Candidate number:	
Desk number:	

King's College London

UNIVERSITY OF LONDON

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B.Sc. EXAMINATION

6CCP3221/CP3221 Spectroscopy and Quantum Mechanics

Examiner: Dr. C. Molteni

Summer 2011
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.

For examiners' use only:

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TURN OVER WHEN INSTRUCTED

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

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

$$\int_0^{+\infty} e^{-\gamma x^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{\gamma}} \qquad \gamma > 0$$

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

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

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

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

For a rigid rotator of moment of inertia $\mathcal{I}$

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

The Laplacian in spherical polar coordinates is

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

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

Let the eigenstates and eigenvalues of the unperturbed Hamiltonian $\hat{H}_0$ be denoted by $\left|\phi_n\right\rangle$ with $E_n^0 = \hbar\omega_n$ respectively.

- In non-degenerate time-independent perturbation theory, the second order energy shift due to the perturbation $\hat{H}_p$, which is added to $\hat{H}_0$, is:

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

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

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

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 the variational method, estimate the ground state energy of the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - V_0\delta(x),$$

knowing that the expectation value of $\hat{H}$ calculated with the trial wavefunction $Ae^{-\beta x^2}$ (where A is the normalization constant and β is a positive parameter that can be varied) is

$$\langle \hat{H} \rangle = \frac{\hbar^2\beta}{2m} - V_0\sqrt{\frac{2\beta}{\pi}}.$$

[5 marks]

1.2) A hydrogen atom is placed in a uniform electric field of magnitude E pointing in the z direction. This results in an additional term in the Hamiltonian equal to $\hat{H}_p = eE\hat{z}$, which can be treated as a perturbation if the field is weak. Show that the ground state energy of the hydrogen atom is not shifted by this perturbation to first order in the field.

[6 marks]

1.3) An electron in a uniform magnetic field in the z direction is described by the Hamiltonian $\hat{H}_0 = \frac{eB_z}{m_e}\hat{S}_z$. A weak magnetic field is turned on in the x direction resulting in the perturbation $\hat{H}_p = \frac{eB_x}{m_e}\hat{S}_x$, where $\hat{S}_x$ and $\hat{S}_z$ can be expressed by the matrices:

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

Using non-degenerate perturbation theory show that the second-order energy shifts to the two energy levels of $\hat{H}_0$ due to the perturbation $\hat{H}_p$ are $\pm\frac{\hbar}{4}\frac{eB_x^2}{m_e B_z}$.

[8 marks]

1.4) Define the particle exchange operator $\hat{P}_{12}$ for a two-particle system and show that $\hat{P}_{12}^2 = \hat{1}$, where $\hat{1}$ is the identity operator. Find its eigenvalues.

[6 marks]

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

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

Where ε is a constant 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]

1.6) Assuming that Hund's rules apply, derive an expression for the spectroscopic terms of the ground state of oxygen (O, atomic number Z=8) and sodium (Na, Z=11).

[6 marks]

1.7) The Hamiltonian of a hydrogen atom in a strong magnetic field $\mathbf{B} = \left(0, 0, B_z\right)$ pointing in the z-direction is

$$\hat{H} = -\frac{\hbar^2}{2m_\mathrm{e}}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} + \frac{\mu_B}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right)B_z ,$$

where $\hat{L}_z$ and $\hat{S}_z$ are the z-components of the orbital angular momentum operator and of the spin operator, respectively.

How many energy levels does the energy of the states characterized by quantum numbers $n = 2$, $l = 1$ split into, when the magnetic field is applied? Calculate the energy shifts of these levels with respect to the case of no magnetic field.

[7 marks]

1.8) The H_2 molecule consists of two protons separated by a distance of 0.75 Å. Calculate the energy needed to excite the molecule from its rotational ground state to its first rotational excited state.

[6 marks]

1.9) A particle of mass M, initially (t=0) in the ground state of a harmonic oscillator of angular frequency ω, is placed in a time-dependent perturbation described by

$$\hat{V}(t) = -V_0 \hat{x} e^{-\frac{t}{\tau}},$$

where V_0 is a constant.

Using first-order time-dependent perturbation theory, show that the probability of finding the particle after a long time ($t \to +\infty$) in the first excited state of the harmonic oscillator is

$$\frac{V_0^2}{2M\hbar\omega}\left(\omega^2 + \frac{1}{\tau^2}\right)^{-1}.$$

[8 marks]

SECTION B – Answer TWO questions

Answer SECTION B in an answer book.

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 eigenfunction of the corresponding Hamiltonian for the n^{th} 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,…

a) Find the exact energies and eigenfunctions 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:

$$\hat{H}_p(x,y)=\begin{cases}\lambda V_0 & 0\le x\le \dfrac{L}{2},\quad 0\le y\le \dfrac{L}{2}\\ 0 & \text{otherwise.}\end{cases}$$

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

[8 marks]

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

[15 marks]

3) Consider a one-dimensional harmonic oscillator of mass *M*, spring constant *k* and angular frequency $\omega = \sqrt{\frac{k}{M}}$. Its Hamiltonian is:

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

Suppose that the spring constant increases slightly, from k to $k(1+\lambda)$, where λ is a small positive number.

a) Write down the Hamiltonian $\hat{H}$ of the harmonic oscillator with the increased spring constant and express it as $\hat{H} = \hat{H}_0 + \hat{H}_p$, where $\hat{H}_p$ is a small perturbation proportional to λ.

[2 marks]

b) For each state $|n\rangle$ of the unperturbed harmonic oscillator, using non-degenerate time-independent perturbation theory, calculate:

i) the first order energy shift due to the perturbation $\hat{H}_p$;

[8 marks]

ii) the second order energy shift due to the perturbation $\hat{H}_p$;

[11 marks]

iii) write down the energy of the perturbed n^{th} state up to second order in λ.

[2 marks]

c) Calculate the exact eigenvalues of the Hamiltonian $\hat{H}$ of the harmonic oscillator with the increased spring constant, expand them as a power series in λ up to second order and compare the result with the energies obtained using perturbation theory in b).

[7 marks]

4 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) In spherical polar coordinates the Hamiltonian of a three-dimensional isotropic harmonic oscillator of mass M and angular frequency ω is

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 + \frac{1}{2}M\omega^2 r^2$$

i) Use the variational method with the trial wavefunction

$$\psi(r,\vartheta,\varphi) = Ae^{-\alpha r^2} ,$$

where A is a normalization constant to be determined and α (>0) is a parameter that can be varied, to show that an upper limit for the ground state energy of the three-dimensional harmonic oscillator as a function of α is:

$$\frac{3\hbar^2}{2M}\alpha + \frac{3M\omega^2}{8\alpha} .$$

[13 marks]

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

[5 marks]

iii) Find the exact ground state energy of the three-dimensional harmonic oscillator and compare it with the result obtained in ii) with the variational method.

[4 marks]