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5.74 Introductory Quantum Mechanics II  
Spring 2009

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**5.74, Problem Set #5**  
**Spring 2009**  
**Due Date: April 6, 2009, 12pm**

**1. Density Matrix Description of the Linear Response Function**

In problem set 2 you showed that the equation of motion for the density matrix in the interaction picture is  $\frac{\partial \rho_I}{\partial t} = -\frac{i}{\hbar} [V_I, \rho_I]$ , where the density matrix in the interaction picture is defined as  $\rho_I = U_0^\dagger \rho_S U_0$ .

- a) How do you express the expectation value of the operator  $A$  in terms of  $\rho_I$ ?
- b) The time development of  $\rho_I$  can be obtained by integrating the equation of motion. Use the first-order solution to the differential equation for  $\rho_I$  above to obtain a density matrix expression for the linear response function.
- c) Explicitly evaluate the expression in (b) for the electric dipole interaction of a field with a two level system

$$H_0 = |a\rangle \epsilon_a \langle a| + |b\rangle \epsilon_b \langle b|$$

in which the dipole operator couples the two states:

$$\mu = |a\rangle \mu_{ab} \langle b| + |b\rangle \mu_{ba} \langle a|.$$

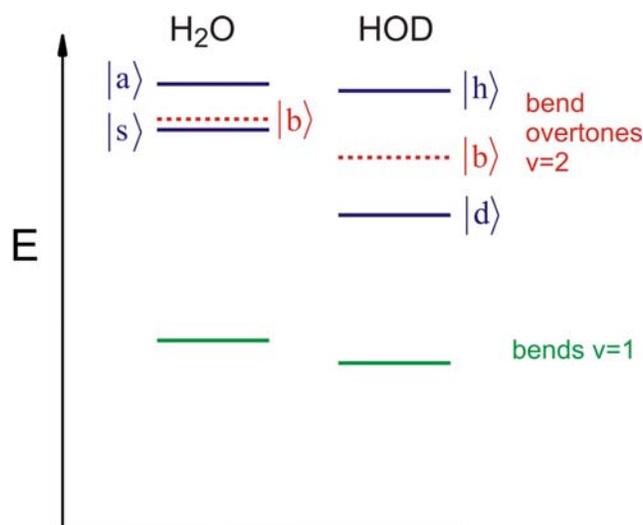
What is the form of  $\rho_{eq}$ ? What is the matrix form of  $U_0$ ? Show that your result is consistent with the Schrödinger representation

$$R(t) = \frac{2}{\hbar} \sum_{n,j} P_n |A_{jn}|^2 \sin \omega_{jn} t$$

## 2. Vibrational relaxation in a triatomic

We'll examine the process of vibrational relaxation commonly found in triatomic molecules, focusing specifically at the case of water. For the case of a nonlinear "ABA" molecule such as H<sub>2</sub>O, the normal modes of vibration are the symmetric and asymmetric O-H stretching modes,  $\nu_a$  and  $\nu_s$ , and the bending mode,  $\delta_{\text{HOH}}$ , with vibrational frequencies of  $\omega_{a0}=3450\text{ cm}^{-1}$ ,  $\omega_{s0}=3200\text{ cm}^{-1}$  and  $\omega_{b0}=1650\text{ cm}^{-1}$ , respectively. The splitting between  $\nu_a$  and  $\nu_s$  arises from coupling between the two OH local mode stretching vibrations. In the case of the nonlinear "ABC" molecule HDO (where D is <sup>2</sup>H), the normal modes are well-approximated by local O-H and O-D stretching vibrations,  $\nu_h$  and  $\nu_d$ , and the bend is  $\delta_{\text{HOD}}$ . The frequencies in this case are  $\omega_{h0}=3400\text{ cm}^{-1}$ ,  $\omega_{d0}=2500\text{ cm}^{-1}$  and  $\omega_{b0}=1450\text{ cm}^{-1}$ , respectively.

For both H<sub>2</sub>O and HOD, the dominant mechanism by which vibrational energy in stretching vibrations dissipates to the environment is through stretch-bend coupling. An anharmonic coupling exists by which vibrational energy flows from the stretch to the  $v=2$  state of the bend (bend overtone). That is, annihilation of one quantum of stretch leads to two quanta in the bend. The energy difference is made up by the bath. We will be investigating this vibrational energy transfer process treating the bend overtone as a sink for vibrational energy in the stretches. For our purposes, we take the energy of the bend overtone states to be  $\omega_b=3250\text{ cm}^{-1}$  and  $\omega_b=2900\text{ cm}^{-1}$  for H<sub>2</sub>O and HOD respectively.



The values of the couplings  $V$  between the stretches and bend overtones are as follows. In the case of H<sub>2</sub>O, the bend overtone has the same symmetry as the symmetric state, leading to strong mixing in comparison to the asymmetric state. Let's take  $V_{ab}=15\text{ cm}^{-1}$  and  $V_{sb}=50\text{ cm}^{-1}$ . In the case of HOD, the coupling of stretch to bend overtone is about the same  $V_{hb}=V_{db}=30\text{ cm}^{-1}$ .

- Assuming that these vibrations interact linearly with a harmonic bath, write expressions for the rate of vibrational energy relaxation from each stretch state of H<sub>2</sub>O and HOD to the bend overtone in terms of the coupling  $V$ , the density of states of the bath  $W$ , and the thermal occupancy of the bath.
- Using the HOD and H<sub>2</sub>O molecules as examples, explain under what circumstances do you expect to:
  - ...observe Arrhenius vibrational relaxation behavior? (That is, when do you have linear scaling between  $\ln[k]$  and  $1/T$ ?)
  - ...observe rates that increase linearly with temperature?
  - What about rates independent of temperature?
- In certain cases it is observed that vibrational relaxation rates *decrease* with increasing temperature. Explain the types of circumstances that can lead to this behavior.

- d) To examine a specific example of temperature dependent vibrational relaxation rates, let's assume that the density of states (DOS) for the bath takes on a normalized Ohmic form

$$W(\omega) = A \frac{\omega}{\omega_c^2} e^{-\omega/\omega_c}$$

where  $\omega_c$  defines the characteristic maximum in the DOS, and that DOS shifts to higher frequencies with temperature. We will describe the shift with temperature through the relationship  $\omega_c = T \cdot (0.3 \text{ cm}^{-1} / \text{K})$  and take  $A = 5$ .

Calculate and plot the temperature-dependent vibrational relaxation rate from each stretch mode to the bend overtone for  $T = 50$  to  $350$  K. Explain the temperature dependence observed. What is the fastest rate observed?

- e) Now, let's numerically calculate time-dependent populations in all vibrational modes during the vibrational relaxation of population prepared in the symmetric stretching mode of  $\text{H}_2\text{O}$ . In addition to the couplings above, we expect that the two stretch modes are coupled by  $V_{as} = 50 \text{ cm}^{-1}$ . Start by writing the first-order rate equations that explain the population flow between the bend and stretch modes. Then numerically evaluate the time-dependent populations in the  $a$ ,  $s$ , and  $b$  states by integrating these differential equations using the same routines you used in Problem Set 1. For simplicity, you may assume that the bend mode is a sink from which population may not return to the bends, i.e.  $k_{ab} = k_{sb} = k_{bb} = 0$ . Examine and explain the population flow for temperatures between  $50$  and  $350$  K.