King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP3221 Spectroscopy and Quantum Mechanics
Examiner: Dr. C. Molteni

Summer 2007

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 a further question from SECTION B.

The approximate mark for each part of a question is indicated in square brackets.

You may only use a College-approved calculator for this paper.

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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}

Spherical polar coordinates:

$x = r\cos\varphi\,\sin\vartheta$

$y = r\sin\varphi\,\sin\vartheta$

$z = r\cos\vartheta$

$r \geq 0; \quad 0 \leq \varphi < 2\pi; \quad 0 \leq \vartheta < \pi$

For a harmonic oscillator of mass m and angular frequency ω the ground state wavefunction is

$$\psi_0 = |0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$$

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

The wavefunctions of the ground and first excited states for the hydrogen atom in spherical polar coordinates are:

$$\psi_{100} = |100\rangle = R_{10}(r)Y_{0,0} = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} \exp\left(-\frac{r}{a_0}\right)$$

$$\psi_{200} = |200\rangle = R_{20}(r)Y_{0,0} = \left(\frac{1}{8\pi a_0^3}\right)^{\frac{1}{2}} \left(1-\frac{r}{2a_0}\right)\exp\left(-\frac{r}{2a_0}\right)$$

$$\psi_{210} = |210\rangle = R_{21}(r)Y_{1,0} = \left(\frac{1}{32\pi a_0^5}\right)^{\frac{1}{2}} r\exp\left(-\frac{r}{2a_0}\right)\cos\vartheta$$

$$\psi_{21\pm1} = |21\pm1\rangle = R_{21}(r)Y_{1,\pm1} = \mp\left(\frac{1}{64\pi a_0^5}\right)^{\frac{1}{2}} r\exp\left(-\frac{r}{2a_0}\right)\sin\vartheta\exp(\pm i\varphi)$$

where a_0 is the Bohr radius.

Useful definite integrals:

$$\int_{-\infty}^{+\infty} x^{2n}e^{-\gamma x^2}dx = \frac{1\cdot3\cdot5\cdots(2n-1)}{2^n(\gamma)^n}\sqrt{\frac{\pi}{\gamma}} \qquad \gamma > 0;\ n \text{ is a positive integer}$$

$$\int_{-\infty}^{+\infty} e^{-\gamma x^2}dx = \sqrt{\frac{\pi}{\gamma}} \qquad \gamma > 0$$

$$\int_{0}^{+\infty} x^{n}e^{-\beta x}dx = \frac{n!}{\beta^{n+1}} \qquad \beta > 0;\ n \text{ is a non-negative integer}$$

SECTION A – Answer ALL parts of this section

1.1) Prove that if the operators $\hat{A}$ and $\hat{B}$ are hermitian, then $i\left[\hat{A},\hat{B}\right]$ is hermitian.

[5 marks]

1.2) An hermitian operator $\hat{H}$ has the property $\hat{H}^4 = \hat{1}$. What are the eigenvalues of the operator $\hat{H}$? What are the eigenvalues of $\hat{H}$ if it is not restricted to be hermitian?

[6 marks]

1.3) For a harmonic oscillator of mass m and angular frequency ω, calculate $\left\langle k\left|\hat{x}\right|n\right\rangle$, where $\left|n\right\rangle$ and $\left|k\right\rangle$ are eigenstates of the harmonic oscillator, and show that it vanishes unless $n = k \pm 1$.

[7 marks]

1.4) Positronium consists of an electron and a positron bound together analogous to the electron and proton in the hydrogen atom. The spin interaction Hamiltonian of the electron and positron can be written as

$$\hat{H} = \beta\hat{S}_1 \bullet \hat{S}_2 ,$$

where $\hat{S}_1$ and $\hat{S}_2$ are the spin operators of the electron and the positron and β is a constant. Derive an expression for the interaction energies of positronium in the singlet and triplet states.

[8 marks]

1.5) State Hund's rules.
Assuming Hund's rules apply, derive an expression for the spectroscopic terms of the ground state of carbon (C, atomic number Z=6) and oxygen (O, Z=8).

[7 marks]

1.6) Radiation with a wavelength of 2.603 mm is absorbed by CO in a transition between the rotational level states J=0 and J=1. Calculate the moment of inertia of the CO molecule and the equilibrium separation between the carbon and oxygen nuclei.

[7 marks]

SECTION B – Answer TWO questions

2a) The hamiltonian of a one-dimensional anharmonic oscillator of mass m and angular frequency ω is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2\hat{x}^2 + \lambda\hat{x}^4 ,$$

where the third term is small compared to the second.

(i) Using time-independent perturbation theory, show, to first order, that the effect of the anharmonic term is to change the energy of the ground state of the harmonic oscillator by

$$3\lambda\left(\frac{\hbar}{2m\omega}\right)^2$$

[10 marks]

(ii) What would be the first-order effect of an additional term proportional to $\hat{x}^3$ in the hamiltonian?

[5 marks]

b) Consider now a system described by the hamiltonian

$$\hat{H}' = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \lambda\hat{x}^4$$

[Note that $\hat{H}'$ is similar to the hamiltonian $\hat{H}$ of part a), but it does not have any term proportional to x^2].

(i) Use the variational method with the trial wavefunction

$$\psi(x) = \left(\frac{\beta}{\sqrt{\pi}}\right)^{1/2} e^{-\beta^2 x^2/2}$$

to show that this system has an upper limit for the ground state energy of

$$\frac{\hbar^2\beta^2}{4m} + \frac{3\lambda}{4\beta^4} .$$

[10 marks]

(ii) Use the variational method to estimate the ground state energy.

[5 marks]

3) For a system of spin $\frac{1}{2}$ the cartesian components of the spin operator $\hat{\mathbf{S}} = \hat{S}_x\mathbf{u_x} + \hat{S}_y\mathbf{u}_y + \hat{S}_z\mathbf{u}_z$, where $\mathbf{u_x}$, $\mathbf{u}_y$ and $\mathbf{u}_z$ are the unit vectors along the *x*, *y* and *z*-direction respectively, can be expressed by the matrices:

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

a) Find the eigenvalues and normalized eigenstates of the spin operator of an electron in the direction of a unit vector $\mathbf{n} = \sin\vartheta\,\mathbf{u_x} + \cos\vartheta\,\mathbf{u}_z$ (i.e. $\hat{\mathbf{S}}\bullet\mathbf{n}$).

[14 marks]

b) A measurement of $\hat{S}_x$ for an electron yields the value $+\frac{\hbar}{2}$. Calculate the expectation value of $\hat{\mathbf{S}}\bullet\mathbf{n}$.

[8 marks]

c) After the measurement made in b), a measurement of $\hat{\mathbf{S}}\bullet\mathbf{n}$ is carried out. What are the probabilities of observing each of the eigenvalues of $\hat{\mathbf{S}}\bullet\mathbf{n}$?

[8 marks]

4) Consider an unperturbed hamiltonian with eigenvalues $\hbar\omega_k$ and eigenfunctions $|\phi_k\rangle$. In first-order time-dependent perturbation theory, the amplitude $c_{k\to m}(t)$ for a transition due to the time-dependent perturbation $\lambda\hat{V}(t)$ from a state $|\phi_k\rangle$ to a state $|\phi_m\rangle$ is:

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

A hydrogen atom, initially in its ground state ($|nlm\rangle = |100\rangle$), is placed in a time-dependent electric field $\mathbf{E} = (0,0,E_z)$ aligned in the z-direction, where

$$E_z = \begin{cases} 0 & t < 0 \\ E_0 \exp(-\gamma t) & t > 0 \end{cases} .$$

This results in the time-dependent perturbation $eE_z\hat{z}$, where e is the elementary charge.

a) Show that the probability of finding the hydrogen atom in the $|200\rangle$ state is zero.

[5 marks]

b) To first order, show that, as $t \to \infty$, the probability that the hydrogen atom has made a transition to the $|210\rangle$ state is

$$\frac{2^{15}}{3^{10}} \frac{a_0^2 e^2 E_0^2}{\hbar^2 (\omega^2 + \gamma^2)},$$

where a_0 is the Bohr radius, and $\hbar\omega$ is the energy difference between the $|210\rangle$ and the ground state. [It is convenient to work in spherical polar coordinates.]

[16 marks]

c) What are the probabilities of finding the atom in the $|211\rangle$ and $|21-1\rangle$ states?

[9 marks]