Chem 532: Problem Set #6

Due in class: Friday., Nov. 4th

(1) A certain unperturbed system has a doubly degenerate energy level for which the perturbation integrals have the values $H_{11}^{(1)} = 4b$, $H_{12}^{(1)} = 2b$, and $H_{22}^{(1)} = 6b$, where b is a positive constant, $H_{ij}^{(1)} \equiv \left\langle \psi_i^{(0)} \middle| H^{(1)} \middle| \psi_j^{(0)} \right\rangle$ and $\left\langle \psi_i^{(0)} \middle| \psi_j^{(0)} \right\rangle = \delta_{ij}$.

(a) In terms of b, find the $E^{(1)}$ values for the perturbed system.

(b) Find the normalized, correct zeroth-order wave functions.

(2) Consider the 4 possible product spin functions for the He atom

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

(a) Explicitly show that all 4 are eigenfunctions of S_z but only 2 are eigenfunctions of S^2. Give the eigenvalues where they exist.

(b) Show that the linear combinations

$$\alpha(1)\beta(2) + \beta(1)\alpha(2)$$
$$\alpha(1)\beta(2) - \beta(1)\alpha(2)$$

are eigenfunctions of both S_z and S^2. Give their eigenvalues.

(3) The 4 normalized spin functions for a 2-electron system are given by

$$\Theta_{11} = \alpha(1)\alpha(2)$$
$$\Theta_{10} = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$
$$\Theta_{1-1} = \beta(1)\beta(2)$$
$$\Theta_{00} = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

(a) Show that Θ_{10} can be obtained from Θ_{1-1} by application of the raising operator S_+.

(b) Obtain Θ_{00} by orthogonalizing the function $c_1\Theta_{11} + c_2\Theta_{1-1} + c_3\alpha(1)\beta(2) + c_4\beta(1)\alpha(2)$ to the other 3 spin functions (Θ_{11} , Θ_{10}, Θ_{1-1}).