

King's College London

UNIVERSITY OF LONDON

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B.Sc. EXAMINATION

CP3221 Spectroscopy and Quantum Mechanics

Summer 2001

Time allowed: THREE Hours

**Candidates should answer SIX parts of SECTION A,
and TWO questions from SECTION B.**

Separate answer books must be used for each Section of the paper.

The approximate mark for each part of a question is indicated in square brackets.

**You must not use your own calculator for this paper.
Where necessary, a College calculator will have been supplied.**

TURN OVER WHEN INSTRUCTED
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Physical constants

Atomic Mass Unit	$m_u = 1.675 \times 10^{-27} \text{ kg}$
Boltzmann constant	$k = 1.380 \times 10^{-23} \text{ J K}^{-1}$
Planck constant	$h = 6.626 \times 10^{-34} \text{ J s}$
Speed of light	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Proton charge	$e = 1.602 \times 10^{-19} \text{ C}$
Bohr magneton	$\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}$

The following information may be helpful:

(i) $\psi_{nlm}(\mathbf{x})$ is the wave function of the electron of a hydrogen atom having principal quantum number n , orbital angular momentum quantum number l and orbital angular momentum component quantum number m .

(ii) The energy of the ground state of a hydrogen-like atom of charge Ze is

$$E_0 = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0}$$

while the corresponding eigenfunction is

$$\psi_{100}(r, \theta, \phi) = \left(\frac{Z^3}{\pi a_0^3}\right)^{\frac{1}{2}} \exp\left(-Z\frac{r}{a_0}\right),$$

where

$$a_0 = 4\pi\frac{\epsilon_0\hbar^2}{me^2}$$

is the Bohr radius, m the electron mass and ϵ_0 the permittivity of a vacuum. The eigenfunction may be shown to satisfy

$$\int \frac{|\psi_{100}(r, \theta, \phi)|^2}{|\mathbf{x}|} d^3x = \frac{Z}{a_0}$$

and

$$\iint \frac{|\psi_{100}(r_1, \theta_1, \phi_1)|^2 |\psi_{100}(r_2, \theta_2, \phi_2)|^2}{|\mathbf{x}_1 - \mathbf{x}_2|} d^3x_1 d^3x_2 = \frac{5}{8} \frac{Z}{a_0}.$$

(iii) The following integrals may be assumed:

$$\int_0^{2\pi} \cos(m\phi) \cos(n\phi) = \pi \delta_{mn}$$

$$\int_0^{2\pi} \sin(m\phi) \cos(n\phi) = 0.$$

SECTION A – Answer SIX parts of this section

- 1.1) Use the time-dependent Schrödinger equation for a wavefunction in one dimension

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

to show that

$$\frac{\partial |\Psi(x,t)|^2}{\partial t} = -i \frac{\hbar}{2m} \frac{\partial j}{\partial x},$$

where the probability current j is

$$j = -i \frac{\hbar}{2m} \left\{ \Psi^* \frac{\partial \Psi}{\partial x} - \frac{\partial \Psi^*}{\partial x} \Psi \right\}.$$

[7 marks]

- 1.2) Show that, if $\phi(x)$ and $\psi(x)$ are eigenfunctions of a Hamiltonian operator corresponding to distinct eigenvalues,

$$\hat{H}\phi(x) = E_1\phi(x)$$

$$\hat{H}\psi(x) = E_2\psi(x),$$

$$E_1 \neq E_2,$$

then,

$$\int_{-\infty}^{\infty} \phi^*(x)\psi(x)dx = 0.$$

[7 marks]

- 1.3) \hat{J}_1 , \hat{J}_2 and \hat{J}_3 are operators of angular momentum which satisfy the commutation relation

$$[\hat{J}_1, \hat{J}_2] = i\hbar\hat{J}_3,$$

together with its cyclic permutations.

Given that the operator

$$\hat{J}^{(+)} = \frac{1}{\sqrt{2}} (\hat{J}_1 + i\hat{J}_2)$$

satisfies

$$[\hat{J}^{(+)}, \hat{J}_3] = i\hbar\hat{J}^{(+)}$$

infer that $\hat{J}^{(+)}$ is the creation operator of a quantum of angular momentum \hbar about the z -axis.

[7 marks]

- 1.4) Define the action of the exchange operator \hat{P}_{12} on the product of two spin $\frac{1}{2}$ states with values $s_1\hbar$ and $s_2\hbar$ along the z -axis

$$\chi(s_1, s_2) = \chi(s_1)\chi(s_2).$$

[2 marks]

Write down the product states that form a symmetric triplet and a anti-symmetric singlet.

[2 marks]

State the relation of such combinations to the ortho and para electronic states of Helium.

[3 marks]

- 1.5) The ground state electronic configuration of atomic zinc is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2.$$

Deduce the term symbols for the states that can be formed when a single electron from the 4s shell is excited into the 5s, 4p or 4d shells.

On the basis of selection rules explain which of the excited states could relax to the ground state with the emission of radiation.

[7 marks]

- 1.6) The D lines of a sodium discharge are examined when the discharge is subject to a magnetic field of strength 5T. The D₁ line corresponds to a $^2P_{1/2} \rightarrow ^2S_{1/2}$ transition. Calculate the Zeeman splitting in the two states and using an energy level diagram predict qualitatively the spectral structure of the observed D₁ line. It may be assumed that

$$g_j = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}.$$

[7 marks]

- 1.7) The total angular momentum A of a diatomic molecule is given by the relationship

$$A^2 = J(J+1)\hbar^2$$

where J can take values $0, 1, 2, \dots$

Use this to show that the rotational energies of a diatomic molecule are given by

$$E = BJ(J+1),$$

where B is a molecular constant.

If B for $H^{35}Cl$ is 10.59 cm^{-1} at what wavelength would the first pure rotational absorption be observed ?

[7 marks]

- 1.8) The first absorption in the P branch of the fundamental vibration-rotation band of $^{12}C^{16}O$ is observed at 2147.08 cm^{-1} while the first absorption in the R branch is observed at 2139.43 cm^{-1} . Assuming the harmonic approximation calculate the vibrational frequency of the CO molecule in cm^{-1} and find the force constant for the CO bond.

[7 marks]

SECTION B – Answer TWO questions

- 2) Consider a rigid rotator with moment of inertia I which is free to move in two dimensions. State the canonical commutation relation between angle and angular momentum, and form the Hamiltonian operator.

[8 marks]

Show that the eigenfunctions of energy are

$$\psi_n(\phi) = c \exp(in\phi) \quad n = 0, \pm 1, \pm 2, \dots,$$

evaluate the corresponding energy eigenvalues and state their degree of degeneracy.

[6 marks]

Calculate the normalisation constant c and determine the value of the angular momentum of the n 'th state.

[4 marks]

The rotator has an electric dipole moment μ . Due to its interaction with an external electric field E the Hamiltonian is perturbed by

$$V(\phi) = \mu E \cos(2\phi).$$

Use perturbation theory to calculate the first order energy shifts of the ground and first excited states, taking account of any degeneracy which is present.

[10 marks]

Draw an energy-level diagram for the lowest two states of the system and show the effect of the perturbing potential on it.

[2 marks]

- 3) Derive the variational inequality for the energy, E_0 of the ground state of a system with Hamiltonian \hat{H} ,

$$E_0 \leq \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

where

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int_{-\infty}^{\infty} \psi^*(x) \hat{H} \psi(x) dx}{\int_{-\infty}^{\infty} |\psi(x)|^2 dx}$$

and state how it may be used to estimate E_0 .

[12 marks]

Write down the Hamiltonian \hat{H} of the Helium atom, ignoring the effects of spin.

[4 marks]

Show that, by approximating the energy eigenfunction of the ground state by the product of two wavefunctions corresponding to the ground states of electrons in hydrogen atoms of nuclear charge Ze , the variational inequality yields

$$E_0 \leq \frac{e^2}{4\pi\epsilon_0 a_0} \left(Z^2 - \frac{27}{8} Z \right).$$

[10 marks]

Determine the value of effective nuclear charge Ze which minimises the bound imposed by the inequality and give a reason why its value is less than 2.

[4 marks]

- 4) By considering the possible LCAO orbitals that can be formed by combination of two atomic 2p orbitals deduce the likely valence shell electronic configurations of the first row diatomic molecules $({}_7\text{N})_2$, $({}_8\text{O})_2$, and $({}_9\text{F})_2$.

[14 marks]

Explain the stability of these molecules in terms of their valence shell molecular electronic configurations and why $({}_{10}\text{Ne})_2$ does not exist.

[6 marks]

The photoelectron spectrum of molecular $({}_1\text{H})_2$ produced using 21 eV photons consists of a progression of peaks corresponding to the various vibrational levels of the $({}_1\text{H})_2^+$ ion. These converge to a limit at 18.10 eV. The lowest (adiabatic) ionization energy for $({}_1\text{H})_2$ is measured as 15.45 eV while the ionisation energy of the ${}_1\text{H}$ atom is known to be 13.60 eV. Use this information to deduce values for the dissociation energy D_0 in eV of the $({}_1\text{H})_2$ molecule and the $({}_1\text{H})_2^+$ ion. Are your values consistent with the ionization of a $1\sigma_g$ bonding electron?

[10 marks]

- 5) By considering the rotational and vibrational selection rules for absorption of radiation by a diatomic molecule show that the energies of absorptions in the vibration-rotation bands associated with an electronic excitation are given by the expressions

$$\Delta E_{P,R} = \Delta E_0 + (B' + B'')m + (B' - B'')m^2.$$

where $m = \pm 1, \pm 2, \pm 3, \dots$, and

$$\Delta E_Q = \Delta E_0 + (B' - B'')m + (B' - B'')m^2.$$

where $m = +1, +2, +3, \dots$, ΔE_0 is the energy of the band centre and B' and B'' are the rotational constants for the excited and ground states respectively.

[20 marks]

The energy of the electronic excitation of an N_2 molecule from the ground state to the lowest vibrational level ($\nu' = 0$) of the ${}^1\Pi_g$ excited state is $\Delta E_0 = 69290 \text{ cm}^{-1}$. Calculate the wavelength at which the band head would be observed given that for the excited state $B' = 1.637 \text{ cm}^{-1}$ and for the ground state $B'' = 2.010 \text{ cm}^{-1}$. State whether the band head will occur in the P or R branch of the band.

[10 marks]