Candidate number:	
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King's College London

UNIVERSITY OF LONDON

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B.Sc. EXAMINATION

CP3221 Spectroscopy and Quantum Mechanics

Examiner: Dr. C. Molteni

Summer 2009
Time allowed: THREE Hours

Answer SECTION A on the question paper.
Candidates may answer as many parts as they wish from SECTION A, but the total mark for this section will be capped at 40.
Candidates should also answer TWO questions from SECTION B.
No credit will be given for answering a further question from this section.
The approximate mark for each part of a question is indicated in square brackets.

Calculators may be used. The following models are permitted: Casio fx83 and Casio fx85.

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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}	$\mathrm{N\ m^{-2}}$

Useful formulae

$$\int_0^{+\infty} x^n e^{-\gamma x}\,dx = \frac{n!}{\gamma^{n+1}} \qquad \gamma>0$$

For a one-dimensional harmonic oscillator of mass M and angular frequency ω

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right) \qquad n = 0,1,2,\ldots$$

$$\hat{x} = \sqrt{\frac{\hbar}{2M\omega}}\left(\hat{a}+\hat{a}^\dagger\right), \qquad \hat{p} = -i\sqrt{\frac{M\omega\hbar}{2}}\left(\hat{a}-\hat{a}^\dagger\right)$$

$$\hat{a}^\dagger\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle, \qquad \hat{a}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle.$$

For a rigid rotator of moment of inertia I

$$E_l = \frac{\hbar^2}{2\mathrm{I}}\,l\left(l+1\right) \qquad l = 0,1,2,\ldots$$

The Laplacian in spherical coordinates is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \vartheta^2} + \cot\vartheta \frac{\partial}{\partial \vartheta}\right) + \frac{1}{r^2 \sin^2\vartheta}\frac{\partial^2}{\partial \varphi^2}\,.$$

For a spin $\frac{1}{2}$ system, the Cartesian components of the spin operator $\hat{\mathbf{S}}$ are

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

SECTION A

Answer SECTION A on the question paper in the space below each question. If you require more space, use an answer book. Answer as many parts of this section as you wish. Your total mark for this section will be capped at 40.

1.1) Using $\left[\hat{x}, \hat{p}_x\right] = i\hbar\hat{1}$, show that $\left[\hat{x}^2, \hat{p}_x\right] = 2i\hbar\hat{x}$.

[5 marks]

1.2) The Hamiltonian of a three-dimensional anisotropic harmonic oscillator with mass M has the form

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \frac{1}{2}M\left(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\right)$$

and can be expressed as a sum of three Hamiltonians H_x, H_y and H_z for one-dimensional harmonic oscillators. For the case $\omega_x = \omega_y = \frac{2}{3}\omega_z = \omega$, calculate the three lowest energy eigenvalues of $\hat{H}$ and show that their degeneracies are 1, 2 and 1.

[*7* marks]

1.3) For the two operators

$$\hat{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 7 & -3i \\ 0 & 3i & 5 \end{pmatrix} \quad \text{and} \quad \hat{B} = \begin{pmatrix} 0 & i & -3i \\ i & 0 & -i \\ -3i & -i & 0 \end{pmatrix}$$

calculate $\hat{A}^\dagger$ and $\hat{B}^\dagger$. Are $\hat{A}$ and $\hat{B}$ Hermitian?

[6 marks]

1.4) Define the parity operator $\hat{P}$ in one-dimension and demonstrate that $\hat{P}^2 = \hat{1}$. Find its eigenvalues.

[6 marks]

1.5) A one-dimensional infinite potential well of length L is described by the potential

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

The normalized eigenfunctions of a particle in the potential $V(x)$ are

$$\phi_n = \begin{cases} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & 0 \le x \le L \\ 0 & \text{elsewhere} \end{cases} \quad n = 1, 2, 3, \ldots$$

The bottom of the well is modified by the perturbation $\hat{H}_p = \begin{cases} V_0 & 0 \le x \le L/2 \\ 0 & \text{elsewhere} \end{cases}$,

where V_0 is a constant.

Show that the first order energy shift due to the perturbation is $\frac{V_0}{2}$ for all n.

[7 marks]

1.6) Find the two eigenvalues and the corresponding eigenstates of the spin operator

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

If a system is in the state $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, find the probabilities that a measurement of $\hat{S}_x$ yields each eigenvalue.

[*7* marks]

1.7) Consider a system of two non-identical spin $\frac{1}{2}$ particles with the Hamiltonian

$$\hat{H} = \frac{\varepsilon_1}{\hbar^2}\left(\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2\right)\cdot\hat{\mathbf{S}}_1 - \frac{\varepsilon_2}{\hbar^2}\left(\hat{S}_{1z} + \hat{S}_{2z}\right)^2$$

where ε_1 and ε_2 are constants with the dimension of energy and $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ are the spin operators for the two particles with z-components $\hat{S}_{1z}$ and $\hat{S}_{2z}$ respectively. Find the energy levels and their degeneracies for this system.

[8 marks]

1.8) Assuming that Hund's rules apply, derive an expression for the spectroscopic terms of the ground state of chlorine (Cl, atomic number Z=17) and magnesium (Mg, Z=12).

[6 marks]

1.9) Calculate the wavelength of the radiation absorbed by a CO molecule in a transition between the rotational level states l=0 and l=1. The equilibrium separation between the carbon (Z=6) and oxygen (Z=8) nuclei is $1.124\times10^{-10}\,\mathrm{m}$.

[8 marks]

SECTION B – Answer TWO questions

Answer SECTION B in an answer book.

2) Let the eigenstates and eigenvalues of the unperturbed Hamiltonian $\hat{H}_0$ be denoted by $|\phi_n\rangle$ with E_n^0 respectively. The second order energy shift due to the time-independent perturbation $\hat{H}_p$ which is added to $\hat{H}_0$ is:

$$\delta E_n^{(2)} = \sum_{k\neq n} \frac{\left|\left\langle \phi_k \left| \hat{H}_p \right| \phi_n \right\rangle\right|^2}{E_n^0 - E_k^0} .$$

The Hamiltonian of a one-dimensional harmonic oscillator of mass M and angular frequency ω is

$$\hat{H}_0 = \frac{\hat{p}^2}{2M} + \frac{1}{2} M \omega^2 \hat{x}^2 .$$

a) A small perturbation $\hat{H}_p = \lambda \hat{x}$ is now added to $\hat{H}_0$.

i) Show that, to first order in λ, the energy levels of the harmonic oscillator are not shifted.

[6 marks]

ii) Show that, to second order in λ, all the energy levels are shifted by

$$-\frac{\lambda^2}{2M\omega^2} .$$

[10 marks]

b) A different perturbation $\hat{H}'_p = \lambda \hat{x}^2$ is now added to $\hat{H}_0$.

i) Show that, to first order in λ, the energy shift of the n^{th} energy level is

$$\frac{\hbar\lambda}{M\omega}\left(n + \frac{1}{2}\right) \quad n = 0,1,2,\dots .$$

[7 marks]

ii) Show that the exact energy levels of the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}'_p$ are

$$\hbar\omega\sqrt{1 + \frac{2\lambda}{M\omega^2}}\left(n + \frac{1}{2}\right) \quad n = 0,1,2,\dots$$

and demonstrate that when $\lambda \ll M\omega^2$ the results obtained with first order perturbation theory are a good approximation of the exact energy levels of $\hat{H}$.

[7 marks]

3 a) Consider a Hamiltonian $\hat{H}$ with a discrete non-degenerate spectrum and ground state energy E_0; for an arbitrary normalized trial wavefunction $|\psi\rangle$ prove that

$$\langle\psi|\hat{H}|\psi\rangle \geq E_0 .$$

[8 marks]

b) A non-relativistic particle of mass M moves subject to a central potential

$$V(r) = -\frac{4\hbar^2}{3Ma^2}e^{-r/a}$$

where r is the distance from the origin and a is a positive constant. It occupies the ground state.

i) Consider a trial wavefunction proportional to $\exp\left(-\frac{\beta r}{2a}\right)$, where β is a positive parameter that can be varied, and normalize it.

[6 marks]

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

$$\frac{\hbar^2}{2M}\left(\frac{\beta}{2a}\right)^2 - \frac{4\hbar^2}{3Ma^2}\left(\frac{\beta}{\beta+1}\right)^3 .$$

[11 marks]

iii) Verify that the upper limit for the ground state energy in ii) has a minimum at $\beta = 1$ and hence estimate the ground state energy for the particle in the central potential $V(r)$.

[5 marks]

4) Let the eigenstates of the unperturbed Hamiltonian be denoted by $|\phi_k\rangle$ with eigenvalues $\hbar\omega_k$.

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

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

A spin $\frac{1}{2}$ system, which is subject to the static magnetic field in the z-direction $(0, \ \ 0, \ \ B_0)$, is described by the Hamiltonian $\hat{H}_0 = -\gamma B_0 \hat{S}_z$.

Initially, at $t_0 = 0$, the spin of the system is pointing in the negative z-direction.

a) At $t_0 = 0$ a rotating weak magnetic field in the xy-plane $(B_1 \cos\omega t, \ \ B_1 \sin\omega t, \ \ 0)$ is switched on. This gives rise to the time-dependent perturbation

$$\hat{V}(t) = -\gamma B_1 \left(\hat{S}_x \cos\omega t + \hat{S}_y \sin\omega t \right).$$

$\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ are the components of the spin operator $\hat{\mathbf{S}}$, a form for which can be found in the rubric.

i) Using first-order time dependent perturbation theory, show that the probability that at time t the spin points in the positive z-direction is

$$\frac{\gamma^2 B_1^{\,2}}{(\omega + \gamma B_0)^2} \sin^2 \frac{(\omega + \gamma B_0)t}{2}.$$

[14 marks]

ii) Evaluate this probability in the case of resonance (i.e. when $\hbar\omega$ is equal to the energy difference for the spin-up and spin-down eigenstates). Show that in this case, perturbation theory must break down for sufficiently large t, however weak B_1 is. How small should t be for perturbation theory to hold?

[6 marks]

b) If the magnetic field that is switched on at $t_0 = 0$ is $\left(B_1 e^{-\beta t}, \quad 0, \quad 0\right)$ where $\beta > 0$, giving rise to the time-dependent perturbation

$$\hat{V}'(t) = -\gamma B_1 \hat{S}_x e^{-\beta t} ,$$

show that, using first-order time-dependent perturbation theory, the probability that at long times ($t \to +\infty$) the spin points in the positive z-direction is

$$\frac{\gamma^2 B_1^{\ 2}}{4\left(\beta^2 + \gamma^2 B_0^{\ 2}\right)} .$$

[10 marks]