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# Phonon transport aspects of non-radiative decay

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**Abstract.** Non-radiative decay in solids depends not only on the particular features of electron–phonon coupling but also on the spatial dissipation process of the energy into the host lattice. A theory is given in which the decay is handled as a generalised Bixon–Jortner process. This allows for a lattice dynamical Green function description, which is a well known computational option. The final result exhibits the interplay of three influences: accepting-mode coupling, promoting-mode coupling and phonon transport. This is made explicit in the calculation of prototypical examples.

## 1. Introduction

A huge amount of theoretical work has been devoted to the non-radiative transition problem. One main stream of investigation has been based on the paper of Huang and Rhys (1950). Later this has become known as the 'adiabatic base' approach, as contrasted to the 'static base' approach which dates back to the work of Helmis (1956). For a broader background description we refer to the extensive article of Stoneham (1981). More recently the discrepancy between the 'static' and 'adiabatic' approaches has led to new theoretical activity (Gutsche 1982, Denner and Wagner 1983, 1984a, b, Bartram and Stoneham 1985, Wagner 1982, 1985a, b), which originally was initiated by Huang (1981) himself.

The present work aims at illuminating an aspect of the non-radiative transition problem which up to now has played almost no role in the discussion. We start from the expectation that the local non-radiative decay process should depend on how the surrounding medium is able to administer the spatial dissipation of the energy, which has been transmuted from the electronic to the oscillatory subsystem. For example it appears conceivable that there may be bottleneck situations against such dissipation. Thus in our concept the local transport properties of phonons play the dominant role.

In our study the decay process is handled as a Fano–Bixon–Jortner process, which is described in section 2. For convenience we assume the initial state to be the relaxed excited electronic state, although our formalism also allows for the treatment of unrelaxed initial states (Zavt *et al* 1984). In section 3 the required phonon formalism is presented, which is needed to describe our electron–phonon model (section 4). The non-radiative decay is characterised by a peculiar 'decay function', which incorporates the interplay and competition of three-parameter sets (spatial extension of the promoting- and accepting-mode coupling, and phonon dispersion); this is given in section

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5. In section 6 the application of our formalism is demonstrated by considering a one-dimensional lattice, and it is found (section 7) that the 'decay function' is of a form which is strongly related to a kind of spatial dissipation which was originally considered by Hamilton (1839). In section 8 we develop a moment method which allows a quick global analysis of the decay characteristics. This is used (section 9) to discuss the interplay and competing influences of the dynamical parameter sets.

## 2. Modified Fano–Bixon–Jortner model

As explained in the following sections, we shall describe the non-radiative decay process as a Fano (1961) mechanism in which a singular state $|s\rangle$ decays into a quasi-continuum of states $\{|n\rangle\}$. This is incorporated in a Hamiltonian of the form

$$H = E_s^{(0)}\,|s\rangle\langle s| + \sum_n E_n^{(0)}\,|n\rangle\langle n| + \sum_n (V_n\,|s\rangle\langle n| + \text{HC}). \tag{1}$$

An exact solution of this problem has been derived by Bixon and Jortner (1968, 1969) for the special case $E_n^{(0)} = n\varepsilon$ and $V_n = V$. This solution later has been generalised in our previous paper (Wagner and Vazquez-Marquez 1988). The basic correlation function of the general solution of the time-dependent Schrödinger equation is shown to be $(\varepsilon = 0_+)$

$$\langle\Psi(0)\Psi(t)\rangle = \frac{\mathrm{i}}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\,\exp(-\mathrm{i}\omega t)\{[\omega + \mathrm{i}\varepsilon - E_s^{(0)} - S(\omega + \mathrm{i}\varepsilon)]^{-1} - [\text{CC}]^{-1}\} \tag{2}$$

where the most natural initial state, which is the singular state $|s\rangle$,

$$|\Psi(0)\rangle = |s\rangle \tag{3}$$

has been chosen. The self-energy function $S(\omega)$ is the crucial quantity for the decay and is given as

$$S(\omega \pm \mathrm{i}\varepsilon) \equiv \sum_n \frac{|V_n|^2}{(\omega \pm \mathrm{i}\varepsilon) - E_n^{(0)}} = \mp \int_{-\infty}^{\infty} \theta(\mp t)F(t)\exp[-\mathrm{i}(\omega \pm \mathrm{i}\varepsilon)t]\,\mathrm{d}t. \tag{4}$$

It will also be the crucial object of our calculation. Its Fourier transformation defines the 'decay function'

$$F(t) = \sum_n |V_n|^2 \exp(\mathrm{i}E_n^{(0)}t) \tag{5}$$

with the inversion

$$\int_{-\infty}^{\infty} S(\omega \pm \mathrm{i}\varepsilon)\exp(\mathrm{i}\omega t) = \mp 2\pi\mathrm{i}\theta(\mp t)\exp(\pm\varepsilon t)\,F(t). \tag{6}$$

For quick and direct physical insight it is convenient to introduce a moment analysis of the distribution $|V_n|^2$, where the moments are given as follows:

$$M_r = \sum_n (E_n^{(0)})^r |V_n|^2 \tag{7}$$

which may be traced back to $F(t)$ (see equation (5)) as its generating function:

$$M_r = \lim_{t\to 0}\left[\left(\frac{\mathrm{d}}{\mathrm{i}\,\mathrm{d}t}\right)^r \sum_n |V_n|^2 \exp(\mathrm{i}E_n^{(0)}t)\right] \tag{8}$$

or

$$M_r = \lim_{t\to 0} \{[\mathrm{d}/(\mathrm{i}\,\mathrm{d}t)]^r F(t)\}. \tag{9}$$

If we content ourselves with the calculation of the first three moments, we may introduce a suitable analytical form for $F(t)$, which is characterised by three parameters, e.g.

$$F(t) = M_0 \exp(\mathrm{i}\omega_0 t) \exp(-\gamma|t|)(1 + \gamma|t|) \qquad \gamma > 0 \tag{10}$$

which yields

$$S(\omega \pm \mathrm{i}\varepsilon) = M_0(\omega - \omega_0 \pm 2\mathrm{i}\gamma)/(\omega - \omega_0 \pm \mathrm{i}\gamma)^2 \tag{11}$$

where $\omega_0$ and $\gamma$ are given by

$$\omega_0 = M_1/M_0 \tag{12}$$

$$\omega_0^2 + \gamma^2 = M_2/M_0. \tag{13}$$

In the following we shall employ these formulae for a global analysis.

## 3. Phonon dynamics

We consider an oscillatory system with a Hamiltonian

$$H_{\mathrm{ph}} = \tfrac{1}{2}\sum_m P_m^2 + \tfrac{1}{2}\sum_{m,n} V_{m,n} X_m X_n \tag{14}$$

where $P_m$, $X_m$ designate the mass-reduced Cartesian coordinates. The Hamiltonian (14) is diagonalised if normal coordinates $\{P_k, Q_k\}$ are introduced:

$$X_m = \sum_k \eta_m(k) Q_k \qquad P_m = \sum_k \eta_m^*(k) P_k \qquad k = 0, \pm 1, \pm 2, \ldots, \pm N/2 \tag{15}$$

with the inversion

$$Q_k = \sum_m \eta_m^*(k) X_m \qquad P_k = \sum_m \eta_m(k) P_m \tag{16}$$

where $\eta_m(k)$ are eigenvectors which satisfy the orthonormality and closure relations

$$\sum_m \eta_m(k)\eta_m^*(k') = \delta_{k,k'} \tag{17}$$

$$\sum_k \eta_m(k)\eta_{m'}^*(k) = \delta_{m,m'}. \tag{18}$$

The linear transformation (15) transmutes the Hamiltonian (14) to

$$H_{\mathrm{ph}} = \tfrac{1}{2}\sum_k (P_k P_k^+ + \Omega_k^2 Q_k Q_k^+) \tag{19}$$

where the quantities $\Omega_k$ and $V_{mn}$ satisfy the sum rule $\Sigma_k \Omega_k^2 = \Sigma_m V_{mm}$.

The solution of the dynamical problem is given by the Heisenberg evolution operators

$$Q_k(t) = \exp(\mathrm{i}H_{\mathrm{ph}}t)\, Q_k(0) \exp(-\mathrm{i}H_{\mathrm{ph}}t) = Q_k(0)\cos(\Omega_k t) + (1/\Omega_k) P_k(0)\sin(\Omega_k t) \tag{20}$$

$$P_k(t) = \exp(\mathrm{i}H_{\mathrm{ph}}t)\, P_k(0) \exp(-\mathrm{i}H_{\mathrm{ph}}t) = P_k(0)\cos(\Omega_k t) - \Omega_k Q_k(0)\sin(\Omega_k t) \tag{21}$$

which in their structural form are identical with the classical operators. For the background of this formulation we refer to the standard literature on lattice dynamics, e.g. to the books by Maradudin *et al* (1963), by Dederichs *et al* (1980) and by Böttger (1983). We introduce the Zubarev Green function (GF) $G^{\mathrm{r,a}}_{m,n}(t) = \langle\langle X_m(t)X_n(0)\rangle\rangle^{\mathrm{r,a}}$ of the system (14) (see, e.g., Zubarev 1960, Stinchcombe 1978)

$$G^{\mathrm{r,a}}_{m,n}(t) = \mp\Theta(\pm t)\sum_k \frac{1}{\Omega_k}\eta_m(k)\eta_n^*(k)\sin(\Omega_k t) \tag{22}$$

and its Fourier transform

$$\begin{aligned} G_{m,n}(\omega \pm \mathrm{i}\varepsilon) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, G_{m,n}(t)\exp[\mathrm{i}(\omega \pm \mathrm{i}\varepsilon)t] = \frac{1}{2\pi}\sum_k \frac{\eta_m(k)\eta_n^*(k)}{(\omega \pm \mathrm{i}\varepsilon)^2 - \Omega_k^2} \\ &= \frac{1}{4\pi}\sum_k \eta_m(k)\eta_n^*(k)\frac{1}{\Omega_k}\left(\frac{1}{\omega \pm \mathrm{i}\varepsilon - \Omega_k} - \frac{1}{\omega \pm \mathrm{i}\varepsilon + \Omega_k}\right). \end{aligned} \tag{23}$$

For the imaginary part of (23) we then find that

$$\begin{aligned} \operatorname{Im} G_{m,n}(\omega \pm \mathrm{i}\varepsilon)|_{\omega>0} &= -\tfrac{1}{4}\sum_k \frac{1}{\Omega_k}\eta_m(k)\eta_n^*(k)\delta(\omega - \Omega_k) \\ &= -\tfrac{1}{4}\frac{1}{\omega}\sum_k \eta_m(k)\eta_n^*(k)\delta(\omega - \Omega_k). \end{aligned} \tag{24}$$

Employing the eigenvector normalisation (see equations (17) and (18)) we arrive at the formula

$$\sum_m \operatorname{Im} G_{m,n}(\omega + \mathrm{i}\varepsilon)|_{\omega>0} = -\tfrac{1}{4}\frac{1}{\omega}\rho(\omega) \qquad \text{for } \omega > 0 \tag{25}$$

where $\rho(\omega)$ designates the density of the oscillatory frequency distribution $\{\Omega_k\}$. It will be this formula which later plays a central role in our calculation.

## 4. Electron–phonon model

We consider an electronic Hilbert subspace of two states $\{|1\rangle, |2\rangle\}$, and a Hamiltonian of the form

$$H = (\Delta + AS_a)\,|2\rangle\langle 2| + BS_b(|2\rangle\langle 1| + \mathrm{HC}) + H_{\mathrm{ph}}(P, X) \tag{26}$$

where $H_{\mathrm{ph}}$ is the oscillatory Hamiltonian (see section 3). $A$ and $B$ characterise the coupling strengths to the 'accepting'- and 'promoting'-mode coordinates $\{S_a, S_b\}$, respectively. These coordinates will be taken as the linear forms

$$S_a = \sum_m \sigma_m^*(a)X_m \qquad P_a = \sum_m \sigma_m(a)P_m \tag{27}$$

$$S_b = \sum_m \sigma_m^*(b)X_m \qquad P_b = \sum_m \sigma_m(b)P_m \qquad m = 0, \pm 1, \ldots, \pm N/2 \tag{28}$$

where $\sigma_m(a)$ and $\sigma_m(b)$ are 'symmetry vectors' belonging to *different* irreducible representation of a local symmetry group. They obey the orthonormality relations

$$\sum_m \sigma_m(a)\sigma_m^*(b) = 0 \tag{29}$$

$$\sum_m \sigma_m(a)\sigma_m^*(a) = 1 = \sum_m \sigma_m(b)\sigma_m^*(b). \tag{30}$$

Insertion of equation (15) into equations (27) and (28) leads to the forms

$$AS_a = \sum_k Q_k A \sum_m \sigma_m^*(a)\eta_m(k) = \sum_k A_k Q_k \tag{31}$$

$$BS_b = \sum_k Q_k B \sum_m \sigma_m^*(b)\eta_m(k) = \sum_k B_k Q_k \tag{32}$$

with abbreviations

$$A_k = A \sum_m \sigma_m^*(a)\eta_m(k) \tag{33}$$

$$B_k = B \sum_m \sigma_m^*(b)\eta_m(k). \tag{34}$$

The respective diagonal projections of the full Hamiltonian (26) onto the two electronic states thus read

$$\langle 1|H|1\rangle = H_{\text{ph}}(P, Q) \tag{35}$$

$$\langle 2|H|2\rangle = H_{\text{ph}}(P, Q) + AS_a + \Delta. \tag{36}$$

The latter amounts to an oscillatory Hamiltonian with displaced equilibrium positions $\{-A_k/\Omega_k^2\}$ and may be expressed by means of a unitary transformation, which is defined by the displacement operator

$$U_{\text{D}} = \exp\left(\mathrm{i}\sum_k \frac{A_k}{\Omega_k^2} P_k\right) \tag{37}$$

and has the properties

$$U_{\text{D}}^{-1}\Phi(Q_k) = \Phi(Q_k + (A_k/\Omega_k^2)) \tag{38}$$

$$U_{\text{D}}^{-1} Q_k U_{\text{D}} = Q_k + (A_k/\Omega_k^2). \tag{39}$$

Employing these we may write

$$\langle 2|H|2\rangle = U_{\text{D}}^{-1} H_{\text{ph}} U_{\text{D}} - \tfrac{1}{2}\sum_k \left(\frac{A_k}{\Omega_k^2}\right)^2. \tag{40}$$

The vibrational wavefunctions of $H_{\text{ph}} \equiv \langle 1|H|1\rangle$, i.e. those pertaining to the lower electronic state $|1\rangle$, are given as

$$|\{m_k\}\rangle_{|1\rangle} = \prod_k \Phi_{m_k}(Q_k) \tag{41}$$

whereas those of $\langle 2|H|2\rangle$, i.e. those pertaining to the upper electronic state $|2\rangle$, are displaced:

$$|\{m_k\}\rangle_{|2\rangle} = U_{\text{D}}|\{m_k\}\rangle_{|1\rangle}. \tag{42}$$

## 5. Decay function

We handle the decay problem as a Fano–Bixon–Jortner problem, as explained in section 2. That is, we consider a single vibrational state pertaining to the upper electronic level $|2\rangle$ (specifically we choose the lowest of these states, $|\{0_k\}\rangle_{(2)}$), and we assume that this state completely decays into the quasi-continuous set of vibrational states (41) pertaining to the lower electronic level $|1\rangle$ via the promoting-mode interaction. We thus refrain from considering a secondary decay process back into the quasi-continuous vibrational set pertaining to the upper electronic level $|2\rangle$.

Referring to the formalism of section 2 we make the identifications

$$|s\rangle \rightarrow |2\rangle|\{0_k\}\rangle_{(2)} = |2\rangle U_{\mathrm{D}}|\{0_k\}\rangle_{(1)} \tag{43}$$

$$|n\rangle \rightarrow |1\rangle|\{m_k\}\rangle_{(1)} \tag{44}$$

$$E_s^{(0)} \rightarrow \Delta - \tfrac{1}{2}\sum_k \left(\frac{A_k}{\Omega_k^2}\right)^2 \equiv E_{\{0_k\}} \tag{45}$$

$$E_n^{(0)} \rightarrow \sum_k \Omega_k m_k \equiv E_{\{m_k\}} \tag{46}$$

$$V_n \rightarrow B\langle\{0_k\}|_{(1)} U_{\mathrm{D}}^{+}(P_k) S_b^{+}(Q_k)|\{m_k\}\rangle_{(1)} \tag{47}$$

where $m_k$ is the quantum number of the state $|m_k\rangle$ of mode $k$. From the identification (47) we obtain for the decay function (5) in section 2

$$F(t) = |B|^2 \sum_{\{m_k\}} \langle\{0_k\}|_{(1)} U_{\mathrm{D}}^{+}(P) S_b^{+}(Q)|\{m_k\}\rangle_{(1)}$$
$$\times \langle\{m_k\}|_{(1)} S_b(Q) U_{\mathrm{D}}(P)|\{0_k\}\rangle_{(1)} \exp(\mathrm{i}E_{\{m_k\}}t) \tag{48}$$
$$= |B|^2 \langle\{0_k\}|_{(1)} U_{\mathrm{D}}^{+}(P) S_b^{+}(Q) \exp(\mathrm{i}H_{\mathrm{ph}}t)\, S_b(Q) U_{\mathrm{D}}(P)|\{0_k\}\rangle_{(1)} \tag{49}$$

where we have exploited the fact that $\{|m_k\rangle\}$ constitutes a complete orthonormal system in the vibrational subspace. In this manner we have succeeded in reducing the multiphonon summation (48) to a single expectation value. Invoking the Heisenberg representation of operators $O(t) = \exp(\mathrm{i}Ht)\, O(0) \exp(-\mathrm{i}Ht)$ and employing equations (20) and (21) we may transcribe equation (49) into

$$F(t) = |B|^2 \langle\{0_k\}|_{(1)} U_{\mathrm{D}}^{+}(P(0)) S_b^{+}(Q(0)) S_b(Q(t)) U_{\mathrm{D}}(P(t))|\{0_k\}\rangle_{(1)}. \tag{50}$$

We can factorise this expression if $\sigma_m(a)$ (which is implicit in $U_{\mathrm{D}}$ via $A_k$; see equation (33)) and $\sigma_m(b)$ (which defines $S_b(Q)$; see equation (27)) are 'symmetry' vectors pertaining to different irreducible representations (henceforth assumed):

$$F(t) = |B|^2 \langle\{0_k\}|_{(1)} U_{\mathrm{D}}(P(0)) U_{\mathrm{D}}(P(t))|\{0_k\}\rangle_{(1)} \langle\{0_k\}|_{(1)} S_b^{+}(Q(0)) S_b(Q(t))|\{0_k\}\rangle_{(1)}. \tag{51}$$

We employ the formula of Baker (1905) and Hausdorff (1906):

$$\exp y \exp z = \exp(\tfrac{1}{2}[y, z]) \exp(y + z) \qquad \text{if } [y, [y, z]] = 0 = [z, [y, z]]. \tag{52}$$

With this formula and using equation (21) we obtain

$$U^{+}(P(0)) U(P(t)) = \exp\left(-\mathrm{i}\sum_k \frac{A_k}{\Omega_k^2} P_k(0)\right) \exp\left(\mathrm{i}\sum_k \frac{A_k}{\Omega_k^2} P_k(t)\right)$$
$$= \exp\left(\frac{\mathrm{i}}{2}\sum_k \frac{|A_k|^2}{\Omega_k^3} \sin(\Omega_k t)\right)$$

$$\times \exp\left(-\mathrm{i}\sum_k \frac{A_k}{\Omega_k^2} P_k(0)[1-\cos(\Omega_k t)] + \Omega_k Q_k^+(0)\sin(\Omega_k t)\}\right). \tag{53}$$

We now employ a special version of the Bloch (1932) formula (Wilcox 1967):

$$\langle\{0_k\}|\exp\left[\mathrm{i}\sum_k\left(\frac{\xi_k}{\Omega_k^{1/2}}P_k + \eta_k\Omega_k^{1/2}Q_k\right)\right]|\{0_k\}\rangle = \exp\left(-\tfrac{1}{4}\sum_k(|\xi_k|^2+|\eta_k|^2)\right). \tag{54}$$

Then the first matrix element in equation (51) simplifies to the form

$$\langle\{0_k\}|U^+(P(0))U(P(t))|\{0_k\}\rangle = \exp\left(-\tfrac{1}{2}\sum_k |A_k|^2\Omega_k^{-3}[1-\exp(\mathrm{i}\Omega_k t)]\right). \tag{55}$$

In the same way, one can calculate the second matrix element in equation (51):

$$|B|^2\langle\{0_k\}|S_b^+(Q(0))S_b(Q(t))|\{0_k\}\rangle = \tfrac{1}{2}\sum_k |B_k|^2\Omega_k^{-1}\exp(\mathrm{i}\Omega_k t). \tag{56}$$

We introduce the abbreviations

$$u(t) = \tfrac{1}{2}\sum_k |A_k|^2\Omega_k^{-3}\exp(\mathrm{i}\Omega_k t) = \tfrac{1}{2}|A|^2\sum_k \Omega_k^{-3}\exp(\mathrm{i}\Omega_k t)\sum_{m,n}\sigma_m^*(a)\eta_m(k)\eta_n^*(k)\sigma_n(a) \tag{57}$$

$$v(t) = \tfrac{1}{2}\sum_k |B_k|^2\Omega_k^{-1}\exp(\mathrm{i}\Omega_k t) = \tfrac{1}{2}|B|^2\sum_k \Omega_k^{-1}\exp(\mathrm{i}\Omega_k t)\sum_{m,n}\sigma_m^*(b)\eta_m(k)\eta_n^*(k)\sigma_n(b) \tag{58}$$

where in the second version of both formulae, respectively, definitions (33) and (34) have been used. Then

$$F(t) = v(t)\exp[u(t)-u(0)]. \tag{59}$$

By use of the identity

$$\sum_k c_k f(\Omega_k) = \int_0^\infty \mathrm{d}\omega\, f(\omega)\sum_k c_k\delta(\omega-\Omega_k) \tag{60}$$

we finally may establish the contact with the GF description in section 3 (see (24)) and transmute (57) and (58) into

$$u(t) = -2|A|^2\int_0^\infty \mathrm{d}\omega\,\exp(\mathrm{i}\omega t)\,\omega^{-2}\sum_{m,n}\sigma_m^*(a)\sigma_n(a)\,\mathrm{Im}\,G_{m,n}(\omega+\mathrm{i}\varepsilon) \tag{61}$$

$$v(t) = -2|B|^2\int_0^\infty \mathrm{d}\omega\,\exp(\mathrm{i}\omega t)\sum_{m,n}\sigma_m^*(b)\sigma_n(b)\,\mathrm{Im}\,G_{m,n}(\omega+\mathrm{i}\varepsilon). \tag{62}$$

The functions $u(t)$ and $v(t)$ are the crucial decay functions which govern the non-radiative transitions. The function $v(t)$ represents the promoting-mode dynamics, whereas $u(t)$ is a representation of the accepting modes. Both functions tend to zero for $t\to\infty$, but the actual evolution in time depends very sensitively on the details of the coupling (parameter sets $A$, $\{\sigma_m(a)\}$ and $B$, $\{\sigma_m(b)\}$) and on the dispersion behaviour of $\Omega_k$ (parameter set $\{\gamma_d\}$); see below.

The main virtue of the GF formulation of the crucial decay functions $u(t)$ and $v(t)$, however, consists of calculational *options for disturbed lattices*, since it allows for the application of a Lifshitz procedure, which later traces the disturbed GFs back to undisturbed GFs. This also explains why we have returned to the Cartesian space, since it is in this projection where the Lifshitz procedure works. Moreover, the $m$, $n$ sums in equations (61) and (62) only involve a few terms given by the Cartesian extension of the promoting- and accepting-mode coupling constants $A\sigma_m(a)$ and $B\sigma_m(b)$.

## 6. One-dimensional visualisation

We demonstrate the computational technique for a one-dimensional chain of atoms with spring interactions between nearest neighbours, next-nearest neighbours, etc. Equation (14) then assumes the form

$$H_{\mathrm{ph}} = \tfrac{1}{2}\sum_m P_m^2 + \tfrac{1}{4}\Omega_{\mathrm{D}}^2 \sum_{m,d} \gamma_d (X_{m+d} - X_m)^2 \qquad (14')$$

where

$$\Omega_{\mathrm{D}}^2 = 2f/M \qquad \gamma_1 = 1 \qquad \gamma_2 = f'/f \qquad \gamma_3 = f''/f \qquad \dots \qquad (63)$$

From this we deduce the dispersion relation

$$\Omega_k^2 = \Omega_{\mathrm{D}}^2 \sum_{d>0} \gamma_d \sin^2\left(\frac{\pi k}{N} d\right) = \Omega_{\mathrm{D}}^2 \sin^2\left(\frac{\pi k}{N}\right)\left\{1 + \gamma_2 4\cos^2\left(\frac{\pi k}{N}\right) + \gamma_3\left[4\cos^2\left(\frac{\pi k}{N}\right) - 1\right]^2 + \dots\right\}. \qquad (64)$$

The eigenvectors (17) now are of simple Bloch form

$$\eta_m(k) = (1/\sqrt{N})\exp[\mathrm{i}(2\pi/N)km] \qquad k = 0, \pm 1, \dots, \pm N/2 \qquad (65)$$

and for the symmetry vectors, which characterise the accepting- and promoting-mode coupling, respectively, we choose the structure

$$\sigma(a) = \left(\sum_m \alpha_m^2\right)^{-1/2} (\dots, -\alpha_m, \dots, -\alpha_2, -\alpha_1, 0, \alpha_1, \alpha_2, \dots, \alpha_m, \dots) \qquad (66a)$$

(Cartesian sites $m$:) $(\dots, (-m), \dots, (-2), (-1), (0), (1), (2), \dots, (m), \dots)$

$$\sigma(b) = \left(\sum_m \beta_m^2\right)^{-1/2} (\dots, \beta_m, \dots, \beta_2, \beta_1, \beta_0, \beta_1, \beta_2, \dots, \beta_m, \dots). \qquad (66b)$$

Upon inserting these in equations (33) and (34) we then find that

$$A_k = \frac{1}{\sqrt{N}}\left(A\Big/\sqrt{\sum_m \alpha_m^2}\right) 2\mathrm{i} \sum_{m=1}^{N/2} \alpha_m \sin\left(\frac{2\pi km}{N}\right) \qquad (67a)$$

$$B_k = \frac{1}{\sqrt{N}}\left(B\Big/\sqrt{\sum_m \beta_m^2}\right) 2 \sum_{m=0}^{N/2} \beta_m \cos\left(\frac{2\pi km}{N}\right). \qquad (67b)$$

Correspondingly one has for the GF (23)

$$G_{m,n}(\omega \pm \mathrm{i}\varepsilon) = \frac{1}{2\pi N} \sum_{k=-N/2}^{N/2} \frac{\exp[\mathrm{i}2\pi k(m-n)/N]}{(\omega \pm \mathrm{i}\varepsilon)^2 - \Omega_k^2} \qquad (68)$$

and finally with equations (66) and (67)

$$\sum_{m,n} \sigma_m^*(a) G_{m,n}(\omega \pm i\varepsilon)\sigma_n(a) = \frac{4}{\pi N}\left(1\Big/\sum_m \alpha_m^2\right)\sum_{k=1}^{N/2} \times \left\{\left[\sum_{m=1}^{N/2} \alpha_m \sin\left(\frac{2\pi k m}{N}\right)\right]^2 \Big/ [(\omega \pm i\varepsilon)^2 - \Omega_k^2]\right] \tag{69a}$$

$$\sum_{m,n} \sigma_m^*(b) G_{m,n}(\omega \pm i\varepsilon)\sigma_n(b) = \frac{4}{\pi N}\left(1\Big/\sum_m \beta_m^2\right)\sum_{k=0}^{N/2} \times \left\{\left[\beta_0 + \sum_{m=1}^{N/2} \beta_m \cos\left(\frac{2\pi k}{N} m\right)\right]^2 \Big/ (\omega \pm i\varepsilon)^2 - \Omega_k^2\right\} \tag{69b}$$

and

$$\mathrm{Im}\left(\sum_{m,n} \sigma_m^*(a) G_{m,n}(\omega \pm i\varepsilon)\sigma_n(a)\right) = \pm\frac{2}{N}\left(1\Big/\sum_m \alpha_m^2\right)\sum_{k=1}^{N/2} \times \left[\!\left[\left\{\left[\sum_m \alpha_m \sin\left(\frac{2\pi k}{N} m\right)\right]^2 \Big/ \Omega_k\right\}[\delta(\omega + \Omega_k) - \delta(\omega - \Omega_k)]\right]\!\right] \tag{70a}$$

$$\mathrm{Im}\left(\sum_{m,n} \sigma_m^*(b) G_{m,n}(\omega \pm i\varepsilon)\sigma_n(b)\right) = \pm\frac{2}{N}\left(1\Big/\sum_m \beta_m^2\right)\sum_{k=0}^{N/2} \times \left[\!\left[\left\{\left[\beta_0 + \sum_m \beta_m \cos\left(\frac{2\pi k}{N} m\right)\right]^2 \Big/ \Omega_k\right\}[\delta(\omega + \Omega_k) - \delta(\omega - \Omega_k)]\right]\!\right]. \tag{70b}$$

Henceforth we shall use the abbreviations

$$a = A(\Sigma\alpha_m^2)^{-1/2} \tag{71}$$

$$b = B(\Sigma\beta_m^2)^{-1/2}. \tag{72}$$

## 7. Transport: Bessel–Hamilton

In the one-dimensional problem there is a prototype case of decay, which permits an exact analytical solution. If we insert equations (71) and (72) into (61) and (62), both characteristic functions $u(t)$ (even modes) and $v(t)$ (odd modes) display decay features of a type first considered by Hamilton (1839) a long time ago. To demonstrate this, we consider the most simple choices for the intrinsic parameter sets:

$$\begin{aligned} &\alpha_1 = 1 \qquad \alpha_2 = -\tfrac{1}{2} \qquad \alpha_3 = \alpha_4 = \ldots = 0 \\ &\beta_0 = 1 \qquad \beta_1 = -1 \qquad \beta_2 = \beta_3 = \ldots = 0 \\ &\Omega_k = \Omega_D \sin(\pi k/N) \qquad \gamma_2 = \gamma_3 = \ldots = 0. \end{aligned} \tag{73}$$

Then (see equations (68) and (69))

$$A_k = i(N)^{-1/2} a \times 2 \times 4 \cos\left(\frac{\pi k}{N}\right)\sin^3\left(\frac{\pi k}{N}\right) \tag{74}$$

$$B_k = (N)^{-1/2} b \times 2 \times 2 \sin^2\left(\frac{\pi k}{N}\right) \tag{75}$$

and equations (71$a$) and (72$a$) assume the form

$$\mathrm{Im}\Big(\sum_{m,n}\sigma_m^*(a)G_{m,n}(\omega+\mathrm{i}\varepsilon)\sigma_n(a)|_{\omega>0}\Big)$$
$$= -\frac{32}{N}|a|^2\sum_{k=1}^{N/2}\frac{[\sin(\pi k/N)]^6[\cos(\pi k/N)]^2}{\Omega_k}\delta(\omega-\Omega_k) \tag{76}$$

$$\mathrm{Im}\Big(\sum_{m,n}\sigma_m^*(b)G_{m,n}(\omega+\mathrm{i}\varepsilon)\sigma_n(b)\Big|_{\omega>0}\Big) = -\frac{8}{N}|b|^2\sum_{k=0}^{N/2}\Big[\sin\Big(\frac{\pi k}{N}\Big)\Big]^4\delta(\omega-\Omega_k). \tag{77}$$

For equations (61) and (62) we finally obtain

$$u(t) = |a|^2\frac{64}{N\Omega_\mathrm{D}^3}\sum_{k=1}^{N/2}\Big[\sin\Big(\frac{\pi k}{N}\Big)\Big]^3\Big[\cos\Big(\frac{\pi k}{N}\Big)\Big]^2\exp\Big[\mathrm{i}\Omega_\mathrm{D}t\sin\Big(\frac{\pi k}{N}\Big)\Big] \tag{78}$$

$$v(t) = |b|^2\frac{16}{N\Omega_\mathrm{D}}\sum_{k=0}^{N/2}\Big[\sin\Big(\frac{\pi k}{N}\Big)\Big]^3\exp\Big[\mathrm{i}\Omega_\mathrm{D}t\sin\Big(\frac{\pi k}{N}\Big)\Big]. \tag{79}$$

In the continuum limit ($N\to\infty$) the remaining integrals are of the Bessel type and may be traced back to the form

$$\frac{1}{\pi}\int_0^\pi \exp[\pm\mathrm{i}(\nu\varphi - z\sin\varphi)]\,\mathrm{d}\varphi = \mathcal{J}_\nu(z)\pm\mathrm{i}\mathbb{E}_\nu(z) \tag{80}$$

(see Erdelyi *et al* 1953, p 35). Exploiting this formula we get for equations (78) and (79)

$$u(t) = (4/\pi)(|a|^2/\Omega_\mathrm{D}^3)\{2\mathbb{E}_1(\Omega_\mathrm{D}t)+\mathbb{E}_3(\Omega_\mathrm{D}t)-\mathbb{E}_5(\Omega_\mathrm{D}t)$$
$$+\mathrm{i}[2\mathcal{J}_1(\Omega_\mathrm{D}t)+\mathcal{J}_3(\Omega_\mathrm{D}t)-\mathcal{J}_5(\Omega_\mathrm{D}t)]\} \tag{81}$$

$$u(0) = [(64\times 4)/15\pi^2](|a|^2/\Omega_\mathrm{D}^3) \tag{82}$$

$$v(t) = (16|b|^2/\pi\Omega_\mathrm{D})\{3\mathbb{E}_1(\Omega_\mathrm{D}t)-\mathbb{E}_3(\Omega_\mathrm{D}t)+\mathrm{i}[3\mathcal{J}_1(\Omega_\mathrm{D}t)-\mathcal{J}_3(\Omega_\mathrm{D}t)]\}. \tag{83}$$

In this manner we recognise that the crucial decay functions are superpositions of Bessel-type functions and thus display a kind of decay behaviour which Hamilton (1839) had found for decay in a classical oscillatory chain. Subsequently, this type of decay was also investigated by Havelock (1910), Schrödinger (1914) and Rubin (1960).

The functions $u(t)$ and $v(t)$ are drawn in figures 1 and 2, whereas $F(t)$ itself is given in figure 3. We observe that $u(t)$ and $v(t)$ display the extended long-time tail of a $(\Omega_\mathrm{D}t)^{-1/2}$-behaviour which is typical for Bessel functions. In particular, we find the asymptotics

$$u(t) = (2a^2/\Omega_\mathrm{D}^3\sqrt{2})(\pi\Omega_\mathrm{D}t)^{-3/2}c\exp[\mathrm{i}(\Omega_\mathrm{D}t-3\pi/4)]$$
$$+O((\Omega_\mathrm{D}t)^{-2})+\exp(\mathrm{i}\pi/2)O((\Omega_\mathrm{D}t)^{-5/2}) \tag{84}$$

$$c = -2\Gamma(\tfrac{5}{2})\Gamma(\tfrac{1}{2})+\Gamma(\tfrac{9}{2})\Gamma(-\tfrac{3}{2})+\Gamma(\tfrac{13}{2})\Gamma(-\tfrac{7}{2})$$

$$v(t) = (2b^2/\Omega_\mathrm{D})\sqrt{32}(\pi\Omega_\mathrm{D}t)^{-1/2}\exp[\mathrm{i}(\Omega_\mathrm{D}t-5\pi/4)]$$
$$+\exp(\mathrm{i}3\pi/4)O((\Omega_\mathrm{D}t)^{-3/2}) \tag{85}$$

$$F(t) = (2b^2/\Omega_\mathrm{D})\sqrt{32}(\pi\Omega_\mathrm{D}t)^{-1/2}\exp[-u(0)]\exp[\mathrm{i}(\Omega_\mathrm{D}t-5\pi/4)]$$
$$+\exp(\mathrm{i}3\pi/4)O((\Omega_\mathrm{D}t)^{-3/2}). \tag{86}$$

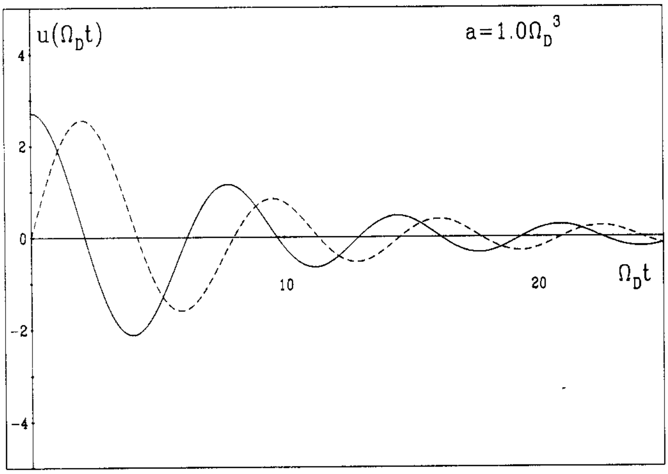


**Figure 1.** Real part (——) and imaginary part (– – –) of the characteristic function of the promoting-mode evolution $u(\Omega_D t)(\Omega_D/b^2)$ for the accepting-mode coupling strength $a = 1.0\Omega_D^{3/2}$.

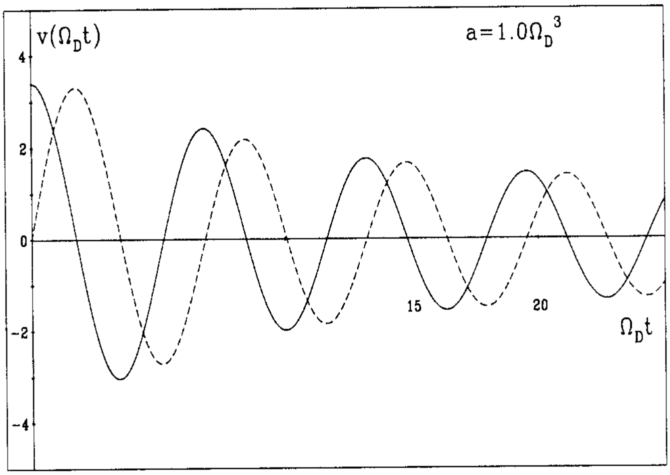


**Figure 2.** Real part (——) and imaginary part (– – –) of the characteristic function of the accepting-mode evolution $v(\Omega_D t)$ for the accepting-mode coupling strength $a = 1.0\Omega_D^{3/2}$.

From figure 3 we notice that the temporal structure does not display a simple damped oscillation but a more complicated form. This is also reflected in the spectral structure of the self-energy function (equation (4)) $S_+(\omega)(= (S(\omega))^*)$, which is drawn in figure 4.

## 8. Global analysis of non-radiative decay

In section 4 we have traced back the self-energy function (4) to two decay functions $u(t)$ and $v(t)$:

$$F(t) = v(t) \exp[-u(0) + u(t)]. \tag{87}$$

There is no major difficulty in computing $u(t)$ and $v(t)$ in their full detail and to form (at

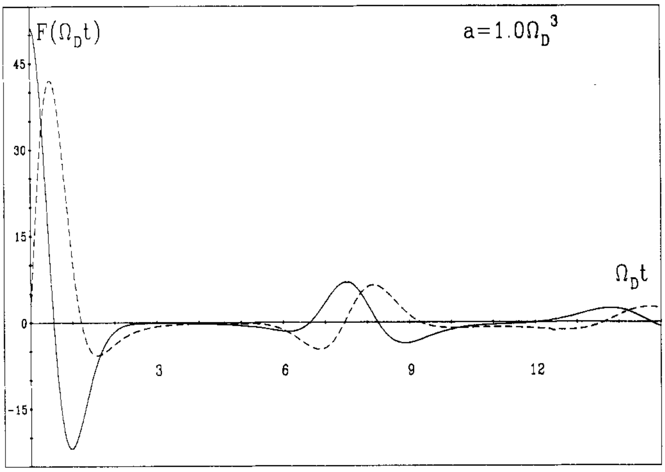


**Figure 3.** Real part (——) and imaginary part (---) of the decay function $F(\Omega_D t)\,(\Omega_D/b^2)$ for the accepting-mode coupling strength $a = 1.0\Omega_D^{3/2}$. $F(\Omega_D t)$ is the Fourier transformation of the self-energy function.

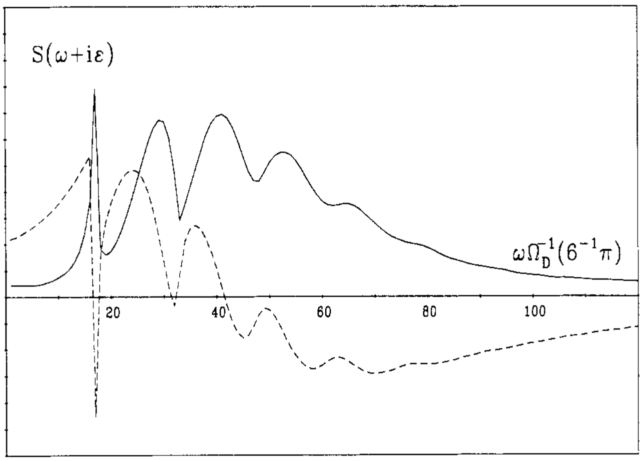


**Figure 4.** Self-energy function $S(\omega + \mathrm{i}\varepsilon)$ for the accepting-mode coupling strength $a = 1.0\Omega_D^{3/2}$: ---, 'damping function'; ——, 'energy shift'.

least numerically) the Fourier inversion of equation (87). However, for direct physical insight it is rather more rewarding to perform a simpler although less accurate, calculation. This is provided for by a moment analysis of equation (87), as explained at the end of section 2. Inserting equation (87) in (9) we find that

$$M_r = \lim_{t\to 0}\{[\mathrm{d}/(\mathrm{i}\,\mathrm{d}t)]^r v(t)\exp[-u(0) + u(t)]\}. \tag{88}$$

Employing equations (78) and (79) this yields

$$M_0 \equiv v(0) \tag{89}$$

$$M_1 = -\mathrm{i}\dot{v}(0) - \mathrm{i}M_0\dot{u}(0) \tag{90}$$

$$M_2 = M_1^2/M_0 - \ddot{v}(0) - M_0\ddot{u}(0) - M_0[\dot{v}(0)/M_0]^2 \tag{91}$$

which still are exact results. We now introduce the analytic form (8), whose characteristic parameters ($M_0$, $\omega_0$, $\gamma$) are given by (12) and (13), and upon employing (89)–(91) we write

$$\omega_0 = -\mathrm{i}\dot{u}(0) - \mathrm{i}\dot{v}(0)/v(0) \tag{92}$$

$$\gamma^2 = -\ddot{v}(0)/v(0) - \ddot{u}(0) - [\dot{v}(0)/v(0)]^2 \tag{93}$$

which determines the functional representation of the self-energy function $S(\omega \pm \mathrm{i}\varepsilon)$ via equation (11):

$$S(\omega \pm \mathrm{i}\varepsilon) = v(0)(\omega - \omega_0 \pm 2\mathrm{i}\gamma)/(\omega - \omega_0 \pm \mathrm{i}\gamma)^2. \tag{11}$$

Inserting this in the decay formula (2) we arrive at

$$\langle\Psi(0)\Psi(t)\rangle = \frac{\mathrm{i}}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\,\omega \exp(-\mathrm{i}\omega t)$$
$$\times \left(\frac{(\omega - \omega_0 + \mathrm{i}\gamma)^2}{(\omega - E_s^{(0)})(\omega - \omega_0 + \mathrm{i}\gamma)^2 - v(0)(\omega - \omega_0 + 2\mathrm{i}\gamma)} + \mathrm{cc}\right). \tag{94}$$

In the integrand of this expression the poles are determined by

$$(\omega - E_s^{(0)})(\omega - \omega_0 + \mathrm{i}\gamma)^2 - v(0)(\omega - \omega_0 + 2\mathrm{i}\gamma) = 0 \tag{95}$$

and those in the lower half-plane we denote by

$$\omega_j = \Omega_j - \mathrm{i}\Gamma_j \qquad j = 1, 2, 3$$

$\Omega_j$ real, $\Gamma_j$ positive. In the upper half-plane we have the complex conjugate solution. Then from equation (94)

$$\begin{aligned}\langle\Psi(0)\Psi(t)\rangle = {} & [(\omega_1 - \omega_0 + \mathrm{i}\gamma)^2/(\omega_1 - \omega_2)(\omega_1 - \omega_3)] \exp(-\mathrm{i}\Omega_1 t) \exp(-\Gamma_1|t|) \\ & + [(\omega_2 - \omega_0 + \mathrm{i}\gamma)^2/(\omega_2 - \omega_1)(\omega_2 - \omega_3)] \exp(-\mathrm{i}\Omega_2 t) \exp(-\Gamma_2|t|) \\ & + [(\omega_3 - \omega_0 + \mathrm{i}\gamma)^2/(\omega_3 - \omega_1)(\omega_3 - \omega_2)] \exp(-\mathrm{i}\Omega_3 t) \exp(-\Gamma_3|t|)\end{aligned} \tag{96}$$

and we observe that there are three decay channels. Since the general solutions of the third-order equations (95) are rather awkward expressions, we refrain from writing them down, but content ourselves with discussing only the physically most interesting case when $v(0)$ (i.e. the promoting-mode coupling) is small. Then the approximate solution of equation (95) reads

$$\Omega_{1,2} - \mathrm{i}\Gamma_{1,2} = \omega_0 - \mathrm{i}\gamma \pm [\mathrm{i}\gamma v(0)/(\omega_0 - E_s^{(0)} - \mathrm{i}\gamma)]^{1/2} = \omega_0 - \mathrm{i}\gamma \pm O(v(0)^{1/2}) \tag{97}$$

$$\Omega_3 = E_s^{(0)} + O(v(0)/\gamma^2) \tag{98}$$

$$\Gamma_3 = 2\gamma^3 v(0)/[(E_s^{(0)} - \omega_0)^2 + \gamma^2]^2 \tag{99}$$

and the approximate decay evolution (96) follows as

$$\begin{aligned}\langle\Psi(0)\Psi(t)\rangle = {} & [\![-\mathrm{i}\{[\mathrm{i}\gamma v(0)]^{1/2}/(\omega_0 - E_s^{(0)} - \mathrm{i}\gamma)^{3/2}\} \exp(-\mathrm{i}\omega_0 t) \exp(-\gamma|t|) \\ & \times \sin\{t[\mathrm{i}\gamma v(0)(\omega_0 - E_s^{(0)} + \mathrm{i}\gamma)]^{1/2}\} + \exp(-\mathrm{i}E_s^{(0)} t) \exp(-\Gamma_3|t|)]\!].\end{aligned} \tag{100}$$

The first two decay channels in this approximation have merged into one and are governed by the decay constant $\gamma$, which is a measure of the accepting-mode coupling strength. However, the weight of these channels is small (about $[v(0)]^{1/2}$). It is the third channel which normally will be of physical interest and will be analysed in the next section.

## 9. Interplay of intrinsic dynamical parameters

In the preceding section we have recognised that the non-radiative decay constant $\Gamma_3$ (see equation (99)) incorporates the quantities $\omega_0$, $\gamma$ and $v(0)$, which are given by equations (89), (92) and (93) and thus via equations (87)–(91) depend on the interplay of the parameter set $\{\alpha_m\}$ characterising the accepting-mode coupling, the set $\{\beta_m\}$ characterising the promoting-mode coupling, and the set $\{\gamma_d\}$ characterising the $k$-dependence of the phonon frequencies $\Omega_k$. Because of the large multitude of parameters involved, a discussion is only feasible if we restrict ourselves to the four most prominent questions. For the present discussion we assume the promoting-mode coupling to be small, such that the non-radiative decay constant is given by

$$\Gamma_3 = 2v(0)\gamma^3/[(E_s^{(0)} - \omega_0)^2 + \gamma^2]^2. \tag{99}$$

From this expression we deduce that $\Gamma_3$ is maximal if $\omega_0$ approaches $E_s^{(0)}$. Then

$$\Gamma_3^{(\max)} = 2v(0)/\gamma \qquad (\text{for } E_s^{(0)} = \omega_0). \tag{101}$$

On the other hand, by inserting (68) in (45) we have (see equation (78))

$$E_s^{(0)} = \Delta + \mathrm{i}\dot{u}(0) \tag{102}$$

and from (92)

$$E_s^{(0)} = \Delta - \omega_0 - \mathrm{i}\dot{v}(0)/v(0) \tag{103}$$

whence the resonance condition for maximal decay, $E_s^{(0)} = \omega_0$, may be rewritten as

$$\omega_0^{\max} = \Delta/2 - i\dot{v}(0)/2v(0). \tag{104}$$

### 9.1. The simplest model

The parameter choice (73) is the simplest. Employing (78) and (79), the elements of equations (89), (92) and (93) assume the values

$$v(0) = \frac{16}{\Omega_0\pi} b^2 \int_0^{\pi/2} \mathrm{d}x \sin^3 x = \frac{32}{3\pi\Omega_\mathrm{D}} b^2 \tag{105}$$

$$\dot{v}(0) = \mathrm{i}\frac{16}{\pi} b^2 \int_0^{\pi/2} \mathrm{d}x \sin^4 x = \mathrm{i}\frac{9\pi}{32}\Omega_\mathrm{D} v(0) \tag{106}$$

$$\ddot{v}(0) = \mathrm{i}^2 \frac{16}{\pi} b^2 \int_0^{\pi/2} \mathrm{d}x \sin^5 x = -\tfrac{4}{5}\Omega_\mathrm{D}^2 v(0) \tag{107}$$

$$\dot{u}(0) = \mathrm{i}\frac{64}{\pi\Omega_\mathrm{D}^2} a^2 \int_0^{\pi/2} \mathrm{d}x\,(\sin^4 x - \sin^6 x) = \mathrm{i}\frac{2}{\Omega_\mathrm{D}^2} a^2 \tag{108}$$

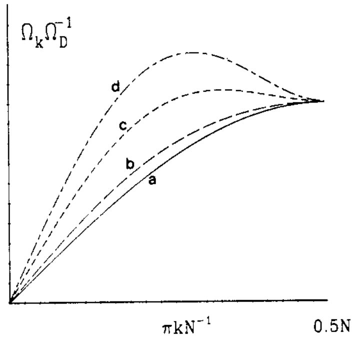


**Figure 5.** Dispersion relation $\Omega_k$ of the one-dimensional lattice in the harmonic approximation for the elastic coupling with nearest (spring constant $f$) and next-nearest (spring constant $f'$): curve A, $\gamma_2 \equiv f'/f = 0$; curve B, $\gamma_2 = 0.1$; curve C, $\gamma_2 = 0.4$; curve D, $\gamma_2 = 0.8$.

$$\ddot{u}(0) = \mathrm{i}^2 \frac{64}{\pi\Omega_D} a^2 \int_0^{\pi/2} \mathrm{d}x\,(\sin^5 x - \sin^7 x) = -\frac{8^3}{3 \times 5 \times 7} \frac{a^2}{\pi\Omega_D}. \tag{109}$$

Then from (92) and (93)

$$\omega_0 = \omega_0^{(a,0)} + \omega_0^{(b,0)} \tag{110}$$

$$\gamma^2 = \gamma^2_{(a,0)} + \gamma^2_{(b,0)} \tag{111}$$

$$E_s^{(0)} = \Delta - (2a^2/\Omega_D^2) \tag{112}$$

where

$$\omega_0^{(b,0)} = (9\pi/32)\Omega_D \qquad \omega_0^{(a,0)} = 2a^2/\Omega_D^2$$

$$\gamma^2_{(b,0)} = [\tfrac{4}{5} + (9\pi/32)^2]\Omega_D^2 \qquad \gamma^2_{(a,0)} = (512/105\pi)(a^2/\Omega_D).$$

From equations (105)–(107) we can only deduce that $v(0)$ is large if the promoting-mode coupling is large. Equations (110) and (111), however, show that the relative promoting-mode influence is larger on $\omega_0$ than on $\gamma^2$. It may be neglected if the dimensionless accepting-mode coupling is large: $a^2/\Omega_D^3 \gg 1$. Then, both $\omega_0$ and $\gamma^2$ grow in proportion to the accepting-mode coupling strength $a^2/\Omega_D^3$ and the maximal decay constant (see equation (101)) takes on the value

$$\Gamma_3^{(\max)} = 5.45\, b^2/a\sqrt{\Omega_D} \qquad (\text{for } a^2/\Omega_D^3 \gg 1). \tag{113}$$

### *9.2. Extended lattice interaction (ideal)*

We now investigate the influence of modified transport properties within the host lattice. We still keep to ideal lattice dynamics, but we change the phonon dispersion by allowing for next-nearest-neighbour spring constants. Thus we choose the set

$$\{\gamma_d\} \equiv (\Omega_D^2/2)\{1, \gamma_2, 0, \ldots, 0\} \tag{114}$$

which yields for the lattice frequencies (see equation (64))

$$\Omega_k = \Omega_D\,|\sin(\pi k/N)|\,[1 + 4\gamma_2 \cos^2(\pi k/N)]^{1/2}. \tag{115}$$

This dispersion relation is drawn in figure 5 for different $\gamma_2$-values. It is noted that the phonon group velocities are remarkably changed in all $k$-regions. The other two intrinsic parameter sets, $\{\alpha_m\}$ and $\{\beta_m\}$, are again chosen as before (see (73)). We then may perform the computational steps which are equivalent to those of equations (104)–(111), and we find that

$$\omega_0 = (9\pi/32 + 2a^2/\Omega_D^3)\Omega_D + [(9\pi/32)\tfrac{4}{5} - (2a^2/\Omega_D^3)\tfrac{3}{4}]\gamma_2\Omega_D + O(\Omega_D\gamma_2^2) \qquad (116)$$

$$\gamma^2 = [\tfrac{4}{5} + (9\pi/32)^2 + 512a^2/105\pi]\,\Omega_D + 4[\tfrac{17}{175} + 9\pi/320 - (512a^2/105\pi)\tfrac{1}{6}]\gamma_2\Omega_D + O(\Omega_D^2\gamma_2^2) \qquad (117)$$

$$E_s^{(0)} = \Delta - (2a^2/\Omega_D^2)(1 - \tfrac{3}{4}\gamma_2) + O(\Omega_D\gamma_2^2) \qquad (118)$$

and for $a^2/\Omega_D^3 \gg 1$ the maximal decay constant (see equation (101)) reads

$$\Gamma_3^{(\max)} = (1 - \tfrac{1}{15}\gamma_2)5.45b^2/a\sqrt{\Omega_D} + O(\gamma_2^2) \qquad (\text{for } a^2/\Omega_D^3 \gg 1). \qquad (119)$$

Disregarding for the moment the oversimplified nature of the model, this result would allow for the physical interpretation that non-radiative decay is slowing down if the locally created oscillatory energy is not transported away from the centre quickly enough.

### 9.3. *Spatially extended promoting-mode coupling*

We now leave the intrinsic sets $\{\alpha_m\}$ and $\{\gamma_d\}$ unchanged (see equation (73)) but assume the promoting-mode coupling to reach farther into the surrounding medium:

$$\beta_0 = 1 \qquad \beta_1 = 0 \qquad \beta_2 = -1 \qquad \beta_3 = \beta_4 = \ldots = 0. \qquad (120)$$

We may thus perform the computation very much along the lines given in the preceding two case studies and arrive at the results

$$\omega_0^{(a)} = \omega_0^{(a,0)} \qquad \omega_0^{(b)} = 0.729\omega_0^{(b,0)} \qquad (121)$$

$$\gamma_{(a)}^2 = \gamma_{(a,0)}^2 \qquad \gamma_{(b)}^2 = \tfrac{4}{5}(0.99) + (9\pi/32)^2 0.53 \qquad (122)$$

$$E_s^{(0)} = \Delta - (2/\Omega_D^2)a^2 \qquad (123)$$

$$\Gamma_3^{(\max)} = 1.37\Gamma_3^{(\max)}(\beta_2 = 0) \qquad (\text{for } a^2/\Omega_D^3 \gg 1) \qquad (124)$$

which again are given in the simplified form pertaining to $a^2/\Omega_D^3 \gg 1$. We thus find a sensibly increased decay with respect to that in section 9.1.

### 9.4. *Spatially extended accepting-mode coupling*

Finally, we may consider a longer spatial extension in the set $\{\alpha_m\}$ of accepting-mode coupling parameters:

$$\alpha_1 = 1 \qquad \alpha_2 = -\tfrac{3}{4} \qquad \alpha_3 = \tfrac{1}{6} \qquad \alpha_4 = \alpha_5 = \ldots = 0 \qquad (125)$$

leaving $\{\beta_m\}$ and $\{\gamma_d\}$ as in the case in section 9.1 (equation (73)). Then computation along the preceding lines yields

$$\omega_0^{(a)} = \omega_0^{(a,0)}0.58 \qquad \omega_0^{(b)} = \omega_0^{(b,0)} \qquad (126)$$

$$\gamma_{(a)}^2 = \gamma_{(a,0)}^2 2 \qquad \gamma_{(b)}^2 = \gamma_{(b,0)}^2 \qquad (127)$$

$$E_s^{(0)} = \Delta - (2a^2/\Omega_D^2)0.58 \qquad (128)$$

$$\Gamma_3^{(\max)} = 0.92\Gamma_3^{(\max)}(\alpha_3 = 0) \qquad (\text{for } a^2/\Omega_D^3 \gg 1) \qquad (129)$$

which is a slightly diminished maximal decay than in the case in section 9.1.

## 10. Summary and remarks

We have presented a GF formalism of non-radiative decay, which is derived by means of a Fano–Bixon–Jortner concept of decay. Our formalism allows investigation of the influence of spatial coupling peculiarities as well as lattice dynamical properties on the decay.

The results, which we deduce from our calculation of prototypical examples, may be summarised as follows. If the range of the elastic coupling within the ideal host is spatially extended (second-neighbour springs, etc), the phonon transport properties deteriorate. This is reflected in a slowing down of non-radiative decay. A slightly slowing down is also achieved via a spatial extension of the range of accepting-mode coupling. On the other hand, a pronounced increase is initiated if the promoting-mode coupling involves the more distant neighbour atoms.

The formalism is given in such a manner that the relevant evolution functions are traced back to standard GFs of lattice dynamics. Thus, also defects within the intrinsic parameter sets of the lattice (masses and spring constants) are easily handled within the well known Lifshitz procedure. For brevity we have not included computations with disturbances in the internal dynamics of the host lattice. This will be given elsewhere. In the further theoretical development it is desirable to calculate also the 'hot' relaxation process within our Bixon–Jortner concept. This is left to future work.

## References

Baker H F 1905 *Proc. London Math. Soc.* **3** 24
Bartram R H and Stoneham A M 1985 *J. Phys. C: Solid State Phys.* **18** L549
Bixon M and Jortner J 1968 *J. Chem. Phys.* **48** 715
—— 1969 *J. Chem. Phys.* **50** 4061
Bloch F 1932 *Z. Phys.* **74** 295
Böttger H 1983 *Principles of the Theory of Lattice Dynamics* (Berlin: Akademie) p 4
Dederichs P H, Zeller R and Schröder K 1980 *Springer Tracts in Modern Physics* vol 87 (Berlin: Springer)
Denner V and Wagner M 1983 *Solid State Commun.* **46** 75
—— 1984a *J. Chem. Phys.* **81** 5034
—— 1984b *J. Phys. C: Solid State Phys.* **17** 153
Erdelyi A, Magnus W, Oberhettinger F and Tricomi F G 1953 *Higher Transcendental Functions* vol II (New York: McGraw-Hill) p 10
Fano U 1961 *Phys. Rev.* **124** 1866
Gutsche E 1982 *Phys. Status Solidi* b **109** 583
Hamilton W R 1839 *Proc. R. Irish Acad.* **267** 341
Hausdorff A 1906 *Ber. Verhandl. Sächs. Akad. Wiss. Lpz. Math. Phys.* **58** 19
Havelock T H 1910 *Phil. Mag.* **19** 160
Helmis G 1956 *Ann. Phys., Lpz.* **19** 41
Huang K 1981 *Sci. Sin.* **24** 27
Huang K and Rhys A 1950 *Proc. R. Soc.* A **204** 406
Maradudin A A, Montroll E W and Weiss G H 1963 *Solid State Physics* Supplement 3 (New York: Academic)
Rubin J R 1960 *J. Math. Phys.* **1** 309
Schrödinger E 1914 *Ann. Phys., Lpz.* **44** 916
Stinchcombe R B 1978 *Correlation Functions and Quasiparticle Interactions in Condensed Matter (NATO ASI Series)* ed J W Halley (New York: Plenum) p 4
Stoneham A M 1981 *Rep. Prog. Phys.* **44** 79
Wagner M 1982 *J. Phys. C: Solid State Phys.* **15** 5077
—— 1985a *J. Chem. Phys.* **82** 3207
—— 1985b *Proc. 13th Int. Conf. on Defects in Semiconductors* ed L E Kimerling and J M Parsey (Warrendale, PA: Metallurgical Society of AIME) pp 229–34

Wagner M and Vazquez-Marquez J 1988 *J. Phys. A: Math. Gen.* **21** 4377
Wilcox R M 1967 *J. Math. Phys.* **8** 962
Zavt G S, Plekhanov V G, Hizhnyakov V V and Shepelev V V 1984 *J. Phys. C: Solid State Phys.* **17** 2839
Zubarev D N 1960 *Sov. Phys.-Usp.* **3** 320