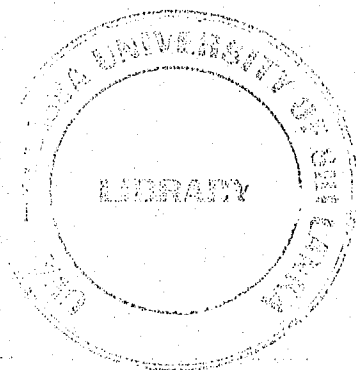




Uva Wellassa University, Sri Lanka
End Semester Examination – Jan 2010
SCT 333-2 Computational Chemistry



Time: Two (02) hours

This examination consists of two parts: Part A and Part B

Part B

Answer three (03) questions only

1.

(a) Define the following:

- (i) Basis function
- (ii) Primitive Gaussian
- (iii) Basis set

Suppose you are performing electronic structure calculations on the ethanol molecule.

- (b) Describe a minimal basis set for ethanol, including the total number of atomic orbitals.
- (c) Describe the 6-31G basis set for ethanol, including the total number of atomic orbitals.
- (d) Describe the 6-311G** basis set for ethanol, including the total number of atomic orbitals.

2.

(a) State the approximations made in

- (i) Hartree method,
- (ii) Hartree – Fock (HF) Method.

State a key difference between these methods.

- (b) State HF equation for a single electron in a many electron system. Identify all operators therein.
- (c) How electron-electron correlation is taken into account in Hartree method and HF method.

- (d) Hartree-Fock calculations that employ basis sets consisting of 8, 25, 50, and 100 basis functions, respectively, are carried out on the ammonia molecule. Sketch a plot of how you would expect the total electronic energy of the ammonia molecule to vary as a function of basis set size. Explain the theoretical principle behind the shape of the plot.

3.

- (a) Describe the major energy components of a molecular mechanics force field.
- (b) Give an equation for the stretching energy of a bond in a molecular mechanics force field. Make sure that you define any symbols that you use. Sketch a plot of the shape of the stretching energy as a function of the bond length.
- (c) Consider the hydrogen peroxide molecule, HOOH. Provide an explicit account of the terms that would be required in a molecular mechanics force field to describe this molecule. Also include a listing of the force field parameters that would be needed for HOOH, including force constants and equilibrium geometrical parameters.

4. A student investigates the bond in the A-B diatomic molecule using a software package for molecular mechanics. The student measures the bond length as 1.25 Å. When the single point energy of the molecule is calculated, the student gets a value of 30.0 kcal/mol. The equilibrium A-B bond length is 1.00 Å.

- (a) Using the information obtained above, determine the force constant for bond stretching. Use units of $\text{kcal mol}^{-1} \text{Å}^{-2}$.
- (b) Plot the stretching energy as a function of bond length for this system.
- (c) What happens to the plot from question (b) if the stretching force constant is doubled?
- (d) What happens to the plot from question (b) if the stretching force constant is halved?