

Answer any **THREE** questions.

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

The simple molecule H_2^+ comprises two protons and an electron. With the aid of a diagram, write down the Hamiltonian, \hat{H} , which the electronic wavefunction of H_2^+ must satisfy. [3]

A suitable trial wavefunction for the electronic ground state of H_2^+ consists of a hydrogen atom $1s$ wavefunction, ϕ_{1s} , centred on each proton.

- (a) Give a function for the electronic wavefunction, of the ground state, Ψ_g . [1]
- (b) Write down an expression for the electronic energy of the H_2^+ ground state in terms of \hat{H} and Ψ_g . [1]
- (c) Substitute the expressions found above for \hat{H} and Ψ_g into your energy expression. Which of these terms can be evaluated directly? [4]
- (d) Using the integrals:

$$I = \int \phi_{1s}^*(r_A)\phi_{1s}(r_B)d\tau,$$

$$G = \int \phi_{1s}^*(r_A)\frac{1}{r_B}\phi_{1s}(r_A)d\tau$$

and

$$S = \int \phi_{1s}^*(r_A)\frac{1}{r_B}\phi_{1s}(r_B)d\tau$$

obtain an expression for the electronic energy of the ground state of H_2^+ . [4]

- (e) Explain the physical significance of the integrals I and G . [2]

A similar procedure can be used to evaluate the electronic energies of many-electron molecules. Explain what new integrals arise for a many electron problem such as H_2 . [2]

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

Explain what is meant by the **orbital approximation** for wavefunctions of many-electron systems. What is the major contribution to the total electronic energy of the system omitted in the orbital approximation? Why is the energy which is omitted in the orbital approximation particularly important when considering molecular bonding? [5]

Within the orbital approximation write down wavefunctions for a two-electron system which satisfies the Pauli Principle and which couple to (a) a singlet and (b) a triplet spin state. [3]

Explain what is meant by the term **Exchange** in the electronic structure of atoms and molecules. How does exchange lead to the separation of singlet and triplet states arising from wavefunctions with the same orbital occupancy. [3]

The lowest and first excited orbitals of the hydrogen molecule, H_2 , can be designated $1\sigma_g$ and $1\sigma_u$ respectively. Give, in energy order, the configuration and spin state of the electronic states of H_2 derived from these orbitals. [4]

The fluorine atom has nuclear spin $i = \frac{1}{2}$ and forms a molecule, F_2 , whose ground state has $^1\Sigma_g^+$ symmetry. At high temperature what is the probability of finding F_2 in a state where the rotational quantum number, J , is even rather than odd? [3]

3. Outline three types of spectra that can be obtained for a heteronuclear diatomic molecule such as CO. What types of motion that give rise to each of these spectra? [4]

At what wavelengths do each of these types of spectra typically occur? [2]

What selection rules govern the allowed transitions in each case? [3]

A cool sample of $^{12}C^{16}O$ is found to absorb infrared radiation at 2135.63, 2139.46, 2147.16, 2151.03 and 2154.94 cm^{-1} . Identify the transitions observed in this spectrum. [3]

Obtain estimates in cm^{-1} for the rotational constant, B , and fundamental vibrational frequency, ω , of $^{12}C^{16}O$. What information about the molecule do these constants contain? [4]

Estimate the absorption frequencies if cool $^{14}C^{16}O$ is used instead of $^{12}C^{16}O$ to obtain the spectrum given above. [4]

4. Describe the **Franck-Condon Principle** as applied to the intensity of transitions in the electronic spectrum of a diatomic molecule. [4]

What assumptions are made when deriving the Franck-Condon Principle? [2]

Consider a diatomic system with three electronic states of the same spin multiplicity: the X ground state, the excited A state and the excited B state. The A state is attractive while the B state is purely repulsive. Explain what is meant by the words **attractive** and **repulsive** in this context. [2]

For which of these states is the concept of an equilibrium bondlength, R_e , useful? [1]

Why is the equilibrium bondlength for an excited state often larger than that of the ground state? [2]

With the aid of sketches explain what transitions one would expect to observe if: (a) the $A \leftarrow X$ spectrum is recorded and $R_e(X) \approx R_e(A)$; (b) the $A \leftarrow X$ spectrum is recorded and $R_e(X) \ll R_e(A)$; and (c) the $B \leftarrow X$ spectrum is recorded. [6]

Give one example of another process where transition probabilities can be determined using the Franck-Condon Principle. Explain why the Franck-Condon Principle is appropriate in this case. [3]

5. Define the terms **total cross section**, **differential cross section** and **inelastic cross section** when applied to the scattering of an electron from a molecule. [3]

Describe ONE experimental method for measuring one of these cross sections to high accuracy. [5]

Describe the mechanisms which give rise to the three different resonances observed in electron-molecule collisions [6]

Comment on the likely width of each type of resonance [3]

Give an example of an electron-molecule process which is reliant on the presence of a resonance. Briefly discuss the role of the resonance width in this process. [3]