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Remarks on Exciton—Phonon Coupling and Exciton Transport

R. W. Munn [a] & R. Silbey [b]

[a] Department of Chemistry, U.M.I.S.T., Manchester, M60 1QD, U.K.

[b] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., 02739, U.S.A.

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Remarks on Exciton–Phonon Coupling and Exciton Transport

R. W. MUNN
Department of Chemistry, U.M.I.S.T., Manchester, M60 1QD, U.K.

and

R. SILBEY
Department of Chemistry
Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A.

A general theory of exciton (and electron) transport in perfect molecular crystals is discussed. The emphasis is on qualitative results and the elucidation of the effect of exciton and phonon bandwidth on the scattering of excitons and on transport. Various microscopic models are discussed in this light.

1. INTRODUCTION

Theories of exciton and charge-carrier transport in molecular crystals are numerous—so numerous that it is hard to appreciate the relationships between the different theories.[1-12] In part, this variety and complexity is essential to molecular crystals. Transport is governed by a large number of parameters: the electronic exchange integrals between different molecules; the electron-phonon coupling strength for different mechanisms and different types of phonons; the frequencies and bandwidths for the phonons; and the temperature. Some of these parameters may be markedly anisotropic and no one of them is necessarily much bigger or smaller than the others. As a result, there is a whole range of different regimes defined by different orderings of the parameters. These regimes correspond not only to different mechanisms of transport, such as hopping or band motion, but also to different physical processes determining these mechanisms.

The available transport theories have usually been constructed specifically for one or two regimes. They have often started from a particular physical picture of transport, such as whether or not localized states are important, using methods and approximations appropriate to that picture (but not always explicitly stated). Direct comparison of such *ad hoc* theories is clearly difficult. However, it is possible to compare the various theories as special cases of a more general theory.

In this paper, we present a general theory of electronic transport in perfect molecular crystals. Inevitably, such a general theory cannot be evaluated exactly: we cannot derive a single algebraic expression for the diffusion coefficient from which the results for all regimes follow on simplification (and even if we could, such an expression would be horrendously complicated). Instead, we show how different regimes permit or require different ways of evaluating the quantities in the general theory. This puts the regimes in a clear relationship to one another. Our treatment thus provides a new and helpful perspective in which to view transport theories.

The theory we describe is necessarily mathematical, but we concentrate on results rather than derivations and on broad principles rather than matters of detail. The different regimes appear initially as mathematical consequences of inequalities among the parameters. We then show how the regimes may be interpreted physically. Some of the results are already available in the literature, but others are presented here for the first time (in particular, for the regime with strong exciton-phonon coupling and wide exciton bands).

The following section introduces the general theory we use. We then examine in detail the various transport regimes obtained for linear exciton-phonon coupling as the exciton bandwidth is increased from being smaller than the phonon bandwidth to being larger than the phonon frequency. Finally, we discuss quadratic exciton-phonon coupling briefly, with particular reference to the problems caused by bound exciton-phonon states. The effects of such states on vibronic spectra were recognized some years ago by Broude and Rashba.[13,14,15]

2. DIFFUSION COEFFICIENT

The results we shall present in this section are sufficiently general to encompass both exciton diffusion and charge-carrier drift mobility. For definiteness, we shall treat diffusion and refer to the diffusing particle as an exciton. The drift mobility μ is obtained from the diffusion coefficient D via the Einstein equation

$$\mu = e\beta D, \tag{1}$$

where e is the proton charge and $\beta = 1/kT$. Hence, μ has all the qualitative features of D except for a temperature dependence modified by the factor β.

The exciton diffusion coefficient describes the rate of relaxation of a nonequilibrium distribution of excitons towards the uniform equilibrium distribution. It can be written as

$$D = \lim_{t \to \infty} \frac{\langle R^2(t) \rangle}{2td} = \frac{1}{2d} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} \langle R^2(t) \rangle \tag{2}$$

where d is the dimensionality of the system (here taken as isotropic for simplicity), and $\langle R^2(t) \rangle$ is the mean-square displacement of an exciton at time t from its position at time zero. Other ways of defining D, for example by the Kubo formalism, are equivalent to Eq. (2). Assuming for simplicity but without loss of generality that the exciton was the origin of coordinates at time zero, we can write the mean-square displacement as

$$\langle R^2(t) \rangle = \sum_n R_n^2 P_n(t) \tag{3}$$

where R_n is the distance of site n from the origin and $P_n(t)$ is the probability of finding the exciton at site n at time t. Calculating D thus depends on calculating the $P_n(t)$, which is a problem of nonequilibrium statistical mechanics.

Before we consider technical aspects of the calculation, we should remark that transport is diffusive only if there is some mechanism for scattering an exciton from one state to another. In the absence of such a mechanism, the exciton moves as a perfect wave through the crystal; this is sometimes called "coherent" transport, but as this term has been used for other types of transport, we shall avoid using it here. In this limit, the mean-square displacement never becomes proportional to time, and no diffusion coefficient can be defined. When there is some mechanism for scattering, repeated scattering events cause the exciton distribution to lose memory of its initial state and to attain equilibrium in a diffusive way. Scattering occurs most commonly from phonons and from impurities or other crystal imperfections. In this paper we shall consider only scattering arising from the exciton-phonon coupling.

Two limiting cases of transport are often distinguished. In *band transport*, the exciton states are labelled by a wavevector **k**, and phonons scatter the exciton from one **k** state to another. The transport is then governed by the scattering times of the **k** states. In *hopping transport*, the exciton is almost localized in states labelled by a site index n, and phonons scatter these states. These two limits and the transition between them have been studied for a number of years, and a great deal is known about them. Calculations of transport may be performed in terms of wavevector or site states, irrespective of which limit applies. Unfortunately, neither choice is ideal: the wavevector states are most suitable for taking account of translational symmetry in a crystal, but the site states are most suitable for calculating D from Eq. (3).

In the general case, a single equation can reproduce the various transport limits. Such generality is obtained at the cost of deriving the density matrix of the system and the equations governing its time behaviour, which are difficult (but not impossibly so). The equilibrium density operator $\hat{\rho}$ of a system is $e^{-\beta H}$, where H is the Hamiltonian operator. When the system is not at equilibrium, $\hat{\rho}$ is a function of time. It contains all the information about that system, and so has a rather complicated structure. Its form cannot be found explicitly for anything but a model system, but equations for the diffusion coefficient can be obtained in terms of matrix elements of the density operator. The application of these equations for a simple model Hamiltonian is described in section 3.

The diagonal matrix elements of the density operator in any choice of basis states give the probabilities that these states are occupied. For the diffusion coefficient, we require the $P_n(t)$, which are diagonal elements of the *exciton* density matrix σ in the site representation. These follow from the density matrix of the coupled exciton-phonon system integrated over all phonon variables:

$$P_n(t) = \sigma_{nn}(t) = [\mathrm{Tr}_L \hat{\rho}(t)]_{nn} \tag{4}$$

where Tr_L is a trace over phonon (lattice) states. The density matrix $\hat{\rho}(t)$ for the coupled system obeys the Liouville equation

$$\dot{\hat{\rho}}(t) = -i[\mathrm{H},\hat{\rho}(t)] \equiv -i\hat{\mathscr{L}}\hat{\rho}(t) \tag{5}$$

where $\hat{\mathscr{L}}$ is the Liouville operator and the superposed dot denotes a time derivative.

Using mathematical procedures derived from irreversible statistical mechanics, one can derive an *exact* equation for $\hat{\sigma}(t)$, or rather its matrix elements in the wavevector representation. The equation assumes only that the exciton and phonon variables were uncoupled at time zero, i.e. that the initial phonon density matrix was thermal. The result is

$$\dot{\sigma}_{\mathbf{kk'}}(t) = -i(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k'}})\sigma_{\mathbf{kk'}}(t) - \int_0^t \mathrm{d}\tau \sum_{\mathbf{q}} K_{\mathbf{kk'};\mathbf{qs}}(t-\tau)\sigma_{\mathbf{qs}}(\tau) \tag{6}$$

where $\varepsilon_{\mathbf{k}}$ is the energy of the exciton state $\mathbf{k}$; because of conservation of wavevector $\mathbf{s} = \mathbf{k'} - \mathbf{k} + \mathbf{q}$. Because this equation is exact, the formula for the kernel K is impossible to evaluate except in the most exceptional (and least interesting) cases, and so need not be given here.

However, in a approximation equivalent to second-order time-dependent perturbation theory in the exciton-phonon coupling $\hat{V}$, Eq. (6) becomes

$$\dot{\sigma}_{\mathbf{kk'}}(t) = -i[E_{\mathbf{k}} - E_{\mathbf{k'}}]\sigma_{\mathbf{kk'}}(t) - \Gamma_{\mathbf{kk'}}\sigma_{\mathbf{kk'}}(t) + \sum_{\mathbf{q}} W_{\mathbf{kk'};\mathbf{qs}}\sigma_{\mathbf{qs}}(\tau) \tag{7}$$

Here, the energies $E_{\mathbf{k}}$ differ from the $\varepsilon_{\mathbf{k}}$ by terms up to second order in the coupling. Because the results are restricted to second order, it is necessary that the coupling $\hat{V}$ should be small, and this may require the Hamiltonian to be transformed in a suitable way (see section 3). Equation (7) is also restricted to a limit where initial transient behaviour has been removed, so that it may not be applicable at short times. For the diffusion coefficient it is the long-time behaviour which is required, and Eq. (7) does give this thermal behaviour correctly.

The quantities $W_{\mathbf{kk}';\mathbf{qs}}$ are given by

$$W_{\mathbf{kk}';\mathbf{qs}} = \int_0^\infty d\tau\{\langle V_{\mathbf{sk}'}V_{\mathbf{kq}}(\tau)\rangle U_{\mathbf{sk}'}(\tau) + \langle V_{\mathbf{sk}'}(\tau)V_{\mathbf{kq}}\rangle U_{\mathbf{kq}}(\tau)\} \tag{8}$$

where the angle brackets denote an average over phonon states and

$$U_{\mathbf{kq}}(\tau) = \exp\{i(E_{\mathbf{k}} - E_{\mathbf{q}})\tau\} \tag{9}$$

The remaining quantities in Eq. (7) are the $\Gamma_{\mathbf{kk}'}$, which satisfy

$$\Gamma_{\mathbf{kk}'} = \tfrac{1}{2}(\Gamma_{\mathbf{kk}} + \Gamma_{\mathbf{k}'\mathbf{k}'}) \tag{10}$$

The nature of the diagonal elements $\Gamma_{\mathbf{kk}}$ can be seen from Eq. (7), which reduces to

$$\dot{\sigma}_{\mathbf{kk}}(t) = -\Gamma_{\mathbf{kk}}\sigma_{\mathbf{kk}}(t) + \sum_{\mathbf{q}} W_{\mathbf{kk};\mathbf{qq}}\sigma_{\mathbf{qq}}(t) \tag{11}$$

This contains only the probabilities of finding the exciton in the states **k**, and is therefore a *master equation.* Equation (11) shows that $\Gamma_{\mathbf{kk}}$ represents the rate of scattering out of exciton state **k**, i.e. the inverse lifetime of the state, while $W_{\mathbf{kk};\mathbf{qq}}$ represents the rate of scattering from exciton state **q** into exciton state **k**. From these considerations, or by summing Eq. (11) over **k**, it follows that

$$\Gamma_{\mathbf{kk}} = \sum_{\mathbf{q}} W_{\mathbf{qq};\mathbf{kk}} \tag{12}$$

The form (8) for W guarantees that

$$W_{\mathbf{qq};\mathbf{kk}} = W_{\mathbf{kk};\mathbf{qq}}e^{-\beta(E_{\mathbf{q}}-E_{\mathbf{k}})}, \tag{13}$$

irrespective of $\hat{V}$, as required by the principle of detailed balance. This ensures that

$$\sigma_{\mathbf{kk}}(\infty) \equiv \sigma_{\mathbf{kk}}^{eq} = \frac{e^{-\beta E_{\mathbf{k}}}}{(\sum_{\mathbf{q}} e^{-\beta E_{\mathbf{q}}})} \tag{14}$$

with off-diagonal elements zero, as expected from the Boltzmann distribution.

Equation (1) shows that the rate at which off-diagonal elements $\sigma_{\mathbf{kk}'}(t)$ decay is related to the decay rates of the occupation probabilities of the individual states **k** and **k**′. This simple result, and the simple form of Eq. (11), where the coefficients Γ and W are independent of time, are valid only in the **k** representation because only in that representation is the equilibrium exciton density matrix diagonal. If one chooses to work in the site representation, Eq. (14) shows that the $\sigma_{nm}(\infty)$ are complicated functions which are in general nonzero for $n \neq m$. Transformation of Eq. (7) to this representation shows that the time derivatives of the diagonal elements σ_{nn} are in general coupled to the off-diagonal elements σ_{nm}, so that a master equation like Eq. (11) cannot be written. However, provided the density matrix $\hat{\rho}$ was diagonal at time zero (for example, with a single exciton at the origin), the off-diagonal elements at time t can be related to the diagonal elements at all previous times. This leads to a *generalized master equation* (GME) of the form[8]

$$\dot{\sigma}_{nn}(t) = \int_0^t \mathrm{d}\tau \sum_m G_{nm}(t - \tau)\sigma_{mm}(\tau) \tag{15}$$

where the kernels G are complicated oscillatory functions. An equation of this form can also describe initial transient behaviour in either representation.

The kernels G in the GME can be viewed as describing the memory of the exciton for its past states. The kernels must clearly decay for diffusive transport to arise, but it has recently been pointed out[16] that a decaying memory is not sufficient. Calculations based on an approximate treatment of a simple hamiltonian[17] show that the mean-square displacement does not eventually become proportional to time. This conclusion also follows from exact treatments of the same model,[6a,18] including a recent treatment giving the exact memory function.[19]

In fact, diffusion cannot ensue because the model studied lacks any dissipative mechanism such as exciton-phonon coupling. The memory function describes the time development of the initially prepared localized nonstationary state towards the delocalized eigenstates of the hamiltonian. The complexity of the memory function and the difficulty of deriving it result from writing the GME in a localized basis when the exact eigenstates are delocalized. What is required for the memory function to produce diffusion can be seen in general terms from Eq. (15). For diffusion the rate of change of the mean square displacement must become constant, whereas for wave-like motion it must diverge as t.[4a,6a] This implies that the memory function must decay faster to yield diffusion than to yield wave-like transport. This faster decay is produced by the dissipative mechanism, as can be seen in other recent work:[20] the electron-phonon coupling introduces extra exponential decays into the memory function.

The diffusion coefficient given by Eqs. (2) and (3) can be written as

$$D = \frac{1}{2d} \lim_{t \to \infty} \sum_n R_n^2 \dot{\sigma}_{nn}. \tag{16}$$

To evaluate D we need either to substitute the complicated expression (15) in this equation, or else to transform to the wavevector representation, with the result[6c]

$$D = \frac{1}{2d}\lim_{t\to\infty}\sum_{\mathbf{k}}\nabla_{\mathbf{K}}^2\dot{\sigma}_{\mathbf{k},\mathbf{k}+\mathbf{K}}(t)|_{\mathbf{K}=0} \tag{17}$$

In the latter case, insertion of Eq. (7) for $\sigma_{\mathbf{kK}'}(t)$ in the limit $t \to \infty$ gives an equation which can be somewhat simplified by neglect of small terms. The result is still rather complicated, and so for present purposes we shall use an approximate formula which gives a good qualitative description of the behaviour of D in various limits.[6c] We take

$$D = \sum_{\mathbf{k}}\sigma_{\mathbf{kk}}^{eq}\left\{\frac{v_{\mathbf{k}}^2}{\Gamma_{\mathbf{kk}}} + \gamma_{\mathbf{kk}}\right\} \tag{18}$$

where $v_{\mathbf{k}} = \nabla_{\mathbf{k}}E_{\mathbf{k}}$ is the exciton velocity in state **k** and the form of $\gamma_{\mathbf{kk}}$ will be described in Section 4.

The first term in Eq. (18) looks like a band theory result (recall that $1/\Gamma_{\mathbf{kk}}$ is the exciton scattering time in state **k**). It can thus be related to the phenomenological theories of exciton diffusion, which often use scattering times or scattering lengths to calculate mean free paths and diffusion coefficients. The second term in Eq. (18), on the other hand, looks like a hopping result. We shall see that these terms can indeed be interpreted in this way. For large $\Gamma_{\mathbf{kk}'}$, small $v_{\mathbf{k}}$, or both, the second term dominates, whereas for large $v_{\mathbf{k}}$ (wide exciton bands) the first term dominates. In general, though, both terms contribute and the transport cannot be described as either pure hopping or pure band motion.

3. CALCULATION OF $\Gamma_{\mathbf{kk}}$

In order to use the results of the last section, we must discuss the form of $\Gamma_{\mathbf{kk}}$ in various limits and approximations. To do this systematically, we will compute $\Gamma_{\mathbf{kk}}$ for a general $\hat{V}$, then apply the formulas to simple linear, simple quadratic coupling and then to transformed linear coupling (i.e. exponential phonon coupling).

In the case of a general exciton-phonon coupling term,

$$\hat{V} = \frac{1}{\sqrt{N}}\sum_{\mathbf{k},\mathbf{q}} a_{\mathbf{k}+\mathbf{q}}^{+}a_{\mathbf{k}}V_{\mathbf{kq}} \tag{19}$$

where $V_{\mathbf{kq}}$ is a phonon operator of unspecified form. Then

$$\Gamma_{\mathbf{kk}} = \frac{1}{N}\sum_{\mathbf{q}}\operatorname{Re}\int_0^\infty d\tau e^{i(E_{\mathbf{k}}-E_{\mathbf{q}})\tau}\langle V_{\mathbf{kq}}V_{\mathbf{qk}}(\tau)\rangle. \tag{20}$$

Let us assume that the phonon correlation function decays on a time scale α^{-1} where α will be proportional to the phonon bandwidth. To avoid mathematical complications, we will assume that this decay is gaussian in time. That is, we take

$$\langle V_{\mathbf{kq}} V_{\mathbf{qk}}(\tau) \rangle = \lambda^2 e^{-\alpha^2 \tau^2/4} \tag{21}$$

and we assume that the exciton band has a Gaussian density of states:

$$N_{\text{exc}}(E) = \frac{1}{\sqrt{\pi} B} e^{-E^2/B^2} \tag{22}$$

where B is the bandwidth. Then we find

$$\Gamma_{\mathbf{kk}} = \frac{\lambda^2}{[B^2 + \alpha^2]^{1/2}} e^{-E_k^2/B^2[1+\alpha^2/B^2]} \tag{23}$$

Thus the scattering rate of an exciton is largest in the center of the band and decreases towards the top and the bottom. This is merely a consequence of there being more processes allowable in the center in this simple picture (where temperature and phonon populations have been neglected). The most important result for our purposes is that Γ_{kk} is inversely proportional to $[B^2 + \alpha^2]^{1/2}$ where α is (proportional to) the phonon bandwidth. This shows that in the limit of a narrow phonon band $\Gamma_{kk} \sim B^{-1}$, while in the limit of a narrow exciton band $\Gamma_{\mathbf{kk}} \sim 1/\alpha$. This corresponds to the slow phonon and slow exciton limits, respectively.[4]

We now go on to study specific microscopic forms of V.

(a) *linear coupling*: for simple linear coupling

$$V_{\mathbf{kq}} = g(\mathbf{q}, \mathbf{k}) \omega_{\mathbf{q}} (b_{\mathbf{q}} + b^{+}_{-\mathbf{q}}) \tag{24}$$

where $\omega_{\mathbf{q}}$ is the phonon frequency of wavevector $\mathbf{q}$ and $g(\mathbf{q}, \mathbf{k})$ is the dimensionless coupling constant for scattering an exciton from state $\mathbf{k}$ to state $\mathbf{k} + \mathbf{q}$ while destroying a phonon of wavevector $\mathbf{q}$ or creating a phonon of wavevector $-\mathbf{q}$. Using this form in Eq. (8), we find

$$\begin{aligned} W_{\mathbf{qq};\mathbf{kk}} = \frac{1}{N} g^2(\mathbf{k} - \mathbf{q}, \mathbf{k}) \omega_{k-q}^2 \{ (\bar{n}_{\mathbf{k}-\mathbf{q}} + 1) \delta(E_{\mathbf{q}} - E_{\mathbf{k}} + \omega_{\mathbf{k}-\mathbf{q}}) \\ + \bar{n}_{\mathbf{k}-\mathbf{q}} \delta(E_{\mathbf{q}} - E_{\mathbf{k}} - \omega_{\mathbf{k}-\mathbf{q}}) \} \end{aligned} \tag{25}$$

and

$$\begin{aligned} \Gamma_{\mathbf{kk}} = \frac{1}{N} \sum_{\mathbf{q}} \omega_{\mathbf{q}}^2 g^2(\mathbf{q}, \mathbf{k}) \{ (\bar{n}_{\mathbf{q}} + 1) \delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} + \omega_{\mathbf{q}}) \\ + n_{\mathbf{q}} \delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} - \omega_{\mathbf{q}}) \} \end{aligned} \tag{26}$$

where $\bar{n}_{\mathbf{q}}$ is the Planck distribution function, $\bar{n}_{\mathbf{q}} = (e^{\beta\omega_{\mathbf{q}}} - 1)^{-1}$. So $\Gamma_{\mathbf{kk}} = 0$ unless the exciton bandwidth is larger than some phonon frequency.

Consider a narrow optical phonon band of width Δ about a frequency ω_0. We will assume $g^2(\mathbf{q}, \mathbf{k}) = g_{\mathrm{eff}}^2$, $\omega_{\mathbf{q}}^2 \simeq \omega_0^2$, $\bar{n}_{\mathbf{q}} = \bar{n}$, and in order for $\Gamma_{\mathbf{kk}}$ to be nonzero, $B > \omega_0$ ($\gg \Delta$), where B is the exciton bandwidth. Then

$$\Gamma_{\mathbf{kk}}^{\mathrm{opt}} = g_{\mathrm{eff}}^2 \omega_0^2[(\bar{n} + 1)N_{\mathrm{exc}}(E_{\mathbf{k}} - \omega_0) + \bar{n}N_{\mathrm{exc}}(E_{\mathbf{k}} + \omega_0)] \qquad (27)$$

where $N_{\mathrm{exc}}(E)$ is the exciton density of states function (centered at $E = 0$) and $E_{\mathbf{k}}$ is the exciton energy. Since $N(E) \sim B^{-1}$, we see that $\Gamma_{\mathbf{kk}} \sim g_{\mathrm{eff}}^2\omega_0^2/B$.

Now consider a Deybe-like acoustic phonon band (Debye frequency ω_D). In this case

$$g^2(\mathbf{q}, \mathbf{k})\Gamma_{\mathbf{q}}^2 \simeq A_{\mathbf{k}}\omega_{\mathbf{q}} \qquad (23)$$

(we are assuming a deformation potential type of coupling). Then

$$\Gamma_{\mathbf{kk}}^{\mathrm{acou}} = \frac{1}{N}\sum_{\mathbf{q}} A_{\mathbf{k}}\omega_{\mathbf{q}}\{(\bar{n}_{\mathbf{q}} + 1)\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} + \omega_{\mathbf{q}}) + \bar{n}_{\mathbf{q}}\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} - \omega_{\mathbf{q}})\} \qquad (29)$$

By defining a joint density of states

$$\rho_{\mathbf{k}}(E, \omega) = \frac{1}{N}\sum_{\mathbf{q}} \delta(\omega - \omega_{\mathbf{q}})\delta(E - E_{\mathbf{k}-\mathbf{q}}) \qquad (30)$$

which satisfies

$$\frac{1}{N}\sum_{\mathbf{k}} \rho_{\mathbf{k}}(E, \omega) = \frac{1}{N}\sum_{\mathbf{q}} \delta(\omega - \omega_{\mathbf{q}})\frac{1}{N}\sum_{\mathbf{k}} \delta(E - E_{\mathbf{k}-\mathbf{q}}) = N_{\mathrm{phon}}(\omega)N_{\mathrm{exc}}(E) \qquad (31)$$

where $N_{\mathrm{phon}}(\omega)$ is the phonon density of states, we find

$$\Gamma_{\mathbf{kk}} = \int \mathrm{d}E \int \mathrm{d}\omega A_{\mathbf{k}}\omega\rho_{\mathbf{k}}(E, \omega)\{(\bar{n}_\omega + 1)\delta(E - E_{\mathbf{k}} + \omega) + \bar{n}_\omega\delta(E - E_{\mathbf{k}} - \omega)\} \qquad (32)$$

If $B \gg \omega_D$, $\rho_{\mathbf{k}}(E, \omega) \sim 1/B$ and so $\Gamma_{\mathbf{kk}} \sim B^{-1}$. If $B \ll \omega_D$, $\rho_{\mathbf{k}}(E, \omega) \sim \omega_D^{-1}$, then $\Gamma_{\mathbf{kk}} \sim \omega_D^{-1}$.

(b) *quadratic coupling*: for simple quadratic coupling

$$V_{\mathbf{kq}} = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}'} \eta(\mathbf{k}', \mathbf{q} - \mathbf{k}')\{(b_{\mathbf{k}'} + b_{-\mathbf{k}'}^{+})(b_{\mathbf{q}-\mathbf{k}'} + b_{-\mathbf{q}+\mathbf{k}'}^{+}) - \delta_{0\mathbf{q}}(2\bar{n}_{\mathbf{k}'} + 1)\} \qquad (33)$$

where $\eta(\mathbf{k}, \mathbf{q} - \mathbf{k})$ is the coupling energy for scattering an exciton from state $\mathbf{k}$ to state $\mathbf{q}$ with the creation or annihilation of two phonons, or the creation of one and annihilation of a second phonon. We find

$$\begin{aligned}\Gamma_{\mathbf{kk}} = \frac{2}{N^2}\sum_{\mathbf{k}',\mathbf{q}} \eta^2(\mathbf{k}', \mathbf{q} - \mathbf{k}')\{&\bar{n}_{\mathbf{k}'}\bar{n}_{\mathbf{q}-\mathbf{k}'}\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} - \omega_{\mathbf{k}'} - \omega_{\mathbf{q}-\mathbf{k}'})\\ &+ \bar{n}_{\mathbf{k}'}(n_{\mathbf{q}-\mathbf{k}'} + 1)\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} - \omega_{\mathbf{k}'} + \omega_{\mathbf{q}-\mathbf{k}'})\\ &+ (\bar{n}_{\mathbf{k}'} + 1)\bar{n}_{\mathbf{q}-\mathbf{k}'}\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} + \omega_{\mathbf{k}'} - \omega_{\mathbf{q}-\mathbf{k}'})\\ &+ (\bar{n}_{\mathbf{k}'} + 1)(\bar{n}_{\mathbf{q}-\mathbf{k}'} + 1)\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} + \omega_{\mathbf{k}'} + \omega_{\mathbf{q}-\mathbf{k}'})\}\end{aligned} \tag{34}$$

For a narrow optical phonon band of width Δ and central frequency ω_0, assuming $B < \omega_0$ so the first and fourth terms do not contribute, we find

$$\begin{aligned}\Gamma_{\mathbf{kk}} \cong \frac{2\eta^2}{N^2}\bar{n}(\bar{n} + 1)\sum_{\mathbf{k}',\mathbf{q}} \{&\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} + \omega_{\mathbf{k}'} - \omega_{\mathbf{q}-\mathbf{k}'})\\ &+ \delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} - \omega_{\mathbf{k}'} + \omega_{\mathbf{q}-\mathbf{k}'})\}\end{aligned} \tag{35}$$

If $B \gg \Delta$

$$\Gamma_{\mathbf{kk}} \simeq 2\eta^2\bar{n}(\bar{n} + 1)\{N_{\text{exc}}(E_{\mathbf{k}} - \Delta) + N_{\text{exc}}(E_{\mathbf{k}} + \Delta)\} \sim B^{-1} \tag{36}$$

If $B \ll \Delta$, then we take $E_{\mathbf{q}} - E_{\mathbf{k}} \approx B$, so

$$\begin{aligned}\Gamma_{\mathbf{kk}} &\approx 2\eta^2\bar{n}(\bar{n} + 1)\frac{1}{N}\sum_{\mathbf{k}'}\{N_{\text{phon}}(\omega_{\mathbf{k}'} + B) + N_{\text{phon}}(\omega_{\mathbf{k}'} - B)\}\\ &\approx \frac{4\eta^2\bar{n}(\bar{n} + 1)}{\Delta}\end{aligned} \tag{37}$$

For an acoustic phonon band, we assume

$$\eta^2(\mathbf{k}', \mathbf{q} - \mathbf{k}') = \bar{\eta}^2\omega_{\mathbf{k}'}\omega_{\mathbf{q}-\mathbf{k}'} \tag{38}$$

where $\bar{\eta}$ is dimensionless. Then, assuming the largest contribution comes from the second and third terms in Eq. (25),

$$\Gamma_{\mathbf{kk}} = \frac{4\bar{\eta}^2}{N^2}\sum_{\mathbf{k}',\mathbf{q}} \omega_{\mathbf{k}'}\omega_{\mathbf{q}-\mathbf{k}'}\bar{n}_{\mathbf{q}-\mathbf{k}'}(\bar{n}_{\mathbf{k}'} + 1)\delta(E_{\mathbf{k}-\mathbf{q}} - E_{\mathbf{k}} + \omega_{\mathbf{k}'} - \omega_{\mathbf{q}-\mathbf{k}'}) \tag{39}$$

If $B \ll \omega_D$, $\Gamma_{\mathbf{kk}}$ is independent of $\mathbf{k}$ and for a Debye spectrum, $\Gamma_{\mathbf{kk}} \sim T^7$.

(c) *transformed linear coupling*: In the case that the standard unitary transformation of polaron theory is applied to linear coupling[6]

$$V_{\mathbf{kk}'} = \left\{\sum_{nm} J_{n-m}e^{i\mathbf{k}\cdot\mathbf{R}_m}e^{-i\mathbf{k}'\cdot\mathbf{R}_m}(\theta_n^+\theta_m - \langle\theta_n^+\theta_m\rangle)\right\} \tag{40}$$

where

$$\theta_m = \exp -\left\{\sum_{\mathbf{q}} N^{-1/2}e^{i\mathbf{q}\cdot\mathbf{R}_m}g(\mathbf{q})(b_{\mathbf{q}} - b_{-\mathbf{q}}^+)\right\} \tag{41}$$

and

$$\langle \theta_n^+ \theta_m \rangle = \exp - \left\{ N^{-1} \sum_{\mathbf{q}} g^2(\mathbf{q})(1 - \cos \mathbf{q} \cdot \mathbf{R}_{nm})(2\bar{n}_{\mathbf{q}} + 1) \right\} \tag{42}$$

For this form of V, Yarkony and Silbey[6c] have evaluated $\Gamma_{\mathbf{kk}}$ in the standard approximations.

4. CALCULATION OF $\gamma_{\mathbf{kk}}$

The other part of D in Eq. (18) is $\gamma_{\mathbf{kk}}$ which is given by

$$\gamma_{\mathbf{kk}} = \left[-\mathrm{Re} \sum_{\mathbf{q}} \frac{\mathrm{d}^2 W_{\mathbf{q},\mathbf{q}+\mathbf{K};\,\mathbf{k},\mathbf{k}+\mathbf{K}}}{\mathrm{d}K^2} \right]_{\mathbf{K}=0} + \frac{\mathrm{d}^2 \Gamma_{\mathbf{kk}}}{\mathrm{d}\mathbf{k}^2} \tag{43}$$

This is extremely difficult to evaluate in any of the models discussed above. However, $\gamma_{\mathbf{kk}}$ can be calculated in the Haken–Strobl model,[1] which has been used in many applications to molecular crystals. In this model the exciton phonon coupling has two parts, the site diagonal (or local) terms V_{nn} and the off diagonal terms V_{nm} which satisfy

$$\langle V_{nn} V_{n'n'}(\tau) \rangle = \delta_{nn'} 2\gamma_0 \delta(\tau)$$

$$\langle V_{nm} V_{n'm'}(\tau) \rangle = [\delta_{nn'} \delta_{mm'} + \delta_{nm'} \delta_{n'm}(1 - \delta_{nn'})] \times 2\gamma_{n-n'} \delta(\tau) \tag{44}$$

Then, it can be shown that (considering only $\gamma_{n-n'}$ for $|n - n'| = 0, 1$), in one dimension

$$W_{\mathbf{k},\mathbf{k}+\mathbf{K};\mathbf{q},\mathbf{q}+\mathbf{K}} = \frac{2\gamma_0}{N} + \frac{4\gamma_1}{N} [\cos \mathbf{K} + \cos(\mathbf{q} + \mathbf{k} + \mathbf{K})] \tag{45}$$

and

$$\Gamma_{\mathbf{kk}} = 2\gamma_0 + 4\gamma_1. \tag{46}$$

Thus, we find the hopping term to be

$$\gamma_{\mathbf{kk}} = +4\gamma_1. \tag{47}$$

A possible microscopic realization of V_{nm} with the above properties is site diagonal quadratic coupling for V_{mn} and phonon assisted hopping for $V_{nn'}$.

The Haken–Strobl model is appropriate only for small exciton bandwidth B relative to the phonon bandwidth Δ (or α) and in the limit λ^2 large [in Eq. (21)].[10] In this case γ_1 is proportional to $1/\Delta$.

5. STRONG QUADRATIC PHONON COUPLING

In the case that there is strong local quadratic phonon coupling, for example,[6d,13]

$$\hat{V} = \sum_n a_n^+ a_n g\omega(b_n + b_n^+)^2 \tag{48}$$

there may be a strong effect on the diffusion constant and spectral function. For weak coupling, Munn and Silbey[6d] treated this problem; however, if g is large enough, the phonon in the excited electronic state has a significantly different frequency from the ground state. This can give rise to bound exciton-phonon states, an effect first discussed by Rashba[13] and Broude.[14,15] This effect is easily understood qualitatively; however, not many quantitative calculations are available.

The bound exciton-phonon state occurs if the change in phonon frequency upon electronic excitation, $\delta\omega$, is greater than the width of the zero phonon exciton band. There is then one bound state per wavevector **k** and $N - 1$ scattering states per wavevector **k**, in the one phonon space.

If bound states occur, then the usual way of computing $\Gamma_{\mathbf{kk}}$ or $W_{\mathbf{kk};\mathbf{qq}}$ given in the above sections breaks down, because the exciton and phonon time dependences are not separable *even in zeroth order*. This means that the correlation functions will have a time dependence consisting, even in the best of cases, of two parts, one like that calculated above and one due to the bound states. The relative contribution of these will be temperature dependent; however, quantitative calculations have not yet been carried out.

6. DISCUSSION

Within the scope of this paper, we have had to be rather selective. We have indicated in Section 2 a general approach to the calculation of the diffusion coefficient from any microscopic model, but have then concentrated on specific aspects of this calculation. The main results are for the exciton scattering rates $\Gamma_{\mathbf{kk}}$, which are easy to visualize physically and prove relatively straightforward to calculate. As the general result in Section 3 shows, the scattering rate may be inversely proportional either to the phonon bandwidth (possibly modified by some temperature-dependent and other factors) or to the exciton bandwidth, whichever is the larger. Our treatment avoids the divergence which occurs in more restrictive theories as either parameter tends to zero. This is not merely a mathematical tidying-up, since even for triplet excitons and molecular phonons the exciton bandwidth may be the larger (and for charge carriers the electronic bandwidth is certainly the larger), though few theories have faced this possibility.

The detailed results in Section 3 illustrate the various limits, showing how the general approach is able to encompass the many different transport regimes. We have concentrated on the dependence of $\Gamma_{\mathbf{kk}}$ on the exciton and phonon bandwidths, but the appropriate temperature dependences can also be deduced from the expressions given. Once transformed exciton-phonon couplings are needed, the effective coupling parameters become temperature dependent and the temperature dependence of $\Gamma_{\mathbf{kk}}$ becomes more complicated. This is true *a fortiori* of the temperature dependence of the diffusion coefficient or mobility, which is important in characterizing the transport but cannot of itself indicate the mechanism.[21]

Some limitations of our treatment are indicated in Sections 4 and 5. The term $\gamma_{\mathbf{kk}}$ in the diffusion coefficient is found to be like $\Gamma_{\mathbf{kk}}$ without local scattering in simple models, but the general result for $\gamma_{\mathbf{kk}}$ is less transparent or tractable. The Haken–Strobl model has proved invaluable in evaluating exact results from transport theories, however, and we are able to use it to illustrate the calculation of $\gamma_{\mathbf{kk}}$. Bound exciton-phonon states present a more fundamental problem which the present treatment is not constructed to solve. Their effect on spectra has been treated on several occasions, but producing a transport theory which accounts properly for the tendency of excitons and phonons to remain close to one another is a more difficult task. Nevertheless, it appears that to solve the problem of bound states some general treatment akin to that presented here will be necessary.

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