Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
2nd Semester, 2021-2022

CHEM F244: Physical Chemistry - III

Tuesday, May 10, 2022 **Duration: 1 hour**

Comprehensive Examination **Part-I (Closed book)** **Maximum Total Marks: 32**

General Instructions: This is the first part of the comprehensive examination. The second part (open book) can be collected only after submitting this part. Suggested duration for solving this part is 1 hour.

1. Write your name and ID number in the space provided. 2. There are 16 questions in this part with four options each for the answers. Choose the most correct answer. 3. ***You have to CIRCLE the correct option with pen. Do not tick or cross or write the answer. Every correct answer carries 2 marks, whereas every wrong answer carries 0 marks.*** *3. Non-programmable scientific calculators may be used for solving this part. Use of calculators with operating systems, smart phones, etc is strictly prohibited.*

Name:		Marks Obtained
ID:	Invigilator's signature:	

1. Amongst the given groups, identify the non-cyclic one(s): (I) C_{2h} ; (II) C_{3h} ; (III) C_4 ; (IV) C_S

(a) I, II and III **(b)** I, II and IV **(c)** I and IV **(d)** I only

2. The order of the C_{5h} group and the number of classes are, respectively equal to

(a) 6, 3 **(b)** 6, 4 **(c)** 10 and 10 **(d)** 10 and 4

3. In the context of Kohn-Sham DFT, the E_{xc} is defined as

(a) $\Delta T[\rho]+\int v_{ex}(r)\rho(r)dr$ **(b)** $\Delta T[\rho]+\Delta V_{ee}$ **(c)** $\Delta T[\rho]+\Delta V_{ee}+\int v_{ex}(r)\rho(r)dr$ **(d)** $\Delta V_{ee}+\int v_{ex}(r)\rho(r)dr$

4. In the context of the Thomas-Fermi model, $\phi(\vec{r})$ appearing in the Euler-Lagrange equation, $\frac{\delta E_{TF}[\rho(\vec{r})]}{\delta\rho}=\frac{1}{2}(3\pi^2)^{2/3}\rho^{2/3}(\vec{r})-\phi(\vec{r})$ represents

(a) electrostatic potential **(b)** chemical potential **(c)** exchange-correlation potential **(d)** external potential

5. In the context of Moller-Plesset perturbation theory, which of the following the statements is/are NOT true?:(I) $E_0^{(0)}+E_0^{(1)}=E_{HF}$; (II) $E_0^{(0)}=E_{HF}$ (III) $E_0^{(1)}=0$

(a) All of them **(b)** I only **(c)** II and III **(d)** III only

6. If $q_X=e(Z_X-N_X)$ is the net atomic charge on atom X , then N_X stands for

(a) gross population **(b)** net population **(c)** overlap population **(d)** effective population

7. The size-extensivity is the property by virtue of which

(a) when the molecule AB dissociates into the fragments A and B , the $E(AB)$ decomposes as $E(A)+E(B)$

(b) the correlation energy of the molecule approximately scales linearly with the number of electrons

(c) the correlation energy of the molecule approximately scales linearly with the number of basis functions

(d) the total energy of the molecule approximately scales linearly with the number of basis functions

8. In cc-pVDZ basis set, the "cc" stands for

(a) correlation correction **(b)** correlated configuration **(c)** coulomb correlation **(d)** correlation consistent

9. For an H_2 molecule in ground electronic state, if the internuclear distance, R is infinitesimally decreased from the equilibrium bond distance, R_{eq} , then

(a) $T_e(R)$ increases **(b)** $V_{el}(R)$ increases **(c)** T_e decreases **(d)** $U(R)$ decreases

10. The great orthogonality theorem reads $\sum_R[\Gamma_i(R_{mn})][\Gamma_i(R_{pq})]^*=\frac{h}{\sqrt{l_i l_j}}\xi$, where ξ is the product of three Kronecker delta functions, as

(a) $\delta_{ij}\delta_{mn}\delta_{pq}$ **(b)** $\delta_{ij}\delta_{mp}\delta_{nq}$ **(c)** $\delta_{ij}\delta_{mq}\delta_{np}$ **(d)** $\delta_{mn}\delta_{ip}\delta_{jq}$

11. The only irreducible representations of a group are A' and A". The symmetry elements present in the group are

(a) E and C_2 **(b)** E and i **(c)** S_4 and its powers **(d)** E and σ_s

12. The number of normal modes of vibration of water corresponding to completely symmetric irreducible representations is

(a) 4 **(b)** 3 **(c)** 2 **(d)** 1

13. If $E_X=E_Y+\sum_{i=1}^{n/2}H_{ii}^{core}$ and $E_Y=\sum_{i=1}^{n/2}H_{ii}^{core}+\sum_{i=1}^{n/2}\sum_{j=1}^{n/2}(2J_{ij}-K_{ij})$ for a closed-shell molecule, then

(a) $E_{HF}=E_X+V_{NN}$ **(b)** $E_{HF}=E_Y+V_{NN}$ **(c)** $E_{HF}=\frac{E_X}{2}+V_{NN}$ **(d)** $E_{HF}=\frac{E_Y}{2}+V_{NN}$

14. For neon atom, if an electronic structure job is set up using 6-31G basis set, then the "6" mean

(a) core orbital split into 6 atomic orbitals **(b)** core orbital formed by contracting 6 gaussians

(c) the polarized d-subshell has 6 orbitals **(d)** 6 gaussians to give 1 s-type and and 3 p-type orbitals

15. According to degenerate perturbation theory where $\{\Psi_j^{(0)}; j=1,...n\}$ are degenerate zeroth-order wavefunctions, while solving $H(\lambda)\Psi_j(\lambda)=E_j(\lambda)\Psi_j(\lambda)$ as $\lambda \to 0$,

(a) Ψ_j tends to $\Psi_j^{(0)}$ and E_j tends to $E_j^{(0)}$.

(b) Ψ_j tends to $\Psi_j^{(0)}$ but E_j may not tend to $E_j^{(0)}$

(c) Ψ_j may not tend to $\Psi_j^{(0)}$ but E_j tends to $E_j^{(0)}$

(d) Ψ_j may not tend to $\Psi_j^{(0)}$ and E_j may not tend to $E_j^{(0)}$

16. Which of the following statements are true about the irreducible representations of symmetry point groups?: (I) The most symmetric irreducible representation for a non-abelian point group can be degenerate. (II) There is at least one irreducible representation that is symmetric with respect to all the classes. (III) Irreducible representations of non-cyclic abelian point groups are necessarily unidimensional.

(a) All of them **(b)** I and II **(c)** I and III **(d)** II and III

---END of Part I---

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CHEM F244: Physical Chemistry - III

Tuesday, May 10, 2022 **Duration: 2 hours**
Comprehensive Examination **Part-II (Open book)** **Maximum Total Marks: 48**

A Restricted Hartree-Fock (RHF) energy computation job of water dimer using STO-6G basis set up on Q-Chem. The atoms were oriented as described by the following cartesian coordinates (in angstroms):

Atom No.	Symbol	X	Y	Z
1	**O**	0.0000000	0.0000000	0.5567556
2	**H**	0.7830366	0.0000000	0.0000000
3	**H**	-0.7830366	0.0000000	0.0000000
4	**O**	0.0000000	0.0000000	-0.5567556
5	**H**	0.0000000	0.7830366	0.0000000
6	**H**	0.0000000	-0.7830366	0.0000000

Upon convergence of the SCF iterations, the AO-MO coefficient matrix was obtained as given below:

MO index→		**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
AO index ↓															
1	$1s(O_1)$	0.7043	0.7045	-0.1551	0.1819	0.0000	0.0000	-0.0645	0.0000	0.0000	0.1085	0.0000	0.0808	0.0000	0.0000
2	$2s(O_1)$	0.0130	0.0146	0.5006	-0.8466	0.0000	0.0000	0.2976	0.0000	0.0000	-0.8711	0.0000	-0.6609	0.0000	0.0000
3	$2p_x(O_1)$	0.0000	0.0000	0.0000	0.0000	-0.4539	0.0000	0.0000	-0.7863	0.0000	0.0000	0.0000	0.0000	0.7425	0.0000
4	$2p_y(O_1)$	0.0000	0.0000	0.0000	0.0000	0.0000	-0.4539	0.0000	0.0000	0.7863	0.0000	0.0000	0.0000	0.0000	0.7425
5	$2p_z(O_1)$	-0.0023	-0.0058	-0.2482	-0.0842	0.0000	0.0000	0.6067	0.0000	0.0000	0.1154	0.0000	1.0317	0.0000	0.0000
6	$1s(H_2)$	-0.0038	0.0000	0.0056	0.0000	-0.3113	0.0000	0.0779	0.0000	0.0000	0.5980	0.8316	0.0000	-1.0392	0.0000
7	$1s(H_3)$	-0.0038	0.0000	0.0056	0.0000	0.3113	0.0000	0.0779	0.0000	0.0000	0.5980	0.8316	0.0000	1.0392	0.0000
8	$1s(O_4)$	0.7043	-0.7045	-0.1551	-0.1819	0.0000	0.0000	-0.0645	0.0000	0.0000	0.1085	0.0000	-0.0808	0.0000	0.0000
9	$2s(O_4)$	0.0130	-0.0146	0.5006	0.8466	0.0000	0.0000	0.2976	0.0000	0.0000	-0.8711	0.0000	0.6609	0.0000	0.0000
10	$2p_x(O_4)$	0.0000	0.0000	0.0000	0.0000	-0.4539	0.0000	0.0000	0.7863	0.0000	0.0000	0.0000	0.0000	0.7425	0.0000
11	$2p_y(O_4)$	0.0000	0.0000	0.0000	0.0000	0.0000	-0.4539	0.0000	0.0000	-0.7863	0.0000	0.0000	0.0000	0.0000	0.7425
12	$2p_z(O_4)$	0.0023	-0.0058	0.2482	-0.0842	0.0000	0.0000	-0.6067	0.0000	0.0000	-0.1154	0.0000	1.0317	0.0000	0.0000
13	$1s(H_5)$	-0.0038	0.0000	0.0056	0.0000	0.0000	-0.3113	0.0779	0.0000	0.0000	0.5980	-0.8316	0.0000	0.0000	-1.0392
14	$1s(H_6)$	-0.0038	0.0000	0.0056	0.0000	0.0000	0.3113	0.0779	0.0000	0.0000	0.5980	-0.8316	0.0000	0.0000	1.0392

The eigenvalues of the MO's (in hartrees) are as follows:

MO	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Energy	-20.621	-20.621	-2.076	-1.093	-1.047	-1.047	-0.662	-0.404	-0.404	0.019	0.391	0.723	0.805	0.805

Based on the given data, answer the following questions:

Q. 1 (a) Identify the symmetry elements (all distinct symmetry operations) in the (dimer) molecule and identify the point group. Is the point group abelian? Justify your answer in one line. **[8+2]**
(b) Identify the largest abelian subgroup of the point group in **(a)** above and find its order. **[2]**
(c) Given that the basis functions (atomic orbitals), $\{\chi_r\}$ are normalized and the molecular orbitals, $\{\phi_i\}$ are orthonormal, express ϕ_4, and ϕ_{11} in terms of the basis functions. Using the character table and without explicitly using the SALC algebra, identify the irreducible representations to which these orbitals belong. **[4+6]**
(d) Identify the HOMO and LUMO (Specify the MO numbers and energies). **[2]**

Q. 2 (a) Evaluate the following elements of the density matrix: $P_{1,2}$, $P_{1,4}$, $P_{1,14}$, $P_{3,5}$ and $P_{5,6}$. **[10]**
(b) Calculate the Mulliken population for the 1s orbital of the H_6 atom. **[2]**
(c) Evaluate the following integrals for a closed-shell molecule: $\langle \Psi_i^a | H | \Psi_{HF} \rangle$, $\langle \Psi_{ij}^{ab} | H^{core} | \Psi_{HF} \rangle$, $\langle \Psi_{ijk}^{abc} | H | \Psi_{HF} \rangle$, and $\langle \Psi_i^a | \vec{\mu}_{el} | \Psi_{HF} \rangle$. **[4]**
(d) If RHF energies of hydrogen fluroide, water, ammonia and methane were computed using 3-21G** basis sets, calculate the number of basis functions produced of each molecule. If CISD correlation energies for these systems were computed, how many singly excited configurations would be generated using the spin-molecular orbitals? **[4+4]**

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