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A TREATMENT OF VIBRATIONAL RELAXATION WITHOUT THE ROTATING WAVE APPROXIMATION

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A harmonic oscillator weakly coupled to a heat bath is studied without invoking the rotating wave approximation. Corrections to the lorentzian lineshape which characterizes the RWA are derived. An expression for the time evolution of the population of the oscillator which is exact in the van Hove weak coupling limit is also obtained. Our results are compared to earlier expressions which were obtained using the rotating wave approximation.

In our equation for the population of the oscillator, we observe an additional transient term, and we examine the time evolution of the population under a variety of conditions. The applicability of the rotating wave approximation is discussed in light of our results.

Relaxation of vibrationally-excited systems in condensed phases has in recent years become accessible to experimental study, with the development of laser-induced fluorescence, stimulated Raman scattering and laser optical double resonance techniques. Concomitantly, a great deal of effort [1] has been expended on theoretical treatments of the vibrational relaxation problem. The usual model is to consider an individual oscillator interacting with a medium by means of a linear coupling. Possible elaborations would include intramolecular coupling of one mode to another [2], use of Morse rather than harmonic oscillators, etc. Possible simplifications include treatment of bath as a collection of oscillators [3,4]. A few treatments have appeared which consider nonlinear coupling. Sun and Rice [5] have examined the problem in a lattice impurity context, and have suggested that impulsive interactions, beyond the linear term in the oscillator displacement, can make the major contribution to the relaxation process. Fischer and Laubereau [6] have very recently examined the dephasing process [7] (loss of phase memory by the oscillator), and have argued that the quadratic terms in the oscillator displacement, which are nearly always neglected in studies of the relaxation process, dominate the dephasing. These higher-order terms can also become important in lineshape studies [8].

Another possible elaboration, with implications which are more conceptual than practical, lies in relaxing the rotating wave approximation (RWA) which was generally invoked in earlier treatments.

The rotating wave approximation [9] consists in neglect of high phase terms compared to those of slowly oscillating (or zero) phase. It was originally developed for oscillator–oscillator interactions, but has been used in numerous cases in which rapidly-varying and weakly-varying terms appear additively. For instance, if one considers dipole–dipole interaction in a two-state, two-site (a and b) system, the interaction hamiltonian is

$$V_{\mathrm{I}}(t) = A\mu_{\mathrm{a}}\mu_{\mathrm{b}}[(a^{\dagger}_{\mathrm{a1}}a_{\mathrm{a0}} + a^{\dagger}_{\mathrm{a0}}a_{\mathrm{a1}})(a^{\dagger}_{\mathrm{b1}}a_{\mathrm{b0}} + a^{\dagger}_{\mathrm{b0}}a_{\mathrm{b1}})](t) \tag{1}$$

$$= A\mu_{\mathrm{a}}\mu_{\mathrm{b}}\{a^{\dagger}_{\mathrm{a1}}a_{\mathrm{a0}}a^{\dagger}_{\mathrm{b0}}a_{\mathrm{b1}} + a^{\dagger}_{\mathrm{a0}}a_{\mathrm{a1}}a^{\dagger}_{\mathrm{b1}}a_{\mathrm{b0}}\}$$

$$+ A\mu_{\mathrm{a}}\mu_{\mathrm{b}}\{a^{\dagger}_{\mathrm{a1}}a_{\mathrm{a0}}a^{\dagger}_{\mathrm{b1}}a_{\mathrm{b0}}\exp(2\mathrm{i}\omega_{10}t) + a^{\dagger}_{\mathrm{a0}}a_{\mathrm{a1}}a^{\dagger}_{\mathrm{b0}}a_{\mathrm{b1}}\exp(-2\mathrm{i}\omega_{10}t)\}\,, \tag{2}$$

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where μ_a is the dipole matrix element on site a, A is a proportionality constant, $a_{a1}^{\dagger}$ creates a particle in level 1 at site a, I denotes interaction representation, and ω_{10} is the energy difference between the two levels. The first bracketed term on the rhs of (2) is the RWA term; it has no phase. The second term is rapidly varying, and is expected to make a relatively small contribution on timescales long compared to ω_{01}^{-1}. Such terms are usually neglected for long-timescale processes [10].

Some treatments of quantum mechanical time evolution problems which do not involve the RWA have been published in the past. Estes, Keil and Narducci [11] have treated the problem of two coupled harmonic oscillators and have shown that the terms neglected in the RWA become important when the coupling between the two oscillators is of the same order of magnitude as the oscillator frequency. Agarwal [12], in his treatment of the brownian motion of the harmonic oscillator, observed that the RWA is justified in the weak coupling limit (oscillator frequency $\gg$ decay width). Agarwal's model is equivalent to the one employed in the present paper apart from his choice of the coupling to be linear in the bath coordinate (a restriction not included in the present work). Also, no systematic study of the effects of the correction terms was carried out by Agarwal. Very recently, Hioe and Montroll [13] have treated the problem of coupling between a harmonic oscillator and a two level system, again without making the RWA.

Recent work, however, has cast some confusion on the possible importance of the RWA. Hioe [14] has shown that in calculating the equilibrium critical properties of the superradiance system, the terms omitted in the RWA are as important as those retained in this approximation. On the other hand, Diestler and Wilson [15] claim to obtain, without invoking the RWA, the same results for the vibrational relaxation problem as obtained previously [16] within this approximation.

In view of these results, and because of the current interest in the vibrational relaxation problem, we decided to reexamine this problem with special attention given to the role played by the RWA. We restrict our attention to an interaction which is linear in the weak coupling limit. We follow the procedure of Nitzan and Silbey [16], except that we do not make the RWA. This procedure is based on the Kubo approach [17] in which the Liouville operator for the time evolution of an observable is expanded in a cumulant series. We employ the weak coupling limit in which only the first non-vanishing cumulant is included. A general result can then be obtained for the time evolution of the oscillator, from which the effects of the RWA on the calculated relaxation process can be deduced. We examine the transients caused by the terms neglected in the RWA and conclude that the corrections to the RWA are small indeed in the weak coupling limit, but definitely non-vanishing.

While additional transient terms arise from non-RWA contributions in the case of a harmonic oscillator, we note that for a two-level system, the RWA expression for the population of the upper level is, indeed, the exact expression. Terms neglected in the RWA do not appear in the equation of motion (see appendix). However, this is not the case for a harmonic oscillator.

Consider then a system with the hamiltonian:

$$H = H_0 + V\,, \tag{3}$$

$$H_0 = \omega a^{\dagger} a + H_B\,, \tag{4}$$

$$V = F^{\dagger} a + F a^{\dagger}\,, \tag{5}$$

where $a^{\dagger}$ and a are the creation and annihilation operators of the harmonic oscillator, ω is the frequency of the oscillator, H_B is the free bath hamiltonian, V is the coupling between the oscillator and bath, and F is a general operator over the states of the bath; we have neglected zero-point motion, and use atomic units ($\hbar = 1$). We assume that the oscillator-medium interaction is linear with respect to the oscillator coordinates. This model is thus descriptive primarily of at-resonance or near-resonance transfer of excitations from the oscillator to the bath.

Consider a general operator P of the oscillator. Since the oscillator is coupled to a heat bath, let us consider the thermally-averaged operator $\langle P \rangle_T$ where the subscript T denotes the average over bath states. This thermally-averaged operator may be expressed as [9]

$$\langle P(t)\rangle_{\mathrm{T}} = \langle \exp_0 [\mathrm{i} \int_0^t V_{\mathrm{I}}^{\times}(\tau)\,\mathrm{d}\tau]\rangle_{\mathrm{T}}\, P_{\mathrm{I}}(t)\,. \tag{6}$$

Here the superscript $\times$ denotes the commutator superoperator, and the notation $\exp_0$ denotes the time-ordered exponential; $V_{\mathrm{I}}(t)$ is the interaction representation of the operator V, given by

$$V_{\mathrm{I}}(t) = F^{\dagger}(t)a\,\mathrm{e}^{-\mathrm{i}\omega t} + F(t)a^{\dagger}\,\mathrm{e}^{\mathrm{i}\omega t}\,.$$

We may express the time evolution of $\langle P(t)\rangle_{\mathrm{T}}$ as a cumulant expansion to second order (consistent with the weak-coupling assumption)

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle P(t)\rangle_{\mathrm{T}} = \langle \exp_0 [\mathrm{i} \int_0^t V_{\mathrm{I}}^{\times}(\tau)\,\mathrm{d}\tau]\rangle_{\mathrm{T}}\, [\tfrac{1}{2} K_2^{\times}(t) P_{\mathrm{I}}(t) + \mathrm{i}[H_0, P_{\mathrm{I}}]]\,, \tag{7}$$

where

$$K_2^{\times}(t)P_{\mathrm{I}} = -2\int_0^t \mathrm{d}\tau\,\langle [V(\tau), [V(t), P_{\mathrm{I}}]]\rangle_{\mathrm{T}}\,. \tag{8}$$

The equations of motion for $\langle a\rangle_{\mathrm{T}}$ and $\langle a^{\dagger}\rangle_{\mathrm{T}}$ may thus be found, using the relations

$$\tfrac{1}{2}K_2^{\times}(t)a_{\mathrm{I}}(t) = -B_1 a_{\mathrm{I}}(t) + D_2 a_{\mathrm{I}}^{\dagger}(t)\,, \qquad \tfrac{1}{2}K_2^{\times}(t)a_{\mathrm{I}}^{\dagger}(t) = D_1 a_{\mathrm{I}}(t) - B_2 a_{\mathrm{I}}^{\dagger}(t)\,, \tag{9}$$

where

$$B_1 = \int_0^t \mathrm{d}\tau\,\langle [F(t), F^{\dagger}(\tau)]\rangle_{\mathrm{T}}\, \mathrm{e}^{\mathrm{i}\omega(t-\tau)}\,, \qquad B_2 = \int_0^t \mathrm{d}\tau\,\langle [F(\tau), F^{\dagger}(t)]\rangle_{\mathrm{T}}\, \mathrm{e}^{-\mathrm{i}\omega(t-\tau)} = B_1^{*}\,,$$

$$D_1 = \int_0^t \mathrm{d}\tau\,\langle [F^{\dagger}(t), F^{\dagger}(\tau)]\rangle_{\mathrm{T}}\, \mathrm{e}^{\mathrm{i}\omega(t-\tau)}\,, \qquad D_2 = \int_0^t \mathrm{d}\tau\,\langle [F(\tau), F(t)]\rangle_{\mathrm{T}}\, \mathrm{e}^{-\mathrm{i}\omega(t-\tau)} = D_1^{*}\,. \tag{10}$$

Using eq. (7), two coupled differential equations are obtained:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle a\rangle_{\mathrm{T}} = -(B_1 + \mathrm{i}\omega)\langle a\rangle_{\mathrm{T}} + D_2\langle a^{\dagger}\rangle_{\mathrm{T}}\,, \qquad \frac{\mathrm{d}}{\mathrm{d}t}\langle a^{\dagger}\rangle_{\mathrm{T}} = -(B_2 - \mathrm{i}\omega)\langle a^{\dagger}\rangle_{\mathrm{T}} + D_1\langle a\rangle_{\mathrm{T}}\,. \tag{11}$$

This system of equations is then solved to give:

$$\langle a\rangle_{\mathrm{T}} = \frac{\mathrm{e}^{-\widetilde{B}_1 t}(k_+\,\mathrm{e}^{k_- t} - k_-\,\mathrm{e}^{k_+ t})}{k_+ - k_-}\langle a\rangle_0 + \frac{\mathrm{e}^{-\widetilde{B}_1 t} D_2(\mathrm{e}^{k_+ t} - \mathrm{e}^{k_- t})}{k_+ - k_-}\langle a^{\dagger}\rangle_0\,, \tag{12}$$

where $\widetilde{B}_1 = B_1 + \mathrm{i}\omega$, $\widetilde{B}_2 = B_2 - \mathrm{i}\omega$, $\langle a\rangle_0 \equiv \langle a\rangle_{\mathrm{T}}(t=0)$, $\langle a^{\dagger}\rangle_0 \equiv \langle a^{\dagger}\rangle_{\mathrm{T}}(t=0)$, and

$$k_{\pm} \equiv \tfrac{1}{2}\,\mathrm{i}\Omega[1 \pm (1 - 4|D_1|^2/\Omega)^{1/2}]\,, \tag{13}$$

where

$$\Omega = (\widetilde{B}_1 - \widetilde{B}_2)/\mathrm{i} = 2(\omega + \mathrm{Im}\,B_1)\,. \tag{14}$$

In general, $|D_1| \ll \tfrac{1}{2}|\Omega|$ and so

$$k_+ \approx \mathrm{i}\Omega\,, \qquad k_- \approx 2\mathrm{i}|D_1|^2/\Omega\,. \tag{15}$$

Hence, the thermally-averaged operator $\langle a \rangle_T$ may be calculated from eq. (16), obtained by substitution into eq. (12):

$$\langle a \rangle_T = e^{-\widetilde{B}_1 t}\left\{\exp\left(2i\frac{|D_1|^2}{\Omega}t\right) - 2\frac{|D_1|^2}{\Omega^2}\exp(i\Omega t)\right\}\langle a \rangle_0 - i\frac{D_2}{\Omega}e^{-\widetilde{B}_1 t}\left\{\exp(i\Omega t) - \exp\left(2i\frac{|D_1|^2}{\Omega}t\right)\right\}\langle a^\dagger \rangle_0 . \tag{16}$$

Similarly, the hermitian conjugate is obtained:

$$\langle a^\dagger \rangle_T = e^{-\widetilde{B}_2 t}\left\{\exp\left(-2i\frac{|D_1|^2}{\Omega}t\right) - 2\frac{|D_1|^2}{\Omega^2}\exp(-i\Omega t)\right\}\langle a^\dagger \rangle_0$$
$$+ i\frac{D_1}{\Omega}e^{-\widetilde{B}_2 t}\left\{\exp(-i\Omega t) - \exp\left(-2i\frac{|D_1|^2}{\Omega}t\right)\right\}\langle a \rangle_0 . \tag{17}$$

From this, we may obtain the Green function for the oscillator:

$$G(t) \equiv -i\,\theta(t)\langle (a(0) + a^\dagger(0))(a(t) + a^\dagger(t))\rangle , \qquad \theta(t) \equiv \begin{cases} 1 & t \geqslant 0 , \\ 0 & t < 0 , \end{cases} \tag{18}$$

which, assuming a bath at zero temperature becomes

$$G(t) = -i\,\theta(t)[\langle a(0)a(t)\rangle + \langle a(0)a^\dagger(t)\rangle] , \tag{19}$$

in which

$$\langle a(0)a(t)\rangle = -i(D_2/\Omega)\{\exp[(i\Omega - \widetilde{B}_1)t] - \exp[(2i|D_1|^2/\Omega - \widetilde{B}_1)t]\}(n(0) + 1) , \tag{20a}$$

$$\langle a(0)a^\dagger(t)\rangle = \{\exp[-(2i|D_1|^2/\Omega + \widetilde{B}_2)t] - 2(|D_1|^2/\Omega^2)\exp[-(i\Omega + \widetilde{B}_2)t]\}(n(0) + 1) , \tag{20b}$$

$n(0)$ being defined as $\langle a^\dagger a \rangle_T (t = 0)$.

As stated previously, it is in general true that $|D_1| \ll \Omega$ and $|D_2| \ll \Omega$, and therefore the major contribution to the lineshape function will be from the first term in eq. (20b):

$$\langle a(0)a^\dagger(t)\rangle \approx [\exp(-\widetilde{B}_2 t)](n(0) + 1) . \tag{21}$$

The lineshape function, given by

$$L(E) \propto \mathrm{Im}\int_{-\infty}^{+\infty}\exp(iEt)\,G(t)\,dt \tag{22}$$

will therefore be approximately

$$L(E) \propto \frac{\mathrm{Re}\,\widetilde{B}_2}{(E - \mathrm{Im}\,\widetilde{B}_2)^2 + (\mathrm{Re}\,\widetilde{B}_2)^2} . \tag{23}$$

Eq. (23) is the correct result in the RWA; the lineshape function is a lorentzian with a maximum shifted by $\mathrm{Im}\,\widetilde{B}_2$ and a linewidth of $\mathrm{Re}\,\widetilde{B}_2$. Without the RWA, the first term in eq. (20b) contributes a term to the lineshape of the form:

$$\frac{\mathrm{Re}(2i|D_1|^2/\Omega + \widetilde{B}_2)}{[E - \mathrm{Im}(2i|D_1|^2/\Omega + \widetilde{B}_2)]^2 - [\mathrm{Re}(2i|D_1|^2/\Omega + \widetilde{B}_2)]^2} .$$

The second term of eq. (20b) and the two terms in eq. (20a) will each contribute a term of similar form to the lineshape function. However, because D_1 and D_2 are very small relative to Ω, these remaining three terms will be small.

We now focus attention on the temporal evolution of the population of the oscillator, again using eqs. (7) and (8). First, we find that:

$$\tfrac{1}{2}K_2^\times(t)a_1^\dagger a_1 = -B a_1^\dagger a_1 + D_1 a_1 a_1 + D_2 a_1^\dagger a_1^\dagger + C,$$

$$\tfrac{1}{2}K_2^\times(t)a_1 a_1 = -2B_1 a_1 a_1 + 2D_2 a_1^\dagger a_1 - 2J_1, \qquad \mathrm{i}[H_0, a_1 a_1] = -2\mathrm{i}\omega\, a_1 a_1, \tag{24}$$

$$\tfrac{1}{2}K_2^\times(t)a_1^\dagger a_1^\dagger = -2B_2 a_1^\dagger a_1^\dagger + 2D_1 a_1^\dagger a_1 - 2J_2, \qquad \mathrm{i}[H_0, a_1^\dagger a_1^\dagger] = 2\mathrm{i}\omega\, a_1^\dagger a_1^\dagger.$$

In these equations, we have defined

$$B = B_1 + B_2 = 2\,\mathrm{Re}\,B_1,$$

$$C = \int_0^t \mathrm{d}\tau \langle F^\dagger(\tau)F(t)\rangle_\mathrm{T} \exp[\mathrm{i}\omega(t-\tau)] + \int_0^t \mathrm{d}\tau \langle F^\dagger(t)F(\tau)\rangle_\mathrm{T} \exp[-\mathrm{i}\omega(t-\tau)], \tag{25}$$

$$J_1 = \int_0^t \mathrm{d}\tau \langle F(\tau)F(0)\rangle_\mathrm{T} \exp(-\mathrm{i}\omega\bar{\tau}), \qquad J_2 = \int_0^t \mathrm{d}\tau \langle F^\dagger(0)F^\dagger(\tau)\rangle_\mathrm{T} \exp(\mathrm{i}\omega\tau) = J_1^*.$$

Hence, we obtain three coupled equations of motion:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle a^\dagger a\rangle_\mathrm{T} = -B\langle a^\dagger a\rangle_\mathrm{T} + D_1\langle aa\rangle_\mathrm{T} + D_2\langle a^\dagger a^\dagger\rangle_\mathrm{T} + C, \tag{26a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle aa\rangle_\mathrm{T} = -2(B_1 + \mathrm{i}\omega)\langle aa\rangle_\mathrm{T} + 2D_2\langle a^\dagger a\rangle_\mathrm{T} - 2J_1, \tag{26b}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle a^\dagger a^\dagger\rangle_\mathrm{T} = -2(B_2 - \mathrm{i}\omega)\langle a^\dagger a^\dagger\rangle_\mathrm{T} + 2D_1\langle a^\dagger a\rangle_\mathrm{T} - 2J_2, \tag{26c}$$

with the initial conditions $\langle A\rangle_\mathrm{T}(t=0) = \langle A\rangle_0$, for $A = a^\dagger a$, aa, and $a^\dagger a^\dagger$.

If one assumes that $B_1, B_2, D_1, D_2, C, J_1$, and J_2 are all independent of time [18], these three coupled, first-order inhomogeneous differential equations may be solved exactly. Thus we have an expression for the time dependence of the operator $\langle a^\dagger a\rangle_\mathrm{T}$

$$\langle a^\dagger a\rangle_\mathrm{T}(t) = \langle a^\dagger a\rangle_0\, q(t) + \langle aa\rangle_0\, r(t) + \langle a^\dagger a^\dagger\rangle_0\, r^*(t) + u(t), \tag{27}$$

where

$$q(t) = \left(\frac{-\Omega^2}{4|D_1|^2 - \Omega^2} + \frac{2|D_1|^2}{4|D_1|^2 - \Omega^2}\{\exp[\mathrm{i}(\Omega^2 - 4|D_1|^2)^{1/2}t] + \exp[-\mathrm{i}(\Omega^2 - 4|D_1|^2)^{1/2}t]\}\right)\mathrm{e}^{-Bt}, \tag{28}$$

$$r(t) = \left(\frac{\mathrm{i}\Omega D_2}{4|D_1|^2 - \Omega^2} - \frac{2\mathrm{i}D_2|D_1|^2\exp[\mathrm{i}(\Omega^2 - 4|D_1|^2)^{1/2}t]}{(4|D_1|^2 - \Omega^2)[(\Omega^2 - 4|D_1|^2)^{1/2} + \Omega]} + \frac{2\mathrm{i}D_2|D_1|^2\exp[-\mathrm{i}(\Omega^2 - 4|D_1|^2)^{1/2}t]}{(4|D_1|^2 - \Omega^2)[(\Omega^2 - 4|D_1|^2)^{1/2} - \Omega]}\right)\mathrm{e}^{-Bt}, \tag{29}$$

$$u(t) = \frac{-\Omega^2 C - 2\mathrm{i}\Omega D_2 J_1 + 2\mathrm{i}\Omega D_1 J_2}{(4|D_1|^2 - \Omega^2)B}(1 - \mathrm{e}^{-Bt}) +$$

$$+\left\{\left(\frac{2|D_1|^2}{4|D_1|^2-\Omega^2}\right)\left(\frac{4|D_1|^2C-2iD_2J_1[(\Omega^2-4|D_1|^2)^{1/2}-\Omega]-2iD_1J_2[(\Omega^2-4|D_1|^2)^{1/2}+\Omega]}{4|D_1|^2[B-i(\Omega^2-4|D_1|^2)^{1/2}]}\right)\right.$$

$$\left.\times\{1-\exp[(-B+i(\Omega^2-4|D_1|^2)^{1/2}t]\}\right\}$$

$$+\left\{\left(\frac{2|D_1|^2}{4|D_1|^2-\Omega^2}\right)\left(\frac{4|D_1|^2C+2iD_2J_1[(\Omega^2-4|D_1|^2)^{1/2}+\Omega]+2iD_1J_2[(\Omega^2-4|D_1|^2)^{1/2}-\Omega]}{4|D_1|^2[B+i(\Omega^2-4|D_1|^2)^{1/2}]}\right)\right.$$

$$\left.\times\{1-\exp[(-B-i(\Omega^2-4|D_1|^2)^{1/2})t]\}\right\}, \tag{30}$$

where Ω is defined by eq. (14).

Note that $\langle a^\dagger a\rangle_T(t)$ is an operator in the oscillator space. If we take the expectation value of this operator over the initial oscillator state, we obtain

$$\langle\langle a^\dagger a\rangle_T\rangle(t)=\langle\langle a^\dagger a\rangle_0\rangle(0)\,q(t)+u(t)=n(0)\,q(t)+u(t). \tag{31}$$

The second equality assumes that the oscillator is initially in an n-state (that is, an eigenstate of the number operator).

Eqs. (27)–(30) provide the general result for the time evolution of the harmonic oscillator interacting linearly with a thermal bath. We note that a general operator F has been used for the bath term in the oscillator–bath interaction. Eq. (27) for the population operator shows that in addition to the diagonal part which appears in the RWA (and is modified here by non-RWA contributions), this operator contains also non-diagonal contributions which are missing in this approximation.

We are now in a position to compare our results to earlier results [4, 16] obtained in the RWA, and to Diestler and Wilson's result [15], which was obtained without explicitly invoking the RWA. To this end it is sufficient to take the bath-molecule interaction to be linear also in the bath coordinate. This is done merely to simplify the presentation and is by no means necessary. A calculation of the relevant correlation functions for more complicated couplings has been presented elsewhere [19] and has no bearing on the issue at hand which is the applicability of the RWA. We thus take

$$F(t)=\alpha\sum_\nu G_\nu b_\nu\exp(-i\omega_\nu t)+\beta\sum_\nu G_\nu^* b_\nu^\dagger\exp(i\omega_\nu t), \tag{32}$$

where $b_\nu^\dagger$ and b_ν are the creation and destruction operators for the normal mode of the bath (considered as an ensemble of oscillators) of frequency ω_ν. Here, α and β are parameters put into the expression to distinguish the terms retained in the rotating wave approximation from those terms disregarded in the RWA. In the RWA, $\alpha=1$ and $\beta=0$. In the treatment exact in the weak-coupling limit, $\alpha=1$ and $\beta=1$. We may now use this expression for $F(t)$ to find explicit expressions for the parameters in our equation for $\langle\langle a^\dagger a\rangle_T\rangle(t)$. We find that

$$B_1=\lim_{\eta\to 0}\left(-\alpha^2\sum_\nu\frac{|G_\nu|^2}{i(\omega-\omega_\nu)-\eta}+\beta^2\sum_\nu\frac{|G_\nu|^2}{i(\omega+\omega_\nu)-\eta}\right) \tag{33}$$

Neglecting the (nonresonant, small) terms involving $(\omega+\omega_\nu)^{-1}$, we have

$$B_1=\alpha^2\lim_{\eta\to 0}\left(i\sum_\nu\frac{|G_\nu|^2}{(\omega-\omega_\nu)+i\eta}\right)=\alpha^2\, i\sum_\nu|G_\nu|^2\left(\mathrm{PP}\frac{1}{\omega-\omega_\nu}-\pi i\,\delta(\omega-\omega_\nu)\right). \tag{34,35}$$

The principal part term will shift the oscillator frequency by a small amount and can be neglected in the present discussion.

Define the decay rate Γ by

$$\Gamma = \pi \sum_\nu |G_\nu|^2 \delta(\omega - \omega_\nu) = \tfrac{1}{2}(B_1 + B_2) = \tfrac{1}{2} B\,, \tag{36}$$

then

$$B_1 = \alpha^2 \Gamma\,. \tag{37}$$

Similarly:

$$D_2 = -\alpha\beta \lim_{\eta \to 0} \sum_\nu |G_\nu|^2 \left(\frac{1}{\mathrm{i}(\omega_\nu - \omega) - \eta} + \frac{1}{\mathrm{i}(\omega_\nu + \omega) + \eta} \right). \tag{38}$$

Again, neglecting terms in $(\omega + \omega_\nu)^{-1}$ and PP terms,

$$D_2 = \alpha\beta\pi \sum_\nu |G_\nu|^2 \delta(\omega_\nu - \omega) = \tag{39}$$

$$= \alpha\beta\Gamma\,. \tag{40}$$

Hence $D_2 = 0$ in the RWA while $D_2 = \Gamma$ in the exact description.

So, we may substitute the values

$$B_1 = B_2 = D_1 = D_2 = \Gamma \tag{41}$$

and $B = 2\,\mathrm{Re}\,B_1 = 2\Gamma$ into our eq. (31) for $\langle\langle a^\dagger a \rangle_\mathrm{T}\rangle$.

We will further assume that J_1 is real, hence $J_1 = J_2$ and rearrange the equation for $\langle\langle a^\dagger a \rangle_\mathrm{T}\rangle$ to obtain

$$\begin{aligned}\langle\langle a^\dagger a \rangle_\mathrm{T}\rangle &= \langle\langle a^\dagger a \rangle_\mathrm{T}\rangle_{t=0} \left(1 - \frac{4\Gamma^2}{S^2} (\cos St - 1) \right) \mathrm{e}^{-2\Gamma t} + \left(\frac{C}{2\Gamma} \right) \left(1 + \frac{4\Gamma^2}{S^2} \right) (1 - \mathrm{e}^{-2\Gamma t}) \\ &+ \left(\frac{-4}{S^2(4\Gamma^2 + S^2)} \right) (2\Gamma^3 C + \Gamma S^2 J_1)(1 - \mathrm{e}^{-2\Gamma t} \cos St) + \left(\frac{-4}{S^2(4\Gamma^2 + S^2)} \right) (\Gamma^2 CS - 2\Gamma^2 J_1 S)(\mathrm{e}^{-2\Gamma t} \sin St)\,,\end{aligned} \tag{42}$$

where $S = (\Omega^2 - 4|D_1|^2)^{1/2}$.

If we let $D_1 = D_2 = 0$, i.e., if we make the rotating wave approximation, we obtain

$$\langle\langle a^\dagger a \rangle_\mathrm{T}\rangle = \langle a^\dagger a \rangle_0\, \mathrm{e}^{-Bt} + C/B(1 - \mathrm{e}^{-Bt}) \tag{43}$$

which is identical to eq. (26) of Nitzan and Silbey [16], to IV.14 of Diestler and Wilson [15], and to (4.6) of Nitzan and Jortner [4]. Our treatment has additional high-phase components (38) which are absent in the rotating wave approximation. The result by Diestler and Wilson is identical to the rotating wave approximation solution because these authors limit themselves to initial conditions where the oscillator is in a number-state (eigenfunction of $a^\dagger a$). Therefore obviously the bath averaged operators $\langle aa \rangle_\mathrm{T}(t)$ and $\langle a^\dagger a^\dagger \rangle_\mathrm{T}(t)$ are of order $|G|^2$ and, in our eq. (15) for $\mathrm{d}\langle a^\dagger a \rangle/\mathrm{d}t$ the terms involving $\langle aa \rangle$ and $\langle a^\dagger a^\dagger \rangle$ are of order $|G|^4$ and can be neglected. Indeed, we see in eq. (42), which also takes $\langle a^\dagger a^\dagger \rangle_{t=0} = \langle aa \rangle_{t=0} = 0$, that the corrections to the RWA result are of order $\Gamma^2 = |G|^4$. On the other hand for other initial conditions (e.g., a Glauber state) one can no longer assume that $\langle aa \rangle$ and $\langle a^\dagger a^\dagger \rangle$ are small at all times and the Diestler–Wilson approach is no longer valid.

To illustrate the validity of the rotating wave approximation, we compare the time evolution of the population of the oscillator in the weak-coupling limit in both the exact description and the rotating wave description for the case of the bath at zero temperature (corresponding to $C = 0$) and for the case $J_1 = J_2 = 0$. In the numerical computations, we have assumed that $\Omega = 2\omega + 2\,\mathrm{Im}\,B_1 \approx 2\omega$. No difference between the exact and RWA descriptions is observable (figs. 1, 2) when $\Gamma = 1\ \mathrm{cm}^{-1}$ and $\omega = 1000\ \mathrm{cm}^{-1}$. For larger values of Γ, the difference becomes

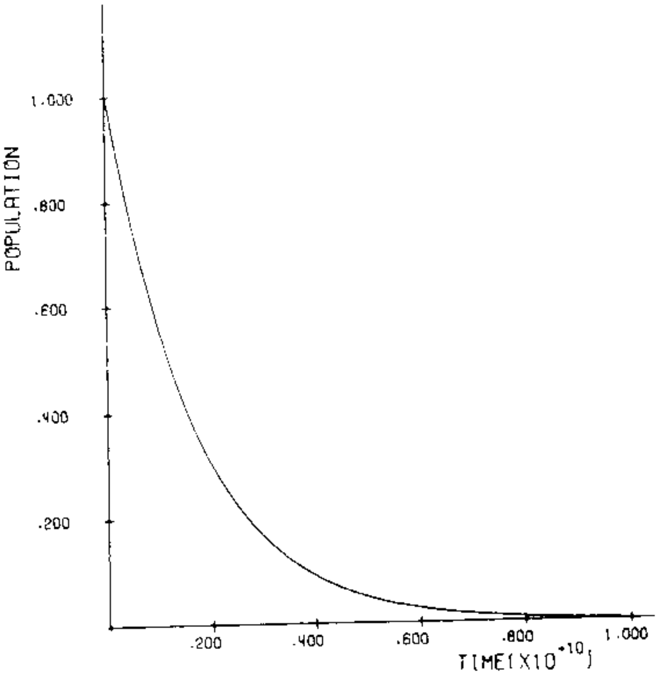

Fig. 1. The population of the oscillator as a function of time in the exact description, for the case $\Gamma = 1$ cm^{-1}, $\omega = 1000$ cm^{-1}, and zero temperature. The graph of the population in the RWA as a function of time is identical to this plot; for this case, the difference between the populations in the exact and RWA descriptions is on the order of 10^{-6}. (See fig. 2.)

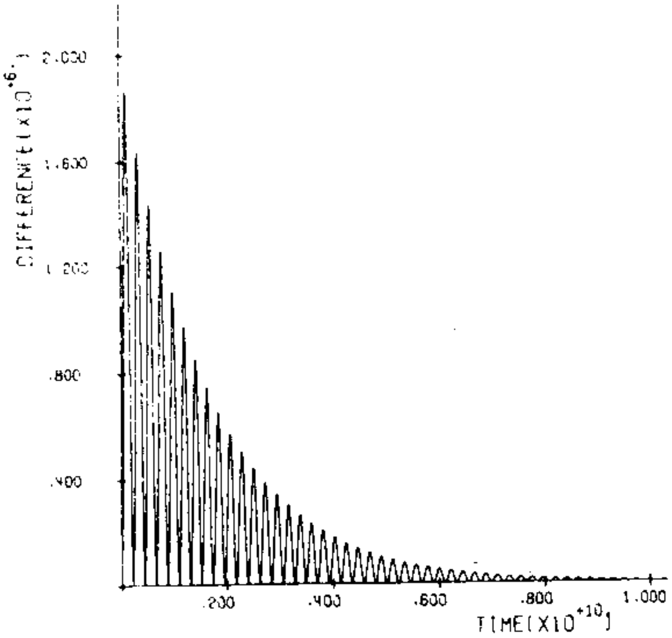

Fig. 2. The difference ($n_{\text{exact}} - n_{\text{RWA}}$) in predicted population as a function of time for the case $\Gamma = 1$ cm^{-1}, $\omega = 1000$ cm^{-1}, and zero temperature.

(figs. 3, 4) more apparent, but it is only in the unphysical situation of $\Gamma = 500$ cm^{-1} and $\omega = 1000$ cm^{-1} that one begins to observe appreciable differences between n_{exact} and n_{RWA}. For the latter case, the error in the rotating wave approximation is 40% or less, and the correction term damps out within 10^{-13} seconds.

An additional ramification of our solution is that, for F hermitian, and assuming $J_1 = J_2 = \frac{1}{2}C$, we obtain for time $\to \infty$:

$$\langle\langle a^\dagger a\rangle_T(\infty)\rangle = \frac{C}{B}\left(1 + \frac{4\Gamma^2}{S^2}\right) - \left(\frac{2}{S^2(4\Gamma^2 + S^2)}\right)(4\Gamma^3 C + \Gamma S^2 C)$$

$$= \frac{C}{B} = [\exp(\omega/kT) - 1]^{-1} = \overline{\langle\langle a^\dagger a\rangle_T\rangle}, \tag{44}$$

which is, as is expected, the thermally-averaged population of the harmonic oscillator. Obtaining the asymptotic behaviour without disregarding the imaginary parts of J_1 and J_2 is an involved mathematical problem which will be dealt with elsewhere.

Thus the exact equation for the temporal evolution of the population of the oscillator in the particular weak coupling system under consideration contains a transient term (an additive "correction" term) which is not obtained when the Rotating Wave Approximation is invoked. However, this correction term is smaller than one part in 10^5 for typical physical situations, and, in any case, damps out in a time of order $3 \times \Gamma^{-1}$. For relaxation processes which are detectable experimentally at this time, the RWA appears to be a very good approximation in the weak coupling limit. The possibility of observing the transients is an intriguing one, but is probably beyond present experimental techniques, which, in the most favorable cases, are in the picosecond range, or at least ten times too slow.

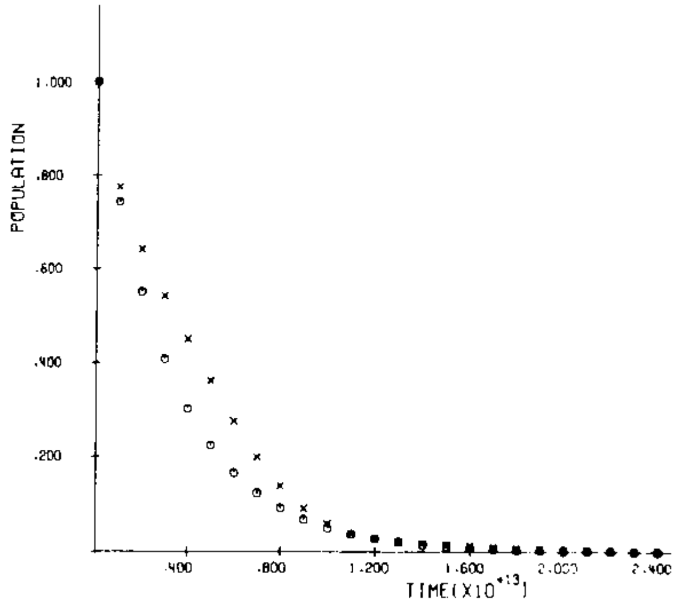

Fig. 3. The populations of the oscillator in the exact and RWA descriptions as functions of time for the (nonphysical) case Γ = 500 cm^{-1}, ω = 1000 cm^{-1}, and zero temperature. ($\circ \equiv n_{\mathrm{RWA}}$; $\times \equiv n_{\mathrm{exact}}$.)

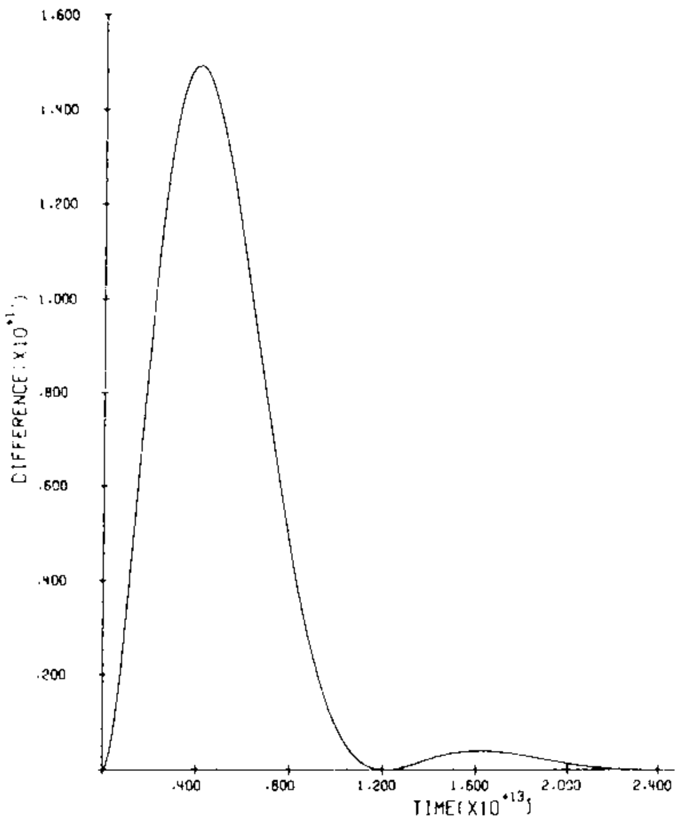

Fig. 4. $n_{\mathrm{exact}}-n_{\mathrm{RWA}}$ as a function of time for the case Γ = 500 cm^{-1}, ω = 1000 cm^{-1} and zero temperature.

Acknowledgement

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Appendix: Relaxation of a two-level system

For a two-level system

—— r

—— s

with the hamiltonian

$$H = H_0 + V\,, \tag{A1}$$

$$H_0 = (\epsilon_r - \epsilon_s) P + H_{\mathrm{bath}}\,, \tag{A2}$$

$$V = F(Q + Q^\dagger)\,, \tag{A3}$$

and operators defined as

$$P = |r\rangle\langle r| , \qquad Q = |s\rangle\langle r| , \qquad Q^\dagger = |r\rangle\langle s|$$

we may employ eq. (7) to obtain the equation of motion for the population $P(t)$ of the upper level. We find that

$$[H_0, P] = 0 \tag{A4}$$

and

$$[V(\tau), [V(t), P_\mathrm{I}(t)]] = F(\tau)F(t)[-(1-P_\mathrm{I})\,\mathrm{e}^{\mathrm{i}\epsilon(t-\tau)} + P_\mathrm{I}\,\mathrm{e}^{-\mathrm{i}\epsilon(t-\tau)}]$$
$$-F(t)F(\tau)[(1-P_\mathrm{I})\,\mathrm{e}^{-\mathrm{i}\epsilon(t-\tau)} - P_\mathrm{I}\,\mathrm{e}^{\mathrm{i}\epsilon(t-\tau)}] , \tag{A5}$$

where we define ϵ as the energy difference between upper and lower levels

$$\epsilon = \epsilon_\mathrm{r} - \epsilon_\mathrm{s} .$$

Substituting into eq. (7), we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle P(t)\rangle = (1-\langle P\rangle)\int_{-\infty}^{+\infty} \mathrm{d}\tau\,\langle F(0)F(\tau)\rangle\,\mathrm{e}^{\mathrm{i}\epsilon\tau} - \langle P\rangle \int_{-\infty}^{+\infty} \mathrm{d}\tau\langle F(\tau)F(0)\rangle\,\mathrm{e}^{\mathrm{i}\epsilon\tau} . \tag{A6}$$

Defining

$$K = \int_{-\infty}^{+\infty} \mathrm{d}\tau\,\mathrm{e}^{\mathrm{i}\epsilon\tau}\langle F(\tau)F(0)\rangle \tag{A7}$$

and noting that

$$\int_{-\infty}^{+\infty} \mathrm{d}\tau\langle F(0)F(\tau)\rangle\,\mathrm{e}^{\mathrm{i}\epsilon\tau} = K\,\mathrm{e}^{-\beta\epsilon} , \tag{A8}$$

eq. (A6) may be rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle P(t)\rangle = -K\langle P\rangle + K\,\mathrm{e}^{-\beta\epsilon}(1-\langle P\rangle) . \tag{A9}$$

All terms in eq. (A9) are retained in the RWA: for the two-level system, higher-energy states which can serve as intermediate states are absent, thus QQ and $Q^\dagger Q^\dagger$ are zero. Hence, the RWA treatment of the second cumulant for the relaxation of a two-level system is exact.

References

[1] An enormous amount of work has been devoted to the problem of a harmonic oscillator linearly coupled to a heat bath. In addition to the references below, cf.
W.H. Louisell, Radiation and Noise in Quantum Electronics (McGraw-Hill, New York, 1964);
B.J. Berne, J. Jortner and R. Gordon, J. Chem. Phys. 97 (1967) 1600;
G.S. Agarwal, Phys. Rev. A4 (1971) 739;
H. Haken, Revs. Mod. Phys. 47 (1975) 67.
A recent review of some experimental aspects of vibrational relaxation is given by
S. Ormonde, Revs. Mod. Phys. 47 (1975) 193,
while the theoretical approaches are discussed by
S.H. Lin and H. Eyring, Annu. Revs. Phys. Chem. 25 (1974) 39.

[2] For example, protonic relaxation in hydrogen-bonded systems has been examined by
N. Rosch, Chem. Phys. 1 (1973) 220, and by
N. Rosch and M.A. Ratner, J. Chem. Phys. 61 (1974) 3344.
[3] I.R. Senitsky, Phys. Rev. 119 (1961) 670; 124 (1961) 642;
J. Schwinger, J. Math. Phys. 2 (1961) 407.
[4] A. Nitzan and J. Jortner, Mol. Phys. 25 (1973) 713.
[5] H.Y. Sun and S.A. Rice, J. Chem. Phys. 42 (1965) 3826.
[6] S.F. Fischer and A. Laubereau, Chem. Phys. Letters 35 (1975) 6.
[7] A. Laubereau, Chem. Phys. Letters 27 (1974) 600.
[8] Cf. e.g. R.G. Gordon, J. Chem. Phys. 43 (1965) 1307.
[9] W.H. Louisell, Coupled Mode and Parametric Electronics (Wiley, New York, 1960);
W.H. Louisell, Quantum Statistical Properties of Radiation (Wiley, New York, 1973) pp. 324, 326.
[10] For an example in dipole–dipole interaction, cf.
K. Godzik and A. Blumen, Phys. Stat. Sol. 17 (1962) 1100.
[11] L.E. Estes, T.H. Keil and L.M. Narducci, Phys. Rev. 175 (1968) 286.
[12] G.S. Agarwal, Phys. Rev. A4 (1971) 739.
[13] F.T. Hioe and E.W. Montroll, J. Math. Phys. 16 (1975) 1259.
[14] F.T. Hioe, Phys. Rev. A8 (1973) 1440.
[15] D.J. Diestler and R.S. Wilson, J. Chem. Phys. 62 (1975) 1572.
[16] A. Nitzan and R. Silbey, J. Chem. Phys. 60 (1974) 4070.
[17] R. Kubo, J. Phys. Soc. Jap. 12 (1957) 5705; 17 (1962) 1100.
[18] This should be true, since the both memory times are very short. Therefore, for times of the order of the oscillator relaxation time, the upper limits of the integrals can all be taken as $+\infty$.
[19] A. Nitzan, S. Mukamel and J. Jortner, J. Chem. Phys. 60 (1974) 3929; 63 (1975) 200.