

King's College London

UNIVERSITY OF LONDON

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B.Sc. EXAMINATION

CP3221 Spectroscopy and Quantum Mechanics

Summer 2003

Time allowed: THREE Hours

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

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	$m_u = 1.660 \times 10^{-27} \text{ kg}$
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	$\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}$
Rydberg constant	$R = 1.097 \times 10^5 \text{ cm}^{-1}$

The following information may be helpful:

(i)

$$\int_0^{\infty} x^n \exp(-ax) dx = n! a^{-(n+1)},$$

where $a > 0$ and n is a non-negative integer.

(ii) The volume element in three dimensions may be expressed in spherical polar coordinates (r, θ, ϕ) , with

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

where

$$0 \leq r < \infty; \quad 0 \leq \theta \leq \pi; \quad 0 \leq \phi < 2\pi,$$

as

$$d^3x = r^2 \sin \theta dr d\theta d\phi,$$

while the second derivative becomes

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right).$$

(iii) $\psi_{n,l,m}(\mathbf{x})$ 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 .

(iv) The following integrals may be assumed:

$$\int \psi_{n,l,m}^*(r, \theta, \phi) r \cos \theta \psi_{n,l',m'}(r, \theta, \phi) d^3x = 0$$

for $n = 1, 2$ and all $l, l' \leq n$, $|m| \leq l$, $|m'| \leq l'$, except

$$\begin{aligned} \int \psi_{2,1,0}^*(r, \theta, \phi) r \cos \theta \psi_{2,0,0}(r, \theta, \phi) d^3x &= \int \psi_{2,0,0}^*(r, \theta, \phi) r \cos \theta \psi_{2,1,0}(r, \theta, \phi) d^3x \\ &= -3a_0, \end{aligned}$$

where

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

is the Bohr radius, e being the charge and m the mass of an electron.

SECTION A – Answer SIX parts of this section

1.1) Show that the eigenvalues of a Hermitian operator are necessarily real.

[7 marks]

1.2) Given a Hamiltonian operator

$$\hat{H} = \omega \left(\hat{A}^\dagger \hat{A} + \frac{1}{2} \hbar \right)$$

where

$$[\hat{A}, \hat{A}^\dagger] = \hbar,$$

show that

$$[\hat{H}, \hat{A}^\dagger] = \hbar\omega\hat{A}^\dagger$$

and deduce that \hat{A}^\dagger may be identified as a creation operator of a quantum of energy $\hbar\omega$.

[7 marks]

1.3) Use the three-dimensional representation of the angular momentum operators

$$L_x = i\hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}; \quad L_y = i\hbar \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}; \quad L_z = i\hbar \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

to show that

$$L^2 = L_x^2 + L_y^2 + L_z^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Hence show that

$$|1\rangle = \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}$$

is a simultaneous eigenvector of L^2 and L_z by finding the corresponding eigenvalues.

[7 marks]

1.4) The wavefunction of electronic states is antisymmetric with respect to exchange of pairs of electrons. Show that this statement leads to the Pauli Exclusion Principle.

[7 marks]

- 1.5) The frequencies $\bar{\nu}$ in cm^{-1} of a series of bands in the UV region of the N_2 absorption spectrum are found to fit the simple relationship

$$\bar{\nu} = 125666 - \frac{R}{(m - 0.655)^2}$$

where $m = 3, 4, 5, \dots$ and R is the Rydberg constant. The expression corresponds to the excitation of a $2p\sigma_g$ electron to various Rydberg states. Use this information to deduce the $(2p\sigma_g)^{-1}$ ionisation energy for N_2 in eV and explain why such a simple expression can describe an electronic excitation process for molecular N_2 .

[7 marks]

- 1.6) Ti has a $4s^23d^2$ ground state configuration. This can lead to 1G , 3F , 1D , 3P and 1S term symbols. Use Hund's rules to predict which term symbol corresponds to the ground state. Explain why a 3G state is not possible for this configuration.

[7 marks]

- 1.7) The first rotational absorption line in the spectrum of $^{23}\text{Na}^{35}\text{Cl}$ is observed at 0.436 cm^{-1} . Use this information to deduce a value for the bond length of diatomic NaCl given that $E_{rot} = J(J + 1) \frac{\hbar^2}{2I}$ where I is the moment of inertia of the molecule.

[7 marks]

- 1.8) Sketch the form of the LCAO molecular orbitals that can be formed by combining two 2s atomic orbitals and two 2p atomic orbitals. Hence write down the valence shell configuration of F_2 which has 14 valence electrons.

[7 marks]

SECTION B – Answer TWO questions

- 2) a) Write down the Hamiltonian operator of the electron of a hydrogen atom and identify the kinetic and potential energy terms.

[6 marks]

- b) Express the Hamiltonian in spherical polar coordinates (r, θ, ϕ) .

[2 marks]

- c) Given that the form of the wave function in the ground state is

$$\psi(r, \theta, \phi) = C \exp \{-ar\},$$

where C and a are both real with $a > 0$, state the normalisation condition and determine the normalisation constant C .

[4 marks]

- d) Determine the average kinetic and potential energies of the electron when it occupies such a state.

[8 marks]

- e) State the variational inequality for the energy of the ground state of a system and use it to obtain an estimate of the energy of the ground state of hydrogen.

[8 marks]

- f) Comment on the value you obtained, compared to the exact value

$$E_0 = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2.$$

[2 marks]

- 3) a) Write down an expression for the interaction potential between an electron of charge e at position \mathbf{x} and an electric field \mathbf{E} in spherical polar coordinates when the field direction is along the z axis.

[4 marks]

- b) State the first order perturbation correction to the energy of a non-degenerate state due to a perturbing potential. Using the information in the rubric, show that there is no perturbation of the ground state of hydrogen by an external electric field.

[10 marks]

- c) Use degenerate perturbation theory to analyse the effect of an external electric field on the first excited state of hydrogen.

[12 marks]

- d) Discuss the effect of the external field on the emission lines of hydrogen due to transitions between the first excited and ground states.

[4 marks]

- 4) The emission spectrum of atomic Zn, which has the closed shell ground state configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$, is found to consist of singlets and triplets. Explain this observation in terms of the possible transitions between the ground state and excited states with configurations of the form $4s^1 ns^1$, $4s^1 np^1$ and $4s^1 nd^1$.

[10 marks]

When triplets in the emission spectrum are studied at high resolution some are seen to be simple triplets, *i.e.* composed of only three lines, while some are seen to be more complicated, consisting of six lines. Use energy level diagrams and selection rules to show how the simple and compound triplet structure arises.

[10 marks]

A line corresponding to a ${}^3D_2 \rightarrow {}^3P_1$ transition is identified in the emission spectrum. The Zn discharge is then exposed to a strong magnetic field. Draw an energy level diagram showing the effect of the field on the energies of the 3D_2 and 3P_1 states and mark on your diagram all possible transitions.

How many lines can be resolved in the Zeeman spectrum for this transition?

[10 marks]

- 5) Show that the frequencies $\bar{\nu}_{\text{PR}}$ in cm^{-1} of lines in the vibration-rotation spectrum of a diatomic molecule are given in the harmonic approximation by

$$\bar{\nu}_{\text{PR}} = \bar{\nu}_0 + 2mB$$

where $m = \pm 1, \pm 2, \pm 3, \dots$, B is the rotational constant and $\bar{\nu}_0$ is the vibrational frequency of the molecule.

[10 marks]

For HCl $B = 10.59 \text{ cm}^{-1}$. Use this information to predict which peak in the R branch ($\Delta J = +1$) of the spectrum of HCl will be most intense at room temperature (300 K).

If the form of the potential energy curve is anharmonic, what effect would you expect this to have on the infra-red vibration-rotation spectrum?

[10 marks]

The dissociation energy D_0 for HCl is 4.43 eV. The first ionisation energy for atomic Cl is 13.01 eV and the first ionisation energy for molecular HCl is 12.74 eV. Indicate these parameters on a diagram showing potential energy curves for HCl and the HCl^+ cation (dissociation products $\text{H} + \text{Cl}^+$). Use this to deduce a value for the dissociation energy of the HCl^+ ion. Comment on the nature of the orbital from which the electron is ionised.

[10 marks]