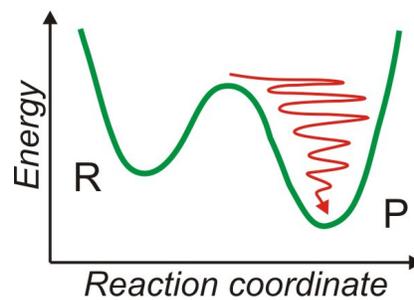


15. QUANTUM RELAXATION PROCESSES

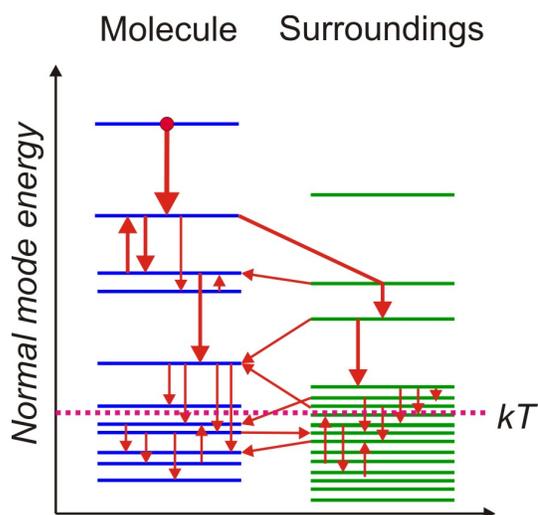
15.1. Vibrational Relaxation

Here we want to address how excess vibrational energy undergoes irreversible energy relaxation as a result of interactions with other intra- and intermolecular degrees of freedom. Why is this process important? It is the fundamental process by which nonequilibrium states thermalize. As chemists, this plays a particularly important role in chemical reactions, where efficient vibrational relaxation of an activated species is important to stabilizing the product and not allowing it to re-cross to the reactant well. Further, the rare activation event for chemical reactions is similar to the reverse of this process. Although we will be looking specifically at vibrational couplings and relaxation, the principles are the same for electronic population relaxation through electron–phonon coupling and spin–lattice relaxation.



For an isolated molecule with few vibrational coordinates, an excited vibrational state must relax by interacting with the remaining internal vibrations or the rotational and translational degrees of freedom. If a lot of energy must be dissipated, radiative relaxation may be more likely. In the condensed phase, relaxation is usually mediated by the interactions with the environment, for instance, the solvent or lattice. The solvent or lattice forms a continuum of intermolecular motions that can absorb the energy of the vibrational relaxation. Quantum mechanically this means that vibrational relaxation (the annihilation of a vibrational quantum) leads to excitation of solvent or lattice motion (creation of an intermolecular vibration that increases the occupation of higher lying states).

For polyatomic molecules it is common to think of energy relaxation from high lying vibrational states ($kT \ll \hbar\omega_0$) in terms of cascaded redistribution of energy through coupled modes of the molecule and its surroundings leading finally to thermal equilibrium. We seek ways of describing these highly non-equilibrium relaxation processes in quantum systems.



Classically vibrational relaxation reflects the surroundings exerting a friction on the vibrational coordinate, which damps its amplitude and heats the sample. We have seen that a Langevin equation for an oscillator experiencing a fluctuating force $f(t)$ describes such a process:

$$\ddot{Q}(t) + \omega_0^2 Q^2 - \gamma \dot{Q} = f(t)/m \quad (15.1)$$

This equation assigns a phenomenological damping rate γ to the vibrational relaxation we wish to describe. However, we know in the long time limit, the system must thermalize and the dissipation of energy is related to the fluctuations of the environment through the classical fluctuation-dissipation relationship. Specifically,

$$\langle f(t)f(0) \rangle = 2m\gamma k_B T \delta(t) \quad (15.2)$$

More general classical descriptions relate the vibrational relaxation rates to the correlation function for the fluctuating forces acting on the excited coordinate.

In these classical pictures, efficient relaxation requires a matching of frequencies between the vibrational period of the excited oscillator and the spectrum of fluctuation of the environment. Since these fluctuations are dominated by motions are of the energy scale of $k_B T$, such models do not work effectively for high frequency vibrations whose frequency $\omega \gg k_B T/\hbar$. We would like to develop a quantum model that allows for these processes and understand the correspondence between these classical pictures and quantum relaxation.

Let's treat the problem of a vibrational system H_S that relaxes through weak coupling V to a continuum of bath states H_B using perturbation theory. The eigenstates of H_S are $|a\rangle$ and those of H_B are $|\alpha\rangle$. Although our earlier perturbative treatment did not satisfy energy conservation, here we can take care of it by explicitly treating the bath states.

$$H = H_0 + V \quad (15.3)$$

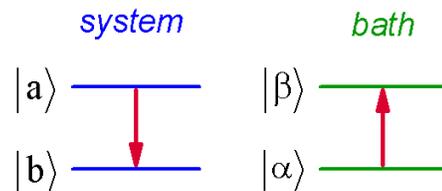
$$H_0 = H_S + H_B \quad (15.4)$$

$$H_S = |a\rangle E_a \langle a| + |b\rangle E_b \langle b| \quad (15.5)$$

$$H_B = \sum_{\alpha} |\alpha\rangle E_{\alpha} \langle \alpha| \quad (15.6)$$

$$H_0 |a\alpha\rangle = (E_a + E_{\alpha}) |a\alpha\rangle \quad (15.7)$$

We will describe transitions from an initial state $|i\rangle = |a\alpha\rangle$ with energy $E_a + E_{\alpha}$ to a final state $|f\rangle = |b\beta\rangle$ with energy $E_b + E_{\beta}$. Since we expect energy conservation to hold, this undoubtedly requires that a change in the system states will require an equal and opposite change of energy in the bath. Initially, we take $p_a = 1$ $p_b = 0$. If the interaction potential is V , Fermi's Golden Rule says the transition from $|i\rangle$ to $|f\rangle$ is given by



$$k_{fi} = \frac{2\pi}{\hbar} \sum_{i,f} p_i |\langle i|V|f\rangle|^2 \delta(E_f - E_i) \quad (15.8)$$

$$= \frac{2\pi}{\hbar} \sum_{a,\alpha,b,\beta} p_{a,\alpha} |\langle a\alpha|V|b\beta\rangle|^2 \delta((E_b + E_\beta) - (E_a + E_\alpha)) \quad (15.9)$$

$$= \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \sum_{\substack{a,\alpha \\ b,\beta}} p_{a,\alpha} \langle a\alpha|V|b\beta\rangle \langle b\beta|V|a\alpha\rangle e^{-i((E_b - E_a) + (E_\beta - E_\alpha))t/\hbar} \quad (15.10)$$

Equation (15.10) is just a restatement of the time domain version of (15.8)

$$k_{fi} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V(t)V(0) \rangle \quad (15.11)$$

$$V(t) = e^{iH_0 t} V e^{-iH_0 t} \quad (15.12)$$

Now, the matrix element involves both evaluation in both the system and bath states, but if we write this in terms of a matrix element in the system coordinate $V_{ab} = \langle a|V|b\rangle$:

$$\langle a\alpha|V|b\beta\rangle = \langle \alpha|V_{ab}|\beta\rangle \quad (15.13)$$

Then we can write the rate as

$$k_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \sum_{\alpha,\beta} p_\alpha \langle \alpha|e^{+iE_\alpha t} V_{ab} e^{-iE_\beta t}|\beta\rangle \langle \beta|V_{ba}|\alpha\rangle e^{-i\omega_{ba}t} \quad (15.14)$$

$$k_{ba} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_{ab}(t)V_{ba}(0) \rangle_B e^{-i\omega_{ba}t} \quad (15.15)$$

$$V_{ab}(t) = e^{iH_B t} V_{ab} e^{-iH_B t} \quad (15.16)$$

Equation (15.15) says that the relaxation rate is determined by a correlation function

$$C_{ba}(t) = \langle V_{ab}(t)V_{ba}(0) \rangle \quad (15.17)$$

which describes the time-dependent changes to the coupling between b and a . The time dependence of the interaction arises from the interaction with the bath; hence its time evolution under H_B . The subscript $\langle \dots \rangle_B$ means an equilibrium thermal average over the bath states

$$\langle \dots \rangle_B = \sum_{\alpha} p_\alpha \langle \alpha|\dots|\alpha\rangle \quad (15.18)$$

Note also that eq. (15.15) is similar but not quite a Fourier transform. This expression says that the relaxation rate is given by the Fourier transform of the correlation function for the fluctuating coupling evaluated at the energy gap between the initial and final state states.

Alternatively we could think of the rate in terms of a vibrational coupling spectral density, and the rate is given by its magnitude at the system energy gap ω_{ba} .

$$k_{ba} = \frac{1}{\hbar^2} \tilde{C}_{ba}(\omega_{ab}) \quad (15.19)$$

where the spectral representation $\tilde{C}_{ba}(\omega_{ab})$ is defined as the Fourier transform of $C_{ba}(t)$.

Vibration coupled to a harmonic bath

To evaluate these expressions, let's begin by consider the specific case of a system vibration coupled to a harmonic bath, which we will describe by a spectral density. Imagine that we prepare the system in an excited vibrational state in $\nu = |1\rangle$ and we want to describe relaxation to $\nu = |0\rangle$.¹

$$H_S = \hbar\omega_0(\tilde{P}^2 + \tilde{Q}^2) \quad (15.20)$$

$$H_B = \sum_{\alpha} \hbar\omega_{\alpha}(\tilde{p}_{\alpha}^2 + \tilde{q}_{\alpha}^2) = \sum_{\alpha} \hbar\omega_{\alpha}(a_{\alpha}^{\dagger}a_{\alpha} + \frac{1}{2}) \quad (15.21)$$

We will take the system–bath interaction to be linear in the bath coordinates:

$$V = H_{SB} = \sum_{\alpha} c_{\alpha} \tilde{Q} \tilde{q}_{\alpha} \quad (15.22)$$

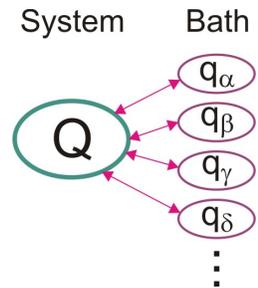
Here c_{α} is a coupling constant which describes the strength of the interaction between the system and bath mode α . Note, that this form suggests that the system vibration is a local mode interacting with a set of normal vibrations of the bath.

For the case of single quantum relaxation from $|a\rangle = |1\rangle$ to $b = |0\rangle$, we can write the coupling matrix element as

$$V_{ba} = \sum_{\alpha} \xi_{ab,\alpha} (a_{\alpha}^{\dagger} + a_{\alpha}) \quad (15.23)$$

where

$$\xi_{ab,\alpha} = c_{\alpha} \frac{\sqrt{m_Q m_q \omega_0 \omega_{\alpha}}}{2\hbar} \langle b | Q | a \rangle \quad (15.24)$$



¹ Note that we are using an equilibrium property, the coupling correlation function, to describe a nonequilibrium process, the relaxation of an excited state. Underlying the validity of the expressions are the principles of linear response. In practice this also implies a time scale separation between the equilibration of the bath and the relaxation of the system state. The bath correlation function should work fine if it has rapidly equilibrated, even though the system may not have. An instance where this would work well is electronic spectroscopy, where relaxation and thermalization in the excited state occurs on picosecond time scales, whereas the electronic population relaxation is on nanosecond time scales.

Here the matrix element $\langle b|Q|a\rangle$ is taken in evaluating $\xi_{ab,\alpha}$. Evaluating eq. (15.17) is now much the same as problems we've had previously:

$$\begin{aligned} \langle V_{ab}(t)V_{ba}(0)\rangle_B &= \langle e^{iH_B t} V_{ab} e^{-iH_B t} V_{ba}\rangle_B \\ &= \sum_{\alpha} \xi_{\alpha}^2 [(\bar{n}_{\alpha} + 1)e^{-i\omega_{\alpha} t} + \bar{n}_{\alpha} e^{+i\omega_{\alpha} t}] \end{aligned} \quad (15.25)$$

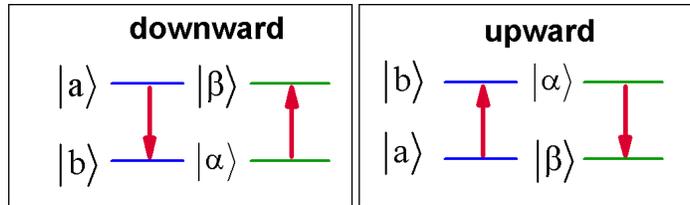
here $\bar{n}_{\alpha} = (e^{\beta\hbar\omega_{\alpha}} - 1)^{-1}$ is the thermally averaged occupation number of the bath mode at ω_{α} . In evaluating this we take advantage of relationships we have used before

$$\begin{aligned} e^{iH_B t} a_{\alpha} e^{-iH_B t} &= a_{\alpha} e^{-i\omega_{\alpha} t} \\ e^{iH_B t} a_{\alpha}^{\dagger} e^{-iH_B t} &= a_{\alpha}^{\dagger} e^{+i\omega_{\alpha} t} \end{aligned} \quad (15.26)$$

$$\begin{aligned} \langle a_{\alpha} a_{\alpha}^{\dagger} \rangle &= \bar{n}_{\alpha} + 1 \\ \langle a_{\alpha}^{\dagger} a_{\alpha} \rangle &= \bar{n}_{\alpha} \end{aligned} \quad (15.27)$$

So, now by Fourier transforming (15.25) we have the rate as

$$k_{ba} = \frac{1}{\hbar^2} \sum_{\alpha} [\xi_{\alpha}]_{ab}^2 [(\bar{n}_{\alpha} + 1)\delta(\omega_{ba} + \omega_{\alpha}) + \bar{n}_{\alpha}\delta(\omega_{ba} - \omega_{\alpha})] \quad (15.28)$$



This expression describes two relaxation processes which depend on temperature. The first is allowed at $T=0$ K and obeys $-\omega_{ba} = \omega_{\alpha}$. This implies that $E_a > E_b$, and that a loss of energy in the system is balanced by an equal rise in energy of the bath. That is $|\beta\rangle = |\alpha+1\rangle$. The second term is only allowed for elevated temperatures. It describes relaxation of the system by transfer to a higher energy state $E_b > E_a$, with a concerted decrease of the energy of the bath ($|\beta\rangle = |\alpha-1\rangle$). Naturally, this process vanishes if there is no thermal energy in the bath.²

To more accurately model the relaxation due to a continuum of modes, we can replace the explicit sum over bath states with an integral over a density of bath states W

² There is an exact analogy between this problem and the interaction of matter with a quantum radiation field. The interaction potential is instead a quantum vector potential and the bath is the photon field of different electromagnetic modes. Equation (15.28) describes has two terms that describe emission and absorption processes. The leading term describes the possibility of spontaneous emission, where a material system can relax in the absence of light by emitting a photon at the same frequency.

$$k_{ba} = \frac{1}{\hbar^2} \int d\omega_\alpha W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \left[(\bar{n}(\omega_\alpha) + 1) \delta(\omega_{ba} + \omega_\alpha) + \bar{n}(\omega_\alpha) \delta(\omega_{ba} - \omega_\alpha) \right] \quad (15.29)$$

We can also define a spectral density, which is the vibrational coupling-weighted density of states:

$$\rho(\omega_\alpha) \equiv W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \quad (15.30)$$

Then the relaxation rate is:

$$\begin{aligned} k_{ba} &= \frac{1}{\hbar^2} \int d\omega_\alpha W(\omega_\alpha) \xi_{ba}^2(\omega_\alpha) \left[(\bar{n}(\omega_\alpha) + 1) \delta(\omega_{ba} + \omega_\alpha) + \bar{n}(\omega_\alpha) \delta(\omega_{ba} - \omega_\alpha) \right] \\ &= \frac{1}{\hbar^2} \left[(\bar{n}(\omega_{ba}) + 1) \rho_{ba}(\omega_{ab}) + \bar{n}(\omega_{ba}) \rho_{ba}(-\omega_{ab}) \right] \end{aligned} \quad (15.31)$$

We see that the Fourier transform of the fluctuating coupling correlation function, is equivalent to the coupling-weighted density of states, which we evaluate at ω_{ba} or $-\omega_{ba}$ depending on whether we are looking at upward or downward transitions. Note that \bar{n} still refers to the occupation number for the bath, although it is evaluated at the energy splitting between the initial and final system states. Equation (15.31) is a full quantum expression, and obeys detailed balance between the upward and downward rates of transition between two states:

$$k_{ba} = \exp(-\beta\hbar\omega_{ab}) k_{ab} \quad (15.32)$$

From our description of the two level system in a harmonic bath, we see that high frequency relaxation ($kT \ll \hbar\omega_0$) only proceeds with energy from the system going into a mode of the bath at the same frequency, but at lower frequencies ($kT \approx \hbar\omega_0$) that energy can flow both into the bath and from the bath back into the system. When the vibration has energies that are thermally populated in the bath, we return to the classical picture of a vibration in a fluctuating environment that can dissipate energy from the vibration as well as giving kicks that increase the energy of the vibration. Note that in a cascaded relaxation scheme, as one approaches kT , the fraction of transitions that increase the system energy increase. Also, note that the bi-linear coupling in eq. (15.22) and used in our treatment of quantum fluctuations can be associated with fluctuations of the bath that induce changes in energy (relaxation) and shifts of frequency (dephasing).

Multiquantum relaxation of polyatomic molecules³

Vibrational relaxation of polyatomic molecules in solids or in solution involves anharmonic coupling of energy between internal vibrations of the molecule, also called IVR (internal vibrational energy redistribution). Mechanical interactions between multiple modes of vibration

³ V. M. Kenkre, A. Tokmakoff and M. D. Fayer, "Theory of vibrational relaxation of polyatomic molecules in liquids," *J. Chem. Phys.*, **101**, 10618 (1994).

of the molecule act to rapidly scramble energy deposited into one vibrational coordinate and lead to cascaded energy flow toward equilibrium.

For this problem the bilinear coupling above doesn't capture the proper relaxation process. Instead we can express the molecular potential energy in terms of well-defined normal modes of vibration for the system and the bath, and these interact weakly through small anharmonic terms in the potential. Then we can extend the perturbative approach above to include the effect of multiple accepting vibrations of the system or bath. For a set of system and bath coordinates, the potential energy for the system and system–bath interaction can be expanded as

$$V_S + V_{SB} = \frac{1}{2} \sum_a \frac{\partial^2 V}{\partial Q_a^2} Q_a^2 + \frac{1}{6} \sum_{a,\alpha,\beta} \frac{\partial^3 V}{\partial Q_a \partial q_\alpha \partial q_\beta} Q_a q_\alpha q_\beta + \frac{1}{6} \sum_{a,b,\alpha} \frac{\partial^3 V}{\partial Q_a \partial Q_b \partial q_\alpha} Q_a Q_b q_\alpha \cdots \quad (15.33)$$

Focusing explicitly on the first cubic expansion term, for one system oscillator:

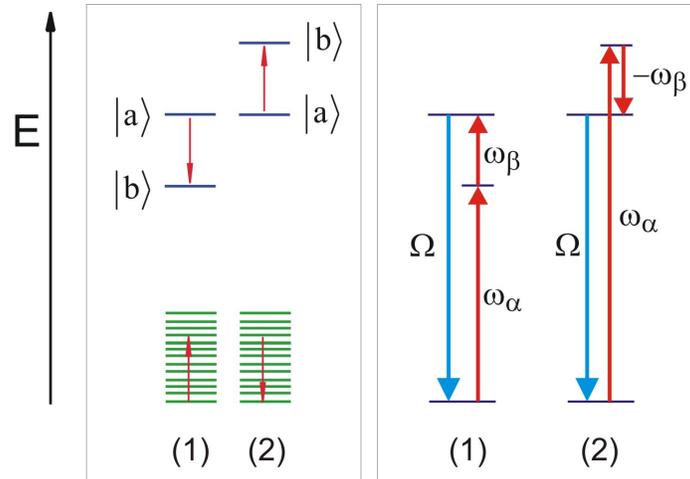
$$V_S + V_{SB} = \frac{1}{2} m \Omega^2 \underline{Q}^2 + V^{(3)} \underline{Q} \underline{q}_\alpha \underline{q}_\beta \quad (15.34)$$

Here, the system–bath interaction potential describes the case for a cubic anharmonic coupling that involves one vibration of the system Q interacting weakly with two vibrations of the bath q_α and q_β , so that $\hbar\Omega \gg V^{(3)}$. Energy deposited in the system vibration will dissipate to the two vibrations of the bath, a three quantum process. Higher-order expansion terms would describe interactions involving four or more quanta.

Working specifically with the cubic example, we can use the harmonic bath model to calculate the rate of energy relaxation. This picture is applicable if a vibrational mode of frequency Ω relaxes by transferring its energy to another vibration nearby in energy (ω_α), and the energy difference ω_β being accounted for by a continuum of intermolecular motions. For this case one can show

$$k_{ba} = \frac{1}{\hbar^2} \left[(\bar{n}(\omega_\alpha) + 1) (\bar{n}(\omega_\beta) + 1) \rho_{ba}(\omega_{ab}) + (\bar{n}(\omega_\alpha) + 1) \bar{n}(\omega_\beta) \rho_{ba}(\omega_{ab}) \right] \quad (15.35)$$

where $\rho(\omega) \equiv W(\omega) (V^{(3)}(\omega))^2$. Here we have taken $\Omega, \omega_\alpha \gg \omega_\beta$. These two terms describe two possible relaxation pathways, the first in which annihilation of a quantum of Ω leads to a creation of one quantum each of ω_α and ω_β . The second term describes the dissipation of energy by coupling to a higher energy vibration, with the excess energy being absorbed from the bath. Annihilation of a quantum of Ω leads to a creation of one quantum of ω_α and the annihilation of one quantum of ω_β . Naturally this latter term is only allowed when there is adequate thermal energy present in the bath.



Rate calculations using classical vibrational relaxation

In general, we would like a practical way to calculate relaxation rates, and calculating quantum correlation functions is not practical. How do we use classical calculations for the bath, for instance drawing on a classical molecular dynamics simulation? Is there a way to get a quantum mechanical rate?

The first problem is that the quantum correlation function is complex $C_{ab}^*(t) = C_{ab}(-t)$ and the classical correlation function is real and even $C_{cl}(t) = C_{cl}(-t)$. In order to connect these two correlation functions, one can derive a quantum correction factor that allows one to predict the quantum correlation function on the basis of the classical one. This is based on the assumption that at high temperature it should be possible to substitute the classical correlation function with the real part of the quantum correlation function

$$C_{cl}(t) \Rightarrow C'_{ba}(t) \quad (15.36)$$

To make this adjustment we start with the frequency domain expression derived from the detailed balance expression $\tilde{C}(-\omega) = e^{-\beta\hbar\omega} \tilde{C}(\omega)$

$$\tilde{C}(\omega) = \frac{2}{1 + \exp(-\beta\hbar\omega)} \tilde{C}'(\omega) \quad (15.37)$$

Here $\tilde{C}'(\omega)$ is defined as the Fourier transform of the real part of the quantum correlation function. So the vibrational relaxation rate is

$$k_{ba} = \frac{4}{\hbar^2 (1 + \exp(-\hbar\omega_{ba}/kT))} \int_0^\infty dt e^{-i\omega_{ba}t} \text{Re}[\langle V_{ab}(t) V_{ba}(0) \rangle] \quad (15.38)$$

Now we will assume that one can replace a classical calculation of the correlation function here as in eq. (15.36). The leading term out front can be considered a “quantum correction factor” that accounts for the detailed balance of rates encoded in the quantum spectral density.

In practice such a calculation might be done with molecular dynamics simulations. Here one has an explicit characterization of the intermolecular forces that would act to damp the excited vibrational mode. One can calculate the system–bath interactions by expanding the vibrational potential of the system in the bath coordinates

$$\begin{aligned} V_S + V_{SB} &= V_0 + \sum_{\alpha} \frac{\partial V^{\alpha}}{\partial Q} Q + \sum_{\alpha} \frac{\partial^2 V^{\alpha}}{\partial Q^2} Q^2 + \dots \\ &= V_0 + FQ + GQ^2 + \dots \end{aligned} \quad (15.39)$$

Here V^{α} represents the potential of an interaction of one solvent coordinate acting on the excited vibrational system coordinate Q . The second term in this expansion FQ depends linearly on the system Q and bath α coordinates, and we can use variation in this parameter to calculate the correlation function for the fluctuating interaction potential. Note that F is the *force* that molecules exert on Q ! Thus the relevant classical correlation function for vibrational relaxation is a force correlation function

$$C_{Cl}(t) = \langle F(t)F(0) \rangle \quad (15.40)$$

$$k_{Cl} = \frac{1}{kT} \int_0^{\infty} dt \cos \omega_{ba} t \langle F(t)F(0) \rangle \quad (15.41)$$

Readings

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15.2. A DENSITY MATRIX DESCRIPTION OF QUANTUM RELAXATION

Here we will more generally formulate a quantum mechanical picture of coherent and incoherent relaxation processes that occur as the result of interaction between a prepared system and its environment. This description will apply to the case where we separate the degrees of freedom in our problem into a system and a bath that interact. We have limited information about the bath degrees of freedom. As a statistical mixture, we only have knowledge of the probability of occupying states of the bath and not of the phase relationships required to describe a deterministic quantum system. For such problems, the density matrix is the natural tool.

Mixed States

How does a system get into a mixed state? Generally, if you have two systems and you put these in contact with each other, interaction between the two will lead to a new system that is inseparable. Imagine that I have two systems H_S and H_B for which the eigenstates of H_S are $|a\rangle$ and those of H_B are $|\alpha\rangle$.

$$H_0 = H_S + H_B \quad (15.42)$$

$$\begin{aligned} H_S |a\rangle &= E_a |a\rangle \\ H_B |\alpha\rangle &= E_\alpha |\alpha\rangle \end{aligned} \quad (15.43)$$

In general, before these systems interact, they can be described in terms of product states in the eigenstates of H_S and H_B :

$$|\psi(t_0)\rangle = |\psi_S^0\rangle |\psi_B^0\rangle \quad (15.44)$$

$$|\psi_S^0\rangle = \sum_a s_a |a\rangle \quad |\psi_B^0\rangle = \sum_\alpha b_\alpha |\alpha\rangle \quad (15.45)$$

$$|\psi_0\rangle = \sum_{a,\alpha} s_a b_\alpha |a\rangle |\alpha\rangle \quad (15.46)$$

After these states are allowed to interact, we have a new state vector $|\psi(t)\rangle$. The new state can still be expressed in the zero-order basis, although this does not represent the eigenstates of the new Hamiltonian

$$H = H_0 + V \quad (15.47)$$

$$|\psi(t)\rangle = \sum_{a,\alpha} c_{a\alpha} |a\alpha\rangle \quad (15.48)$$

For any point in time, $c_{a\alpha}$ is the joint probability amplitude for finding particle of $|\psi_S\rangle$ in $|a\rangle$ and simultaneously finding particle of $|\psi_B\rangle$ in $|\alpha\rangle$. At $t = t_0$, $c_{a\alpha} = s_a b_\alpha$.

Now suppose that you have an operator A that is only an operator in the $|\psi_S\rangle$ coordinates. This might represent an observable for the system that you wish to measure. Let's calculate the expectation value of A

$$\langle A(t) \rangle = \langle \psi(t) | A | \psi(t) \rangle = \langle \psi_S | A | \psi_S \rangle \quad (15.49)$$

$$\begin{aligned} \langle A(t) \rangle &= \sum_{\substack{a,\alpha \\ b,\beta}} c_{a\alpha}^* c_{b\beta} \langle a\alpha | A | b,\beta \rangle \\ &= \sum_{\substack{a,\alpha \\ b,\beta}} c_{a\alpha}^* c_{b\beta} \langle a | A | b \rangle \delta_{\alpha\beta} \\ &= \sum_{a,b} \left(\sum_{\alpha} c_{a\alpha}^* c_{b\alpha} \right) A_{ab} \\ &\equiv \sum_{a,b} (\rho_S)_{ba} A_{ab} \\ &= Tr[\rho_S A] \end{aligned} \quad (15.50)$$

Here we have defined a density matrix for the degrees of freedom in $|\psi_S\rangle$

$$\rho_S = |\psi_S\rangle \langle \psi_S| \quad (15.51)$$

with density matrix elements that traced over the $|\psi_B\rangle$ states, that is, that are averaged over the probability of occupying the $|\psi_B\rangle$ states.

$$|b\rangle \rho_S \langle a| = \sum_{\alpha} c_{a\alpha}^* c_{b\alpha} \quad (15.52)$$

Here the matrix elements in direct product states involve elements of a four-dimensional matrix, which are specified by the tetradic notation.

We have defined a trace of the density matrix over the unobserved degrees of freedom in $|\psi_B\rangle$, i.e. a sum over diagonal elements in α . To relate this to our similar prior expression: $\langle A(t) \rangle = Tr[\rho A]$, the following definitions are useful:

$$\begin{aligned} \rho_S &= Tr_B(\rho) \\ &= \sum_{a,b} (\rho_S)_{ba} A_{ab} \\ &= Tr(\rho_S A) \end{aligned} \quad (15.53)$$

Also,
$$Tr(A \times B) = Tr(A) Tr(B) \quad (15.54)$$

Since ρ_S is Hermitian, it can be diagonalized by a unitary transformation T , where the new eigenbasis $|m\rangle$ represents the mixed states of the $|\psi_S\rangle$ system.

$$\rho_S = \sum_m |m\rangle\langle m| \rho_{mm} \quad (15.55)$$

$$\sum_m \rho_{mm} = 1 \quad (15.56)$$

The density matrix elements represent the probability of occupying state $|m\rangle$ averaged over the bath degrees of freedom

$$\begin{aligned} \rho_{mm} &= \sum_{a,b} T_{mb} \rho_{ba} T_{am}^\dagger \\ &= \sum_{a,b,\alpha} a_{b\alpha} T_{mb} a_{a\alpha}^* T_{ma}^* \\ &= \sum_{\alpha} f_{m\alpha} f_{m\alpha}^* \\ &= \sum_{\alpha} |f_{m\alpha}|^2 = p_m \geq 0 \end{aligned} \quad (15.57)$$

The quantum mechanical interaction of one system with another causes the system to be in a mixed state after the interaction. The mixed states are generally not separable into the original states. The mixed state is described by

$$|\psi_S\rangle = \sum_m d_m |m\rangle \quad (15.58)$$

$$d_m = \sum_{\alpha} f_{m\alpha} \quad (15.59)$$

If we only observe a few degrees of freedom, we can calculate observables by tracing over unobserved degrees of freedom. This forms the basis for treating relaxation phenomena. A few degrees of freedom that we observe, coupled to many other degrees of freedom, which lead to irreversible relaxation.

Equation of motion for the reduced density matrix

So now to describe irreversible processes in quantum systems, let's look at the case where we have partitioned the problem so that we have a few degrees of freedom that we are most interested in (the system), which is governed by H_S and which we observe with a system operator A . The remaining degrees of freedom are a bath, which interact with the system. The Hamiltonian is given by eqs. (15.42) and (15.47). In our observations, we will be interested in expectation values in A which we have seen are written

$$\begin{aligned}
\langle A_S \rangle &= Tr[\rho(t)A] \\
&= Tr_S[\sigma(t)A] \\
&= \sum_{a,b} \sigma_{ab}(t) A_{ba} \\
&= Tr_S Tr_B[\rho(t)A]
\end{aligned} \tag{15.60}$$

Here σ is the reduced density operator for the system degrees of freedom. This is the more commonly variable used for ρ_S .

$$\sigma_{ab} = \sum_{\alpha} \langle a\alpha | \rho | b\alpha \rangle = Tr_B \rho_{ab} \tag{15.61}$$

Tr_B and Tr_S are partial traces over the bath and system respectively. Note, that since $Tr(A \times B) = TrA TrB$ for direct product states, all we need to do is describe time evolution of σ to understand the time dependence to A .

We obtain the equation of motion for the reduced density matrix beginning with

$$\rho(t) = U(t)\rho(0)U^\dagger(t) \tag{15.62}$$

and tracing over bath:

$$\sigma(t) = Tr_B[U\rho U^\dagger] \tag{15.63}$$

We can treat the time evolution of the reduced density matrix in the interaction picture. From our earlier discussion of the density matrix, we integrate the equation of motion

$$\dot{\rho}_I = -\frac{i}{\hbar}[V_I(t), \rho_I(t)] \tag{15.64}$$

to obtain

$$\rho_I(t) = \rho_I(0) - \frac{i}{\hbar} \int_0^t d\tau [V_I(\tau), \rho_I(\tau)] \tag{15.65}$$

Remember that the density matrix in the interaction picture is

$$\rho_I(t) = U_0^\dagger \rho(t) U_0 = e^{i(H_S+H_B)t/\hbar} \rho(t) e^{-i(H_S+H_B)t/\hbar} \tag{15.66}$$

and similarly

$$V_I(t) = U_0^\dagger V U_0 = e^{i(H_S+H_B)t/\hbar} V(t) e^{-i(H_S+H_B)t/\hbar} \tag{15.67}$$

Substituting (15.65) into (15.64) we have

$$\dot{\rho}_I(t) = -\frac{i}{\hbar}[V_I(t), \rho_I(t_0)] - \frac{1}{\hbar^2} \int_0^t dt' [V_I(t), [V_I(t'), \rho_I(t')]] \tag{15.68}$$

Now taking a trace over the bath states

$$\dot{\sigma}_I(t) = -\frac{i}{\hbar} Tr_B[V_I(t), \rho_I(t_0)] - \frac{1}{\hbar^2} \int_0^t dt' Tr_B[V_I(t), [V_I(t'), \rho_I(t')]] \tag{15.69}$$

If we assume that the interaction of the system and bath is small enough that the system cannot change the bath

$$\rho_I(t) \approx \sigma_I(t) \rho_B(0) = \sigma_I(t) \rho_{eq}^B \quad (15.70)$$

$$\rho_{eq}^B = \frac{e^{-\beta H_B}}{Z} \quad (15.71)$$

Then we obtain an equation of motion for σ to second order:

$$\dot{\sigma}_I(t) = -\frac{i}{\hbar} Tr_B [V_I(t), \sigma_I(0) \rho_{eq}^B] - \frac{1}{\hbar^2} \int_0^t dt' Tr_B [V_I(t), [V_I(t'), \sigma_I(t') \rho_{eq}^B]] \quad (15.72)$$

The last term involves an integral over a correlation function for a fluctuating interaction potential. This looks similar to a linear response function, and also the same form as the relaxation rates from Fermi's Golden Rule that we just discussed. The first term in eq. (15.72) involves a thermal average over the interaction potential, $\langle V \rangle_B = Tr_B [V \rho_{eq}^B]$. If this average value is zero, which would be the case for an off-diagonal form of V , we can drop the first term in the equation of motion for σ_I . If it were not zero, it is possible to redefine the Hamiltonian such that $H_0 \rightarrow H_0 + \langle V \rangle_B$ and $V(t) \rightarrow V(t) - \langle V \rangle_B$, which recasts it in a form where $\langle V \rangle_B \rightarrow 0$ and the first term can be neglected.

Now let's evaluate the equation of motion for the case where the system-bath interaction can be written as a product of operators in the system \hat{A} and bath $\hat{\beta}$:

$$H_{SB} = V = \hat{A} \hat{\beta} \quad (15.73)$$

This is equivalent to the bilinear coupling form that was used in our prior description of dephasing and population relaxation. There we took the interaction to be linearly proportional to the system and bath coordinate(s): $V = c \underline{Q} \underline{q}$. The time evolution in the two variables is separable and given by

$$\begin{aligned} \hat{A}(t) &= U_S^\dagger \hat{A}(t_0) U_S \\ \hat{\beta}(t) &= U_B^\dagger \hat{\beta}(t_0) U_B \end{aligned} \quad (15.74)$$

The equation of motion for σ_I becomes

$$\begin{aligned} \dot{\sigma}_I(t) &= \frac{1}{\hbar^2} \int_0^t dt' \left[\hat{A}(t) \hat{A}(t') \sigma(t') - \hat{A}(t') \sigma(t') \hat{A}(t) \right] Tr_B \left(\hat{\beta}(t) \hat{\beta}(t') \rho_{eq}^B \right) \\ &\quad - \left[\hat{A}(t) \sigma(t') \hat{A}(t') - \sigma(t') \hat{A}(t') \hat{A}(t) \right] Tr_B \left(\hat{\beta}(t') \hat{\beta}(t) \rho_{eq}^B \right) \end{aligned} \quad (15.75)$$

Here the history of the evolution of \hat{A} depends on the time dependence of the bath variables coupled to the system. The time dependence of the bath enters as a bath correlation function

$$\begin{aligned}
C_{\beta\beta}(t-t') &= \text{Tr}_B(\hat{\beta}(t)\hat{\beta}(t')\rho_{eq}^B) \\
&= \langle \hat{\beta}(t)\hat{\beta}(t') \rangle_B = \langle \hat{\beta}(t-t')\hat{\beta}(0) \rangle_B
\end{aligned} \tag{15.76}$$

The bath correlation function can be evaluated using the methods that we have used in the Energy Gap Hamiltonian and Brownian Oscillator Models. Switching integration variables to the time interval prior to observation

$$\tau = t - t' \tag{15.77}$$

we obtain

$$\dot{\sigma}_I(t) = -\frac{1}{\hbar^2} \int_0^t d\tau \left[\hat{A}(t), \hat{A}(t-\tau) \sigma_I(t-\tau) \right] C_{\beta\beta}(\tau) - \left[\hat{A}(t), \sigma_I(t-\tau) \hat{A}(t-\tau) \right] C_{\beta\beta}^*(\tau). \tag{15.78}$$

Here we have made use of $C_{\beta\beta}^*(\tau) = C_{\beta\beta}(-\tau)$. For the case that the system–bath interaction is a result of interactions with many bath coordinates

$$V = \sum_{\alpha} \hat{A} \hat{\beta}_{\alpha} \tag{15.79}$$

then eq. (15.78) becomes

$$\dot{\sigma}_I(t) = -\frac{1}{\hbar^2} \sum_{\alpha, \beta} \int_0^t d\tau \left[\hat{A}(t), \hat{A}(t-\tau) \sigma_I(t-\tau) \right] C_{\alpha\beta}(\tau) - \left[\hat{A}(t), \sigma_I(t-\tau) \hat{A}(t-\tau) \right] C_{\alpha\beta}^*(\tau) \tag{15.80}$$

with the bath correlation function

$$C_{\alpha\beta}(\tau) = \langle \hat{\beta}_{\alpha}(\tau) \hat{\beta}_{\beta}(0) \rangle_B \tag{15.81}$$

Equation (15.78) or (15.80) indicates that the rates of exchange of amplitude between the system states carries memory of the bath's influence on the system, that is, $\sigma_I(t)$ is dependent on $\sigma_I(t-\tau)$. If we make the Markov approximation, for which the dynamics of the bath are much faster than the evolution of the system and where the system has no memory of its past, we would replace

$$\sigma(t') = \sigma(t') \delta(t-t') \Rightarrow \sigma(t) \tag{15.82}$$

in eq. (15.75), or equivalently in eq. (15.78) set

$$\sigma_I(t-\tau) \Rightarrow \sigma_I(t) \tag{15.83}$$

For the subsequent work, we use this approximation. Similarly, the presence of a time scale separation between a slow system and a fast bath allows us to change the upper integration limit in eq. (15.78) from t to ∞ .

Evaluating the equation of motion: Redfield equations

To describe the exchange of amplitude between system states induced by the bath, we will want to evaluate the matrix elements of the reduced density matrix in the system eigenstates. To begin, we use eq. (15.78) to write the time-dependent matrix elements as

$$\begin{aligned} \dot{\sigma}_{ab}^I(t) = & -\sum_{c,d} \frac{1}{\hbar^2} \int_0^\infty d\tau \left[\hat{A}_{ac}(t) \hat{A}_{cd}(t-\tau) \sigma_{db}^I(t) - \hat{A}_{ac}(t-\tau) \sigma_{cd}^I(t) \hat{A}_{db}(t) \right] C_{\beta\beta}(\tau) \\ & - \left[\hat{A}_{ac}(t) \sigma_{cd}^I(t) \hat{A}_{db}(t-\tau) - \sigma_{ac}^I(t) \hat{A}_{cd}(t-\tau) \hat{A}_{db}(t) \right] C_{\beta\beta}^*(\tau) \end{aligned} \quad (15.84)$$

Now, let's convert the time dependence expressed in terms of the interaction picture into a Schrodinger representation using $\langle a | A(t) | b \rangle = e^{i\omega_{ab}t} A_{ab}$

$$\langle a | \sigma^I | b \rangle = e^{i\omega_{ab}t} \sigma_{ab} \quad (15.85)$$

To see how this turns out, consider the first term in eq. (15.84):

$$\dot{\sigma}_{ab}^I(t) = -\sum_{c,d} \frac{1}{\hbar^2} \int_0^\infty d\tau \hat{A}_{ac}(t) \hat{A}_{cd}(t-\tau) \sigma_{db}^I(t) C_{\beta\beta}(\tau) \quad (15.86)$$

$$\dot{\sigma}_{ab}(t) e^{i\omega_{ab}t} + i\omega_{ab} e^{i\omega_{ab}t} \sigma_{ab} = -\sum_{c,d} \frac{1}{\hbar^2} \hat{A}_{ac} \hat{A}_{cd} \sigma_{db}(t) e^{i\omega_{ac}t + i\omega_{cd}t + i\omega_{ab}t} \int_0^\infty d\tau e^{-i\omega_{cd}\tau} C_{\beta\beta}(\tau) \quad (15.87)$$

Defining the Fourier-Laplace transform of the bath correlation function:

$$\tilde{C}_{\beta\beta}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} C_{\beta\beta}(\tau) \quad (15.88)$$

We have

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab} \sigma_{ab} - \sum_{c,d} \frac{1}{\hbar^2} \hat{A}_{ac} \hat{A}_{cd} \sigma_{db}(t) \tilde{C}_{\beta\beta}(\omega_{dc}) \quad (15.89)$$

Here the spectral representation of the bath correlation function is being evaluated at the energy gap between system states ω_{dc} . So the evolution of coherences and populations in the system states is governed by their interactions with other system states, governed by the matrix elements, and this is modified depending on the fluctuations of the bath at different system state energy gaps. In this manner, eq. (15.84) becomes

$$\begin{aligned} \dot{\sigma}_{ab}(t) = & -i\omega_{ab} \sigma_{ab}(t) - \frac{1}{\hbar^2} \sum_{c,d} \left[\hat{A}_{ac} \hat{A}_{cd} \sigma_{db}(t) \tilde{C}_{\beta\beta}(\omega_{dc}) - \hat{A}_{ac} \hat{A}_{db} \sigma_{cd}(t) \tilde{C}_{\beta\beta}(\omega_{ca}) \right. \\ & \left. - \hat{A}_{ac} \hat{A}_{db} \sigma_{cd}(t) \tilde{C}_{\beta\beta}^*(-\omega_{db}) + \hat{A}_{cd} \hat{A}_{db} \sigma_{ac}(t) \tilde{C}_{\beta\beta}^*(-\omega_{cd}) \right] \end{aligned} \quad (15.90)$$

$$= -i\omega_{ab} \sigma_{ab}(t) - \sum_{c,d} \left[\Gamma_{ac,cd}^+ \sigma_{db}(t) - \Gamma_{ac,db}^- \sigma_{cd}(t) - \Gamma_{ac,db}^+ \sigma_{cd}(t) + \Gamma_{cd,db}^- \sigma_{ac}(t) \right]. \quad (15.91)$$

The rate constants are defined through:

$$\Gamma_{ab,cd}^+ = \frac{1}{\hbar^2} A_{ab} A_{cd} \tilde{C}_{\beta\beta}(\omega_{dc}) \quad (15.92)$$

$$\Gamma_{ab,cd}^- = \frac{1}{\hbar^2} A_{ab} A_{cd} \tilde{C}_{\beta\beta}(\omega_{ba}) \quad (15.93)$$

Here we made use of $\tilde{C}_{\beta\beta}^*(\omega) = \tilde{C}_{\beta\beta}(-\omega)$. Also, it is helpful to note that

$$\Gamma_{ab,cd}^+ = [\Gamma_{dc,ba}^-]^* \quad (15.94)$$

The coupled differential equations in eq. (15.91) express the relaxation dynamics of the system states almost entirely in terms of the system Hamiltonian. The influence of the bath only enters through the bath correlation function.

The common alternate way of writing these expressions is in terms of the relaxation super-operator \mathbf{R}

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab}\sigma_{ab} - \sum_{c,d} R_{ab,cd} \sigma_{cd}(t) \quad (15.95)$$

or in the interaction picture

$$\dot{\sigma}_{ab}^I(t) = \sum_{c,d} \sigma_{cd}^I(t) R_{ab,cd} e^{i(E_a - E_b - E_c + E_d)t/\hbar} \quad (15.96)$$

Equation (15.95), the reduced density matrix equation of motion for a Markovian bath, is known as the Redfield equation. It describes the irreversible and oscillatory components of the amplitude in the $|a\rangle\langle b|$ coherence as a result of dissipation to the bath and feeding from other states. \mathbf{R} describes the rates of change of the diagonal and off-diagonal elements of σ_I and is expressed as:

$$R_{ab,cd} = \delta_{db} \sum_k \Gamma_{ak,kc}^+ - \Gamma_{db,ad}^+ - \Gamma_{db,ad}^- + \delta_{ac} \sum_k \Gamma_{dk,kb}^- \quad (15.97)$$

where k refers to a system state.

The derivation described above can be performed without assuming a form to the system–bath interaction potential as we did in eq. (15.73). If so, one can write the relaxation operator in terms of a correlation function for the system–bath interaction

$$\Gamma_{ab,cd}^+ = \frac{1}{\hbar^2} \int_0^\infty d\tau \langle V_{ab}(\tau) V_{cd}(0) \rangle_B e^{-i\omega_{cd}\tau} \quad (15.98)$$

$$\Gamma_{ab,cd}^- = \frac{1}{\hbar^2} \int_0^\infty d\tau \langle V_{ab}(0) V_{cd}(\tau) \rangle_B e^{-i\omega_{ab}\tau} \quad (15.99)$$

The tetradic notation for the Redfield relaxation operator allows us to identify four classes of relaxation processes, depending on the number of states involved:

aa, aa : Population relaxation (rate of loss of the population in a)

ab, ab : Coherence relaxation or dephasing (damping of the coherence ab)

aa, bb : Population transfer (rate of transfer of population from state b to state a)

ab, cd : Coherence transfer (rate at which amplitude in an oscillating superposition between two states (c and d) couples to form oscillating amplitude between two other states (a and b))

The origin and meaning of these terms will be discussed below.

Secular Approximation

From eq. (15.96) we note that the largest changes in matrix elements of σ_I result from a resonance condition:

$$\begin{aligned} \exp\left[i(E_a - E_b - E_c + E_d)t / \hbar\right] &\approx 1 \\ E_a - E_b - E_c + E_d &\approx 0 \end{aligned} \quad (15.100)$$

which is satisfied when:

$$\begin{aligned} a = c ; b = d &\quad \Rightarrow R_{ab,ab} \\ a = b ; c = d &\quad \Rightarrow R_{aa,cc} \\ a = b = c = d &\quad \Rightarrow R_{aa,aa} \end{aligned} \quad (15.101)$$

In evaluating relaxation rates, often only these *secular* terms are retained. Whether this approximation is valid must be considered on a case by case basis and depends on the nature of the system eigenvalues and the bath correlation function.

Population Relaxation and the Master Equation

To understand the information in the relaxation operator and the classification of relaxation processes, let's first consider the relaxation of the diagonal elements of the reduced density matrix. Using the secular approximation,

$$\dot{\sigma}_{aa}(t) = -\sum_b R_{aa,bb} \sigma_{bb}(t) \quad (15.102)$$

Considering first the case that $a \neq b$, eq. (15.97) gives the relaxation operator as

$$R_{aa,bb} = -\Gamma_{ba,ab}^+ - \Gamma_{ba,ab}^- \quad (15.103)$$

Recognizing that Γ^+ and Γ^- are Hermitian conjugates,

$$\begin{aligned}
R_{aa,bb} &= -\frac{1}{\hbar^2} |A_{ab}|^2 \int_0^\infty d\tau C_{\beta\beta}(\tau) e^{-i\omega_{ba}\tau} + c.c. \\
&= -\frac{1}{\hbar^2} \int_0^\infty d\tau \langle V_{ba}(\tau) V_{ab}(0) \rangle_B e^{-i\omega_{ab}\tau} + c.c.
\end{aligned} \tag{15.104}$$

So $R_{aa,bb}$ is a real valued quantity. However, since $\langle V_{ba}(\tau) V_{ab}(0) \rangle = \langle V_{ba}(0) V_{ab}(-\tau) \rangle$,

$$R_{aa,bb} = -\frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_{ba}(\tau) V_{ab}(0) \rangle_B e^{i\omega_{ba}\tau} \tag{15.105}$$

So we see that the relaxation tensor gives the population relaxation rate between states a and b that we derived from Fermi's Golden rule:

$$R_{aa,bb} = -w_{ab} \quad (a \neq b). \tag{15.106}$$

For the case that $a = b$, eq. (15.97) gives the relaxation operator as

$$\begin{aligned}
R_{aa,aa} &= -(\Gamma_{aa,aa}^+ + \Gamma_{aa,aa}^-) + \sum_k (\Gamma_{ak,ka}^+ + \Gamma_{ak,ka}^-) \\
&= \sum_{k \neq a} (\Gamma_{ak,ka}^+ + \Gamma_{ak,ka}^-)
\end{aligned} \tag{15.107}$$

The relaxation accounts for the bath-induced dissipation for interactions with all states of the system (last term), but with the influence of self-relaxation (first term) removed. The net result is that we are left with the net rate of relaxation from a to all other system states ($a \neq k$)

$$R_{aa,aa} = \sum_{k \neq a} w_{ka} \tag{15.108}$$

This term $R_{aa,aa}$ is also referred to as the inverse of T_1 , the population lifetime of the a state.

The combination of these observations shows that the diagonal elements of the reduced density matrix follow a master equation that describes the net gain and loss of population in a particular state

$$\dot{\sigma}_{aa}(t) = \sum_{b \neq a} w_{ab} \sigma_{bb}(t) - \sum_{k \neq a} w_{ka} \sigma_{aa}(t) \tag{15.109}$$

Coherence Relaxation

Now let's consider the relaxation of the off-diagonal elements of the reduced density matrix. It is instructive to limit ourselves at first to one term in the relaxation operator, so that we write the equation of motion as

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab} \sigma_{ab}(t) - R_{ab,ab} \sigma_{ab}(t) + \dots \tag{15.110}$$

The relaxation operator gives

$$R_{ab,ab} = -\left(\Gamma_{aa,bb}^+ + \Gamma_{aa,bb}^-\right) + \sum_k \left(\Gamma_{ak,ka}^+ + \Gamma_{bk,kb}^-\right) \quad (15.111)$$

$$= -\left(\Gamma_{aa,bb}^+ + \Gamma_{aa,bb}^- - \Gamma_{aa,aa}^+ - \Gamma_{bb,bb}^-\right) + \left(\sum_{k \neq a} \Gamma_{ak,ka}^+ + \sum_{k \neq b} \Gamma_{bk,kb}^-\right) \quad (15.112)$$

In the second step, we have separated the sum into two terms, one involving relaxation constants for the two coherent states, and the second involving all other states. The latter term looks very similar to the relaxation rates in eq. (15.107). In fact, if we factor out the imaginary parts of these terms and add them as a correction to the frequency in eq. (15.110), $\omega_{ab} \rightarrow \omega_{ab} + \text{Im}[\text{term 2}]$, then the remaining expression is directly related to the population lifetimes of the a and b states:

$$\begin{aligned} \text{Re} \left(\sum_{k \neq a} \Gamma_{ak,ka}^+ + \sum_{k \neq b} \Gamma_{bk,kb}^- \right) &= \frac{1}{2} \sum_{k \neq b} w_{kb} - \frac{1}{2} \sum_{k \neq a} w_{ka} \\ &= \frac{1}{2} \left(\frac{1}{T_{1,a}} + \frac{1}{T_{1,b}} \right) \end{aligned} \quad (15.113)$$

This term accounts for the decay of the coherence as a sum of the rates of relaxation of the a and b states.

The meaning of the first term on the right hand side of eq. (15.112) is a little less obvious. If we write out the four contributing relaxation factors explicitly using the system–bath correlation functions in eqs. (15.98) and (15.99), the real part can be written as

$$\begin{aligned} \text{Re} \left(\Gamma_{aa,bb}^+ + \Gamma_{aa,bb}^- - \Gamma_{aa,aa}^+ - \Gamma_{bb,bb}^- \right) &= \int_0^\infty d\tau \left\langle \left[V_{bb}(\tau) - V_{aa}(\tau) \right] \left[V_{bb}(0) - V_{aa}(0) \right] \right\rangle_B \\ &\equiv \int_0^\infty d\tau \left\langle \Delta V(\tau) \Delta V(0) \right\rangle_B \end{aligned} \quad (15.114)$$

In essence, this term involves an integral over a correlation function that describes variations in the a - b energy gap that varies as a result of its interactions with the bath. So this term, in essence, accounts for the fluctuations of the energy gap that we previously treated with stochastic models. Of course in the current case, we have made a Markovian bath assumption, so the fluctuations are treated as rapid and only assigned an interaction strength Γ which is related to the linewidth. In an identical manner to the fast modulation limit of the stochastic model we see that the relaxation rate is related to the square of the amplitude of modulation times the correlation time for the bath:

$$\begin{aligned}
 \int_0^{\infty} d\tau \langle \Delta V(\tau) \Delta V(0) \rangle_B &= \langle \Delta V^2 \rangle \tau_c \\
 &\equiv \Gamma \\
 &= \frac{1}{T_2^*}
 \end{aligned}
 \tag{15.115}$$

As earlier this is how the pure dephasing contribution to the Lorentzian lineshape is defined. It is also assigned a time scale T_2^* .

So to summarize, we see that the relaxation of coherences has a contribution from pure-dephasing and from the lifetime of the states involved. Explicitly, the equation of motion in eq. (15.110) can be re-written

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab}\sigma_{ab}(t) - \frac{1}{T_2}\sigma_{ab}(t)
 \tag{15.116}$$

where the dephasing time is

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2} \left(\frac{1}{T_{1,a}} + \frac{1}{T_{1,b}} \right)
 \tag{15.117}$$

and the frequency has been corrected as a result interactions with the bath with the (small) imaginary contributions to $R_{ab,ab}$:

$$\omega_{ab} = \omega_{ab} + \text{Im}[R_{ab,ab}]
 \tag{15.118}$$

Readings

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