Uva Wellassa University, Sri Lanka

End Semester Examination – June 2009

CHE 331-2 Applied Molecular Chemistry

Time Two (02) hours

Total number of questions: Part I (**10**), Part II (**3**)
Answer: **Part I:** all questions. **Part II:** two questions only
All symbols carry standard meanings

Index No:

Part I (Return this section)

Answer all questions. Use the space given. No additional sheets are needed.
Total pages: Two (2).

1. **(6 marks)** What is the Hamiltonian operator for the LiH molecule within the Born-Oppenheimer approximation? Express the Hamiltonian operator for LiH molecule in atomic units (Li Z= 3, H Z=1).

2. **(6 marks)** "The energy of a molecule calculated by Hartree Fock (HF) theory is always higher than the true energy of the molecule". Give your answer in one sentence as to why this occurs.

3. **(6 marks)** State the Slater determinant of the wave function of He (Z= 2)?

4. **(6 marks)** State the major energy components of a molecular mechanics force field.

5. **(6 marks)** State the Koopmans' theorem and the two assumptions made in the derivation.

6. **(6 marks)** In density functional theory (DFT), what is the quantity (property) of interest? Why DFT is, in principle, more useful than HF theory for calculating molecular properties, i.e. vibration frequency, of a given molecule (give one reason)?

7. **(10 marks)** How electron-electron correlation is accounted for within the HF framework?

8. **(6 marks)** State the Hartree Fock equation for n number of electrons system (use standard symbols).

9. **(6 marks)** Define the following terms:

   (i). CNDO (ii). Cusps behavior

10. **(2 marks)** Name two Noble Laureates in **Computational Chemistry**.

Part II (Retain this section)

Answer **two** questions only. All questions in this section carry **equal marks**

Question 1 (total 20 marks)

(i) **(5 marks)** State variation principle?

(ii) Given below are results from Hartree-Fock calculations for the formaldehyde molecule.

Basis Set	*Energy (a.u.)*	r_{CO} *(Å)*	r_{CH} *(Å)*	*HCO (°)*
STO-3G	*–112.35435*	*1.217*	*1.101*	*122.74*
3-21G	*–113.22182*	*1.207*	*1.083*	*122.53*
6-31G	*–113.80837*	*1.210*	*1.082*	*121.71*
*6-31G**	*–113.86633*	*1.184*	*1.092*	*122.16*

a) **(5 marks)** Are these results in agreement with the Variation Principle? Explain.

b) **(5 marks)** For each basis set listed in the table above, give the basis set type (for example, minimal basis, double zeta basis, triple zeta basis, split valence basis, etc.).

c) **(5 marks)** Suppose you are performing electronic structure calculations on the ethanol molecule. Describe the 6-311G** basis set for ethanol, including the total number of atomic orbitals and basic functions.

Question 2 (total 20 marks)

(i) **(5 marks)** Consider the hydrogen peroxide molecule, HOOH. Provide an account of the terms that would be required in a molecular mechanics force field to describe this molecule. Also include the listing of the force field parameters that would be needed for HOOH, including force constants and equilibrium geometrical parameters.

(ii) The atoms in a sulfur dioxide molecule (SO_2) have the following Cartesian coordinates (in Å):

Atom	x	y	z
S	0.00	0.00	0.00
O1	0.00	–0.91	0.95
O2	0.00	1.32	1.19

Consider a simple harmonic stretching and bending force field with the following parameters:

k_{SO} = *1250 kcal mol^{-1} Å^{-2}*

$r_{SO,equil}$ = *1.42 Å*

k_{OSO} = *760 kcal mol^{-1} radian^{-2}*

$\theta_{OSO,equil}$ = *125.3° (2.187 radians)*

a). **(5 marks)** What is the stretching energy (in kcal/mol) for sulfur dioxide at this geometry?

b). **(5 marks)** What is the bending energy (in kcal/mol) for sulfur dioxide at this geometry?

c). **(5 marks)** What is the total energy (in kcal/mol) for sulfur dioxide at this geometry?

Question 3 (total marks 20)

(i) (10 marks) The input file to a molecular modeling program must specify the coordinates of the atoms that comprise the molecule. Determine the Z matrix of the atoms in the molecule CH_3Cl. The HCH bond angle is 110.0^0 and the C-H and C-Cl bond lengths are 109.0 and 178.1 pm.

(ii) (10 marks) State the Fock operator. Write down the Hartree Fock equation for an i^{th} electron (no derivations are needed). Derive the Roothan-Hall equation for <u>many electrons</u> system (you may use standard symbols without definition).