Chem 542

Homework for Part 5: Two-level systems

1. Consider 2 dipoles, one with a transition frequency on-resonance with the applied field at ω, the other off resonance by $\Delta\omega$. Write down in terms of the Bloch equation, and sketch in a "u,v,w" density matrix figure, how a $\pi/2$ pulse followed by an evolution period t_1, followed by a π pulse leads to a maximum output signal at t_1 after the second pulse. How do homogeneous and inhomogeneous line broadening affect the intensity of the output signal?

2. N two-level systems (TLS) with total transition dipole operator

$$\hat{P} = \begin{pmatrix} 0 & N\mu \\ N\mu & 0 \end{pmatrix}$$

have just been excited by a $\pi/2$ pulse, so that now u=0, v=-1, w=0. To find out how P decays with time after the pulse, solve the following:

a. Write down the Bloch equations letting $T_1=T_2=\tau$, $\omega = \omega_{10}$ (on resonance), E=R=0 (free propagation after the pulse) and choosing $w_{eq} = -1$ (T = 0 K).

b. Solve these Bloch equations for v(t) and w(t) using the above initial conditions for v and w (u should be zero always). What are the values of $v(\infty)$ and $w(\infty)$ after the TLS have fully relaxed?

c. Transform u,v,w back to s_1, s_2, s_3 using

$$\begin{pmatrix} s_1 \\ s_2 \\ s_3 \end{pmatrix} = \begin{pmatrix} \cos\omega t & -\sin\omega t & 0 \\ \sin\omega t & \cos\omega t & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix}.$$

d. Using your s_i from c., solve the three equations which we derived in lecture,

$$s_1 = c_0 c_1^* + c_0^* c_1$$
$$s_2 = -i(c_0 c_1^* - c_0^* c_1)$$
$$s_3 = |c_1|^2 - |c_0|^2$$

for $|c_1|^2$, $|c_0|^2$, and $c_0 c_1^*$. (Hint: $\mathrm{Tr}(\rho) = |c_1|^2 + |c_0|^2 = 1$ always.) Write down the 2 by 2 density matrix $\rho(t)$.

e. Calculate the expectation value of P by evaluating the appropriate matrix product and trace. The result is the time dependent polarization decay of the exited TLS, also known as the 'free induction decay.' Plot it against time. (The electromagnetic field radiated by the TLS is generated by the polarization P by the usual wave equation, and looks very similar to this plot also.)

3. The spontaneous emission rate or Einstein A-coefficient (derived in section 10 of the notes) is:

$$\Gamma_{sp} = \frac{4\omega^3}{3\hbar c^3} |\vec{\mu}_{fi}|^2 = \frac{1}{\tau_{sp}} = \mathrm{A} \ \ (\text{in sec}^{-1}). \qquad [1]$$

The absorption rate for a transition by a narrow-bandwidth laser field is related to laser intensity by,

$$\Gamma_{abs}(\omega) = \frac{\pi^2 c^2}{\omega^3 \hbar \tau_{sp}} I(\omega) \ \ (\text{in sec}^{-1}), \qquad [2]$$

where I(ω) is the laser intensity per unit frequency, in J/(m^2 s Hz) or erg/(cm^2 s Hz).

This can be used to derive Planck's black-body radiation law for the energy density u in a cavity of temperature T, without doing heavy-duty statistical mechanics:

$$u(\omega,T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1},$$

Here $\hbar$ is the constant first introduced by Planck in this very equation as an arbitrary fitting factor. <u>You'll find the information at the end of ch. 11 helpful when working through this</u>.

a. How are intensity I(ω) and energy density u (ω) (J/[m^3 Hz] or erg/[cm^2 Hz]) related by the propagation velocity c? Given $\Gamma_{abs}(\omega) = Bu(\omega)$ defines the Einstein B coefficient, derive the Einstein B-coefficient.

b. Imagine a cavity cooled near zero degrees Kelvin, filled with molecules M. In that case, [M*]/[M] ≈ 0 of course. If we shine in a laser beam of energy density u (ω) resonant with the molecules, the molecules will start absorbing, as well as spontaneously and stimulated emitting. Write down the rate equation for d[M]*/dt which holds before equilibrium is reached due to these three processes, in terms of [M], A, B and u.

c. When steady-state is reached, u (ω) is the same for the cavity as for the laser, and the molecular populations obey [M*]/[M] = exp[-ΔE/kT], where T is the temperature to which the laser has heated the cavity. What is d[M*]/dt at steady-state? Use this and your result from b. to show that at steady-state,

$$\frac{[M^*]}{[M]} = \frac{Bu}{\Gamma_{sp} + Bu} = e^{-\hbar\omega/kT}.$$

d. Rearrange this to derive Planck's black body radiation law shown above.

e. Based on your result in c., can an intense laser field induce a <u>static</u> population inversion where [M*] > [M]? What is the highest ratio [M*]/[M] possible? Give an example of a device that proves that this does not hold for <u>dynamical</u> population inversions.