Candidate number:	
Desk number:	

King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

6CCP3221/CP3221 Spectroscopy and Quantum Mechanics

Examiner: Dr. C. Molteni

Summer 2010
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

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

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

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

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

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

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

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

The Laplacian in spherical coordinates is

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

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

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

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

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

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

SEE NEXT PAGE

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) A spin $\frac{1}{2}$ system, immersed in a magnetic field $\mathbf{B}$, is described by the Hamiltonian $\hat{H} = -\gamma \mathbf{B} \bullet \hat{\mathbf{S}}$, where $\hat{\mathbf{S}}$ is the spin operator whose Cartesian components are:

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

$\mathbf{B} = \left(B_0 \sin\vartheta, 0, B_0 \cos\vartheta\right)$ lies in the xz plane. What are the energy values that can be measured for this system?

[6 marks]

1.2) 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

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

Show that the perturbation $\hat{H}_p = \lambda V_0 \delta\left(x - \dfrac{L}{2}\right)$ shifts the energy level of the n^{th} excited state by $\dfrac{2\lambda V_0}{L}$ when n is odd, but does not shift the energy level of the n^{th} excited state when n is even.

[6 marks]

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

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

[8 marks]

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

[6 marks]

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

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

where ε is a constant having 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.

For this system, find the energy levels and their degeneracies.

[8 marks]

1.6) Assuming that Hund’s rules apply, derive an expression for the spectroscopic terms of the ground state of boron (B, atomic number Z=5) and nitrogen (N, Z=7).

[6 marks]

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

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

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 number $n = 2,\ l = 1$ split into, when the magnetic field is applied? Calculate the energy shifts of such levels with respect to the case of no magnetic field.

[7 marks]

1.8) Estimate the energy difference between the lowest and the first excited rotational state of the HCl molecule, knowing that the moment of inertia for this molecule is equal to 2.66×10^{-47} kg m^{2}.

[5 marks]

1.9) A one-dimensional harmonic oscillator is subject to the time-dependent perturbation $\hat{V}(t) = \lambda \hat{x}^2 f(t)$, where $f(t)$ is a function of time only. Using first-order time-dependent perturbation theory show that if the harmonic oscillator is initially in its n^{th} excited state $|n\rangle$, the only possible transitions are to the $(n \pm 2)^{\text{th}}$ excited states $|n \pm 2\rangle$.

[8 marks]

SECTION B – Answer TWO questions

Answer SECTION B in an answer book.

2) Consider a one-dimensional harmonic oscillator of mass M and angular frequency ω with Hamiltonian

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

a) A small perturbation $\hat{H}_p = \lambda\left(\hat{a}^2 + \hat{a}^{\dagger 2}\right)$, where $\hat{a}$ and $\hat{a}^\dagger$ are the annihilation and creation operators, is added to $\hat{H}_0$. Using time-independent perturbation theory show that:

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

[6 marks]

ii) To second order in λ, the energy level of n^{th} excited state is shifted by

$$-\frac{\lambda^2\left(2n+1\right)}{\hbar\omega} .$$

[9 marks]

b) Initially the harmonic oscillator (described by the Hamiltonian $\hat{H}_0$) is in its ground state. A small constant force F is then applied for a time interval τ .

i) Evaluate the potential energy operator corresponding to this force.

[2 marks]

ii) Using first-order time-dependent perturbation theory show that the probability to find the harmonic oscillator in its first excited state after a time interval τ is

$$\frac{2F^2}{M\hbar\omega^3}\sin^2\left(\frac{\omega\tau}{2}\right) .$$

[9 marks]

iii) What values of τ give the greatest chance that the oscillator will be found in its first excited state?

[4 marks]

3) A system, with an unperturbed Hamiltonian $\hat{H}_0$, is subject to a perturbation $\hat{H}_p$ with

$$\hat{H}_0 = \varepsilon \begin{pmatrix} 15 & 0 & 0 & 0 \\ 0 & 3 & 0 & 0 \\ 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}, \qquad \hat{H}_p = \frac{\varepsilon}{100} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

The total Hamiltonian is $\hat{H} = \hat{H}_0 + \hat{H}_p$.

a) Find the exact eigenvalues and the corresponding eigenstates of the unperturbed Hamiltonian $\hat{H}_0$ and specify their degeneracies.

[4 marks]

b) Using non-degenerate and/or degenerate perturbation theory as appropriate, show that two of the energy levels of $\hat{H}_0$ are not shifted by the perturbation $\hat{H}_p$, while the other two are shifted by $\pm\frac{\varepsilon}{100}$. Evaluate the energy levels to first order perturbation theory.

[19 marks]

c) Calculate the exact eigenvalues of $\hat{H}$ and compare them with the energy levels evaluated in b).

[7 marks]

4) Consider the Hamiltonian of the hydrogen atom in spherical polar coordinates.

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

Its exact ground state energy is $E_0 = -\frac{e^2}{8\pi\varepsilon_0 a_0}$, where $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$ is the Bohr radius.

a)

i) Use the variational method with the trial wavefunction

$$\psi(r,\vartheta,\varphi) = \begin{cases} A\left(1-\frac{r}{\alpha}\right) & 0 \le r \le \alpha \\ 0 & r > \alpha \end{cases} ,$$

where A is a normalization constant to be determined and α is a parameter that can be varied, to show that an upper limit for the ground state energy of the hydrogen atom as a function of α is:

$$5\left(\frac{\hbar^2}{m_e\alpha^2} - \frac{e^2}{8\pi\varepsilon_0\alpha}\right).$$

[11 marks]

ii) Use the variational method to estimate the ground state energy. Compare the result with the exact ground state energy and comment on the outcome.

[4 marks]

b)

i) Use the variational method with the trial wavefunction

$$\phi(r,\vartheta,\varphi) = Be^{-\beta r} ,$$

where B is a normalization constant to be determined and β is a parameter that can be varied $(\beta > 0)$, to show that an upper limit for the ground state energy of the hydrogen atom as a function of β is:

$$\frac{\hbar^2\beta^2}{2m_e} - \frac{e^2\beta}{4\pi\varepsilon_0} .$$

[11 marks]

ii) Use the variational method to estimate the ground state energy. Compare the result with the exact ground state energy and comment on the outcome.

[4 marks]