King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/3221 Spectroscopy and Quantum Mechanics

Summer 1999

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

Physical constants

Atomic Mass Unit	$m_u = 1.66 \times 10^{-27}$ kg
Boltzmann constant	$k = 1.38 \times 10^{-23}$ J K^{-1}
Planck constant	$h = 6.63 \times 10^{-34}$ J s
Speed of light	$c = 3.00 \times 10^{8}$ m s^{-1}
Charge on a proton	$\mathrm{e} = 1.60 \times 10^{-19}$ C

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 wave-function of the ground state of a hydrogen-like atom of charge Ze is

$$\psi_{1,0,0}(r,\theta,\phi) = \left(\frac{Z^3}{\pi a_0^3}\right)^{\frac{1}{2}} \exp\left(-Z\frac{r}{a_0}\right),$$

where

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

is the Bohr radius.

(iii) The following integrals may be assumed:

$$\int_{-\infty}^{\infty} \exp\left(-a^2x^2\right) dx = \frac{\pi^{\frac{1}{2}}}{a}$$

$$\int_{-\infty}^{\infty} x^2 \exp\left(-a^2x^2\right) dx = \frac{\pi^{\frac{1}{2}}}{2a^3}$$

$$\int_{-\infty}^{\infty} x^4 \exp\left(-a^2x^2\right) dx = \frac{3\pi^{\frac{1}{2}}}{4a^5}$$

SECTION A – Answer SIX parts of this section

1.1) Define a hermitian operator.
Prove that the momentum operator

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

is hermitian.

[7 marks]

1.2) Describe how the connection between spin and statistics for half-integer spin particles leads to the Pauli Exclusion Principle.

[7 marks]

1.3) Define the parity operator $\hat{P}$ in terms of its effect upon eigenfunctions $\psi(\mathbf{x})$ of position.
Deduce that

$$\hat{P}^2 = \hat{\mathbf{1}}.$$

Infer that the eigenvalues of parity are ± 1.

[7 marks]

1.4) The quantum operators of angular momentum

$$\hat{L_x} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$
$$\hat{L_y} = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$
$$\hat{L_z} = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right),$$

satisfy the commutation relation

$$\left[\hat{L_x}, \hat{L_y}\right] = i\hbar\hat{L_z}.$$

By defining the operator

$$\hat{L^+} = \hat{L_x} + i\hat{L_y}$$

show that

$$\left[\hat{L^+}, \hat{L_z}\right] = -\hbar\hat{L^+}$$

and hence deduce that $\hat{L^+}$ may be interpreted as a creation operator of a quantum of spin $\hbar$.

[7 marks]

1.5) An excited state of carbon has the electronic configuration

$$1s^2 2s^2 2p^1 3p^1.$$

Deduce the term symbols for the states that can be formed for this configuration and explain why these states would not all be possible for the

$$1s^2 2s^2 2p^2$$

ground state configuration.

[7 marks]

1.6) The shift ΔE, in the energy of a state resulting from spin-orbit coupling between the different states of a spin-orbit multiplet is given by

$$\Delta E = A\,\vec{L}\cdot\vec{S}$$

where A is a constant. Show that the energy differences between the states with $J = 3$ and $J = 2$, and between the states with $J = 2$ and $J = 1$ for a ^{3}D multiplet are in the ratio 3 : 2.

[7 marks]

1.7) The total angular momentum L of a particle about a point is given by the relationship

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

where l can take values $0, 1, 2, 3, \ldots$.
Use this to show that the rotational energies of a diatomic molecule are given by

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

where

$$B = \frac{\hbar^2}{2I}$$

and I is the moment of inertia of the molecule.

[7 marks]

1.8) The electronic configuration of molecular nitrogen is

$$1\sigma_g^2, 1\sigma_u^2, 2\sigma_g^2, 2\sigma_u^2, 3\sigma_g^2 1\pi_u^4.$$

Explain the significance of the symbols used to describe the configuration.
Use simple LCAO diagrams for the valence shell molecular orbitals to explain the stability of molecular N_2.

[7 marks]

SECTION B – Answer TWO questions

2) Consider a particle of mass m in one dimension at position x which is acted on by the potential

$$V(x) = \frac{1}{2}\mu x^2.$$

Write down the total energy of the particle and use it to derive the time-independent Schrödinger equation of the particle.

[6 marks]

State the conditions which the solutions must satisfy and explain the physical significance of the conditions.

[4 marks]

Given that

$$\psi_0(x) = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\alpha x^2\right)$$

and

$$\psi_1(x) = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} 2\alpha^{\frac{1}{2}} x \exp\left(-\alpha x^2\right),$$

with $\alpha^2 = \frac{m\mu}{4\hbar^2}$, are both normalised eigenfunctions of energy, find their corresponding eigenvalues.

[8 marks]

Determine the frequency of the spectral line corresponding to the emission or absorption of a photon whenever the particle undergoes a transition between the two states.

[4 marks]

The particle is subject to a perturbing potential

$$U(x) = \kappa x^2 \exp\left(-2\alpha x^2\right).$$

Determine the changes in energy of the two states to first-order in the perturbation and hence the change in frequency of the spectral line.

[8 marks]

3) The Hamiltonian of a hydrogen molecular ion, which consists of two protons and a shared electron, is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0|\mathbf{x}_A|} - \frac{e^2}{4\pi\epsilon_0|\mathbf{x}_B|} + \frac{e^2}{4\pi\epsilon_0|\mathbf{X}|},$$

where the position-vector of the electron is $\mathbf{x}$, the distance-vectors from the nuclei to the electron are $\mathbf{x}_A$ and $\mathbf{x}_B$ and the vector between the nucleii is $\mathbf{X}$.

Justify that the wave-function of the ground state may be approximated by

$$\psi(\mathbf{x}) = c_1\phi_A(\mathbf{x}) + c_2\phi_B(\mathbf{x}),$$

where $\mathbf{x}$ is the position of the electron and $\phi_A(\mathbf{x})$ and $\phi_B(\mathbf{x})$ are the wave-functions of an electron in the ground-states of nuclei A and B respectively.

[6 marks]

Apply the variational inequality to the above wave-function to show that the energy of the ground state satisfies

$$E \leq \frac{(c_1^2 + c_2^2)\int \phi_A(\mathbf{x})\hat{H}\phi_A(\mathbf{x})d^3x + 2c_1c_2\int \phi_A(\mathbf{x})\hat{H}\phi_B(\mathbf{x})d^3x}{(c_1^2 + c_2^2) + 2c_1c_2\int \phi_A(\mathbf{x})\phi_B(\mathbf{x})d^3x},$$

where $\hat{H}$ is the Hamiltonian of the system.

[12 marks]

Hence obtain an approximation to the energy of the lowest-energy state.

[12 marks]

4) Potassium has a ground state configuration $1s^22s^22p^63s^23p^64s^1$ while Ca has a ground state configuration $1s^22s^22p^63s^23p^64s^2$. In K and Ca discharges single 4s electrons are excited to 5s or 4d orbitals to form excited states. Predict the fine structure for the emission that would be observed if these relax to a 4p orbital.

[15 marks]

In solids electronic core levels remain largely atomic and may be described using the nomenclature of atomic spectroscopy. 1s ionization energies can be measured by X-ray photoelectron spectroscopy and, since these are atomic properties, the detection of a particular 1s ionization energy can be used to identify the presence of an element. Discuss briefly how this is achieved experimentally.

[15 marks]

5) By considering the rotational and vibrational selection rules for absorption of infrared radiation by a heteronuclear diatomic molecule show that the energies of absorptions in the fundamental vibration-rotation absorption band are given by the expression

$$\Delta E = \Delta E_0 + (B_1 + B_0)\, m + (B_1 - B_0)\, m^2$$

where $m = \pm 1, \pm 2, \pm 3, \ldots$, ΔE_0 is the energy of the fundamental vibrational transition and B_0 and B_1 are the rotational constants for the $\nu = 0$ and $\nu = 1$ vibrational states.
Why is it necessary to assume that B is a function of ν ?

[15 marks]

For the molecule $^{12}\mathrm{C}^{16}\mathrm{O}$, $r_0 = 0.1128\mathrm{nm}$. Assuming that the atomic masses may be taken as the atomic mass numbers in $\mathrm{m_u}$ sketch the form of the absorption band for the harmonic case where $B_0 = B_1$, indicating line separations in cm^{-1} and which absorptions will be most intense in the P and R branches.

[15 marks]