48

RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Special) Degree in Chemistry
Fourth Year - Semester I Examination – Oct/Nov 2017

CHE 4201 – Applied Molecular Chemistry / Computational Chemistry

Time:Two (2) hours

1.

a) The Hamiltonian for multi electron system composed of several nuclei consists of various parts. Write equations for the following terms in the Hamiltonian.

i. The Kinetic energy of electrons
ii. The kinetic energy of nuclei
iii. The Coulombic interactions between the nuclei and the electrons
iv. The Coulombic interactions between the electrons
v. The Coulombic interactions between nuclei

(25 marks)

b) State the Born Oppenheimer approximation and indicate the important part of the electronic Hamiltonian after the approximation

(25 marks)

c) Each one electron molecular orbital is approximated by linear combinations of atomic orbitals called basis functions. A basis set is a set of mathematical functions centered on nuclei with radial and angular distributions of electron density used to represent the atomic orbitals.

i. State the number of basis functions and primitive Guassians of the basis set 6-31+G

(10 maks)

ii. State the major difference between Slater type Orbital (STO) and Gaussian type orbital (GTO)

(15 marks)

d) Compare the Restricted Hartree Fock (RHF) method and Unrestricted Hartree Fock method with an appropriate example.

(25 marks)

2.

a) Briefly describe the following molecular representations used in electronic structure calculations:

Cartesian coordinate, Z-matrix

(20 marks)

b)

i. Define a potential energy surface (PES). Identify following structures on PES: Saddle point, local minimum and global minimum

(15 marks)

ii. Why geometrical optimization methods are important in computational chemical calculations. .

(10 marks)

c) Write Z-matrixes of following molecules (i) Ethanol (ii) Formic acid

(20 marks)

d) Why is a KS (Kohn and Sham) calculation of density functional method is much faster than direct solution of the Schrodinger equation?

(20 marks)

e) What is "dispersion"? How do different modeling techniques both classical and quantum mechanical include (or fail to include) dispersion? What kinds of "mistakes" would you expect to make in molecular modeling if your model fails accurately to account for dispersion?

(15 marks)

3.

a) How would you use molecular simulation methods to refine potential parameters?

(25 marks)

b) Briefly explain following terms

I. Periodic boundary condition

II. Minimum image convention

(20 marks)

c) For a given intermolecular potential function, U(r), $\left(\frac{dU(r)}{dr}\right)_{r=r_e} = 0$. Show that $r_e = \left(\frac{n}{6}\right)^{\frac{1}{n-6}}\sigma$ for Lennard-Jones (n-6) potential function. If Lennard-Jones (12-6) potential parameters for element "A" are 281 K and 0.379 nm respectively, calculate r_e for A-A interaction.

(25 marks)

d) Two spherical particles are at the positions A and B with coordinates (x_1,y_1,z_1) and (x_2,y_2,z_2) respectively. Dispersion interaction of these particles is represented by Lennard-Jones (12-6) potential function,

$$U(r) = 4\varepsilon\left[\frac{\sigma^{12}}{r_{12}^{12}} - \frac{\sigma^{6}}{r_{12}^{6}}\right]$$

wherer_{12} is the distance between two particles. Evaluate an expression for the force acting on the particle 2 in the X-direction.

$$\left[r_{12} = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}\right]$$

(30 marks)

4.

a) Write down the main steps of a Monte Carlo simulation of a molecular system

(25 marks)

b) What is the expected acceptance ratio of a MC simulation? What are the remedies can be taken if the acceptance ratio is below the required value and that of above the required value?

(25 marks)

c) At a particular Monte Carlo step of the simulation the potential energy of the system was -4211.528 kJ mol^{-1}. After the next trial move the potential energy was found to be -4210.985 kJ mol^{-1}. If the selected random number was 0.5387 can this trial move be accepted at 300 K?

(25 marks)

d) GROMACS is a molecular dynamics simulation package mostly used for biomolecular simulations. Molecular mechanics force field parameters for proteins and/or DNA are readily available. However, if one wants to use small organic molecule, may be as a ligand bound to a protein, main difficulty is finding correct force field parameters. What are the steps can be taken to obtain reasonable classical (molecular mechanics) force field parameters for small organic molecules? (brief stepwise explanation is sufficient).

(25 marks)

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