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63/1 (SEM-5) CC12/CHMHC5126

2023

CHEMISTRY

Paper : CHMHC5126

(Physical Chemistry-V)

Full Marks : 60

Pass Marks : 24

Time : Three hours

**The figures in the margin indicate
full marks for the questions.**

1. Choose the correct answer : **(any five)**
1×5=5

(a) For a d-electron, the orbital angular momentum is

(i) $\sqrt{6} \hbar$

(ii) $\sqrt{2} \hbar$

(iii) \hbar

(iv) $2\hbar$

Contd.

(b) If the uncertainty in position and momentum are equal, the uncertainty in velocity is

(i) $\frac{1}{2m} \sqrt{\frac{h}{\pi}}$

(ii) $\sqrt{\frac{h}{2\pi}}$

(iii) $\frac{1}{m} \sqrt{\frac{h}{\pi}}$

(iv) $\sqrt{\frac{h}{\pi}}$

(c) Which one of the following statements is wrong about photon ?

(i) Photon energy is $h\nu$.

(ii) Photon rest mass is zero.

(iii) Momentum of photon is $h\nu/c$.

(iv) Photon exerts no pressure.

(d) The momentum operator in one dimension is

(i) $\frac{h}{2\pi} \frac{\partial}{\partial x}$

(ii) $\frac{2\pi i}{h} \frac{\partial}{\partial x}$

(iii) $\frac{h}{2\pi i} \frac{\partial}{\partial x}$

(iv) $\frac{2\pi i}{h} \frac{\partial}{\partial i}$

(e) Which one of the following has maximum no. of nodal planes ?

(i) σ_{1s}^*

(ii) σ_{2pz}^*

(iii) π_{2px}

(iv) π_{2py}^*

- (f) Proton magnetic resonance (PMR) is studied in
- (i) UV region
 - (ii) IR region
 - (iii) Radio frequency region
 - (iv) γ -ray region
- (g) Electromagnetic radiation is characterised by
- (i) electric and magnetic field
 - (ii) wave and particle character
 - (iii) wavelength and wavenumber
 - (iv) All of the above
- (h) Which one of the following is IR active ?
- (i) O_2
 - (ii) H_2
 - (iii) CO
 - (iv) CH_4

- (i) In photochemical reactions the absorption of light takes place in
- (i) primary process only
 - (ii) secondary process only
 - (iii) both primary and secondary processes
 - (iv) either primary or secondary process
- (j) The delayed fluorescence is called
- (i) chemiluminescence
 - (ii) phosphorescence
 - (iii) photosensitization
 - (iv) photolysis

2. Answer **any five** of the following questions :
2×5=10

- (a) What are normalised and orthogonal wavefunctions ?

- (b) How many normal modes of vibration are there in HCl and SO_2 (bent) molecules ?
- (c) Justify the variation theorem. What is its applicability ?
- (d) Mention the selection rules of vibrational-rotational spectra.
- (e) What is molar extinction co-efficient ? Write its unit.
- (f) Give a schematic diagram of an absorption spectrometer.
- (g) Calculate the energy associated with one Einstein of radiation of wavelength 400 nm .

3. Answer **any five** of the following questions :
5×5=25

- (a) (i) Explain briefly the Born interpretation of wavefunction. 3

(ii) What are eigenfunction and eigenvalue ? 2

(b) (i) Explain are Hermitian operators ?

Examine if $\frac{d^2}{dx^2}$ is a Hermitian operator or not. 3

(ii) Explain the quantum mechanical significance of *four* quantum nos. 2

(c) (i) An electron in one-dimensional box of width 1 \AA undergoes a transition from the ground state ($n = 1$) to the first excited state ($n = 2$). Calculate the transition energy in eV. 3

(ii) What is zero point energy of a particle in one-dimesional box ? Explain. 2

(d) Define force constant. The fundamental vibrational frequency of HCl is $2,890\text{ cm}^{-1}$. Calculate the force constant of the molecule. $1+4=5$

(e) Explain briefly the NMR instrumentation with diagram. Justify with suitable applications.

(f) (i) What is Born-Oppenheimer approximation? Elaborate. 3

(ii) What factors effect the width of spectral lines? Discuss in brief. 2

(g) What is spin-spin splittings of NMR signals? Explain the high resolution spectra of acidified ethanol (CH_3CH_2OH). $2+3=5$

(h) What do you mean by quenching of fluorescence? Derive Stern-Volmer equation. $1+4=5$

(i) Distinguish between the following :
 $2\frac{1}{2}+2\frac{1}{2}=5$

(i) Absorption spectra and emission spectra

(ii) Singlet and triplet states

4. Answer **any two** of the following questions :
 $10\times 2=20$

(a) (i) Derive an expression for the total energy of a particle in a three-dimensional box. Explain the concept of degeneracy. $5+2=7$

(ii) What are radial probability distribution curves? Draw the radial probability distribution curve for the valence electron of Na-atom. 3

(b) (i) What is the difference between atomic orbital and molecular orbital? Give the salient features of molecular orbital theory. $1+4=5$

- (ii) Draw molecular orbital energy level diagram of O_2 molecule. Predict bond order and magnetic behaviour of the molecule from the diagram. 2
- (iii) Explain sp-hybridization with an example. 3
- (c) (i) Discuss the principles and applications of ESR spectroscopy. 6
- (ii) State and explain Franck-Condon principle. 2
- (iii) List all the electronic transitions possible for 2
- (i) CH_4 ;
- (ii) $H_2C=O$;
- (d) (i) Derive the expression for the energies (in terms of wavenumber) of rotational levels of diatomic molecules based on the rigid rotator. 6
- (ii) The rotational spectrum for HCl shows a series of lines separated by 20.6 cm^{-1} . Find the moment of inertia and the internuclear distance of the molecule. 4
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