BITS Pilani, Pilani Campus; Semester-II, 2016-17

SET-A

CHEM F244: Physical Chemistry – III

Thursday, May 11, 2017 **Comprehensive Examination** **Duration: 1.5 (+1.5) hours**

Part I: Closed-book Quiz **Maximum Marks for Part I: 60 out of 120**

Instructions: *This examination has two parts. This part, (Part I) is a closed-book. Part II is open-book. Part I is to be solved on the question paper only. No supplements will be provided for solving Part I. Part I is having* ***20 questions*** *over three pages.*

Name: ____ ID: ____________________ Marks obtained ____

1. A HF calculation for LiH^{2+} is carried out with minimal basis function and with 6-31G* basis set. How the nuclear repulsion energy and number of occupied orbital will vary? **[2]**

Nuclear repulsion energy: ....

Number of occupied orbital: ....

2. A particle is subject to the potential energy $V = ax^5 + by^5 + cz^5$. If the ground state energy of the particle is 10 eV, calculate,

(i) $\langle T\rangle$ = ... eV and $\langle V\rangle$ = ... eV **[2]**

3. Determine $\langle x^2\rangle$ for one-dimensional simple harmonic oscillator in terms of v, ν, h, and k. **[3]**

[v = vibrational quantum no., ν = frequency, h = Planck's constant, k = force constant]

$\langle x^2\rangle$ = ...

4. Fill in the blanks [1×2]

(i) The permanent dipole moment of a many electron atom in a stationary state is always ....

(ii) Under Møller-Plesset perturbation theory: $E_0^{(0)} + E_0^{(1)}$ = ...

5. The gross populations (N) of the basis functions on each atom of H_2O are, N_O = (2.00 + 1.83+ 2 + 1.12 + 1.50), N_{H1} = 0.77 = N_{H2}. Calculate the net charges on O-atom (q_O) and H-atom (q_H). **[2]**

q_O = ... and q_H = ...

6. Time dependent expansion coefficients [$\mathbf{b_m(t')}$]for a transition from stationary state **m** to stationary state **n** are obtained using time dependent perturbation theory to describe the interaction of radiation and matter. The expression is,

$$b_m(t') \approx \delta_{mn} + \frac{\mathscr{E}_0}{2\hbar i}\langle\psi_m^0|\sum_i Q_i x_i|\psi_n^0\rangle\left[\frac{e^{i(\omega_{mn}+\omega)t'}-1}{\omega_{mn}+\omega} - \frac{e^{i(\omega_{mn}-\omega)t'}-1}{\omega_{mn}-\omega}\right]$$

In which $\omega \equiv 2\pi\nu$ and $\omega_{mn} = (E^m{}_0 - E^n{}_0)/\hbar$

Using the above expression describe the situation for, **[4]**

Induced absorption: ....

Induced emission: ....

7. Write down the expression of the one electron Fock operator for electron ***p*** in a ***q*** electron molecule which is having $\boldsymbol{\alpha}$ nuclei. **[4]**

$\hat{f}$(p) =

8. State whether following statements are **True** or **False** [Write down **True** or **False** after the statement] [1×4]

(i) Two external potentials v_a (r_i) and v_b (r_i) can give rise to the same ground-state electron density ρ_0 ....

(ii) The spatial parts of the wave function of ***He*** atom in the ground and lowest excited state are, antisymmetric and symmetric respectively. ....

(iii) First order energy correction obtained from non-degenerate perturbation theory treatment $E^{(1)} = \langle \psi^{(0)} | \widehat{H'} | \psi^{(0)} \rangle$ applies only to the ground state ....

(iv) For non-linear polyatomic molecules angular momentum classification of electronic terms can not be used as $[\widehat{L_z}, \widehat{H}] = 0$ ....

9. Express nuclear-electron attraction ($\overline{V_{ne}}$) in terms of ground state electron density and external potential: **[2]**

$\overline{V_{ne}}$ =

10. Use the concepts of Møller-Plesset perturbation theory to answer the following questions for a molecular system of 3 electrons. Fock operators can be represented as $\hat{f}$(i), spin orbitals as u(i) with an eigen value ϵ(i). **[2×3]**

(i) Form of the unperturbed Hamiltonian ($\widehat{H^0}$) = ...

(ii) Form of the zeroth order wavefunction (ϕ_0) = ...

(iii) Eigen value of the state represented in previous question, $E^{(0)}$ = ...

11. Consider perturbation theory treatment of the ground state of ***He*** atom. The first order energy correction can be written in terms of 1s energy of the hydrogen atom as E' = $(-\frac{5}{8}z)$ E_{1s} (H). Calculate the energy of the ground state of the ***He*** atom using the first order correction term. [E_{1s} (H) = -13.6 eV] **[2]**

Energy = ...eV

12. Given that D_e = 4.75 eV and R_e = 0.741 Å for the ground electronic state of H_2. Find, **[4]**

$U(R_e)$ = ...eV

$\langle T_{el} \rangle_{Re}$ **=** .... **eV**.

13. Consider an electronic state of H_2O molecule with 2 unpaired electrons. and electronic wavefunction remain unchanged by all four symmetry operations. **[2]**

Determine the molecular electronic term of H_2O molecule: ....

14. Consider simple model system, H_2, in minimal basis molecular orbital treatment using linear combination of atomic orbitals. The bonding and anti-bonding molecular orbitals are represented by Ψ_1 and Ψ_2. Represent all spin orbitals of H_2 using molecular orbitals, Ψ_1 and Ψ_2. **[4]**

15. Represent HF approximated ground state wavefunction in terms of the spin orbitals obtained in **Q14** **[2]**

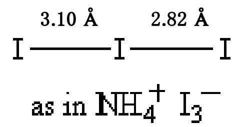
Ψ_0 **(1,2) =** ....

16. Express correlation energy in terms of energy obtained through CI and HF methods: **[2]**

E = ...

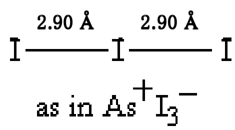
17. Assign point group to I_3^-: **[2]**

(a)



Point group: ____________________

(b)



Point group: ____________________

18. The character of the matrix representing the effect of identity operation on the set of Cartesian displacement coordinates for CO_3^{2-} is .... **[2]**

19. In case of H_2O, the linear combination of the two hydrogen 1s AOs (H_1 1s + H_2 1s) belong to the symmetry species .... **[1]**

20. (i) Determine all the symmetry elements in cis-hydroquinone (cis-1,4-dihydroxyphenol). (ii) How many classes are present in the point group to which the molecule belongs? Represent all those classes. (iii) Construct the character table. (iv) Assign Mulliken symbol to each of the representations. **[2+2+2+2]**

--- END OF PART I ---

Do not write any answer on this page

BITS Pilani, Pilani Campus; Semester-II, 2016-17

SET-B

CHEM F244: Physical Chemistry – III

Thursday, May 11, 2017 **Comprehensive Examination** **Duration: 1.5 (+1.5) hours**

Part I: Closed-book Quiz **Maximum Marks for Part I: 60 out of 120**

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Name: ____ ID: ____________________ Marks obtained ____

1. Use the concepts of Møller-Plesset perturbation theory to answer the following questions for a molecular system of 3 electrons. Fock operators can be represented as $\hat{f}$(i), spin orbitals as u(i) with an eigen value ϵ(i). **[2×3]**

(i) Form of the unperturbed Hamiltonian ($\widehat{H^0}$) = ...

(ii) Form of the zeroth order wavefunction (ϕ_0) = ...

(iii) Eigen value of the state represented in previous question, $E^{(0)}$ = ...

2. A particle is subject to the potential energy $V = ax^5 + by^5 + cz^5$**.** If the ground state energy of the particle is 10 eV, calculate,

(i) <T> = ... eV and <V> = ... eV **[2]**

3. Determine $\langle x^2 \rangle$ for one-dimensional simple harmonic oscillator in terms of v, ν, h, and k. **[3]**

[v = vibrational quantum no., ν = frequency, h = Planck's constant, k = force constant]

$\langle x^2 \rangle$ = ...

4. Fill in the blanks [1×2]

(i) Under Møller-Plesset perturbation theory: $E_0^{(0)} + E_0^{(1)}$ = ...

(ii) The permanent dipole moment of a many electron atom in a stationary state is always ....

5. The gross populations (*N*) of the basis functions on each atom of H_2O are, N_O = (2.00 + 1.83+ 2 + 1.12 + 1.50), N_{H1} = 0.77 = N_{H2}. Calculate the net charges on O-atom (q_O) and H-atom (q_H). **[2]**

q_H = ... and q_O = ...

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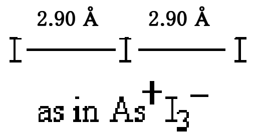
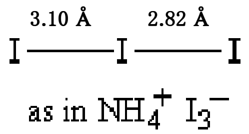


Point group: ____________________

(b)



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species .... **[1]**

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--- END OF PART A ---

Do not write any answer on this page

Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
Second Semester 2016-2017
CHEM F244 Physical Chemistry - III
Comprehensive Examination (Open Book)

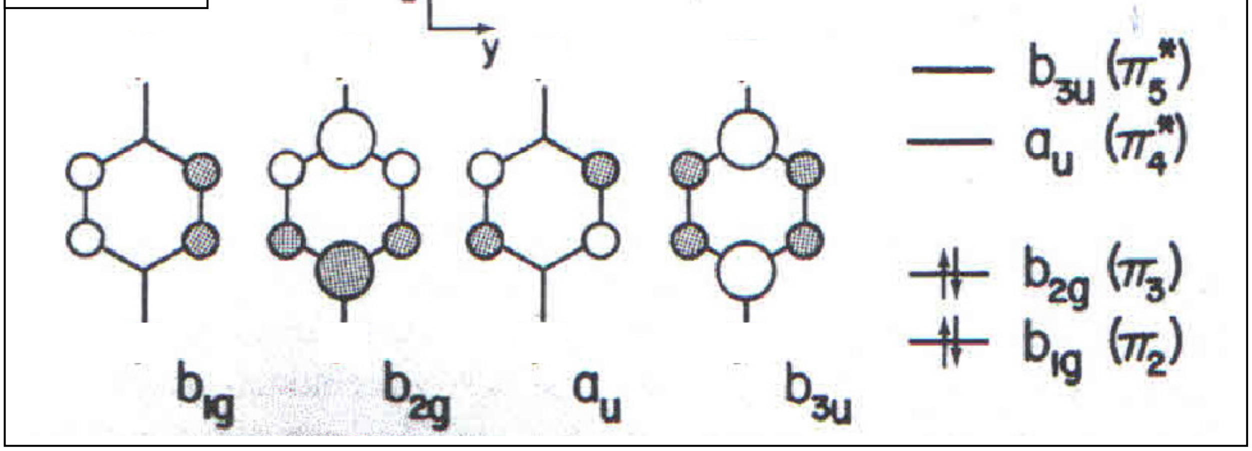
Part II **Time: 90 minutes** **Date: 11.05.2017 (08.00 - 11.00 hrs.)** **Marks: 60 out of 120**

Don't scribble on the question paper

Instructions: *Irrelevant writing for a question would not be considered for evaluation and may lead to deduction of marks*

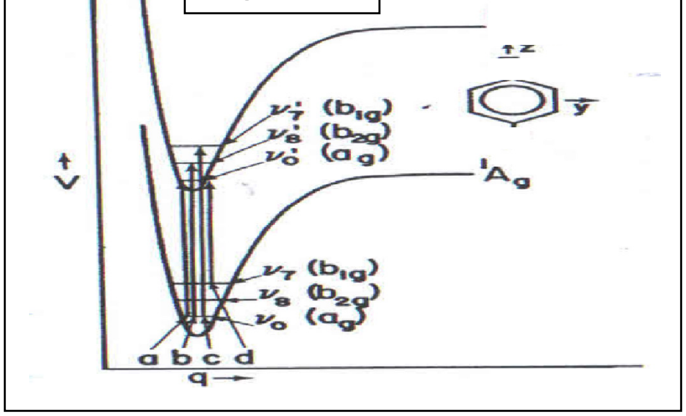
1 Approximate drawings of the highest filled and lowest unfilled π-orbitals of p-disubstitutedbenzene, p-$C_6H_4X_2$, where X is an atom (p-DSB, Figure 1). Shown are the upper lobes of the C($2p_x$) orbitals which lie perpendicular to the plane of the molecule. Shaded and unshaded orbitals are of opposite sign.

Figure 1



A schematic representation of the S_0 and S_1 electronic potential wells of p-DSB showing the vibrational ground states and vibrational levels ν_7 and ν_8 (Figure 2). The transitions are designated as follows: a, 0-0; b, 8^1_0; c, 7^1_0; and d, 7^0_1. Ground state of p-DSB is ^1A_g. Symmetry of the vibrational modes are represented in parentheses. Answer the following questions in brief.

Figure 2



i) Point group of p-DSB. **[3]**

ii) Determine the Symmetry of S_1 state. **[5]**

iii) Is the spin-allowed pure electronic transition $S_0 \rightarrow S_1$ of p-DSB orbitally allowed? Justify your answer with key points. **[6]**

iv) Consider the vibronic transition 'a', i.e. 0-0 transition and comments on polarization in case this transition is allowed. **[3]**

v) What about the vibronic transition 'b', i.e 8_0^1 if ν_8 has b_{2g} symmetry? Do mention the polarization in case the transition is allowed. **[3]**

vi) Are the vibronic transitions 'c' (7_0^1) and 'd' (7_1^0) allowed? Do mention the polarization in case the transition is allowed. **[5]**

vii) Can you identify transitions 'c' and 'd' in terms of fundamental, combination, and hot bands. **[2]**

viii) How do you differentiate band 'c' and 'd' experimentally. You need to consider (Figure 2) that the transition energy of band 'c' and 'd' would be different. Thus, this is not the answer. **[3]**

2 (a) Calculate the number of molecular orbitals for the given molecules and the basis sets: **[2×3]**
[Tabulate you answer in the following way]

Molecule	Basis set	Number of molecular orbitals
LiH_2	6-311G	
C_2H_5OH	6-31+G	
C_6H_6O	6-31G**	

(b) A HF calculation was carried out followed by Full CI for H_2 molecule. 6-31G* basis set was used for this calculation. Only singlet spin states (S=0) are used. Calculate,

i) the number of singly-excited configurations; **[3]**

ii) the number of doubly-excited configurations; and **[2]**

iii) the total number of configurations. **[4]**

(c) NH_3 molecule is perturbed by the application of an electric field in the x-direction. Which orbitals of N atom in NH_3 molecule would mix with a d-orbital under this perturbation? **[4]**

(d) Use time-independent perturbation theory to calculate an expression for the first order shift in the zero point energy of a one dimensional harmonic oscillator if the oscillator is perturbed by a small anharmonic term containing x^4. **[6]**

(e) Expression of the integral $\langle\psi_m^0|Qx|\psi_n^0\rangle$ for the particle in a one-dimensional box is: $\langle\psi_m^0|Qx|\psi_n^0\rangle = \frac{Ql^2}{a\pi^2}\,[(-1)^{m-n} - 1]\,[\frac{1}{(m-n)^2} - \frac{1}{(m+n)^2}]$. What is the selection rule for transition of the particle in a one-dimensional box? Use this result to predict the lowest energy allowed transition in a three-dimensional box in terms of three quantum numbers, n_x, n_y, and n_z. [a, Q, and l are constants and having usual meanings] **[5]**

****** End ******