RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Joint Major) Degree in Chemistry & Physics
Fourth Year Semester II Examination- September/November 2014

CHE 4201 APPLIED MOLECULAR CHEMISTRY

Answer both Parts I and II Time allowed: 2 hours

All symbols carry their standard meanings. Any standard symbol may be used without defining it.

PART I

Answer in the spaces provided. Return this section.

1. State the value of following quantities in atomic units:

   (a) Mass of electron (2) Charge of electron (3) Planck constant

2. Write down the Slate determinant for He (Z = 2)

3. State variational principle. What is meant by the term "self consistence"?

4. How a potential energy surface for a molecule is resulted from Bon Oppenheimer approximation? How many dimensionalities do occur for H_2O in PES?

5. Why Hatree method is not accepted? Give brief answers.

6. Write the electronic Hamiltonian for H_2O.

7. What is the major difference between *ab initio* and semi-empirical methods of electronic structure calculations?

8. Write the operators for following observables:

   Electron – electron interaction term

   Electron – nuclear interaction term

9. Why molecular mechanics methods cannot be used to describe chemical reactivity?

10. A 6-32G basis set notation is given. Calculate the number of primitive Gaussians in 6-31 G for Li (Z=3).

PART II

Answer in separate sheets. Retain this section.

1. (a) Discuss the advantages of Hatree-Fock theory in comparison to Hatree method.

   (b) State Hartree Fock equation of a many electrons system. Clearly identify all terms used.

   (c) Derive Roothan Hall equation using basis set terminology.

   (d) A single point energy calculation was performed for formaldehyde with Gaussian09^{TM} code. A section of the output file is attached. Answer following questions.

      (i) The level of theory used in the calculation
      (ii) State the wave functions of HOMO-LUMO orbitals
      (iii) Prove that these wave functions are normalized.

2. (a) What is a force field of a given molecule? How they are used in MM codes?

   (b) The atoms in a methylene molecule (CH2) have the following cartesian coordinates (in Å):

Atom	**x**	**y**	**z**
C	0.000	0.000	0.000
H1	0.000	–0.785	0.901
H2	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 an $\theta_{HCH,eq}$ = 103.3°.

   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}.

Sample printout

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 ---------------------------------------
 Gaussian 09:  IA32W-G09RevB.01 12-Aug-2010
               10-Oct-2014
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 ----------------------
 #T RHF/6-31G(d) Pop=Reg Test
 ----------------------
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 Formaldehyde Single Point
 ----------------------
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Occupied (A1) (A1) (A1) (A1) (B2) (A1) (B1) (B2)
Virtual (B1) (A1) (B2) (A1) (B1) (A1) (B2) (A1) (A1) (B2)
(A1) (B1) (B2) (A1) (A2) (B1) (A1) (B2) (A2) (A1)
(A1) (B1) (B2) (A1) (A1) (A1)

Molecular Orbital Coefficients:

				4	5	6	7	8
				(A1)--O	(B2)--O	(A1)--O	(B1)--O	(B2)--O
	Eigenvalues --			-0.87257	-0.69706	-0.63916	-0.52290	-0.44043
1	1	C	1S	-0.16261	0.00000	0.01957	0.00000	0.00000
2			2S	0.33954	0.00000	-0.06111	0.00000	0.00000
3			2PX	0.00000	0.00000	0.00000	0.32484	0.00000
4			2PY	0.00000	0.42032	0.00000	0.00000	-0.19770
5			2PZ	-0.12475	0.00000	-0.37609	0.00000	0.00000
6			3S	0.31305	0.00000	0.03916	0.00000	0.00000
7			3PX	0.00000	0.00000	0.00000	0.21194	0.00000
8			3PY	0.00000	0.15769	0.00000	0.00000	-0.04436
9			3PZ	-0.07978	0.00000	-0.08877	0.00000	0.00000
10			4XX	-0.01333	0.00000	0.00548	0.00000	0.00000
11			4YY	0.03021	0.00000	0.02730	0.00000	0.00000
12			4ZZ	-0.00166	0.00000	-0.01928	0.00000	0.00000
13			4XY	0.00000	0.00000	0.00000	0.00000	0.00000
14			4XZ	0.00000	0.00000	0.00000	0.03560	0.00000
15			4YZ	0.00000	-0.01398	0.00000	0.00000	0.06037
16	2	O	1S	0.08887	0.00000	-0.06975	0.00000	0.00000
17			2S	-0.20345	0.00000	0.15375	0.00000	0.00000
18			2PX	0.00000	0.00000	0.00000	0.49070	0.00000
19			2PY	0.00000	0.32078	0.00000	0.00000	0.56595
20			2PZ	-0.14181	0.00000	0.50921	0.00000	0.00000
21			3S	-0.27033	0.00000	0.32427	0.00000	0.00000
22			3PX	0.00000	0.00000	0.00000	0.35378	0.00000
23			3PY	0.00000	0.17549	0.00000	0.00000	0.44356
24			3PZ	-0.06784	0.00000	0.28713	0.00000	0.00000
25			4XX	-0.00041	0.00000	0.00484	0.00000	0.00000
26			4YY	-0.00412	0.00000	0.00743	0.00000	0.00000
27			4ZZ	0.00905	0.00000	-0.03499	0.00000	0.00000
28			4XY	0.00000	0.00000	0.00000	0.00000	0.00000
29			4XZ	0.00000	0.00000	0.00000	-0.04165	0.00000
30			4YZ	0.00000	-0.02339	0.00000	0.00000	-0.01932
31	3	H	1S	0.17907	0.19092	0.09090	0.00000	-0.18058
32			2S	0.06482	0.12037	0.07400	0.00000	-0.22518
33	4	H	1S	0.17907	-0.19092	0.09090	0.00000	0.18058
34			2S	0.06482	-0.12037	0.07400	0.00000	0.22518

				9	10	11	12	13
				(B1)--V	(A1)--V	(B2)--V	(A1)--V	(B1)--V
	Eigenvalues --			0.13577	0.24838	0.33337	0.37335	0.73665
1	1	C	1S	0.00000	-0.12210	0.00000	0.05347	0.00000
2			2S	0.00000	0.14892	0.00000	0.00027	0.00000
3			2PX	0.40261	0.00000	0.00000	0.00000	-1.07309
4			2PY	0.00000	0.00000	-0.43254	0.00000	0.00000
5			2PZ	0.00000	-0.21094	0.00000	-0.05318	0.00000
6			3S	0.00000	1.98075	0.00000	-1.80268	0.00000
7			3PX	0.71157	0.00000	0.00000	0.00000	1.10559
8			3PY	0.00000	0.00000	-1.64055	0.00000	0.00000
9			3PZ	0.00000	-0.74992	0.00000	-1.99713	0.00000
10			4XX	0.00000	-0.00273	0.00000	-0.00207	0.00000
11			4YY	0.00000	-0.01265	0.00000	-0.01784	0.00000
12			4ZZ	0.00000	-0.00457	0.00000	-0.00327	0.00000
13			4XY	0.00000	0.00000	0.00000	0.00000	0.00000
14			4XZ	-0.03288	0.00000	0.00000	0.00000	-0.01572
15			4YZ	0.00000	0.00000	0.00599	0.00000	0.00000
16	2	O	1S	0.00000	-0.00101	0.00000	-0.10774	0.00000
17			2S	0.00000	-0.01033	0.00000	0.02902	0.00000
18			2PX	-0.38114	0.00000	0.00000	0.00000	-0.01906
19			2PY	0.00000	0.00000	0.12594	0.00000	0.00000
20			2PZ	0.00000	0.05330	0.00000	-0.15411	0.00000
21			3S	0.00000	0.10056	0.00000	2.27053	0.00000
22			3PX	-0.52769	0.00000	0.00000	0.00000	-0.09028
23			3PY	0.00000	0.00000	0.39608	0.00000	0.00000
24			3PZ	0.00000	0.05062	0.00000	-0.94543	0.00000
25			4XX	0.00000	0.00129	0.00000	-0.08344	0.00000
26			4YY	0.00000	-0.01009	0.00000	-0.08067	0.00000
27			4ZZ	0.00000	-0.00050	0.00000	0.00148	0.00000
28			4XY	0.00000	0.00000	0.00000	0.00000	0.00000
29			4XZ	0.00355	0.00000	0.00000	0.00000	0.08787
30			4YZ	0.00000	0.00000	0.00368	0.00000	0.00000
31	3	H	1S	0.00000	-0.04750	-0.03426	-0.01673	0.00000
32			2S	0.00000	-1.47347	1.83003	-0.04451	0.00000
33	4	H	1S	0.00000	-0.04750	0.03426	-0.01673	0.00000
34			2S	0.00000	-1.47347	-1.83003	-0.04451	0.00000