

Thursday, May 05, 2016
Part A: Closed-book Quiz

BITS Pilani, Pilani Campus; Semester-II, 2015-16
CHEM F244: Physical Chemistry – III
Comprehensive Examination

Duration: 1 (+2) hours

Maximum Marks for Part A: 40 out of 120

Instructions: This examination has two parts. This part, (Part A) is a closed-book quiz. Part B is open-book. Part A is to be solved on the question paper only. No supplements will be provided for solving Part A.

Name: _____ ID: _____ Marks obtained _____

1. Complete the following table: For the systems given in the first column, state whether the Virial theorem simplifies to $2\langle T \rangle = n\langle V \rangle$ by circling the correct option between Yes and No in the second column. Complete the third column as per the given instructions. [2X3]

| System | Virial theorem simplifies to $2\langle T \rangle = n\langle V \rangle$? | If "Yes" in the second column, write the value of n, if "No" in the second column, explain in no more than 2-3 words |
|------------------------------------|--|--|
| Hydrogen atom | Yes / No | |
| 3D-Isotropic anharmonic oscillator | Yes / No | |
| 3D-anisotropic harmonic oscillator | Yes / No | |

2. For each of the following quantities obtained in a quantum chemical calculation, state whether it is independent of the choice of the basis-set or not. Circle "Yes" or "No" accordingly. [1X3]

| | | | |
|--------------------------|----------|-----------------------------|----------|
| Orbital energies | Yes / No | Hartree-Fock energy | Yes / No |
| Nuclear Repulsion energy | Yes / No | Dipole moment | Yes / No |
| Mulliken population | Yes / No | Number of occupied orbitals | Yes / No |

3. Choose the most correct answer among the given choices for the following questions: [1X4]

- (I) In Hartree-Fock Roothan method, if P is the charge-density bond-order matrix, so that P_{xy} is the matrix element corresponding to xth row and yth column, then
(a) x and y label the molecular orbitals.
(b) x and y label the basis functions.
(c) x labels the molecular orbitals, whereas y labels the basis functions.
(d) x labels the basis functions, whereas y labels the molecular orbitals.

- (II) In the context of Mulliken population analysis, _____
(a) net atomic population is equal to gross atomic population plus a fraction of overlap population.
(b) gross atomic population is equal to net atomic population plus a fraction of overlap population.
(c) gross atomic population is net atomic charge minus net atomic population.
(d) gross and net atomic populations are just different names for the same quantity.

- (III) Zeeman effect on first excited electronic level of Hydrogen atom can be studied using degenerate perturbation theory. Which of the following sets of zeroth-order wave-functions would yield the secular matrix with all off-diagonal elements zero?
(a) the orbitals: $2s, 2p_{+1}, 2p_{-1}, 2p_0$
(b) two sp-hybrid orbitals and two p-type orbitals
(c) the orbitals: $2s, 2p_x, 2p_y, 2p_z$
(d) the four sp^3 -hybrid orbitals

- (IV) In the context of density functional theory, the external potential refers to
(a) inter-electronic repulsion energy
(b) nuclear-electron attraction energy
(c) exchange energy
(d) correlation energy

4. Determine the number of normal modes of vibration in BCl_3 . [1]

5. State whether the following statements are True or False. (Circle the correct option).

| 5. State whether the following statements are True or False. (Circle the correct option). | | [1x7] |
|---|--|--------------|
| I. | In Moller-Plesset perturbation theory, Hartree-Fock wavefunction happens to be the zeroth-order wavefunction. | True / False |
| II. | In Moller-Plesset perturbation theory, Hartree-Fock energy happens to be the zeroth-order energy for the ground state. | True / False |
| III. | In Moller-Plesset perturbation theory, the first order correction to the energy is zero. | True / False |
| IV. | The Columb integral in Hartree-Fock theory is the consequence of antisymmetry in the wavefunction. | True / False |
| V. | Inclusion of only singly excited determinants (in addition to the RHF reference) does not correct the energy. This is the consequence of Koopmans' theorem. | True / False |
| VI. | The directional properties of a system can be more accurately determined if the basis-set consists of adequate number of polarization functions. | True / False |
| VII. | According to Hohenberg-Kohn theorem, the external potential for the ground electronic state the quantum mechanical system is completely determined by the ground-state electron probability density. | True / False |

9. E

6. Answer the following questions for D_{2h} point group by filling up the blanks:

[3+1+2]

| D_{2h} | E | | | $C_2(x)$ | | | | |
|----------|-------|-------|-------|----------|-------|-------|-------|-------|
| | | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| X | | X | X | X | X | X | X | X |
| X | | X | X | X | X | X | X | X |
| X | | X | X | X | X | X | X | X |
| X | | X | X | X | X | X | X | X |
| X | | X | X | X | X | X | X | X |
| X | | X | X | X | X | X | X | X |
| X | | X | X | X | X | X | X | X |

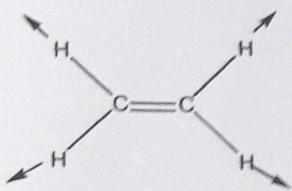
7. Stokes' lines are more intense than anti-Stokes' lines: Explain briefly.

[2]

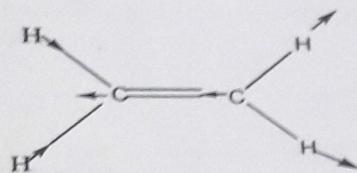
8. Does the product, xyz , necessarily vanish when integrated over C_{3v} point group.? [2]

9. Explain the IR activity of the following two vibrational modes of ethylene: [2]

(i)



(ii)



10. Which orbitals of N atom in NH_3 molecule would mix with a d-orbital when it is perturbed by the application of an electric field in the x-direction. [3]

11. Show that C_2 and σ_v do commute in case of H_2O molecule using matrix representation. [4]

--- END OF PART A ---

Date: May 05, 2016

Comprehensive Examination: Part B (Open Book)

General Instructions:

- 1.. Write your name, ID no., Course No., Course Title, Date and Day legibly, correctly, and completely on the main answer sheet as well as on the supplement(s) used.
2. All the questions are compulsory. Attempt each question on a new sheet and solve all the sub-questions of a question before going to next question.
3. Only scientific and non-programmable calculators, Chemistry book(s), and lecture-notes may be used for solving this part. Use of calculators with operating systems, mobile phones, iPhones, pagers, solution manuals, etc. is strictly prohibited.

Time: (1+) 2 hours

Max. Total Marks 80 out of 120

- a) Calculate the number of molecular orbitals for the given molecules and the basis sets: [2+2+2]
 [Tabulate your answers in the following format]

| Molecule | Basis set | Number of molecular orbitals |
|--------------------------------|-----------|------------------------------|
| BeH ₂ | 6-311G | |
| NH ₄ OH | 6-31+G | |
| C ₆ H ₁₂ | 6-31G** | |

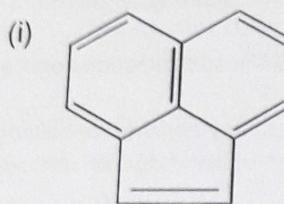
- b) An RHF calculation was done for HeH⁺ molecule using 6-31G* basis set, followed by [2+2+1] Full CI. Taking into consideration the singlet spin-adaptation (spin-part = $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$; S=0) , calculate
 - the number of singly-excited configurations;
 - the number of doubly excited configurations; and
 - the total number of configurations;
 in the Full CI wavefunction.

- c) Consider a molecule in external electric field of strength \vec{F} . The Hamiltonian of the [3+6] system is given by $\hat{H} = H^0 - \vec{\mu} \cdot \vec{F}$, where the unperturbed Hamiltonian corresponds to the system when no external electric field acts on it. Compare this with the non-degenerate perturbation method and recognize that polarizability is change in the dipole moment with respect to the change in the external field, write the expressions for
 - the ground-state permanent dipole moment
 - the ground-state static polarizability
 of the molecule in terms of the perturbation parameter and the set of the unperturbed wavefunctions, $\{\Psi_n^{(0)}; n=0,1,2,\dots\}$.

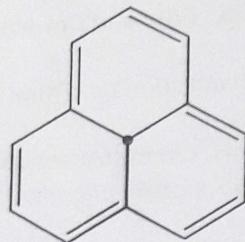
- a) Determine whether the following operators (**O**) are linear or non-linear operator: (i) **O**₁ = [2+2] d/dx and (ii) **O**₂ = $\log(x)$.

- b) Given the set of operations {E, C₄, σ_h}, answer the following questions: [7]
 - Determine the other operations that must be present to form a complete point group? [1]
 - What is the order of the group? [2]
 - Identify the point group for the complete set of operations. [2]
 - What would be the order of the subgroup(s)? [2]
 - Identify one subgroup for each order. [2]

3 a) Determine symmetry elements, symmetry operations, and point group of the following molecules:

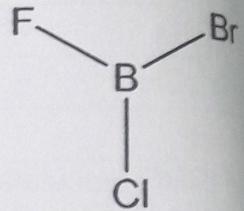
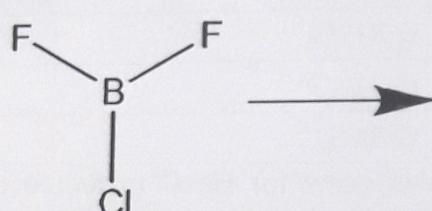
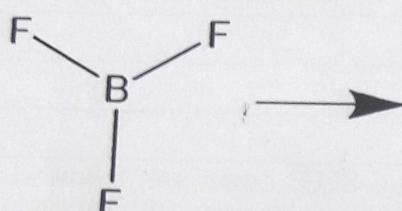


(ii)



These molecules may have doubly degenerate orbitals - Comment in one or two sentences.

b) Consider the following sequential structural changes:



I $\{D_{3h}\}$

Answer the following:

II $\{C_{2v}\}$

III $\{C_s\}$

- The specific symmetry elements that are lost or gained in the transition I \rightarrow II
- Comment whether the point groups II and III, and point groups I and III are having group and sub-group relation.
- Whether the transition II \rightarrow III represent descent or ascent in symmetry?

4 a) p-Difluorobenzene belongs to D_{2h} point group Electronic ground and excited states are represented by A_g and B_{2u} irreducible representations, respectively. Answer the following questions (Show all relevant steps):

- Is the spin allowed transition $^1A_g \rightarrow ^1B_{2u}$ is orbitally allowed?
- Comments on the polarization of the transition(s).
- Determine whether the vibronic transition for the normal mode of vibration, v_8 , having B_{2g} symmetry is allowed?

b) Two electronic states are described by the following two spin functions:

State-1: $\frac{1}{\sqrt{2}} [\alpha\beta - \beta\alpha]$ and State-2: $[\alpha\alpha]$. Is the transition from State-1 to State-2 is allowed?

--- END OF PART B ---