Uva Wellassa University, Sri Lanka
Faculty of Science and Technology
Science and Technology Degree Programme
3rd Year 2nd Semester Examination –Dec 2017/Jan 2018
SCT 333-2 Computational Chemistry

Uva Wellassa University



1. The Hartree-Fock (HF) theory forms the basis of the entire computational chemistry. Yet HF theory provides neither correct, nor even very accurate solution to the molecular electronic structure problem (= molecular Schrodinger equation).

   (i) Why, then, is HF theory so important?

   (ii) What is the major drawback of HF that demands use of different (higher-level) methods?

   (iii) There are several approximations of HF methodology in practical use. In particular, we distinguish between the so-called *ab initio* HF and semi-empirical HF methods. Describe the difference between them.

   (iv) Density functional methods account for the vast majority of quantum-chemical calculations done today and over the last two or so decades. Why are DFT methods so popular?

2.

   (i) What sorts of information can be reliably predicted from molecular mechanics methods. Give some examples and expected accuracies.

   (ii) In what sorts of situations would you expect the predictions of molecular mechanics type methods to be unreliable? Give some examples.

   (iii) Describe a way in which non- bonded interactions are typically included in molecular mechanics force fields.

   (iv) The atoms in a methylene molecule ($CH_2$) have the following Cartesian coordinates (in Å):

| Atom | x | y | z |
|---|---|---|---|
| C | 0.000 | 0.000 | 0.000 |
| $H_1$ | 0.000 | −0.785 | 0.901 |
| $H_2$ | 0.000 | 1.096 | 1.143 |

   The molecule is described by a harmonic stretching and bending force field with the following equilibrium values for the bond lengths and bond angle, respectively,

   $r_{CH,eq}$ = 1.150 Å
   $\theta_{HCH,eq}$ = 103.3°.

4b

When the molecular mechanics energy of the system is calculated using the MMFF force field at the geometry listed above, the total energy is 42.82 kcal/mol. The stretching force constant for the two C-H bonds is $k_{s,CH}$ = 406.0 kcal $mol^{-1}Å^{-2}$. From this information, determine the bending force constant, $k_{b,HCH}$. Express your answer in units of kcal $mol^{-1}deg^{-2}$.

3.

(i) Briefly define the following terms and discuss their role in molecular orbital calculations.

a) Variation Principle b) Basis Set

(ii) Sketch approximate plots of a Gaussian type orbital and a Slater type orbital.

(iii) Discuss the advantages and disadvantages of using Gaussian type orbitals compared to Slater type orbitals in molecular orbital calculations.

(iv) If a 6-311G (d) basis set were employed for a calculation of phenol, $C_6H_5OH$, describe the basis set and the total number of basis functions required for calculations.