King's College London

UNIVERSITY OF LONDON

This paper is part of an examination of the College counting towards the award of a degree. Examinations are governed by the College Regulations under the authority of the Academic Board.

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.

Physical constants

Atomic Mass Unit	$m_u = 1.660 \times 10^{-27}$ kg
Boltzmann constant	$k = 1.380 \times 10^{-23}$ J K^{-1}
Planck constant	$h = 6.626 \times 10^{-34}$ J s
Speed of light	$c = 2.998 \times 10^8$ m s^{-1}
Proton charge	$e = 1.602 \times 10^{-19}$ C
Bohr magneton	$\mu_B = 9.274 \times 10^{-24}$ 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

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

with

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

where a_0 is the Bohr radius, m_e the electron mass and ϵ_0 the permittivity of a vacuum.

(iii) The following integral may be assumed:

$$\int_0^\pi \sin(Mx)\sin(Nx)dx = \frac{\pi}{2}\delta_{MN},$$

M and N being integers.

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SECTION A – Answer SIX parts of this section

1.1) Show that the operators

$$\hat{x} = x; \quad \hat{p} = -i\hbar \frac{d}{dx}$$

satisfy the canonical commutation relations

$$[\hat{x}, \hat{p}] = (\hat{x}\hat{p} - \hat{p}\hat{x})$$
$$= i\hbar \hat{1}.$$

when acting on a wavefunction, $\psi(x)$.

[7 marks]

1.2) Define the reflection operator $\hat{P}$ in terms of its action on a wavefunction.
Show that $\hat{P}$ is a hermitian operator.

[7 marks]

1.3) Show by explicit evaluation that the matrices

$$\sigma_1 = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \sigma_2 = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \quad \sigma_3 = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

satisfy the commutation relations of angular momentum

$$\left[\hat{L}_1, \hat{L}_2 \right] = i\hbar \hat{L}_3.$$

State how the wave function of the electron of a hydrogen atom $\psi_{nlm}(\mathbf{x})$ may be extended to take account of spin.

[7 marks]

1.4) Define the exchange-operator $\hat{P}_{12}$ in terms of its action on a two-particle wavefunction $\psi(x_1, x_2)$.
What effect does it have if the particles are identical bosons or fermions?
How is this property related to the statistics of a collection of bosons?

[7 marks]

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1.5) The energies $E(n)$ of the $3s^1np^1$, ^2P states of atomic Na may be written

$$E(n) = -\frac{R}{\left(n - \delta^2\right)^2},$$

where the Rydberg constant $R = 1.097373 \times 10^7$ m^{-1} and the quantum defect $\delta = 0.88$.
Explain the significance of the quantum defect and calculate the ionisation energy in cm^{-1} of the n $= 50$ Rydberg state.

[7 marks]

1.6) A line corresponding to a $^3D_2 \rightarrow^3 P_2$ transition is observed in a calcium emission spectrum. The Ca 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 $^3P_2$ states and mark on your diagram all possible transitions.
How many lines can be resolved in the Zeeman spectrum for this transition?

[7 marks]

1.7) The angular momentum L of a body is given by the expression

$$L = \sqrt{l\left(l+1\right)}\hbar,$$

where $l = 0, 1, 2, 3, \ldots.$
Use this to show that the rotational energy E_{Rot} of a diatomic molecule can be written
$$E_{Rot} = J\left(J+1\right)B,$$

where B is the rotational constant.

[7 marks]

1.8) Sketch the form of the two LCAO molecular orbitals that can be formed by combining two 1s atomic orbitals to form the molecular orbitals of H_2.
Explain in terms of the expected energies of these orbitals why the $1\sigma_g^2$ ground state of molecular hydrogen is stable but the $1\sigma_g^1 1\sigma_u^1$ excited state is not.
Explain whether you expect any higher excited states of molecular hydrogen to be stable.

[7 marks]

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SECTION B – Answer TWO questions

2) Consider a system having Hamiltonian

$$\hat{H} = \hat{H}^0 + \lambda \hat{U}$$

where $\hat{H}^0$ has orthonormal non-degenerate eigenfunctions $\phi_i^0(x), i = 1, 2, \dots$ with corresponding eigenvalues E_i^0.

Show that the first-order perturbation of the energy of the i'th state is $\lambda E_i^{(1)}$ where

$$E_i^{(1)} = \int_{-\infty}^{\infty} \phi_i^*(x) \hat{U} \phi_i(x) dx.$$

[12 marks]

A hydrogen atom is exposed to a constant magnetic field $\mathbf{B}$ derived from the vector potential

$$\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{x},$$

where $\mathbf{x}$ is the position vector.

Show that the interaction between the electron of the atom and the magnetic field may be expressed as

$$\hat{U} = -\frac{e}{2m_e} \mathbf{B} \cdot \hat{\mathbf{L}},$$

where m_e is the mass of the electron and $\hat{L}$ is its orbital angular momentum.

[6 marks]

Assuming that non-degenerate perturbation theory may be applied and ignoring the effect of electron-spin, determine the first-order perturbations of the ground and first excited states of the electron.

[12 marks]

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3) Given that the energy, E_0 of the ground state of a system with Hamiltonian $\hat{H}$, satisfies the inequality

$$E_0 \leq \frac{\int_{-\infty}^{\infty} \psi^*(x)\hat{H}\psi(x)dx}{\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx}$$

where $\psi(x)$ is any normalisable wavefunction. Describe how it may be used to estimate E_0.

[4 marks]

Derive the Ritz determinental condition on the upper bound for the energy of a system by supposing that the wave function of the ground state may be approximated by the sum of two trial wave functions.

[12 marks]

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

$$V(x) = 0 \qquad 0 \leq x \leq \pi$$
$$= \infty \qquad x < 0 \quad \text{or} \quad x > a.$$

Write down the Hamiltonian and, by taking a trial wave function that is a linear combination of

$$\phi_1(x) = \sin(x)$$
$$\phi_2(x) = \sin(2x)$$

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

[14 marks]

4) Write down in full the electronic configuration of the ground state of $^{40}_{20}$Ca and deduce the term symbol for this configuration.
In a Ca discharge 4s electrons can be excited to the 3d, 4p or 5s levels. Deduce terms symbols for all possible excited states corresponding to these excited configurations. Deduce which of these states can undergo allowed transitions to the ground state.

[12 marks]

LS coupling in a state results in an energy shift E where $E = A\mathbf{L} \cdot \mathbf{S}$.
Use this to show that the energy separation between two adjacent components of an LS multiplet is proportional to the higher J value.

[10 marks]

How would you expect the LS coupling to be apparent in the emission spectrum of Ca?

[8 marks]

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

$$\bar{\nu}_{\mathrm{PR}} = \bar{\nu}_0 + (B_1 + B_0)\, m + (B_1 - B_0)\, m^2$$

where $m = \pm 1, \pm 2, \pm 3, \ldots$, and B_0 and B_1 are the rotational constants for the $\nu = 0$ and $\nu = 1$ vibrational states.

[15 marks]

The energies of the vibrational levels of a diatomic harmonic oscillator with respect to the lowest point in the anharmonic potential may be approximated by

$$E_\nu = \left(\nu + \frac{1}{2}\right)\bar{\nu}_e - \left(\nu + \frac{1}{2}\right)^2 \bar{\nu}_e x_e.$$

For $^{14}\mathrm{C}^{16}O$, $\bar{\nu}_e = 2169.74$ cm^{-1} and $x_e = 0.0061$ cm^{-1}. Show how this information may be used to calculate the force constant for the CO bond and to deduce an approximate value for D_e the dissociation energy.

[15 marks]

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