King's College London

UNIVERSITY OF LONDON

B.Sc. EXAMINATION

CP3221 Spectroscopy and Quantum Mechanics

Examiner: Dr. C. MOLTENI

Summer 2008

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.

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

DO NOT REMOVE THIS EXAM PAPER FROM THE EXAMINATION ROOM

TURN OVER WHEN INSTRUCTED

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}

Useful expressions

$$\int_{-\infty}^{+\infty} x^2 e^{-\lambda x^2} = \frac{1}{2\lambda}\left(\frac{\pi}{\lambda}\right)^{1/2}$$

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

$$\int_{-\infty}^{+\infty} e^{-\left(ax^2+bx+c\right)} dx = \sqrt{\frac{\pi}{a}} e^{\left(b^2-4ac\right)/4a}$$

$$\sin\vartheta \sin\varphi = \frac{1}{2}\left(\cos\left(\vartheta-\varphi\right)-\cos\left(\vartheta+\varphi\right)\right)$$

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

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

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

SECTION A – Answer all parts of this section

1.1) Prove that, for any pair of linear operators $\hat{A}$ and $\hat{B}$, $\left[\hat{A},\hat{B}^2\right]=\left[\hat{A},\hat{B}\right]\hat{B}+\hat{B}\left[\hat{A},\hat{B}\right]$.
Using $\left[\hat{x},\hat{p}_x\right]=i\hbar\hat{1}$, show that $\left[\hat{x},\hat{p}_x^2\right]=2i\hbar\hat{p}_x$.

[5 marks]

1.2) Calculate the expectation value and the uncertainty of the position operator $\hat{x}$ for a particle in a state described by the normalized wavefunction

$$\psi(x)=\left(\frac{a}{\pi}\right)^{1/4}e^{-ax^2/2} \qquad -\infty < x < +\infty$$

where a is a real positive constant.

[6 marks]

1.3) Show that, for a harmonic oscillator of mass m and angular frequency ω with eigenstates $|n\rangle$,

$$\langle n|\hat{x}^2|n\rangle=\frac{\hbar}{2m\omega}(2n+1)\,.$$

[8 marks]

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

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

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

[8 marks]

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

$$\hat{H}=\frac{\varepsilon_0}{\hbar^2}\left(\hat{S}_1+\hat{S}_2\right)^2+\frac{\varepsilon_0}{\hbar^2}\left(\hat{S}_{1z}+\hat{S}_{2z}\right)^2$$

where ε_0 is a constant with the dimensions of energy and $\hat{S}_1$ and $\hat{S}_2$ 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.

[7 marks]

1.6) Assuming Hund's rules apply, derive an expression for the spectroscopic terms of the ground state of fluorine (F, atomic number Z=9) and sodium (Na, Z=11).

[6 marks]

SECTION B – Answer TWO questions

2)

a) Consider a Hamiltonian $\hat{H}$ with a discrete non-degenerate spectrum and ground state energy E_0, and an arbitrary trial wavefunction $|\psi\rangle$, chosen to be normalized. Prove that

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

[8 marks]

b) A particle of mass m is moving in a one-dimensional triangular quantum well described by the potential energy

$$V(x) = \begin{cases} +\infty & x < 0 \\ V_0 x & x \geq 0 \end{cases}$$

i) For $x \geq 0$, use a trial wavefunction proportional to $x\exp(-\beta x)$, where β is a positive parameter that can be varied. Explain why this trial wavefunction is a plausible choice and normalize it.

[6 marks]

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

$$\frac{\hbar^2}{2m}\beta^2 + \frac{3V_0}{2\beta}$$

[10 marks]

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

[6 marks]

3) A two-dimensional isotropic harmonic oscillator of mass m and angular frequency ω has the Hamiltonian

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

a) Show that the energy levels are given by

$$E_{n_x n_y} = \hbar\omega\left(n_x + n_y + 1\right); \quad n_x = 0,1,2,... \ ; n_y = 0,1,2,...$$

Find the energies and eigenstates for the ground and first excited states (in terms of the eigenstates $|n\rangle \quad n = 0,1,2,...$ of the one-dimensional harmonic oscillator). Show that the ground state is non-degenerate and that the first excited state is doubly-degenerate.

[7 marks]

b) Now add the following perturbation to the two-dimensional harmonic oscillator Hamiltonian:

$$\hat{H}_p = 2\lambda\hat{x}\hat{y}.$$

i) Using first-order non-degenerate perturbation theory, show that the energy shift in the ground state due to $\hat{H}_p$ is zero.

[8 marks]

ii) Calculate the matrix elements of $\hat{H}_p$ between the eigenstates corresponding to the first excited state level. Hence, using first-order degenerate perturbation theory, show that the energy shifts in the first excited state due to $\hat{H}_p$ are equal to $\pm\frac{\hbar\lambda}{m\omega}$.

[15 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 $\lambda\hat{V}_1(t)$ from a state $|\phi_k\rangle$ to a state $|\phi_l\rangle$ is:

$$c_{k\to l}(t) = \frac{1}{i\hbar}\int_{t_0}^{t}\left\langle \phi_l \left| \lambda\hat{V}_1(\tilde{t}) \right| \phi_k \right\rangle e^{i(\omega_l-\omega_k)\tilde{t}}\, d\tilde{t}\ .$$

Consider a particle of mass m in a one-dimensional quantum well described by the potential energy

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

The energy and the normalized eigenstate for the n^{th} excited state of the corresponding Hamiltonian are respectively

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad \text{and} \quad \phi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

where n=1,2,3,… and $0 \le x \le L$.

In the range $0 \le x \le L$ the system is perturbed by the additional time-dependent term

$$\lambda\hat{V}_1(x,t) = \lambda\left(x - \frac{L}{2}\right)e^{-t^2/\tau^2}\ .$$

a) Using first-order time-dependent perturbation theory show that the probability that a particle in the ground state (n=1) at $t=-\infty$ makes a transition to the first excited state (n=2) at $t=+\infty$ is equal to

$$\frac{256\lambda^2L^2\tau^2}{81\hbar^2\pi^3}\exp\left(-\frac{9\pi^4\hbar^2\tau^2}{8m^2L^4}\right)\ .$$

[18 marks]

b) Show that the transition probability from the ground state to the second excited state (n=3) is zero.

[8 marks]

c) What happens to the transition probability calculated in a) for a very slowly varying perturbation (i.e. $\tau \to +\infty$)?

[4 marks]