UNIVERSITY COLLEGE LONDON

University of London

EXAMINATION FOR INTERNAL STUDENTS

For the following qualifications :-

B.Sc.   *M.Sci.*

Physics 4431: Molecular Physics

COURSE CODE	:	**PHYS4431**
UNIT VALUE	:	**0.50**
DATE	:	**13-MAY-02**
TIME	:	**10.00**
TIME ALLOWED	:	**2 hours 30 minutes**

02-C1098-3-30

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. How is the orbital approximation related to the independent particle model? [3]

   The lowest excited states of the hydrogen molecule have the configuration $1\sigma_g^1 1\sigma_u^1$. A wavefunction corresponding to this configuration can be written

   $$\Psi = \frac{1}{\sqrt{2}}\left(1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)\right)\alpha(1)\alpha(2)$$

   where α is a normalized spin function. What state of H_2 is represented by Ψ? Consider the electron-electron interaction operator r_{12}^{-1}. Derive an expression for the expectation value of this operator in the form:

   $$< \Psi|r_{12}^{-1}|\Psi >= J - K$$

   and explain the nature of the two integrals J and K. [11]

   The $1\sigma_g^1 1\sigma_u^1$ configuration of H_2 gives rise to a state,Ψ', which has different spin multiplicity from Ψ. Write down a possible wavefunction for Ψ' and, without mathematical derivation, state the expectation value the operator r_{12}^{-1} with Ψ' in terms of J and K. Use this expression to explain whether state Ψ or state Ψ' is the lower in energy. [6]

2. Define what is meant by the **reduced mass** of a system containing two particles of mass M_A and M_B. How does the harmonic frequency, ω, and the rotational constant, B, of a diatomic system depend on the reduced mass? [5]

   Absorption spectra are recorded for three molecules N_2, HF and CO_2 at (a) microwave, (b) infrared and (c) ultraviolet wavelengths. For each case explain if any spectral features will be observed, and if so which motions will be excited. [9]

   For HF, $B = 20.94$ cm^{-1} and $\omega = 4138.52$ cm^{-1}. An HF molecule is prepared in its $v = 1, J = 3$ state. Calculate the frequencies at which you expect to observe emission lines from this state. If the molecule DF in its $v = 1, J = 3$ state is observed instead, estimate at what frequency the emissions will now occur. Assume that $M_H = 1$ u, $M_D = 2$ u and $M_F = 19$ u and state any other assumptions made in deriving these estimates. [6]

3. Consider the interaction between species X and Y. Briefly discuss the how wavefunctions of X and Y are altered on the formation of the molecule XY if the main bonding is (a) ionic, (b) covalent and (c) Van der Waals. **[6]**

For the case where species X and Y are both closed shell atoms in their electronic ground state, how does this interaction depend on R, the distance between X and Y? Explain the behaviour with R at both short and long range. **[3]**

Consider the six molecules that can be formed by combining any two of the following closed shell species (a) Cl^-, (b) Li^+, (c) Ne and (d) LiF. Rank these molecules according to the approximate strength of their binding energy. **[5]**

A Li and a F atom are brought together. Sketch the curves that are involved in forming the LiF molecule in its electronic ground state. What determines the dissociation energy in this system? Explain how you would expect the dissociation energy of LiCl to compare with that of LiF. **[6]**

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

Define what is meant by the processes **dissociative attachment** (DA) and **dissociative recombination** (DR). Explain both the role of resonances and the nature of the resonances involved in the following processes:

(a) Dissociative attachment;

(b) Direct dissociative recombination;

(c) Indirect dissociative recombination. **[9]**

Briefly describe an experimental set-up used to measure dissociative recombination. **[4]** The dissociation energy, D_0, of H_2 is 4.75 eV and the electron affinity, A, of H is 0.25 eV. Assuming that the vibrational states of H_2 are evenly separated by 0.55 eV, which vibrational states of H_2 can undergo dissociative attachment if the molecule is bombarded by 2.5 eV electrons. What other considerations will determine if dissociative attachment will actually occur? **[5]**

5. Describe the **Franck-Condon Principle** as applied to the intensity of transitions in the electronic spectrum of a diatomic molecule. What assumptions are made when deriving the Franck-Condon Principle? **[6]**

A diatomic molecule in its ground (X) electronic state and $v'' = 0$ vibrational state is excited to a number of electronically excited states using light of the appropriate wavelength.

(a) Electronic state A is found to give only a continuous spectrum;

(b) Electronic state B is populated entirely in the $v' = 0$ vibrational state;

(c) Electronic state C is largely populated in vibrational states v' equals 5 to 8.

Given an approximate sketch of the potential energy curves involved in each case. **[6]**

The X – B spectrum is recorded at high enough resolution that individual rotational transitions are observed. For a cold sample of the molecule absorption features are observed at 25665.36, 25668.38, 25674.40, 25677.42 and 25680.42 cm^{-1}. Suggest a possible set of rotational assignments for these transition. What information about the molecule can be obtained from this spectrum? Briefly explain why this spectrum has the structure characteristic of a spectrum recorded in the infrared and why rotationally resolved electronic spectra are usually more complicated than this. **[8]**

END OF PAPER