HW set 2 Justin Estee

Ex 3

a.) $$\Phi^{AS} = \frac{1}{\sqrt{6}} \sum_P (-)^P P \prod_{i=1}^{3} \psi_{\alpha_i}(x_i)$$

$$= \frac{1}{\sqrt{6}} \Big[\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\psi_{\alpha_3}(x_3) - \psi_{\alpha_1}(x_2)\psi_{\alpha_2}(x_1)\psi_{\alpha_3}(x_3)$$
$$- \psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_3)\psi_{\alpha_3}(x_2) - \psi_{\alpha_1}(x_3)\psi_{\alpha_2}(x_2)\psi_{3}(x_1)$$
$$- \psi_{\alpha_1}(x_3)\psi_{\alpha_2}(x_2)\psi_{\alpha_3}(x_1) + \psi_{\alpha_1}(x_3)\psi_{\alpha_2}(x_1)\psi_{\alpha_3}(x_2)$$
$$+ \psi_{\alpha_1}(x_2)\psi_{\alpha_2}(x_3)\psi_{\alpha_3}(x_1)$$

b.) In the configuration space any ~~permute~~ permutation of the Hartree function is orthogonal to another permutation

$$\iiint dx_1 dx_2 dx_3 \psi^*_{\alpha_1}(x_1)\psi^*_{\alpha_2}(x_2)\psi^*_{\alpha_3}(x_3) \; \psi_{\alpha_1}(x_2)\psi_{\alpha_2}(x_1)\psi_{\alpha_3}(x_3)$$
$$= \iint \psi^*_{\alpha_2}(x_2)\psi^*_{\alpha_3}(x_3) \times \psi_{\alpha_1}(x_2)\psi_{\alpha_3}(x_3) \underbrace{\int dx_1 \psi^*_{\alpha_1}(x_1)\psi_{\alpha_2}(x_1)}_{=0}$$

due to $\langle \psi_{\alpha_i} | \psi_{\alpha_j} \rangle = \delta_{ij}$

we show that only the conjugate of a permutation survives. Thus in the case $N=3$ above we have the six terms

$$\iiint dx_1 dx_2 dx_3 \; |\Phi^{AS}|^2 = \frac{6}{6} = 1$$

$\hat{f}\varphi_{\alpha_1} = \varepsilon_{\alpha_1}\varphi_{\alpha_1}$

c.) $\langle \Phi^{AS}_{\alpha_1\alpha_2} | \hat{F} | \Phi^{AS}_{\alpha_1\alpha_2} \rangle$

$$= \iint dx_1 dx_2\, \varphi^*_{\alpha_1}(x_1)\varphi^*_{\alpha_2}(x_2)\left(\hat{f}(x_1)+\hat{f}(x_2)\right)$$
$$\left(\varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_1}(x_2)\varphi_{\alpha_2}(x_1)\right)$$

$$= \iint dx_1 dx_2\, \varphi^*_{\alpha_1}(x_1)\varphi^*_{\alpha_2}(x_2)\, f(x_1)\,\varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2)$$
$$+ \iint dx_1 dx_2\, \varphi^*_{\alpha_1}(x_1)\varphi^*_{\alpha_2}(x_2)\, f(x_2)\,\varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2)$$
$$- \cancel{\int dx_1\, \varphi^*_{\alpha_1}(x_1) f(x_1)\varphi_{\alpha_2}(x_1)} \int dx_2\, \underbrace{\varphi^*_{\alpha_2}(x_2)\varphi_{\alpha_1}(x_2)}_{=0} \to 0$$
$$- \int dx_1\, \underbrace{\varphi^*_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_1)}_{=0} \int dx_2\, \varphi^*_{\alpha_2}(x_2) f(x_2)\varphi_{\alpha_1}(x_2) \to 0$$

$$\boxed{\langle \Phi^{AS}_{\alpha_1\alpha_2} | \hat{F} | \Phi^{AS} \rangle = \sum_{i=1}^{N} \varepsilon_{\alpha_i}} \quad \boxed{\text{if } \hat{f}\varphi_{\alpha_1} = \varepsilon_{\alpha_1}\varphi_{\alpha_1}}$$

$$\langle \varphi^{AS}_{\alpha_1\alpha_2} | \hat{G} | \varphi^{AS}_{\alpha_1\alpha_2} \rangle = \int dx_1 dx_2\, \varphi^*_{\alpha_1}(x_1)\varphi^*_{\alpha_2}(x_2)\,\hat{g}(x_2, x_1)$$
$$\left(\varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2) - \varphi_{\alpha_1}(x_2)\varphi_{\alpha_2}(x_1)\right)$$
$$= \int dx_1 dx_2\, \varphi^*_{\alpha_1}(x_1)\varphi^*_{\alpha_2}(x_2)\,\hat{g}\,\varphi_{\alpha_1}(x_1)\varphi_{\alpha_2}(x_2)$$
$$- \int dx_1 dx_2\, \varphi^*_{\alpha_1}(x_1)\varphi^*_{\alpha_2}(x_2)\,\hat{g}\,\varphi_{\alpha_1}(x_2)\varphi_{\alpha_2}(x_1)$$
$$= \langle \alpha_1\alpha_2 | \hat{g} | \alpha_1\alpha_2 \rangle - \langle \alpha_1\alpha_2 | \hat{g} | \alpha_2\alpha_1 \rangle$$

c.) cont.

The notation $|\alpha_1 \alpha_2\rangle$ denotes the particular permutation of the hartree function $\phi_{\alpha_1}(x_1)\cdot\phi_{\alpha_2}(x_2)$ in configuration space

Ex 4

a.) 6

$$\left\{\begin{matrix} |11\rangle, & & |23\rangle & |32\rangle, \\ |12\rangle & |21\rangle, & & \\ |13\rangle & |31\rangle, & & \\ |33\rangle, & & & \\ |22\rangle, & & & \end{matrix}\right\}$$

b.)

$$\langle 11|\hat{H}_0|11\rangle = \sum_{i=1}^{2} \varepsilon_{\alpha_i} = d(p=1) + d(p=1) = 2d$$

$$\langle 22|\hat{H}_0|22\rangle = \sum_{i=1}^{2} \varepsilon_{\alpha_i} = 4d \quad (p=2)$$

$$= 2d + 2d =$$

$$\hat{H}_0 = \begin{pmatrix} 2d & 0 \\ 0 & 4d \end{pmatrix} \qquad \hat{H}_1 = \begin{pmatrix} -g & -g \\ -g & -g \end{pmatrix}$$

$$\hat{H} = \begin{pmatrix} 2d-g & -g \\ -g & 4d-g \end{pmatrix}$$

Solving the eigenvalues equates to solving for λ

$$(2d-g-\lambda)(4d-g-\lambda) + g^2 = 0$$

$$\lambda^2 + (2g-6d)\lambda + 8d^2 - 6dg$$

$$\lambda = \frac{-(2g-6d) \pm \sqrt{(2g-6d)^2 - 4(8d^2-6dg)}}{2} = 3d - g \pm (d^2+g^2)^{1/2}$$

b.) cont. Solving for the eigen values

$$\lambda = 3d - g + (d^2+g^2)^{1/2}$$

$$\begin{pmatrix} -d-(d^2+g^2)^{1/2} & -g \\ -g & d-(d^2+g^2)^{1/2} \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \vec{0}$$

$$g\, a_1 = d - (d^2+g^2)^{1/2}\, a_2$$

set $a_2 = 1 \Rightarrow a_1 = \dfrac{d-(d^2+g^2)^{1/2}}{g}$

first eigen vector is

for $\lambda = 3d-g+(d^2+g^2)^{1/2}$ $\begin{pmatrix} \frac{d-(d^2+g^2)^{1/2}}{g} \\ 1 \end{pmatrix}$

for the second eigen ~~value~~ vector we must solve

$$\begin{pmatrix} -d+(d^2+g^2)^{1/2} & -g \\ -g & d+(d^2+g^2)^{1/2} \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \vec{0}$$

~~eq~~ $a_2 = 1 \Rightarrow a_1 = d + (d^2+g^2)^{1/2}$

thus for eigen ~~vector~~ value $3d-g-(d^2+g^2)^{1/2}$

the eigen vector is $\begin{pmatrix} d+(d^2+g^2)^{1/2} \\ 1 \end{pmatrix}$

We can normalize these vectors since it can get a bit messy lets call the normalized eigen vectors

$$\vec{e}_1 = \frac{1}{\sqrt{A}}\begin{pmatrix} \frac{d-(g^2+d^2)^{1/2}}{g} \\ 1 \end{pmatrix} \qquad A = \frac{1}{1+\left(\frac{d-(d^2+g^2)^{1/2}}{g}\right)^2}$$

$$\vec{e}_2 = \frac{1}{\sqrt{B}}\begin{pmatrix} \frac{d+(g^2+d^2)^{1/2}}{g} \\ 1 \end{pmatrix} \qquad B = \frac{1}{1+\left(\frac{d+(d^2+g^2)^{1/2}}{g}\right)^2}$$

b.) cont. Expressing these new eigen vectors in terms of the old eigen vectors, that is eigen vectors of the diagonal ($g=0$) hamiltonian. These ~~old~~ eigenvectors of the diagonal hamiltonian $\begin{pmatrix}1\\0\end{pmatrix}$ $\begin{pmatrix}0\\1\end{pmatrix}$ represent the 2-particle slater determinant for the ~~states~~ 1p1p state and 2p2p state respectively

$$\begin{pmatrix}1\\0\end{pmatrix} \Leftrightarrow |1p1p\rangle \text{ S.D.}$$

$$\begin{pmatrix}0\\1\end{pmatrix} \Leftrightarrow |2p2p\rangle \text{ S.D.}$$

The overlap of the new eigen vectors is trivial that is

$$\vec{e}_1 = \frac{d-(g^2+d^2)^{1/2}}{\sqrt{A}\,g}|1p1p\rangle + \frac{1}{\sqrt{A}}|2p2p\rangle$$

$$\vec{e}_2 = \frac{d+(g^2+d^2)^{1/2}}{\sqrt{B}\,g}|1p1p\rangle + \frac{1}{\sqrt{B}}|2p2p\rangle$$