

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]

At an internuclear separation of R , a diatomic molecule has two electronic states with wavefunctions $\Psi_1(R)$ and $\Psi_2(R)$. Without proof, explain why in general the potential energy curves associated with $\Psi_1(R)$ and $\Psi_2(R)$ do not cross. Give a sketch of potential energy curves in the vicinity of an avoided crossing and explain how the nature of the wavefunction changes in this region. Under what circumstances can curves cross? [6]

The LiCl molecule is ionically bonded. Sketch the potential energy curves involved in bringing atoms of Li and Cl together. Indicate the role of:

- (a) The ionisation potential of Li, I .
- (b) The electron affinity of Cl, A .
- (c) The dissociation energy, D_e .
- (d) The equilibrium bondlength, R_e .

You may assume that $I > A$. [6]

Obtain an expression for R_c , the internuclear separation where the bonding changes between covalent and ionic. How would you expect the curves to behave in this region? [3]

How would you expect the curves to differ for an ionic molecule for which $I < A$? [2]

2. The hydrogen molecule comprises two protons and two electrons. 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 **orbital approximation** and which physical interactions are approximated in the approximation. [4]

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

$$\Psi^S = 1\sigma_g(1)1\sigma_g(2) \times \chi^S$$

where χ^S is a two electron singlet spin function, and the molecular orbital for electron i is given by:

$$1\sigma_g(i) = N[\phi_{1s}(r_{Ai}) + \phi_{1s}(r_{Bi})]$$

and $\phi_{1s}(r_{Ai})$ is a hydrogen atom $1s$ orbital centred on atom A for electron i . Obtain an expression for the normalisation factor N in terms of the integral

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

Explain the physical significance of the integral I . [5]

Using this wavefunction, the energy of the ground state of H_2 can be shown to be:

$$2E(H_2^+) - \frac{1}{R} + \int \frac{|1\sigma_g(1)1\sigma_g(2)|^2}{r_{12}} dV_1 dV_2$$

where $E(H_2^+)$ is the energy of the ground state of H_2^+ . Explain the physical significance of the final term in this expression. [2]

Explain why Ψ^S gives a poor approximation to the wavefunction of H_2 as it dissociates. Suggest how one might construct a wavefunction which gives a better representation of the molecule as it dissociates. [4]

3. A heteronuclear diatomic molecule is found to show absorption features in
- (a) the microwave,
 - (b) the infrared,
 - (c) the ultraviolet.

Explain what motions of the molecule give rise to absorption features in each of the three spectral regions. What quantum numbers govern allowed transitions for each type of spectrum? [7]

With the aid of a diagram, describe in detail an experiment which records the absorption spectrum of a molecule in the infrared. [5]

Explain in detail what information about the molecule and its environment can be obtained from analysing its infrared spectrum. Be careful to state any assumptions made. [8]

4. Define the term **resonance** as used in electron-molecule collisions. [2]

Describe the three types of resonances that can occur in electron molecule collisions, explaining the physical process that gives rise to each of them. What level of theoretical treatment is required to model each type of resonance? [8]

List the various non-ionizing inelastic processes that can occur in electron molecule collisions. For which of these are resonances particularly important? [5]

Electrons collide with molecular hydrogen in its vibrational ground state. You can assume that H_2 is a harmonic oscillator whose vibrational states are separated by approximately 0.5 eV.

- (a) What vibrationally excited states of H_2 would you expect to observe for electrons colliding with the (non-resonant) energy of 2.5 eV?
- (b) What vibrationally excited states of H_2 would you expect to observe for electrons colliding at the resonance energy of 2.8 eV? What determines the distribution between different vibrational states in this case?
- (c) If D_2 is substituted for H_2 , what changes in the vibrational spectrum would you expect to observe for electrons colliding at the resonance energy of 2.8 eV? [5]

5. Explain the **Franck-Condon Principle** as it is used to predict the intensity of vibrational transitions within the electronic spectrum of a diatomic molecule. [3]

Electronic spectra often display a **Band Head**. Explain how this might arise. [3]

Molecular hydrogen undergoes an electronic transition from the $X^1\Sigma_g^+$ ground state to the $B^1\Sigma_u^+$ excited state. There is no Q branch for this transition. The potential energy minima of these two electronic states are separated by $T_e = 91689.9 \text{ cm}^{-1}$. The energy levels of the ground state can be characterised by the constants $\hbar\omega'' = 4395.9 \text{ cm}^{-1}$ and $B'' = 60.8 \text{ cm}^{-1}$; the corresponding levels of the excited state are given by $\hbar\omega' = 1356.9 \text{ cm}^{-1}$ and $B' = 19.9 \text{ cm}^{-1}$. You may assume that both states behave as rigid rotors and harmonic oscillators.

An absorption spectrum is recorded in cold H_2 so that only the $J'' = 0$ and $J'' = 1$ rotational levels are occupied. Calculate the wavenumbers where you would expect to find transitions to the $v' = 0$ and 1 vibrational levels of the excited electronic state. [8]

Given that $R_e(X) \ll R_e(B)$, which vibrational bands would you expect to be strongest? The $b^3\Sigma_u^+$ state of H_2 is purely repulsive and absorbs weakly from the $X^1\Sigma_g^+$ ground state. What would you expect this absorption spectrum to look like? [3]

It is observed that for H_2 transitions starting from the $J'' = 1$ rotational level are three times as strong as those starting from the $J'' = 0$ level. Would you expect this to be true for D_2 ? Give your reasoning. [3]