Physics 531: Lecture 13 – ~~Hartree-Fock~~

Hartree-Fock Equations

How do we find the effective mean field? Firstly, this will depend on the state of the electrons, so no single effective potential can be used to find all multielectron states. As a first approximation we will assume that the multielectron orbital is described by a single Slater determinant, constructed from "spin orbitals" $\{\phi_\alpha = \psi_{n,m}(\vec{r}) s\}$. Then we will use the variational principle to find these orbitals.

Example: Two electrons $\Psi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_\alpha(1) & \phi_\beta(1) \\ \phi_\alpha(2) & \phi_\beta(2) \end{vmatrix}$

Employ constraint that $\langle \phi_\alpha | \phi_\beta \rangle = \delta_{\alpha\beta}$

$$\hat{H} = \sum_i \underbrace{\left(\frac{\vec{p}_i^{\,2}}{2} - \frac{Z}{r_i} \right)}_{H_0(i)} + \sum_{i<j} \frac{1}{r_{ij}}$$

$$\Rightarrow E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \langle \phi_\alpha(1) | \hat{H}_0(1) | \phi_\alpha(1) \rangle + \langle \phi_\beta(1) | \hat{H}_0(1) | \phi_\beta(1) \rangle$$

$$+ \langle \phi_\alpha(1)\phi_\beta(2) | \frac{1}{r_{12}} | \phi_\alpha(1)\phi_\beta(2) \rangle$$

$$- \langle \phi_\alpha(1)\phi_\beta(2) | \frac{1}{r_{12}} | \phi_\alpha(2)\phi_\beta(1) \rangle$$

$$\Rightarrow E[\Psi] = \sum_{\lambda=\alpha,\beta} E_\lambda^{(0)} + \frac{1}{2}\sum'_{\lambda,\mu=\alpha,\beta} \left(J_{\lambda\mu} - K_{\lambda\mu}\right)$$

where $J_{\alpha\beta} = \langle \phi_\alpha(1)\phi_\beta(2) \mid \frac{1}{r_{12}} \mid \phi_\alpha(1)\phi_\beta(2)\rangle$

$$= \int d^3x_1 d^3x_2 \; |u_\alpha(\vec{r}_1)|^2 \, |u_\beta(\vec{r}_2)|^2 \, \frac{1}{r_{12}}$$

$$K_{\alpha\beta} = \langle \phi_\alpha(1)\phi_\beta(2) \mid \frac{1}{r_{12}} \mid \phi_\alpha(2)\phi_\beta(1)\rangle$$

$$= \delta_{m_{s_\alpha} m_{s_\beta}} \int d^3x_1 d^3x_2 \, (u_\alpha(\vec{r}_1) u_\beta(\vec{r}_2))^* \frac{1}{r_{12}} (u_\alpha(\vec{r}_2) u_\beta(\vec{r}_1))$$

We seek to minimize this functional subject to the constraint $\langle \phi_\lambda | \phi_\mu \rangle = \delta_{\lambda\mu}$ $\Rightarrow$ Use Lagrange multiplier $\epsilon_{\lambda\mu}$

$$\Gamma[\Psi] = E[\Psi] - \sum_{\lambda,\mu} \epsilon_{\lambda\mu} \langle \phi_\lambda | \phi_\mu \rangle$$

$$\delta\Gamma = 0 \Rightarrow \delta E[\Psi] - \sum_{\lambda\mu} \epsilon_{\lambda,\mu} \, \delta\langle \phi_\lambda | \phi_\mu \rangle = 0$$

Can It follows that $\epsilon_{\lambda\mu} = \epsilon^*_{\mu\lambda}$

Thus the matrix of Lagrange Multipliers is Hermitian $\Rightarrow$ Can diagonalize and thus always choose spin orbitals to be orthogonal consistent with constraints

(Note: Orthogonal spin-orbital may not be for central potential)

Take functional derivative:

$$\frac{\delta F}{\delta \phi_\alpha^*} = 0 \Rightarrow \left\{ -\frac{1}{2}\nabla_{r_1}^2 - \frac{Z}{r_1} + \int d^3x_2 \, |u_\beta(\vec{r}_2)|^2 \frac{1}{r_{12}} \right\} \phi_\alpha(\vec{r}_1)$$

$$- \left(\delta_{m_s^\alpha m_s^\beta} \int d^3x_2 \, u_\beta^*(\vec{r}_2) u_\alpha(\vec{r}_2) \frac{1}{r_{12}} \right) \phi_\beta(\vec{r}_1)$$

$$= \epsilon_\alpha \phi_\alpha(\vec{r}_1)$$

$$\frac{\delta F}{\delta \phi_\beta^*} = 0 \Rightarrow \left\{ -\frac{1}{2}\nabla_{r_1}^2 - \frac{Z}{r_1} + \int d^3x_2 \, |u_\alpha(\vec{r}_2)|^2 \frac{1}{r_{12}} \right\} \phi_\beta(\vec{r}_1)$$

$$- \left(\delta_{m_s^\alpha m_s^\beta} \int d^3x_2 \, u_\alpha^*(\vec{r}_2) u_\beta(\vec{r}_2) \frac{1}{r_{12}} 3 \right) \phi_\alpha(\vec{r}_1)$$

$$= \epsilon_\beta \phi_\beta(\vec{r}_1)$$

Generally

$$H_0^{(1)} u_\lambda(\vec{r}_1) + \left(\sum_{\mu \neq \lambda} \int |u_\mu(\vec{r}_2)|^2 \frac{1}{r_{12}} d^3x_2 \right) u_\lambda(\vec{r}_1)$$

$$- \sum_{\mu \neq \lambda} \left[\left(\int u_\mu^*(\vec{r}_2) u_\lambda(\vec{r}_2) \frac{1}{r_{12}} d^3x_2 \right) u_\mu(\vec{r}_1) \right] \delta_{m_s^\lambda m_s^\mu}$$

$$= \epsilon_\lambda u_\lambda(\vec{r}_1)$$

Coupled set of integro-differential equation

for spin orbitals $\{\phi_\alpha\}$

Interpretation

$\left[\int d^3x_2 \, |\psi_\mu(\vec{r}_2)|^2 \, \frac{1}{r_{12}}\right]$ = Repulsive energy of electron 2 acting on 1, averaged over the orbital $\psi_\mu(\vec{r})$

$-\left[\delta_{m_s^\mu m_s^\lambda} \int \psi_\mu^*(\vec{r}_2)\, \psi_\lambda(\vec{r}_2)\, \frac{1}{r_{12}}\right]$ = exchange effect

= Negative contribution due to the fact that electrons in the same spin state cannot be at the same position = "Fermi Hole"

As an operator equation

$$\underbrace{\left[-\frac{\vec{\nabla}_i^2}{2} - \frac{Z}{r_i} + \hat{V}^{direct}(\vec{r}_i) + \hat{V}^{exchg}(i)\right]}_{\hat{H}_{HF}} |\phi_\lambda(i)\rangle = \epsilon_\lambda |\phi_\lambda(i)\rangle$$

$$\hat{V}^{direct}(\vec{r}_i) = \sum_\mu V_\mu^{direct}(\vec{r}_i), \quad V_\mu^{direct} = \int d^3x_j \, |\psi_\mu(\vec{r}_j)|^2 \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\hat{V}^{ex}(i) = \sum_\mu \hat{V}_\mu^{ex}(i), \quad \hat{V}_\mu^{ex}(i)\,|\phi_\lambda(i)\rangle$$

$$= \delta_{m_s^\mu m_s^\lambda}\left[\int d^3x_j \, \frac{\psi_\mu^*(\vec{r}_i)\,\psi_\lambda(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|}\right] |\phi_\mu(i)\rangle$$

Properties of Hartree-Fock solutions

- Interpretation of eigenvalues ϵ_λ

$$E = \sum_\lambda E_\lambda^{(0)} + \sum_{\mu<\lambda} \left(J(\mu,\lambda) - K(\mu,\lambda) \right)$$

Now, if we take H-F equation and project on $\langle \phi_\lambda |$

$$\Rightarrow E_\lambda^{(0)} + \sum_\mu \left(J(\mu,\lambda) - K(\mu,\lambda) \right) = \epsilon_\lambda$$

$$\therefore \sum_\lambda \epsilon_\lambda = \sum_\lambda E_\lambda^{(0)} + \sum_{\lambda,\mu} \left(J(\mu,\lambda) - K(\mu,\lambda) \right)$$

$$= \sum_\lambda E_\lambda^{(0)} + \frac{1}{2} \sum_{\lambda,\mu} \left(J(\mu,\lambda) - K(\mu,\lambda) \right)$$

$$+ E$$

- Thus $E \neq$ Sum of individual electron energies.

they are correlated

- However ϵ_λ = Energy difference between $N+1$ electrons and N electrons in the Hartree-Fock solution when the $(N+1)^{st}$ is in orbital $|\phi_\lambda\rangle$

$\Rightarrow$ Ionization energy (in this approx.)

Proof:

$$E_{N+1} = \underbrace{\sum_{\alpha=1}^{N} E_\alpha^{(0)} + \sum_{\alpha<\beta}^{N} (J_{\alpha\beta} - K_{\alpha\beta})}_{E_N} + E_\lambda^{(0)} + \sum_{\beta}^{N} (J_{\lambda\beta} - K_{\lambda\beta})$$

$$\therefore E_{N+1} - E_N = E_\lambda^{(0)} + \sum_{\beta}^{N} (J_{\lambda\beta} - K_{\lambda\beta}) = \epsilon_\lambda$$

This is a crude approximation, since removing an electron will change the mean field equations.

- For a closed shell, the H-F solutions are those of central field.

Closed shell $\Rightarrow$ 2 spin states for every orbital

Let N = # of spatial orbitals $= 2l+1$

$$\Rightarrow \hat{H}_{HF} = \hat{H}_0 + \sum_{\alpha}^{N} (2V_\alpha^{direct} - V_\alpha^{exchange})$$

↑ both spin up/down contribute

Eigenenergy:

$$E = 2\sum_{\alpha}^{N} E_\alpha^{(0)} + \sum_{\alpha\beta}^{N} (2J_{\alpha\beta} - K_{\alpha\beta})$$

$$= 2\sum_{\alpha}^{N} \epsilon_\alpha - \sum_{\alpha\beta}^{N} (2J_{\alpha\beta} - K_{\alpha\beta})$$

Assume orbital for spherical symmetry

$$U(\vec{r}) = R_{nl}(r)\, Y_{lm}(\theta, \phi)$$

⇒ Sum over spatial orbitals in a closed shell = Sum over m_ℓ values in $2\ell+1$

$$\sum_m^{\text{occ}} \hat{V}_m^{\text{direct}} = \sum_{m=-\ell}^{\ell} \int |\psi_{n\ell m}(\vec{r})|^2 \frac{1}{r_{12}}$$

$$= \int r_2^2 dr_2 \frac{R_{n\ell}(r_2)}{r_{12}} \left[\sum_{m_\ell=-\ell}^{\ell} |Y_{\ell,m}(\theta_2,\phi_2)|^2 d\Omega_2 \right]$$

Use addition theorem

$$\Rightarrow \sum_m^{\text{occ}} \hat{V}_m^{\text{direct}} = \frac{(2\ell+1)}{\sqrt{4\pi}} \int \frac{(r_2 R_{n\ell}(r_2))^2}{r_>} dr_2$$

For r inside closed shell $r_> = r_2 \Rightarrow$ constant

For r outside $r_> = r_1 \Rightarrow$ Like uniformly spherical distribution

With more elbow grease, can show exchange term is spherically symmetric

⇒ Self-consistent solutions of Hartree-Fock for a closed shell are made of central-field orbitals