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, \( H_{ij}^{(1)} = \langle \psi_i^{(0)} | H^{(1)} | \psi_j^{(0)} \rangle \) and \( \langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = \delta_{ij} \).

(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 \( \Theta_{10} \) can be obtained from \( \Theta_{1-1} \) by application of the raising operator \( S_+ \).
(b) Obtain $\Theta_{00}$ 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 $(\Theta_{11}, \Theta_{10}, \Theta_{1-1})$. 