A general treatment of relaxation phenomena
(reservoir/subsystems/Liouville equation/density motion/singular perturbation method)

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ABSTRACT The singular perturbation method has been applied to solve the quantum mechanical Liouville equation for the relaxation phenomenon of the system in thermal contact with a heat bath. The master equation derived gives the proper expressions for both diagonal and off-diagonal elements of the density matrix and is capable of describing the time-dependent behavior of the system in the time range comparable with the reciprocal of the damping constants and the time range $t \to \infty$ compared with the reciprocal of the damping constants.

1. Introduction

The singular perturbation method has been applied to solve problems in fluid mechanics (1), nonlinear mechanics (2), kinetic theory of gases and plasmas (3, 4), chemical kinetics (5, 6), spontaneous radiation process (7), etc. In this paper, we shall show how to apply the singular perturbation method to the solution of the quantum mechanical Liouville equation of the relaxation phenomenon. Using this method, we shall derive a master equation for a system in contact with a heat bath which can give a proper time-dependent behavior of both diagonal and off-diagonal parts of the density matrix of the system so that the master equation can be employed to study the optical phenomena where the resonance effect is important.

The starting point of the present investigation is to take advantage of the general ideas developed by Zwanzig, Wangness and Bloch, Argyres, Emch and Sewell, Fano, etc. (refs. 8–11; references given in ref. 8); the idea is to consider an isolated system which can be divided into a "reservoir" (or "heat bath") and a "system" (or "system of interest") and to eliminate the irrelevant part of the density matrix to obtain the equation of motion for the reduced density matrix of the system. The value of such an equation is that macroscopic variables of the reservoir occur in a natural way in the equation of motion and that only a statistical assumption at an initial time is used.

2. General consideration

The dependence of the density matrix $\hat{p}(t)$ is determined by the Liouville equation of motion

$$\frac{\partial \hat{p}}{\partial t} = -\frac{i}{\hbar} (\hat{H} - \hat{\rho} \hat{H}) = -iL \hat{p} \quad [2-1]$$

in which $L$ represents the Liouville operator. The total system consists of a part called the system of interest with Hamiltonian $\hat{H}_s$ and of a heat bath with Hamiltonian $\hat{H}_b$. If we let $\hat{H}_s$ represent the interaction between the two parts, then the Hamiltonian of the total system can be written as

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_1 = \hat{H}_0 + \hat{H}_1. \quad [2-2]$$

In accordance with Eq. 2-1, the corresponding Liouville operator takes the form

$$\hat{L} = \hat{L}_s + \hat{L}_b + \hat{L}_1 = \hat{L}_0 + \hat{L}_1 \quad [2-3]$$

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In this section, we are mainly concerned with the elimination of the heat bath variables and the derivation of the equation of motion for the density matrix of the system of interest. For this purpose many approaches have been developed (8–11). Here Fano's method will be used, although some minor details will be different. For convenience of discussion, the derivation is briefly outlined in the following.

Applying the Laplace transformation to Eq. 2-1 yields

$$\hat{\rho}(p) = \frac{1}{p + iL} \hat{\rho}(0) \quad [2-4]$$

in which $\hat{\rho}(0)$ represents the density matrix of the total system at $t = 0$ and $\hat{\rho}(p)$ denotes the Laplace transform of $\hat{\rho}(t)$,

$$\hat{\rho}(p) = \int_0^\infty e^{-pt} \hat{\rho}(t) dt. \quad [2-5]$$

Following Fano (9), we introduce transition operator $\hat{M}(p)$ defined by

$$\hat{M}(p) = \frac{1}{p + iL_0} \left[ 1 + \hat{M}(p) \frac{1}{p + iL_0} \right]. \quad [2-6]$$

$\hat{M}(p)$ can be put into the following form,

$$\hat{M}(p) = (-iL_1) + (iL_1) \frac{1}{p + iL} (-iL_1). \quad [2-7]$$

Substituting Eq. 2-6 into Eq. 2-4 yields

$$\hat{\rho}(p) = \frac{1}{p + iL_0} \left[ 1 + \hat{M}(p) \frac{1}{p + iL_0} \right] \hat{\rho}(0). \quad [2-8]$$

Notice that the density matrix of the system of interest at time $t$ can be found by

$$\hat{\rho}^{(s)}(t) = T_{bs}[\hat{\rho}(t)] \quad [2-9]$$

or equivalently

$$\hat{\rho}^{(s)}(p) = T_{bs}[\hat{\rho}(p)] \quad [2-10]$$

in which $T_{bs}$ represents the operation of carrying out a trace over the quantum states of the heat bath. To eliminate the reservoir variables we shall assume that at $t = 0$,

$$\hat{\rho}(0) = \hat{\rho}^{(s)}(0) \hat{\rho}^{(b)}(0) \quad [2-11]$$

Combining Eqs. 2-11 and 2-10 with Eq. 2-8, we obtain

$$\hat{\rho}^{(s)}(p) = \frac{1}{p + iL_0} \left( 1 + \langle M(p) \rangle \frac{1}{p + iL_0} \right) \hat{\rho}^{(s)}(0) \quad [2-12]$$

in which $\langle M(p) \rangle = T_{bs}[\hat{M}(p) \hat{\rho}^{(b)}(0)]$.

Eq. 2-12 can be conveniently expressed as (9)

$$\hat{\rho}^{(s)}(p) = \frac{1}{p + iL_0 + \langle M_c(p) \rangle} \hat{\rho}^{(s)}(0) \quad [2-13]$$

in which

$$\langle M_c(p) \rangle = \frac{1}{1 + \langle M(p) \rangle (p + iL_0)^{-1}} \left( -\langle \hat{M}(p) \rangle \right) \quad [2-14]$$

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or
\[ \langle \dot{M}(p) \rangle = \langle \dot{M}_c(p) \rangle + \frac{1}{1 + \langle \dot{M}_c(p) \rangle (p + it_n)^{-1}}. \]  

Eq. 2-13 was obtained previously by Fano and Zwanzig. Notice that Eq. 2-13 can be rewritten as
\[ p \dot{\rho}^{(0)}(p) - \dot{\rho}^{(0)}(p) = -iL_\epsilon \dot{\rho}^{(0)}(p) - \langle \dot{M}_c(p) \rangle \dot{\rho}^{(0)}(p). \]  

Inverting the Laplace transformation of Eq. 2-16, we obtain
\[ \frac{\partial \hat{p}^{(s)}(t)}{\partial t} = -iL_\epsilon \hat{p}^{(s)}(t) - \int_0^t d\tau \langle \dot{M}_c(\tau) \rangle \hat{p}^{(s)}(t - \tau) \]  

in which
\[ \langle \dot{M}_c(p) \rangle = \int_0^\infty e^{-pt} \langle \dot{M}_c(t) \rangle dt. \]

Eq. 2-13 and 2-17 are equivalent and both are useful for finding the density matrix of the system of interest at \( t > 0 \).

Next we consider Eq. 2-17. Notice that
\[ \hat{p}^{(s)}(t - \tau) = \sum \frac{1}{n!} (-\tau)^n \frac{\partial^n \hat{p}^{(s)}(t)}{\partial \tau^n}. \]

Using Eq. 2-19, Eq. 2-20 becomes
\[ \frac{\partial \hat{p}^{(s)}(t)}{\partial t} = -iL_\epsilon \hat{p}^{(s)}(t) - \hat{\Gamma}(t) \hat{p}^{(s)}(t) \]  

in which
\[ \hat{\Gamma}(t) = \int_0^t d\tau \langle \dot{M}_c(\tau) \rangle. \]

In the Markoff approximation, \( \hat{\Gamma}(\omega) \) plays the role of the damping matrix in the approximate expression of the equation of motion of \( \hat{p}^{(s)}(t) \) given by Eq. 2-21.

3. Singular perturbation method

According to the singular perturbation method, we replace the original single time variable \( t \) by \( t_0, t_1, t_2 \ldots \) in which \( t_n = \lambda^n t \) and \( \lambda \) represents the perturbation parameter associated with \( L_1 \). All \( t_n \) values are treated as independent variables. \( \hat{p}^{(s)}(t) \) is expanded as follows
\[ \hat{p}^{(s)}(t) = \hat{p}^{(s)}(0) + \lambda \hat{p}^{(1)}(0) + \lambda^2 \hat{p}^{(2)}(0) + \ldots \]  

Notice that
\[ \hat{K}_n(t) = \lambda \hat{K}_n^{(1)}(t) + \lambda^2 \hat{K}_n^{(2)}(t) + \ldots \]  

in which
\[ \hat{K}_n^{(m)}(t) = \frac{1}{n!} \int_0^{t_n} d\tau (-\tau)^m \langle \dot{M}_c^{(m)}(\tau) \rangle \]  

and
\[ \langle \dot{M}_c(\tau) \rangle = \lambda \langle \dot{M}_c(\tau) \rangle + \lambda^2 \langle \dot{M}_c^{(2)}(\tau) \rangle + \ldots \]  

with
\[ \langle \dot{M}_c^{(1)}(\tau) \rangle = 2t \langle \dot{L}_1 \delta(\tau) \rangle \]  
\[ \langle \dot{M}_c^{(2)}(\tau) \rangle = \langle \dot{L}_1 e^{-i\tau L_0} \dot{L}_1 \rangle - \langle \dot{L}_1 \rangle e^{-i\tau L_1} \]  

etc.

Substituting Eqs. 3-1 and 3-2 into Eq. 2-20, we obtain in the zeroth-order approximation,
\[ \frac{\partial \hat{p}^{(0)}(t)}{\partial t} = -iL_\epsilon \hat{p}^{(0)}(t); \]

in the first-order approximation,
\[ \frac{\partial \hat{p}^{(0)}(t)}{\partial t} + \frac{\partial \hat{p}^{(1)}(t)}{\partial t_0} = -iL_\epsilon \hat{p}^{(0)}(t) - \sum_{n=0}^{\infty} \hat{K}_n^{(1)}(t) \frac{\partial^n \hat{p}^{(0)}(t)}{\partial t_0^n}; \]

in the second-order approximation,
\[ \frac{\partial \hat{p}^{(0)}(t)}{\partial t_2} + \frac{\partial \hat{p}^{(1)}(t)}{\partial t_1} + \frac{\partial \hat{p}^{(2)}(t)}{\partial t_0} = -iL_\epsilon \hat{p}^{(0)}(t) - \sum_{n=0}^{\infty} \left[ \hat{K}_n^{(1)}(t) \frac{\partial^n \hat{p}^{(0)}(t)}{\partial t_0^n} + n \frac{\partial^n \hat{p}^{(0)}(t)}{\partial t_0^n} \right] \]  

etc.

Here the following relation has been used
\[ \frac{\partial}{\partial t} = \frac{\partial}{\partial t_0} + \lambda \frac{\partial}{\partial t_1} + \lambda^2 \frac{\partial}{\partial t_2} + \ldots \]

We first consider the zeroth-order equation, Eq. 3-7, which can be solved to yield
\[ \hat{p}^{(0)}(t)_{m,n} = \exp(\lambda t \omega_{m,n}) \hat{p}^{(0)}(t_0)_{m,n} \]

which can formally be written as
\[ \hat{\rho}^{(s)}(t) = \exp(\lambda t L_\epsilon) \hat{\rho}^{(0)}(t_0) \]

in which \( \hat{\rho}^{(0)}(t) = \hat{\rho}^{(0)}(t_0) \).

Next we consider the first-order approximation. Using the fact that
\[ \hat{K}^{(1)}(t) = \delta(L_1); \hat{K}^{(1)}(t) = 0 \quad n > 0 \]

Eq. 3-8 can be written as
\[ \frac{\partial \hat{p}^{(0)}(t)}{\partial t_1} + \frac{\partial \hat{p}^{(1)}(t)}{\partial t_0} = -\frac{\partial \hat{p}^{(0)}(t)}{\partial t_0} - iL_\epsilon \hat{p}^{(1)}(t) \]  

In terms of matrix elements, Eq. 3-14 becomes
\[ \frac{\partial}{\partial t_0} \rho_{01}(t_0)_{m,n} + \frac{i}{\hbar} \left( \langle \hat{H} \rangle_{m,m} - \langle \hat{H} \rangle_{n,n} \right) \rho_{01}(t_0)_{m,n} \]

\[ + \frac{i}{\hbar} \left( \sum_{m} \langle \hat{H} \rangle_{m,m} \text{exp}(it \omega_{m,n}) \rho_{01}(t_0)_{m,n} \right) \]

\[ - \sum_{n} \langle \hat{H} \rangle_{n,n} \text{exp}(it \omega_{n,n}) \rho_{01}(t_0)_{m,n} \]

\[ = - \frac{\partial}{\partial t_0} \left[ \text{exp}(it \omega_{m,n}) \rho_{01}(t_0)_{m,n} \right]. \]

In the limit of large \( t_0 \), the first two terms on the left-hand side of Eq. 3-15, which are independent of \( t_0 \), diverge linearly as \( t_0 \). This secular behavior of \( \rho_{01}(t_0)_{m,n} \) due to these terms may be eliminated by imposing the condition
\[ \frac{\partial}{\partial t_0} \rho_{01}(t_0)_{m,n} + \frac{i}{\hbar} \left( \langle \hat{H} \rangle_{m,m} - \langle \hat{H} \rangle_{n,n} \right) \rho_{01}(t_0)_{m,n} = 0. \]

This simply means that
\[ - \frac{\partial}{\partial t_0} \left[ \text{exp}(it \omega_{m,n}) \rho_{01}(t_0)_{m,n} \right] \]

\[ = \frac{i}{\hbar} \sum_{m} \langle \hat{H} \rangle_{m,m} \text{exp}(it \omega_{m,n}) \rho_{01}(t_0)_{m,n} \]

\[ - \frac{i}{\hbar} \sum_{n} \langle \hat{H} \rangle_{n,n} \text{exp}(it \omega_{n,n}) \rho_{01}(t_0)_{m,n}. \]
which can be integrated

\[ \rho_{1(t)}(t)_{m,n} = \exp(-it\omega_{m,n})\rho_{1(t)}(t)_{m,n} \]

\[ - \sum_{m'} \frac{(\hat{H}')_{m,n}}{\hbar\omega_{m,n'}} \rho^0(t)_{m,n} \]

\[ + \sum_{m'} \frac{(\hat{H}')_{m,n}}{\hbar\omega_{m,n'}} \rho^0(t)_{m,n'} \]  \[ [3-18] \]

in which \( \rho_{1(t)}(t)_{m,n} \) represents an arbitrary function. Eq. 3-16 shows that the effect of energy level shift enters in the first-order approximation, i.e.,

\[ \rho_{01(t)}(t)_{m,n} = \exp \left[ -\frac{\hbar}{\hbar} \left( (\hat{H}')_{m,n} \right) \right] \rho_{01(t)}(t)_{m,n}. \]  \[ [3-19] \]

Notice that \( \rho_{1(t)}(t)_{m,n} \) is given by

\[ \rho_{1(t)}(t)_{m,n} = \rho_{11(t)}(t)_{m,n} + \sum_{m'} \frac{(\hat{H}')_{m,n}}{\hbar\omega_{m,n'}} \rho^0(t)_{m,n} \]

\[ - \left( \hat{H}' \right)_{m,n} \]  \[ [3-20] \]

Now we consider the second-order approximation. Eq. 3-9 can be rewritten as

\[ \left[ \frac{\partial}{\partial t} \right] \rho_{1(t)}(t)_{m,n} + \left[ \frac{\partial}{\partial t} \right] \rho^0(t)_{m,n} + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{1(t)}^{(2)}(t)_{n,m,n} \rho_{1(t)}(t)_{m,n} \]

\[ - \hat{H}'_{m,n} \rho_{1(t)}(t)_{m,n} = \sum_{m'} \frac{(\hat{H}')_{m,n}}{\hbar\omega_{m,n'}} \rho^0(t)_{m,n} \]

\[ - i\omega_{m,n'} \rho^0(t)_{m,n'} \]  \[ [3-21] \]

or

\[ \left[ \frac{\partial}{\partial t} \right] \rho_{1(t)}(t)_{m,n} + \sum_{m'} \frac{(\hat{H}')_{m,n}}{\hbar\omega_{m,n'}} \rho^0(t)_{m,n} \]

\[ + \left[ \frac{\partial}{\partial t} \right] \rho^0(t)_{m,n} + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{1(t)}^{(2)}(t)_{n,m,n} \rho_{1(t)}(t)_{m,n} \]

\[ - \hat{H}'_{m,n} \rho_{1(t)}(t)_{m,n} = -i\omega_{m,n'} \rho^0(t)_{m,n'} \]  \[ [3-22] \]

Using the same argument as that used in the first-order approximation for removing the secular behavior of the density matrix elements, we obtain

\[ \frac{\partial}{\partial t} \rho_{02(t)}(t)_{m,n} + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{02(t)}^{(2)}(t)_{n,m,n} \rho_{02(t)}(t)_{m,n} \]

\[ + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{1(t)}^{(2)}(t)_{n,m,n} \rho_{1(t)}(t)_{m,n} \]

\[ \rho_{02(t)}(t)_{m,n} = 0, \]  \[ [3-23] \]

and

\[ \frac{\partial}{\partial t} \rho_{11(t)}(t)_{m,n} + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{1(t)}^{(2)}(t)_{n,m,n} \rho_{11(t)}(t)_{m,n} \]

\[ - \hat{H}'_{m,n} \rho_{11(t)}(t)_{m,n} = 0, \]  \[ [3-24] \]

and

\[ \frac{\partial}{\partial t} \rho_{12(t)}(t)_{m,n} = i\omega_{m,n} \rho_{12(t)}(t)_{m,n} \]

\[ + \sum_{m'} \frac{(\hat{H}')_{m,n}}{\hbar\omega_{m,n'}} \rho^0(t)_{m,n} \]

\[ + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{2(t)}^{(2)}(t)_{n,m,n} \rho_{12(t)}(t)_{m,n} \]

\[ \left[ \frac{\partial}{\partial t} \right] \rho_{12(t)}(t)_{m,n} \left[ \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{2(t)}^{(2)}(t)_{n,m,n} \rho_{12(t)}(t)_{m,n} \right] \]

\[ \left[ \frac{\partial}{\partial t} \right] \rho_{12(t)}(t)_{m,n} = 0, \]  \[ [3-25] \]

in which

\[ K_{n,m,n',n'}^{(2)} = \sum_{n=0}^{\infty} (-i\omega_{m,n})^n K_{n,m,n',n'}^{(2)}(t)_{m,n,n',n'} \]  \[ [3-26] \]

The terms like \( \sum_{n=0}^{\infty} \left( \hat{H}' \right)_{m,n} \) and \( \sum_{n=0}^{\infty} \left( \hat{H}' \right)_{n,m} \) are the second-order energy of the \( m \) and \( n \) states \( E_{m}^{(2)}(t) \) and \( E_{n}^{(2)} \).

For the diagonal elements of the density matrix, we have

\[ \frac{\partial}{\partial t} \rho_{11(t)}(t)_{m,n} = 0, \]  \[ [3-27] \]

\[ \frac{\partial}{\partial t} \rho_{02(t)}(t)_{m,n} + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{02(t)}^{(2)}(t)_{n,m,n} \rho_{02(t)}(t)_{m,n} \]

\[ + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{1(t)}^{(2)}(t)_{n,m,n} \rho_{1(t)}(t)_{m,n} \]

\[ \rho_{02(t)}(t)_{m,n} = 0, \]  \[ [3-28] \]

and

\[ \frac{\partial}{\partial t} \rho_{12(t)}(t)_{m,n} = i\omega_{m,n} \rho_{12(t)}(t)_{m,n} \]

\[ + \frac{\omega}{\hbar} \sum_{n=0}^{\infty} K_{1(t)}^{(2)}(t)_{n,m,n} \rho_{12(t)}(t)_{m,n} \]

\[ \rho_{12(t)}(t)_{m,n} = 0, \]  \[ [3-29] \]

in which

\[ K_{n,m,n',n'}^{(2)} = \sum_{n=0}^{\infty} (-i\omega_{m,n})^n K_{n,m,n',n'}^{(2)}(t)_{m,n,n',n'} \]  \[ [3-30] \]

In the limit \( t \to \infty \) which corresponds to the Markov approximation, we have

\[ K_{n,m,n',n'}^{(2)}(t)_{m,n,n',n'} = \frac{-2\pi}{\hbar^2} \sum_{n=0}^{\infty} \rho^0(t)_{n,m,n} \left| H_{n,m,n,n'} \right|^2 \]

\[ \times \delta(\omega_{m,n}) \]  \[ [3-31] \]

\[ K_{n,m,n',n'}^{(2)}(t)_{m,n,n',n'} = \frac{-2\pi}{\hbar^2} \sum_{n=0}^{\infty} \rho^0(t)_{n,m,n} \left| H_{n,m,n,n'} \right|^2 \]

\[ \times \delta(\omega_{n,m,n,n'}) \]  \[ [3-32] \]

and

\[ \sum_{n=0}^{\infty} K_{n,m,n',n'}^{(2)}(t)_{m,n,n',n'} = \sum_{n=0}^{\infty} \left| \left( \hat{H}' \right)_{n,m,n} \right|^2 \delta(\omega_{n,m,n,n'}) \]  \[ [3-33] \]

in which

\[ k_{n,m,n} = \frac{-2\pi}{\hbar^2} \sum_{n=0}^{\infty} \rho^0(t)_{n,m,n} \left| H_{n,m,n,n'} \right|^2 \delta(\omega_{n,m,n,n'}) \]  \[ [3-34] \]
and
\[ i\eta(\omega_{n,m_{n,n'}}) = \int_0^\infty dt \exp(\frac{i\eta}{\hbar} t\omega_{n,m_{n,n'}}). \]  \[3-35\]

The constant \( K^{(2)}_{n,m_{n,n'}} \) consists of the imaginary part, which yields the second-order energy level shift, and the real part, which plays the role of the relaxation rate constant of the off-diagonal density matrix element. Notice that the real part of \( K^{(2)}_{n,m_{n,n'}} \) is related to \( K^{(2)}(\omega)_{n,m_{n,n'}} \) and \( K^{(2)}(\omega)_{m_{n,m_{n}}} \) by the relation
\[ \text{Re}(K^{(2)}_{m_{n,m_{n}}}) = \frac{1}{2} [K^{(2)}(\omega)_{n,m_{n,n'}} + K^{(2)}(\omega)_{m_{n,m_{n}}}] + \frac{1}{\hbar^2} \]
\[ \times \sum_{m_{n}} \sum_{m_{n'}} \rho^{(b)}(t)_{n,m_{n}} |H'_{n,m_{n,n'}}|^2 + |H'_{m_{n,m_{n}}}|^2 \]
\[ \times \delta(\omega_{n,m_{n}}). \]  \[3-36\]

If \( H'_{n,m_{n,n'}} = H'_{m_{n,m_{n}}} = 0 \), then
\[ \text{Re}(K^{(2)}_{m_{n,m_{n}}}) = \frac{1}{2} [K^{(2)}(\omega)_{n,m_{n,n'}} + K^{(2)}(\omega)_{m_{n,m_{n}}}] ] . \]  \[3-37\]

Eq. 3-36 or Eq. 3-37 is a well-known relation (11–14); it has been derived only for the case in which the perturbation is the interaction between the radiation and molecules. Here we have shown that it holds in general.

Now we summarize the results for the time-dependent behavior of \( \rho^{(s)}(t) \). To the second-order approximation (or to the approximation valid up to the time scale \( t_2 \)), the solution of the Liouville equation by the singular perturbation method yields
\[ \frac{\partial}{\partial t} \rho^{(s)}(t)_{n,n'} = -\sum_{n''} K^{(2)}(\omega)_{n,n',n''} \rho^{(s)}(t)_{n'',n'} \]  \[3-38\]
and
\[ \frac{\partial}{\partial t} \rho^{(s)}(t)_{m_{n,n}} = -\left[ \omega_{m_{n,n}} + \frac{i}{\hbar} \left( \langle \hat{H}' \rangle_{m_{n,n}} + E_{m_{n}} \right) \right. \]
\[ \left. - \langle \hat{H}' \rangle_{n_{n,n'}} - E_{n_{n}} \right] + K^{(2)}_{m_{n,m_{n}}} \]  \[3-39\]
for \( m_{n} \neq n_{n} \), In other words, Eqs. 3-38 and 3-39 can be put in the form
\[ \frac{\partial}{\partial t} \hat{\rho}^{(s)} = -i\hat{L}_0 \hat{\rho}^{(s)} - \hat{\Gamma}^{(s)} \]  \[3-40\]
in which
\[ \Gamma^{(s)}_{m_{n,n},n_{n}} = \delta_{m_{n},n_{n}} K^{(2)}(\omega)_{n,n,n_{n}} \]  \[3-41\]
and
\[ \Gamma^{(s)}_{m_{n,m_{n},n_{n}}} = \delta_{m_{n},m_{n}} \delta_{n_{n},n_{n}} \left[ \frac{i}{\hbar} \left( \langle \hat{H}' \rangle_{m_{n},n_{n}} + E_{m_{n}} \right) \right. \]
\[ \left. - \langle \hat{H}' \rangle_{n_{n},n_{n}} - E_{n_{n}} \right] + K^{(2)}_{m_{n},m_{n}} \]  \[3-42\]
for \( m_{n} \neq n_{n} \), In terms of the damping matrix elements \( \Gamma^{(d)}_{m_{n},m_{n}} \), Eq. 3-35 becomes
\[ \text{Re}(\Gamma^{(d)}_{m_{n},m_{n}}) = \frac{1}{2} (\Gamma^{(d)}_{m_{n},m_{n}} + \Gamma^{(d)}_{m_{n},m_{n}}) \]
\[ + \Gamma^{(d)}_{m_{n},m_{n}} \]  \[3-43\]
in which \( \Gamma^{(d)}_{m_{n},m_{n}} \) is defined by
\[ \Gamma^{(d)}_{m_{n},m_{n}} = \frac{1}{\hbar^2} \sum_{m_{n}} \sum_{m_{n'}} \rho^{(b)}(0)_{m_{n},m_{n'}} |\langle H' \rangle_{m_{n},m_{n}}|^2 \]
\[ + |H'_{m_{n},m_{n}}|^2 \delta(\omega_{m_{n},m_{n}}). \]  \[3-44\]

Notice that in terms of the relaxation rate constants \( k_{m_{n}} \), we have
\[ \Gamma^{(d)}_{m_{n},m_{n}} = K^{(2)}(\omega)_{m_{n},m_{n}} = -k_{m_{n}} \]  \[3-45\]
and
\[ \Gamma^{(d)}_{m_{n},m_{n}} = \sum_{m_{n}} k_{m_{n}}. \]  \[3-46\]

The master equation given by Eq. 3-40 is widely used in nonlinear optics (13–15) and magnetic resonance (16). How the damping matrix results from interaction of the system with random fields has been a subject of extensive studies in magnetic resonance (16), but is not well understood in optical cases. However, it is usually believed that the lifetime broadening often dominates the linewidth of an optical transition (13–15). In this paper we derive Eq. 3-40 by using the singular perturbation method and give the damping constants (especially off-diagonal ones) a rigorous theoretical basis. From the above discussion, we can see that \( \Gamma \) should result from not only the radiative process but also other non-radiative processes that can deplete and/or populate the state or states involved in \( \Gamma \).

In the above derivation, we have only carried out the singular perturbation calculation up to the second-order approximation. Higher-order calculations can be carried out similarly and will not be pursued here. The vibrational dephasing process in condensed phases has been of recent interest both experimentally and theoretically. In this case, the off-diagonal portion of Eq. 3-40 is important; the investigation of this dephasing process is not yet complete.