

# King's College London

UNIVERSITY OF LONDON

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**B.Sc. EXAMINATION**

**CP3221 Spectroscopy and Quantum Mechanics**

**Summer 1998**

**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.**

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## Physical constants

Atomic Mass Unit	$m_u = 1.66 \times 10^{-27} \text{ kg}$
Boltzmann constant	$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$
Planck constant	$h = 6.63 \times 10^{-34} \text{ Js}$
Speed of light	$c = 3.00 \times 10^8 \text{ ms}^{-1}$

The following information may be helpful:

- (i)  $\psi_{n,l,m}(\mathbf{x})$  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  $m$ .
- (ii) The following integrals may be assumed:

$$\int \psi_{2,l,m}^*(r, \theta, \phi) r \cos \theta \psi_{2,l',m'}(r, \theta, \phi) d^3x = 0$$

for all  $l, l' \leq 2$ ,  $|m| \leq l$ ,  $|m'| \leq l'$ , 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,  $m$  being the mass of an electron.

(iii)

$$\begin{aligned} I_{mn} &\equiv \int_0^a x^m (a-x)^n dx \\ &= \frac{m! n! a^{m+n+1}}{(m+n+1)!} \quad \text{with } m, n \geq 0. \end{aligned}$$

## SECTION A – Answer SIX parts of this section

1.1) Show that the operators

$$\hat{A} = x + \hbar \frac{d}{dx}$$

$$\hat{A}^\dagger = x - \hbar \frac{d}{dx}$$

satisfy the commutation relation

$$[\hat{A}, \hat{A}^\dagger] = 2\hbar.$$

Given that a Hamiltonian operator  $\hat{H}$  satisfies

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

explain how  $\hat{A}^\dagger$  may be interpreted as a creation operator of a quantum of energy  $\hbar$ .

[7 marks]

1.2) Define the operation of inversion  $\hat{P}$  by its action on a wave function  $\psi(\mathbf{x})$ .  
Given that the eigenfunctions of the electron of a hydrogen atom satisfy

$$\psi_{n,l,m}(-\mathbf{x}) = (-1)^l \psi_{n,l,m}(\mathbf{x}),$$

deduce that

$$\langle n, l, m | \hat{U} | n', l', m' \rangle \equiv e \int \psi_{n,l,m}^*(\mathbf{x}) \mathbf{E} \cdot \mathbf{x} \psi_{n',l',m'}(\mathbf{x}) d^3x$$

is zero unless  $l$  and  $l'$  differ by an odd integer. In the above integral  $\mathbf{E}$  is an electric field.

[7 marks]

1.3) Describe how the wave function of an electron may be extended to take account of spin and use first-order perturbation theory to calculate the shift in energy caused by the potential

$$\hat{V} = -\frac{e}{m_0} \hat{\mathbf{s}} \cdot \mathbf{B}$$

due to the interaction of an electron of charge  $e$  and mass  $m_0$  with a magnetic field  $\mathbf{B}$  via its spin-operator  $\hat{\mathbf{s}}$ .

[7 marks]

- 1.4) Define the operator  $\hat{P}_{12}$  that exchanges electrons in two-electron wave functions  $\psi(\mathbf{x}_1, \mathbf{x}_2)$ .  
Construct eigenfunctions of  $\hat{P}_{12}$  and determine the corresponding eigenvalues.  
Show that a pair of electron spin states may be expressed as a symmetric triplet and an anti-symmetric singlet.

[7 marks]

- 1.5) Write down the full electronic configuration for atomic  ${}^1_7\text{N}$  and for atomic  ${}^{45}_{21}\text{Sc}$ .  
Deduce the term symbol describing the ground state of each atom giving your reasoning for each choice.

[7 marks]

- 1.6) The angular momentum  $L$  of a particle can be shown to be quantized according to the expression

$$L^2 = l(l+1)\hbar^2.$$

Use this to show that the rotational energy  $E_{Rot}$  of a diatomic molecule may be written

$$E_{Rot} = BJ(J+1),$$

where  $B$  is a molecular constant.

Draw the rotational energy level diagram for  $J = 0$  to  $J = 5$  indicating possible excitations at room temperature.

[7 marks]

- 1.7) Write down the electronic configuration of  $({}^{14}_7\text{N})_2$ .  
Sketch the form of the molecular orbitals that are formed by linear combination of atomic 2p orbitals and discuss their bonding character.

[7 marks]

- 1.8) Draw an energy-level diagram showing the first four rotational levels of the  $\nu = 0$  and  $\nu = 1$  vibrational states of a diatomic molecule. Indicate the P and R transitions from the  $\nu = 0, J'' = 0$  and 1 levels to rotational levels of the  $\nu = 1$  state and deduce their energy separation in terms of the rotational constant  $B$ .  
In the IR spectrum of  $\text{H}^{35}\text{Cl}$  the  $\text{P}_1$  line is measured at  $2865 \text{ cm}^{-1}$  and the  $\text{R}_0$  line is measured at  $2906 \text{ cm}^{-1}$ . Use this information to estimate the length of the HCl bond.

The rotational constant  $B = \frac{\hbar^2}{2I}$  where  $I$  is the moment of inertia of the molecule.

[7 marks]

**SECTION B – Answer TWO questions**

- 2) State an expression for the interaction potential between an electron of charge  $e$  at position  $\mathbf{x}$  and an electric field  $\mathbf{E}$  and express it in spherical polar coordinates.

[4 marks]

Show that an electron in the ground state of a hydrogen atom is unaffected by an external electric field to first order of perturbation.

[10 marks]

Show that the energy of the first excited state of an electron of a hydrogen atom splits as a result of an external electric field and calculate the magnitude of the splitting to first order in the field-strength.

[12 marks]

Discuss the effect of the splitting on the emission line of hydrogen due to transitions between the first excited and ground states.

[4 marks]

- 3) State the variational inequality for the energy of the ground state of a system. [4 marks]

Suppose that the wave function of the ground state may be expressed as the sum of two approximate wave functions and derive the Ritz determinantal condition on the upper bound for the energy.

[10 marks]

A particle of mass  $m$  at position  $x$  in one dimension is subject to the potential

$$\begin{aligned} V(x) &= 0 & 0 \leq x \leq a \\ &= \infty & x < 0 \quad \text{or} \quad x > a. \end{aligned}$$

Take a trial wave function that is a linear combination of

$$\begin{aligned} \phi_1(x) &= x^2(a-x) \\ \phi_2(x) &= x(a-x)^2 \end{aligned}$$

and use the Ritz formulation of the variational inequality to obtain an approximation to the energy of the ground state.

[14 marks]

Compare your result to the exact value

$$E_0 = \frac{h^2}{8ma^2}.$$

[2 marks]

- 4) The emission spectrum of He consists of two series of lines, one corresponding to transitions between singlet states, the other between triplet states. Explain why this is so and draw an energy level diagram showing the ground state and states derived by exciting one electron to the  $n = 2$  or  $n = 3$  levels together with their term symbols. Show the possible transitions between these states and explain the basis for the information given in the diagram.

[10 marks]

If the He discharge is positioned in a 1 T magnetic field the emission line produced by a  $^1P_1 \rightarrow ^1S_0$  transition is observed to split into three equispaced lines with an energy separation of  $9.27 \times 10^{-24}$  J.

Explain this observation and use the information to calculate a value for the Bohr magneton.

[5 marks]

A  $^3P_2 \rightarrow ^3S_1$  transition results in more complicated fine structure than that observed for the singlet transition. Explain why this is so and sketch the form of the fine structure that you would expect with a 1 T magnetic field. You may assume that

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

where the symbols have their usual meanings.

[15 marks]

- 5) Show that the energy  $\Delta E_{PR}$  of the absorption lines in the P and R branches of the absorption band associated with an electronic transition for a diatomic molecule can be written as

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

where  $M = \pm 1, 2, 3, \dots$  and a  $\nu' = 0 \rightarrow \nu'' = 0$  transition is assumed.

Explain the significance of the various terms in the expression.

[15 marks]

For the molecule CO the  $\nu'' = 0 \rightarrow \nu' = 0$  transition associated with the first electronic excitation occurs at  $65076 \text{ cm}^{-1}$ .  $B''$  for the ground state is  $1.931 \text{ cm}^{-1}$  and  $B'$  for the electronically excited state is  $1.612 \text{ cm}^{-1}$ . Calculate the position of the band head and state whether it occurs in the P or R branch of the spectrum. Calculate the fractional change in bond length which occurs on excitation. The rotational constant  $B = \frac{\hbar^2}{2I}$  where  $I$  is the moment of inertia of the molecule.

[15 marks]