

DO NOT ASK ANY QUESTIONS; USE YOUR INTERPRETATION WHERE NEEDED.

Q1. You are told that the intensities of spectroscopic transitions between the vibrational states of a diatomic molecule are proportional to the square of the integral $\int_{\text{all space}} \psi_v' x \psi_v dx$.

(A) Deduce a relationship between v and v' from this integral. (10)

(B) Evaluate the integral in terms of α and v based on your results from part (A). (10)

Q2. This question deals with the rotational spectra of diatomics. The intensities of spectral lines increase with increasing l (the orbital angular momentum quantum number) and pass through a maxima before decreasing as l becomes large. The most important reason for the maximum in intensity is the existence of a maximum in the population of rotational levels. The Boltzmann distribution implies that the population of each state decays exponentially with increasing l , but the degeneracy of the level increases. Specifically, the population of a rotational level l is given by the Boltzmann expression: $N_l = N g_l \exp(-E_l/k_B T)$, where N is the total number of molecules and the g_l is the degeneracy of the level l (k_B is the Boltzmann constant). Derive an expression for the value of l [in terms of rotational constant \bar{B} (in cm^{-1})] corresponding to the most highly populated rotational energy level (i.e., l_{max}) of a diatomic rigid rotor at temperature T . Calculate the l_{max} (as an integer) for a diatomic molecule ICl (for which $\bar{B} = 0.1142 \text{ cm}^{-1}$) at 25°C . (15 + 5 = 20)

Q3. Consider a particle in a spherical box of radius a . The Hamiltonian operator for this system is

$$\hat{H} = -\frac{\hbar^2}{2ma^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{\hbar^2 l(l+1)}{2mr^2}; 0 < r \leq a. \text{ As in the case of a particle in a rectangular box, } \psi(a) = 0.$$

Use $\phi(r) = (a-r)$ to calculate an upper bound to the ground-state energy of this system. Specify if variational theorem is obeyed if the exact ground-state energy is $\pi^2 \hbar^2 / 2ma^2$. (15 + 5 = 20)

Q4. A normalized wavefunction for hydrogen atom is $\psi_H = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) \exp\left(-\frac{r}{2a_0}\right)$.

(A) Assign n, l, m_l and name the atomic orbital. (4)

(B) Calculate the most probable distance of this electron from the nucleus in terms of a_0 . (4)

(C) Calculate the average distance of this electron from the nucleus in terms of a_0 . (4)

(D) Calculate the most probable point for this electron in terms of a_0 . (4)

(E) Sketch the radial wavefunction and the radial distribution function versus r for this orbital. (4)

Q5. Using LCAO-MO approach, a trial wavefunction for H_2^+ may be written as

$\psi = c_1 \psi_{1s_A} + c_2 \psi_{1s_B}$, where ψ_{1s_A} and ψ_{1s_B} are hydrogenic atomic orbitals centered on nuclei A and B, respectively.

(A) Write the expressions for Overlap integral, Coulomb integral, and Exchange integral (in their integral forms) clearly explaining each term in every expression. (6)

(B) What is the energy in terms of Coulomb integral, Exchange integral, Overlap integral and energy of the hydrogenic atomic orbital? (4)

(C) What is the energy of H_2^+ relative to completely dissociated species H^+ and H ? (2)

(D) Plot the energy obtained in part (C) versus the internuclear separation R . (2)

(E) Plot the separate contributions of the Coulomb integral and the Exchange integral to the stability of H_2^+ versus the internuclear separation R . (4)

(F) Based on your plots in part (E), indicate which integral is responsible for chemical bonding in H_2^+ . (2)