UIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL II) EXAMINATION
JULY- 2016

SUBJECT: Chemistry
COURSE UNIT: CHE 4493   TIME: Two (02) hours

Answer **three (03)** questions only

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01. Answer **all** parts

In the search of minimum energy conformations of ammonia molecule, initial geometry of molecule is set up in reference to the Lab-fixed coordinate system and x,y,z coordinates are given as

N	1.0000	1.0000	0.1165
H	1.0000	1.9397	-0.2718
H	1.8138	0.5301	-0.2718
H	0.1862	0.5301	-0.2718

All distances have the unit of length and relative atomic masses of N, H are 14 and 1, respectively.

(a) Calculate the center of mass of the molecule.

(40 marks)

(b) Express the coordinate of each atom of the molecule with respect to the Body-fixed frame of reference.

(20 marks)

(c) Express the center of mass as a position vector with reference to the origin of the Lab-fixed coordinate system and hence calculate the unit vector.

(20 marks)

(d) Express the Cartesian coordinate of the center of mass as polar coordinates and calculate corresponding two angles.

(20 marks)

02. Answer **all** parts

In the quantum mechanical simulation, molecular specification and the selection of suitable basis set are the key steps. A student was asked to run the *ab intio* calculation on glyoxal (ethanedial) molecule $H_2C_2O_2$.

(a) Construct the Z-matrix for glyoxal molecule using appropriate symbols for bond distances and angles.

(40 marks)

(b) Explaining the types of basis functions that are employed on each atom of glyoxal molecule ($H_2C_2O_2$), find the total number of basis functions and primitive Gaussian type orbitals for the basis set 3-21G and 6-311G, 6-31+G* and 6-31++G**

(60 marks)

03. Answer **all** parts

(a) In molecular dynamic simulation technique, there are several step by step procedures to follow. It includes setting up the initial configurations, velocities and accelerations.

(i) Explain briefly how you would use random numbers generated in uniform distribution to obtain the velocities of particles at desired temperature.

(20 marks)

(ii) Use the Newton's second law to get the differential equation to represent the motion of a particle.

(20 marks)

(b) You are provided with the ensembles of atoms in which pair interactions of atoms are suitably assumed to be represented by the Morse potential, $V(r) = D_{eq}(1 - e^{-a(r-r_e)})^2$. Here a is a constant for a particular atom pair, D_{eq} and r_e are the dissociation energy and the separation at the minimum interaction energy, respectively. Derive the vector expression for the force acting on the particles.
Position vector, $\bar{r} = xi + yj + zk$.

(40 marks)

(c) Write the corrections for position derivatives in fifth order Gear predictor-corrector method.

(20 marks)

04. Answer **all** parts

Complete conformational analysis for butane was carried out by using MOE molecular modeling program. The variation of force field energy function with respect to the dihedral angle is given in figure below.

Diheadral angle
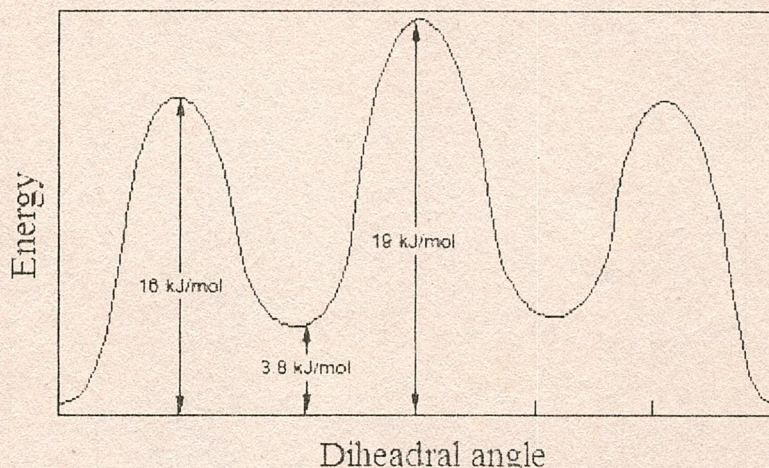
(a)   Giving the corresponding torsion angle, identify the structural conformer at each extreme.   (30 marks)

(b)   Write down the full torsional energy term in the total force fields for the butane molecule using the parameters (values) given in the diagram.

(10 marks)

(c)   Characterize each of the extrema of the potential energy surface.

(15 marks)

(d)   Calculate the equilibrium constant for the equilibrium in transformation of gauche to anti forms using the energy difference between two isomers at standard temperature and pressure.

(30 marks)

(e)   Distinguish the behavior of first and second derivatives of a potential energy function with respect to the relevant coordinate at a maximum and minimum.

(15 marks)

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