPIED STATES}} |\psi_i^{(0)}(\vec{r})|^2$$

$\cdot e$



STEP 2

$$\left(-\frac{\hbar^2\nabla^2}{2m} + V^{ION}(r) - e\int \frac{\rho^{(0)}(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}' \right)\psi = E\psi \;\Rightarrow\; \begin{cases}\psi^{(1)} \\ \varepsilon_n^{(1)}\end{cases}$$

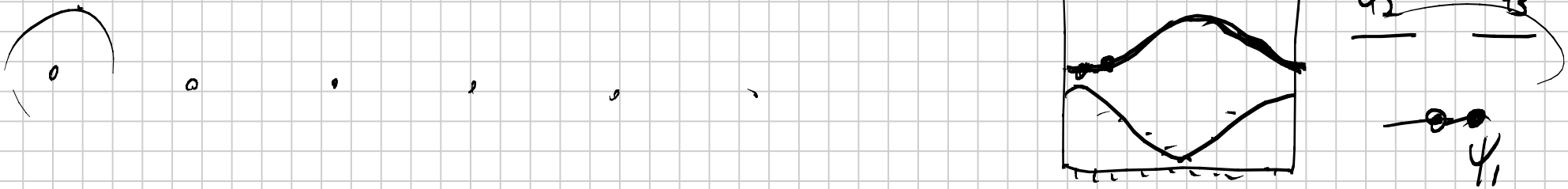
$V^{(H)}_{(r)}$ HARTREE

$$\rho^{(1)} \longrightarrow V^{(1)} \longrightarrow \rho^{(2)} \longrightarrow V^{H(2)} \cdots$$

ITERATION — STOP WHEN $\rho^{(m+1)} \sim \rho^{(m)}$

$$\Psi_H(r_1 s_1, \ldots r_N s_N) = \psi_1^H(r_1 s_1) \times \cdots \times \psi_N^H(r_N, s_N)$$

NO CORRELATIONS



$$\rho(r) = |\psi_1(r)|^2 + |\psi_2(r)|^2$$

$|\psi_1(4)|^2 + |\psi_3(4)|^2$

$e^{-\alpha|r_1 - r_2|}$

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

$\Rightarrow$ HARTREE - FOCK APPROXIMATION

$\psi_1 \qquad \psi_N$

$\varphi_{1s}(r_1)\varphi_{1s}(r_2)\otimes$

$(|\uparrow\rangle - |\downarrow\rangle)$

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

ANSATZ $\Longleftrightarrow$ VARIATIONAL PRINCIPLE

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

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

$$\frac{d\,E(\alpha)}{d\,\alpha} = 0$$

VARIATIONAL APPROACH WITH RESPECT TO 1 ELECTRON FUNCTIONS INSTEAD OF PARAMETERS

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

$$\langle \Psi_H | H^{TOT} | \Psi_H \rangle = E_{TOT}\left[\{\psi_i(r_i s_i)\}\right] \rightarrow \text{FUNCTIONAL}$$

$$E^{\text{HARTREE}}_{TOT}\left[\{\psi_i^*, \psi_i\}\right] = \sum_i \int dr_i\, \psi_i^*(r_i)\left(T^i + V^{ion}\right)\psi_i(r) \; +$$

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

$$N = \sum_i \int dr_i \, |\psi_i(r_i)|^2$$

MINIMIZE

LAGRANGE MULTIPLIER

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

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

$$N = \sum_J \int dr \; \psi_J^* \psi_J = \int [\{\psi_J^* \psi_J\}]$$

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

$$\frac{\delta E_{TOT}^{HARTREE}[\{\psi_i^*, \psi_i\}]}{\delta \psi_j^*} = \left(-\frac{\hbar^2 \nabla^2}{2m} + V^{ION}(\vec{r})\right)\psi_j(\vec{r})$$

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

ENERGY