

CHEM F213: Physical Chemistry-II

Date: December 13, 2023

Time: 1 (+2) hours

Comprehensive Examination

Part I (Closed Book)

Max. 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. Maximum duration for solving this part is 1 hour.

Write your name and ID number in the space provided. There are 16 MCQs with four options each (2 marks for each correct answer, none for wrong answer.). Choose the most correct option and CIRCLE the same using blue or black pen. Do not tick or cross. Non-programmable scientific calculators may be used for solving this part.

Name: _____ ID: _____ Marks Obtained: _____

- In the context of Hückel MO theory, the molecular orbital of ethene corresponding to energy $E_{MO} = \alpha + \beta$ is
(A) a bonding π MO (B) an anti-bonding π MO
(C) a spin-contaminated MO (D) a non-bonding MO
- Amongst the molecules, methane, benzene, sulphur hexafluoride, water and ammonia, the examples of a spherical top rotor are
(A) benzene and methane (B) methane, ammonia and water
(C) methane only (D) methane and sulphur hexafluoride
- Amongst the molecules, methane, benzene, carbon dioxide, water and ammonia the rotationally active molecules are
(A) water and carbon dioxide (B) ammonia and water
(C) methane, ammonia and water (D) carbon dioxide only
- The product of uncertainties in simultaneous measurements of magnitude of orbital angular momentum and energy of a hydrogen atom in absence of any external forces would be
(A) equal to \hbar (B) greater than \hbar
(C) equal to zero (D) greater than or equal to $\hbar/2$
- For shorter wavelengths, the Planck's expression from his quantum hypothesis for explaining the black-body radiation reduces to the
(A) Stefan-Boltzmann law (B) Wein's displacement law
(C) Rayleigh and Jeans' law (D) Wein's formula for energy density
- For a one-particle system, a wavefunction is given by $\psi = A \sin \frac{\pi X}{a_0} e^{-x^2/a_0^2 + iEt/\hbar}$, where, A is the normalization constant. The SI units of A must be
(A) m^{-3} (B) $m^{-3/2}$ (C) $m^{-3/2} s^{-1/2}$ (D) none (it's dimensionless)
- If the angular part of a hydrogenic orbital is $\sin^2 \theta \sin 2\phi$ and its radial part is $(12 Z^2 r^2 / a_0^2 - Z^3 r^3 / a_0^3) e^{-Zr/a_0}$, then the orbital must be
(A) $4d_{zx}$ (B) $4d_{xy}$ (C) $3p_x$ (D) $4f_z^3$
- Probability current corresponding to stationary state of a one-particle quantum mechanical system must be
(A) zero (B) an irrotational vector (C) a solenoidal vector (D) time-independent
- The degree of degeneracy of the first excited energy level in a 3D isotropic harmonic oscillator is
(A) 2 (B) 3 (C) 4 (D) 1 (non-degenerate)
- The ground state electronic configuration of Titanium atom CANNOT give rise to which of the following terms?
(A) 3F (B) 3P (C) 3S (D) 1S
- The numbers of respectively, angular and radial nodes in a $6f_z$ orbital of hydrogen atom are
(A) 3 and 5 (B) 4 and 6 (C) 2 and 3 (D) 3 and 2
- A 3D rigid rotor was found in an energy level with degree of degeneracy equal to m . The number of states with energy lower than this energy equals to n . The maximum value of m such that $m > n$ is
(A) 7 (B) 9 (C) 3 (D) 5

13. Using the orthonormal pure atomic orbitals of hydrogen, four states $\phi_1 = \frac{1}{\sqrt{2}}(\phi_{3d_z} + \phi_{2p_z})$, $\phi_2 = \frac{1}{\sqrt{2}}(\phi_{3p_x} + \phi_{2p_y})$, $\phi_3 = \frac{1}{\sqrt{2}}(\phi_{2p_x} + \phi_{2p_y})$ and $\phi_4 = \frac{1}{\sqrt{2}}(\phi_{3p_x} + \phi_{3d_{xy}})$ were set up and studied with respect to the measurements of the observables corresponding to the operators, \hat{H} , $\hat{\mathcal{L}}^2$ and $\hat{\mathcal{L}}_z$. Three of them have some similarities and one option stands out. Identify the option that stands out.

- (A) ϕ_1 (B) ϕ_2 (C) ϕ_3 (D) ϕ_4

14. Out of the operator pairs: (I) \hat{z} and \hat{p}_z ; (II) \hat{z} and $\hat{\mathcal{L}}_z$; and (III) \hat{p}_z and $\hat{\mathcal{L}}_z$; simultaneous and exact measurement of the corresponding observables is not possible for which pairs?

- (A) All of them (B) I and II (C) I and III (D) II and III

15. Koopmans' theorem enables us to approximately consider

- (A) a many-electron wavefunction expressible as a single determinant of spin-orbitals
 (B) the first ionization energy to be equal to negative of the energy of the HOMO
 (C) the nuclear motion to be negligible while solving for electronic wavefunction
 (D) the spin-orbit interactions in the many-electron Hamiltonian to be negligible

16. The term symbol for oxygen molecule in ground electronic state is

- (A) ${}^3\Pi_g$ (B) ${}^1\Delta_g$ (C) ${}^1\Sigma_g$ (D) ${}^3\Sigma_g$

---END of Part I---

CHEM F213: Physical Chemistry-II

Date: December 13, 2023

Time: (1+) 2 hours

Comprehensive Examination

Part II (Open Book)

Max. Total Marks 48

General Instructions: Stick to the following values of constants/conversion factors in numerical calculations:
 $\hbar = 1.0546 \times 10^{-34} \text{ J.s}$; $c = 3 \times 10^{10} \text{ cm s}^{-1}$; $\pi = 3.14159$; $1 \text{ a.m.u.} = 1.673 \times 10^{-27} \text{ kg}$.

Q. 1. (a) A computational calculation reveals that sulphur difluoride (SF_2) molecule has a singlet ground electronic state with $F-S-F$ bond-angle to be 98.2132° , which is significantly different from the regular tetrahedral bond angles. The bonded and non-bonded hybrid orbitals of sulphur thus have very different hybridizations. The molecule is oriented in XY plane with sulphur nucleus at origin fluorines in +X side of the plane and the X-axis bisecting the $F-S-F$ bond-angle. The pure atomic orbitals of sulphur, namely, ϕ_{3s} , ϕ_{3p_x} , ϕ_{3p_y} and ϕ_{3p_z} are mutually orthonormal. The hybrid orbitals, ϕ_1 , ϕ_2 , ϕ_3 and ϕ_4 too are mutually orthonormal, The orbitals ϕ_1 and ϕ_2 participate in bonding with the two fluorine atoms, whereas the orbitals ϕ_3 and ϕ_4 possess lone pairs of electrons. Obtain the expressions for all the hybrid orbitals (in terms of ϕ_{3s} , ϕ_{3p_x} , ϕ_{3p_y} and ϕ_{3p_z}). Determine the hybridization and %s-character in ϕ_1 and ϕ_2 . Similarly, determine the hybridization and %s-character in ϕ_3 and ϕ_4 . Also determine the angle between the ϕ_3 and ϕ_4 . [8+2+2+2]

(b) In the vibrational-rotational spectrum of a heteronuclear diatomic molecule, the first lines of P and R bands, respectively appear at 2057.989 cm^{-1} and 2078.552 cm^{-1} , whereas the second line in the R band appears at 2087.928 cm^{-1} . The reduced mass of the molecule is 1.89189 a.m.u. and the force constant is 514.5 kg s^{-2} . Using this data, calculate **(I)** \bar{B}_0 , \bar{B}_1 , \bar{v}_0 , (all in cm^{-1}); **(II)** $\bar{\alpha}_e$, \bar{B}_e , (both in cm^{-1}); **(III)** \bar{v}_e and the centrifugal distortion constant (both in cm^{-1}) **(IV)** the equilibrium bond length (in \AA) and the anharmonicity constant. [4+2+2+2]

Q. 2. (a) Consider the system is 1D anharmonic oscillator with the potential energy approximated as $U(x) = kx^2/2 + \gamma x^3$. Use non-degenerate time-independent perturbation theory with The 1D harmonic oscillator to model the unperturbed states, **(I)** Identify the quantities, H' , $\Psi_0^{(0)}$, $E_0^{(0)}$ (write the relevant expressions); **(II)** evaluate $E_0^{(1)}$ **(III)** Note that $E_0^{(2)}$ is sum of several terms (in principle, a series of terms) corresponding to all possible values of m , with $m \neq 0$. Identify m corresponding to the most dominant term in the series. Justify your answer in no more than one line explanation. [3+2+1]

(b) The wavefunction $\Psi(1,2) = 0.5[\phi_{1s}(1)\phi_{2p_z}(2) + \phi_{2p_z}(1)\phi_{1s}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$ describes an excited electronic state of Helium atom. **(I)** Write the term symbols corresponding to these states. **(II)** The total electronic orbital angular momentum of the system is the resultant of the orbital angular momenta of the individual electrons, that is, $\vec{L} = \vec{L}_1 + \vec{L}_2$. Similarly, the total electronic spin angular momentum of the system is the resultant of the spin angular momenta of the individual electrons, that is, $\vec{S} = \vec{S}_1 + \vec{S}_2$. If \hat{L}_\pm and \hat{S}_\pm are the corresponding ladder operators, then without explicitly using the forms of the operators, and just based on your knowledge about ladder operator algebra, evaluate $\hat{L}_+ \Psi(1,2)$; $\hat{L}_- \Psi(1,2)$; $\hat{S}_+ \Psi(1,2)$ and $\hat{S}_- \Psi(1,2)$. [2+4]

(c) Given $F = \{f_1, f_2, f_3, f_4\}$ is a complete orthonormal set of eigen-functions of hermitian operator, \hat{A} with the eigenvalues, $a_1 = 5$; $a_2 = a_3 = 7$; $a_4 = 9$, respectively. Similarly, $G = \{g_1, g_2, g_3, g_4\}$ is a complete orthonormal set of eigen-functions of operator, \hat{B} with the corresponding eigenvalues, $b_1 = 6$; $b_2 = b_3 = 8$; $b_4 = 10$. The sets, F and G are related to each other by: $g_1 = 0.7071(f_1 + f_4)$; $g_2 = 0.7071(f_2 + f_3)$; $g_3 = 0.7071(f_2 - f_3)$ and $g_4 = 0.7071(f_1 - f_4)$. The functions in both F and G independently form complete orthonormal sets of eigenfunctions of yet another operator, \hat{D} , with the eigenvalue, $d = 25$ for each. Based on this data and the theorems about operators, attempt the following: **(I)** State whether any pairs of the given operators commute with each other or not. **(II)** If measurement is made with operator \hat{A} and value 9 is found, what is the state of the system immediately after the measurement? **(III)** Immediately after this, if measurement with operator \hat{B} is done, what is the probability of getting the value 6 of the measurement? **(IV)** If measurement with operator \hat{B} is done and value 8 is found, and immediately after this, the measurement with operator \hat{A} is done, then what is the probability that value 7 will be found? **(V)** If the system is prepared to be in the normalized state: $\psi = 0.57735f_1 + 0.5(f_2 + f_3) + c_4f_4$, then find the magnitude of the coefficient, c_4 . **(VI)** If the system is in the state, ψ described above, and measurement with \hat{D} is done, what would be the value obtained? [2+2+2+2+2+2]