King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP/3221 Spectroscopy and Quantum Mechanics

Summer 2000

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}
Proton charge	$\mathrm{e} = 1.60 \times 10^{-19}$ C
Bohr magneton	$\mu_B = 9.274 \times 10^{-24}$ J T^{-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 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, m the electron mass and ϵ_0 the permittivity of a vacuum.

(iii) The following integrals may be assumed:

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

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

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

SECTION A – Answer SIX parts of this section

1.1) Write down the Hamiltonian of a particle of mass m moving in one dimension under the action of a three-dimensional velocity-independent potential $V(\mathbf{x})$. Show that the components of the position vector $\mathbf{x} = x\hat{\mathbf{i}}+y\hat{\mathbf{j}}+z\hat{\mathbf{k}}$ and the partial derivative operator $-i\hbar\nabla = -i\hbar\left\{\frac{\partial}{\partial x}\hat{\mathbf{i}} + \frac{\partial}{\partial y}\hat{\mathbf{j}} + \frac{\partial}{\partial z}\hat{\mathbf{k}}\right\}$ satisfy the canonical commutation relations between the quantum-mechanical position and momentum operators and hence derive the time-independent Schrödinger equation in three dimensions.

[7 marks]

1.2) A Hamiltonian H_0 has two orthogonal eigenfunctions $\psi_1(x)$ and $\psi_2(x)$ which both correspond to the same eigenvalue E_0.
A perturbing term U is added to the Hamiltonian. Show that the perturbations ΔE of the energies of the two eigenfunctions are solutions of

$$\begin{vmatrix} <1|U|1> -\Delta E & <1|U|2> \\ <2|U|1> & <2|U|2> -\Delta E \end{vmatrix} = 0$$

where

$$<i|U|j> = \int_{-\infty}^{\infty} \psi_i^*(x)U(x)\psi_j(x)dx, \quad i,j = 1,2.$$

[7 marks]

1.3) Define the exchange operator $\hat{P}_{12}$ for a wavefunction $\psi(\mathbf{x}_1, \mathbf{x}_2)$ of two identical particles having position vectors $\mathbf{x}_1$ and $\mathbf{x}_2$ respectively and construct its normalised eigenfunctions.
State the connection between spin and statistics.

[7 marks]

1.4) Show that the matrices

$$J_1 = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \; J_2 = \frac{-i\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}; \; J_3 = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

satisfy the commutation relations of angular momentum

$$[J_1, J_2] = i\hbar J_3$$

and that

$$J_1^2 + J_2^2 + J_3^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

How may it be inferred from the above equation that these matrices represent spin-1 particles?

[7 marks]

1.5) The emission spectrum of atomic Ca, ground state configuration $1s^2 2s^2 2p^6 3p^6 4s^2$, ${}^1S_0$, is found to consist of singlets and triplets which may be grouped into series showing convergence in a way similar to that observed for atomic hydrogen.
Explain this observation in terms of the possible transitions between the ground state, and excited states of the form $4s^1 n s^1$, $4s^1 n p^1$ and $4s^1 n d^1$.

[7 marks]

1.6) When triplets in the emission spectrum of atomic Ca are studied with 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 to show how the simple and compound triplet structures arise.

[7 marks]

1.7) When a calcium discharge is placed in a magnetic field of flux density B the high resolution spectra of emission lines, viewed at right angles to the field, all show additional splitting. Although the fine structure of the triplets is complicated, all singlet lines are split into three equally spaced components with an energy separation of 4.637×10^{-24}J.
Explain these observations and deduce the value of B for the magnetic field.

[7 marks]

1.8) The fundamental infra-red absorption spectrum of ${}^1H^{35}Cl$ consists of two branches, a P and an R branch . The components of the P and R branches are approximately equally spaced with a separation of 21.18 cm^{-1}. The equivalent spectrum for ${}^2H^{35}Cl$ is similar but the separation between the components of the P and R branches is reduced. Calculate this separation.
N.B. The rotational constant B for a diatomic molecule is given by $B = \hbar^2/(2I)$ where I is the moment of inertia of the molecule.

[7 marks]

SECTION B – Answer TWO questions

2) The Hamiltonian of a particle of mass m, which is subject to the one dimensional simple harmonic potential

$$V(x) = m\omega^2 x^2,$$

may be expressed as

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

where

$$\hat{A} = \left(\frac{m\omega}{2}\right)^{\frac{1}{2}} x + \frac{\hbar}{(2m\omega)^{\frac{1}{2}}}\frac{d}{dx}$$

and

$$\hat{A}^\dagger = \left(\frac{m\omega}{2}\right)^{\frac{1}{2}} x - \frac{\hbar}{(2m\omega)^{\frac{1}{2}}}\frac{d}{dx}.$$

Show that the commutator $\left[\hat{A}, \hat{A}^\dagger\right] = \hbar$.

[6 marks]

Show also that

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

[6 marks]

Hence deduce that, if $\psi_E(x)$ is an eigenfunction of the Hamiltonian corresponding to energy E, then $\hat{A}^\dagger\psi_E(x)$ is an eigenfunction corresponding to energy $E + \hbar\omega$ and that $\hat{A}^\dagger$ is, therefore, a creation operator.

[6 marks]

Define the eigenfunctions of the ground and first excited state, $\psi_0(x)$ and $\psi_1(x)$ respectively, using the annihilation and creation operators and state the normalistation condition that they satisfy.

[4 marks]

Determine the first-order effect on the ground and first excited states of the perturbing potential

$$U = \lambda\left(\hat{A} - \hat{A}^\dagger\right)^2$$

where λ is a constant.

[8 marks]

3) State briefly how the variational inequality for the energy, E_0 of the ground state of a system with Hamiltonian $\hat{H}$,

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

may be used to obtain an estimate of E_0.

[5 marks]

A particle of mass m is subject to the one dimensional potential

$$V(x) \begin{cases} = \lambda x, & x \geq 0 \\ = \infty, & x < 0 \end{cases}$$

where λ is a constant and can be represented by the trial wavefunction

$$\psi(x) \begin{cases} = ax \exp(-bx), & x \geq 0 \\ = 0, & x < 0 \quad \text{where } b > 0. \end{cases}$$

a) Show that normalisation of the wavefunction requires that

$$a = 2b^{\frac{3}{2}}.$$

[5 marks]

b) Use the variational inequality to show that the lowest energy, E, of the particle satisfies

$$E \leq \frac{\hbar^2 b^2}{2m} + \frac{3\lambda}{2b}.$$

[10 marks]

c) Hence obtain an expression for the minimum value of E corresponding to such a wavefunction.

[7 marks]

d) Sketch the form of the wavefunction and determine the most probable location of the particle when it is in this state.

[3 marks]

4) 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 of a diatomic molecule may be written

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

where B is a molecular constant.

[8 marks]

Using this information calculate the energies, in cm^{-1}, of the first four lines in the rotational spectrum that you would expect to observe for diatomic $^{23}Na^{35}Cl$ at 1000 K.
You may assume that atomic masses are equal to atomic mass numbers in m_u.
Calculate the position of the most intense line in the spectrum.

[16 marks]

Indicate the type of equipment that you would need to record this spectrum.

[6 marks]

5) By considering the rotational selection rules for the electronic excitation of a diatomic molecule show that the energies of the components of the P and R branches in the $\nu'' = 0 \rightarrow \nu' = 0$ vibration-rotation band are given by the expression

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

In this expression $m = \pm 1, \pm 2, \pm 3, \ldots$, ΔE_0 is the energy of the electronic excitation and B' and B'' are the rotational constants for the $\nu' = 0$ and $\nu'' = 0$ vibrational states.

[15 marks]

Derive a similar expression for the Q branch.

[5 marks]

For the N_2 molecule the lowest energy electronic transition corresponds to the excitation of a $2p\sigma_g$ electron to a $2p\pi_g$ orbital. B'' for the $\nu'' = 0$ level of the ground state is 2.01 cm^{-1} and B' for the $\nu' = 0$ level of the excited state is 1.637 cm^{-1}.
Calculate m for the band head of the $\nu'' = 0 \rightarrow \nu' = 0$ vibration-rotation band and state whether this occurs in the P or R branch of the spectrum.

[5 marks]

Calculate the fractional change in bond length that occurs for this excitation and comment on what this tells you about the bonding nature of the π_g orbital.

[5 marks]