



1. Attempt any *five* :

5×3

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

(b) State and briefly explain the rule of mutual exclusion.

(c) Evaluate the commutator  $[\hat{L}_x, \hat{L}_y]$ , 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. (a) Write the expression for the Hamiltonian for the helium atom explaining briefly the terms involved.

(b) For a one-electron diatomic molecule the molecular orbitals have been formed as a linear combination of two atomic orbitals centred to the two atoms. The normalized atomic orbitals are represented by  $\phi_A$  and  $\phi_B$ .

(i) Derive the expression for the normalized wavefunctions of the molecular orbitals formed and their corresponding energy.

(ii) The values of the integrals are :

$$\int \varphi_A \hat{H} \varphi_A d\tau = -2\text{a.u.}; \quad \int \varphi_B \hat{H} \varphi_B d\tau = -2\text{a.u.};$$

$$\int \varphi_A \hat{H} \varphi_B d\tau = -1\text{a.u.}; \quad \int \varphi_A \varphi_B d\tau = 0.25\text{a.u.}$$

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

Calculate the energy of the bonding and anti-bonding molecular orbitals. 3,6+3

3. (a) For a diatomic molecule undergoing rotational motion :

(i) why does the population of the rotational level attain a maximum value at  $J_{\max}$  ?

(ii) derive an expression for  $J_{\max}$ .

(iii) evaluate the rotational energy corresponding to  $J_{\max}$  and show that under certain conditions this value is in accordance with classical theory.

(b) Draw an energy level diagram to explain bonding in the linear beryllium hydride molecule. 2+3+3,4

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

- (b) A substance shows a vibration Raman line at 456.8 nm when the incident radiation is at 433.2 nm. Calculate the wavelength for the Stokes' and Anti-Stokes' line for this substance when the incident radiation is at 403.6 nm.
- (c) Consider a particle of mass ' $m$ ' in a cubic box of edge length ' $L$ '. What is the degeneracy of the level that has energy three times the lowest energy? Write the mathematical expressions for the degenerate wavefunctions. 4,3,5
5. (a) Calculate the average distance for the 2s electron from the nucleus of the hydrogen atom given that  $\phi_{2s} = (1/32\pi)^{1/2} (2 - r) \exp(-r/2)$  in atomic units, and that :
- $$\int r^n \exp(-ar) dr = n! / a^{(n+1)} .$$
- (b) State variation theorem.
- (c) 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  $h^2/8ma^2$ , does this function satisfy the variation theorem? 4,2,6
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 the nuclear  $g$ -factor,  $g_N$ , for  $^1\text{H}$  is 5.585.

- (b) Sketch and explain the low and high resolution  $^1\text{H}$  NMR spectrum of ethyl alcohol.
- (c) Derive the mathematical expression to evaluate the rotational constant, B, from a spectrum which is observed as a PQR contour. 4,4,4

7. (a) Explain briefly the Huckel Molecular Orbital theory approximations.
- (b) The  $\pi \rightarrow \pi^*$  transition for 1,3-butadiene is observed at  $46083 \text{ cm}^{-1}$ . Evaluate the value of the resonance integral  $\beta$ .
- (c) What are the factors that influence the linewidth of a spectral line ? 4,4,4
8. (a) With the help of an energy level diagram, explain fluorescence and phosphorescence.
- (b) Sketch and explain the ESR spectrum of the  $\bullet\text{CH}_2$  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  $728 \text{ kJmol}^{-1}$ . What will be the wavelength of light absorbed by this bond ? Will a 254 nm mercury source be effective in breaking this bond ? 4,2+2,4

9. Write short notes on :

(a) Franck-Condon principle

(b) Comparison of the valence bond and molecular orbital approaches to bonding in the hydrogen molecule

(c) Larmor precessional frequency.

4,4,4