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Tutorial 5

Kumar Satyam 200050064

1) for n electron atom with ~~a~~ nuclear charge Z

$$\hat{H} = \frac{-\hbar^2}{2m_n}\nabla_n^2 - \sum_{i=1}^{n} \frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{1}{4\pi\epsilon_0}\sum_{i=1}^{n}\frac{Z_n e^2}{r_i} + \frac{1}{4\pi\epsilon_0}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{e^2}{r_{ij}}$$

$$\therefore \hat{H} = \hat{H}_n + \sum_{i=1}^{n}\hat{H}_{e_i} - \frac{Z_n e^2}{4\pi\epsilon_0}\sum_{i=1}^{n}\frac{1}{r_i} + \frac{e^2}{4\pi\epsilon_0}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\frac{1}{r_{ij}}$$

2)

Orbital Approximation is Just approximating the Total ψ which is function of $(r_1\theta_1\phi_1\, r_2\theta_2\phi_2 \ldots r_n\theta_n\phi_n)$ as product of n, one electron wavefunctions $\psi_{ie}(r_i\theta_i\phi_i)$ just for getting a first hand approach to solve the ψ.

It doesn't include neglecting of interelectronic repulsion as still for $2e^-$ system the TDSE can be written with Orbital Approximation as.

$$\hat{H}_e\Psi_T = \hat{H}_1\psi_{1e}(r_1\theta_1\phi_1)\psi_{2e}(r_2\theta_2\phi_2) + \hat{H}_2\psi_{1e}(r_1\theta_1\phi_1)\psi_2(r_2\theta_2\phi_2) + \frac{e^2}{4\pi\epsilon_0}\psi_{1e}(r_1\theta_1\phi_1)\psi_{2e}(r_2\theta_2\phi_2)$$

Here $\hat{H}_1 = \frac{-\hbar^2}{2m_{e_1}}\nabla_1^2 - \frac{QZ_n e^2}{r_1}$

3) $\alpha(1)\beta(2)$ & $\alpha(2)\beta(1)$ spin functions for $2e^-$ system ain't acceptable because they doesn't fit into the exchange operator thus are distinguishable but being fermions, electrons are indistinguishable.

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C

$$\psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 2s(1)\alpha(1) & 3s(1)\beta(1) \\ 2s(2)\alpha(2) & 3s(2)\beta(2) \end{vmatrix}$$

Changing (1,2) to (2,1) in ψ'

$$\psi' = \frac{1}{\sqrt{2}} \begin{vmatrix} 2s(2)\alpha(2) & 3s(2)\beta(2) \\ 2s(1)\alpha(1) & 3s(1)\beta(1) \end{vmatrix}$$

$$= -\frac{1}{\sqrt{2}} \begin{vmatrix} 2s(1)\alpha(1) & 3s(1)\beta(1) \\ 2s(2)\alpha(2) & 3s(2)\beta(2) \end{vmatrix}$$

$\therefore \psi'(2,1) = -\psi(1,2) \quad \therefore |\psi(2,1)|^2 = |\psi(1,2)|^2$

Thus force its a valid wavefunction with He in one of its excited state.

$$\text{Here } \psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 2s(1)\alpha(1) & 3s(1)\beta(1) \\ 2s(2)\alpha(2) & 3s(2)\beta(2) \end{vmatrix}$$

Here α(●) & β(●) are specifically ~~added~~ attached to the 2s & 3s spatial orbits resp & since spatial & spin functions must be independent

And even it comes out that they are one part of the actual wave function which is sum / difference of 2 separate slaters determinants having (α & β) associated with (2s & 3s) and (3s & 2s) resp in each determinant.

4) Let assume Given Slater's determinant, He has e in 2s & 3s orbitals each

$\therefore$ Spatial part can be $\frac{1}{\sqrt{2}}\left(2s(1)\,3s(2) + 2s(2)\,3s(1)\right)$ $\xrightarrow{\text{Spin part}}$ $\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$

or $\frac{1}{\sqrt{2}}\left(2s(1)\,3s(2) - 2s(2)\,3s(1)\right)$ $\xrightarrow{\text{Spin part}}$ $\alpha(1)\alpha(2)$

$\beta(1)\beta(2)$

$\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \alpha(2)\beta(1)\right)$

$\therefore$ Possible Ψ can be

$$\Psi = \frac{1}{\sqrt{2}}\begin{vmatrix} 2s(1)\alpha(1) & 3s(1)\alpha(1) \\ 2s(2)\alpha(2) & 3s(2)\alpha(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} 2s(1)\beta(1) & 3s(1)\beta(1) \\ 2s(2)\beta(2) & 3s(2)\beta(2) \end{vmatrix}$$

$$= \frac{1}{2}\left\{\begin{vmatrix} 2s(1)\alpha(1) & 3s(1)\beta(1) \\ 2s(2)\alpha(2) & 3s(2)\beta(2) \end{vmatrix} + \begin{vmatrix} 2s(1)\beta(1) & 3s(1)\alpha(1) \\ 2s(2)\beta(2) & 3s(2)\alpha(2) \end{vmatrix}\right\}$$

or $$\frac{1}{2}\left\{\begin{vmatrix} 2s(1)\alpha(1) & 3s(1)\beta(1) \\ 2s(2)\alpha(2) & 3s(2)\beta(2) \end{vmatrix} - \begin{vmatrix} 2s(1)\beta(1) & 3s(1)\alpha(1) \\ 2s(2)\beta(2) & 3s(2)\alpha(2) \end{vmatrix}\right\}$$

~~Given~~ $\cancel{\Psi = \frac{1}{\sqrt{2}}\begin{vmatrix} 2s(1)\alpha(1) & 3s(1)\beta(1) \\ 2s(2)\alpha(2) & 3s(2)\beta(2) \end{vmatrix}}$

$\cancel{= \frac{1}{\sqrt{2}}\left\{2s(1)\,3s(2)\,\alpha(1)\beta(2) - 2s(2)\,3s(1)\,\alpha(2)\beta(1)\right\}}$

5) a) Since both spin α are possible only when the 2 e's are in diff orbitals. So lets assume them to be in 1s & 2s

$$\therefore \Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}} \left\{ 1s(1)2s(2)\alpha(1)\alpha(2) - 1s(2)2s(1)\alpha(1)\alpha(2) \right\}$$

$$\therefore \hat{S}^2_{\Psi} = \frac{1}{\sqrt{2}} 1s(1)2s(2)\, \hat{S}^2(\alpha(1)\alpha(2)) - \frac{1}{\sqrt{2}} 1s(2)2s(1)\, \hat{S}^2(\alpha(1)\alpha(2))$$

$$= \frac{1}{\sqrt{2}} \left(1s(1)2s(2) - 1s(2)2s(1)\right) \hat{S}^2(\alpha(1)\alpha(2))$$

$$\hat{S}^2(\alpha(1)\alpha(2)) = \hat{S}_1^2(\alpha(1)\alpha(2)) + \hat{S}_2^2(\alpha(1)\alpha(2)) + 2\left\{ \hat{S}_{1x}\cdot\hat{S}_{2x}(\alpha(1)\alpha(2)) + \hat{S}_{1y}\cdot\hat{S}_{2y}(\alpha(1)\alpha(2)) + \hat{S}_{1z}\cdot\hat{S}_{2z}(\alpha(1)\alpha(2)) \right\}$$

$$= \left\{ \alpha(2)\left[\cancel{\frac{\hbar^2}{4}\alpha(1)} - \cancel{\frac{\hbar^2}{4}\alpha(1)} + \frac{\hbar^2}{4}\alpha(1)\right] + \alpha(1)\left[\cancel{\frac{\hbar^2}{4}\alpha(2)} - \cancel{\frac{\hbar^2}{4}\alpha(2)} + \frac{\hbar^2}{4}\alpha(2)\right] \right\}$$

$$+ 2\left\{ \cancel{\frac{\hbar^2}{4}\beta(1)\beta(2)} - \cancel{\frac{\hbar^2}{4}\beta(1)\beta(2)} + \frac{\hbar^2}{4}\alpha(1)\alpha(2) \right\}$$

$$= \left\{ \frac{\hbar^2}{4}\alpha(1)\alpha(2) \right\}$$

$$\therefore \hat{S}^2 \Psi = \frac{1}{\sqrt{2}} \left(1s(1)2s(2) - 1s(2)2s(1) \right\} \cdot \cancel{2}\hbar^2 \alpha(1)\alpha(2)$$

$$= \cancel{2}\hbar^2 \Psi$$

$\therefore$ Yes its an eigen function of $\hat{S}^2$ with $\cancel{2}\hbar^2$ as eigen value