Problem Set 12
On Applications of Perturbation Theory

1. The molecular rotation eigenfunctions of a rigid linear molecule are the spherical harmonic functions $Y_{J,M}(\theta, \phi)$ and the Hamiltonian is $\mathcal{H} = (1/2I)\mathbf{J}^2$ where I is the moment of inertia. We can examine the effects of an external static electric field **E** on the rotational energy levels of linear molecules with electric dipole moment μ, the perturbation is

$$h = -\mu \mathbf{E} \cos\theta.$$

(a) Set up the matrix representation of operator h (in the zeroth order functions) in terms of μ **E**.

Recall that in the hydrogen atom angular functions, it had been found that the following relation holds:

$$\cos\theta\, Y_{\ell m} = \{(\ell^2 - m^2)/[(2\ell-1)(2\ell+1)]\}^{1/2}\, Y_{\ell-1, m} + \{[(\ell+1)^2 - m^2]/[(2\ell+1)(2\ell+3)]\}^{1/2}\, Y_{\ell+1, m}$$

For this problem, we use different letters (J,M) for the angular momentum quantum numbers since the physical problem is that of a rigid rotor

$$\cos\theta \cdot Y_{J,M}(\theta, \phi) = \{(J^2-M^2)/[(2J-1)(2J+1)]\}^{1/2} \cdot Y_{J-1,M}(\theta, \phi) + \{[(J+1)^2-M^2)]/[(2J+1)(2J+3)]\}^{1/2} \cdot Y_{J+1,M}(\theta, \phi).$$

(b) Determine the ENERGY correct to second order for the lowest two energy levels in terms of μ **E**.

(c) Determine the wavefunction correct to first order for the lowest energy level.

(d) Transitions between rotational levels of a linear molecule can be observed in the microwave region of the spectrum, and for the light polarized parallel to the static electric field, the intensities are related to

$$\left| \int_0^{2\pi}\int_0^{\pi} Y_{J,M}(\theta, \phi)\, \mu \cos\theta\, Y_{J',M'}(\theta, \phi) \sin\theta\, d\theta\, d\phi \right|^2.$$

Draw the energy levels and the rotational transitions for a linear molecule at zero external field, and in the presence of a static external electric field **E** .

Typical magnitudes: For HCN molecule ($\hbar^2/2I$)= 44 315.99 MHz and for **E** = 3000 volts/cm, μ **E** = 4500 MHz

(e) If **E** is known accurately, show explicitly how the electric dipole moment of the molecule is determined from the spectrum.

This is known as the STARK EFFECT.

2. The Zeeman effect on the spectrum of benzene can be treated approximately by considering the case of a single electron on a ring. The ring is in the xy plane and in polar coordinates the Hamiltonian is

$$\mathcal{H}_1 = (-\hbar^2/2m_eR^2)\, d^2/d\phi^2.$$

(a) What are the eigenfunctions of $\mathcal{H}_1$?

(b) What are the eigenvalues?

(c) The electron on a ring is subjected to a uniform magnetic field B_z perpendicular to the plane of the ring. Using the classical expression for the interaction of a particle of charge -e and mass m_e with a magnetic field, the new Hamiltonian is

$$\mathcal{H}_2 = (-\hbar^2/2m_eR^2)\, d^2/d\phi^2 + (\mu_B/\hbar)\, L_zB_z + (e^2B_z^2/8m_ec^2)(x^2+y^2)$$

where μ_B is a constant called the Bohr magneton. Does $\mathcal{H}_2$ commute with $\mathcal{H}_1$? Show this. (Remember the function which describes a circle!)

(d) What are the eigenfunctions of $\mathcal{H}_2$? What are the eigenvalues of $\mathcal{H}_2$?

(e) Draw the energy level diagram without and with the magnetic field.

(f) Use the non-interacting-six-electrons-on-a-ring model for benzene pi electrons. Impose the constraint of assigning no more than 2 electrons to a given one-electron state. What is the ground state energy of the 6 electrons without the field? What is the ground state energy with the magnetic field?

(g) The magnetic susceptibility of a molecule is the second derivative of the energy,

$$(-\partial^2E/\partial B_z^2) = \chi_{zz}$$

Given what you have found in parts (a) through (f) of this problem, use the non-interacting-electrons-on-a-ring model to calculate the ring current contribution to the magnetic susceptibility of benzene.

3. The matrix representation of x in the basis set of eigenfunctions for a particle in an infinite one-dimensional potential well (i.e., a particle constrained to move on a line from x = 0 to x = a), $\Psi_n(x) = (2/a)^{1/2} \sin\{(n\pi/a)x\}$ is given by:

$$x_{nn} = a/2 \qquad x_{mn} = (4a/\pi^2)mn\{(-1)^{m-n} - 1\}\{m^2 - n^2\}^{-2} \text{ for } m \neq n$$

Some of these terms are shown in the matrix below:

$$
x = -8a/\pi^2 \left|\begin{array}{cccccccc}
\text{////////} & 2/9 & 0 & 4/225 & 0 & 6/1225 & 0 & \ldots \\
2/9 & \text{////////} & 6/25 & 0 & 10/441 & 0 & 14/2025 & \ldots \\
0 & 6/25 & \text{////////} & 12/49 & 0 & 18/729 & 0 & \ldots \\
4/225 & 0 & 12/49 & \text{////////} & 20/81 & 0 & 28/1089 & \ldots \\
0 & 10/441 & 0 & 20/81 & \text{////////} & 30/121 & 0 & \ldots \\
6/1225 & 0 & 18/729 & 0 & 30/121 & \text{////////} & 42/169 & \ldots \\
0 & 14/2025 & 0 & 28/1089 & 0 & 42/169 & \text{////////} & \ldots \\
8/3969 & 0 & 24/3025 & 0 & 40/1521 & 0 & 56/225 & \ldots \\
: & : & : & : & : & : & : & \\
: & : & : & : & : & : & : &
\end{array}\right|
$$

Consider a particle of charge q and mass m constrained to move on a line from x = 0 to x = a. Place this system in a uniform electric field along the x direction, that is, add a term

$$h = -q \mathbf{E} x$$

to the original Hamiltonian. Calculate the energy of the perturbed states $\Psi_n(x)$, correct to second order for the two lowest levels. This simple model can be applied to the system of a linear polyene in an electric field.