

Relaxation in simple quantum systems*

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The decay of an oscillator and a two level system into a general heat bath is studied using a truncated cumulant expression for the time evolution operator. Expressions for the decay rate in the weak coupling and rotating wave approximations are derived, and the temperature dependence of the rate examined in all cases. We find the temperature dependence to be strongly dependent on the nature of the system and bath.

I. INTRODUCTION

The harmonic oscillator and the two level system, when weakly coupled to heat baths, have been widely applied as models for studying quantum relaxation phenomena.¹⁻⁵ Relaxation of a harmonic oscillator is used as a model for studying decay of optical modes in laser and maser cavities,^{1b} vibrational relaxation in molecules interacting with their surroundings,² and relaxation of phonons in solids due to anharmonic interactions.³ Relaxing two level systems are encountered in spin lattice relaxation problems⁴ and also in most of the studies on atomic and molecular electronic transitions when one focuses attention on only two particular levels.⁵

Theoretical studies of these relaxation phenomena have utilized both stochastic methods using phenomenological rate laws⁶ and approximate solution of the equations of motion obtained from various model Hamiltonians.¹⁻⁵ In this paper we study these processes by applying Kubo's⁷ cumulant expansion method to the time evolution operator of the system. This approach enables us to obtain approximate results for the time evolution of a harmonic oscillator or a two level system in contact with a thermal bath of general nature. This generalizes the results of recent work² which considered only a bath of harmonic oscillators, and is equivalent to the earlier work of Senitzky.⁸ The present derivation is much simpler than that of Senitzky and leads to a simple general expression for the relaxation rate in terms of an equilibrium time correlation function in the bath operators. It also provides a better understanding of the approximations invoked in previous work.

We first study the relaxation of a harmonic oscillator. We then repeat the derivation for the relaxation of a two level system. Next we investigate the expressions obtained for the decay rates, in particular their temperature dependence, for different types of baths. Finally we discuss the application of our results to radiative decay processes.

II. RELAXATION OF A HARMONIC OSCILLATOR

Consider a system characterized by the Hamiltonian

$$H = H_0 + V, \quad (1a)$$

$$H_0 = \epsilon \alpha^\dagger \alpha + H_B, \quad (1b)$$

$$V = F^\dagger \alpha + F \alpha^\dagger, \quad (1c)$$

where α^\dagger and α are creation and annihilation operators

for the harmonic oscillator, and ϵ is its frequency; H_B is the Hamiltonian of the free thermal bath, F is an operator in the medium's degrees of freedom, F^\dagger is its Hermitian conjugate. The oscillator-bath coupling is assumed to be of the form (1c). The operators F and F^\dagger are assumed to have no diagonal matrix elements in the bath eigenstates. \hbar is taken to be 1 throughout the calculation.

We shall be interested in the time evolution of the population of the oscillator which, for the free oscillator, is given by the expectation value of the operator

$$n = \alpha^\dagger \alpha. \quad (2)$$

The meaningful quantity for an oscillator coupled to a heat bath is the thermally averaged operator

$$\langle n \rangle = \text{tr}_B (\rho_B^{\text{eq}} n), \quad (3)$$

where ρ_B^{eq} is the equilibrium density operator of the bath and tr_B denotes the trace over bath states. We now consider the time evolution of this bath-averaged operator. Starting from the Heisenberg form of the population operator written in the Liouville operator notation, we have

$$n(t) = \exp(iH^\times t) n \quad (H^\times A \equiv [H, A]), \quad (4)$$

we separate H_0 and V in the standard way

$$\exp(iH^\times t) = \exp_o \left[i \int_0^t V^\times(\tau) d\tau \right] \exp(iH_0^\times t), \quad (5)$$

where \exp_o denotes a time ordered exponential. Noting that

$$\exp(iH_0^\times t) \alpha^\dagger \alpha = \exp(iH_0 t) \alpha^\dagger \alpha \exp(-iH_0 t) = \alpha^\dagger \alpha \quad (6)$$

we obtain

$$n(t) = \exp_o \left[i \int_0^t V^\times(\tau) d\tau \right] \alpha^\dagger \alpha \quad (7)$$

and, taking the thermal average over a canonical ensemble of bath states

$$\langle n(t) \rangle = \langle \exp_o \left[i \int_0^t V^\times(\tau) d\tau \right] \alpha^\dagger \alpha \rangle. \quad (8)$$

Next we make a cumulant expansion⁷ of the thermally averaged quantity

$$\left\langle \exp_o \left[i \int_0^t V^\times(\tau) d\tau \right] \right\rangle = \exp_o \left[\sum_{n=1}^{\infty} \int_0^t d\tau \frac{K_n^\times(\tau)}{n!} \right], \quad (9)$$

where $K_n^\times(\tau)$, $n = 1, 2, \dots$ are the cumulants and the ordering prescription is given below. In particular $K_1^\times(\tau)$ is equal to $i \langle V^\times(\tau) \rangle$ and vanishes as the bath operators F and F^\dagger have no diagonal matrix elements in the bath ei-

genstates representation. The second cumulant is given by

$$K_2^x(\tau) d\tau = -2 \int_0^\tau \langle V^x(\tau) V^x(\tau') \rangle d\tau' \quad (10)$$

We now assume that the coupling is weak enough to neglect higher order cumulants. Thus

$$\langle \exp_0 [i \int_0^t V^x(\tau) d\tau] \rangle \simeq \exp_0 \left[\frac{1}{2} \int_0^t K_2^x(\tau) \right] \quad (11)$$

For the cumulant expansion (9), the ordering prescription is chosen such that⁹

$$\begin{aligned} & \frac{d}{dt} \left[\exp_0 \int_0^t \frac{K_n^x(\tau)}{n!} d\tau \right] \\ &= \exp_0 \left[\int_0^t \sum_n \frac{K_n^x(\tau)}{n!} d\tau \right] \left[\sum_n \frac{1}{n!} K_n^x(t) \right] \end{aligned} \quad (12)$$

Following this prescription we thus have

$$\begin{aligned} & \frac{d}{dt} \left\langle \exp_0 \left[i \int_0^t V^x(\tau) d\tau \right] \right\rangle \\ & \simeq \left\langle \exp_0 \left[i \int_0^t V^x(\tau) d\tau \right] \right\rangle \left[\frac{1}{2} K_2^x(t) \right] \end{aligned} \quad (13)$$

Equations (8) and (13) then lead to

$$\frac{d}{dt} \langle n(t) \rangle = \left\langle \exp_0 \left[i \int_0^t V^x(\tau) d\tau \right] \right\rangle \frac{1}{2} K_2^x(t) \alpha^\dagger \alpha \quad (14)$$

Note that up to this point we have not used any property of the operator $\alpha^\dagger \alpha$. Equation (14) may thus be used as a starting point for a general derivation.

Next we calculate the factor $\frac{1}{2} K_2^x(t) \alpha^\dagger \alpha$ appearing in Eq. (14);

$$\begin{aligned} \frac{1}{2} K_2^x(t) \alpha^\dagger \alpha &= - \int_0^t d\tau \langle V^x(t) V^x(\tau) \rangle \alpha^\dagger \alpha \\ &= - \int_0^t d\tau \langle [V(t), [V(\tau), \alpha^\dagger \alpha]] \rangle \end{aligned} \quad (15)$$

Here

$$V(t) = F^\dagger(t) \alpha \exp(-i\epsilon t) + F(t) \alpha^\dagger \exp(i\epsilon t) \quad (16)$$

Utilizing the commutation relations of the operators α and α^\dagger , the commutators in Eq. (15) may be disentangled. This leads to

$$\frac{1}{2} K_2^x(t) \alpha^\dagger \alpha = (A_1 + A_2) \alpha^\dagger \alpha + A_3 \alpha \alpha + A_4 \alpha^\dagger \alpha^\dagger + A_5 + A_6 \quad (17)$$

where

$$A_1 = - \int_0^t d\tau \exp[i\epsilon(t-\tau)] \langle [F(t), F^\dagger(\tau)] \rangle \quad (18a)$$

$$A_2 = \int_0^t d\tau \exp[-i\epsilon(t-\tau)] \langle [F^\dagger(t), F(\tau)] \rangle \quad (18b)$$

$$A_3 = - \int_0^t d\tau \exp[-i\epsilon(t+\tau)] \langle [F^\dagger(t), F^\dagger(\tau)] \rangle \quad (18c)$$

$$A_4 = \int_0^t d\tau \exp[i\epsilon(t+\tau)] \langle [F(t), F(\tau)] \rangle \quad (18d)$$

$$A_5 = \int_0^t d\tau \exp[i\epsilon(t-\tau)] \langle F^\dagger(\tau) F(t) \rangle \quad (18e)$$

$$A_6 = \int_0^t d\tau \exp[-i\epsilon(t-\tau)] \langle F^\dagger(t) F(\tau) \rangle \quad (18f)$$

The contribution of the terms A_3 and A_4 is expected to be small and these terms will be neglected. This is equivalent to the rotating wave approximation involved in previous works.² The equilibrium time correlation functions appearing in Eqs. (18) depend only on the time displacements between their parameters.

$$\langle A(t) B(\tau) \rangle = \langle A(t-\tau) B(0) \rangle = \langle A(0) B(\tau-t) \rangle \quad (19)$$

Using this property it is easy to show that

$$B(t) \equiv - (A_1 + A_2) = \int_{-\infty}^t d\tau \exp(i\epsilon\tau) \langle [F(\tau), F^\dagger(0)] \rangle \quad (20)$$

$$C(t) \equiv A_5 + A_6 = \int_{-\infty}^t d\tau \exp(i\epsilon\tau) \langle F^\dagger(0), F(\tau) \rangle \quad (21)$$

Equation (17) then takes the form

$$\frac{1}{2} K_2^x(t) \alpha^\dagger \alpha = -B(t) \alpha^\dagger \alpha + C(t) \quad (22)$$

Inserting this result into Eq. (14) and applying Eq. (18) we get a closed equation for $\langle n(t) \rangle$

$$\frac{d}{dt} \langle n(t) \rangle = -B(t) \langle n(t) \rangle + C(t) \quad (23)$$

We now assume that the bath correlation time is much shorter than the inverse relaxation time. Equation (23) may then be recast in the form

$$\frac{d}{dt} \langle n(t) \rangle = -B \langle n(t) \rangle + C \quad (24)$$

where

$$B = B(\infty); \quad C = C(\infty) \quad (25)$$

The solution of Eq. (24) subject to the initial condition $n(0) = n$ is given by

$$\langle n(t) \rangle = (C/B) + [n - (C/B)] \exp(-Bt) \quad (26)$$

in which the decay rate is

$$B = \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle [F(\tau), F^\dagger(0)] \rangle \quad (27)$$

and the equilibrium ($t = \infty$) solution is

$$\begin{aligned} \langle n(\infty) \rangle &= \frac{C}{B} = \left[\frac{\int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle F(\tau) F^\dagger(0) \rangle}{\int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle F^\dagger(0) F(\tau) \rangle} - 1 \right]^{-1} \\ &= (\exp \beta \epsilon - 1)^{-1} \end{aligned} \quad (28)$$

which indeed characterizes a thermally averaged boson population. In the last step in Eq. (28) we have used the well known identity

$$\int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle A(\tau) B(0) \rangle = \exp(\beta\epsilon) \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle B(0) A(\tau) \rangle \quad (29)$$

for any two operators A and B .

The same method can be applied for obtaining the time evolution of operators other than $n = \alpha^\dagger \alpha$. In particular for the operator $e^{\alpha n} = e^{\alpha \alpha^\dagger \alpha}$ (where α is a number) which is the generating function for higher powers $(\alpha^\dagger \alpha)^n$ of the population operator, this procedure leads to the following partial differential equation for $\langle e^{\alpha n(t)} \rangle$.

$$\frac{\partial}{\partial t} \langle e^{\alpha n(t)} \rangle = B(\alpha) \frac{\partial}{\partial \alpha} \langle e^{\alpha n(t)} \rangle - C(\alpha) \langle e^{\alpha n(t)} \rangle \quad (30)$$

where

$$B(\alpha) = e^{-\alpha} (1 - e^\alpha) \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle [F(\tau), F^\dagger(0)]_\alpha \rangle \quad (31)$$

$$C(\alpha) = (1 - e^\alpha) \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle F^\dagger(0) F(\tau) \rangle \quad (32)$$

and where

$$[A, B]_\alpha \equiv AB - BAe^\alpha \quad (33)$$

Equation (30) is to be solved under the initial condition

$\langle e^{\alpha n(t=0)} \rangle = e^{\alpha n} = e^{\alpha \alpha^\dagger \alpha}$. The equilibrium solution is easily obtained from the ordinary differential equation,

$$B(\alpha) \frac{\partial}{\partial \alpha} \langle \exp[\alpha n(\infty)] \rangle - C(\alpha) \langle \exp[\alpha n(\infty)] \rangle = 0 \quad (34)$$

which leads to

$$\langle \exp[\alpha n(\infty)] \rangle = \langle \exp(\alpha \alpha^\dagger \alpha) \rangle_{t=\infty} = \frac{\exp(\beta \epsilon) - 1}{\exp(\beta \epsilon) - \exp(\alpha)} \quad (35)$$

For the operators α and α^\dagger themselves, we can again repeat the same procedure to obtain

$$d\langle \alpha(t) \rangle / dt = -B_1 \langle \alpha(t) \rangle; \quad \langle \alpha(t) \rangle = \alpha \exp(-B_1 t) \quad (36a)$$

$$d\langle \alpha^\dagger(t) \rangle / dt = -B_2 \langle \alpha^\dagger(t) \rangle; \quad \langle \alpha^\dagger(t) \rangle = \alpha^\dagger \exp(-B_2 t), \quad (36b)$$

where

$$B_1 = \int_{-\infty}^0 d\tau \exp(i\epsilon\tau) \langle [F(\tau), F^\dagger(0)] \rangle, \quad (37a)$$

$$B_2 = \int_{-\infty}^0 d\tau \exp(i\epsilon\tau) \langle [F(\tau), F^\dagger(0)] \rangle. \quad (37b)$$

Note that $B_1 = B_2^*$ and $B_1 + B_2 = B$. From this we can obtain the Green's function associated with the relaxing oscillator.

$$G(t) \equiv -i\theta(t) \langle \alpha(0) \alpha^\dagger(t) \rangle = -i\theta(t) [n(0) + 1] \exp(-B_2 t),$$

$$\theta(t) = \begin{cases} 1, & t \geq 0 \\ 0, & t < 0 \end{cases} \quad (38)$$

which is related, e. g., to the line shape by

$$L(E) \propto \text{Im} \int_{-\infty}^{\infty} \exp(iEt) G(t) \quad (39)$$

giving

$$L(E) \propto \frac{\text{Re } B_2}{(E - \text{Im } B_2)^2 + (\text{Re } B_2)^2} \quad (40)$$

$\text{Re } B_2 = B/2$ is half the decay width while $\text{Im } B_2$ is a re-normalized oscillator frequency (for explicit expressions see Ref. 2a).

We end this part of our discussion by summarizing the assumption and approximations employed in the present approach. These are

- (1) The weak coupling limit is invoked in neglecting higher than second order terms in the cumulant expansion, Eq. (9).
- (2) The rotating wave approximation is employed in neglecting the highly oscillating terms A_3 and A_4 [Eqs. (18c-d)].
- (3) The Markoffian assumption is invoked in replacing Eq. (23) by Eqs. (24), (25).

In other equivalent treatments of this problem^{2,8} a random phase approximation has been used instead of the weak coupling assumption. It is seen that both approximations lead to identical results.

There is another route to get to the same result as above, which depends on a projection operator procedure. This has been employed successfully in the theory of Brownian motion.¹⁰ In this method, one derives an exact equation of motion for $\langle n(t) \rangle$, which contains a correlation function $\langle FF^\dagger(t) \rangle$ of the same form as above except that the zeroth order time development operator has

been replaced by a modified operator, $\exp(i(1-P)H^\dagger t)$, where P is a suitable projection operator. Except in the case of completely harmonic systems where it is possible to show that this modified propagator can be replaced by the zeroth order term,¹¹ it is extremely difficult to use this exact form. Some perturbation schemes have been employed¹⁰ but the usual (weak coupling) procedure is to simply replace the modified propagator by the zeroth order propagator. This then reproduces our results when the rotating wave and Markoffian approximations are employed.

III. RELAXATION OF A TWO LEVEL SYSTEM

We now consider the Hamiltonian

$$H = H_0 + V, \quad (41a)$$

$$H_0 = \epsilon_1 |1\rangle \langle 1| + \epsilon_2 |2\rangle \langle 2| + H_B, \quad (41b)$$

$$V = F^\dagger |1\rangle \langle 2| + F |2\rangle \langle 1|, \quad (41c)$$

representing a two level system with states $|1\rangle$, $|2\rangle$ and corresponding energies ϵ_1 , ϵ_2 , interacting with a heat bath characterized by the same operator H_B , F , F^\dagger , as before. The unperturbed Hamiltonian H_0 , Eq. (41b), may be simplified by noting that

$$\epsilon_1 |1\rangle \langle 1| + \epsilon_2 |2\rangle \langle 2| = \epsilon_1 + \epsilon |2\rangle \langle 2|, \quad (42)$$

where

$$\epsilon = \epsilon_2 - \epsilon_1. \quad (43)$$

The constant ϵ_1 may then be disregarded; Eq. (41b) is thus replaced by

$$H_0 = \epsilon |2\rangle \langle 2| + H_B. \quad (44)$$

For brevity we make the notations

$$|2\rangle \langle 2| \equiv P, \quad (45a)$$

$$|1\rangle \langle 2| \equiv Q, \quad (45b)$$

$$|2\rangle \langle 1| \equiv Q^\dagger. \quad (45c)$$

In terms of the operators P and Q we now have

$$H_0 = \epsilon P + H_B, \quad (46a)$$

$$V = F^\dagger Q + F Q^\dagger. \quad (46b)$$

The following commutation relations follow directly from the definitions (45):

$$[Q^\dagger, P] = -Q^\dagger, \quad (47a)$$

$$[Q, P] = Q, \quad (47b)$$

$$[Q^\dagger Q] = 2P - 1; \quad Q^\dagger Q = P. \quad (47c)$$

We shall study the thermally averaged time evolution of the operator P . We may start from Eq. (14) by replacing $\alpha^\dagger \alpha$ by P ,

$$\frac{d}{dt} \langle P(t) \rangle = \langle \exp_o [i \int_0^t V^\dagger(\tau) d\tau] \rangle \frac{1}{2} K_2^\dagger(t) P. \quad (48)$$

The analogs of Eq. (15) and (16) are now

$$\frac{1}{2} K_2^\dagger(t) P = - \int_0^t d\tau \langle V^\dagger(t) V^\dagger(\tau) \rangle P \quad (49)$$

$$= - \int_0^t d\tau \langle [V(t), [V(\tau), P]] \rangle,$$

$$V(t) = F^\dagger(t) Q \exp(-i\epsilon t) + F(t) Q^\dagger \exp(i\epsilon t). \quad (50)$$

Inserting Eq. (50) into Eq. (49) and applying relations (42), then neglecting terms with highly oscillating integrands and making use of relations (19) in simplifying the remaining terms, we finally get the analog of Eq. (22),

$$\frac{1}{2}K_2^x(t)P = -B'(t)P + C'(t), \quad (51)$$

where the function $C'(t)$ is identical to the function $C(t)$, Eq. (21), but the function $B'(t)$ is different from $B(t)$, Eq. (20), in that the commutator in Eq. (20) is replaced by an anticommutator

$$B'(t) = \int_{-t}^t d\tau \exp(i\epsilon\tau) \langle \{F(\tau), F^\dagger(0)\} \rangle, \quad (52)$$

$$C'(t) = \int_{-t}^t d\tau \exp(i\epsilon\tau) \langle F^\dagger(0)F(\tau) \rangle. \quad (53)$$

Equations (51) and (48) now lead to

$$d\langle P(t) \rangle / dt = -B'\langle P(t) \rangle + C', \quad (54)$$

where here again we make a Markoffian approximation in replacing $B'(t)$ and $C'(t)$ by $B' = B'(\infty)$ and $C' = C'(\infty)$.

Equation (54) with the initial condition $\langle P(0) \rangle = P$ yields the final solution

$$\langle P(t) \rangle = (C'/B') + [P - (C'/B')] \exp(-B't) \quad (55)$$

with the decay rate

$$B' = \int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle \{F(\tau), F^\dagger(0)\} \rangle \quad (56)$$

and an equilibrium ($t = \infty$) solution

$$\frac{C'}{B'} = \left[\frac{\int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle F(\tau)F^\dagger(0) \rangle}{\int_{-\infty}^{\infty} d\tau \exp(i\epsilon\tau) \langle F(0)F^\dagger(\tau) \rangle} + 1 \right]^{-1} = [\exp\beta\epsilon + 1]^{-1} \quad (57)$$

as expected. Note that the time evolution of the generating function $e^{\alpha P}$ is easily obtained from the identity

$$e^{\alpha P} = 1 + P \sum_{n=1}^{\infty} \frac{\alpha^n}{n!} = 1 + P(e^\alpha - 1)$$

which yields

$$\langle \exp(\alpha P(t)) \rangle = 1 + \langle P(t) \rangle (e^\alpha - 1). \quad (58)$$

Analogously to the time evolution of the averaged operators $\langle Q \rangle$ and $\langle Q^\dagger \rangle$ studied in the previous section, we can obtain expressions also for the evolution of the operators $\langle Q \rangle$ and $\langle Q^\dagger \rangle$. Starting from Eq. (49) with Q replacing P we get in the same way

$$\frac{d\langle Q(t) \rangle}{dt} = -B'_1 \langle Q(t) \rangle; \quad \langle Q(t) \rangle = Q \exp(-B'_1 t), \quad (59a)$$

$$\frac{d\langle Q^\dagger(t) \rangle}{dt} = -B'_2 \langle Q^\dagger(t) \rangle; \quad \langle Q^\dagger(t) \rangle = Q^\dagger \exp(-B'_2 t), \quad (59b)$$

with

$$B'_1 = \int_{-\infty}^0 d\tau \exp(i\epsilon\tau) \langle \{F(\tau), F^\dagger(0)\} \rangle, \quad (60a)$$

$$B'_2 = \int_0^{\infty} d\tau \exp(i\epsilon\tau) \langle \{F(\tau), F^\dagger(0)\} \rangle. \quad (60b)$$

This leads to the following expression for the time dependent Green's function:

$$G(t) = -i\theta(t) \langle Q(0)Q^\dagger(t) \rangle \propto \exp(-B'_2 t) \quad (61)$$

and to the line shape function

$$L(E) \propto \frac{B'}{(E - \text{Im} B'_2)^2 + (\frac{1}{2}B')^2}. \quad (62)$$

IV. TEMPERATURE DEPENDENCE OF THE DECAY RATES

Equations (27) and (56) together with the identity (29) yield the following forms of the relaxation rates: for the harmonic oscillator

$$B = [\exp(\beta\epsilon) - 1] \int_{-\infty}^{\infty} dt \exp(i\epsilon t) \langle F^\dagger(0)F(t) \rangle \quad (63)$$

and for the two level system

$$B' = [\exp(\beta\epsilon) + 1] \int_{-\infty}^{\infty} dt \exp(i\epsilon t) \langle F^\dagger(0)F(t) \rangle. \quad (64)$$

The difference in the pre-integral factors indicates a difference in the temperature dependence of the two rates (for the same bath) which disappears in low temperature

$$\frac{B}{B'} = \frac{e^{\beta\epsilon} - 1}{e^{\beta\epsilon} + 1} \begin{matrix} \xrightarrow{\tau \rightarrow \infty} T^{-1} \\ \xrightarrow{\tau \rightarrow 0} 1 \end{matrix}. \quad (65)$$

To obtain explicit expressions for the temperature dependence of the relaxation rates we have to study specific models for the bath and for the coupling operator F . A model employed recently by Nitzan and Jortner² for studying vibrational relaxation of molecules imbedded in solid matrices take the bath as a collection of harmonic phonons and the coupling operators as

$$F = \sum_{\nu} G_{\nu} B_{\nu}; \quad F^\dagger = \sum_{\nu} G_{\nu}^{\dagger} B_{\nu}^{\dagger}, \quad (66)$$

where ν is a set of phonon indices, G_{ν} are coupling constants, and where

$$B_{\nu} \equiv \prod_{\nu} b_{\nu} \quad (67)$$

in which b_{ν} are phonon annihilation operators. Within this model, the time correlation function in Eqs. (63) and (64) becomes

$$\langle F^\dagger(0)F^\dagger(t) \rangle = \sum_{\nu} |G_{\nu}|^2 \prod_{\nu} \langle b_{\nu}^{\dagger} b_{\nu} \rangle \exp \left[-i \left(\sum_{\nu} \omega_{\nu} \right) t \right] \quad (68)$$

and the rate becomes

$$B, B' = (e^{\beta\epsilon} \mp 1) \sum_{\nu} |G_{\nu}|^2 \delta \left(\epsilon - \sum_{\nu} \omega_{\nu} \right) \prod_{\nu} [\exp(\beta\omega_{\nu}) - 1]^{-1}, \quad (69)$$

where the upper sign is for B and the lower for B' . The expression for B was recently studied by Nitzan, Mukamel, and Jortner.^{2b} A particularly simple result is obtained for an Einstein type model where all ω_{ν} are taken as constants $\omega_{\nu} = \omega$ in Eq. (69). Then the temperature dependent parts of B and B' are simply

$$B, B' \sim (e^{\beta\epsilon} \mp 1) / (e^{\beta\omega} - 1)^N, \quad (70)$$

where

$$N = \epsilon / \omega \quad (71)$$

is the number of bath phonons participating in the transition. The approximation (70) fits well the experimental results of Legay *et al.*¹² on the temperature dependence of the vibrational relaxation rates of matrix isolated NH_3 and CO molecules. It should be pointed out that these

experiments were performed in low temperatures ($5^\circ < T < 30^\circ$) and cannot distinguish between the expressions for B and for B' , as both converge into the same low temperature limit. The difference between B and B' will become significant for $kT > \epsilon$. It is interesting that this quantum effect becomes significant in the high temperature limit.

In a recent paper, Rackovsky and Silbey^{5b} have discussed a particular relaxing two level system (as a model of electronic energy transfer) into a phonon bath. In this case, the coupling operator is given as

$$F = \exp \left\{ \sum_{\nu} G_{\nu} (b_{\nu} - b_{\nu}^{\dagger}) \right\} - \left\langle \exp \left\{ \sum_{\nu} G_{\nu} (b_{\nu} - b_{\nu}^{\dagger}) \right\} \right\rangle. \quad (72)$$

Thus this form contains a sum of many terms like that of Eq. (66). For this case, it is found that there is again a marked dependence on $N (= \epsilon/\omega)$. Recently, Abram and Silbey¹³ have extended this to include electron phonon coupling operators which are diagonal in two level (electronic) system. In these papers, an additional coupling between the two levels which is independent of the bath variables, is also postulated. This makes only a minor modification in the calculation of the rate of decay.

A different possible model for a thermal bath is a bath composed of two level systems. Equation (68) will retain its form but the operators b_{ν} and b_{ν}^{\dagger} are now fermion annihilation and creation operators. Equation (69) will be replaced by

$$B, B' = (e^{\beta\epsilon} \mp 1) \sum_{\nu} |G_{\nu}|^2 \delta \left(\epsilon - \sum_{\nu} \omega_{\nu} \right) \left\{ \prod_{\nu} [\exp(\beta\omega_{\nu}) + 1] \right\}^{-1} \quad (73)$$

and the Einstein approximation results now in

$$B, B' \sim (e^{\beta\epsilon} \mp 1) / (e^{\beta\epsilon} + 1)^N. \quad (74)$$

As an example consider the case of one quantum decay [$N=1$, $\omega = \epsilon$ in Eqs. (70) and (74)]. This is usually the case where the bath is the radiation field and also when the bath is a solid whose Debye frequency is larger than ϵ . In this case we get the following results.

(a) A phonon bath: the decay of a harmonic oscillator is temperature independent. The decay of a two level system is temperature dependent for $kT \geq \epsilon$, and becomes proportional to T in the high temperature limit.

(b) A bath of two level systems: the decay of a two level system is temperature independent while that of a harmonic oscillator becomes inversely proportional to T in the high temperature limit.

V. RELAXATION IN A RADIATION FIELD

As was mentioned in the previous section, radiative relaxation is included in our theory as a particular case—a one quantum relaxation (neglecting multiphonon processes) of a system in contact with a boson bath. For our purpose the field is adequately described by the Hamiltonian

$$H_B = \sum_{\nu} \omega_{\nu} b_{\nu}^{\dagger} b_{\nu}, \quad (75)$$

and the coupling operators are

$$F = \sum_{\nu} G_{\nu} b_{\nu}; \quad F^{\dagger} = \sum_{\nu} G_{\nu}^* b_{\nu}^{\dagger}. \quad (76)$$

Equation (76) leads to the following expressions for the correlation functions appearing in Eqs. (17) and (52)

$$\langle [F(\tau), F^{\dagger}(0)] \rangle = \sum_{\nu} |G_{\nu}|^2 \exp(-i\omega_{\nu}\tau) \quad (77)$$

$$\langle \{F(\tau), F^{\dagger}(0)\} \rangle = \sum_{\nu} |G_{\nu}|^2 \exp(-i\omega_{\nu}\tau) (2n_{\nu} + 1), \quad (78)$$

where

$$n_{\nu} = \langle b_{\nu}^{\dagger} b_{\nu} \rangle \quad (79)$$

is the average number of photons in the mode ν . The radiative relaxation rate of a harmonic oscillator is now obtained from Eqs. (27) and (77)

$$B = \sum_{\nu} |G_{\nu}|^2 \delta(\epsilon - \omega_{\nu}) \quad (80)$$

while the radiative relaxation rate of a two level system is [from Eq. (52) with $t = \infty$ and Eq. (78)]

$$B' = \sum_{\nu} |G_{\nu}|^2 (2n_{\nu} + 1) \delta(\epsilon - \omega_{\nu}). \quad (81)$$

Note that Eqs. (78) and (81) were obtained using the assumption that the density operator of the field is diagonal in the number representation. An alternative description of the field such that its density operator is diagonal in the coherent state representation leads to a similar result with n_{ν} replaced by $|\alpha_{\nu}|^2$, α_{ν} being the coherent state amplitude of the mode ν .

Equation (80), originally obtained in this form by Glauber and Arecchi,¹⁴ indicates that, to the approximations employed in this paper, stimulated processes do not change the radiative relaxation rate of a harmonic oscillator. On the other hand, the radiative relaxation rate of a two level system, Eq. (81) contains, as expected, a term proportional to the radiation intensity which results from stimulated emission and absorption.

VI. FINAL REMARKS

In the above discussion, it has been shown how to calculate the rate for an oscillator or a two level system decaying into a bath of oscillators or two level systems. The calculation is approximate, but should be valid in the weak coupling limit as long as the rotating wave approximation is also valid. The temperature dependence of the rate calculated in this manner is strongly dependent on the nature of the system and its heat bath. The four possible cases are summarized in Eqs. (70) and (74). Since the temperature dependence is so different for these cases, it is hoped that further experiments over larger temperature ranges will lead to further testing of these simple, yet physically appealing models.

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