10.02.2013

Lecture - 10 :

Many-electron atom :

$$H = -\frac{1}{2m}\sum_{i=1}^{N}\vec{\nabla}_i^2 - \sum_i \frac{Ze^2}{r_i} + e^2\sum_{i<j}\frac{1}{r_{ij}}$$

$r_{ij} = |\vec{r}_i - \vec{r}_j|$

$\psi(\vec{r}_1, m_{s_1}, \vec{r}_2, m_{s_2}, \ldots, \vec{r}_N, m_{s_N})$ → wavefunction of the system

means ⇒ we can choose a basis $|\vec{r}_1, m_{s_1}, \ldots \vec{r}_N, m_{s_N}\rangle$

$$\psi = \langle \vec{r}_1, m_{s_1}, \ldots \vec{r}_N, m_{s_N} | \psi \rangle$$

$\{\vec{r}_i, m_{s_i}\} \Rightarrow q_i \qquad m_{s_i} = \frac{1}{2}$ or $-1/2$ $(\forall\ i)$.

1 particle case : $\begin{pmatrix} \psi(\vec{r}_1, 1/2) \\ \psi(\vec{r}_1, -\frac{1}{2}) \end{pmatrix}$

- Symmetries are easy to implement.

- $\psi(q_1, \ldots q_N)$ is antisymmetric under $q_i \leftrightarrow q_j$ for any pair (i, j).

- Goal : Find eigenstates of $H\psi = E\psi$

(At least ground state wavefunction & energy)

A simplified approach

Think of each electron experiencing an effective potential due to the nucleus & other electrons.

denote by $V(\vec{r})$

(assumed to be central) $\equiv V(r)$

- A scheme of calculations where this is the starting pt.

$$H = H_0 + H_1 \quad | \quad H_0 = \sum_{i=1}^{N}\left(-\frac{1}{2m}\nabla_i^2 + V(r_i)\right)$$

$$H_1 = -\sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_i V(r_i) .$$

- Choose $V(r)$ such that H_1 has small matrix elements for the states.
- To find $V(r)$? LATER . . . .

Some general rules (Think $V(r)$ as given)

- Given $V(r)$, we can solve the 1-particle SE.

$$\left(-\frac{1}{2m} \vec{\nabla}^2 + V(r) \right) u_{n l m_l}(\vec{r}) - E_{nl}\, u_{n l m_l}(\vec{r}) = 0 .$$

  - $n = n_r + l$.
  - $n_r = 1, 2, 3, \ldots$ (for given l)
  - l can take values of $0, 1, \ldots (n-1)$.

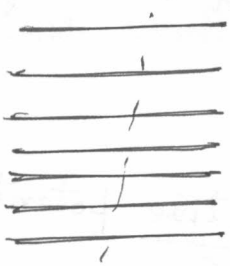
(Notice that we've assumed $V(r)$ doesn't depend on spin)

- Spin $\rightarrow$ $u_{n l m_l} \Rightarrow u_{n l m_l m_s}(\vec{r}, \tilde{m}_s)$

$$\| $$

$$\langle \vec{r}, \tilde{m}_s \mid n\, l\, m_l\, m_s \rangle = \delta_{m_s \tilde{m}_s}\, u_{n l m_l}(\vec{r})$$

- FERMIONS



fill states

$\alpha \leftrightarrow (n, l, m_l, m_s)$ labels single-particle energy levels.

$q \leftrightarrow (\vec{r}, m_s)$

$u_\alpha(q)$: single particle wavefunctions.

- Suppose, the ground state contains particles in single-particle states $\alpha_1, \ldots, \alpha_N$ (N: no. of electrons)

$$\Psi(q_1, q_2, \ldots q_N) = \frac{1}{\sqrt{N!}} \left| u_{\alpha_1}(q_1)\, u_{\alpha_2}(q_2) \cdots u_{\alpha_N}(q_N) \right| + (N! - 1) \text{ other terms w/ a sign !}$$

$$E = \sum_{i=1}^{N} E_{\alpha i}$$

(ground state energy)

One can write Ψ as a determinant (aka Slater Determinant)

$$\Psi(q_1, \ldots, q_N) = \frac{1}{\sqrt{N!}} \times \begin{vmatrix} u_{\alpha_1}(q_1) & u_{\alpha_2}(q_1) & \cdots & u_{\alpha_N}(q_1) \\ u_{\alpha_1}(q_2) & u_{\alpha_2}(q_2) & \cdots & u_{\alpha_N}(q_2) \\ \vdots & \vdots & & \vdots \\ u_{\alpha_1}(q_N) & u_{\alpha_2}(q_N) & \cdots & u_{\alpha_N}(q_N) \end{vmatrix}$$

Second Quantized Description

$$\left[a_{\alpha_1}^{\dagger} \cdots a_{\alpha_N}^{\dagger} |0\rangle \right]$$

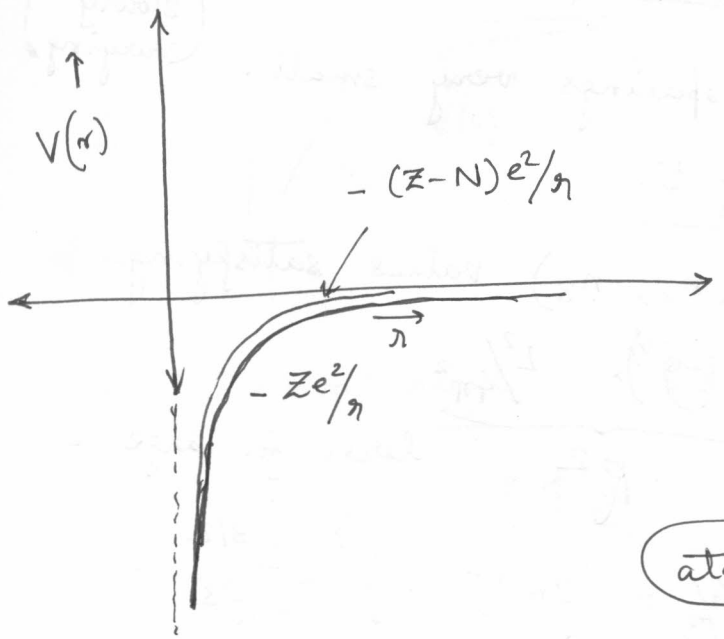
$$a_{\alpha_i} |0\rangle = 0 .$$

$$\{ a_\alpha, a_\beta^{\dagger} \} = \delta_{\alpha\beta}$$

$$\{ a_\alpha, a_\beta \} = 0 = \{ a_\alpha^{\dagger}, a_\beta^{\dagger} \}$$

$$H = \sum_\alpha E_\alpha a_\alpha^{\dagger} a_\alpha$$

- (What do we expect qualitatively ?)



- Additional forces are repulsive
- For small r, $V(r)$ should approach $-\frac{Ze^2}{r}$
- For $r \longrightarrow \infty$, $V(r)$ should approach $-\frac{(Z-N)e^2}{r}$

atomic no. — no. of electrons − 1

$E - E^0_{n\ell}$ → energy levels due to $-Ze^2/r$ potential

- As we increase n & ℓ, how should this behave ??

{ should go up as n goes up for fixed ℓ }

{ should go up as ℓ goes up for fixed n }

Degeneracy (of approximate ground state)

Suppose, (n_0, l_0, m_l, m_s) is the highest filled level.

$(2l_0 + 1) \times 2 \longrightarrow$ 8 states

Suppose, we have ν electrons in this level.

- Degeneracy of atomic ground state = $\binom{8}{\nu} = {}^8C_\nu$.

$\longrightarrow$ COME BACK TO Calculation of $V(r)$

- Thomas - Fermi model
- Free electrons in a periodic box with constant potential V.

$$\psi_{n_1, n_2, n_3}(\vec{r}) = \frac{1}{\sqrt{L^3}} e^{2\pi i/L (n_1 x + n_2 y + n_3 z)}$$

$$E_{n_1, n_2, n_3} = \frac{1}{2m} \frac{4\pi^2}{L^2} (n_1^2 + n_2^2 + n_3^2) + V$$

(slowly varying)

- Large box $\longrightarrow$ level spacings very small.

# of states below energy E.

$= 2 \times$ no. of (n_1, n_2, n_3) values satisfying

$$n_1^2 + n_2^2 + n_3^2 < \underbrace{(2m(E-V)) \times L^2/4\pi^2}_{R^2}$$

large for large L

$$\frac{2 \times \frac{4}{3}\pi R^3}{} = 2 \times \frac{4}{3}\pi \left(2m(E-V)\right)^{3/2} \frac{L^{3/2}}{8\pi^3}.$$

Suppose, you have n electrons inside the box.

$$n = \frac{1}{3\pi^2} L^3 \left\{2m(E_F - V)\right\}^{3/2}.$$

n = # of electrons

If $\rho = n/L^3 \longrightarrow$ no. density,

$$\rho = \frac{1}{3\pi^2} \left\{2m(E_F - V)\right\}^{3/2}.$$

Suppose, $\rho(r)$ = average electron density
$V(r)$ = " potential energy } at r

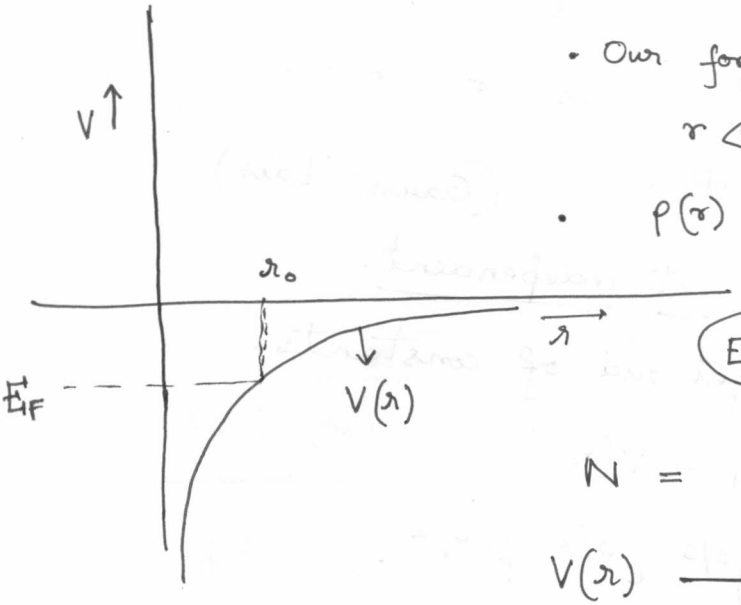
$E_F(r)$ ⇒ defined by

$$\rho(r) = \frac{1}{3\pi^2} \cdot \left\{ 2m \left(E_F(r) - V(r) \right) \right\}^{3/2}$$

- Assumption: Large # of electrons.
- Fermi energy as a function of r.
- For ground state, E_F can't be dependent on r

REASON? (✓)

- Draw up a physical picture



- Our formula is valid only for $r < r_0$.
- $\rho(r)$ must vanish for $r > r_0$

$E_F < 0$.

$$N = 4\pi \int_0^{r_0} r^2 \rho(r)\, dr$$

$V(r) \longrightarrow -\left(\frac{Ze^2}{r} + \text{const.} \right)$ as $r \to 0$

- Functional relationship? $\longrightarrow -\frac{(Z-N)e^2}{r}$ as $r \to \infty$

- $V(r) = -e\phi(r)$ → electrostatic potential

$$\nabla^2 \phi = -4\pi(e\rho) = 4\pi e \rho.$$

$$\Rightarrow \quad \nabla^2 V = -4\pi e^2 \rho(r) \quad \text{(Poisson's equation)}$$

Substitute ρ in terms of V

⇒ Find V. ✓

14.02.2013

Lecture - 11 :

$\rho(r)$: number density of electrons at r

$V(r)$: potential experienced by the electron at r.

$$\rho(r) = \frac{1}{3\pi^2}(2m)^{3/2}\left(\epsilon_F - V(r)\right)^{3/2} \quad \text{for } r < r_0$$

$$= 0 \quad \text{for } r \geq r_0 .$$

- r_0 is defined as the point where $\epsilon_F = V(r)$.
- $\nabla^2 V(r) = -4\pi e^2 \rho(r)$ (Differential equation for $V(r)$.)
- $V(r) \longrightarrow -\frac{Ze^2}{r} + \text{const.}$ as $r \longrightarrow 0$

$$\longrightarrow -\frac{(Z-N)e^2}{r} \quad \text{as} \quad r \longrightarrow \infty .$$

- $N = 4\pi \int_0^{r_0} r^2 \rho(r)\, dr$. (Gauss' Law)
- All the relations are <u>not independent</u>.
- Scale variables to get rid of constants.

Define $\psi = \frac{1}{e}\left(\epsilon_F - V(r)\right)$

$$\rho(r) = \frac{1}{3\pi^2}(2m)^{3/2} e^{3/2} \psi^{3/2} .$$

Substituting in the differential equation, we get –

$$\nabla^2\psi = \frac{4}{3\pi} e^{5/2} (2m)^{3/2} \psi^{3/2} .$$

$$\Downarrow \qquad \longleftrightarrow \qquad \downarrow$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d\psi}{dr}\right) . \qquad \text{Rescale} \quad r = bx, \quad r\psi = Ze\Phi$$

$$= \frac{1}{r}\frac{d^2}{dr^2}(r\psi)$$

$$b = \frac{(3\pi)^{2/3}}{2^{7/3}} Z^{-1/3} \cdot \frac{1}{me^2}$$

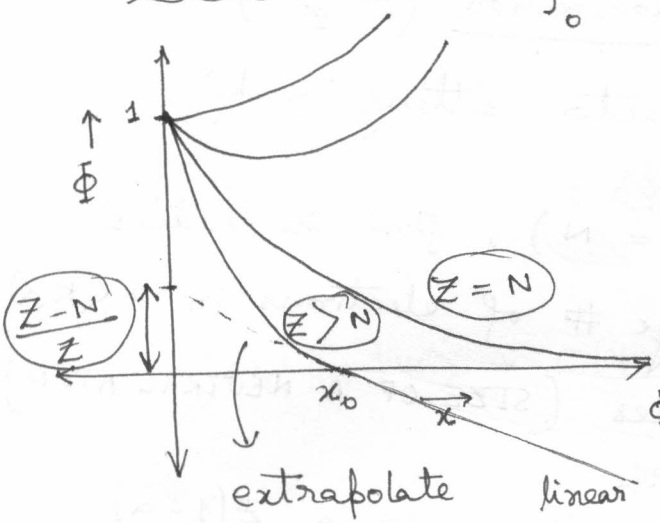
Exercise $\longrightarrow$ Show that

$$\frac{d^2\Phi}{dx^2} = x^{-1/2}\Phi^{3/2} .$$

$\Phi(x) \longrightarrow 1$ as $x \longrightarrow 0$.

$\longrightarrow + \frac{1}{Ze^2}\left(\epsilon_F b x + (Z-N)e^2\right)$ as $x \longrightarrow \infty$.

Show that – $\int_0^{x_0} x^{1/2}\, dx\, \Phi^{3/2} = N/Z$.



$\frac{d^2\Phi}{dx^2} = x^{-1/2}\Phi^{3/2}$, for $x < x_0$

$= 0$, for $x \geq x_0$

$\Phi = C(x - x_0)$

$\Phi'(x_0)$

- Intercept determines what solution you should choose.
- Our method works only for positively charged / neutral atoms.

$-Cx_0 = \frac{Z-N}{Z}$

$\Rightarrow \boxed{-x_0\Phi'(x_0) = \frac{Z-N}{Z}}$

Is the condition $\int_0^{x_0} x^{1/2}\, dx\, \Phi^{3/2} = N/Z$ satisfied ?

$\int_0^{x_0} x^{1/2}\, \Phi^{3/2}\, dx$

$= \int_0^{x_0} x^{1/2}\, dx \cdot x^{1/2}\, \frac{d^2\Phi}{dx^2}$

$= -\int_0^{x_0} dx\, \frac{d\Phi}{dx} + x\, \frac{d\Phi}{dx}\Big|_0^{x_0}$

(Integrating by parts)

$= -\Phi(x_0) + 1 + x_0\Phi'(x_0)$

$\Phi(x_0) = 0$

$= 1 + \frac{N-Z}{Z} = \frac{N}{Z}$. (Proved)

- What's the size of the atom?
- Problem with $x_0 \longrightarrow$ goes to ∞ for neutral atom

$$b = (3\pi)^{2/3} / 2^{7/3} \quad Z^{-1/3} \quad \frac{1}{me^2}.$$

- For fixed fractional ionization $\left(\frac{Z-N}{Z}\right)$,

$r_0 \propto Z^{-1/3}$ (factor sitting in b).

- For a neutral atom $(Z = N)$, find the radius $R(\alpha)$ such that the average # of electrons in $r < R(\alpha)$ is $(1-\alpha)Z$. $\Rightarrow$ Defines (SIZE OF A NEUTRAL ATOM)

$$X(\alpha) = \frac{R(\alpha)}{b} \qquad 4\pi \int_0^{R(\alpha)} r^2 \rho(r)\, dr = Z(1-\alpha)$$

$\Downarrow$ change variables

$$(1-\alpha) = \int_0^{x(\alpha)} x^{1/2}\, dx\, \Phi^{3/2}. \qquad \text{(Exercise)}$$

$$= \int_0^{x(\alpha)} x\, dx\, \frac{d^2\Phi}{dx^2}$$

$$= x(\alpha)\, \Phi'(X(\alpha)) - \underbrace{\Phi(X(\alpha))}_{\text{extra term}} + 1$$

$\Phi \longrightarrow$ solution to a DE with a fixed boundary condition

$X(\alpha) \longrightarrow$ universal function of α.

(α small)

$$R(\alpha) = X(\alpha) \frac{(3\pi)^{2/3}}{2^{7/3}} Z^{-1/3} \cdot \frac{1}{me^2}$$

For higher and higher atomic numbers, radius shrinks.

The Hartree-Fock Approximation

Take any system with Hamiltonian H.

$\langle H \rangle = \langle \psi | H | \psi \rangle$ → trial wavefunction

Extremize (minimize) $\langle H \rangle$ subject to the condition (constraint)

$$\langle \psi | \psi \rangle = 1.$$

$$\delta \langle \psi | H | \psi \rangle + C \, \delta \langle \psi | \psi \rangle = 0$$

C → Lagrange multiplier

$$\Rightarrow \quad \langle \delta\psi | \left(H | \psi \rangle + C | \psi \rangle \right) + \left(\langle \psi | H + \langle \psi | C \right) | \delta\psi \rangle = 0.$$

$|\delta\psi\rangle$ & $\langle \delta\psi |$ → treat as independent ⇝

$$H|\psi\rangle + C|\psi\rangle = 0$$

$C = C^*$

$$\Rightarrow \quad \langle \psi | H + \langle \psi | C = 0$$

$$H|\psi\rangle = -C|\psi\rangle$$ → eigenvalue equation with energy eigenvalue $= -C$.

- Compare <u>variational principle</u> in general.

$$H = -\frac{1}{2m} \sum_i \vec{\nabla}_i^2 - \sum_i \frac{Ze^2}{r_i} + e^2 \sum_{i<j} \frac{1}{r_{ij}}.$$

$\psi(q_1 \cdots q_N)$ → $(\vec{r}_N, m_{SN})$

- Hartree - Fock wavefunction (trial)

$$-\frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(q_1) & \cdots & u_N(q_1) \\ \vdots & & \vdots \\ u_1(q_N) & \cdots & u_N(q_N) \end{vmatrix}$$ → free functions

$$\langle u_\alpha | u_\beta \rangle = \delta_{\alpha\beta}$$ (only constraint)

$a_1^\dagger a_2^\dagger |0\rangle \longrightarrow$ Slater det.

$\frac{1}{2}(a_1^\dagger + a_3^\dagger)(a_2^\dagger + a_4^\dagger)|0\rangle \longrightarrow$ Slater det. ? (YES)

Define $\frac{1}{\sqrt{2}}(a_1 + a_3) = v_1 \qquad \tilde{a}_1^\dagger = \frac{1}{\sqrt{2}}(a_1^\dagger + a_3^\dagger)$

$\frac{1}{\sqrt{2}}(a_2 + a_4) = v_2 \qquad \tilde{a}_2^\dagger = \frac{1}{\sqrt{2}}(a_2^\dagger + a_4^\dagger)$

$a_1^\dagger a_2^\dagger |0\rangle + a_3^\dagger a_4^\dagger |0\rangle \longrightarrow$ {NOT A Slater Determinant}

20.02.2013 Lecture - 12

Hartree - Fock Theory

$$H = -\frac{1}{2m}\sum_i \vec{\nabla}_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} + e^2 \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Ansatz : $\psi = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} u_1(q_1) & \cdots & u_{N+1}(q_N) \\ \vdots & & \vdots \\ u_N(q_1) & \cdots & u_N(q_N) \end{pmatrix}$

$q \equiv (\vec{r}, m_s)$

- Take arbitrary variations within this class of functions and extremize $\langle \psi | H | \psi \rangle$ subject to $\langle u_\alpha | u_\beta \rangle = \delta_{\alpha\beta}$

- $\langle \psi | H | \psi \rangle = ?$

$H = H_1 + H_2$. (H_2 = two-body part)

$$\langle \psi | H_1 | \psi \rangle = \sum_{\alpha=1}^N \int d^3r \sum_{m_s} u_\alpha^*(\vec{r}, m_s) \left(-\frac{\vec{\nabla}_1^2}{2m} - \frac{Ze^2}{r} \right) u_\alpha(\vec{r}, m_s)$$

$$H_1 = \sum_{\alpha\beta} \langle u_\alpha | \hat{h} | u_\beta \rangle a_\alpha^\dagger a_\beta$$

$$\langle 0 | a_N \cdots a_1 \hat{H}_1 a_1^\dagger \cdots a_N^\dagger | 0 \rangle$$

$$\langle \Psi | H_2 | \Psi \rangle = \frac{1}{2} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \int d^3r \int d^3r' \sum_{m_s} \sum_{m_s'} u_\alpha^* (\vec{r}, m_s)$$

$$u_\beta^* (\vec{r}', m_s') \frac{e^2}{|\vec{r} - \vec{r}'|} \left(u_\alpha (\vec{r}, m_s) u_\beta (\vec{r}', m_s') \right.$$

$$\left. - u_\beta (\vec{r}, m_s) u_\alpha (\vec{r}', m_s') \right)$$

$$\left(\hat{H}_2 = \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} V_{\alpha\beta\gamma\delta} a_\beta^\dagger a_\alpha^\dagger a_\gamma a_\delta \right.$$

$$= \int d^3r \, d^3r' \sum_{m_s} \sum_{m_s'} u_\alpha^* (\vec{r}, m_s) \times$$

$$u_\beta^* (\vec{r}', m_s') \frac{e^2}{|\vec{r} - \vec{r}'|} u_\gamma (\vec{r}, m_s) u_\delta (\vec{r}', m_s') \Big)$$

$$\delta \langle \Psi | H | \Psi \rangle$$

$$= \int d^3r \sum_{m_s} \delta u_\alpha^* (\vec{r}, m_s) \left[\left(-\tfrac{1}{2m} \vec{\nabla}^2 - Ze^2/r \right) u_\alpha (\vec{r}, m_s) \right.$$

$$+ \int d^3r' \sum_{m_s'} u_\beta^* (\vec{r}', m_s') \times \left(\frac{e^2}{|\vec{r} - \vec{r}'|} \times \right.$$

$$\left. \left. u_\alpha (\vec{r}, m_s) u_\beta (\vec{r}', m_s') - u_\beta (\vec{r}, m_s) u_\alpha (\vec{r}', m_s') \right\} \right]$$

$$+ \text{c.c.} \Rightarrow \underbrace{e_{\alpha\beta} \, \delta \langle u_\alpha | u_\beta \rangle}$$ (repeated indices summed over)

$$= \int d^3r \sum_{m_s} \delta u_\alpha^* (\vec{r}) e_{\alpha\beta} u_\beta (\vec{r}) +$$

$$(\vec{r}) \to (\vec{r}, m_s) \quad \int d^3r \sum_{m_s} \delta u_\alpha (\vec{r}) e_{\beta\alpha} u_\beta^* (\vec{r})$$

$$\delta \langle \Psi | H | \Psi \rangle - e_{\alpha\beta} \, \delta \langle u_\alpha | u_\beta \rangle = 0 .$$

$$e_{\alpha\beta} u_\beta (\vec{r}, m_s) = \left(-\frac{1}{2m} \vec{\nabla}_r^2 - \frac{Ze^2}{r} \right) u_\alpha (\vec{r}, m_s) +$$

$$e^2 \int d^3r' \sum_{m_s'} \frac{e^2}{|\vec{r} - \vec{r}'|} u_\beta^* (\vec{r}', m_s') \times$$

$$u_\beta (\vec{r}', m_s') u_\alpha (\vec{r}, m_s)$$

$$- e^2 \int d^3r' \sum_{m_s'} \frac{e^2}{|\vec{r} - \vec{r}'|} u_\beta^* (\vec{r}', m_s') u_\alpha (\vec{r}', m_s')$$

$$u_\beta (\vec{r}, m_s)$$

$\underline{e_{\alpha\beta} = e^*_{\beta\alpha}}$ (so that c.c. equation is consistent)

$\Rightarrow$ 'e' is hermitian

$$\psi = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} u_1(q_1) & \cdots & u_N(q_1) \\ \vdots & & \vdots \\ u_1(q_N) & \cdots & u_N(q_N) \end{pmatrix}$$

$\tilde{\psi} = \psi$

$v_r(q) = W_{rs}\, u_s(q)$ $\qquad \tilde{\psi} = \frac{1}{\sqrt{N!}} \begin{pmatrix} v_1(q_1) & \cdots & v_N(q_1) \\ \vdots & & \vdots \\ v_1(q_N) & \cdots & v_N(q_N) \end{pmatrix}$

W : SU(N) matrix

Substitute $u_\beta = W_{\beta r} v_r$ in the $e_{\alpha\beta}$ equation. $\quad e \longrightarrow (W^{-1} e W)$

v's satisfy same equation with $e \longrightarrow \tilde{e}$.

. We'll look for solutions in that basis where e is 'diagonal'. $\qquad e_{\alpha\beta} = e_\alpha \delta_{\alpha\beta}$

$$V^d(\vec{r}) = e^2 \int d^3r' \sum_{m_s'} \frac{1}{|\vec{r} - \vec{r}'|} u^*_\beta(\vec{r}', m_s') u_\beta(\vec{r}', m_s')$$

(function) (Direct interaction)

$$\hat{V}^{ex} \neq f(\vec{r}, m_s) = -\int d^3r' \sum_{m_s'} \frac{e^2}{|\vec{r} - \vec{r}'|} u^*_\beta(\vec{r}', m_s') \times f(\vec{r}', m_s')\, u_\beta(\vec{r}, m_s).$$

(operator) (NON-LOCAL OPERATOR)

for a fixed set of u's

$$\left(-\frac{1}{2m}\vec{\nabla}_r^2 - \frac{Ze^2}{r} + V^d(\vec{r}) + \hat{V}^{ex}\right) u_\alpha(\vec{r}, m_s)$$

$$= \epsilon_\alpha u_\alpha(\vec{r}, m_s)$$

NOT A LINEAR OPERATOR + Non-local . . .

- Self-consistent field approximation.

21.02.2013

Lecture - 13

- No central field approximation done!

$$\left[-\frac{1}{2m}\vec{\nabla}_r^2 + V^d(\vec{r}) - \frac{Ze^2}{r} - \hat{V}^{ex}\right] u_\alpha(\vec{r}, \tilde{m}_s)$$

change in convention

$$= \epsilon_\alpha u_\alpha(\vec{r}, \tilde{m}_s)$$

spin variable

$u_\alpha(\vec{r}, \tilde{m}_s)$ contains m_s information.

$$V^d(\vec{r}) = \sum_\alpha \int d^3r' \sum_{\tilde{m}_s'} u_\alpha^*(\vec{r}', \tilde{m}_s') \frac{e^2}{|\vec{r} - \vec{r}'|} u_\alpha(\vec{r}', \tilde{m}_s')$$

$$\hat{V}^{ex} f(\vec{r}, \tilde{m}_s) = \sum_\alpha \int d^3r' \sum_{\tilde{m}_s'} u_\alpha^*(\vec{r}', \tilde{m}_s') \frac{e^2}{|\vec{r} - \vec{r}'|} \times f(\vec{r}', \tilde{m}_s') u_\alpha(\vec{r}, \tilde{m}_s)$$

$$\langle E \rangle = \langle \Psi | H | \Psi \rangle = \sum_{\alpha=1}^{N} I_\alpha + \frac{1}{2} \sum_{\alpha \neq \beta} (J_{\alpha\beta} - K_{\alpha\beta})$$

$$I_\alpha = \int d^3r \sum_{\tilde{m}_s} u_\alpha^*(\vec{r}, \tilde{m}_s) \left(-\frac{1}{2m}\vec{\nabla}_r^2 - \frac{Ze^2}{r}\right) u_\alpha(\vec{r}, \tilde{m}_s)$$

$$J_{\alpha\beta} = e^2 \int d^3r \int d^3r' \sum_{\tilde{m}_s, \tilde{m}_s'} u_\alpha^*(\vec{r}, \tilde{m}_s) u_\beta^*(\vec{r}', \tilde{m}_s') \times \frac{1}{|\vec{r} - \vec{r}'|} u_\alpha(\vec{r}, \tilde{m}_s) u_\beta(\vec{r}', \tilde{m}_s')$$

$$K_{\alpha\beta} = e^2 \int d^3r \int d^3r' \sum_{\tilde{m}_s, \tilde{m}_s'} u_\alpha^*(\vec{r}, \tilde{m}_s) u_\beta^*(\vec{r}', \tilde{m}_s') \times \frac{1}{|\vec{r} - \vec{r}'|} u_\beta(\vec{r}, \tilde{m}_s) u_\alpha(\vec{r}', \tilde{m}_s')$$

① $\sum_{\alpha=1}^{N} e_\alpha = \sum_{\alpha=1}^{N} I_\alpha + \sum_{\alpha \neq \beta} (J_{\alpha\beta} - K_{\alpha\beta})$.

② If $e_\alpha \neq e_\beta$, then $\langle u_\alpha | u_\beta \rangle = 0$.

$\langle u_\alpha |$ Hartree Fock eq. (l.h.s.) $\rangle$

$= e_\alpha \langle u_\beta | u_\alpha \rangle$

Take $\beta \leftrightarrow \alpha$ equation $= e_\beta \langle u_\alpha | u_\beta \rangle$

$\Rightarrow$ (Take complex conjugate) $\rightarrow \langle u_\alpha | u_\beta \rangle = 0$ for $\alpha \neq \beta$.

③ Suppose, $u_N' \neq u_1 \ldots u_N$ & satisfies

$$\left(-\frac{1}{2m} \vec{\nabla}_r^2 - \frac{Ze^2}{r} + V^d(\vec{r}) - \hat{V}^{ex} \right) u_N' = e_N' u_N' \quad (\vec{r}, \tilde{m}_s)$$

Hermitian

$\langle u_N' | u_\alpha \rangle = 0 \quad \forall \quad \alpha = 1(1) N$.

$$\phi(q_1, \ldots q_N) = \det \begin{vmatrix} u_1(q_1) & \cdots & u_{N-1}(q_1) & u_N'(q_1) \\ \vdots & & \vdots & \vdots \\ u_1(q_N) & \cdots & u_{N-1}(q_N) & u_N'(q_N) \end{vmatrix}$$

Replace any column by a new one $\rightarrow$ "excited state"

$\Rightarrow \langle \phi | \Psi \rangle = 0$.

Exercise To show that $\langle \phi | H | \Psi \rangle = 0$.

(Note : $|\Psi\rangle$ is not an eigenstate of H)

- Central fields.

Suppose, we begin with central V^d & V^{ex}.

$\Rightarrow u_\alpha(\vec{r}, \tilde{m}_s) = u_{n l m_l m_s}(\vec{r}, \tilde{m}_s)$

$= R_{nl}(r) \, \delta_{m_s \tilde{m}_s} \, Y_{l m_l}(\theta, \phi)$

Result : The new V^d & $V^{ex.}$ are central if all m_l, m_s values for given l, n are either fully occupied or fully unoccupied. (NOBLE GASES ...)

Direct : $\sum_d \longrightarrow$ fix n, l sum over m_l, m_s

$$\tilde{V}^d_{(nl)} = \sum_{m_l, m_s} \int d^3r' \sum_{\tilde{m}_s'} R^*_{nl}(r')\, \delta_{m_s \tilde{m}_s'}\, Y^*_{lm_l}(\theta', \phi') \frac{e^2}{|\vec{r} - \vec{r}'|} R_{nl}(r')\, \delta_{m_s \tilde{m}_s'} \times Y_{lm_l}(\theta', \phi')$$

~~$= 2 \int d^3r'$~~

Now $\sum_{m_l=-l}^{l} Y^*_{lm_l}(\theta', \phi')\, Y_{lm_l}(\theta', \phi') = \frac{(2l+1)}{4\pi}$

$$V^d_{(nl)} = 2 \int r'^2 dr' \sin\theta' d\theta' d\phi' \times (2l+1)\, e^2 \times R^*_{nl}(r')\, R_{nl}(r') \times \frac{1}{|\vec{r} - \vec{r}'|} \times \frac{1}{4\pi}.$$

$= ?$

$$\int \sin\theta' d\theta' d\phi' \frac{1}{|\vec{r} - \vec{r}'|} = \frac{4\pi}{r_>}$$

$\left\{ \hookrightarrow \begin{array}{l} r \text{ for } r > r' \\ r' \text{ " } r < r' \end{array} \right\}$

$$V^d_{(nl)} = 2(2l+1)e^2 \int_0^\infty r'^2 dr'\, R^*_{nl}(r')\, R_{nl}(r') \cdot \frac{1}{r_>}$$

$$\left[\frac{1}{r} \int_0^r r'^2 dr' \left| R_{nl}(r') \right|^2 + \int_r^\infty r'^2 dr' \left| R_{nl}(r) \right|^2 \frac{1}{r'} \right]$$

$$\overset{?}{\sum_{m_s} \sum_{\tilde{m}_s'}} \delta_{m_s \tilde{m}_s'}\, \delta_{\tilde{m}_s' m_s}$$

Direct term $\longrightarrow$ no spin dependence.

$V^{ex}_{(nl)}$ $f(\vec{r}, \tilde{m}_s)$

$\Downarrow$ choose a basis such that

$$f = \delta_{\hat{m}_s \tilde{m}_s} \; F(r) \; Y_{\hat{l}\hat{m}_l}(\theta, \phi)$$

To prove : $V^{ex}_{(nl)} \; f(\vec{r}, \tilde{m}_s)$

$$= G(r) \; \delta_{\hat{m}_s \tilde{m}_s} \; Y_{\hat{l}\hat{m}_l}(\theta, \phi)$$

(Dependence on $\hat{m}_s$, θ, ϕ don't change)

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Lecture – 14

$$V^{ex}_{(nl)} f \bullet (\vec{r}, \tilde{m}_s) = \sum_{\alpha} \int d^3r' \sum_{\tilde{m}_s'} u^*_\alpha (\vec{r}', \tilde{m}_s') \times$$

$\{$ fixed $n,l\}$ $\swarrow$

$$\frac{e^2}{|\vec{r} - \vec{r}'|} f(\vec{r}', \tilde{m}_s') \; u_\alpha (\vec{r}, \tilde{m}_s)$$

$\Rightarrow$ $V^{ex}_{(nl)} f(\vec{r}, \tilde{m}_s)$ $\longrightarrow$ what do we mean by the statement $V^{ex}_{(nl)}$ is spherically symmetric ?

$= \sum_{m_l, m_s}$?

Suppose, $f(\vec{r}, \tilde{m}_s) = F(r) \; Y_{\hat{l}\hat{m}_l}(\theta, \phi) \; \delta_{\tilde{m}_s \hat{m}_s}$

We want to prove, $V^{ex}_{(nl)} f = G(r) \; Y_{\hat{l}\hat{m}_l}(\theta, \phi) \; \delta_{\tilde{m}_s \hat{m}_s}$.

$$V^{ex}_{(nl)} f = \sum_{m_l, m_s} \int d^3r' \sum_{\tilde{m}_s'} \Big\{ R^*_{nl}(r') \; \delta_{m_s', \tilde{m}_s'} \times$$

$$Y^*_{l m_l}(\theta', \phi') \Big\} F(r') \frac{e^2}{|\vec{r} - \vec{r}'|} \; \delta_{\hat{m}_s, \tilde{m}_s'} \; Y_{\hat{l}\hat{m}_l}(\theta', \phi')$$

$$\{\delta_{m_s', \tilde{m}_s} \; Y_{l m_l}(\theta, \phi) \; R_{nl}(r)\}$$

- Spin sum gives $\delta_{\tilde{m}_s \hat{m}_s}$.
- Expand $\frac{1}{|\vec{r} - \vec{r}'|}$ in spherical harmonics.

$$e^2 \sum_{l'=0}^{\infty} \sum_{m_l' = -l'}^{l'} \frac{4\pi}{2l' + 1} \frac{(r_<)^{l'}}{(r_>)^{l'+1}} \; Y_{l'm_l'}(\theta, \phi) \times$$

$$Y^*_{l'm_l'}(\theta', \phi')$$

$$\int \sin\theta' \, d\theta' \, d\phi' \; Y^*_{L,m_L}(\theta',\phi') \; Y^*_{l'm_{l'}}(\theta',\phi') \; Y_{\hat{l}\hat{m}_l}(\theta',\phi')$$

$$= K^*(\hat{l}, l^*, l') \begin{pmatrix} \hat{l} & l & l' \\ \hat{m}_l & m_L & m_{l'} \end{pmatrix}^* \times 1 .$$

↓ is calculable

- Use the orthonormality of Clebsch-Gordon coefficients and work this out.

$$Y_{L,m_L}(\theta,\phi) \; Y_{l'm_{l'}}(\theta,\phi) = \sum_L K(L, l', l) \; Y_{LM}(\theta,\phi) ,$$

(l, l', L) $\quad C^{L\,l\,l'}_{M\,l\,l'\,M\,m_{l'}}$

Homework 4

- Remember : $\langle \psi | H | \psi \rangle = \sum_{\alpha=1}^{N} I_\alpha + \frac{1}{2} \sum_{\alpha,\beta=1}^{N} (J_{\alpha\beta} - K_{\alpha\beta})$

$$\neq \sum_\alpha e_\alpha .$$

$$e_\alpha = I_\alpha + \sum_\beta (J_{\alpha\beta} - K_{\alpha\beta})$$

factor of 2 mismatch

$$\therefore \; e_\alpha = \sum_\alpha I_\alpha + \sum_{\alpha,\beta=1}^{N} (J_{\alpha\beta} - K_{\alpha\beta})$$

→ Is there any interpretation of e_α ?

(Yes, under a certain approximation)

$$E_N = \sum_{\alpha=1}^{N} I_\alpha + \frac{1}{2} \sum_{\alpha,\beta=1}^{N} (J_{\alpha\beta} - K_{\alpha\beta})$$

$$E_{N-1} = \sum_{\alpha=1}^{N-1} I_\alpha + \frac{1}{2} \sum_{\alpha,\beta=1}^{N-1} (J_{\alpha\beta} - K_{\alpha\beta})$$

Let's calculate $E_N - E_{N-1}$ (Koopman's Theorem)

$$= I_N + \sum_{\beta=1}^{N-1} (J_{N\beta} - K_{N\beta})$$

(under the approximation that other electrons remain in same energy)

$$= e_N \; (\text{Ionization energy})$$

- The Hartree Approximation

$$\psi^d u_\beta(\vec{r}, \tilde{m}_s) = \sum_\alpha \int d^3r' \sum_{\tilde{m}_s'} u_\alpha^*(\vec{r}', \tilde{m}_s') \frac{e^2}{|\vec{r}-\vec{r}'|} u_\alpha(\vec{r}', \tilde{m}_s') \, u_\beta(\vec{r}, \tilde{m}_s)$$

$$\psi^{ex} u_\beta(\vec{r}, \tilde{m}_s) = \sum_\alpha \int d^3r' \sum_{\tilde{m}_s'} u_\alpha^*(\vec{r}', \tilde{m}_s') \frac{e^2}{|\vec{r}-\vec{r}'|} u_\beta(\vec{r}', \tilde{m}_s') \, u_\alpha(\vec{r}, \tilde{m}_s)$$

For $\alpha = \beta$, ψ^d & ψ^{ex} cancel

- In Hartree approximation, we drop $\alpha \neq \beta$ terms
- Comes from a different starting pt.
  (Extremize with product wavefunctions)
- Two products can't have same u's.
  (IMPOSE BY HAND!)
- Replace $(\psi^d - \psi^{ex}) u_\beta$ by

$$\sum_{\alpha \neq \beta} \left\{ \int d^3r' \sum_{\tilde{m}_s'} u_\alpha^*(\vec{r}, \tilde{m}_s') \frac{e^2}{|\vec{r}-\vec{r}'|} u_\alpha(\vec{r}', \tilde{m}_s') \right\} \times u_\beta(\vec{r}, \tilde{m}_s) .$$

- A simple, linear operator acts on u_β.

Electronic structures

(n, ℓ)

H $1s$ ($n \to 1$, $\ell = 0$)

He $1s^2$

Li $1s^2 2s^1$

Be $1s^2 2s^2$

⋮ ⋮

- Issue of taking spherical averaging.

How to go Beyond Hartree-Fock ??

$$H_{HF} = \sum_{i=1}^{N} \left(-\frac{1}{2m} \vec{\nabla}_i^2 - \frac{Ze^2}{r_i} + \psi_i^d - \hat{\psi}_i^{ex} \right)$$

(Hartree-Fock operator)

Define $H_1 = H - H_{HF}$. (correlation effects)

$$H = H_{HF} + H_1 .$$

$$\Psi = \det \begin{pmatrix} u_1(\vec{r}_1, \tilde{m}_{s_1}) & \cdots & u_N(\vec{r}_1, \tilde{m}_{s_N}) \\ \vdots & & \vdots \\ u_1(\vec{r}_N, \tilde{m}_{s_N}) & \cdots & u_N(\vec{r}_N, \tilde{m}_{s_N}) \end{pmatrix}$$

$$H_{HF} |\Psi\rangle = \sum_{\alpha=1}^{N} e_\alpha |\Psi\rangle$$

- Calculation of the correction (upto first order)

$$\langle \Psi | H_1 | \Psi \rangle$$

Total energy to first order —

$$= \sum_{\alpha=1}^{N} e_\alpha + \langle \Psi | H_1 | \Psi \rangle$$

$$= \langle \Psi | H_{HF} | \Psi \rangle + \langle \Psi | H_1 | \Psi \rangle$$

$$= \langle \Psi | H | \Psi \rangle = E_{HF} \quad \text{(correct result !)}$$

- 2^{nd} order onwards $\longrightarrow$ Beyond Hartree-Fock.
- Degenerate Perturbation Theory ?
- Choice of convenient basis ?

$\vec{L} = \sum_i \vec{L}_i$ $\quad$ $\vec{L}^2, \vec{S}^2, L_z, S_z$

$\vec{S} = \sum_i \vec{S}_i$ $\quad$ ✓

- We can do non-degenerate pert. theory.

electronic structure

He $\quad (1s^2) \quad {}^1S$

1 combination

$2(2l+1)C_{2(2l+1)}$

terms

^{2S+1}L

$\downarrow$

S, P, D, F, ...

Hund's Rule

(empirical)

NEXT $\rightarrow$ **Molecules**