UNIVERSITY COLLEGE LONDON

University of London

EXAMINATION FOR INTERNAL STUDENTS

For The Following Qualification:-

M.Sci.

Physics 4431: Molecular Physics

COURSE CODE	:	**PHYS4431**
UNIT VALUE	:	**0.50**
DATE	:	**20-MAY-04**
TIME	:	**14.30**
TIME ALLOWED	:	**2 Hours 30 Minutes**

04-C1102-3-40

TURN OVER

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. Explain what is meant by the **orbital approximation** for the wavefunction of a many-electron system. Briefly describe one method used to generate orbitals for a many electron molecule. [4]

   In atomic units the Hamiltonian for the hydrogen molecule can be written:

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}} + \frac{1}{R}.$$

   Explain the physical origin of each of these terms. [4]

   The ground state electronic wavefunction of the hydrogen molecule can be expressed in terms of the H atomic orbitals $\phi_{1s}(r_A)$ and $\phi_{1s}(r_B)$. Give an expression for this wavefunction in (a) the valence bond model and (b) the molecular orbital model. [6]

   As $R \longrightarrow \infty$, use the valence bond wavefunction to obtain an expression for the energy of the hydrogen molecule. Comment on the physical correctness of this result and, without derivation, on the result obtained using the molecular orbital wavefunction. [6]

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

   Explain how the Pauli Principle leads to exchange forces and the effect these have on molecular bonding. Discuss one other way in which the Pauli Principle influences the level structure of simple molecules such as H_2. [6]

   The lowest two molecular orbitals of the hydrogen molecule are denoted $1\sigma_g$ and $1\sigma_u$. What electronic states can arise from placing two electrons in these orbital? Give the spectroscopic designation for each of these states. Order these states according to their energies, giving reasons for your choice. Which of these states would you expect to be stable with respect to (a) autoionisation and (b) dissociation? [12]

3. The atoms in a triatomic molecule have nine degrees of freedom. Explain how these degrees of freedom are distributed among the classes of motion when the triatomic is (a) linear and (b) bent. [3]

What physical criteria determine whether (a) a diatomic and (b) a triatomic molecule absorbs light (i) at microwave wavelengths and (ii) at wavelengths in the mid infrared? [5]

Using this information, explain the role of N_2, O_2, O_3, H_2O and CO_2 molecules in determining the Earth's radiation budget. Why is water particularly important? [10]

Oil wells release significant quantities of methane (CH_4) and atomic helium. Suggest how increasing the concentration of these species might influence the the Earth's radiation budget. [2]

4. Describe the **Franck-Condon Principle** and explain the assumptions upon which it is based. [5]

Consider a very cold sample of gaseous molecular hydrogen. The Franck-Condon Principle is used to model the following processes:

(a) photoionisation;

(b) electron impact dissociation via the repulsive, first-excited electronic state;

(c) the electronic spectrum for the X $^1\Sigma_g^+$ – C $^1\Pi_u$ band.

For each case, give a sketch of the curves involved. State which vibrational wavefunctions need to be considered for each process and hence comment on the distribution of the final product in each case. [10]

Considering the X $^1\Sigma_g^+$ – C $^1\Pi_u$ electronic transition in detail. At what frequency would you expect to observe transitions into the $v = 0$ and $v = 1$ vibrational states of the C $^1\Pi_u$ state? [5]

The following information should be used as needed.

H_2 State	T_e	ω_e	B
X $^1\Sigma_g^+$	0	4401.2	60.9
C $^1\Pi_u$	100089.8	2443.8	31.4

5. Explain what is meant by the term **resonance** in an electron – molecule collision. [2]

What are the three distinct types of resonances that occur in electron – molecule collisions? For each type, describe the physical processes that create the resonance state and how this effects the typical width of the associated resonance. Explain the role of each type of resonance in processes leading to dissociation in low energy collisions. [10]

Give an actual example of a resonance system for two of the resonance types. [2]

Electrons collide with the HF molecule. Consider HF as a harmonic oscillator whose vibrational states are separated by approximately 0.4 eV.

(a) What vibrationally excited states of HF would you expect to observe for electrons colliding with the (non-resonant) energy of 2.0 eV?

(b) What vibrationally excited states of HF would you expect to observe for electrons colliding at the resonance energy of 2.2 eV? What determines the distribution between different vibrational states in this case?

(c) If DF is substituted for HF, what changes in the vibrational spectrum would you expect to observe for electrons colliding at the resonance energy of 2.2 eV? [6]

END OF PAPER