King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP3221 Spectroscopy and Quantum Mechanics

Summer 2004

Time allowed: THREE Hours

Candidates should answer no more than SIX parts of SECTION A, and no more than TWO questions from SECTION B. No credit will be given for answering further questions.

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

Permittivity of free space	ϵ_0	$=$	8.854×10^{-12}	$\mathrm{F\,m^{-1}}$
Permeability of free space	μ_0	$=$	$4\pi \times 10^{-7}$	$\mathrm{H\,m^{-1}}$
Speed of light in free space	c	$=$	2.998×10^{8}	$\mathrm{m\,s^{-1}}$
Gravitational constant	G	$=$	6.673×10^{-11}	$\mathrm{N\,m^2\,kg^{-2}}$
Elementary charge	e	$=$	1.602×10^{-19}	C
Electron rest mass	m_{e}	$=$	9.109×10^{-31}	kg
Unified atomic mass unit	m_{u}	$=$	1.661×10^{-27}	kg
Proton rest mass	m_{p}	$=$	1.673×10^{-27}	kg
Neutron rest mass	m_{n}	$=$	1.675×10^{-27}	kg
Planck constant	h	$=$	6.626×10^{-34}	$\mathrm{J\,s}$
Boltzmann constant	k_{B}	$=$	1.381×10^{-23}	$\mathrm{J\,K^{-1}}$
Stefan-Boltzmann constant	σ	$=$	5.670×10^{-8}	$\mathrm{W\,m^2\,K^{-4}}$
Gas constant	R	$=$	8.314	$\mathrm{J\,mol^{-1}\,K^{-1}}$
Avogadro constant	N_{A}	$=$	6.022×10^{23}	$\mathrm{mol^{-1}}$
Molar volume of ideal gas at STP		$=$	2.241×10^{-2}	$\mathrm{m^3}$
One standard atmosphere	P_0	$=$	1.013×10^{5}	$\mathrm{N\,m^{-2}}$

The following integral may be assumed:

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

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

The Pauli matrices are

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

The energy of a quantum mechanical rigid rotator of angular momentum J is given by

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

where the rotational constant is

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

I being the moment of inertia.

SECTION A – Answer SIX parts of this section

1.1) State the condition under which an operator $\hat{q}$ is hermitian and use it to demonstrate that the momentum operator

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

is hermitian.

[7 marks]

1.2) Show that the Pauli matrices satisfy the commutation relation of angular momentum

$$[\sigma_2, \sigma_3] = i\hbar\sigma_1.$$

Determine the eigenvalues and eigenvectors of σ_3.

[7 marks]

1.3) State the physical quantities determined by, and their relationship to, the quantum numbers (n, l, m, s) of a hydrogen-electron wave function $\psi_{n,l,m,s}(\mathbf{x})$.
The interaction of a magnetic field $\mathbf{B}$ with an electron may be described by the potential

$$\hat{V} = \frac{e}{m_e c} \hat{\mathbf{s}} \cdot \mathbf{B}$$

where $\hat{\mathbf{s}}$ is the spin-operator of the electron of charge e and mass m_e.
Use first-order perturbation theory to calculate the energy-shift caused by the potential.

[7 marks]

1.4) Define the operator $\hat{P}_{12}$ that exchanges electrons in two-electron wave-functions, $\psi(\mathbf{x}_1, \mathbf{x}_2)$.
Write down eigenfunctions of $\hat{P}_{12}$ in terms of wavefunctions $\psi(\mathbf{x}_1, \mathbf{x}_2)$ and determine the corresponding eigenvalues.
A pair of electrons may be represented by triplet and singlet states. The triplet states are

$$\left\{ \begin{array}{c} \chi\left(\frac{1}{2}; \frac{1}{2}\right) \\ \frac{1}{\sqrt{2}}\left(\chi\left(\frac{1}{2}; -\frac{1}{2}\right) + \chi\left(-\frac{1}{2}; \frac{1}{2}\right)\right) \\ \chi\left(-\frac{1}{2}; -\frac{1}{2}\right) \end{array} \right\}.$$

What are the eigenvalues of $\hat{P}_{12}$ for each state?

[7 marks]

1.5) By assuming that HCl may be approximated by a rigid rotator, given that the bond length for the molecule $^{1}H^{35}Cl$ is 0.12746 nm, calculate the energy difference in Joules corresponding to the $J = 0$ to $J = 1$ rotational excitation for HCl.

[7 marks]

1.6) The energies of the states of the $2s^2 2p^4 3p^1$ ^4D spin-orbit multiplet of the Ne^+ ion relative to its $^2P_0$ ground-state are 30.8895 eV, 30.9315 eV, 30.9625 eV and 30.9803 eV.

Deduce the allowed J values.

The energy separation between the J and $J-1$ states of a spin-orbit multiplet is given by

$$\Delta E = \hbar^2 AJ,$$

where A is the spin-orbit coupling constant.

Use this to assign J values to the states.

[7 marks]

1.7) Show that the angular momentum of the state of maximum probability of occupancy by a diatomic molecule at a temperature T is

$$J = \sqrt{\frac{k_B T}{2B}} - \frac{1}{2},$$

where B is the rotational constant of the molecule.

Given that $B = 7.09 \times 10^{-24}$ J for the molecule BrF, determine the most probable rotational state of this molecule at 315 K.

[7 marks]

1.8) Use sketches to describe the molecular orbitals of homonuclear diatomic molecules that are formed by linear combinations of s and p atomic orbitals.

[7 marks]

SECTION B – Answer TWO questions

2) Consider a spin-one system, with the Hamiltonian

$$\hat{H} = a\mathbf{S}_z^2 + b\left(\mathbf{S}_x^2 - \mathbf{S}_y^2\right)$$

where $\mathbf{S}_x, \mathbf{S}_y$ and $\mathbf{S}_z$ are the component matrices

$$\mathbf{S}_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad \mathbf{S}_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}; \quad \mathbf{S}_z = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}.$$

By evaluating $\mathbf{S}_z^2$, show that the states

$$|1> = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; \quad |0> = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; \quad |-1> = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

are eigenstates of

$$\hat{H}_0 = a\mathbf{S}_z^2$$

where $|1>$ and $|-1>$ are degenerate, while $|0>$ is non-degenerate.

[8 marks]

Treat

$$\hat{U} = b\left(\mathbf{S}_x^2 - \mathbf{S}_y^2\right)$$

as a perturbation to $\hat{H}_0$ and evaluate the first-order energy shift of $|0>$.

[10 marks]

Write down the determinant for the first-order energy shifts of doubly-degenerate states and hence determine the first-order effect of $\hat{U}$ on combinations of the states $|1>$ and $|-1>$.

[12 marks]

3) Explain how the variational inequality for the energy E of the ground state of a system having Hamiltonian $\hat{H}$ can be used to estimate the energy, given that the average expectation value of an operator $\hat{q}$ in a state with wavefunction $\psi(x)$ is

$$< q >= \frac{\int_{-\infty}^{\infty} \psi^*(x)\hat{q}\psi(x)dx}{\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx}$$

[10 marks]

Use the variational method to derive an approximation for the ground state energy of a particle of mass m subject to the one dimensional potential

$$V(x) \begin{cases} = \lambda x^2, & x \geq 0 \\ = \infty, & x < 0 \end{cases}$$

where λ is a constant, by assuming the trial wavefunction

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

[16 marks]

State briefly how the approximation might be improved.

[4 marks]

4) State the electronic configuration of the ground state of potassium ${}^{38}_{19}$K and deduce the corresponding term symbol.

[8 marks]

Single 4s electrons of potassium are excited to 5s or 4d orbitals. Give a sketch of the energy diagram and a specification of the selection rules to describe the fine structure of the resulting emission spectrum when the electrons relax to the 4p orbitals.

[12 marks]

Describe the processes of X-ray fluorescence and Auger emission.

[10 marks]

5) The energy of rotation of a diatomic molecule having rotational quantum number J is,

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

State the selection rules of angular momentum for the absorption of radiation by the molecule.

[4 marks]

Show that the energies ϵ of absorption lines in the vibration-rotation bands of a diatomic molecule are given by

$$\epsilon_{P,R} = \epsilon_0 + (B_1 + B_0)m + (B_1 - B_0)m^2$$

where $m = \pm 1, \pm 2, \pm 3, \ldots$, and

$$\epsilon_Q = \epsilon_0 + (B_1 - B_0)m + (B_1 - B_0)m^2$$

where $m = +1, +2, +3, \ldots$. ϵ_0 is the energy of the band centre, while B_0 and B_1 are the rotational constants for the ground and first excited vibrational states respectively.

[14 marks]

Show that the band head occurs at

$$m = -\frac{1}{2}\frac{B_1 + B_0}{B_1 - B_0}.$$

The rotational constants for a C_2 molecule are $B_0 = 3.4817 \times 10^{-23}$ J and $B_1 = 3.2431 \times 10^{-23}$ J for the ground and first excited vibrational states respectively. Use these to calculate the value of m for the band head of the vibration-rotation band. Given that the energy of excitation between the vibrational states is $\epsilon_0 = 3.8446 \times 10^{-19}$ J, determine the energy, in Joules, of the band head.

[12 marks]