QUADRATIC EFFECTS IN MULTIPHONON TRANSITION RATES IN SOLIDS

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In this paper we explore the contribution of quadratic impurity–phonon coupling terms on nonradiative multiphonon transition rates in solids. It is demonstrated that the quadratic terms may increase substantially the transition rate and may modify quantitatively the energy gap law. Such effects will be exhibited even when the quadratic coupling is too weak to be observable in the optical spectra.

1. Introduction

Multiphonon relaxation processes occurring during the decay of excited states of impurity molecules embedded in solid matrices have long been a subject of active experimental and theoretical research [1–13]. So far, all theoretical studies have assumed some form of a linear coupling between the impurity levels and the lattice phonon, e.g., a shift in the phonon equilibrium positions induced by transitions between the impurity levels or, alternatively, an interaction potential between the lattice and the impurity molecule which is exponential in the phonon coordinates. Quadratic contributions to the coupling, originating from frequency changes and mode-mixing induced by impurity transitions, have been considered on several occasions [14,15]. It is well established that such terms bring about temperature dependent broadening and the spectral shift of the zero phonon lines associated with the impurity transitions [14–16]. In the theory of radiationless electronic transitions in large molecules frequency changes have been considered and have been found to have a profound quantitative effect on the transition rates [17,18].

In this paper we report the results of a study of the effect of quadratic coupling terms on multiphonon relaxation rates between impurity levels of molecules embedded in solid matrices. The formalism developed in the theory of thermal broadening and shift of zero phonon lines [14] is utilized together with a formal analogy which exists between the terms contributed by the quadratic coupling and these arising in the linear case. It is found that in a zero-temperature calculation the quadratic contributions to the coupling substantially modify the multiphonon transition rate without necessarily having a visible effect on the zero-temperature absorption or emission spectrum of the same impurity molecule. In particular, the "energy gap law" which predicts a rapid decrease of the transition rate as a function of the impurity electronic energy gap is modified to yield a weaker dependence of the nonradiative rate on the energy gap.

Recently, Bondebey [19] has measured several multiphonon transition rates involving the vibronic levels corresponding to the $A\,^2\Pi$ and $X\,^2\Sigma$ electronic states of the CN radical. The energy gap dependence deduced from his results is much weaker than what the conventional rate expressions (based on linear coupling terms) predict [20]. Inclusion of quadratic coupling terms shifts the calculated rates substantially in the desired direction.

2. Multiphonon transition rates

We consider a multiphonon transition between two levels of an impurity interacting with phonon bath at zero temperature. Denoting H_u (H_ℓ) the hamiltonian of the phonon system when the upper (lower) level of the impurity is occupied, we may write

$$H_\ell = H_u - \hbar\omega_0 + V, \tag{1}$$

where V denotes the difference between the phonon potential surfaces associated with the two impurity states and where $\hbar\omega_0$ is the energy difference between the (zero phonon) impurity levels. In the harmonic approximation V can be described by second order Taylor expansion in the normal coordinates

$$V = \sum_s V_s q_s + \tfrac{1}{2}\sum_{s,s'} V_{s,s'} q_s q_{s'} = \int \mathrm{d}\omega \rho(\omega) V(\omega) q_\omega + \tfrac{1}{2}\int \mathrm{d}\omega\,\mathrm{d}\omega' \rho(\omega)\rho(\omega') V(\omega,\omega') q_\omega q_{\omega'}. \tag{2}$$

In the second identity the ω integrals are taken over the phonon spectrum and $\rho(\omega)$ is the phonon density of states. The normalized line shape $G(\Omega)$ at the frequency Ω can be systematically computed from the Lax formula [21] with the Condon approximation

$$G(\Omega) = \tfrac{1}{2}\pi^{-1}\int_{-\infty}^{\infty} \exp(-\mathrm{i}\Omega t) \times \langle \exp(\mathrm{i}H_u t/\hbar)\exp(-\mathrm{i}H_\ell t/\hbar)\rangle\,\mathrm{d}t$$

$$= \tfrac{1}{2}\pi^{-1}\int_{-\infty}^{\infty} \exp[-\mathrm{i}(\Omega-\omega_0)t] \times \langle T\exp[-\mathrm{i}\hbar^{-1}\int_0^t V(t_1)\,\mathrm{d}t_1]\rangle\,\mathrm{d}t, \tag{3}$$

where T is the time ordering operator, $\langle\ \rangle$ denotes temperature average in H_u states and

$$V(t) = \exp(\mathrm{i}tH_u/\hbar) V \exp(-\mathrm{i}tH_u/\hbar). \tag{4}$$

The time ordered thermal average which appears in eq. (3) can be calculated, in principle, to any order in V. To second order in V at $T = 0$ K, $G(\Omega)$ can be represented (see appendix) as follows [14]

$$G(\Omega) = \tfrac{1}{2}\pi^{-1}\exp(-S_1 - S_2) \times \int_{-\infty}^{\infty} \mathrm{d}t \exp[-\mathrm{i}(\Omega-\omega_0+\Omega_0)t + g_1(t) + g_2(t)], \tag{5}$$

where

$$\Omega_0 = \tfrac{1}{2}\hbar^{-1}\int_0^\infty \mathrm{d}\omega V(\omega,\omega)\rho(\omega) - \hbar^{-2}\int_0^\infty \mathrm{d}\omega \frac{V^2(\omega)}{\omega}\rho(\omega), \tag{6}$$

$$g_1(t) = \hbar^{-2}\int_0^\infty \mathrm{d}\omega \left[\frac{V(\omega)}{\omega}\right]^2 \exp(-\mathrm{i}\omega t)\rho(\omega), \tag{7}$$

$$g_2(t) = \tfrac{1}{2}\hbar^{-2}\int_0^\infty \mathrm{d}\omega_1\,\mathrm{d}\omega_2 \frac{V(\omega_1,\omega_2)}{(\omega_1+\omega_2)^2}\rho(\omega_1)\rho(\omega_2) \times \exp[-\mathrm{i}(\omega_1+\omega_2)t], \tag{8}$$

$$S_1 = g_1(0), \quad S_2 = g_2(0). \tag{9}$$

The function $g_1(t)$ is familiar from the linear coupling multiphonon theory [3], while the effect of the quadratic terms in the expression of V, eq. (2), manifests itself mainly through $g_2(t)$. Nevertheless, the present zero-temperature case can be formally reduced to an effective linear coupling case. We introduce $A_2(\omega)$, the Fourier transform of $g_2(t)$,

$$g_2(t) = \int_0^\infty A_2(\omega)\exp(-\mathrm{i}\omega t)\,\mathrm{d}\omega, \tag{10}$$

where

$$A_2(\omega) = \tfrac{1}{2}\pi^{-1}\int_{-\infty}^{\infty}\exp(\mathrm{i}\omega t) g_2(t)\,\mathrm{d}t = \tfrac{1}{2}\hbar^{-2}\omega^{-2}\int_0^\infty \mathrm{d}\omega_1 V^2(\omega_1,\omega-\omega_1)\rho(\omega_1)\rho(\omega-\omega_1). \tag{11}$$

We introduce similarly $A_1(\omega)$, the Fourier transform of $g_1(t)$,

$$g_1(t) = \int_0^\infty A_1(\omega)\exp(-\mathrm{i}\omega t)\,\mathrm{d}\omega. \tag{12}$$

Inspection of eqs. (5)–(9) reveals that our zero-temperature system is equivalent (up to an energy shift) to a linearly coupled system with coupling function $A_1 + A_2$. We thus can apply to the present case all approximation methods (Perlin, ref. [1]) developed for the line shape of the linearly coupled system.

In general, there are no universal relations between $A_1(\omega)$ and $A_2(\omega)$. However, taking into account that $\rho(\omega)$ has a cutoff at a certain frequency ω_D, it is evident that $A_1(\omega)$ extends up to ω_D, while $A_2(\omega)$ extends up to $2\omega_D$. Therefore, it is expected that at sufficiently high frequencies Ω, eq. (5), the contribution of $A_2(\omega)$ to the line shape function will dominate, no matter how small the ratio S_2/S_1 is. This conclusion is of considerable importance in the study of multiphonon transition rates in which relatively high energy gaps are involved.

In order to obtain semi-quantitative information regarding the effect of $A_2(\omega)$ on the line shape, we performed a numerical calculation on a model system. For convenience we have chosen

$$A_1(\omega) = S_1(2\pi\sigma_1^2)^{-1/2} \exp[-(\omega-\omega_0)^2/2\sigma^2]. \quad (13)$$

In order to avoid significant non-physical contributions from the negative tail of the gaussian function we have limited ourselves only to the cases in which

$$\sigma/\omega_0 \ll 1. \quad (14)$$

We have further invoked the ansatz which has been used successfully in the theory of zero phonon linewidth [14,15]

$$V(\omega_1, \omega_2) = \gamma V(\omega_1) V(\omega_2). \quad (15)$$

In view of eqs. (11), (14) and (15), we can approximate $A_2(\omega)$ by a gaussian

$$A_2(\omega) \approx S_2(4\pi\sigma^2)^{-1/2} \exp[-(\omega-2\omega_0)^2/4\sigma^2], \quad (16)$$

where

$$S_2 = \tfrac{1}{8}(S_1 \hbar\gamma\omega_0)^2. \quad (17)$$

From zero phonon linewidth data [14,15] it is possible to estimate $S_2/S_1 \approx O(10^{-1})$. The total relative frequency change of the phonon modes is of the order $(S_2)^{1/2}/S_1$. In order to calculate $G(\Omega)$ we expand the integrand in eq. (5) in power series

$$G(\Omega) = \frac{\exp(-S_1-S_2)}{2\pi} \sum_{n_1,n_2=0}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}t \times \exp[-\mathrm{i}(\Omega-\omega_0+\Omega_0)t] \, \frac{[g_1(t)]^{n_1}}{n_1!} \, \frac{[g_2(t)]^{n_2}}{n_2!} . \quad (18)$$

The terms in the sum are convolutions of the functions $A_1(\omega)$ and $A_2(\omega)$. Since both functions are gaussians these convolutions can be easily calculated, provided that we extend $A_1(\omega)$ and $A_2(\omega)$ to negative values of ω. This procedure, justified by inequality (14), has been adopted in the course of the calculation. The final formula for the calculation of $G(\Omega)$ is

$$G(x) = \exp(-S_1-S_2) \sum_{m=1}^{\infty} K(m)(2\pi m y^2)^{-1/2} \times \exp[-(x-m)^2/2my^2], \quad (19)$$

where

$$K(m) = \sum_{n=0}^{[m/2]} \frac{S_1^{m-2n}}{(m-2n)!} \frac{S_2^n}{n!}, \quad (20)$$

$$x = \frac{\Omega - \omega_0 + \Omega_0}{\omega_0}, \quad (21)$$

$$y = \sigma/\omega_0. \quad (22)$$

Fig. 1 displays the results of a numerical calculation of $\log_{10} G$ as a function of x, [eq. (19)] for $y = 0.1$, $S_1 = 1$, and $S_2 = 0.5, 0.05$ and 0. As expected, the presence of the nonlinear interaction affects dramatically the line shape function for large values of x. For relatively small values of x, where $G(\Omega)$ is large, the effect of the quadratic interaction is small. This range of small values of x is monitored by measurements of the optical line shapes. We conclude that for

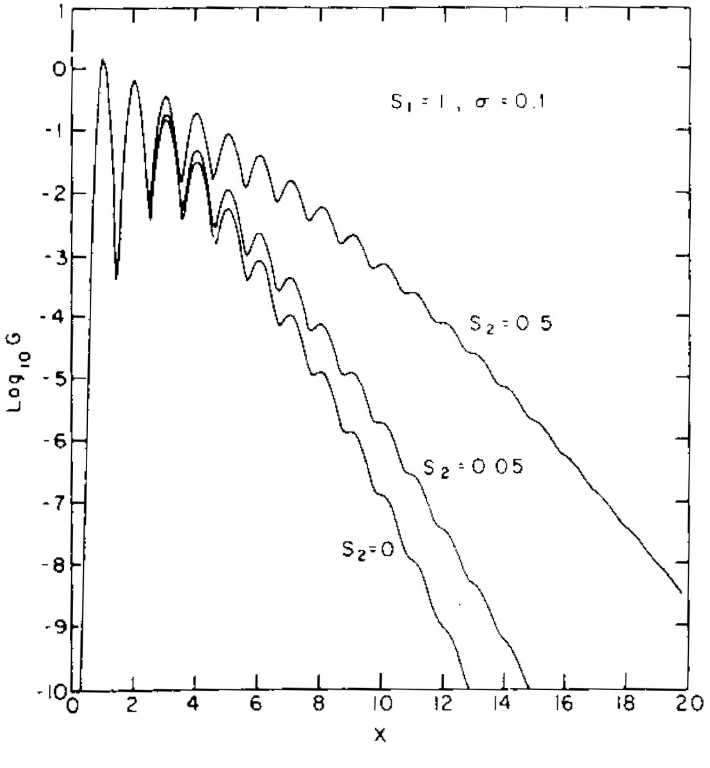

Fig. 1. The overall behavior of the transition rate at $T = 0$ K as calculated from eq. (19) for three values of the quadratic coupling S_2. The different peaks correspond to transitions involving different numbers of phonons.

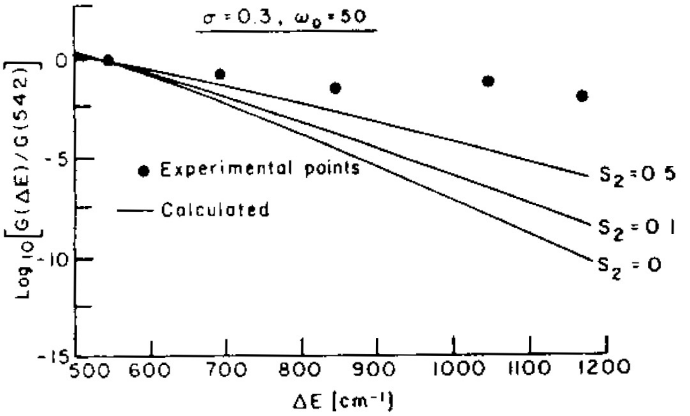

Fig. 2. An attempt to fit the gaussian model [eq. (19)] (continuous line) to Bondebey's experimental results [7]. The $S_2 = 0$ case corresponds to the linear coupling model which was utilized previously [20].

$S_2/S_1 < 0.5$ the effects of quadratic coupling terms on the optical spectra is small and the major contribution to the phonon structure will be due to linear coupling terms. In fig. 2 we show a comparison of the calculated results [using eq. (19)] with and without quadratic effects and the experimental results obtained by Bondebey on the CN systems. Clearly the quadratic terms have an important effect in shifting the calculated results towards the experimental ones. It should be kept in mind that in making these calculations we assumed that the molecule–lattice coupling [V of eq. (1)] is the same for all the transitions involved. This assumption is not quite correct; it might be the source of the remaining discrepancy. Other important factors, which were not included in our treatment, are corrections higher than quadratic and higher order terms in V which are discussed below.

3. Discussion

We have demonstrated that quadratic terms in the impurity–lattice coupling, which represent mode-mixing and frequency changes are important in both the qualitative and the quantitative behavior of the multiphonon relaxation rate between the impurity levels. It should be pointed out that the effect observed here is of a different nature than the effect of frequency changes on intramolecular radiationless transition rates. In the latter case, taking frequency changes into account has mainly the effect of adding active accepting modes which are not characterized by a shift of their equilibrium position between different electronic levels. Such molecular modes are usually of low frequency and when they become important in determining the nonradiative rate the energy gap dependence may become steeper [17]. In the lattice case the main effect of incorporating the quadratic terms is to increase the effective cutoff frequency from ω_D to $2\omega_D$. This moderates the energy gap dependence of the transition rate. This conclusion does not depend on the particular nature of the model used here [as represented by eqs. (13), (14)] and is expected to hold generally.

The observation that the quadratic terms have such a profound effect on the nonradiative rates for large energy gaps suggests that other higher order terms, both in V, eq. (1), (resulting from anharmonicities) and in the cumulant expansion, which was truncated beyond second-order contributions to eq. (5), may be important. Such terms will give rise to higher cutoff frequencies in the effective phonon spectrum. We have made this point before with respect to the effect of frequency changes on intramolecular radiationless transitions [18]. With this in mind we conclude that the results obtained in the present paper should not be considered as exact model results but rather to be viewed as a demonstration of the importance of nonlinear coupling terms on nonradiative decay rates in solids.

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Appendix

In this appendix we present an outline of the derivation of eqs. (5)–(9). The normal mode coordinate operator $A_s(t)$ in the Heisenberg picture is given by

$$A_s(t) = b_s \exp(-\mathrm{i}\omega_s t) + b_s^\dagger \exp(\mathrm{i}\omega_s t), \tag{A.1}$$

where $b_s^\dagger$ and b_s are the boson creation and annihilation operators of the mode s, respectively. The time dependent potential $V(t)$ is given by

$$V(t) = \sum_s V_s A_s(t) + \tfrac{1}{2} \sum_{s,s'} V_{s,s'} A_s(t) A_{s'}(t). \tag{A.2}$$

We introduce $g(t)$:

$$\exp[g(t)] = \langle T \exp\left(-\mathrm{i}\hbar^{-1} \int_0^t V(t_1)\,\mathrm{d}t_1\right)\rangle. \tag{A.3}$$

The function $g(t)$ can be evaluated to any order in $V(t)$ by utilizing cumulant expansion of the right-hand-side of eq. (A.3)

$$g(t) = \sum_{n=1}^{\infty} (-\mathrm{i}\hbar^{-1})^n \int_0^t \prod_{j=1}^{n} \mathrm{d}t_j \langle T \prod_{k=1}^{n} V(t_k)\rangle_\mathrm{c}, \tag{A.4}$$

where the subscript c denotes cumulant average. The first two cumulant averages are related to ordinary averages as follows [22]:

$$\langle x\rangle_\mathrm{c} = \langle x\rangle, \quad \langle x^2\rangle_\mathrm{c} = \langle x^2\rangle - \langle x\rangle^2, \tag{A.5}$$

where $\langle\ \rangle$ denotes ordinary average. Using eqs. (A.4) and (A.5) we have to second-order in $V(t)$:

$$g(t) = -\mathrm{i}\hbar^{-1} \int_0^t \langle V(t_1)\rangle\,\mathrm{d}t_1 + \tfrac{1}{2}(-\mathrm{i}\hbar^{-1})^2 \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 [\langle TV(t_1)V(t_2)\rangle - \langle V(t_1)\rangle\langle V(t_2)\rangle]. \tag{A.6}$$

The calculation of the first term in this expression is straightforward:

$$\langle V(t)\rangle = \sum_s V_s \langle A_s(t)\rangle + \tfrac{1}{2} \sum_{s_1,s_2} V_{s_1,s_2} \langle A_{s_1}(t) A_{s_2}(t)\rangle = \tfrac{1}{2} \sum_s V_{s,s}(2n_s + 1), \tag{A.7}$$

where n_s is the average phonon occupation number of the s mode:

$$n_s = [\exp(\hbar\omega_s/kT) - 1]^{-1}. \tag{A.8}$$

We turn now to the second term in eq. (A.6). The first thermal average appearing in the integrand is given by:

$$\langle TV(t_1)V(t_2)\rangle = \sum_{s_1,s_2} V_{s_1} V_{s_2} \langle TA_{s_1}(t_1) A_{s_2}(t_2)\rangle + \tfrac{1}{4} \sum_{s_1,s_1'} \sum_{s_2,s_2'} V_{s_1,s_1'} V_{s_2,s_2'} \langle TA_{s_1}(t_1) A_{s_1'}(t_1) A_{s_2}(t_2) A_{s_2'}(t_2)\rangle. \tag{A.9}$$

The first term on the right-hand-side of eq. (A.9) is calculated as follows:

$$\langle A_{s_1}(t_1) A_{s_2}(t_2)\rangle = (n_{s_1}+1) \exp(-\mathrm{i}\omega_{s_1}\tau)\delta_{s_1 s_2} + n_{s_1} \exp(\mathrm{i}\omega_{s_1}\tau)\delta_{s_1 s_2}, \tag{A.10}$$

where $\tau = t_1 - t_2$. Using eq. (A.10) we obtain:

$$\sum_{s_1,s_2} V_{s_1} V_{s_2} \langle TA_{s_1}(t_1) A_{s_2}(t_2)\rangle = \sum_s V_s^2 [(n_s+1) \exp(-\mathrm{i}\omega_s|\tau|) + n_s \exp(\mathrm{i}\omega_s|\tau|)]. \tag{A.11}$$

In order to calculate the second term on the right-hand-side of eq. (A.10) we need thermal averages of products of four boson operators. These are given in the following equations [23]:

$$\langle b_{s_1} b_{s_1'} b_{s_2}^\dagger b_{s_2'}^\dagger\rangle = (n_{s_1}+1)(n_{s_1'}+1)(\delta_{s_1 s_2}\delta_{s_1' s_2'} + \delta_{s_1 s_2'}\delta_{s_1' s_2}), \tag{A.12a}$$

$$\langle b_{s_1} b_{s_1'}^\dagger b_{s_2} b_{s_2'}^\dagger\rangle = (n_{s_1}+1)(n_{s_2}+1)\delta_{s_1 s_1'}\delta_{s_2 s_2'} + (n_{s_1}+1) n_{s_2} \delta_{s_1 s_2'}\delta_{s_1' s_2}, \tag{A.12b}$$

$$\langle b_{s_1} b^\dagger_{s_1'} b^\dagger_{s_2} b_{s_2'} \rangle = (n_{s_1}+1) n_{s_1'} \delta_{s_1 s_2} \delta_{s_1' s_2'} + (n_{s_1}+1) n_{s_2} \delta_{s_2 s_2'} \delta_{s_1 s_1'}, \tag{A.12c}$$

$$\langle b^\dagger_{s_1} b_{s_1'} b_{s_2} b^\dagger_{s_2'} \rangle = n_{s_1} (n_{s_2}+1) \delta_{s_1 s_1'} \delta_{s_2 s_2'} + n_{s_1} (n_{s_1'}+1) \delta_{s_1 s_2} \delta_{s_1' s_2'}, \tag{A.12d}$$

$$\langle b^\dagger_{s_1} b_{s_1'} b^\dagger_{s_2} b_{s_2'} \rangle = n_{s_1} n_{s_2} \delta_{s_1 s_1'} \delta_{s_2 s_2'} + n_{s_1} (n_{s_2}+1) \delta_{s_1 s_2'} \delta_{s_1' s_2}. \tag{A.12e}$$

$$\langle b^\dagger_{s_1} b^\dagger_{s_1'} b_{s_2} b_{s_2'} \rangle = n_{s_1} n_{s_1'} (\delta_{s_1 s_2} \delta_{s_1' s_2'} + \delta_{s_1 s_2'} \delta_{s_1' s_2}). \tag{A.12f}$$

With the help of eqs. (A.12) we can evaluate the thermal average of products of four A operators:

$$\begin{aligned}
&\langle A_{s_1}(t_1) A_{s_1'}(t_1) A_{s_2}(t_2) A_{s_2'}(t_2) \rangle \\
&\quad = \{(n_{s_1}+1)(n_{s_2}+1) \exp[-\mathrm{i}(\omega_{s_1}+\omega_{s_2})\tau] + (n_{s_1}+1) n_{s_2} \exp[\mathrm{i}(\omega_{s_2} - \omega_{s_1})\tau] + n_{s_1}(n_{s_2}+1) \exp[\mathrm{i}(\omega_{s_1}-\omega_{s_2})\tau] \\
&\quad + n_{s_1} n_{s_2} \exp[\mathrm{i}(\omega_{s_1}+\omega_{s_2})\tau]\} (\delta_{s_1 s_2} \delta_{s_1' s_2'} + \delta_{s_1 s_2'} \delta_{s_1' s_2}) \\
&\quad + [(n_{s_1}+1)(n_{s_2}+1) + (n_{s_1}+1) n_{s_2} + n_{s_1}(n_{s_2}+1) + n_{s_1} n_{s_2}] \delta_{s_1 s_1'} \delta_{s_2 s_2'},
\end{aligned} \tag{A.13}$$

where again $\tau = t_1 - t_2$. We can proceed now to the calculation of the second sum in eq. (A.9):

$$\begin{aligned}
&\sum_{s_1, s_1'} \sum_{s_2, s_2'} V_{s_1, s_1'} V_{s_2, s_2'} \langle T A_{s_1}(t_1) A_{s_1'}(t_1) A_{s_2}(t_2) A_{s_2'}(t_2) \rangle \\
&\quad = 2 \sum_{s_1, s_1'} V^2_{s_1, s_1'} \{(n_{s_1}+1)(n_{s_1'}+1) \exp[-\mathrm{i}(\omega_{s_1}+\omega_{s_1'})|\tau|] + (n_{s_1}+1) n_{s_1'} \exp[\mathrm{i}(\omega_{s_1'} - \omega_{s_1})|\tau|] \\
&\quad + n_{s_1}(n_{s_1'}+1) \exp[\mathrm{i}(\omega_{s_1}-\omega_{s_1'})|\tau|] + n_{s_1} n_{s_1'} \exp[\mathrm{i}(\omega_{s_1}+\omega_{s_1'})|\tau|] + \left[\sum_s V_{s,s}(2n_s+1)\right]^2,
\end{aligned} \tag{A.14}$$

where we took advantage of the fact that $V_{s_1, s_2} = V_{s_2, s_1}$.

In the course of the evaluation of the integrals occurring in eq. (A.6), the following formula is useful:

$$\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \exp(\mathrm{i}\omega |t_2 - t_1|) = 2\omega^{-2}[1 - \exp(\mathrm{i}\omega t)] + 2\mathrm{i}t/\omega. \tag{A.15}$$

Substituting eqs. (A.7), (A.11) and (A.14) in eq. (A.6), and utilizing eq. (A.15), a general expression for $g(t)$ is obtained [14].

The $T = 0$ K version of $g(t)$ (obtained by taking $n \equiv 0$) is presented in eqs. (5)–(9).

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