# 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 : **12-MAY-05**

TIME : **10.00**

TIME ALLOWED : **2 Hours 30 Minutes**

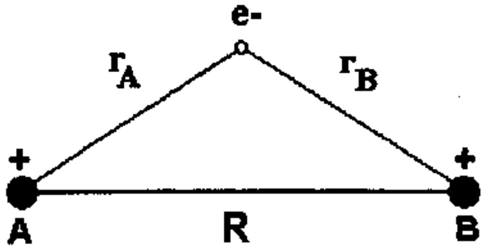
**TURN OVER**

**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. (i) Give a brief account of the significance and basis of the Born-Oppenheimer approximation in the quantum mechanical treatment of molecular structure. [6]

The $H_2^+$ molecular ion consists of the stable arrangement of two protons, A and B, and an electron as depicted below



The electronic Hamiltonian for $H_2^+$ in the Born-Oppenheimer approximation is given by

$$H = -\frac{\hbar^2}{2m}\nabla_e^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R}.$$

A trial electronic wavefunction for $H_2^+$ is given by

$$|\Psi_T\rangle = |\phi_{1S}(r_A)\rangle$$

and is equivalent to a hydrogen 1S atomic orbital centred on proton A.

(ii) Using the trial wave function above derive an expression for the expectation value of the electronic energy $\langle E(R)\rangle$ and briefly discuss the physical significance of each of the various contributions to $\langle E(R)\rangle$. [3]

(iii) Show why the trial wavefunction does not lead to bonding in $H_2^+$. [7]

(iv) Explain in physical terms what the trial wavefunction fails to account for and suggest a more realistic form for $|\Psi_T\rangle$ [4]

You will need to use the following:

(a) $\langle\phi_{1S}(r_A)|\frac{e^2}{r_B}|\phi_{1S}(r_A)\rangle = \frac{2E_I}{r}[1-(1+r)\exp(-2r)]$ where $E_I$ is the ionisation energy of a hydrogen atom in its ground electronic state and $r$ is $R/a_o$.

(b) $e^2/2a_o = E_I$.

2. (i) Explain what is understood by a sudden perturbation in relation to the induced transition between two quantum states $|\phi_i\rangle$ and $|\phi_f\rangle$. [4]

A quantum mechanical system at time $t < 0$ is described by a Hamiltonian $\boldsymbol{H}$ with eigenstates $|\phi_k\rangle$; at time $t=0$ the Hamiltonian undergoes a sudden change to $\boldsymbol{H}'$ which has its own set of eigenstates $|\phi'_n\rangle$.

(ii) If the system is initially in an eigenstate $|\phi_i\rangle$ of $\boldsymbol{H}$, show that the probability of subsequently finding it in $|\phi'_f\rangle$ at $t = 0$ is given by

$$P_{(i\to f)} = \left|\langle\phi'_f|\phi_i\rangle\right|^2 \qquad (1)$$

[6]

The electronic rearrangement that accompanies the absorption or emission of a photon in transitions between molecular electronic states occurs on a timescale that is sudden in comparison to molecular vibrational and rotational periods. The Born-Oppenheimer nuclear wavefunctions for two electronic states $\boldsymbol{i}$ and $\boldsymbol{f}$ of a diatomic molecule are given by products of rotational and vibrational wavefunctions

$$\chi_i = \Psi^i_{VIB} \times Y_{JM}(\theta,\phi)$$
$$\chi_f = \Psi^f_{VIB} \times Y_{J'M'}(\theta,\phi)$$

(iii) From (1) what would you infer to be the vibrational and rotational selection rules for electronic transitions in diatomic molecules?

[4]

(iv) How do you reconcile this with the observation of P, Q and R branches? [2]

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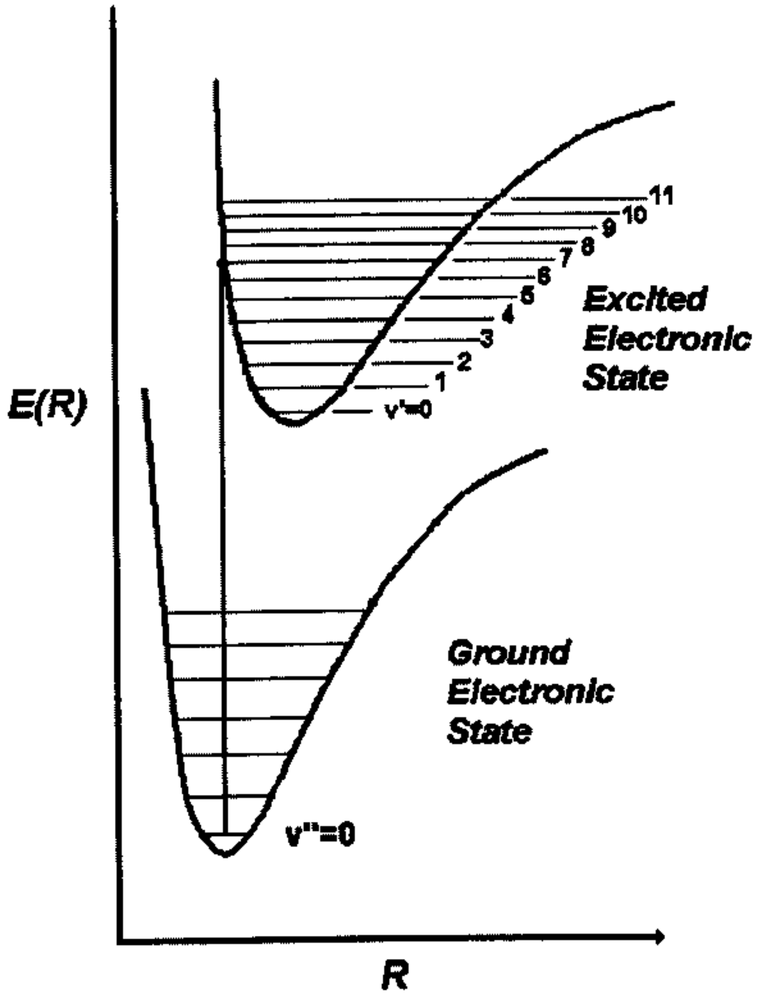
**2. Continued.**

(v) The potential energy curves for the ground and excited electronic states of a diatomic molecule are shown below; sketch the vibrational structure of the electronic transition that you would expect to observe. [4]



3. (i) Briefly state the physical basis of the electric dipole approximation as applied to the interaction of electromagnetic radiation with molecules [2]

From Fermi's Golden Rule, the transition rate between two eigenstates i and f induced by a radiation field of angular frequency $\omega$, wavevector $\bar{k}$, propagation direction $\bar{r}$ and polarisation vector $\bar{e}$ is given by

$$R_{if} = \frac{\pi}{\varepsilon_0 \hbar^2} \left| \left\langle f \middle| \bar{\mu} \cdot \bar{e} \times \exp\left( i\bar{k} \cdot \bar{r} \right) \middle| i \right\rangle \right|^2 \rho\left(\omega_{fi}\right)$$

where $\rho(\omega_{fi})$ is the average energy density per unit angular frequency in the region of $\omega = \left(\mathrm{E}_f - \mathrm{E}_i\right)/\hbar$ and $\bar{\mu}$ is the dipole moment operator.

(ii) Show that in the electric dipole approximation the Einstein coefficient for the induced transition probability is given by

$$B_{if} = \frac{\pi}{\varepsilon_0 \hbar^2} \left| \left\langle f \middle| \bar{\mu} \cdot \bar{e} \middle| i \right\rangle \right|^2 \qquad \text{(A).}$$ [4]

For a blackbody radiation field at temperature $T$ in a medium of refractive index $n$, $\rho(\omega)$ is given by

$$\rho(\omega) = \frac{\hbar \omega^3 n^3}{\pi^2 c^3} \left( \frac{1}{\exp\left(\hbar\omega/kT\right) - 1} \right).$$

If a population of atoms or molecules (in non-degenerate energy levels) are in thermal equilibrium with this field, the population balance between $i$ and $f$ is governed by Boltzmann statistics

$$N_f / N_i = \exp\left(-\left(\left(E_f - E_i\right)/kT\right)\right) = \exp\left(-\left(\hbar\omega_{fi}/kT\right)\right).$$

(iii) By considering the population flow between $i$ and $f$ show that the relationship between the Einstein A and B coefficients for the transition $f$ to $i$ is given by

$$\mathrm{A}_{fi} = \mathrm{B}_{fi} \frac{\hbar \omega_{fi}{}^3 n^3}{\pi^2 c^3} \qquad \text{(B)}$$ [6]

(iv) Use these results ((A) and (B)) to explain the following observations:

(1) Water can be heated in a microwave oven,

(2) Strong radio frequency emission can be detected from diffuse clouds of OH radicals in interstellar space,

(3) Nitrogen is transparent to infra-red radiation but can be used to efficiently store and transfer vibrational energy in $CO_2$ laser systems.

(4) Under continuous illumination the emission from a single molecular probe is characterised by periods where no absorption or emission takes place [8]

4. (i) Briefly explain what is understood by the term *photoselection* in the context of the interaction of polarised electromagnetic radiation with an initially isotropic distribution of fluorescent probe molecules in solution. [3]

(ii) Draw a diagram setting out the experimental arrangement for investigating the time resolved fluorescence decay from a population of fluorescent probe molecules in solution. Explain clearly what experimental observables are required in order to determine the fluorescence anisotropy and explain why it is essential to take account of molecular order in the determination of the fluorescence lifetime. [8]

The probability for a single-photon induced transition between the ground electronic state $|i\rangle$ and excited electronic state $|f\rangle$ of a condensed phase molecular probe $P_{if}$ is given by

$$P_{if} \propto \left|\langle f|\mu\cdot\bar{e}|i\rangle\right|^2$$

Where $\bar{e}$ is the polarisation vector of the incident laser pulse and $\mu$ is the transition dipole moment operator.

(iii) Show that for linearly polarised photoselection the initial distribution of transition dipole moment directions in the laboratory frame axis system is given by

$$P(\theta,\phi) = \frac{3}{4\pi}\cos^2\theta,$$

where $\theta$ denotes the angle between the polarisation vector of the light and the absorption transition dipole moment direction in the molecular frame. [3]

If absorption and emission transition dipole moments are parallel then the initial fluorescence anisotropy is given by

$$R = \frac{1}{2}\left[3\langle\cos^2\theta\rangle - 1\right]$$

where $\langle\ \rangle$ denotes the average value of $\cos^2\theta$ given by

$$\int_0^{2\pi} d\phi \int_0^{\pi} P(\theta,\phi)\cos^2\theta\sin\theta d\theta = \langle\cos^2\theta\rangle$$

(iv) Show that the initial fluorescence anisotropy is 2/5. [2]

(v) What could you infer from an $R$ value of below 2/5? [2]

(vi) How might a value of $R$ above 2/5 arise? [2]

5. The population $N_J$ of a rotational level $J$ within a given vibrational state of a molecule at a temperature of $T$ is, from Boltzmann statistics, given by

$$N_J = \frac{N_{TOTAL}}{Z}(2J+1)\exp\left(-\frac{BJ(J+1)}{kT}\right)$$

Where $N_{TOTAL}$ is the total population in the vibrational level, $Z$ is the rotational partition function, $BJ(J+1)$ is the rotational energy and $k$ is Boltzmann's constant.

(i) Show that the rotational population is maximised in level $J_{MAX}$ given by

$$J_{MAX} = \frac{1}{2}\left(\left(\frac{2kT}{B}\right)^{\frac{1}{2}} - 1\right)$$

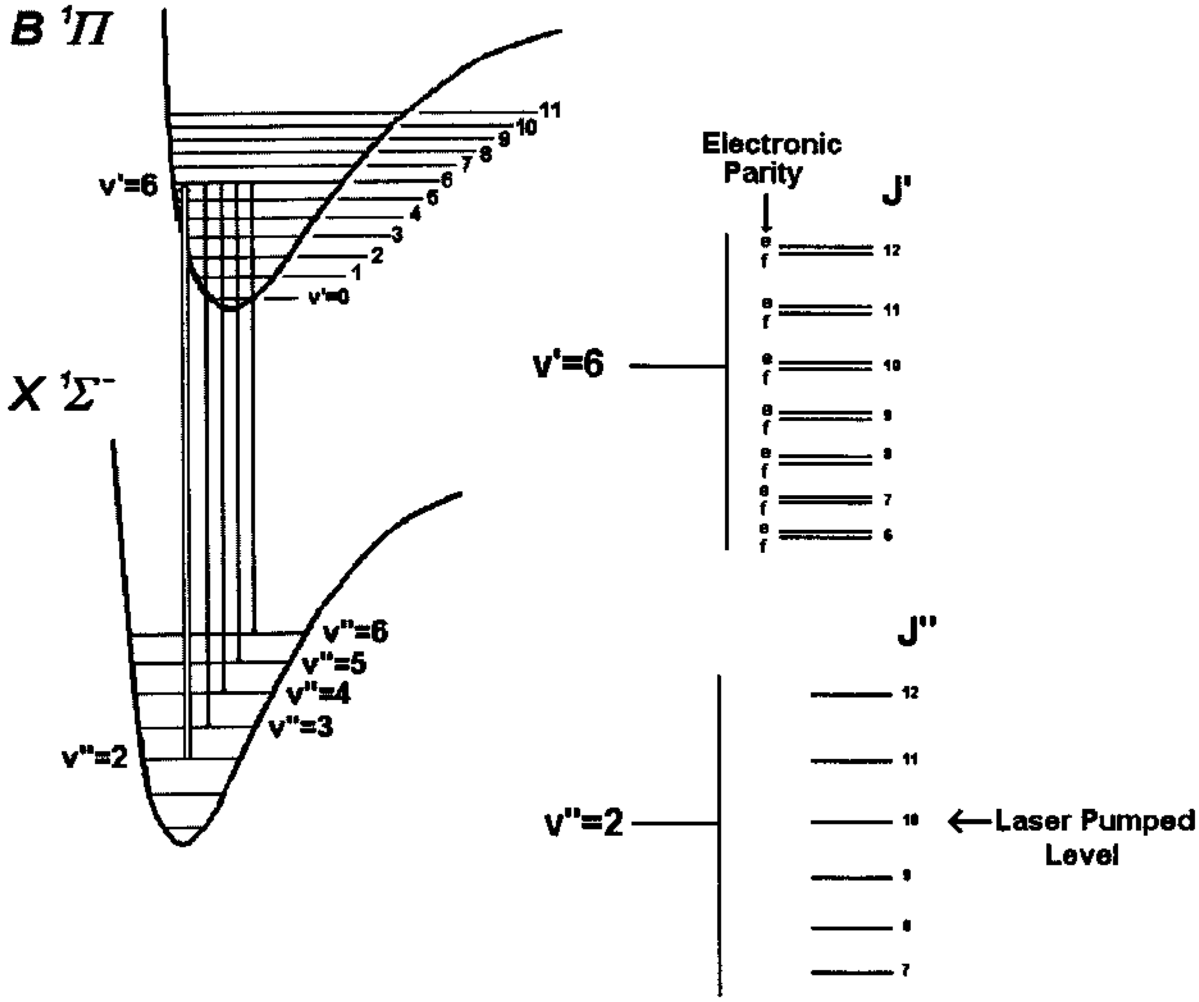
[4]

(ii) For molecular Iodine $B=0.037\text{cm}^{-1}$, calculate $J_{MAX}$ at for $I_2$ vapour at 298K ($k=0.695\text{cm}^{-1}\ \text{K}^{-1}$). [2]

(iii) What is the effect of such a distribution as determined in (ii) on the structure of the $I_2$ electronic absorption spectrum? How would you expect the absorption spectrum to be modified if the $I_2$ was observed in a supersonic jet? [4]

(iv) Briefly explain what specific advantages dispersed laser induced fluorescence brings to the study of molecular electronic spectra at ambient and elevated temperatures. [4]

(v) The $v''=2$ to $v'=6$ component of the $X^1\Sigma^- \rightarrow B^1\Pi$ transition in a heteronuclear diatomic molecule (see diagram) is probed using a tuneable laser. Population is pumped from $v''=2\ J''=10$ and the resulting $B \rightarrow X$ fluorescence spectrum to $v''= 6, 5, 4\ 3$ is recorded using a high resolution spectrometer. The $B^1\Pi$ electronic state is split into two closely spaced components of **e** (even) and **f** (odd) parity (see diagram). Draw a rotational level diagram indicating the total parity of ground and excited state rotational levels and use total parity arguments to determine which emission transitions are allowed for Q excitation from $J''=10$. Sketch the dispersed laser induced fluorescence spectra you would expect to observe [6]


B ¹Π
X ¹Σ⁻
v'=6
11
10
9
8
7
6
5
4
3
2
1
v'=0
v"=6
v"=5
v"=4
v"=3
v"=2
Electronic Parity
J'
e f 12
e f 11
e f 10
e f 9
e f 8
e f 7
e f 6
v'=6
J"
12
11
10
9
8
7
v"=2
Laser Pumped Level