The Journal of Chemical Physics

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Citation: J. Chem. Phys. **78**, 4193 (1983); doi: 10.1063/1.445096
View online: http://dx.doi.org/10.1063/1.445096
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v78/i6
Published by the American Institute of Physics.

On the calculation of transfer rates between impurity states in solids

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(Received 30 July 1982; accepted 10 September 1982)

We comment on the calculation of energy transfer in solids, showing that the calculation can be done to infinite order in the phonon-impurity interaction using the small-polaron transformation. When the final result is expanded, the results of low order perturbation theory are recovered, and, in addition, new terms are found which are due to cross products.

I. INTRODUCTION

Recently, there have been a number of beautiful experiments on energy transfer and spectral diffusion in inhomogeneously broadened spectral lines in electronic excitations[1] and vibrational excitations.[2] In order to understand the dynamics, the energy transfer rate between impurities must be calculated. These rates are derivable from the general Hamiltonian

$$H = H_0 + V_J + V_g \,, \tag{1}$$

where V_J is the electronic transfer interaction coupling the impurity states of H_0 and V_g is a local coupling to the phonon bath, usually taken to be linear or quadratic in the phonon variables. We discuss this in greater detail below.

Most calculations of the probability amplitude for transfer, including those of recent articles[3] use standard perturbation theory, taking V_J to first order and V_g to first or second order (describing one or two phonon processes, respectively, for a linear coupling). Each order of perturbation theory in V_g, as well as each choice for the form of the coupling results in a different dependence on temperature, energy, and other parameters. Since the simplest connection to make between theory and experiment is to compare the observed and predicted temperature dependencies of transfer rates, optical linewidths, etc., one must be careful to include all orders of the bath–molecule interaction in order to avoid spurious results. We wish to point out that this can be accomplished easily by using the small polaron transformation,[4–10] which gives the transfer rate exactly to all orders in V_g and lowest order in V_J. In fact, at higher temperatures for moderate to strong coupling to the bath, it is absolutely necessary to use the small polaron transformation, assuming the resonance interaction is small enough to warrant a first order calculation in V_J.

Although the equivalence of this approach to infinite order perturbation theory in the bath interaction has been previously noted,[6] it has never been examined rigorously and seems to be relatively unknown. This examination also reveals that there is another term second order in the phonon interaction in addition to the one usually calculated by perturbation theory, which cannot necessarily be neglected. Even though we address only the impurity transfer problem here, it should be noted that our comments apply equally well to the case of a pure crystal, or indeed to the calculation of transfer rates or line shapes for any system linearly or quadratically coupled to a bath of boson excitations.

II. MODEL CALCULATION

As an example, consider the transfer of energy between two impurity molecules doped into inequivalent sites at r_1 and r_2 in some host. The Hamiltonian is

$$\begin{aligned} H_0 &= \epsilon_1 a_1^\dagger a_1 + \epsilon_2 a_2^\dagger a_2 + \sum_q \omega_q (b_q^\dagger b_q + \tfrac{1}{2}) \,, \\ V_J &= J(a_1^\dagger a_2 + a_2^\dagger a_1) \,, \\ V_g &= N^{-1/2} \sum_q g_q \omega_q (b_q + b_{-q}^\dagger)[a_1^\dagger a_1 \exp(iq\cdot r_1) \\ &\quad + Z_q a_2^\dagger a_2 \exp(iq\cdot r_2)] \,, \end{aligned} \tag{2}$$

where J is the resonance interaction, g_q is the coupling to the phonon of wave vector q, $Z_q \neq 1$ allows for different coupling to sites 1 and 2, and $a_n^\dagger$ and a_n ($b_q^\dagger$ and b_q) create and annihilate excitations (phonons) on site n (of wave vector q).

Effecting the transformation $\tilde{H} = e^S H e^{-S}$, where

$$\begin{aligned} S &= -N^{-1/2} \sum_q g_q (b_q - b_{-q}^\dagger)\,[a_1^\dagger a_1 \exp(iq\cdot r_1) \\ &\quad + a_2^\dagger a_2 Z_q \exp(iq\cdot r_2)] \,, \end{aligned} \tag{3}$$

we find

$$\tilde{H} = H_0 - \sum_q g_q^2 \omega_q [a_1^\dagger a_1 + Z_q^2 a_2^\dagger a_2] + \tilde{V} \,, \tag{4}$$

$$\tilde{V} = J(a_1^\dagger a_2\, \theta_1^\dagger \theta_2 + a_2^\dagger a_1 \theta_2^\dagger \theta_1) \,,$$

where

$$\theta_1^\dagger = \exp\left[-N^{-1/2} \sum_q g_q \exp(iq\cdot r_1)(b_q - b_{-q}^\dagger)\right] , \tag{5}$$

and

$$\theta_2^\dagger = \exp\left[-N^{-1/2} \sum_q g_q \exp(iq\cdot r_2)\, Z_q (b_q - b_{-q}^\dagger)\right] .$$

$\theta_1^\dagger$ is the "clothing" operator responsible for the lattice distortion about the excitation on site 1. Thus we have replaced the linear coupling term with a phonon modulated resonance interaction which transfers both

the excitation and its associated "phonon cloud."

We use simple first order perturbation theory[11] in $\tilde{V}$ to calculate the transfer rate between the clothed states on sites 1 and 2. We must use the clothed states with the transformed Hamiltonian since we want to compare the results with the bare transfer rates calculated by using perturbation theory with the bare Hamiltonian. That is,

$$|\langle 2|\, e^{-iHt}\,|1\rangle|^2 \equiv |\langle \mathrm{II}\,|\, e^{-i\tilde{H}t}\,|\mathrm{I}\rangle|^2 \,, \tag{6}$$

where $|1\rangle$ is the state vector for the bare excitation on site 1 and $|\mathrm{I}\rangle = e^{s}|1\rangle = \theta_1^{\dagger}|1\rangle$ is its clothed equivalent. We use the Fermi Golden Rule in integral form[11(a)]

$$W_{\mathrm{I}\to\mathrm{II}} = \sum_{i,j} |\langle \mathrm{I}, i|\,\tilde{V}\,|\mathrm{II}, j\rangle|^2 p_i \delta(E_i + \epsilon_{\mathrm{I}} - E_j - \epsilon_{\mathrm{II}}) \,,$$

$$= \mathrm{Re}\int_0^\infty dt \exp[i(\epsilon_1 - \epsilon_2)t]\langle \tilde{V}_{\mathrm{I},\mathrm{II}}(t)\tilde{V}_{\mathrm{II},\mathrm{I}}\rangle \,,$$

where $|\mathrm{I}, i\rangle$ is a state with the excitation on site 1 and the bath (phonons) in state i (energy $= E_i$). p_i is the canonical probability of being in state i at temperature T $[\sim\exp(-\beta E_i)]$, the brackets represent a canonical average over the phonon states,

$$\tilde{V}_{\mathrm{I},\mathrm{II}}(t) = \exp(iH_{\mathrm{ph}}t)\,\tilde{V}_{\mathrm{I},\mathrm{II}}\exp(-iH_{\mathrm{ph}}t) \,, \tag{7}$$

and $\tilde{V}_{\mathrm{I},\mathrm{II}}$ is the phonon operator resulting when the electronic matrix element of $\tilde{V}$ is taken.

The result, for $\epsilon_1 \neq \epsilon_2$, is (see Refs. 6 or 8 for details)

$$W_{1\to 2} = [J^2\exp(-\phi(0))]\,\mathrm{Re}\int_0^\infty dt \exp[i(\epsilon_1 - \epsilon_2)t] \times e^{\phi(t)}e^{A(t)} \,, \tag{8}$$

where

$$\phi(t) = 2N^{-1}\sum_q X_q^2[n_q\exp(i\omega_q t) + (n_q+1)\exp(-i\omega_q t)] \,,$$

$$X_q^2 = g_q^2[\tfrac{1}{2}(1+Z_q^2) - Z_q\cos q\cdot(r_1 - r_2)] \,,$$

$$n_q = (e^{\beta\omega_q} - 1)^{-1} \,.$$

The term in brackets is often written as $\tilde{J}^2$, where $\tilde{J} < J$ is the renormalized transfer integral ($e^{-\phi(0)}$ is simply the Debye–Waller factor). When $\epsilon_1 = \epsilon_2$, a more careful job must be done on $W_{1\to 2}$ because of the degeneracy. The effect is to subtract 1 from $\exp[\phi(t) + A(t)]$ in the integrand of Eq. (8).

If we were to calculate $W_{1\to 2}$ using $\tilde{V}$ with the bare states, we would arrive at Eq. (8) without the factor $e^{A(t)}$. Within the limits of our approximation, however, these two expressions are equivalent since

$$A(t) = 2iN^{-1}\sum_q g_q^2(1 - Z_q\exp[iq\cdot(r_1 - r_2)])\sin\omega_q t \,,$$

and $A(t)$ goes to 0 for times longer than a few picoseconds. Our Fermi Golden Rule expression is only valid for times longer than this, and we henceforth set $e^{A(t)} = 1$. If one is interested in short time behavior (comparable to clothing times), however, one must be careful about the proper choice of basis sets and initial states.

Let us expand the exponential in the integrand of Eq. (8) and look at the second and third terms, setting $e^{-\phi(0)} = 1$ for now:

$$2N^{-1}\int_0^\infty dt \exp[i(\epsilon_1 - \epsilon_2)t]\sum_q X_q^2[n_q\exp(i\omega_q t) + (n_q+1)\exp(-i\omega_q t)] \tag{9}$$

and

$$2N^{-2}\int_0^\infty dt \exp[i(\epsilon_1 - \epsilon_2)t]\sum_{q,q'} X_q^2 X_{q'}^2 \times[n_q\exp(i\omega_q t) + (n_q+1)\exp(-i\omega_q t)] \times[n_{q'}\exp(i\omega_{q'}t) + (n_{q'}+1)\exp(-i\omega_{q'}t)] \,. \tag{10}$$

These terms, proportional to g^2 and g^4, respectively, can easily be shown to be identical to the one and two phonon assisted rates as calculated by Holstein, Lyo, and Orbach[3] using perturbation theory.

To compute the bare transfer rate perturbatively to all orders in V_g and lowest order in V_J, we use the exact form of the transition rate using the T matrix,[11(b)]

$$W_{1\to 2} = \sum_{i,j} |\langle 1, i|\,T\,|2, j\rangle|^2 p_i \delta(E_i + \epsilon_1 = E_j - \epsilon_2) \,,$$

where $T \equiv V + VGT$ where G is the zeroth order Green's function. We write $W_{1\to 2}$ in integral form as before except that the matrix elements of T replace those of $\tilde{V}$,

$$W_{1\to 2} = \mathrm{Re}\int_0^\infty dt\langle T_{12}(t)T_{21}^{\dagger}\rangle\exp[i(\epsilon_1 - \epsilon_2)t] \,, \tag{11}$$

where we may break up T_{12} into terms of first order in V_g, second order in V_g, etc.:

$$T_{12} = [T^{(1)}]_{12} + [T^{(2)}]_{12} + [T^{(3)}]_{12} + \cdots \,. \tag{12}$$

The phonon operator $T_{12}(t)$ is T_{12} in the interaction representation with respect to the zeroth order phonon Hamiltonian. Care must be taken when using Eq. (11) since G (and hence T) contains an energy E which must be evaluated correctly (in all terms which we shall study, this turns out to be obvious from energy conservation and the form of V).

$T^{(3)}$ for example is the set of all third order evolution operators using V_J once and V_g twice. The first nonzero term arises from $\langle[T^{(2)}(t)]_{12}\,[T^{(2)}]_{21}\rangle$ where the phonon matrix elements of $[T^{(2)}]_{21}$ are given by

$$\langle j\,|\,[T^{(2)}]_{21}\,|\,i\rangle = \sum_{M,m}\frac{\langle 2j|V_g|Mm\rangle\langle Mm|V_J|1i\rangle}{(\epsilon_1 + E_i - \epsilon_M - E_m)} + \sum_{M,m}\frac{\langle 2j|V_J|Mm\rangle\langle Mm|V_g|1i\rangle}{(\epsilon_1 + E_i - \epsilon_M - E_m)} \,, \tag{13}$$

with $|Mm\rangle$ labeling the intermediate electronic and phonon states. Using V_J and V_g from Eq. (2), we easily arrive at Eq. (9), the single phonon assisted rate.

The next contribution comes from the square of the third order propagator, where a typical matrix element of $T^{(3)}$ is of the form

$$\langle j|[T^{(3)}]_{21}|i\rangle = \sum_{\substack{M_1 m_1 \\ M_2 m_2}} \frac{\langle 2j|V_g|M_2 m_2\rangle\langle M_2 m_2|V_g|M_1 m_1\rangle\langle M_1 m|V_J|1i\rangle}{[\epsilon_1 + E_i - \epsilon_{M_1} - E_{m_1}][\epsilon_1 + E_1 - \epsilon_{M_2} - E_{m_2}]} , \tag{14}$$

plus two similar terms with the ordering of the V's permuted. Using this expression with Eqs. (11) and (2), a bit of algebra exactly reproduces the two-phonon rate of Eq. (10). Similarly, the square of the fourth order propagator gives us the three-phonon assisted rate, and so on, to all orders in the bath interaction.

However, we see that there is another contribution of the same order as the two-phonon rate ($J^2 g^4$) from the product of the second terms in the expansions of each of the exponentials in Eq. (8):

$$2N^{-1}\left[\sum_q X_q^2 \coth\left(\frac{\beta\omega_q}{2}\right)\right]\left\{2N^{-1}\sum_{q'} X_{q'}^2 \times \int_0^\infty dt \exp[i(\epsilon_1 - \epsilon_2)t][n_{q'}\exp(i\omega_{q'}t) + (n_{q'}+1)\exp(-i\omega_{q'}t)]\right\} . \tag{15}$$

The origin of this expression is a cross term between the second and fourth order propagators of Eq. (12). In fact, all of the contributions arising from the expansion of the Debye–Waller factor are due to similar cross terms, which are usually ignored in perturbative approaches. The above term is a bit laborious to calculate directly from Eqs. (11) and (12) since it involves such a high order propagator, illustrating another advantage of using the small polaron transformation. For low temperatures or weak coupling, where an expansion up to g^4 might be valid, this cross term is not at all negligible for $|\epsilon_1 - \epsilon_2| \gtrsim kT$ when compared with the usual two phonon rate, and cannot be ignored. This is especially true for species doped into amorphous hosts, where the inhomogeneous broadening can give rise to large $\Delta\epsilon$'s (100 cm^{-1} or more for rare earth ions in hard glasses for example).

In certain instances, as for molecular modes of particular symmetries,[9] the linear phonon coupling is small and one must introduce a perturbation explicitly quadratic in the phonon interaction. It is possible to perform a similar transformation for this V_g, or even for a system with both linear and quadratic coupling to the bath.[9]

In the weak coupling limit g is small, and Eq. (8) can be expanded to whatever order in g is deemed proper, reproducing the results of a correct perturbation treatment. In the strong coupling high temperature limit, $\exp[\phi(t) - \phi(0)]$ decays quickly and we can expand it about $t = 0$. This limit has been examined by Holstein[4] and Soules and Duke,[6] as well as Mahan[12] and Toyozawa,[13] who consider the small polaron line shape. Grover and Silbey[5,7] and Silbey and Munn[10] have evaluated $W_{1\to 2}$ for more general values of g and T, and Munn and Silbey[9] have examined the quadratic coupling case. Before concluding, we should note that various other approaches reproduce the same result. Holstein[4] and Gelbart, Freed, and Rice[14] both present first quantized derivations of Eq. (8). Mahan[12] and Toyozawa,[13] following more intuitive approaches, provide interesting derivations of similar expressions for the line shape.

Our purpose was to examine the various approaches to the problem of phonon assisted transport, and show how they are equivalent to, or limiting cases of, the exact small polaron rate. For completeness, we should also mention that the Förster–Dexter rate is equivalent to the small polaron rate in the limit that we treat the phonon interactions on sites 1 and 2 as uncorrelated. This is not necessarily valid, as discussed by Soules and Duke.[6] We also wish to point out that when second order treatments are valid, one should include the contribution from the cross term [Eq. (15)] when $|\Delta\epsilon| \gtrsim kT$.

Thus, one can calculate these transition rates to all orders in the bath interaction, including cross terms, by simply using the small polaron transformation. The methods of Ref. 3 are valid in the low temperature, weak coupling regime, except for the neglect of the aforementioned cross term. However, such calculations are more easily performed by expanding Eq. (8) to the desired order in g, thus avoiding the tedium inherent in higher order perturbation methods. At higher temperatures, or for moderate to strong coupling, one must use the small polaron transformation if J is not too large. When J is large, the second order result breaks down and more elaborate methods are necessary. However, for low concentrations of impurity states the procedure given here will be valid.

ACKNOWLEDGMENT

This research was supported in part by the NSF under grant CHE81-00407.

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