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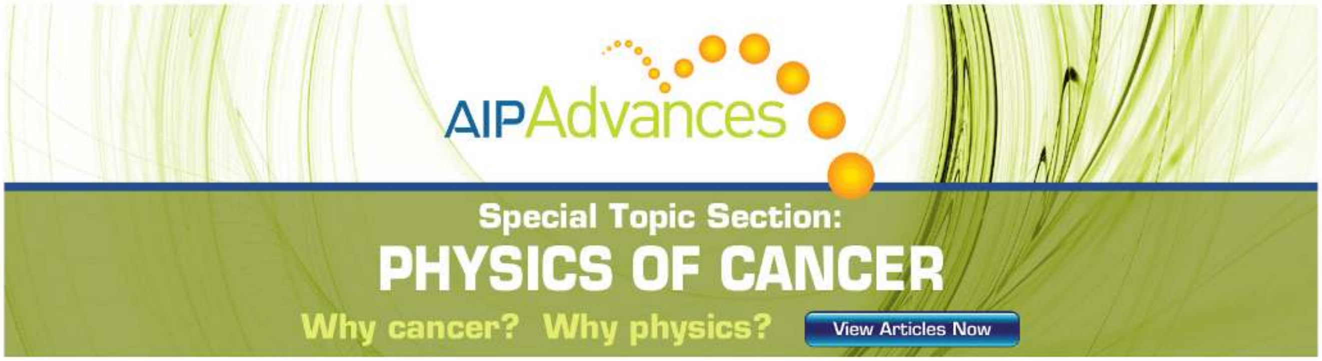

Theory of exciton transport with quadratic exciton–phonon coupling[a]

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The coupling of excitons with phonons is an important process determining the mechanism of exciton transport in molecular crystals. Although linear exciton–phonon coupling has been extensively treated before, there has been little work on quadratic coupling. In this paper the theory of exciton transport is extended to take weak quadratic coupling into account, and the diffusion constant computed for a simple model. The results are qualitatively similar to those obtained from other treatments of linear and quadratic coupling, and may show a rather weak temperature dependence.

I. INTRODUCTION

Exciton transport in molecular solids depends strongly on the coupling of excitons to phonons. In recent years there has been a number of theoretical papers dealing with subject from a variety of viewpoints.[1–8] The later papers[4–8] attempt to derive an equation for the transport of excitons from a model Hamiltonian without assuming a transport mechanism (i.e., hopping or bandlike) and then finding the mean square displacement and diffusion constant. In some of these[6–8] the exciton–phonon coupling is assumed to be a Gaussian stochastic process which allows an exact equation to be found. However, in order for the strength of the coupling to be related to the parameters of the crystal in some way, a particular form of the exciton–phonon coupling must be assumed. In other papers[3–5] such a form is assumed from the outset and an approximate equation derived using some variant of time dependent perturbation theory. Kenkre and Knox[5] use a form which leads them to a generalized master equation, while Grover and Silbey's treatment[4(a)] leads to an equation similar to that of Haken *et al.*[6]

Grover and Silbey[4(a)] assume a *linear* phonon–exciton coupling, i.e., one which assumes that the frequency of the mode is unchanged while the equilibrium position is changed upon electronic excitation. This approach is similar in spirit to the work on the small polaron.[9] In contrast, Munn and Siebrand[3] assume quadratic coupling, i.e., that the frequency changes while the equilibrium position does not. If the mode we are speaking of is a symmetric intramolecular mode, then usually the linear coupling dominates; however, for modes of certain symmetries (e.g., out of plane bending modes in aromatic hydrocarbons) the linear term vanishes and quadratic coupling then dominates.[10] Certain aspects of the Munn–Siebrand treatment were criticized recently by Druger[11] because they had not been derived from the Hamiltonian directly, but instead were assumed "heuristically." In the present paper we investigate exciton transport for a model Hamiltonian with both linear and quadratic coupling. The results are *broadly* consistent with earlier treatments[3–6] and with the experimental results.

In addition to its effect on exciton transport, quadratic exciton–phonon coupling has a marked effect on spectral properties.[12,13] In fact, one of the principal reasons for treating quadratic coupling is that it is the dominant mechanism for broadening the zero phonon line for a single impurity[14] and for an exciton.[6] In the theory to be presented here, which is valid for the case of an exciton bandwidth much smaller than the vibrational frequency, the local scattering term[6] arises entirely from quadratic terms.[15] This theory treats relaxed exciton transport and so neglects relaxation effects which may also contribute to the local scattering.

In the present paper we assume a model exciton–phonon Hamiltonian containing both linear and quadratic coupling terms; after some transformations an equation of motion for the density matrix is derived, which is solved to give the diffusion constant. Various limiting cases are discussed.

There is a major difference between the treatment of linear and quadratic coupling terms: All (local) linear terms can be removed by a unitary transformation, while this is *impossible* for quadratic terms. It is this which gives rise to the local scattering terms as well as to *bound* multiple particle states.[12,16] This can cause trouble for the perturbation theory we use if the quadratic coupling is too large. In the present paper we deal with weak quadratic coupling, reserving the treatment of strong coupling to a later paper.

II. MODEL HAMILTONIAN AND TRANSFORMATION

The Hamiltonian we consider for an exciton interacting both linearly and quadratically with phonons (for *one* exciton band and one phonon band) is given in site space by

$$H=\sum_n \epsilon a_n^+ a_n+\sum_{n,m} J_{nm} a_n^+ a_m+\sum_n \omega(b_n^+ b_n+\tfrac{1}{2}) + \sum_{nm} K_{nm}\, b_n^+ b_m + g\sum_n a_n^+ a_n (b_n+b_n^+)^2+\sum_{nm} G_{nm}\, a_n^+ a_n (b_m+b_m^+) \qquad (2.1)$$

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and in wave vector space by

$$H=\sum_{\mathbf{k}}\epsilon_{\mathbf{k}}a^{+}_{\mathbf{k}}a_{\mathbf{k}}+\sum\omega_{\boldsymbol{\lambda}}(b^{+}_{\boldsymbol{\lambda}}b_{\boldsymbol{\lambda}}+\tfrac{1}{2})+\frac{1}{N^{1/2}}\sum_{\mathbf{k},\boldsymbol{\lambda}}\hat{G}_{\boldsymbol{\lambda}}a^{+}_{\mathbf{k}+\boldsymbol{\lambda}}a_{\mathbf{k}}$$
$$\times(b_{\boldsymbol{\lambda}}+b^{+}_{-\boldsymbol{\lambda}})+\frac{1}{N}\sum_{\mathbf{k},\boldsymbol{\lambda},\boldsymbol{\lambda}'}g\,a^{+}_{\mathbf{k}+\boldsymbol{\lambda}+\boldsymbol{\lambda}'}a_{\mathbf{k}}(b_{\boldsymbol{\lambda}}+b^{+}_{-\boldsymbol{\lambda}})(b_{\boldsymbol{\lambda}'}+b^{+}_{-\boldsymbol{\lambda}'}) \tag{2.2}$$

where

$$\epsilon_{\mathbf{k}}=\epsilon+\sum_{n}J_{nm}e^{i\mathbf{k}\cdot(\mathbf{n}-\mathbf{m})}\ , \tag{2.3a}$$

$$\omega_{\boldsymbol{\lambda}}=\omega+\sum_{n}K_{nm}e^{i\boldsymbol{\lambda}\cdot(\mathbf{n}-\mathbf{m})}\ , \tag{2.3b}$$

$$\hat{G}_{\boldsymbol{\lambda}}=\frac{1}{N}\sum_{n}G_{nm}e^{i\boldsymbol{\lambda}\cdot(\mathbf{n}-\mathbf{m})}\ , \tag{2.3c}$$

and J_{nm} and G_{nm} are functions of $n-m$ only. In these equations $a^{+}_{n}(a_{n})$ represents the creation (destruction) operator for an exciton on site n, while $b^{+}_{n}(b_{n})$ is a creation (destruction) operator of a phonon on site n. Note that we have neglected nonlocal contributions (i.e., $\sim a^{+}_{n}a_{m}$) to the exciton–phonon coupling. Many of these can be handled by the present treatment; however, in order to avoid unnecessary complications we have left them out.

The linear coupling constant G_{n-m} is proportional to the change of the energy of an exciton on site n when the phonon coordinate on site m is changed. It is therefore directly related to the change in equilibrium position of the mode upon electronic excitation. If the mode we are considering is a molecular vibration, then G_0 may be large, while $G_n(n\neq 0)$ will usually be quite small. In this case the "polaron" binding energy (difference between the energy of the excited molecule in the equilibrium positions of the ground and excited states) will be G_0^2/ω. In the case of extended modes the polaron binding energy will be $\sum_{\mathbf{q}}(\hat{G}^2_{\mathbf{q}}/\omega_{\mathbf{q}})$. The quadratic coupling constant g is related to the change in frequency of the oscillator upon electronic excitation.

In order to make these statements clearer, as well as motivate the transformations to follow, we will consider a simplified Hamiltonian—that of a single molecule:

$$h=\epsilon a^{+}a+\omega(b^{+}b+\tfrac{1}{2})+g\,a^{+}a(b+b^{+})^{2}+Ga^{+}a(b+b^{+})\ . \tag{2.4}$$

If $g=0$, then a transformation of the phonon coordinate will diagonalize h [under the condition that $(a^{+}a)^{2}=a^{+}a$ which is obeyed for excitons]. The transformation is given by the following:

$$h_1\equiv e^{u_1}he^{-u_1}=(\epsilon-G^2/\omega)a^{+}a+\omega(b^{+}b+\tfrac{1}{2})\ , \tag{2.5}$$

$$u_1(G)=-(G/\omega)\,a^{+}a(b-b^{+})\ , \tag{2.6}$$

so that

$$e^{u_1(G)}be^{-u_1(G)}=b-(G/\omega)a^{+}a\ . \tag{2.7}$$

If $G=0$, then in order to bring h into a simple form the required transformation is given by

$$h_2\equiv e^{u_2}he^{-u_2}=\epsilon(a^{+}a)+(\omega'-\omega)a^{+}a(b^{+}b+\tfrac{1}{2})+\omega(b^{+}b+\tfrac{1}{2})\ , \tag{2.8}$$

$$u_2=\gamma a^{+}a(b^2-b^{+2})\ , \tag{2.9}$$

$$e^{u_2}be^{-u_2}=b\cosh 2\gamma+b^{+}\sinh 2\gamma\ , \tag{2.10}$$

$$\gamma=-\tfrac{1}{8}\log(1+4g/\omega)=-\tfrac{1}{4}\log(\omega'/\omega)\ , \tag{2.11}$$

where ω' is the frequency of the mode in the excited electronic state and ω is the frequency in the ground state. Note that h_2 still contains terms which couple exciton operators and phonon operators, so that removal of the coupling is not possible. However, the eigenstates of h_2 are still easily found [they are $(b^{+})^{n}|0\rangle$, and $(a^{+})(b^{+})^{n}|0\rangle$, all n].

In the case in which $g\neq 0$ and $G\neq 0$, h can still be transformed into a form like h_2 by a sequence of transformations. The simplest procedure is to remove the quadratic terms using u_2. This changes the linear coupling constant from G to $Ge^{2\gamma}$ since $(b+b^{+})\rightarrow e^{2\gamma}(b+b^{+})$ under u_2. Then apply u_1 with G replaced by $Ge^{2\gamma}\omega/\omega'=Ge^{6\gamma}$. Thus,

$$h_3=e^{u_1(Ge^{6\gamma})}e^{u_2}he^{-u_2}e^{-u_1(Ge^{6\gamma})}=(\epsilon-G^2e^{8\gamma}/\omega)\,a^{+}a$$
$$+(\omega'-\omega)a^{+}a(b^{+}b+\tfrac{1}{2})+\omega(b^{+}b+\tfrac{1}{2})\ . \tag{2.12}$$

This may be rewritten as

$$h=e^{-u_2}e^{-u_1(Ge^{6\gamma})}h_3e^{u_1(Ge^{6\gamma})}e^{-u_2}$$
$$=\left(\epsilon-\frac{G^2e^{8\gamma}}{\omega}\right)A^{+}A+(\omega'-\omega)A^{+}A(B^{+}B+\tfrac{1}{2})+\omega(B^{+}B+\tfrac{1}{2})\ , \tag{2.13}$$

where $A\equiv e^{-u_2}e^{-u_1(Ge^{6\gamma})}a\,e^{u_1(Ge^{6\gamma})}e^{u_2}$, etc. This transformation could be accomplished in a reverse order, by first removing all the linear terms (including those produced from the quadratic term when u_1 is applied) and then removing the quadratic terms. The results are, of course, identical. For completeness we present the details of this order of performing the transformations. Beginning with Eq. (2.4) we transform h as in Eq. (2.5) with $G/(1+4g/\omega)=Ge^{8\gamma}$ replacing G; this results in a Hamiltonian like Eq. (2.4) except that the linear coupling is absent. We then transform as in Eq. (2.8) with γ as given before.

Thus, the total transformation which brings h [Eq. (2.4)] into the form of Eq. (2.13) can be written as

$$e^{-u_2}e^{-u_1(Ge^{8\gamma})}\ ,\quad\text{or}\ e^{-u_1(Ge^{6\gamma})}e^{-u_2}\ . \tag{2.14}$$

These can be combined into one exponential form[13] by noting that

$$[u_2,\ u_1(G)]=-2\gamma u_1(G)\ . \tag{2.15}$$

Using standard algebraic manipulations[17] we find

$$e^{-u_2}e^{-u_1(G)}=\exp-\left[u_2+\left(\frac{2\gamma}{1-e^{-2\gamma}}\right)u_1(G)\right]\ , \tag{2.16a}$$

$$e^{-u_1(G)}e^{-u_2}=\exp-\left[u_2+\left(\frac{2\gamma}{e^{2\gamma}-1}\right)u_1(G)\right]\ , \tag{2.16b}$$

so that both transformations in Eq. (2.14) can be written as

$$\exp\left[-\gamma(b^2-b^{+2})+\left(\frac{2\gamma e^{8\gamma}}{1-e^{-2\gamma}}\right)\frac{G}{\omega}\,(b-b^{+})\right]\ . \tag{2.17}$$

We are now in a position to apply these results to the exciton–phonon Hamiltonian of Eq. (2.1). We first transform Eq. (2.1) with $\exp(S)$, with

$$S=-N^{-1/2}\sum_{n,\boldsymbol{\lambda}}e^{-i\boldsymbol{\lambda}\cdot\mathbf{n}}Q_{\boldsymbol{\lambda}}a^{+}_{n}a_{n}(b_{\boldsymbol{\lambda}}-b^{+}_{-\boldsymbol{\lambda}}) \tag{2.18}$$

and

$$Q_\lambda = Q^*_{-\lambda} = G_\lambda \omega_\lambda^{-1} - 4g \times\left(N^{-1}\sum_{\lambda'} G_{\lambda'}\,\omega_{\lambda'}^{-1}\right)\Big/\left(1+4gN^{-1}\sum_{\lambda'}\omega_{\lambda'}^{-1}\right), \qquad (2.19)$$

so that if $\omega_\lambda = \omega$, $G_\lambda = G$, all λ, $Q = G(1+4g/\omega)^{-1}$ as in the simplified case discussed above. Under this transformation we find

$$H_1 \equiv e^{+S} H e^{-S} = \sum \epsilon' a_n^+ a_n + \sum_{nm} J_{nm}\, a_n^+ \psi_n^+ \psi_m a_m + \sum_n \omega(b_n^+ b_n + \tfrac{1}{2}) + \sum_{n,m} K_{nm} b_n^+ b_m + \sum_n g a_n^+ a_n (b_n + b_n^+)^2 , \qquad (2.20)$$

where

$$\psi_n = \exp\left[N^{-1/2}\sum_\lambda e^{-i\lambda\cdot\mathbf{n}} Q_\lambda (b_\lambda - b^+_{-\lambda})\right] ,$$

$$\epsilon' = \epsilon - N^{-1}\sum_\lambda |G_\lambda|^2 \omega_\lambda^{-1} + 4g \times\left(N^{-1}\sum_\lambda G_\lambda \omega_\lambda^{-1}\right)^2 \left(1 + 4gN^{-1}\sum_\lambda \omega_\lambda^{-1}\right)^{-1} . \qquad (2.21)$$

We now transform H_1 so as to remove the terms in b_n^2 and b_n^{+2}:

$$H_2 \equiv e^T H_1 e^{-T} = \sum_n \epsilon' a_n^+ a_n + \sum_{nm} J_{nm} a_n^+ \theta_n^+ e^T \psi_n^+ \psi_m e^{-T} \theta_m a_m + \sum_n (\omega' - \omega) a_n^+ a_n (b_n^+ b_n + \tfrac{1}{2}) + \sum_n \omega (b_n^+ b_n + \tfrac{1}{2})$$
$$+ \sum_{nm} K_{nm} b_n^+ b_m + (\cosh 2\gamma - 1)\sum_{nm} K_{nm} b_n^+ b_m (a_n^+ a_n + a_m^+ a_m) + \sinh 2\gamma \sum_{nm} K_{nm} a^+{}_m a_m (b_n^+ b_m^+ + b_n b_m) , \qquad (2.22)$$

with

$$T = \gamma \sum_n a_n^+ a_n (b_n^2 - b_n^{+2}) , \qquad (2.23a)$$

$$\theta_n = \exp[-\gamma(b_n^2 - b_n^{+2})] . \qquad (2.23b)$$

Thus,

$$H_2 = \sum_n [\epsilon' + (\omega' - \omega)/2] a_n^+ a_n + \sum_{nm} J_{nm} a_n^+ \theta_n^+ e^T \psi_n^+ \psi_m e_n^{-T} \theta_m a_m + \sum_\lambda \omega_\lambda (b_\lambda^+ b_\lambda + \tfrac{1}{2})$$
$$+ N^{-1}\sum_{n\lambda\lambda'} a_n^+ a_n \{ e^{i(\lambda-\lambda')\cdot\mathbf{n}} b_\lambda^+ b_{\lambda'} [\omega' - \omega + (\cosh 2\gamma - 1)(\hat{K}_\lambda + \hat{K}_{\lambda'})] + \hat{K}_\lambda \sinh 2\gamma (e^{i(\lambda+\lambda')\cdot\mathbf{n}} b_\lambda^+ b_{\lambda'}^+ + e^{-i(\lambda+\lambda')\cdot\mathbf{n}} b_\lambda b_{\lambda'})\} , \qquad (2.24)$$

where

$$\omega_\lambda = \omega + \hat{K}_\lambda . \qquad (2.25)$$

Note that the term $e^T \psi_n^+ \psi_m e^{-T}$ appears to the left of an exciton destruction operator and to the right of an exciton creation operator, so in one exciton space $e^T \psi_n^+ \psi_m e^{-T}$ can be replaced by $\psi_n^+ \psi_m$.

With this form of H_2 we can now rewrite H in terms of the transformed operators

$$A_n = e^{-S} e^{-T} a_n e^T e^S , \qquad (2.26a)$$

$$B_n = e^{-S} e^{-T} b_n e^T e^S , \qquad (2.26b)$$

to find

$$H = \sum_n [\epsilon' + (\omega' - \omega)/2] A_n^+ A_n + \sum_{nm} J_{nm} A_n^+ \theta_n^+ \psi_n^+ \psi_m \theta_m A_m + \sum_\lambda \omega_\lambda (B_\lambda^+ B_\lambda + \tfrac{1}{2})$$
$$+ \frac{1}{N}\sum_{n\lambda\lambda'} A_n^+ A_n [Q_{\lambda\lambda'} e^{i(\lambda-\lambda')\cdot\mathbf{n}} B_\lambda^+ B_{\lambda'} + K_\lambda \sinh 2\gamma (e^{i(\lambda+\lambda')\cdot\mathbf{n}} B_\lambda^+ B_{\lambda'}^+ + e^{-i(\lambda+\lambda')\cdot\mathbf{n}} B_\lambda B_{\lambda'})] , \qquad (2.27)$$

where $Q_{qq'} = \omega' - \omega + (\cosh 2\gamma^{-1})(K_q + K_{q'})$. We follow the usual procedure of averaging exciton–phonon coupling terms over a canonical ensemble of phonons, and add and subtract the average to find

$$H = H_0 + V , \qquad (2.28)$$

$$H_0 = \sum_n [\epsilon' + (\omega' - \omega)/2] A_n^+ A_n + \sum \tilde{J}_{nm} A_n^+ A_m + \sum_\lambda (\omega_\lambda + N^{-1} Q_{\lambda\lambda}) B_\lambda^+ B_\lambda \equiv H_{0,\mathrm{ex}} + H_{0,\mathrm{ph}} , \qquad (2.29)$$

$$V = \sum_{nm} J_{nm} (\theta_n^+ \psi_n^+ \psi_m \theta_m - \langle \theta_n^+ \psi_n^+ \psi_m \theta_m \rangle) A_n^+ A_m + \sum_n V_{nn} A_n^+ A_n , \qquad (2.30)$$

$$\tilde{J}_{nm} = J_{nm} \langle \theta_n^+ \psi_n^+ \psi_m \theta_m \rangle , \qquad (2.31)$$

$$V_{nn} = N^{-1}\sum_{\lambda\lambda'} [Q_{\lambda\lambda'}(1 - \delta_{\lambda\lambda'}) e^{i(\lambda-\lambda')\cdot\mathbf{n}} B_\lambda^+ B_{\lambda'} + K_\lambda \sinh 2\gamma (e^{i(\lambda+\lambda')\cdot\mathbf{n}} B_\lambda^+ B_{\lambda'}^+ + e^{-i(\lambda+\lambda')\cdot\mathbf{n}} B_\lambda B_{\lambda'})] . \qquad (2.32)$$

In the above we have taken the Q_{qq} term into H_0 by noting that $\sum_n A_n^+ A_n = 1$ in one exciton space. This choice of H_0 is reasonable on several grounds: (1) the eigenstates of H_0 are also eigenstates of total wavevector; (2) the perturbation V has zero average and will not give rise to secular terms in perturbation theory; and (3) this procedure is close in spirit to the modified Rayleigh Schrödinger perturbation theory of Rubinstejn and Yaris.[18]

Before going on to the approximate exciton transport equations, we must mention a problem which restricts our results to weak quadratic coupling. In the case of strong quadratic coupling the coupled exciton–phonon system can have a spectrum which is greatly modified from that of H_0. This occurs when the frequency change $(\omega' - \omega)$ is large enough so that bound exciton-n phonon $(n \geq 1)$ bands appear.[12,16] The precursor occurs for $J_{nm} = K_{nm} = 0$ when the one exciton-one phonon levels can have two energies $\epsilon + \omega$ $(N^2 - N$ states) and $\epsilon + \omega'$ (N states). When J_{nm} and K_{nm} are nonzero these states broaden into two bands (a bound state band and a band of scattering states). If the perturbation $(\omega' - \omega)$ is large enough, the time dependence of the density matrix will be very complicated due to the bound state band. However, if $\omega' - \omega$ is small, the bound states and scattering states will be well mixed, so that the effect of the bound states on the time dependence will be small. In what follows we assume that the eigenstates of H_0 are close to those of H, i.e., that bound states are unimportant.

III. DERIVATION OF TRANSPORT EQUATIONS

The equation of motion for the elements of the exciton density matrix in the site representation was derived by Grover and Silbey.[4(a)] In the approximation $(\exp iH_{0,\mathrm{ext}})_{pq} = \delta_{pq}$, valid for weak intersite coupling J, the result can be written as

$$\mathring{\rho}_{nm}(t) = -i \sum_p [\tilde{J}_{np}\rho_{pm}(t) - \rho_{np}(t)\tilde{J}_{pm}] - \sum_{p,r} \int_0^t d\tau$$

$$\times [h_{nppr}(t-\tau)\rho_{rm}(\tau) + h_{rppm}(\tau - t)\rho_{nr}(\tau) - h_{rmnp}(t-\tau)\rho_{pr}(\tau) - h_{rmnp}(\tau - t)\rho_{pr}(\tau)] , \qquad (3.1)$$

where

$$h_{pqrs}(t) = \langle V_{pq}(t) V_{rs}\rangle = \langle V_{pq} V_{rs}(-t)\rangle . \qquad (3.2)$$

(The quantities h_{pqrs} differ somewhat from the g_{pqrs} used previously.[4(a),19,20])

We simplify Eq. (3.1) to the case of a linear chain with nearest-neighbor coupling. There are then four significant types of correlation h_{pqrs}:

h_0 when $p = q = r = s$;

h_1 when $p = s$ and $q = r = s \pm 1$

or $p = r$ and $q = s = r \pm 1$;

h_3 when $p = q = r = s \pm 1$

or $p \pm 1 = q = r = s$;

h_5 when $p = q = r \pm 1 = s \pm 1$.

Equations of motion involving h_0 and h_1 have been published previously.[4(a),6,21] The terms in h_3 arise from cross coupling between the local and nonlocal parts of V, those in h_5 from coupling between the local parts at adjacent sites. Here h_3 turns out to be negligible but h_5 is comparable with h_0 (see Sec. IV.B), contrary to the usual assumption[6] that h_5 is negligible compared with h_0.

The simplified equation of motion is

$$\mathring{\rho}_{nm}(t) = -i\tilde{J}[\rho_{n+1,m}(t) + \rho_{n-1,m}(t) - \rho_{n,m+1}(t) - \rho_{n,m-1}(t)] - 2\{[2h_1 + (1-\delta_{nm})h_0] * \rho_{nm} - h_1 * (\rho_{n-1,n-1} + \rho_{n+1,n+1})\delta_{nm}$$
$$- (1-\delta_{nm})h_3 * (\rho_{n+1,m} + \rho_{n-1,m} + \rho_{n,m+1} + \rho_{n,m-1}) + (\delta_{n,m+1} + \delta_{n,m-1})[h_3 * (\rho_{nn} + \rho_{mm}) - h_1 * \rho_{mn} - h_5 * \rho_{nm}]\} , \qquad (3.2)$$

where the asterisk denotes a convolution

$$f * g \equiv \int_0^t dt f(t-\tau) g(\tau) = \int_0^t dt f(\tau) g(t-\tau) . \qquad (3.3)$$

The equation of motion (3.2) assumes that $h_{nmmn} = h_{nmnm}$, which is valid at long times, when each is equal to h_1. However, at short times h_{nmnm} is a different quantity, denoted by h_4, which replaces h_1 in the last term of Eq. (3.2). This changes the off-diagonal terms, but not the diagonal ones.[20]

We now make the conventional assumption[4(a),5] that vibrational relaxation is fast compared with exciton transfer $\tilde{J} \ll K$ (the "slow-exciton" limit[7]). This means that $h(t-\tau)$ is significant only for times τ close to t, allowing the separation

$$\int_0^t h(t-\tau)\rho(\tau) d\tau \approx \rho(t) \int_0^t h(t-\tau)\, d\tau . \qquad (3.4)$$

Furthermore, the integral of h will have reached its asymptotic value for times less than a nanosecond, which are short compared with triplet exciton lifetimes. We can therefore replace the right-hand side of Eq. (3.4) by $\gamma_n \rho(t)$ for $t \gtrsim 1$ ns, where

$$\gamma_n \equiv \int_0^\infty d\tau\, h_n(\tau)\, d\tau . \qquad (3.5)$$

Transport is studied through the exciton mean square displacement

$$\langle R^2(t)\rangle = a^2 \sum_n n^2 \rho_{nn}(t) , \qquad (3.6)$$

where a is the lattice spacing. We are concerned here mainly with the diffusion coefficient D, given by[19]

$$2D/a^2 = \sum_n n^2 \mathring{\rho}_{nn}(t) \qquad (3.7)$$

as $t \to \infty$. Since h_0 and the new terms h_3 and h_5 do not contribute to $\mathring{\rho}_{nn}$, the expression for D is exactly the same as derived previously,[19] and can be written as

$$D/2a^2 = \gamma_1 + i\tilde{J}X_1 , \qquad (3.8)$$

where

$$X_p = \sum_n n\rho_{n,n+p} . \qquad (3.9)$$

These results arise because the trace of the density matrix is unity, and can be derived[19] before making the assumption (3.4). Differences from the previous results arise from the inclusion of γ_0 and γ_5, and, more fundamentally, of γ_3. The equation of motion of X_1 is obtained, after relabeling of the summation variable, in the form

$$\dot{X}_1 = -i\tilde{J} - 2(3\gamma_1 + \gamma_0 - \gamma_5)X_1 + 4\gamma_3 X_2 . \qquad (3.10)$$

As can be seen, γ_3 couples X_1 to the next member of the set X_p. The higher members are related through the equations for $p \geq 2$:

$$\dot{X}_p = -2(2\gamma_1 + \gamma_0)X_p + 4\gamma_3(X_{p-1} + X_{p+1}) \ . \tag{3.11}$$

The coupled equations (3.10) and (3.11) can be solved in a straightforward way for small γ_3 by Laplace transformation, yielding X_1 as a complicated combination of exponential and hyperbolic functions of time. For long times the equations are readily soluble for arbitrary γ_3 by applying the steady-state condition $\dot{X}_p = 0$ for all p (necessary to obtain a constant diffusion coefficient). The equations (3.11) have the solution

$$X_p = YZ^p \ , \tag{3.12}$$

$$Z = [1 - (1 - W^2)^{1/2}]/W \ , \tag{3.13}$$

$$W = 4\gamma_3/(2\gamma_1 + \gamma_0) \ . \tag{3.14}$$

The value of Y is obtained by substitution in Eq. (3.10), with the result

$$Y = \frac{-i\tilde{J}}{2Z[3\gamma_1 + \gamma_0 - \gamma_5 - 2\gamma_3 Z]} \ . \tag{3.15}$$

Finally, X_1 is found to be

$$X_1 = -i\tilde{J}/\{4\gamma_1 + \gamma_0 - 2\gamma_5 + [(2\gamma_1 + \gamma_0)^2 - 16\gamma_3^2]^{1/2}\} \ , \tag{3.16}$$

yielding D on substitution in Eq. (3.8). All these results assume $W<1$, appropriate for small γ_3. In the limit $\gamma_3 = 0$ we obtain

$$X_1 = -i\tilde{J}/[2(3\gamma_1 + \gamma_0 - \gamma_5)] \ , \tag{3.17}$$

as follows directly from Eq. (3.10) in this limit. Henceforth, γ_3 will be treated as zero (see Sec. IV.D).

The diffusion coefficient is found to be

$$D/2a^2 = \gamma_1 + \tilde{J}^2/[2(3\gamma_1 + \gamma_0 - \gamma_5)] \ , \tag{3.18}$$

an algebraic form similar to that obtained previously.[4(a)] This expression apparently allows the unphysical result that D can be negative if γ_5 is large enough, but this is not so since γ_0 and γ_5 each arise from the correlation h_{nmmm} (with $n=m$ and $n=m\pm 1$, respectively) in such a way that $\gamma_0 > \gamma_5$.

Transport at short times is readily treated, because the results are the same as for linear coupling.[20] The mean square displacement changes at a rate

$$\frac{d\langle R^2(t)\rangle}{dt} = 4a^2[\gamma_1(t) + i\tilde{J}X_1(t)] \ , \tag{3.19}$$

where $\gamma_1(t)$ is given by Eq. (3.5) with the upper limit of the integral as t instead of ∞. For an exciton density matrix which is diagonal at $t=0$ the right-hand side of Eq. (3.19) is zero at $t=0$, so that $\langle R^2(t)\rangle$ varies initially as t^2. The proportionality constant depends on $\dot{X}_1(0) = -i\tilde{J}$ and $\dot{\gamma}_1(0) = h_1(0)$. Now

$$h_1(0) = J^2(\langle \theta_n^+\psi_n^+\psi_m\theta_m\theta_m^+\psi_m^+\psi_n\theta_n\rangle - \langle\theta_n^+\psi_n^+\psi_m\theta_m\rangle\langle\theta_m^+\psi_m^+\psi_n\theta_n\rangle) \ , \tag{3.20}$$

where $m = n \pm 1$, and since $\theta_n^+\psi_n^+\psi_n\theta_n = 1$,

$$h_1(0) = J^2 - \tilde{J}^2 \ , \tag{3.21}$$

a result which is seen to depend on the unitary nature of the canonical transformation. Combining these results we find that at short times the exciton moves with a constant *acceleration* $4a^2J^2$ governed by the *bare* exciton transfer integral. Since transfer of the bare exciton is involved, the result is the same as for linear coupling: The nature of the coupling affects only the clothing time and the subsequent clothed transport.

IV. CALCULATION OF CORRELATION FUNCTIONS

A. Principles

Calculating the correlation functions is the core of the transport problem. Apart from $\tilde{J}$, the correlation functions are the only place where details of the phonons enter and the temperature dependence arises. These calculations carry the treatment beyond the phenomenological theory[6] and give expression to the formal results of the GME treatment.[5] Such advantages are bought at the cost of complexity, and we are unable to perform the calculations exactly for quadratic coupling, unlike linear coupling.[4] A guide to suitable approximations is provided by considering what properties the correlations must have. In order to make the presentation simple *we neglect linear coupling from here on*; such terms can be handled in the same manner as before.

We have to calculate the correlations $h_n(t)$ which are then integrated over time from 0 to ∞ to give the γ_n. It is therefore necessary for the $h_n(t)$ to decay to zero sufficiently rapidly as $t \to \infty$, i.e., for the correlations to die away. This "ergodicity" arises because of the coarse graining or averaging over the phonon distribution,[5] which causes detailed information to be lost and ensures irreversibility. A further consequence is that the phonon distribution must be continuous. This requirement is satisfied by transforming sums over phonon states into integrals over a phonon frequency distribution. Although the present treatment has been simplified to apply to a linear-chain model of a crystal, a strictly one-dimensional phonon frequency distribution is not admissible because the infinites at the band edges cause the diffusion to diverge.[3,4(a)]

B. Local correlations

Here we treat the correlations $h_{nnmm}(t)$ which arise from the terms

$$V_{nn} = N^{-1}\sum_{\lambda,\mu}[e^{i(\lambda-\mu)n}(1-\delta_{\lambda\mu})Q_{\lambda\mu}B_\lambda^+B_\mu - \sinh 2\gamma K_\lambda(e^{i(\lambda+\mu)n}B_\lambda^+B_\mu^+ + e^{-i(\lambda+\mu)n}B_\lambda B_\mu)] \ , \tag{4.1}$$

where

$$Q_{\lambda\mu} = \omega' - \omega + (\cosh 2\gamma - 1)(K_\lambda + K_\mu) \ . \tag{4.2}$$

The thermal averaging over products of phonon operators is straightforward and eliminates terms containing different numbers of creation and annihilation operators, leaving

$$h_{nnmm}(t) = N^{-2}\sum_{\lambda\mu}\{e^{i(\lambda-\mu)(n-m)}(1-\delta_{\lambda\mu})Q_{\lambda\mu}^2 e^{i(\omega_\lambda-\omega_\mu)t}\nu_\lambda(\nu_\mu+1) + \sinh^2 2\gamma\sum_{\lambda\mu}K_\lambda(K_\lambda+K_\mu)[e^{i(\lambda+\mu)(n-m)}e^{i(\omega_\lambda+\omega_\mu)t}\nu_\lambda\nu_\mu$$

$$+e^{-i(\lambda+\mu)(n-m)}e^{-i(\omega_\lambda+\omega_\mu)t}(v_\lambda+1)(v_\mu+1)] , \qquad (4.3)$$

where

$$v_\lambda=(e^{\beta\omega_\lambda}-1)^{-1} \qquad (4.4)$$

is the thermal average number of phonons is a mode of frequency $\omega_\lambda(\beta=1/kT)$. It can be seen that $h_{nnmm}(t)$ depends on $n-m$ through the leading exponential in each term of Eq. (4.3). When $n=m$, i.e., in h_0, these terms are unity; when $n=m+1$, i.e., in h_5 these terms vary like $\cos(\lambda\pm\mu)$, so that $h_0-h_5>0$ as stated earlier. The problem now is to transform the sums into integrals over the phonon distribution. This causes the oscillatory exponentials to decay and permits $\gamma_0-\gamma_5$ to be evaluated.

Perhaps the most convenient form of frequency distribution for optical phonons is the Lorentzian

$$\rho(\omega_1)=\frac{\Delta/\pi}{\Delta^2+\omega_1^2} , \qquad (4.5)$$

where Δ characterizes the width and ω_1 is the frequency measured from the mean frequency ω. However, in the present case this density of states does not give a convergent integral for the terms involving $K^2\sim\omega_1^2$. In practice, these terms would be small, varying as $\Delta^2\gamma^2$ compared with $\omega^2\gamma^2$, and we shall omit them, so that we take

$$h_{nnmm}(t)=N^{-2}(\omega'-\omega)^2\sum_{\lambda\neq\mu}e^{i(\lambda-\mu)(n-m)}e^{i(\omega_\lambda-\omega_\mu)t}\,v_\lambda(v_\mu+1) . \qquad (4.6)$$

Alternatively, convergence can be ensured by using the Gaussian frequency distribution[22]

$$\rho'(\omega_1)=\frac{1}{\Delta\pi^{1/2}}\exp(-\omega_1^2/\Delta^2) \qquad (4.7)$$

although this is mathematically more involved. In addition to $\rho(\omega_1)$ we need the corresponding dispersion law, because the summand in Eq. (4.6) depends explicitly on wave vector as well as on frequency. The result, derived in Appendix A, is

$$\omega_1^{\pm}(\lambda)=\pm\Delta\tan\tfrac{1}{2}\lambda . \qquad (4.8)$$

Using standard trigonometric formulae to obtain $\cos\lambda$ and $\sin\lambda$ as functions of ω_1 we find

$$e^{i\lambda}=(\Delta\pm i\omega_1^{\pm})/(\Delta\mp i\omega_1^{\pm}) , \qquad (4.9)$$

which now permits Eq. (4.6) to be evaluated. In order to obtain a correlation function which decays as $t\to\infty$ it is necessary to choose the upper sign in Eq. (4.9) when $m>n$ and the lower sign when $m<n$.

We ignore the small variation of v_λ with ω_λ and replace it by its value for the central frequency $v\equiv v(\omega)$. Then the sums in Eq. (4.6) can be expressed as integrals which are found to be equal

$$h_{nnmm}(t)=v(v+1)(\omega'-\omega)^2 I_{n-m}^2 , \qquad (4.10)$$

where for $n>m$ we can express I_{n-m} as

$$I_{n-m}=\left(\frac{\Delta}{2\pi}\right)\int_{-\infty}^{+\infty}d\omega_1\,\frac{(\Delta-i\omega_1)^{n-m-1}}{(\Delta+i\omega_1)^{n-m+1}}\,e^{i\omega_1 t} \qquad (4.11)$$

and $\rho(\omega_1)$ has been halved because only one branch of the dispersion curve has been used. For $n=m$ the dispersion curve is not needed, $\rho(\omega_1)$ is not halved, and I_0 is the Fourier transform of $\rho(\omega_1)$, i.e.,

$$I_0=e^{-\Delta t} . \qquad (4.12)$$

The other integrals can be evaluated by contour integration, closing the contour in the upper half-plane. As a function of $u=\omega_1-i\Delta$ the integrand is

$$(-1)^r e^{-\Delta t}e^{itu}(u+2i\Delta)^{r-1}/u^{r+1} , \qquad (4.13)$$

where $r=n-m\geq 1$. The residue at $\omega_1=i\Delta$ is the coefficient of u^{-1} in the series expansion of Eq. (4.13), which is found to be

$$it\,e^{-\Delta t}(r-1)!\sum_{s=0}^{r-1}(-2\Delta t)^s/s!(s+1)!(r-1-s)! . \qquad (4.14)$$

The integral thus becomes

$$I_r=(-1)^{r+1}\Delta t\,e^{-\Delta t}\sum_{s=0}^{r-1}\frac{(r-1)!(-2\Delta t)^s}{s!(s+1)!(r-1-s)!} , \qquad (4.15)$$

which can be expressed in terms of the gamma function as

$$I_r=(-1)^{r+1}\Delta t\,e^{-\Delta t}\sum_{s=0}^{r-1}\frac{\Gamma(2)}{\Gamma(s+2)}\,\frac{\Gamma(r)}{\Gamma(r-s)}\,\frac{(-2\Delta t)^s}{s!} . \qquad (4.16)$$

Using the result[23]

$$\Gamma(r)/\Gamma(r-s)=(-1)^s(-r+1)_s , \qquad (4.17)$$

where

$$(\alpha)_s\equiv\alpha(\alpha+1)\cdots(\alpha+s-1) , \qquad (4.18)$$

we obtain

$$I_r=(-1)^{r+1}\Delta t\,e^{-\Delta t}\sum_{s=0}^{r-1}\frac{(-r+1)_s}{(2)_s}\,\frac{(2\Delta t)^s}{s!} \qquad (4.19)$$

$$=(-1)^{r+1}\Delta t\,e^{-\Delta t}\,{}_1F_1(-r+1;2;2\Delta t) , \qquad (4.20)$$

where ${}_1F_1(\alpha;\beta;z)$ is the confluent hypergeometric function. But according to one definition[24] the associated Laguerre polynomials are given by

$$L_n^\alpha(x)=\frac{(n+\alpha)!}{n!\,\alpha!}\,{}_1F_1(-n;\alpha+1;x) , \qquad (4.21)$$

so that finally we can write

$$I_r=(-1)^{r+1}\Delta t\,e^{-\Delta t}L_{r-1}^1(2\Delta t)/r . \qquad (4.22)$$

The required correlation functions are

$$\gamma_{nnmm}=v(v+1)(\omega'-\omega)^2\int_0^\infty[I_{n-m}(t)]^2\,dt . \qquad (4.23)$$

For γ_0 the integration with Eq. (4.12) is standard, yielding

$$\gamma_0=v(v+1)\,\frac{(\omega'-\omega)^2}{2\Delta} . \qquad (4.24)$$

For the other correlation functions the required quantity is

$$\alpha^{(r)}\equiv[v(v+1)(\omega'-\omega)^2/8r^2\Delta]\int_0^\infty L_{r-1}^1(x)^2x^2e^{-x}\,dx . \qquad (4.25)$$

But from Ref. 24, Eq. (7.414.10),

$$\int_0^\infty dx\, e^{-bx}x^{2a}[L_n^a(x)]^2 = \frac{2^{2a}\Gamma(a+\frac{1}{2})\Gamma(n+\frac{1}{2})}{\pi b^{2a+1}(n!)^2}\ {}_2F_1\left[-n,\ a+\tfrac{1}{2};\ \tfrac{1}{2}-n;\ \left(1-\frac{2}{b}\right)^2\right], \tag{4.26}$$

where Re$a > -\frac{1}{2}$, Re$b > 0$, n is an integer, and ${}_2F_1(\alpha,\ \beta;\ \gamma;\ z)$ is the hypergeometric function. For the integral in Eq. (4.25) we require $a = 1 = b$ and $n = r - 1$. This makes the argument of the hypergeometric function unity, when it is given by (Ref. 23, p. 23)

$${}_2F_1(-n,\ \beta;\ \gamma;\ 1) = (\gamma-\beta)_n/(\gamma)_n\ . \tag{4.27a}$$

The integral in Eq. (4.25) is then equal to

$$\frac{4\Gamma(\frac{3}{2})\Gamma(r-\frac{1}{2})(-r)_{r-1}}{\pi[(r-1)!]^2(\frac{3}{2}-r)_{r-1}}\ , \tag{4.27b}$$

which with Eq. (4.17) and the result (Ref. 23, p. 17)

$$(1-\alpha-n)_s = (-1)^s(\alpha)_n/(\alpha)_{n-s} \tag{4.28}$$

yields

$$-2r\Gamma(3/2)\Gamma(-\tfrac{1}{2})/\pi(r-1)! \tag{4.29}$$

Finally, using $\Gamma(n+1) = n\ \Gamma(n)$ and $\Gamma(\frac{1}{2}) = \pi^{1/2}$ we evaluate Eq. (4.29) as $2r/(r-1)!$, which leads to

$$\alpha^{(r)} = v(v+1)(\omega'-\omega)^2/4\Delta r! \tag{4.30}$$

In particular, for $r = 1$ we have

$$\gamma_5 = v(v+1)(\omega'-\omega)^2/4\Delta = \tfrac{1}{2}\gamma_0\ , \tag{4.31}$$

so that $\gamma_0 - \gamma_5 > 0$ as stated earlier. The next correlation function, with $r = 2$, is only a further factor of 2 smaller; if included in Eq. (3.2) it would introduce a next-nearest-neighbor coupling term which has no effect on transport for $\gamma_3 = 0$ but otherwise would considerably complicate Eqs. (3.10) and (3.11).

C. Nonlocal correlations

Here we treat the correlations $h_{nmmn}(t)$ which arise from the term for $m = n \pm 1$:

$$V_{nm} = J(\theta_n^+\theta_m - \langle\theta_n^+\theta_m\rangle)\ , \tag{4.32}$$

which leads to

$$h_{nmmn}(t) = J^2[\langle\theta_n^+(t)\theta_m(t)\theta_m^+\theta_n\rangle - \langle\theta_n^+\theta_m\rangle\langle\theta_m^+\theta_n\rangle]\ . \tag{4.33}$$

Evaluation of this quantity also entails evaluating the renormalized transfer integral

$$\tilde{J} = J\langle\theta_n^+\theta_{n+1}\rangle\ . \tag{4.34}$$

Because θ_n is an exponential operator in the site representation, evaluating the thermal averages over the phonon distribution in the momentum representation proves to be difficult, particularly since the exponent is quadratic in the phonon operators. In the evaluation we have used both operator disentangling and coordinate-momentum representation techniques, which are described elsewhere.[25] We proceed through successively more complicated averages, aided by arguments from analogy and comparison with the results for linear coupling.

For Einstein phonons the thermal averages decouple into averages for individual sites which are independent of site. We find

$$\langle\theta^+\rangle_E = \langle\theta\rangle_E = \{1 + 2\sinh^2(2\gamma)[v^2 + (v+1)^2]\}^{-1/2}\ , \tag{4.35}$$

so that in this limit $\tilde{J}/J$ is the square of Eq. (4.35). Similarly, after lengthier algebra we obtain

$$\langle\theta^+(t)\theta\rangle_E = \langle\theta(t)\theta^+\rangle_E = \{1 + [v^2 + (v+1)^2 - v^2e^{2i\omega t} - (v+1)^2e^{-2i\omega t}]\sinh^2 2\gamma\}^{-1/2}\ , \tag{4.36}$$

from which $h(t)$ follows. Without dispersion the correlations do not decay, but with the *ad hoc* assumption that the time-dependent terms in Eq. (4.36) decay to zero, $h_1(t)$ given by Eq. (4.33) tends to zero to second order in γ.

Once vibrational coupling is introduced, and the frequencies are not equal, the algebra becomes extremely complicated since the exponent in $\theta_n^+\theta_m$ contains terms coupling different momentum states. We proceed as follows: For a dimer the calculation of $\langle\theta_1^+\theta_2\rangle$ and $\langle\theta_1^+(t)\theta_2(t)\theta_2^+\theta_1\rangle$ can be done exactly, but for an N-mer we have not succeeded in doing the calculation exactly. We therefore rely on the fact that in the limit that N is large the phonon coordinates are distributed in a Gaussian way and perform an approximate calculation of the necessary correlation functions. To low order in γ^2 our results agree with the exact answers where they are known.

For a dimer with frequencies ω_+ and ω_- we find

$$\langle\theta_1^+\theta_2\rangle = \{1 + 2\sinh^2\gamma[v_+v_- + (v_++1)(v_-+1)]\}^{-1}\ , \tag{4.37}$$

which reduces to $\langle\theta\rangle^2$ in the Einstein limit. In addition, we find

$$\langle\theta_1^+(t)\theta_2(t)\theta_2^+\theta_1\rangle = [1 + \sinh^2 2\gamma(v_+v_- + (v_++1)(v_-+1) - v_+v_-e^{i(\omega_++\omega_-)t} - (v_++1)(v_-+1)e^{-i(\omega_++\omega_-)t}]^{-1}\ . \tag{4.38}$$

For N coupled oscillators we use the fact that as $N \to \infty$ the phonons are Gaussian distributed, so that averages of products of phonon operators break up into pairs. For example,

$$\langle\theta_n^+\theta_{n+1}\rangle = \langle\exp(-\gamma C)\rangle \tag{4.39}$$

$$= 1 + \gamma^2\langle C^2\rangle/2! + \gamma^4\langle C^4\rangle/4! + \cdots\ , \tag{4.40}$$

where $C = (B_n^2 - B_n^{+2} + B_{n+1}^2 - B_{n+1}^{+2})$ and averages of odd powers of C are zero. Now C^4 can be broken into three pairs of averages $\langle C^2\rangle$ because of the Gaussian property, leaving

$$\langle\theta_n^+\theta_{n+1}\rangle = 1 + \gamma^2\langle C^2\rangle/2 + \gamma^4\langle C^2\rangle^2/8 + \cdots\ . \tag{4.41}$$

Similarly,

$$\langle\theta_1^+(t)\theta_2(t)\theta_2^+\theta_1\rangle = \langle\exp[\gamma C(t)]\exp(-\gamma C)\rangle \tag{4.42}$$

$$= 1 + \gamma^2/2!\,[\langle C\rangle^2 - 2\langle C(t)C\rangle + \langle C(t)\rangle^2] + \gamma^4/4!\,[\langle C^4\rangle - 4\langle C(t)C^3\rangle + 6\langle C(t)^2C^2\rangle - 4\langle C(t)^3C\rangle + \langle C(t)^4\rangle] + \cdots\ , \tag{4.43}$$

which yields eventually

$$1+\gamma^2[\langle C^2\rangle - \langle C(t)C(0)\rangle] + \tfrac{1}{2}\gamma^4[\langle C^2\rangle - \langle C(t)C(0)\rangle]^2 + \cdots \,, \tag{4.44}$$

where we have used $\langle C(t)^2\rangle = \langle C^2\rangle$. Equation (4.44) correctly reduces to 1 as $t \to 0$.

We can now proceed to construct functions for which Eqs. (4.41) and (4.4) are the leading terms in the series expansion in powers of γ^2. Because the results are not valid to all orders in γ, more than one function may be admissible. For example, by analogy with the results for Einstein phonons Eqs. (4.35) and (4.36) we may equate equations. (4.41) and (4.44) to the leading terms in the expansion of the inverse square root of a biquadratic function of γ. This yields

$$\langle \theta_n^+\theta_{n+1}\rangle \approx [1-\gamma^2\langle C^2\rangle + \tfrac{1}{2}\gamma^4\langle C^2\rangle^2]^{-1/2} \,, \tag{4.45}$$

$$\langle \theta_n^+(t)\theta_{n+1}(t)\theta_{n+1}^+\theta_n\rangle \approx [1-2\gamma^2 D(t) + 2\gamma^4 D^2(t)]^{-1/2} \,, \tag{4.46}$$

where

$$D(t) = \langle C^2\rangle - \langle C(t)C\rangle \,. \tag{4.47}$$

Alternatively, we can recognize Eqs. (4.41) and (4.44) as the leading terms in exponential series, so that

$$\langle \theta_n^+\theta_{n+1}\rangle \approx \exp[\tfrac{1}{2}\gamma^2\langle C^2\rangle] \,, \tag{4.48}$$

$$\langle \theta_n^+(t)\theta_{n+1}(t)\theta_{n+1}^+\theta_n\rangle \approx \exp\{\gamma^2[\langle C^2\rangle - \langle C(t)C\rangle]\} \,. \tag{4.49}$$

Although the forms (4.45) and (4.46) have perhaps better *a priori* justification, the exponential forms are equally good to $0(\gamma^4)$, and have the advantage of being mathematically more tractable. Moreover, the exponential forms constructed in a similar way for linear coupling happen to give the exact result in that case. We therefore use Eqs. (4.48) and (4.49) from now on.

The averages $\langle C^2\rangle$ and $D(t)$ are evaluated by generalizing the results for the dimer expressed as double sums over the two momentum states. This procedure yields

$$\langle C^2\rangle = -(4/N^2)\sum_{\lambda\mu}[v_\lambda v_\mu + (v_\lambda+1)(v_\mu+1)][1-\cos(\lambda+\mu)] \tag{4.50a}$$

$$\cong -(4/N^2)\sum_{\lambda\mu}[v_\lambda v_\mu + (v_\lambda+1)(v_\mu+1)] \,, \tag{4.50b}$$

where, in the last equation, we have assumed that the phonon frequencies are close enough to an Einstein distribution so that the cos term is small. In addition, within this approximation

$$D(t) = -(4/N^2)\sum_{\lambda\mu}\{v_\lambda v_\mu(1-e^{i(\omega_\lambda+\omega_\mu)t}) + (v_\lambda+1)(v_\mu+1)(1-e^{-i(\omega_\lambda+\omega_\mu)t})\} \,. \tag{4.51}$$

We now replace the sums by integrals over frequency as in Sec. IV.B, setting $v_\lambda \approx v$ and introducing the Lorentzian density of states (4.5). Then we obtain

$$\langle C^2\rangle = -4[v^2+(v+1)^2] \tag{4.52}$$

$$D(t) = -4\{v^2+(v+1)^2 - e^{-2\Delta t}[v^2e^{2i\omega t}+(v+1)^2e^{-2i\omega t}]\} \,, \tag{4.53}$$

so that as $t\to\infty$, $D(t)$ becomes constant. With this assumption we finally find

$$\tilde{J} = J\exp\{-2\gamma^2[v^2+(v+1)^2]\} \,, \tag{4.54}$$

$$h_1(t) = \tilde{J}^2(\exp\{4\gamma^2[v^2e^{2i\omega t}+(v+1)^2e^{-i2\omega t}]e^{-2\Delta t}\}-1) \,, \tag{4.55}$$

where it can be seen that $h_1(t)\to 0$ as $t\to\infty$, so that ergodic behavior is ensured.

The correlation function γ_1 required for transport is given by

$$\gamma_1 = \int_0^\infty dt\, h_1(t) \tag{4.56}$$

$$= \tilde{J}^2\int_0^\infty dt\{\exp[f(t)]-1\} \,. \tag{4.57}$$

Now $f(t)$ can be written as

$$f(t) = 4\gamma^2 e^{-2\Delta t}v(v+1)\left(\frac{v}{v+1}\,e^{2i\omega t} + \frac{v+1}{v}\,e^{-2i\omega t}\right) \,, \tag{4.58}$$

where the two terms in the parentheses are inverse to one another. But the generating function for the modified Bessel functions is[24]

$$\exp[\tfrac{1}{2}a(z+z^{-1})] = \sum_{k=-\infty}^{+\infty} z^k I_k(a) \,, \tag{4.59}$$

so that we have

$$\exp[f(t)] = \sum_{k=-\infty}^{+\infty}\left(\frac{v}{v+1}\right)^k e^{2ik\omega t} I_k[8\gamma^2 v(v+1)e^{-2\Delta t}] \,. \tag{4.60}$$

We assume as before[4(a)] that the oscillating terms can be discarded, leaving

$$\exp[f(t)] \approx I_0[8\gamma^2 v(v+1)e^{-2\Delta t}] \,. \tag{4.61}$$

Since $\gamma^2 \ll 1$, we approximate the modified Bessel function by the first two terms in its series expansion, when Eq. (4.57) is readily evaluated to give

$$\gamma_1 = 4\tilde{J}^2\gamma^4 v^2(v+1)^2/\Delta \,. \tag{4.62}$$

As this result has been evaluated only to lowest order in γ, the same result is obtained to the same order if the square-root forms for the thermal averages are used [Eqs. (4.45) and (4.46)], but more manipulation is required.

The relative sizes of γ_1 and γ_0 can now be examined. From Eq. (4.24) for γ_0 with the result $(\omega'-\omega)^2 = 16\gamma^2\omega^2$ valid for small γ we find that

$$\gamma_1/\gamma_0 = \tilde{J}^2\gamma^2 v(v+1)/2\omega^2 \,, \tag{4.63}$$

since $\tilde{J}^2 \ll \omega^2$ and $\gamma^2 \ll 1$, and we see that the nonlocal scattering described by γ_1 is much weaker than the local scattering described by γ_0 (except at very high temperatures where molecular crystals would certainly have melted and the preceding teatment would be invalid). This conclusion accords with deductions from spectra and diffusion measurements for triplet excitons in anthracene.[2]

D. Cross correlations

For the cross correlations $h_{nnnm}(t)$ we take only the leading term in V_{nn} which gave the dominant contribution to γ_0. Then we have, with $m = n \pm 1$,

$$h_{nnnm}(t) = JN^{-1}\sum_{\lambda\neq\mu} e^{i(\lambda-\mu)n}Q_{\lambda\mu}e^{-i(\omega_\lambda-\omega_\mu)t}\langle B_\lambda^+B_\mu\theta_n^+\theta_m\rangle$$

or, on transformation to the site representation in the average,

$$h_{nnnm}(t) = JN^{-2} \sum_{\lambda \neq \mu} e^{i(\lambda-\mu)n} Q_{\lambda\mu} e^{-i(\omega_\lambda - \omega_\mu)t} \times \sum_{p,q} e^{-i(\lambda p - \mu q)} \langle B_p^+ B_q \theta_n^+ \theta_m \rangle \ . \tag{4.65}$$

Note that because the time-dependent factor involves $\omega_\lambda - \omega_\mu$, the required average is not just $\langle B_n^+ B_n \theta_n^+ \theta_m \rangle$. In the Einstein limit the average in Eq. (4.65) is zero unless $p=q$, because θ_n^+ and θ_m create an annihilate pairs of phonons at different sites. The average when $p=q$ is independent of p except when $p=n$ or m, i.e., two cases in N. Then the second double sum in Eq. (4.65), ignoring the cases $p=n$ or m, becomes proportional to

$$\sum_p e^{i(\lambda-\mu)p} = N\delta_{\lambda\mu} \ . \tag{4.66}$$

This is nonzero only if $\lambda = \mu$, but this term is excluded from the first double sum, leaving $h_{nnnm}(t)$ zero. The same result follows directly from Eq. (4.64) if one argues that the averages over θ_n^+ and θ_m can be performed separately. Similar results follow for the other terms in V_{nn} involving B^2 and B^{+2}; they end up proportional to K_{pq} with $p=q$, which is zero.

V. RESULTS AND DISCUSSION

A. Applicability of treatment

Before discussing our results for the diffusion coefficient we review the basic assumptions of the calculation, the systems in which they may be valid, and the appropriate order of magnitude of the various parameters.

The basic assumptions are as follows:

(i) the exciton–phonon coupling is pure quadratic;

(ii) the frequency shift upon excitation $\omega' - \omega$ is the main term responsible for the exciton–phonon scattering, but is not large enough to produce bound states whose time dependence would invalidate our perturbation theory;

(iii) the exciton bandwidth is smaller than the phonon bandwidth (vibrational relaxation fast compared to transport) and the phonon bandwidth is small compared to the frequency, i.e., $J < \Delta \ll \omega$.

Assumption (i) can be relaxed rather easily, as outlined in Sec. V.D. Assumptions (ii) and (iii) are crucial to our calculations: without (ii) the theory would have to take account of the bound states, while without (iii) the calculations would have to be performed in momentum space so that proper account could be taken of the exciton bandwidth in the correlation functions.

As already noted, pure quadratic coupling is expected to occur in certain intramolecular modes of vibration, such as the out-of-plane bending modes in aromatic hydrocarbons, which also have rather low frequencies. Such coupling is estimated to be of importance in exciton transport but probably not in charge-carrier transport,[26] where polarization fluctuations have to be considered. The precise conditions under which assumption (ii) is valid cannot be quantified, but it is clear that the frequency shift must not be too large a fraction of the frequency itself. Normally, the frequency falls on excitation; a fall not exceeding a third of ω requires $\gamma < 0.1$.

The phonon bandwidth Δ for molecular modes in the crystal environment can be estimated from calculations for naphthalene.[27] These show widths of up to 16 cm^{-1} for out-of-plane modes, corresponding to Δ/ω of 3%–6% for the lower frequencies. These are lower limits, since they refer only to wave vectors parallel to the crystal **b** axis, and would be further increased for larger molecules with weaker force fields and lower frequencies, so that Δ/ω could easily reach 0.1. These estimates confirm that Δ/ω is likely to be consistent with assumption (iii), and require J to be less than about 10 cm^{-1}. For singlet excitations the transfer interactions are too long range and strong, but for triplet excitons in anthracene J is calculated[28] to be 10 cm^{-1} or less and measured[2(b)] to be about 2.5 cm^{-1} (including a Franck–Condon factor). Our assumptions should thus be valid for triplet excitons in aromatic hydrocarbon crystals.

B. Diffusion coefficient

The diffusion coefficient is given by Eq. (3.18). Substituting Eqs. (4.24), (4.31), (4.54), and (4.62) we find, to leading order in γ,

$$D/2a^2 = (\tilde{J}^2/\Delta)(y^2 + \Delta^2/4y\omega^2) \tag{5.1}$$

$$= (J^2/\Delta)e^{-4\gamma^2}e^{-4y}(y^2 + \Delta^2/4y\omega) \ , \tag{5.2}$$

where

$$y = 2\gamma^2 v(v+1) \ . \tag{5.3}$$

As $T \to 0$, v and $y \to 0$, and D diverges because there is no scattering. As T increases, D goes through a minimum near $y = \frac{1}{2}(\Delta/\omega)^{2/3}$. It then increases slowly to reach a maximum near $y = \frac{1}{2}$, finally falling to zero as $T \to \infty$.

Figure 1 shows $D/(2a^2J^2/\Delta)$ for $(\Delta/\omega)^2 = 0.005$ and various values of γ plotted as a function of $1/\beta\omega$ (which is proportional to T). Apart from the factor $e^{-4\gamma^2}$, which is nearly constant for $\gamma \leq 0.1$, D depends on γ only through y. Decreasing γ increases the value of $1/\beta\omega$ required to give the same y, so that the curves are stretched to higher temperatures while retaining the same maximum and minimum values.

Figure 2 shows $D/(2a^2J^2/\Delta)$ as a function of $1/\beta\omega$ for $\gamma^2 = 0.01$ and various values of $(\Delta/\omega)^2$. Increasing $(\Delta/\omega)^2$ makes the term in $1/y$ larger compared wity y^2, causing the minimum between the falloff of $1/y$ and the rise of y^2 to become shallower and move to higher temperatures (eventually disappearing completely, although this is not shown). At the highest values of $1/\beta\omega$, $1/y$ becomes so small that the curves become independent of $(\Delta/\omega)^2$.

If we loosely associate the low-temperature divergent part of these curves with "coherent" or band motion

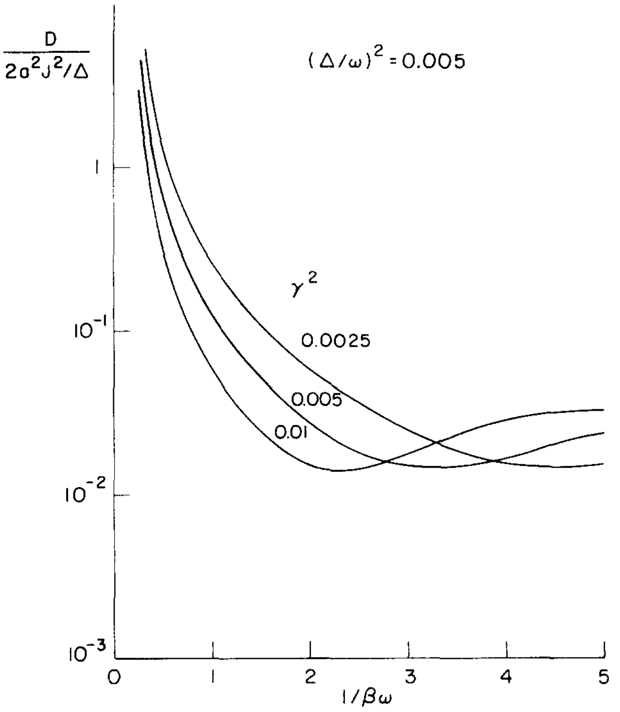

FIG. 1. Reduced diffusion coefficient $D/(2a^2J^2/\Delta)$ as a function of $1/\beta\omega$ for $(\Delta/\omega)^2=0.005$ and various values of γ^2. As γ^2 decreases, the curves remain similar in shape but are stretched towards higher temperatures.

dominated by γ_0, and the higher-temperature slowly rising part with "incoherent" or hopping motion dominated by γ_1, then we see that the smaller γ and the larger Δ, the more coherent the low-temperature motion. For some parameter values D may be relatively constant over a wide temperature range. Note that organic crystals melt well below $1/\beta\omega=5$ for any reasonable molecular frequency ω.

The scaling factor $2a^2J^2/\Delta$ is found to be 2×10^{-3} cm^2 s^{-1} for $a=6$ Å and $J=\Delta=10$ cm^{-1}. With the curves in Figs. 1 and 2 lying around 10^{-2} cm^2 s^{-1} or above, the resultant diffusion coefficients are compatible with measured values[2(b)] when allowance is made for the extra contributions to transport in a three-dimensional lattice as opposed to our one-dimensional model. These measurements[2(b)] also indicate that for triplet excitons in anthracene the *aa* component of the diffusion tensor decreases by a factor to 2–3 between 120 and 300 K, remaining constant or increasing slightly at higher temperatures. Our results are also compatible with this temperature dependence for suitable parameter values, but we do not think it profitable to obtain any "best" set of parameters.

C. Comparison with previous work

For linear exciton–phonon coupling the diffusion coefficient is found[4(a)] to depend on temperature in a way qualitatively similar to that found here: From an infinite value at $T=0$, D decreases as T increases, goes through a minimum and a maximum, and eventually falls to zero as $T\to\infty$. Closer examination reveals significant differences. The temperature dependence of D for linear coupling arises through the parameter

$$z=(G/\omega)^2[v(v+1)]^{1/2}\ , \qquad (5.4)$$

as opposed to y in Eq. (5.3) which is related to z^2, although this difference is partly offset by the fact that $G/\omega\sim1$ while we take $\gamma\le0.1$. With linear coupling there is no local scattering γ_0, whereas this term dominates the "coherent" contribution to D for quadratic coupling. As a result, the importance of the coherent contribution relative to the "incoherent" one depends on $(\Delta/J)^2$ for linear coupling but $(\Delta/\omega)^2$ for quadratic coupling, with other important differences between the relative temperature dependences of the contributions.

As noted in the Introduction, a treatment of quadratic coupling was given by Munn and Siebrand[3] with the help of various *ad hoc* assumptions, some of which give rise to interesting features of the results.[11] This treatment assumed that the coupling was strong enough to produce the bound states which we have excluded here by assumption (ii). It also assumed *a prior* that coherent transport would prevail at low temperatures and hopping transport at higher temperatures. This automatically gives a temperature dependence resembling that in the first two portions of the curves for D obtained here (or for linear coupling[4(a)]). In the slow-exciton limit, corresponding to our assumption (ii), the diffusion coefficient falls rather rapidly as the temperature rises from $T=0$, but once hopping sets in the diffusion coefficient increases only slowly with increasing temperature. Clearly, there is only a broad correspondence between these results and the present ones, but it is not possible to attribute the difference definitely to the empirical assumptions in the light of the other assumption that bound states are formed.

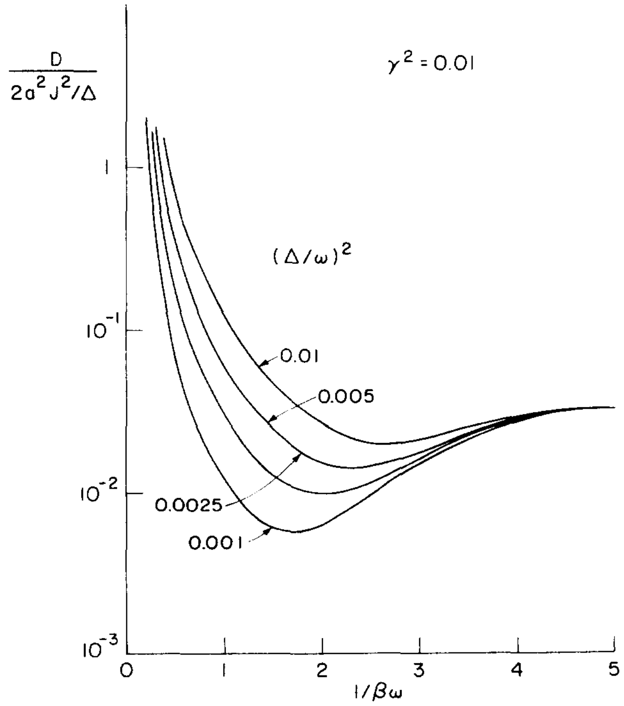

FIG. 2. Reduced diffusion coefficient $D/(2a^2J^2/\Delta)$ as a function of $1/\beta\omega$ for $\gamma^2=0.01$ and various values of $(\Delta/\omega)^2$. As $(\Delta/\omega)^2$ increases, the depth of the minimum decreases but the high-temperature behavior is unchanged.

A treatment of carrier transport including quadratic interactions with *lattice* (intermolecular) vibrations has recently been given,[29] using methods similar to those of Gosar.[30] Including quadratic coupling decreases the carrier mobility significantly, but the two-phonon processes have rather a weak temperature dependence and hence do not affect the total temperature dependence. As a result, the inclusion of this quadratic coupling cannot yield a weakly temperature-dependent mobility (or diffusion coefficient); such coupling has only a quantitative effect. Apart from the method used, which involves resummation of a selected class of diagrams for the carrier Green function, this work differs from the present work in treating all nonlocal couplings rather than the strictly local quadratic coupling of our Eq. (2.1).

D. Further work

Our assumption (ii) is that the exciton–phonon coupling is pure quadratic. Perhaps the most straightforward approach to relaxing this assumption is to postulate that two phonon bands are coupled to the exciton, one linearly, the other quadratically. Then applying the theory outlined here we would find the same γ_0 and γ_5 but a new γ_1:

$$\gamma_1^{\mathrm{NEW}} = \int_0^\infty \tilde{\tilde{J}}^2 (e^{f_1(t)} e^{f_2(t)} - 1)\, dt , \tag{5.4}$$

where

$$f_1(t) = 4\gamma^2 [v_1^2 e^{2i\omega_1 t} + (v_1+1)^2 e^{-2i\omega_1 t}] , \tag{5.5}$$

$$f_2(t) = 2(G/\omega)^2 [v_2 e^{i\omega_2 t} + (v_2+1) e^{-i\omega_2 t}] , \tag{5.6}$$

$$\tilde{\tilde{J}} = J \langle \theta_n^+ \theta_{n+1} \rangle_1 \langle \psi_n^+ \psi_{n+1} \rangle_2 , \tag{5.7}$$

$$= J e^{-2\gamma^2} e^{-4\gamma^2 v_1 (v_1+1)} e^{-(G/\omega)^2 (2v_2+1)} , \tag{5.8}$$

$$v_i = (e^{\beta\omega_i} - 1)^{-1} , \tag{5.9}$$

and the mode of frequency ω_1 is coupled quadratically and that of frequency ω_2 linearly to the exciton. Since γ^2 is usually very small, the Bessel function expansion of $\exp f_1(t)$ can be truncated at the $n=0$ term. Keeping only the nonoscillating part of the integral we find

$$\gamma_1^{\mathrm{NEW}} = \tilde{\tilde{J}}^2 \int_0^\infty dt \{ I_0 [8\gamma^2 v_1 (v_1+1)\, e^{-2\Delta_1 t}] \times I_0 [4(G/\omega)^2 v_2^{1/2} (v_2+1)^{1/2} e^{-\Delta_2 t}] - 1 \} \tag{5.10}$$

$$= \tilde{\tilde{J}}^2 \int_0^\infty dt \{ I_0 [4(G/\omega)^2 v_2^{1/2} (v_2+1)^{1/2} e^{-\Delta_2 t}] - 1 + O(\gamma^4) \} \tag{5.11}$$

$$\approx \gamma_1^L e^{-2\gamma^2} e^{-4y} , \tag{5.12}$$

where γ_1^L is the γ_1 for pure linear coupling. For low to moderate temperatures $\gamma_1^{\mathrm{NEW}} \approx \gamma_1^L$, and the theory reduces to linear coupling for γ_1 and quadratic for γ_0 and γ_5. However, if γ^2 or y are large enough, then γ_1^{NEW} is changed from the pure linear coupling result. As can be seen, in unfavorable cases the transport is a very complicated function of the two phonon frequencies and bandwidths and the two coupling strengths.

In future studies we plan to relax the other assumptions to permit the study of band states and wider exciton bands, so extending the range of validity of the theory. For the present it is apparent that our results are qualitatively similar to those of earlier theories and to the rather meager experimental results, so that quadratic coupling with molecular vibrations must be taken into account in proper theories.

ACKNOWLEDGMENT

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APPENDIX A. PHONON DISPERSION LAW

The Lorentzion frequency distribution normalized to unity is given by Eq. (4.5):

$$\rho(\omega_1) = (\Delta/\pi)/(\Delta^2 + \omega_1^2) . \tag{A1}$$

Let $\omega_1 = \omega_1(\lambda) = \omega_1(2\pi l/N)$, where the integers $l = 1, \cdots, N$ enumerate the modes in a crystal of N sites. Then

$$\rho(\omega_1) = N \Big/ \left| \frac{d\omega_1}{dl} \right| \tag{A2}$$

$$= \left(2\pi \left| \frac{d\omega_1}{d\lambda} \right| \right)^{-1} , \tag{A3}$$

so that

$$\frac{d\omega_1}{\Delta^2 + \omega_1^2} = \pm \frac{d\lambda}{2\Delta} . \tag{A4}$$

Integration with the condition $\omega(0) = 0$ yields

$$\omega_1^\pm(\lambda) = \pm \Delta \tan \tfrac{1}{2}\lambda , \tag{A5}$$

where both signs must be retained to make $\omega_1(\lambda)$ symmetric about $\lambda = 0$ and $\omega_1 = 0$. This result is equivalent to

$$\omega_\lambda^\pm = \omega \pm \Delta \tan \tfrac{1}{2}\lambda . \tag{A6}$$

For the Gaussian frequency distribution, given by Eq. (4.7), a similar procedure yields

$$\mathrm{erf}(\omega_1/\Delta) = \pm \lambda/\pi , \tag{A7}$$

which is not readily inverted.

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[10] For the free molecule the linear exciton–vibration coupling constant in electronic state α for mode Q_i is given by[26] $g_{i\alpha} = \langle \psi_\alpha | (\partial H/\partial Q_i) | \psi_\alpha \rangle_0$, where the zero implies that the integral is evaluated at the ground state equilibrium position. The state ψ_α transforms as an irreducible representation of the molecular symmetry group, as does Q_i; thus, $g_{i\alpha} = 0$ if

Q_i is non-totally symmetric and ψ_α is nondegenerate. (If ψ_α is degenerate, then $g_{i\alpha} \neq 0$ by the Jahn–Teller theorem.) When the molecule is put into the crystal only a few of the molecular symmetry elements still remain; all intramolecular modes which are still non-totally symmetric in the new symmetry group of the molecule in the crystal field (C_i in anthracene, for example) still have zero *site diagonal* linear coupling. Those modes which are non-totally symmetric in the free molecule but are symmetric in the crystal site group, will, in general, have nonzero site diagonal coupling; however, since the geometry of the molecule generally is only slightly perturbed by the crystal field, we expect these coupling constants to be very small. In addition, the lowest excited states of most aromatic hydrocarbons are nondegenerate, so that Jahn–Teller effects are not present.

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$$\gamma_0 = \mathrm{Re}\int_0^\infty d\tau\ \langle V_{mm}(\tau) V_{mm}\rangle\ ,$$

where V_{mm} is the phonon operator which is the coefficient of the term $a_m^+ a_m$ in V. For linear coupling [see Eq. (2.1)]

$$\gamma_0^L = N^{-2} \sum_{k,\lambda} |G_\lambda|^2 [\bar{n}_\lambda \delta(\epsilon_k - \epsilon_{k-\lambda} + \omega_\lambda) + (\bar{n}_\lambda + 1)\delta(\epsilon_k - \epsilon_{k+\lambda} - \omega_\lambda)].$$

For an exciton bandwidth much smaller than the phonon energy conservation of energy is impossible in a one phonon process, so $\gamma_0^L = 0$.

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