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 2006

Time allowed: THREE Hours

Candidates should answer ALL 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} F m^{-1}
Permeability of free space	μ_0	$=$	$4\pi \times 10^{-7}$ H m^{-1}
Speed of light in free space	c	$=$	2.998×10^{8} m s^{-1}
Gravitational constant	G	$=$	6.673×10^{-11} 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} J s
Boltzmann constant	k_B	$=$	1.381×10^{-23} J K^{-1}
Stefan-Boltzmann constant	σ	$=$	5.670×10^{-8} W m^{-2} K^{-4}
Gas constant	R	$=$	8.314 J mol^{-1} K^{-1}
Avogadro constant	N_A	$=$	6.022×10^{23} mol^{-1}
Molar volume of ideal gas at STP		$=$	2.241×10^{-2} m^3
One standard atmosphere	P_0	$=$	1.013×10^{5} N m^{-2}

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SECTION A − Answer ALL parts of this section

1.1) Given two operators $\hat{A}$ and $\hat{B}$ define their commutator $\left[\hat{A},\hat{B}\right]$.

Prove that $\left[\hat{A}\hat{B},\hat{C}\right] = \hat{A}\left[\hat{B},\hat{C}\right] + \left[\hat{A},\hat{C}\right]\hat{B}$, where $\hat{C}$ is also an operator.

[5 marks]

1.2) Consider a spin $\frac{1}{2}$ system represented by the normalised spinor $\frac{1}{\sqrt{65}}\begin{pmatrix} 4 \\ 7 \end{pmatrix}$. Show that

the probability that a measurement of $\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ yields the value $-\frac{\hbar}{2}$ is equal

to $\frac{1}{2}$.

[8 marks]

1.3) Consider the normalised trial wavefunction

$$\psi(x) = \begin{cases} \sqrt{\dfrac{15}{16a^5}}\left(a^2 - x^2\right) & -a \le x \le a \\ 0 & \text{otherwise} \end{cases}$$

where a is a positive parameter that can be varied. Use this wavefunction to show that an upper limit for the ground state energy of a one-dimensional harmonic oscillator with mass M and angular frequency ω is

$$E(a) = \frac{5\hbar^2}{4Ma^2} + \frac{M\omega^2 a^2}{14}.$$

[8 marks]

1.4) Estimate the ground state energy of the one-dimensional harmonic oscillator by minimizing the expression for $E(a)$ given in question 1.3).

[6 marks]

1.5) Write down the ground state electronic configuration for Neon (Ne, Atomic Number Z = 10). Specify the angular momentum properties of the ground state using the notation ${}^{2S+1}L_J$.

[6 marks]

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1.6) The energy spectrum of an hydrogenic atom is given by the formula

$$E(n) = -\frac{Z^2 R_\infty}{n^2} \quad ,$$

where Z is the Atomic Number and $R_\infty \simeq 13.6$ eV is the Rydberg constant. Write down the energy spectrum $E(n_1, n_2)$ of the Helium atom (He, Atomic Number $Z=2$) at zero order in perturbation theory (i.e. ignoring the mutual repulsion of the two electrons).

Show that in this approximation all doubly-excited states of He have a higher energy than the ground state of He$^+$, the singly ionized helium atom.

[7 marks]

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$$\frac{Z^2 R_\infty}{n^2} \quad ,$$

SECTION B – Answer TWO questions

2) Consider a particle of mass M in a one-dimensional quantum well defined by the potential

$$V(x) = \begin{cases} 0 & \text{if } 0 \le x \le L \\ +\infty & \text{otherwise.} \end{cases}$$

The energy and normalised wavefunction of the corresponding Hamiltonian for the nth state are respectively $E_n = \dfrac{n^2 \pi^2 \hbar^2}{2ML^2}$ and $\phi_n(x) = \sqrt{\dfrac{2}{L}} \sin\left(\dfrac{n\pi x}{L}\right)$, where $n=1,2,3,\ldots$

a) Find the exact energies and wavefunctions for the ground and first excited states for an infinite two-dimensional potential well defined by the potential:

$$V(x,y) = \begin{cases} 0 & \text{if } 0 \le x \le L, \quad 0 \le y \le L \\ +\infty & \text{otherwise.} \end{cases}$$

Show that the ground state is non-degenerate and that the first excited state is doubly degenerate.

[7 marks]

b) Add the following perturbation to the infinite two-dimensional quantum well:

$$\hat{H}_p = \lambda V_0 L^2 \delta\left(x - \frac{L}{4}\right)\delta\left(y - \frac{3L}{4}\right)$$

where $\delta(x)$ is the Dirac delta function.

Using first-order (non-degenerate) perturbation theory, calculate the energy of the ground state.

[8 marks]

c) Calculate the matrix elements of $\hat{H}_p$ among the wavefunctions of the first excited state. Hence, using first-order (degenerate) perturbation theory, calculate the energy of the first excited state.

[15 marks]

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3) Let the eigenvectors of the unperturbed Hamiltonian be denoted by $|\phi_k\rangle$.

In first-order time-dependent perturbation theory, the amplitude $c_{k \to l}(t)$ for a transition due to the time-dependent perturbation $\lambda \hat{V}(t)$ from a state $|\phi_k\rangle$ to a state $|\phi_l\rangle$ is:

$$c_{k \to l}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} \left\langle \phi_l \left| \lambda \hat{V}(\tilde{t}) \right| \phi_k \right\rangle e^{i(\omega_l - \omega_k)\tilde{t}} \, d\tilde{t} \,.$$

Consider a particle in the nth state $|\phi_n\rangle$ of a one-dimensional harmonic oscillator, with mass M and angular frequency ω, with energy eigenvalues $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ and eigenvectors $|\phi_n\rangle = |n\rangle$.

Suppose that the system is perturbed by the potential:

$$\lambda \hat{V}(t) = \begin{cases} 0 & t < 0 \\ \lambda \hat{x} \cos(\omega_1 t) e^{-\beta t} & t \geq 0 \end{cases}.$$

a) Demonstrate that transitions to a state $|\phi_m\rangle$ are only allowed for $m = n \pm 1$.

[10 marks]

b) Show that the asymptotic probability of transition $P_{n \to m}$ to the mth state as $t \to \infty$ is given by:

$$P_{n \to m} = \begin{cases} \dfrac{\lambda^2 n}{2\hbar M \omega} \dfrac{\omega^2 + \beta^2}{\left(\omega_1^2 - \omega^2 + \beta^2\right)^2 + 4\omega^2 \beta^2} & m = n - 1 \\[4mm] \dfrac{\lambda^2 (n+1)}{2\hbar M \omega} \dfrac{\omega^2 + \beta^2}{\left(\omega_1^2 - \omega^2 + \beta^2\right)^2 + 4\omega^2 \beta^2} & m = n + 1 \end{cases}.$$

[15 marks]

c) Discuss the behaviour of $P_{n \to m}$ when $\omega_1 \to \omega$ and/or $\beta \to 0$. Is time-dependent perturbation theory applicable in these limiting cases?

[5 marks]

The following expressions might be useful:

$$\hat{x} = \sqrt{\frac{\hbar}{2M\omega}}\left(\hat{a} + \hat{a}^\dagger\right), \qquad \hat{a}^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle, \qquad \hat{a}|n\rangle = \sqrt{n}\,|n-1\rangle.$$

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4) Consider the H_2 , D_2 , HD and HCl (hydrogen chloride) molecules. The atomic masses of the Hydrogen, Deuterium and Chlorine atoms are approximately 1, 2, and 35, respectively.

a) State which of the H_2, D_2 and HD molecules has the largest and which has the smallest binding energy, and explain why.

[7 marks]

b) Consider an experiment aimed at inducing vibrational motion in molecules by means of electric fields oscillating at the vibrational frequencies of the molecules. For each of the molecules H_2, HD and HCl discuss if such motion can arise.

[7 marks]

c) Consider HCl and the chemically equivalent DCl molecule in which the hydrogen atom is substituted by a deuterium atom D (atomic mass 2). The roto-vibrational spectra of the two molecules can be written respectively as:

$$E_H\left(n,l\right) \ = \ A_H\left(n \ +\frac{1}{2}\right) \ + \ B_H \ l(l+1)$$

and

$$E_D\left(n,l\right) \ = \ A_D\left(n \ +\frac{1}{2}\right) \ + \ B_D \ l(l+1).$$

Here n and l are the vibrational and rotational quantum numbers, respectively. Determine A_D and B_D, knowing that $A_H = 0.37$ eV and $B_H = 1.32\times10^{-3}$ eV, respectively.

[7 marks]

d) A gas of HCl molecules de-excites from roto-vibrational states with $n=1$ to states with $n=0$. Sketch the energy spectrum that would be observed in this process. How would the value of A_H , defined in part c) above, be found from this spectrum?

[5 marks]

e) Suppose that, in a new experiment on a gas of HCl, the molecules first absorb an incoming photon which takes them momentarily to an electronically excited state, and then return to their electronic ground state by emitting a photon. Assuming that the molecules do not change their vibrational state during this process, determine the possible values for the energy difference between the incoming and the outgoing photons. Would an analogous spectrum of energies be obtained in a similar experiment conducted on a gas of H_2 molecules?

[4 marks]

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