Problem Set 13

Many-Electron Wavefunctions

Consider a set of two orthonormal spatial orbitals: $\{\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_1)\}$.

1. Write down the spin orbitals that can be constructed from these spatial orbitals.
2. How many Slater determinants can be formed that include two electrons and are eigenfunctions of $\hat{S}_z$ with an eigenvalue of 0. Write down each of these determinants.
3. Form all unique configuration state functions (CSFs) as linear combinations of those Slater determinants. What are the eigenvalues of $\hat{S}^2$ for each of these CSFs?
4. Evaluate the expectation value of the Hamiltonian for each Slater determinant.
5. Evaluate the expectation value of the Hamiltonian for each CSF.
6. Construct a matrix representation of the Hamiltonian in the basis of Slater determinants.
7. Construct a matrix representation of the Hamiltonian in the basis of CSFs.
8. What other Slater determinants can be formed from these spin orbitals? (That is, those with $\hat{S}_z$ eigenvalues different from 0.) Repeat parts 3-7 for each set of Slater determinants sharing the same $\hat{S}_z$ eigenvalue.

For additional practice, repeat for a set of three orthonormal spatial orbitals, $\{\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_1), \phi_3(\mathbf{r}_1)\}$, with three electrons and a set of four orthonormal spatial orbitals, $\{\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_1), \phi_3(\mathbf{r}_1), \phi_4(\mathbf{r}_1)\}$, with four electrons. (Note that for the three electron case you should initially consider Slater determinants with $\hat{S}_z$ eigenvalues of $\hbar/2$.)

Some Potentially Useful Equations

$$\hat{H} = -\sum_{i}^{\text{elec}} \frac{\hbar}{2m}\nabla_i^2 - \sum_{i}^{\text{elec}}\sum_{A}^{\text{nuc}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i>j}^{\text{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

$$\hat{h}(i) = -\frac{\hbar}{2m}\nabla_i^2 - \sum_{A}^{\text{nuc}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}}$$

$$\hat{H} = \sum_{i}^{\text{elec}} \hat{h}(i) + \sum_{i>j}^{\text{elec}} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A>B}^{\text{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

$$|\phi_i\sigma\phi_j\sigma\ldots\phi_k\sigma\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_i(\mathbf{r}_1)\sigma(\omega_1) & \phi_j(\mathbf{r}_1)\sigma(\omega_1) & \cdots & \phi_k(\mathbf{r}_1)\sigma(\omega_1) \\ \phi_i(\mathbf{r}_2)\sigma(\omega_2) & \phi_j(\mathbf{r}_2)\sigma(\omega_2) & \cdots & \phi_k(\mathbf{r}_2)\sigma(\omega_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_i(\mathbf{r}_N)\sigma(\omega_N) & \phi_j(\mathbf{r}_N)\sigma(\omega_N) & \cdots & \phi_k(\mathbf{r}_N)\sigma(\omega_N) \end{vmatrix}$$

$$\sigma(\omega) = \begin{cases} \alpha(\omega) \\ \beta(\omega) \end{cases}$$

$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$ $\qquad$ $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$

$\hat{S}_x|\alpha\rangle = \frac{\hbar}{2}|\beta\rangle$ $\qquad$ $\hat{S}_x|\beta\rangle = \frac{\hbar}{2}|\alpha\rangle$

$\hat{S}_y|\alpha\rangle = \frac{i\hbar}{2}|\beta\rangle$ $\qquad$ $\hat{S}_y|\beta\rangle = -\frac{i\hbar}{2}|\alpha\rangle$

$\hat{S}_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle$ $\qquad$ $\hat{S}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle$

$\hat{S}_+ = \hat{S}_x + i\hat{S}_y$ $\qquad$ $\hat{S}_- = \hat{S}_x - i\hat{S}_y$

$\hat{S}_+|\alpha\rangle = 0$ $\qquad$ $\hat{S}_+|\beta\rangle = \hbar|\alpha\rangle$

$\hat{S}_-|\alpha\rangle = \hbar|\beta\rangle$ $\qquad$ $\hat{S}_-|\beta\rangle = 0$

$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$ $\qquad$ $[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x$

$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \hat{S}_+\hat{S}_- - \hbar\hat{S}_z + \hat{S}_z^2 = \hat{S}_-\hat{S}_+ + \hbar\hat{S}_z + \hat{S}_z^2$$