UNIVERSITY COLLEGE LONDON

University of London

EXAMINATION FOR INTERNAL STUDENTS

For The Following Qualifications:-

M.Sci.

Physics 4431: Molecular Physics

COURSE CODE : **PHYS4431**

UNIT VALUE : **0.50**

DATE : **09-MAY-06**

TIME : **10.00**

TIME ALLOWED : **2 Hours 30 Minutes**

TURN OVER

Answer any THREE questions

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

1 Explain briefly what is understood by the Pauli Exclusion Principle for fermions. [2]

An approximate electronic wavefunction for the hydrogen molecule can be written as

$$\Psi = \frac{1}{\sqrt{N}}[\phi_A(1)\phi_B(2) + C_1\phi_A(2)\phi_B(1)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + C_2\alpha(2)\beta(1)]$$

where ϕ_A and ϕ_B correspond to hydrogen 1s orbitals centred on proton A and proton B respectively, containing either electron (1) or electron (2), α and β are the spin functions $S_Z = +1/2$ and $-1/2$ respectively, N is an appropriate normalisation factor and C_1 and C_2 are constants where $|C_1|=|C_2|=1$. By considering the properties of the space and spin functions under particle exchange show that in order to satisfy the Pauli Exclusion Principle the only two acceptable wavefunctions are

$$\Psi[X] = \frac{1}{\sqrt{N}}[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$
$$\Psi[Y] = \frac{1}{\sqrt{N}}[\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

[6]

Identify which wave functions give rise to bounding and antibonding states in hydrogen. Justify your answer and give a physical interpretation based on a consideration of the Pauli Exclusion Principle.

[4]

Given that the ionisation potential of lithium and the electron affinity fluorine are 5.4eV and 3.4eV, respectively, calculate the Coulomb radius for lithium fluoride and explain its physical significance.

[4]

In the ground state of lithium fluoride the equilibrium bond length is $1.564\,\mathring{A}$. What do you deduce as to the major contribution to the attractive term in the potential energy? Briefly explain the origin of the dominant counteracting repulsive force.

[4]

You may wish to make use of the following:
$e=1.6\times10^{-19}$C, $\frac{1}{4\pi\varepsilon_0} = 9.0\times10^{9}\,\mathrm{Fm}^{-1}$

2 The electric dipole transition rate R[n→n′] between two vibrational eigenstates $|n\rangle$ and $|n'\rangle$ of a diatomic molecule is determined by

$$R[n \to n'] \propto \left|\langle n'|\mu(q)|n\rangle\right|^2$$

where $\mu(q)$ is the molecular dipole moment whose dependence on the inter-nuclear displacement q from equilibrium can be expressed as a Taylor expansion about the equilibrium internuclear separation (q=0)

$$\mu(q) = \mu(q=0) + \left(\frac{d\mu}{dq}\right)_{q=0} q + \frac{1}{2}\left(\frac{d^2\mu}{dq^2}\right)_{q=0} q^2 + \ldots\ldots \frac{1}{n!}\left(\frac{d^n\mu}{dq^n}\right)_{q=0} q^n$$

Show that the presence of a permanent dipole moment (i.e. a non-zero value of $\mu(q=0)$) does not in itself lead to transitions between the vibrational states of a molecule.

[3]

Use symmetry arguments to show that for Δn =(n′-n)= ±1 and Δn =±2 transitions to be observed requires non-zero values for $\left(\frac{d\mu}{dq}\right)_{q=0}$ and $\left(\frac{d^2\mu}{dq^2}\right)_{q=0}$ respectively.

[4]

The variation of $\mu(q)$ in the vicinity of the equilibrium internuclear separation R_e for molecules A and B is given respectively by,

Molecule A: $\mu_A(q) = \mu_0 + a\cos(q/R_e)$

Molecule B: $\mu_B(q) = \mu_0 + b\sin(q/R_e)$

Discuss what infra-red transitions would you expect to observe in A and B and justify your conclusions. [8]

Explain why there is no strict Δn selection rule for the vibrational structure of electronic transitions in diatomic molecules. What factor determines the strength of the observed vibrational features?

[5]

3 The electronic energy for the bound electronic states of a diatomic molecule can be approximated by the Morse potential which has the form,

$$V(q) = D_e[1 - \exp(-\alpha q)]^2 \qquad \text{(eq.1)}$$

$q = R - R_e$ is the displacement of the internuclear separation from equilibrium (R_e), D_e is the depth of the potential well and α is a constant for the particular electronic state.

By expanding (eq.1) in the vicinity of $q = 0$ show that α is given by

$$\alpha = (k/2D_e)^{\frac{1}{2}}$$

where k is the force constant for the oscillator. [5]

For the Morse potential the vibrational energy levels are given by

$$E_V = h\nu\left(V + \frac{1}{2}\right) - \left(V + \frac{1}{2}\right)^2 h\nu X_e$$

where $X_e = (\alpha^2 h/8\pi^2 \mu\nu)$ is the anharmonicity constant for the oscillator and μ is the reduced mass of the molecule. Show that the maximum vibrational quantum number V_{max} that the oscillator can possess is given by

$$V_{max} = \frac{2D_e}{h\nu} - \frac{1}{2}$$

and explain the physical significance of this result. [6]

The ground and first excited state of a diatomic molecule have the following properties

	D_e (cm^{-1})	ν (cm^{-1})
Ground State (X)	10,000	1,000
First Excited State (A)	6,000	700

Use this information to;

(a) Calculate V_{max} for the ground and excited states [4]

(b) Sketch the vibrational structure of the X→A transition at room temperature; you may assume favourable Franck-Condon factors. [5]

You may wish to make use of the following information:

$$k = \left(\frac{d^2V(q)}{dq^2}\right)_{q=0} \qquad \nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

4 Explain briefly what is understood by excitation energy transfer between an electronically excited molecule (donor D*) and the ground state of an acceptor (A), distinguishing between radiative transfer, non-radiative transfer, hetero-transfer and homo-transfer. [4]

What donor-acceptor distances differentiate radiative and non-radiative transfer mechanisms? [2]

Given that the interaction energy between two dipoles is proportional to the inverse cube of their separation r, explain why the transfer rate in Förster energy transfer varies as r^{-6}. [3]

The Förster energy transfer rate k_T is given by

$$k_T = \frac{1}{\tau_D^0}\left(\frac{R_0}{r}\right)^6$$

where τ_D^0 is the fluorescence lifetime of the donor molecule in the absence of energy transfer and R_0 is the critical Förster radius for the donor-acceptor interaction. Show that the modification of the fluorescence lifetime due to energy transfer is given by

$$\frac{\tau_D}{\tau_D^0} = \frac{1}{\left(\frac{R_0}{r}\right)^6 + 1}$$

[3]

Sketch $\frac{\tau_D}{\tau_D^0}$ versus $\left(\frac{r}{R_0}\right)$. Over what range are the effects of Förster energy transfer most noticeable?

[4]

The critical Förster radii and fluorescence lifetimes for two donor-acceptor pairs are tabulated below

D-A Pair	R_0 (Å)	τ_D^0 (ns)
(1): Rhodamine 6G (D) Malachite Green (A)	61	3.5
(2): Fluorescein (D) Tetramethyl Rhodamine (A)	55	4.0

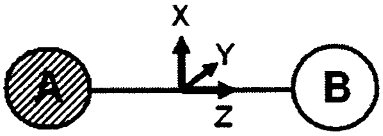
The donor fluorescence lifetimes in the presence of the acceptor τ_D were measured to be (1) 1.6ns and (2) 400ps. Calculate the donor-acceptor distances for each pair.

[4]

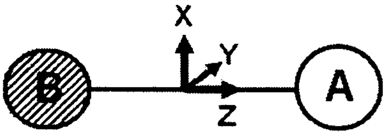
5 Diagram 1(a) below shows a homonuclear diatomic molecule (in its vibrational ground state) comprised of identical nuclei whose nuclear spin labels are denoted by the shaded and un-shaded circles. A coordinate system **(X,Y,Z)** located at the centre of mass of the molecule is also shown. Exchange of the nuclei is equivalent to a transition between diagram 1(a) and 1(b). Show how this can be accomplished by a 180° rotation about X (C_2), followed by a reflection of the electronic wave function in the plane perpendicular to X (σ_h^E) , and inversion through the origin (i_h^E) and an exchange of spin labels.

[8]

1(a)



1(b)



Nuclear Spin Labels ▨ ○

What are the effects of these operations on the signs of the rotational, electronic and nuclear spin wavefunctions for the molecule? [4]

What rotational levels are allowed in the following

$^{12}C_2\ X\ ^1\Sigma_g^+$	[^{12}C, I=0]	[3]
$^{13}C_2\ X\ ^1\Sigma_g^+$	[^{13}C, I=1/2]	[3]

How might such rotational structure be observed given that the C_2 molecule is transparent to microwave radiation? [2]