King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP3221 Spectroscopy and Quantum Mechanics

Summer 1997

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

Constants

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

The following integrals may be assumed: m and n are positive integers, $a > 0$.

$$\int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx = \frac{a}{2}\delta_{nm}$$

$$\int_0^a x^2 \sin^2\left(\frac{n\pi x}{a}\right)dx = \frac{a^3}{6} - \frac{a^3}{4\pi^2 n^2}$$

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

SECTION A – Answer SIX parts of this section

1.1) A system is in a state $|a>$ that is an eigenstate of an operator $\hat{A}$ corresponding to eigenvalue a. A measurement is made of a physical observable represented by an operator $\hat{B}$ with non-degenerate eigenstates $|b>$ corresponding to eigenvalues b.

(i) Write down the probability $P(a, b)$ of observing a value b.

(ii) What is the state of the system after the measurement if a value of b has been observed?

(iii) What is the condition that the $\hat{A}$ and $\hat{B}$ must satisfy if a subsequent measurement of $\hat{A}$ is to be certain to yield the value a ?

[7 marks]

1.2) 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

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

Determine the eigenvectors of σ_1.

[7 marks]

1.3) Consider a Hamiltonian, H_0, with two orthonormal eigenstates, $|1>$ and $|2>$, which both correspond to the same eigenvalue, E_0, *viz.*

$$H_0|1> = E_0|1>$$
$$H_0|2> = E_0|2> .$$

Show that, if a perturbing term, U, is added to the Hamiltonian, then the first-order perturbations, ΔE, of the energies of the two states are solutions of the equation

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

[7 marks]

1.4) State the connection between spin and statistics. Show how the connection for half-integer spin particles leads to the Pauli Exclusion Principle.

[7 marks]

1.5) Atomic zinc has a ground state electronic configuration

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2.$$

Consider the ground state and the excited states that can be formed by exciting 4s electrons to 4p and 5s orbitals, in that energy order, and deduce the term symbols for these states.
State the selection rules that apply for transitions between the states and indicate on energy level diagrams the possible emissions that can occur.

[7 marks]

1.6) The rotational energy of a diatomic molecule can be written as

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

where B is a molecular constant and J is the rotational quantum number.
Using this, write an expression for the ratio N_J/N_0, where N_J is the number of molecules with energy E_J due to thermal excitation and N_0 is the number with $J = 0$.
If $B = 2.104 \times 10^{-22}$ Joules for HCl, find J for the state with the highest molecular population at 300^0 K.

[7 marks]

1.7) The outer valence shell electronic configuration for molecular oxygen can be written $1\pi_u^4\ 1\pi_g^2$. The vibrational frequency for neutral oxygen is 1568 cm^{-1}, while the frequencies for the $1\pi_u^{-1}$ and $1\pi_g^{-1}$ ions are 1025 cm^{-1} and 1860 cm^{-1} respectively. Calculate the fractional change in the force constant for the O-O bond occurring on ionisation from these two orbitals and interpret the results in terms of the bonding character of the molecular orbital involved.
You may assume that the vibrational frequency ν of a diatomic molecule with force constant k and reduced mass μ is given by the expression

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}.$$

[7 marks]

1.8) Sketch the proton NMR spectrum produced by ethyl bromide CH_3CH_2Br and explain the observed structure in terms of chemical shift and spin-coupling processes.

[7 marks]

SECTION B – Answer TWO questions

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

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

Write down the time-independent Schrödinger equation. Show that the energy eigenvalues are

$$E_n = \frac{(\hbar n \pi)^2}{2ma^2} \qquad n = 1, 2, \ldots,$$

and evaluate the corresponding normalised wave-functions.

[15 marks]

Determine the first-order effect of the perturbing potential

$$V = ex^2$$

on the energies of the ground and first excited states.

[15 marks]

3) Show that the lowest eigenvalue E_0 of a Hamiltonian, H, satisfies

$$E_0 \leq \frac{< \psi | H | \psi >}{< \psi | \psi >}$$

where $| \psi >$ is any normalisable state.

[10 marks]

Hence determine an upper bound for the energy of the ground state of a particle of mass m in one dimension that is subject to the potential

$$\begin{aligned} V(x) &= \infty \qquad x \leq 0 \\ &= \lambda x \qquad x > 0, \end{aligned}$$

by assuming the trial wave-function

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

[20 marks]

4) Explain what determines whether the vibration of a diatomic molecule will be infrared or Raman active.

[4 marks]

By considering the selection rules involved, deduce the form of the $\nu = 0$ to $\nu = 1$ vibration-rotation bands observed in the infrared spectrum and the Raman spectrum of HCl. Assume that HCl behaves as a harmonic oscillator.

[18 marks]

If the line in the P branch of the IR spectrum of $H^{35}Cl$ corresponding to an excitation to the $\nu = 1, J = 0$ state is observed at 2865 cm^{-1} and the line in the R branch corresponding to the $\nu = 1, J = 1$ excited state is observed at 2906 cm^{-1} calculate the bond length for $H^{35}Cl$. Assume that atomic mass is equal to the atomic mass number in atomic mass units.
You may assume that the rotational constant B for a diatomic molecule with moment of inertia I is given by the expression

$$B = \frac{h^2}{8\pi^2 I}.$$

[8 marks]

5) In the LCAO approach the orbitals of the hydrogen molecular ion can be regarded as being formed from a combination of two atomic 1s orbitals. Show how application of the variation theorem to a trial LCAO wave function leads to two functions corresponding to one bonding and one antibonding molecular orbital. Deduce expressions for these orbitals and also for the energies of the orbitals.

[22 marks]

If the ionisation energy for H is 13.6 eV, the adiabatic ionisation energy for H_2 is 15.45 eV and the dissociation energy for H_2^+ is 2.65 eV, find the dissociation energy for H_2.

[8 marks]