CH 107 Tutorial 5

Please solve these problems BEFORE the tutorial session

1. Write the general (complete) Hamiltonian for an *n* electron atom with nuclear charge Z. *Additional problem not to be done in tutorial.* Write the Hamiltonian for a molecule with *m* nuclei (same charge Z?) and *n* electrons, under Born-Oppenheimer Approximation.

2. What is orbital approximation? Does it involve neglect of the inter-electronic repulsion?

3. Why are 2-e spin-functions α(1)β(2) or β(1)α(2) not acceptable? Consider the following slater determinant for a two electron system. Comment whether this is a valid wavefunction for He atom in one of it's excited states.

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

4. Evaluate the spin wavefunctions of He atom in an excited state where the 2 electrons are in two different orbitals. Write the Slater determinant for the *singlet* wavefunction.

5. Formulate the Hamiltonian for a triangular H_3^+ molecular ion (equal H – H bond lengths) under the Born-Opperheimer approximation.
   b) Write the LCAO expression for the lowest energy MO using the AOs of H. Sketch the contour plot of this MO (show appropriate signs).
   a) What is the spin wavefunction of this molecule in the ground state?
   b) Express the ground state wavefunction of this molecule as a *single* Slater determinant

6. Qualitatively plot the overlap integral, S_{AB}, as a function of inter-nuclear distance (R_{AB}) for the following LCAO-MOs (below).
   b) Write the MOs (LCAO expressions) for bonding and anti-bonding situations for each.
   c) Sketch MO contours with appropriate signs and assign their symmetries (g/u).