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 2005

Time allowed: THREE Hours

Candidates should answer all 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

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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}	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 z-component of the orbital angular momentum operator $\hat{\mathbf{L}}$ can be expressed in terms of the components of the position and momentum operators as

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \,.$$

Two operators $\hat{A}$ and $\hat{B}$ anticommute if $\hat{A}\hat{B} + \hat{B}\hat{A} = 0$.

SECTION A – Answer all SIX parts of this section

1.1) An operator $\hat{A}$, corresponding to an observable A, has two normalized eigenfunctions ϕ_1 and ϕ_2, with distinct eigenvalues a_1 and a_2. An operator $\hat{B}$, corresponding to an observable B, has normalized eigenfunctions χ_1 and χ_2, with distinct eigenvalues b_1 and b_2. The eigenfunctions are related by

$$\phi_1 = \frac{2\chi_1 + 3\chi_2}{\sqrt{13}} \qquad \phi_2 = \frac{3\chi_1 - 2\chi_2}{\sqrt{13}} .$$

A is measured and the value a_1 is obtained. If B is then measured and then A again, show that the probability of obtaining a_1 a second time is 97/169.

[7 marks]

1.2) A one-dimensional harmonic oscillator with angular frequency ω is known to have energy eigenvalues equal to $\left(n' + \frac{1}{2}\right)\hbar\omega$, where n' is zero or a positive integer. The Hamiltonian of a three-dimensional isotropic harmonic oscillator with mass m and angular frequency ω has the form

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{1}{2}m\omega^2\left(x^2 + y^2 + z^2\right)$$

By expressing H as a sum of three similar Hamiltonians H_x, H_y and H_z for one-dimensional harmonic oscillators, show that the energy eigenvalues are equal to $\left(n + \frac{3}{2}\right)\hbar\omega$, where n is zero or a positive integer. Show, moreover, that the degeneracies of the three lowest energy eigenvalues are 1, 3 and 6.

[7 marks]

1.3) Show that the matrices

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

satisfy the commutation relation of angular momentum

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

and that

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

[7 marks]

1.4) Define the particle exchange operator $\hat{P}_{12}$ that exchanges particles in a two-particle wavefunction $\psi(1,2)$ and demonstrate that $\hat{P}_{12}^2 = \hat{1}$. Find the eigenvalues of $\hat{P}_{12}$.

[7 marks]

1.5) The atomic number of titanium (Ti) is Z=22. Write down the ground state electronic configuration of titanium and determine the quantum number *S* for the total electronic spin of the atom, using the appropriate Hund's rule.

[7 marks]

1.6) Sketch the form of the LCAO molecular orbitals which can be obtained by combining two 2*p* atomic orbitals, ordering them by ascending value of the associated energy levels. Assume that lower–lying levels associated with molecular orbitals obtained from 1*s* and 2*s* electrons and not considered here do not influence this ordering.

[7 marks]

SECTION B – Answer TWO questions

2) A spinless particle of mass m is moving in a one-dimensional infinite potential well of length $2L$, with walls at x=0 and x=$2L$, described by the potential:

$$V(x) = \begin{cases} 0 & 0 \le x \le 2L \\ +\infty & \text{otherwise} \end{cases}$$

a) Write down the time-independent Schroedinger equation and show that the energy of the n^{th} excited states is

$$E_n = \frac{\hbar^2 \pi^2}{8mL^2} n^2 \ ,$$

where n is a positive integer.
Find the corresponding normalized wavefunction.

[10 marks]

b) Calculate to first order perturbation theory the energy of the n^{th} excited state when the bottom of the potential well is modified by the following two perturbations:

(α) $V_{P1}(x) = \lambda V_0 \sin\left(\frac{\pi x}{2L}\right)$

and

(β) $V_{P2}(x) = \lambda V_0 \delta(x - L)$

where $\lambda \ll 1$.

[20 marks]

[The following expression might be useful:

$$\int \cos(nx)\sin(mx)\,dx = -\frac{\cos\left[(m-n)x\right]}{2(m-n)} - \frac{\cos\left[(m+n)x\right]}{2(m+n)} + \text{constant} \qquad m \neq \pm n$$

where m and n are integers.]

SEE NEXT PAGE

3a) Explain the variational method and its use in the evaluation of the ground state energy of a system. Write down the variational inequality for the ground state energy E_0 for a system with Hamiltonian $\hat{H}$.

[10 marks]

b) A particle of mass *m* is moving in the potential

$$V(x)=\begin{cases}\frac{1}{2}m\omega^2x^2 & x>0\\ +\infty & x\le 0\end{cases}$$

i) Consider a trial wavefunction proportional to $x\exp\left(-\beta x^2\right)$ for $x>0$. β is a positive parameter that can be varied. Explain why this trial wavefunction is a plausible choice and normalize it.

ii) Use the variational method to show that an upper limit for the ground state energy (as a function of the variable parameter β) for the particle moving in the potential $V(x)$ is

$$\frac{3\hbar^2}{2m}\beta+\frac{3m\omega^2}{8\beta}$$

iii) Use the variational method to estimate the ground state energy for this particle.

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

[20 marks]

[The following expression might be useful:

$$\int_0^{+\infty} x^{2n}e^{-\gamma x^2}dx=\frac{1\cdot 3\cdot 5\cdots(2n-1)}{2^{n+1}(\gamma)^n}\sqrt{\frac{\pi}{\gamma}} \qquad \gamma>0\,.]$$

.

SEE NEXT PAGE

4) For many applications, alkali atoms can be considered to consist of one (valence) electron interacting with an effective central potential $V_{eff}(r)$. This potential is generated by the atomic nucleus and the remaining electrons which are supposed to be "frozen" in their core orbitals.

a) Write down the Hamiltonian H of an alkali atom in the presence of an external electric field **E** oriented along the z axis, i.e $\mathbf{E} = E\mathbf{e}_z$, where $\mathbf{e}_z$ is the unit vector along the z direction. Assume that $V_{eff}(r)$ is known.

[7 marks]

b) Determine whether H is symmetric with respect to inversion of each of the Cartesian coordinates. Show that the term in the Hamiltonian associated with the external electric field anticommutes with the parity operator.

[8 marks]

c) Show that within first-order perturbation theory the energy levels of the atom are not influenced by the interaction with the external field.
[Hint: ignore the electron spin and consider the generic atomic state ψ_{nlm} with quantum numbers n, l and m. Use the fact that the perturbation term and the parity operator anticommute and the fact that ψ_{nlm} are parity eigenstates with eigenvalues $(-1)^l$.]

[7 marks]

d) Consider now the *exact* energy spectrum of an alkali atom in an electric field Show that the eigenstates of H are still classifiable as eigenstates of the angular momentum component operator L_z.
[Hint: consider the commutation relation between H and L_z.]

[8 marks]