

16.2: 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 $|\alpha\rangle$.

$$H_0 = H_S + H_B \quad (16.2.1)$$

with

$$H_S|a\rangle = E_a|a\rangle \quad (16.2.2)$$

$$H_B|\alpha\rangle = E_\alpha|\alpha\rangle \quad (16.2.3)$$

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

$$|\psi(t_0)\rangle = |\psi_S^0\rangle|\psi_B^0\rangle \quad (16.2.4)$$

with

$$|\psi_S^0\rangle = \sum_a s_a |a\rangle \quad (16.2.5)$$

$$|\psi_B^0\rangle = \sum_\alpha b_\alpha |\alpha\rangle \quad (16.2.6)$$

$$|\psi_0\rangle = \sum_{a,\alpha} s_a b_\alpha |a\rangle |\alpha\rangle \quad (16.2.7)$$

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

$$H = H_0 + V \quad (16.2.8)$$

$$|\psi(t)\rangle = \sum_{a,\alpha} c_{a\alpha} |a\rangle |\alpha\rangle \quad (16.2.9)$$

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

$$\langle A(t) \rangle = \langle \psi(t) | A | \psi(t) \rangle = \langle \psi_S | A | \psi_S \rangle \quad (16.2.10)$$

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

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

$$\rho_S = |\psi_S\rangle\langle\psi_S| \quad (16.2.11)$$

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.

$$|b\rangle\rho_S\langle a| = \sum_{\alpha} c_{a\alpha}^* c_{b\alpha} \quad (16.2.12)$$

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: $\langle A(t) \rangle = \text{Tr}[\rho A]$, the following definitions are useful:

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

Also,

$$\text{Tr}(A \times B) = \text{Tr}(A) \text{Tr}(B) \quad (16.2.13)$$

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.

$$\rho_S = \sum_m |m\rangle\langle m| \rho_{mm} \quad (16.2.14)$$

$$\sum_m \rho_{mm} = 1 \quad (16.2.15)$$

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

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

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

$$|\psi_S\rangle = \sum_m d_m |m\rangle \quad (16.2.16)$$

$$d_m = \sum_{\alpha} f_{m\alpha} \quad (16.2.17)$$

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 Equation 16.2.1 and 16.2.8. In our observations, we will be interested in expectation values in A which we have seen are written

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

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

$$\sigma_{ab} = \sum_{\alpha} \langle a\alpha | \rho | b\alpha \rangle = \text{Tr}_B \rho_{ab} \quad (16.2.18)$$

Tr_B and Tr_S are partial traces over the bath and system respectively. Note, that since

$$\text{Tr}(A \times B) = \text{Tr} A \text{Tr} B \quad (16.2.19)$$

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

$$\rho(t) = U(t)\rho(0)U^\dagger(t) \quad (16.2.20)$$

and tracing over bath:

$$\sigma(t) = \text{Tr}_B [U\rho U^\dagger] \quad (16.2.21)$$

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

$$\dot{\rho}_I = -\frac{i}{\hbar} [V_I(t), \rho_I(t)] \quad (16.2.22)$$

to obtain

$$\rho_I(t) = \rho_I(0) - \frac{i}{\hbar} \int_0^t d\tau [V_I(\tau), \rho_I(\tau)] \quad (16.2.23)$$

Remember that the density matrix in the interaction picture is

$$\rho_I(t) = U_0^\dagger \rho(t) U_0 = e^{i(H_S+H_B)t/\hbar} \rho(t) e^{-i(H_S+H_B)t/\hbar} \quad (16.2.24)$$

and similarly

$$V_I(t) = U_0^\dagger V U_0 = e^{i(H_S+H_B)t/\hbar} V(t) e^{-i(H_S+H_B)t/\hbar} \quad (16.2.25)$$

Substituting Equation 16.2.23 into Equation 16.2.22 we have

$$\dot{\rho}_I(t) = -\frac{i}{\hbar} [V_I(t), \rho_I(t_0)] - \frac{1}{\hbar^2} \int_0^t dt' [V_I(t), [V_I(t'), \rho_I(t')]] \quad (16.2.26)$$

Now taking a trace over the bath states

$$\dot{\sigma}_I(t) = -\frac{i}{\hbar} \text{Tr}_B [V_I(t), \rho_I(t_0)] - \frac{1}{\hbar^2} \int_0^t dt' \text{Tr}_B [V_I(t), [V_I(t'), \rho_I(t')]] \quad (16.2.27)$$

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

$$\rho_I(t) \approx \sigma_I(t) \rho_B(0) = \sigma_I(t) \rho_{eq}^B \quad (16.2.28)$$

$$\rho_{eq}^B = \frac{e^{-\beta H_B}}{Z} \quad (16.2.29)$$

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

$$\dot{\sigma}_I(t) = -\frac{i}{\hbar} \text{Tr}_B [V_I(t), \sigma_I(0) \rho_{eq}^B] - \frac{1}{\hbar^2} \int_0^t dt' \text{Tr}_B [V_I(t), [V_I(t'), \sigma_I(t') \rho_{eq}^B]] \quad (16.2.30)$$

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 Equation 16.2.30 involves a thermal average over the interaction potential,

$$\langle V \rangle_B = \text{Tr}_B [V \rho_{eq}^B]. \quad (16.2.31)$$

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 $\hat{\beta}$

$$H_{sB} = V = \hat{A} \hat{\beta} \quad (16.2.32)$$

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): $V = c \rho q$. The time evolution in the two variables is separable and given by

$$\begin{aligned} \hat{A}(t) &= U_S^\dagger \hat{A}(t_0) U_S \\ \hat{\beta}(t) &= U_B^\dagger \hat{\beta}(t_0) U_B \end{aligned} \quad (16.2.33)$$

The equation of motion for σ_I becomes

$$\begin{aligned} \dot{\sigma}_I(t) &= \frac{1}{\hbar^2} \int_0^t dt' \left[\hat{A}(t) \hat{A}(t') \sigma(t') - \hat{A}(t') \sigma(t') \hat{A}(t) \right] \text{Tr}_B \left(\hat{\beta}(t) \hat{\beta}(t') \rho_{eq}^B \right) \\ &\quad - \left[\hat{A}(t) \sigma(t') \hat{A}(t') - \sigma(t') \hat{A}(t') \hat{A}(t) \right] \text{Tr}_B \left(\hat{\beta}(t') \hat{\beta}(t) \rho_{eq}^B \right) \end{aligned} \quad (16.2.34)$$

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

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

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

$$\tau = t - t' \quad (16.2.35)$$

we obtain

$$\dot{\sigma}_I(t) = -\frac{1}{\hbar^2} \int_0^t d\tau \left[\hat{A}(t), \hat{A}(t-\tau) \sigma_I(t-\tau) \right] C_{\beta\beta}(\tau) - \left[\hat{A}(t), \sigma_I(t-\tau) \hat{A}(t-\tau) \right] C_{\beta\beta}^*(\tau) \quad (16.2.36)$$

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

$$V = \sum_{\alpha} \hat{A} \hat{\beta}_{\alpha} \quad (16.2.37)$$

then Equation 16.2.36 becomes

$$\dot{\sigma}_I(t) = -\frac{1}{\hbar^2} \sum_{\alpha, \beta} \int_0^t d\tau \left[\hat{A}(t), \hat{A}(t-\tau) \sigma_I(t-\tau) \right] C_{\alpha\beta}(\tau) - \left[\hat{A}(t), \sigma_I(t-\tau) \hat{A}(t-\tau) \right] C_{\alpha\beta}^*(\tau) \quad (16.2.38)$$

with the bath correlation function

$$C_{\alpha\beta}(\tau) = \langle \hat{\beta}_{\alpha}(\tau) \hat{\beta}_{\beta}(0) \rangle_B \quad (16.2.39)$$

Equation 16.2.36 or 16.2.38 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

$$\sigma(t') = \sigma(t') \delta(t - t') \Rightarrow \sigma(t) \quad (16.2.40)$$

in Equation 16.2.34 or equivalently in Equation 16.2.36 set

$$\sigma_I(t - \tau) \Rightarrow \sigma_I(t) \quad (16.2.41)$$

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 Equation 16.2.36 from t to ∞ .

$$\begin{aligned} \dot{\sigma}_{ab}(t) = & -i\omega_{ab}\sigma_{ab}(t) - \frac{1}{\hbar^2} \sum_{c,d} [\hat{A}_{ac}\hat{A}_{cd}\sigma_{db}(t)\tilde{C}_{\beta\beta}(\omega_{dc}) - \hat{A}_{ac}\hat{A}_{db}\sigma_{cd}(t)\tilde{C}_{\beta\beta}(\omega_{ca}) - \hat{A}^2\hat{A}_{db}\sigma_{cd}(t)\tilde{C}_{\beta\beta}^*(-\omega_{db}) \\ & + \hat{A}_{cd}\hat{A}_{db}\sigma_{ac}(t)\tilde{C}_{\beta\beta}^*(-\omega_{cd})] \end{aligned} \quad (16.2.42)$$

$$\begin{aligned} \dot{\sigma}_{ab}(t) = & -i\omega_{ab}\sigma_{ab}(t) - \frac{1}{\hbar^2} \sum_{c,d} [\hat{A}_{ac}\hat{A}_{cd}\sigma_{db}(t)\tilde{C}_{\beta\beta}(\omega_{dc}) - \hat{A}_{ac}\hat{A}_{db}\sigma_{cd}(t)\tilde{C}_{\beta\beta}(\omega_{ca}) - \hat{A}^2\hat{A}_{db}\sigma_{cd}(t)\tilde{C}_{\beta\beta}^*(-\omega_{db}) \\ & + \hat{A}_{cd}\hat{A}_{db}\sigma_{ac}(t)\tilde{C}_{\beta\beta}^*(-\omega_{cd})] \end{aligned} \quad (16.2.43)$$

The rate constants are defined through:

$$\Gamma_{ab,cd}^+ = \frac{1}{\hbar^2} A_{ab} A_{cd} \tilde{C}_{\beta\beta}(\omega_{dc}) \quad (16.2.44)$$

$$\Gamma_{ab,cd}^- = \frac{1}{\hbar^2} A_{ab} A_{cd} \tilde{C}_{\beta\beta}(\omega_{ba}) \quad (16.2.45)$$

Here we made use of

$$\tilde{C}_{\beta\beta}^*(\omega) = \tilde{C}_{\beta\beta}(-\omega). \quad (16.2.46)$$

Also, it is helpful to note that

$$\Gamma_{ab,cd}^+ = [\Gamma_{dc,ba}^-]^* \quad (16.2.47)$$

The coupled differential equations in Equation 16.2.43 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.

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 Equation 16.2.36 to write the time-dependent matrix elements as

$$\dot{\sigma}_I(t) = -\frac{1}{\hbar^2} \sum_{\alpha,\beta} \int_0^t d\tau [\hat{A}(t), \hat{A}(t-\tau)\sigma_I(t-\tau)] C_{\alpha\beta}(\tau) - [\hat{A}(t), \sigma_I(t-\tau)\hat{A}(t-\tau)] C_{\alpha\beta}^*(\tau) \quad (16.2.48)$$

Now, let's convert the time dependence expressed in terms of the interaction picture into a Schrödinger representation using

$$\langle a | A(t) | b \rangle = e^{i\omega_{ab}t} A_{ab} \quad (16.2.49)$$

$$\langle a | \sigma^I | b \rangle = e^{i\omega_{ab}t} \sigma_{ab} \quad (16.2.50)$$

with

$$\sigma_{ab} = \frac{\partial}{\partial t} \langle a | \sigma^I | b \rangle \quad (16.2.51)$$

To see how this turns out, consider the first term in Equation 16.2.48

$$\dot{\sigma}_{ab}^I(t) = - \sum_{c,d} \frac{1}{\hbar^2} \int_0^\infty d\tau \hat{A}_{ac}(t) \hat{A}_{cd}(t-\tau) \sigma_{db}^I(t) C_{\beta\beta}(\tau) \quad (16.2.52)$$

$$\dot{\sigma}_{ab}(t)e^{i\omega_{bb}t} + i\omega_{ab}e^{i\omega_{bb}t}\sigma_{ab} = -\sum_{c,d} \frac{1}{\hbar^2} \hat{A}_{ac} \hat{A}_{cd} \sigma_{db}(t) e^{i\omega_a t + i\omega_{cd}t + i\omega_{bb}t} \int_0^\infty d\tau e^{-i\omega_{ct}\tau} C_{\beta\beta}(\tau) \quad (16.2.53)$$

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

$$\tilde{C}_{\beta\beta}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} C_{\beta\beta}(\tau) \quad (16.2.54)$$

We have

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab}\sigma_{ab} - \sum_{c,d} \frac{1}{\hbar^2} \hat{A}_{ac} \hat{A}_{cd} \sigma_{db}(t) \tilde{C}_{\beta\beta}(\omega_{dc}) \quad (16.2.55)$$

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, Equation 16.2.48 becomes

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

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab}\sigma_{ab} - \sum_{c,d} R_{ab,cd} \sigma_{cd}(t) \quad (16.2.56)$$

or in the interaction picture

$$\dot{\sigma}_{ab}^I(t) = \sum_{c,d} \sigma_{cd}^I(t) R_{ab,cd} e^{i(E_a - E_b - E_c + E_d)t/\hbar} \quad (16.2.57)$$

Equation 16.2.56 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:

$$R_{ab,cd} = \delta_{db} \sum_k \Gamma_{ak,kc}^+ - \Gamma_{db,ad}^+ - \Gamma_{db,ad}^- + \delta_{ac} \sum_k \Gamma_{dk,kb}^- \quad (16.2.58)$$

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 Equation 16.2.32. If so, one can write the relaxation operator in terms of a correlation function for the system–bath interaction,

$$\Gamma_{ab,cd}^+ = \frac{1}{\hbar^2} \int_0^\infty d\tau \langle V_{ab}(\tau) V_{cd}(0) \rangle_B e^{-i\omega_{cd}\tau} \quad (16.2.59)$$

$$\Gamma_{ab,cd}^- = \frac{1}{\hbar^2} \int_0^\infty d\tau \langle V_{ab}(0) V_{cd}(\tau) \rangle_B e^{-i\omega_{ab}\tau} \quad (16.2.60)$$

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 Equation 16.2.57 we note that the largest changes in matrix elements of σ_I result from a resonance condition:

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

which is satisfied when:

$$\begin{aligned}
 a = c; b = d &\Rightarrow R_{ab,ab} \\
 a = b; c = d &\Rightarrow R_{aa,cc} \\
 a = b = c = d &\Rightarrow R_{aa,aa}
 \end{aligned}
 \tag{16.2.61}$$

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,

$$\dot{\sigma}_{aa}(t) = - \sum_b R_{aa,bb} \sigma_{bb}(t) \tag{16.2.62}$$

Considering first the case that $a \neq b$, Equation 16.2.58 gives the relaxation operator as

$$R_{aa,bb} = -\Gamma_{ba,ab}^+ - \Gamma_{ba,ab}^- \tag{16.2.63}$$

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

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

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

$$R_{aa,bb} = -\frac{1}{\hbar^2} \int_{-\infty}^{+\infty} dt \langle V_{ba}(\tau) V_{ab}(0) \rangle_B e^{i\omega_{ab}\tau} \tag{16.2.64}$$

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:

$$R_{aa,bb} = -w_{ab} \tag{16.2.65}$$

if $a \neq b$.

For the case that $a = b$, Equation 16.2.58 gives the relaxation operator as

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

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 ($a \neq k$)

$$R_{aa,aa} = \sum_{k \neq a} w_{ka} \tag{16.2.66}$$

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

$$\dot{\sigma}_{aa}(t) = \sum_{b \neq a} w_{ab} \sigma_{bb}(t) - \sum_{k \neq a} w_{ka} \sigma_{aa}(t) \tag{16.2.67}$$

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

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab} \sigma_{ab}(t) - R_{ab,ab} \sigma_{ab}(t) + \dots \tag{16.2.68}$$

The relaxation operator gives

$$R_{ab,ab} = -\left(\Gamma_{aa,bb}^+ + \Gamma_{aa,bb}^-\right) + \sum_k \left(\Gamma_{ak,ka}^+ + \Gamma_{bk,kb}^-\right) \quad (16.2.69)$$

$$= -\left(\Gamma_{aa,bb}^+ + \Gamma_{aa,bb}^- - \Gamma_{aa,aa}^+ - \Gamma_{bb,bb}^-\right) + \left(\sum_{k \neq a} \Gamma_{ak,ka}^+ + \sum_{k \neq b} \Gamma_{bk,kb}^-\right) \quad (16.2.70)$$

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 fact, if we factor out the imaginary parts of these terms and add them as a correction to the frequency in Equation 16.2.68 $\omega_{ab} \rightarrow \omega_{ab} + \text{Im}[term2]$, then the remaining expression is directly related to the population lifetimes of the a and b states:

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

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 Equation 16.2.70 is a little less obvious. If we write out the four contributing relaxation factors explicitly using the system–bath correlation functions in Equation 16.2.59 and 16.2.60 the real part can be written as

$$\text{Re}\left(\Gamma_{aa,bb}^+ + \Gamma_{aa,bb}^- - \Gamma_{bb,ab}^+ - \Gamma_{bb,bb}^-\right) = \int_0^\infty d\tau \langle [V_{bb}(\tau) - V_{aa}(\tau)] [V_{bb}(0) - V_{aa}(0)] \rangle_B \quad (16.2.71)$$

$$\equiv \int_0^\infty d\tau \langle \Delta V(\tau) \Delta V(0) \rangle_B \quad (16.2.72)$$

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:

$$\int_0^\infty d\tau \langle \Delta V(\tau) \Delta V(0) \rangle_B = \langle \Delta V^2 \rangle \tau_c \quad (16.2.73)$$

$$\equiv \Gamma \quad (16.2.74)$$

$$= \frac{1}{T_2^*} \quad (16.2.75)$$

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 Equation 16.2.68 can be re-written

$$\dot{\sigma}_{ab}(t) = -i\omega_{ab}\sigma_{ab}(t) - \frac{1}{T_2}\sigma_{ab}(t) \quad (16.2.76)$$

where the dephasing time is

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2} \left(\frac{1}{T_{1,a}} + \frac{1}{T_{1,b}} \right) \quad (16.2.77)$$

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

$$\omega_{ab} = \omega_{ab} + \text{Im}[R_{ab,ab}] \quad (16.2.78)$$

Readings

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