5.74 Introductory Quantum Mechanics II
Spring 2009

5.74, Problem Set #2
Spring 2009
Due Date: March 3, 2009

1. Magnetic Dipole and Electric Quadrupole Transitions

In the light-matter interaction Hamiltonian

$$V(t) = -\sum_i \frac{q_i}{m_i} \bar{A} \cdot \bar{p}_i$$

$$\bar{A} = A_0 \hat{\varepsilon} \exp\left[-i\left(\bar{k} \cdot \bar{r} - \omega t\right)\right] + c.c.$$

the leading term in the long wavelength expansion

$$e^{i\bar{k} \cdot \bar{r}} = 1 + i\bar{k} \cdot \bar{r} + \cdots$$

leads to the electric dipole transitions. The second term leads to magnetic dipole and electric quadrupole transitions, which we will describe here. We can use the identity

$$\left(\hat{\varepsilon} \cdot \bar{p}\right)\left(\bar{k} \cdot \bar{r}\right) = \hat{\varepsilon} \cdot \left(\overline{pr}\right) \cdot \bar{k}$$

$$= \frac{1}{2} \hat{\varepsilon} \left(\overline{pr} - \overline{rp}\right) \bar{k} + \frac{1}{2} \hat{\varepsilon} \left(\overline{pr} + \overline{rp}\right) \bar{k}$$

to separate $V(t)$ into two distinct light-matter intereaction terms where the first gives rise to magnetic dipole transitions, and the second leads to electric quadrupole transitions. For the notation above, $\overline{pr}$ represents an outer product (tensor product $\bar{p} : \bar{r}$), so that

$$\hat{\varepsilon} \cdot \left(\overline{pr}\right) \cdot \bar{k} = \begin{pmatrix} \varepsilon_x & \varepsilon_y & \varepsilon_z \end{pmatrix} \begin{pmatrix} p_x r_x & p_x r_y & p_x r_z \\ p_y r_x & p_y r_y & p_y r_z \\ p_z r_x & p_z r_y & p_z r_z \end{pmatrix} \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}$$

This expression is meant to imply that the component of r that lies along k can influence the magnitude of p along ε. Alternatively this term could be written $\sum_{a,b=x,y,z} \varepsilon_a \left(p_a r_b\right) k_b$.

a) From the first term, express the magnetic dipole interaction in terms of the magnetic field $\bar{B}$ and the orbital angular momentum $\bar{L}$. What is the form of the magnetic dipole moment?

   A useful vector identity is $\left(\mathbf{A} \times \mathbf{B}\right) \cdot \left(\mathbf{C} \times \mathbf{D}\right) = \left(\mathbf{A} \cdot \mathbf{C}\right)\left(\mathbf{B} \cdot \mathbf{D}\right) - \left(\mathbf{A} \cdot \mathbf{D}\right)\left(\mathbf{B} \cdot \mathbf{C}\right)$

b) From the second term, derive the matrix elements for electric quadrupole transitions in analogy to the electric dipole moment, and show that it is a tensor quantity.

2. **The infrared rotational-vibrational spectrum of a diatomic**

Let's study the correlation function for the rotational-vibrational infrared absorption spectrum of a heteronuclear diatomic molecule. We are considering the transitions induced by infrared light that is resonant with a vibrational transition with frequency much greater than kT, and the frequency of the infrared light is much higher frequency than the splitting between rotational levels. We will use the harmonic oscillator and rigid rotor Hamiltonians to describe the vibrational and rotational degrees of freedom:

$$H_0 = H_{vib} + H_{rot}$$

$$H_{vib} = \frac{p^2}{2M_R} + \frac{1}{2}kq^2 = \hbar\Omega_0\left(n + \frac{1}{2}\right)$$

$$H_{rot} = \frac{L^2}{2I} \qquad\qquad I = M_R R^2$$

Here where M_R is the reduced mass and q is the vibrational coordinate. I is the moment of inertia, which is related to the rotational constant by $\bar{B} = \hbar/4\pi Ic$. So, the state of the system will be described by three quantum numbers $|n\,J\,M\rangle$.

The diatomic will interact with the light through the transition dipole moment. Since we assume that there are no interactions between the vibrational and rotational degrees of freedom, we will also partition the dipole operator into two parts:

$$\bar{\mu} = \hat{\mu}\,m$$

where $\hat{\mu}$ is a unit vector oriented along the transition moment (and along the vibrational coordinate in this case), and m is the magnitude of the dipole moment, which we take to be a weak function of the nuclear coordinate:

$$m = m_0 + \left(\frac{\partial m}{\partial q}\right)_{q_0} q$$
$$= m_0 + m_1 q$$

m_0 is the magnitude of the permanent dipole moment and m_1 is the amplitude of the transition dipole moment.

For the following, the system will interact with an electric field oriented along the $\hat{\varepsilon} = \hat{z}$ axis of the laboratory. Remember that in describing the probability of occupying an initial state, we need to consider both probability of occupying the initial state at temperature T and the probability of having a particular orientation in the laboratory frame. The initial state of the system will always be isotropically distributed, i.e. equal probability of finding a dipole oriented in any direction.

a) Evaluate the dipole matrix element $\langle k | \hat{\varepsilon} \cdot \bar{\mu} | \ell \rangle$ for the interactions between an initial state $| \ell \rangle = | n\, J\, M \rangle$ and a final state $| k \rangle = | n'\, J'\, M' \rangle$ using the separation of orientational and vibrational variables. Calculate this only to the leading order expansion coefficient for m.

b) Evaluate the correlation function $\langle \bar{\mu}(t)\bar{\mu}(0) \rangle$ for a gas phase ensemble of molecules at pressures low enough to neglect interactions between molecules.

c) Plot the correlation function for temperatures such that $\bar{B}/kT \gg 1$, $\bar{B} = kT$, and $\bar{B}/kT \ll 1$ (but neglect temperatures high enough that you need to consider $n=2$). Be sure to point out the important features of the time-dependent behavior. You will probably want to plot the rotational, vibrational and combined contributions separately. For the purpose of plotting results, you can use $\Omega_0 = 2000$ cm^{-1} and $\bar{B} = 5$ cm^{-1}.

d) Calculate the analytical form of the spectrum corresponding to the correlation functions in (b) and plot the lineshapes. Point out how the frequency resolved features in the spectrum were manifested in the time-dependent behavior in (b).

3. Numerical calculation of correlation function from a trajectory

The file **cf.dat** on the 5.74 web site contains a trajectory of instantaneous transition frequencies $\omega_i(t)$ for the vibration of a molecule in a fluctuating environment. The file is a set of roughly 32000 consecutive frequencies in cm^{-1} for points separated by 10 femtoseconds (10×10^{-15} sec). We will calculate the correlation function using the time-averaging expression for a single molecule valid for an ergodic system.

a) Express the integral version of the time-correlation function $C(t) = \overline{\delta\omega(t)\delta\omega(0)}$ as an explicit summation over all pairs of points for a finite discrete data set.

b) Calculate $\overline{\omega_0}$ and plot the trajectory $\delta\omega(t)$.

c) Plot the correlation function for the frequency fluctuations using the expression you found in (a). What is the correlation time τ_c for these fluctuations? How does this value compare to an exponential fit?

d) Make a histogram for occurrences of $\delta\omega$ and compare to a Gaussian distribution with a standard deviation $\sqrt{C(0)}$.