

Answer any **THREE** questions.

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question.

1. State the **Born-Oppenheimer** approximation as applied to the wavefunctions of molecules. [3]

The Hamiltonian for the coupled vibration-rotation motion of a diatomic molecule can be written

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu R^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + V \quad (1)$$

where R is the separation between the nuclei and (θ, ϕ) gives the orientation of the molecule. Explain carefully what is meant by the symbols μ and V , and upon what they depend. [4]

An approximate wavefunction for the vibration-rotation motion can be written:

$$\Psi_{VR}(R, \theta, \phi) = \psi_V(R) Y_{J,K}(\theta, \phi) \quad (2)$$

where $Y_{J,K}(\theta, \phi)$ is a spherical harmonic. Use (2) to obtain an effective vibrational Hamiltonian in terms of the rotational angular momentum quantum number J . [3]

By considering the $J = 0$ case, derive the harmonic oscillator form of the Hamiltonian

$$\hat{H}_{HO} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} k (R - R_e)^2 \quad (3)$$

carefully defining the parameters k and R_e . Give an expression for the energy levels of this system. How do the actual vibrational energy levels differ from this? [5]

Give an expression for the energy levels of a rigidly rotating diatomic molecule in terms of the parameters J , μ and R_e . The lowest energy level of the ${}^7\text{Li}^{35}\text{Cl}$ molecule is found to absorb light strongly at 1.413 cm^{-1} . Estimate the wavenumber of the corresponding transition in ${}^7\text{Li}^{37}\text{Cl}$ being careful to state any assumptions you make. [5]

2. State the **Pauli Principle** as it applies to the wavefunction of a many-electron system. [2]

Consider the interaction between species X and Y, where X and Y are both closed shell systems in their electronic ground state. Explain what causes the two species to repel each other as they are brought close together. How does this interaction depend on R , the distance between the centre-of-mass of X and the centre-of-mass of Y? [3]

For each of the following pairs of X and Y, give the leading term in the long range interaction and its dependence on R :

- (a) $X = \text{Cl}^-$, $Y = \text{Li}^+$.
- (b) $X = \text{Cl}^-$, $Y = \text{He}$.
- (c) $X = \text{Cl}^-$, $Y = \text{HCN}$.
- (d) $X = \text{He}$, $Y = \text{He}$.

Rank the $X - Y$ pairs in order of the probable strength of their long range interaction. [8]

Consider the $X \ ^1\Sigma_g^+$ ground state of the He_2 complex. Given that ^4He has nuclear spin $i = 0$ and ^3He has nuclear spin $i = \frac{1}{2}$, comment on the relative probability of finding the complex in its $J = 0$ or $J = 1$ state at high temperature for (a) $^4\text{He}_2$, (b) $^3\text{He}_2$ and (c) $^3\text{He}^4\text{He}$. [7]

3. The hydrogen molecule comprises two protons (A and B) and two electrons (1 and 2). Give a diagram defining the inter-particle coordinates used for the hydrogen molecule and hence give an expression for the Hamiltonian governing the motions of the electrons in H_2 . [5]

Explain what is meant by the phrase **linear combination of atomic orbitals** (LCAO) when representing the electronic structure of a molecule. [2]

Within the molecular orbital model of molecular bonding, a wavefunction for the ground state of H_2 can be written:

$$\Psi_{MO}^S = N_{MO}^S [\phi_{1s}(\mathcal{L}_{A1}) + \phi_{1s}(\mathcal{L}_{B1})][\phi_{1s}(\mathcal{L}_{A2}) + \phi_{1s}(\mathcal{L}_{B2})] \times \chi^S$$

where N_{MO}^S is normalization constant, χ^S is a two electron singlet spin function and $\phi_{1s}(\mathcal{L}_{Ai})$ is a hydrogen atom 1s orbital centred on atom A for electron i . Write down the corresponding expression for

- (a) Ψ_{MO}^T , the wavefunction of the first excited triplet state of H_2 within the molecular orbital model.
 (b) Ψ_{VB}^S , the wavefunction of H_2 within the valence bond model of molecular bonding. [4]

Obtain an expression for the normalization factor for both Ψ_{MO}^S and Ψ_{VB}^S in terms of the integral

$$I = \int \phi_{1s}(\mathcal{L}_{Ai})^* \phi_{1s}(\mathcal{L}_{Bi}) dV_i.$$

Explain the physical significance of the integral I and discuss its value as the H – H separation becomes large. [6]

Contrast the behaviour of Ψ_{MO}^S and Ψ_{VB}^S at large H – H separations. Which model is more reliable in this region? [3]

4. A molecule contains N atoms. Explain, with reasons, how many vibrational modes the molecule will have if it is (a) bent and (b) linear. [4]

Explain the physical processes whereby CO_2 can be made to undergo laser emission. Why does the CO_2 laser lase at several frequencies? Would you expect the number of lasing frequencies to depend on temperature? [7]

A cold sample of the LiF molecule is found to absorb light from a CO_2 laser at 976.48, 979.50, 985.52, 988.53 and 991.53 cm^{-1} . Identify the transitions observed in this spectrum. Obtain estimates of the rotational constant, B , and the fundamental frequency, ω . Why do these constants not give an exact fit to the spectrum? What changes would you expect the absorption spectrum of (a) a room temperature and (b) a very hot sample of LiF to show if they were recorded in the CO_2 region? [9]

5. Explain what is meant by the terms **shape resonance** and **Feshbach resonance** as used in electron-molecule collisions. Give a physical model for both types of resonance. Give an example of each type of resonance for electron collisions with molecular hydrogen. [6]

Electrons are scattered from molecular hydrogen over a range of energies below 10 eV. What electron impact processes can be observed? Explain how these processes can be modified in the region of a resonance. [9]

A beam of 100 eV electrons is used to ionize molecular hydrogen. Discuss what factors determine the vibrational population of the resulting H_2^+ ions. Would you expect this population to be altered if the H_2 was photoionized with 100 eV photons instead? [5]