Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
1st Semester, 2017-2018

CHEM F213: Physical Chemistry-II

Date: December 01, 2017 **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.

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: _____ ID:_____ Marks obtained_____

Useful data: m_e= 9.11 X 10^{-31} kg; c = 3 X 10^8 ms^{-1}; h=6.626 X 10^{-34} Js; p = 3.14159

1. Term symbols for the ground states of O_2^+ and O_2 molecules are, respectively:
(a) $^2\Pi$ and $^1\Pi$ **(b)** $^2\Pi$ and $^3\Sigma$ **(c)** $^2\Pi$ and $^1\Delta$ **(d)** $^2\Sigma$ and $^1\Sigma$

2. The operators A, B, C and D satisfy the following relationships: [A,B] = 0, [A,C]= 0 and D=B +*i*C. Which of the following statements is/are true: (i) [A, D] = 0 (ii) [B, C] = - [C, B] (iii) B and C may not commute
(a) All of them **(b)** (i) and (ii) only **(c)** (i) and (iii) only **(d)** (ii) and (iii) only

3. Which of the following statements are true about a stationary state of a quantum mechanical system?:
(i) The wavefunction does not obey time-dependent Schrodinger equation. (ii) The wavefunction is multiplicatively separable into time-dependent and time-independent functions. (iii) Probability density is time-independent
(a) All of them **(b)** (i) and (ii) only **(c)** (i) and (iii) only **(d)** (ii) and (iii) only

4. Given that V_{ee} and E_{so} are respectively, the electron-electron repulsion energy and spin-orbit coupling energy, the spin-orbit coupling scheme suggested by Russell and Saunders works well for atoms for which
(a) $V_{ee} \ll E_{so}$ **(b)** $V_{ee} \approx E_{so}$ **(c)** $E_{so} \ll V_{ee}$ **(d)** $V_{ee} \approx 0$

5. In quantum tunnelling, the reflection coefficient reduces with _____ in barrier height and _____ in barrier width.
(a) increase, increase **(b)** decrease, decrease **(c)** increase, decrease **(d)** decrease, increase

6. Which of the following is eigenfunction of $\hat{L}_y$ -operator (x-component of angular momentum)?
(a) $\cos\theta$ **(b)** $\cos\theta\sin\phi$ **(c)** $\sin\theta\sin\phi$ **(d)** $\sin\theta\cos\phi$

7. Which of the following statements are NOT true for a 3D non-rigid rotor?: (i) Eigenfunctions are expressible as $R(r)Y(\theta,\phi)$. (ii) Neither the angular momentum nor any one of its components is conserved. (iii) The quantum numbers l and m_l may not be integers.
(a) All of them **(b)** (i) and (ii) only **(c)** (i) and (iii) only **(d)** (ii) and (iii) only

8. The de-Broglie wave-length of an electron travelling with 0.1% of the speed of light would be
(a) 2.43 nm **(b)** 2.43 Å **(c)** 2.43 pm **(d)** 24.3 nm

9. Translation operator $\hat{T}_h$ is defined as follows: $\hat{T}_h f(x) = f(x+h)$. What is the value of $(\hat{T}_2 - 2\hat{T}_1 + 1)x^2$?
(a) 2 **(b)** $2x+3$ **(c)** $2-x^2$ **(d)** x^2-2x+1

10. If the molecular orbitals, σ_g and σ_u of H_2 molecule are obtained by linear combinations of $1s$ orbitals of the bonding atoms a and b : $\sigma_g = N_g(1s_a + 1s_b); \sigma_u = N_u(1s_a - 1s_b)$; then in the orbital approximation, spatial part of the two-electron wave-function $\Psi_{ex}(1,2)$ for the doubly excited singlet state corresponding to the electronic configuration σ_u^2 would reduces to

(a) $\Psi_{ex}(1,2) = \Psi_{cov} + \Psi_{ion}$ **(b)** $\Psi_{ex}(1,2) = \Psi_{ion} - \Psi_{cov}$ **(c)** $\Psi_{ex}(1,2) = \Psi_{ion}$ **(d)** $\Psi_{ex}(1,2) = \Psi_{cov}$

11. Time-dependent perturbation treatment is used to study spectroscopic transition probabilities because
(i) Molecular transitions cannot be described by a stationary state. (ii) Molecules do not have stationary states. (iii) Electromagnetic field oscillates with time.

(a) All of them **(b)** (i) and (ii) only **(c)** (i) and (iii) only **(d)** (ii) and (iii) only

12. For time-independent non-degenerate perturbation theory, which of the following statements are NOT true?: (i) The first order energy correction does not depend on first order correction to wavefunction. (ii) The first order energy correction depends on second order wavefunction. (iii) The first order wavefunction correction is required for calculating second order energy correction.

(a) All of them **(b)** (i) and (ii) only **(c)** (i) and (iii) only **(d)** (ii) and (iii) only

13. If the orbital angular momentum of sp^2-hybrid orbitals is measured, the probability of getting the value, zero, is

(a) 0.8164 **(b)** 1/3 **(c)** 2/3 **(d)** 0.5774

14. The orbital angular momentum vector of which of the following orbitals does not lie in xy-plane?
(i) $2p_x$ (ii) $4f_{-1}$ (iii) $3d_{xy}$

(a) All of them **(b)** (i) and (ii) only **(c)** (i) and (iii) only **(d)** (ii) and (iii) only

15. Consider a particle in a 1-D box with potential energy defined as follows: $V(x) = \infty$ for $x < 0; x > a$ and $V(x) = \xi x$ for $0 \le x \le a$ where, ξ is a constant. If the potential energy inside the box is considered as perturbation to the unperturbed system (with $V = 0$ inside the box), the first order correction to the ground state energy of the box would be

(a) $a/2$ **(b)** $\xi/2$ **(c)** $\xi a/2$ **(d)** ξ

16. The constant ξ in the question **15** has the dimensions of

(a) energy **(b)** momentum **(c)** force constant **(d)** force

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