RAJARATA UNIVERSITY OF SRI LANKA

FACULTY OF APPLIED SCIENCES

B. Sc (Joint Major) Degree in Chemistry and Physics

Third Year Semester I Examination – Oct / Nov 2015

CHE 4201 APPLIED MOLECULAR CHEMISTRY

Answer **all** questions   Time: **02** hours

All symbols carry standard meanings

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

   (i)   Variation principle
   (ii)   Potential energy surface
   (iii)   Born Oppenheimer approximation

   (b) A Gaussian type orbital g(r) has the general form

   $$g(r) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}$$

   while a Slater type orbital has the general form

   $$s(r) = \left(\frac{\xi^3}{\pi}\right)^{1/2} e^{-\xi r}$$

   Sketch approximate plots of a Gaussian and Slater type orbital (Qualitative plots are acceptable answers)

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

   (d) If a 6-31G basis set were employed for a calculation of CH_4 describe the basis set and the total number of basis functions required.

2. (a) Define a force field in a molecular mechanics calculation. List two types of commonly used force fields in modern computer codes.

(b) Indicate whether it would be appropriate to carry out a molecular mechanics calculation using a typical force field (such as MMFF) to determine the minimized energy for the molecular systems listed below.

(i).   porphyrin   (ii).   Fe(CO)$_4$

(c) Sketch a plot of the force field for rotation of ethane about its C-C axis. Sketch the energy of ethane as the torsion angle varies from 0° to 360°. What is a simple functional form that would have the same qualitative shape as your plot?

(d) In most molecular mechanics software packages, the bond lengths and other geometrical parameters of a molecule are determined by knowledge of the Cartesian coordinates of each atom. For example, the bond distance AB between two atoms A and B can be calculated from the equation

$$r_{AB} = \left[(x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2 \right]^{1/2}$$

where (x_A, y_A, z_A) are the Cartesian coordinates of atom A and (x_B, y_B, z_B) are the Cartesian coordinates of atom B. Consider a water molecule with atoms having the following Cartesian coordinates (in Å):

Atom	x	y	z
O	0.00	0.00	0.00
H$_1$	0.00	−0.65	0.60
H$_2$	0.00	0.65	0.60

k_{OH} = 700 kcal mol−1 Å^{-2}, $r_{OH,equil}$ = 0.93 Å, k_{HOH} = 100 kcal mol^{-1} radian^{-2}, $\theta_{HOH,equil}$ = 104.5°. What is the total energy of the system?

3. (a) Define following terms as applied to molecular modeling

(i)   Ab initio method
(ii)   Frontier orbitals
(iii) Self consistency as applied to molecular modeling

Parts (b) – (d)

State all steps to be followed to simulate the vibration spectrum of gas phase HCHO. A portion of output generated from a molecular modeling code for vibration energy calculations of HCHO is shown below:

(b) State the level of theory used in the calculation.

(c) State orbital energy and wave function of the HOMO orbital of HCHO. What is the difference of HOMO-LUMO energy?

(d) State the wave function for HOMO orbital. Is the wave function is normalized?

4. (i) What is the Hamiltonian operator for the CH_4 molecule within Born- Oppenheimer approximation? Express the operators in <u>atomic units.</u>

(ii) Write down the Slater determinant for the wave function of electrons in C atom (Z = 6).

(iii) "The energy of a molecule calculated by HF theory is always higher than the true energy" Why?

(iv) State the approximations made in Hartree – Fock (HF) Method. State HF equation for a single electron in a many electron system. Identify all operators therein (no derivations are required).

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Gaussian 09:  IA32W-G09RevB.01 12-Aug-2010

             16-Sep-2015

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rhf/6-31g(d) geom=connectivity pop=reg test

Formaldehyde Single Point

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	0.	0.	0.
O	0.	1.22	0.
H	0.94	-0.54	0.
H	-0.94	-0.54	0.

Stoichiometry   CH2O Framework group C2V[C2(CO),SGV(H2)]

Deg. of freedom   3

Full point group   C2V   NOp   4

Largest Abelian subgroup   C2V   NOp   4

Largest concise Abelian subgroup C2   NOp   2

                    Standard orientation:

Standard basis: 6-31G(d) (6D, 7F)

There are   18 symmetry adapted basis functions of A1 symmetry.

There are   2 symmetry adapted basis functions of A2 symmetry.

There are   6 symmetry adapted basis functions of B1 symmetry.

There are   8 symmetry adapted basis functions of B2 symmetry.

Integral buffers will be   262144 words long.

Raffenetti 1 integral format.

Two-electron integral symmetry is turned on.

    34 basis functions,   64 primitive gaussians,   34 cartesian basis functions

     8 alpha electrons   8 beta electrons

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        nuclear repulsion energy       31.2026569090 Hartrees.
Initial guess orbital symmetries:
        Occupied  (A1) (A1) (A1) (A1) (B2) (A1) (B1) (B2)
        Virtual   (B1) (A1) (B2) (A1) (B1) (A1) (B2) (A1) (A1) (B2)
                  (A1) (B1) (B2) (A1) (B1) (A2) (A1) (B2) (A2) (A1)
                  (A1) (B1) (B2) (A1) (A1) (A1)
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The electronic state of the initial guess is 1-A1.

Requested convergence on RMS density matrix=1.00D-08 within 128 cycles.

Requested convergence on MAX density matrix=1.00D-06.

Requested convergence on energy=1.00D-06.

No special actions if energy rises.

Keep R1 ints in memory in canonical form, NReq=1019381.

SCF Done: E(RHF) = -113.863703683   A.U. after   11 cycles

          Convg =   0.3952D-08   -V/T = 2.0031

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        Population analysis using the SCF density.

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Orbital symmetries:

```
        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)
```

The electronic state is 1-A1.

```
Alpha  occ. eigenvalues --  -20.58203 -11.33927  -1.39235  -0.87257  -0.69706
Alpha  occ. eigenvalues --   -0.63916  -0.52290  -0.44043
Alpha  virt. eigenvalues --    0.13577   0.24838   0.33337   0.37335   0.73665
Alpha  virt. eigenvalues --    0.80780   0.84690   0.94701   1.10471   1.10702
Alpha  virt. eigenvalues --    1.13933   1.27161   1.33554   1.62068   1.78202
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Alpha virt. eigenvalues --   1.79430   1.99262   2.18363   2.23706   2.45521

Alpha virt. eigenvalues --   2.64528   2.87183   2.97630   3.27601   4.09824

Alpha virt. eigenvalues --   4.47642

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	0.33994	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	-0.18475	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	0.17949	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	-0.01006
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