THE UNIVERSITY OF WESTERN ONTARIO

DEPARTMENT OF CHEMISTRY

CHEMISTRY 474B

MIDTERM

TUESDAY, MARCH 6, 2007
7:00 - 9:00 P.M.

There are 5 questions on 3 pages. Please answer all parts of all questions in the booklet provided. Show all your work. The value of each question is given in square brackets. Total mark value per question is given below. Useful formulae can be found on page 4.

Question 1	20
Question 2	20
Question 3	20
Question 4	20
Question 5	20
Total	**100**

1.) Consider a system which is described by the state $|\psi\rangle = \sqrt{\frac{3}{8}}Y_{1,1} + \sqrt{\frac{1}{8}}Y_{1,0} + AY_{1,-1}$,
where A is a real constant, and $Y_{\ell,m}$ is a spherical harmonic (often noted as $|\ell, m_\ell>$).

(a) Show that A = $\sqrt{\frac{1}{2}}$ if $|\psi\rangle$ is normalized.
(b) Calculate the expectation values of L_z and L^2 in the state $|\psi\rangle$.
(c) Find the probability associated with a measurement that gives zero for the z-component of the angular momentum.

2.) a) Do the following matrices commute?

$$\tilde{A} = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \qquad \tilde{B} = \begin{pmatrix} 2 & 1 & 1 \\ 1 & 0 & -1 \\ 1 & -1 & 2 \end{pmatrix}$$

b) Are any of the following matrices Hermitian? If so, which ones?

$$\tilde{A} = \begin{pmatrix} 9 & 1 \\ 3 & 4 \end{pmatrix} \qquad \tilde{B} = \begin{pmatrix} 9i & 4+4i \\ -4+4i & 7i \end{pmatrix} \qquad \tilde{C} = \begin{pmatrix} 9 & 4-4i \\ 4+4i & 7 \end{pmatrix}$$

c) Find the eigenvalues and normalized eigenvectors of the following matrix:

$$\tilde{A} = \begin{pmatrix} 3 & 4 \\ 4 & -3 \end{pmatrix}$$

3.) Consider the following Hamiltonian $\tilde{H}$ for the first four levels of a perturbed harmonic oscillator:

$$\tilde{H} = \tilde{H}^{(0)} + \tilde{H}^{(1)} = \hbar\omega_o \begin{pmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & \frac{3}{2} & 0 & 0 \\ 0 & 0 & \frac{5}{2} & 0 \\ 0 & 0 & 0 & \frac{7}{2} \end{pmatrix} + \varepsilon\hbar\omega_0 \begin{pmatrix} 1 & 0 & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 0 \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

where $\varepsilon << 1$ and ω_o is the characteristic frequency of the oscillator.

Use time independent non degenerate perturbation theory to calculate the energy of the third level to second order, and the first order correction to the third wave function.

4.) Consider the following Hamiltonian matrix:

$$\tilde{H} = \tilde{H}^{(0)} + \tilde{H}^{(1)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + \begin{pmatrix} 0 & \varepsilon & 0 \\ \varepsilon & 0 & \varepsilon \\ 0 & \varepsilon & 0 \end{pmatrix}$$

a) Use degenerate perturbation theory to find the first order corrections to the energy for any degenerate levels in this 3 level system.

b) Find the "correct" zeroth order eigenfunctions corresponding to the first order energies deduced in part a)

c) Find the second order energy corrections for the degenerate levels.

5.) In class, the following expression was derived for the transition probability for absorption, $P_q(t)$, using time-dependent perturbation theory for an oscillating light field interacting with the electric dipole moment of the system:

$$P_q(t) = \frac{4\left|H_{jq}^{(1)} H_{qj}^{(1)}\right|}{\hbar^2} \cdot \frac{\sin^2\left(\frac{1}{2}(\omega_{qj} - \omega)t\right)}{(\omega_{qj} - \omega)^2}$$

Briefly define all the symbols in this result, and explain how this expression incorporates features that are important to spectroscopy.

Useful Formulae

$$\hat{L}^2 \mid \ell, m_\ell >= \ell(\ell+1)\hbar^2 \mid \ell, m_\ell > \qquad \hat{L}_z \mid \ell, m_\ell >= m_\ell \hbar \mid \ell, m_\ell >$$

$$ax^2 + bx + c = 0; \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad \left|\tilde{A} - \lambda\tilde{I}\right| = 0; \quad \tilde{I} = \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & 0 \\ 0 & 0 & \cdots & 1 \end{pmatrix}$$

$$\hat{H}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

$$E_q^{(1)} =< \psi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_q^{(0)} >$$

$$E_q^{(2)} = -\sum_{k \neq q} \frac{\mid H_{kq}^{(1`)} \mid^2}{E_k^{(0)} - E_q^{(0)}}$$

$$\psi_q^{(1)} = \sum_{k \neq q} a_k \psi_k^{(0)} \text{ where } \mathrm{a}_k = \frac{-H_{kq}^{(1)}}{E_k^{(0)} - E_q^{(0)}}$$

$$\left| H_{qj}^{(1)} - E_j^{(1)}\delta_{qj} \right| = 0$$

$$\sum_{i=1}^{g} \left(H_{qj}^{(1)} - E_j^{(1)}\delta_{ij} \right) c_j = 0 \qquad q = 1, 2, \ldots, g$$

$$E_q^{(2)} = -\sum_{k \neq q} \frac{\left|< \psi_k^{(0)} \mid H^{(1)} \mid \phi_q^{(0)} >\right|^2}{E_k^{(0)} - E_q^{(0)}}$$