(8 pages)   Reg. No. : ....

Code No. : 5408   Sub. Code : ZCHM 13

M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2023

First Semester

Chemistry – Core

QUANTUM MECHANICS AND SPECTROSCOPY – I

(For those who joined in July 2021 onwards)

Time : Three hours   Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

Choose the correct answer :

1. Linear momentum operator along 'x'axis - P_x is known as

    (a) $(h/i)\left(\frac{\partial^2}{\partial x}\right)$ (b) $(h/i)\left(\frac{\partial}{\partial x}\right)$

    (c) $\left(\frac{h}{i}\right)\left(\frac{\partial}{\partial x}\right)$ (d) $\left(\frac{h}{i}\right)\left(\frac{\partial^2}{\partial x^2}\right)$

2. All quantum mechanical operators

    (a) Linear only

    (b) Hermitian only

    (c) Linear and Hermitian

    (d) Neither Linear nor Hermitian

3. The normalized wave function must have _____ norm

    (a) Finite   (b) Infinite

    (c) Zero   (d) Complex

4. If 'n' denotes the quantum number and 'c' the velocity of light, thr energy of particle of mass 'm' in a box of length 'l' is proportional to _____

    (a) l^2 (b) m^2

    (c) n^2 (d) $c^{1/2}$

5. Which of the following highlights the Variation Principle?

    (a) $E_{True} - E_{Cal} > 0$ (b) $E_{True} - E_{Cal} \geq 0$

    (c) $E_{True} > E_{Cal}$ (d) $E_{True} \leq E_{Cal}$

6. The bond order of O_2^+ molecule is

    (a) 3   (b) 2.5

    (c) 3.5   (d) 4

7. The wave number transition is 200 cm^{-1}. In what part of the electromagnetic spectrum does this come?

    (a) Microwave

    (b) Ultra violet - visible

    (c) Infrared

    (d) Radiowave

8. Which of the following radiation brings about rotational transitions?

    (a) IR   (b) UV

    (c) Microwave   (d) Visible

9. Which of the region of IR spectra appears between (1400 to 600) cm

    (a) Functional group region

    (b) Finger Print region

    (c) Low Frequency region

    (d) None of the mentioned

10. In Raman spectroscopy, the radiation lies in the _____

    (a) Microwave region (b) Visible region

    (c) UV region   (d) x - ray

PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).

11. (a) State the Heisenberg's uncertainity Principle. Calculate the uncertainity in the velocity of an electron with an uncertainity 10^{-15} m in its position.

    Or

    (b) Which of the following are Eigen Function with respect to the $\frac{d^2}{dx^2}$ operator? Find the Eigen values for the Eigen Functions

        (i)   Cos X

        (ii) Sin x

        (iii) exponential (x^2)

        (iv) x^3

        (v)   log x

12. (a) Calculate the length of a one – dimensional box for which the difference between the lowest energy levels of a molecule becomes comparable to it's average kinetic energy at a given temperature.

    Or

(b) Calculate for the spacing between energy levels for an electron (mass = 9.1×10^{-31} Kg) in a one – dimensional box of length $1.0 \, A^0$

13. (a) Show that the probability of having three electrons in a '*1s*' orbital is zero.

Or

(b) Why does He_2^+ exist, while He_2 does not?

14. (a) Discuss the factors which determine the width and intensity of spectral lines.

Or

(b) Discuss the effect of isotopic subsitution on the energy levels and rotational spectrum of a diatomic molecule.

15. (a) Discuss Mutual exclusion principle with suitable examples.

Or

(b) (i) Define Stokes and anti – Stokes lines and explain their origin.

(ii) Which set of lines, Stokes or anti-Stokes is weaker?

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

16. (a) Prove that P_x and L_x operators are hermitian.

Or

(b) Show that if two operators $\hat{A}$ and $\hat{C}$ are Hermitian then the product ($\hat{A}\,\hat{C}$) is also Hermitian if and only if $\hat{A}$ and $\hat{C}$ commute.

17. (a) (i) What do you mean by degeneracy? What is the degeneracy of a particle of mass 'm' in a three dimensional cubical box of width 'a' having the energy equal to 6 in unit of $[(h^2)/(8ma^2)]$

(ii) What are spherical harmonics? How are they obtained for 'd' – orbitals?

Or

(b) Verify that the following functions are eigen functions of the simple harmonic oscillator

(i) $\psi = \exp\left(-1/2\,\beta x^2\right)$

(ii) $\psi = x \exp\left(-1/2\,\beta x^2\right)$

18. (a) State Harte's Fock Self consistent field theory.

Or

(b) Discuss the salient Features of HMO method and explain it's application to ethylene.

19. (a) (i) Why is the rotational spectroscopy studied only in gaseous state of atoms or molecules?

(ii) The roaqional energy and rotational constant of CO molecule are $6.5 \times 10^{-13} s^{-1}$ and $1.743 \times 10^{11} s^{-1}$ respectively. Find the rotational quantum number.

Or

(b) (i) What are the degenaracies of the following diatomic rotational energy levels?

(1) 0 (2) $h^2/4\pi^2 I$

(ii) HCl, but not Cl_2 absorbs microwave radiation and gives pure rotational spectrum. Explain.

20. (a) Explain in detail about the anharmonic oscillator model in vibrational spectroscopy.

Or

(b) (i) Explain the origin of Rayleigh and Raman scattering.

(ii) Discuss the applications of Raman spectroscopy.

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