This question paper contains 7 printed pages]

*Your Roll No.* .....

**1232**

**B.Sc. (Hons.)/III** **A**

PHYSICS—Paper XXII (*i*)

(Modern Chemistry)

*Time* : 3 *Hours* *Maximum Marks* : 38

*(Write your Roll No. on the top immediately on receipt of this question paper.)*

Total *six* questions to be answered.

Question **one** is compulsory.

Answer any *five* other questions at least *two* from each Section.

Use of Calculators is allowed but they cannot be shared.

Log tables can be provided if required.

**Physical Constants :**

| | |
|---|---|
| Planck's constant | $6.626 \times 10^{-34}$ Js |
| Velocity of light | $3 \times 10^{8}$ $ms^{-1}$ |
| Boltzmann constant | $1.381 \times 10^{-23}$ $JK^{-1}$ |
| Avogadro's number | $6.023 \times 10^{23}$ $mol^{-1}$ |

P.T.O.

| | |
|---|---|
| Atomic mass unit | $1.661 \times 10^{-27}$ kg |
| Mass of electron | $9.109 \times 10^{-31}$ kg |
| Nuclear magneton | $5.051 \times 10^{-27}$ $JT^{-1}$ |
| Bohr magneton | $9.274 \times 10^{-31}$ $JT^{-1}$ |

1. Attempt any *four* :

(*a*) Show that if two operators $\hat{A}$ and $\hat{B}$ are Hermitian, their product $\hat{A}\hat{B}$ is Hermitian only if operators $\hat{A}$ and $\hat{B}$ commute.

(*b*) State the variation theorem.

(*c*) Evaluate $[\hat{l}_x, \hat{l}_y]$, where $\hat{l}_x$ and $\hat{l}_y$ are the angular momentum operators along the $x$ and $y$-direction respectively.

(*d*) For a particle of mass $m$ in a one-dimensional box of length '$a$' show that $\Psi_1$ and $\Psi_2$ are orthogonal.

(*e*) Explain briefly the appearance of "hotbands" in infrared spectroscopy.

(*f*) ESR spectrum of atomic hydrogen is observed with a spectrometer operating at 9.5 GHz. If the Lande *g*-factor is 2.0026, calculate the value of the external magnetic field required to record the spectrum. $2 \times 4$

**Section A**

2. (*a*) Write the expression for the Hamiltonian for the helium atom explaining briefly the terms involved.

(*b*) For a 1-electron diatomic molecule the molecular orbitals have been formed as a linear combination of two atomic orbitals centred on the two atoms. The normalized atomic orbitals are represented by $\varphi_A$ and $\varphi_B$.

The values of some relevant integrals are :

$$\int \varphi A \hat{H} \varphi_A \, d\tau = -2 a.u. ; \quad \int \varphi B \hat{H} \varphi_B \, d\tau = -2 a.u. ;$$

$$\int \varphi A \hat{H} \varphi_B \, d\tau = -1 a.u. ;$$

$$\int \varphi A \, \varphi B \, d\tau = 0.25 \; a.u.$$

[$\hat{H}$ represents the Hamiltonian operator]

Evaluate the expression for the wavefunction of the bonding molecular orbital and the corresponding energy. 2, 4

3. (*a*) For a diatomic molecule undergoing rotational motion; why does the population of the rotational level attain a maximum value at $J_{max}$ ? Derive an expression to evaluate the rotational constant B for this molecule; from the value of $J_{max}$.

(*b*) Draw an energy level diagram to explain bonding in the linear beryllium hydride molecule. 3, 3

4. (*a*) The fundamental and first overtone of hydrogen chloride are centred at 2886 $cm^{-1}$ and 5668 $cm^{-1}$ respectively. Evaluate the equilibrium vibrational frequency, the anharmonicity constant and the zero point energy.

(*b*) A substance shows a Raman line at 456.8 nm when the exciting line is at 433.2 nm. Calculate the wavelength for the Stokes' and Anti-Stokes' lines for this substance when the exciting line is at 403.6 nm.

(*c*) State the rule of mutual exclusion. 3, 2, 1

5. (*a*) Calculate the average distance for the 2s electron from the nucleus of the hydrogen atom given that :

$$\varphi_{2s} = (1/32\pi)^{1/2} (2-r)\exp(-r/2)$$

in atomic units and that :

$$\int_0^\infty r^n \exp(-ar)\, dr = n\,!/a^{(n+1)}$$

(*b*) A particle of mass '*m*' is confined within a one-dimensional box of length '*a*' extending along the *x*-axis. Using $\psi(x) = x(a-x)$ as a trial function estimate the ground state energy of this particle. If the exact ground state energy is $h^2/8\,ma^2$, does this function satisfy the variation theorem ? 3, 3

## Section B

6. (*a*) A sample containing protons is placed in a magnetic field of strength 2 Tesla. Calculate the ratio of the number of proton spins in the lower state to the higher state at 298 K given that $g_n$ for $^1H$ is 5.585.

(*b*) Sketch the low and high resolution $^1H$ NMR spectrum of methyl alcohol.

(*c*) How will this spectrum be affected if deuterated water, $D_2O$, is added ? 2, 3, 1

7. (*a*) Explain briefly the Hückel Molecular-Orbital theory approximations.

(*b*) The $\pi \rightarrow \pi^*$ transition for 1, 3-butadiene is observed at 46083 $cm^{-1}$. Evaluate the value of the resonance integral $\beta$.

(*c*) What are the factors that influence the linewidth of a spectral line ? 2, 2, 2

8. (*a*) With the help of an energy level diagram, explain fluorescence and phosphorescence.

(*b*) Sketch the ESR spectrum of the $\cdot CH_2$ free radical when :

(*i*) the two protons are equivalent;

(*ii*) the two protons are not equivalent.

(*c*) The bond energy of the carbonyl bond in acetone is 728 kJ $mol^{-1}$. What will be the wavelength of light absorbed by this bond ? Will a 254 nm mercury source be effective in breaking this bond ? 2, 2, 2

9. Write short notes on any *two* :

(*a*) Franck Condon Principle

(*b*) Self consistent field method for many electron systems

(*c*) Larmor precessional frequency. 3, 3