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General theory of electronic transport in molecular crystals. I. Local linear electron–phonon coupling

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An improved general theory of electronic transport in molecular crystals with local linear electron–phonon coupling is presented. It is valid for arbitrary electronic and phonon bandwidths and for arbitrary electron–phonon coupling strength, yielding small-polaron theory for narrow electronic bands and strong coupling, and semiconductor theory for wide electronic bands and weak coupling. Detailed results are derived for electronic excitations fully clothed with phonons and having a bandwidth no larger than the phonon frequency; the electronic and phonon densities of states are taken as Gaussian for simplicity. The dependence of the diffusion coefficient on temperature and on the other parameters is analyzed thoroughly. The calculated behavior provides a rational interpretation of observed trends in the magnitude and temperature dependence of charge-carrier drift mobilities in molecular crystals.

I. INTRODUCTION

Electronic transport in molecular crystals is a complicated phenomenon for two reasons. The first is the complexity of the vibrations. In all molecular crystals the phonons include molecular modes and translational and vibrational lattice modes, each with its characteristic frequency and bandwidth. The various modes also have different mechanisms of electron-phonon coupling, again with different strengths. The second reason why transport is complicated is the absence of any clear ordering of the different parameters. The electronic bandwidths may range from being larger than most phonon frequencies and bandwidths (for charge carriers) to being smaller than either (for triplet excitons). The electron–phonon coupling energy may be large or small compared with electronic and vibrational energies, and if large may cause the electronic bandwidth to narrow rapidly with increasing temperature, so changing the parameter ordering.

Early transport theories were restricted in scope and did not reflect these complications. As well as treating only a single phonon band, for simplicity, the theories would assume a particular parameter ordering and a transport mechanism. More recent work has adopted less restricted approaches.[1–11] Transport has been described by the mean-square particle displacement as a function of time, so permitting study of the clothing of the particle by phonons and the development of diffusive motion. These approaches also reveal the change from hopping to band motion as the temperature is lowered in systems with strong electron–phonon coupling.

However, the available theories have still been restricted to selected parameter orderings. In particular, it has been assumed in theories of exciton transport that the exciton bandwidth is narrower than the phonon bandwidth, and this assumption has been carried over to theories of carrier transport. In fact, carrier bandwidths may well be much larger than phonon bandwidths at low temperatures, becoming smaller than phonon bandwidths as the temperature is raised, owing to polaron band narrowing effects. There is therefore a need for a theory which can treat both wide and narrow electronic bands in molecular crystals with either strong or weak electron–phonon coupling. We have already discussed how such a theory may be developed,[12] and here we describe the theory in detail.

In Sec. II we describe the model Hamiltonian used here and summarize our method. In Sec. III we show how the method gives the diffusion coefficient in the simple case of weak electron–phonon coupling. Then in Sec. IV we apply the method for strong local linear electron–phonon coupling treated by the usual canonical transformation. We derive a general expression for the diffusion coefficient and show the form it takes in various limiting cases of temperature and bandwidths. We also show in Sec. V that the simple weak-coupling results are included in our general result. Finally, in Sec. VI we discuss our results and future work.

II. PRINCIPLES

We start from the following model Hamiltonian, in which we take $\hbar = 1$:

$$H = \sum_{n} \epsilon a_n^{+} a_n + \sum_{n,m} J_{nm} a_n^{+} a_m + \sum_{q} \omega_q (b_q^{+} b_q + \tfrac{1}{2}) + N^{-1/2} \sum_{nq} g_q^n \omega_q (b_{-q}^{+} + b_q) a_n^{+} a_n \,. \qquad (2.1)$$

Here the operators a_n^{+} and a_n create and destroy an electronic excitation (exciton or charge carrier) of energy ϵ at site n, while the operators b_q^{+} and b_q create and destroy a phonon of frequency ω_q and wave vector **q**. The quantity $J_{nm} = J_{mn}$ is the transfer integral between sites n and m. The last term is the electron–phonon coupling term, of magnitude determined by the dimensionless parameters $g_q^n = g_q e^{i\mathbf{q}\cdot\mathbf{R}_n}$, where $\mathbf{R}_n$ is the position vector of site n. The coupling is local (diagonal) in excitation site. Such a coupling can arise from molecular distortion in the excited or ionized state, in which case g_q and ω_q are expected to be almost independent of **q**, or from vibrational fluctuations in the exciton site

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shift or charge carrier polarization energy, in which case g_q and ω_q may vary more markedly with q.

If the electron phonon coupling is weak ($|g_q| \ll 1$ for all $\mathbf{q}$), the Hamiltonian may be used directly to study transport, as in Sec. III. If the coupling is strong, the Hamiltonian is transformed to yield a weaker coupling, as in Sec. IV. In either case, the Hamiltonian is written

$$H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + N^{-1/2} \sum_{\mathbf{k},\mathbf{q}} V_{\mathbf{kq}} a_{\mathbf{k}}^{+} a_{\mathbf{q}} , \tag{2.2}$$

where H_{ex} and H_{ph} are operators diagonal in excitation wave vector k and phonon wave vector q, and $V_{\mathbf{kq}}$ is a function of phonon operators.

Transport is studied in terms of the mean-square displacement of an excitation created at the origin at time zero. At long times, the rate of change of this quantity gives the diffusion coefficient; we shall not consider the transport before it becomes diffusive. The mean-square displacement is obtained from the excitation density matrix, which is the full density matrix of the coupled system integrated over all phonon states. Exact formal expressions for this quantity can be obtained, but more tractable expressions follow if only terms up to second order in the V_{kq} are retained. After further neglect of small quantities, the diffusion coefficient can be expressed as[12]

$$D = \langle\langle v_k^2 \Gamma_{kk}^{-1} + \gamma_{kk} \rangle\rangle, \tag{2.3}$$

where the double angle brackets denote a thermal average over excitation states of energy E_k, and $\mathbf{v}_k$ is the velocity $\nabla_k E_k$. The Γ_{kk} are the rates of scattering out of state $\mathbf{k}$, so that the first term in Eq. (2.3) has the usual form for band transport, and the γ_{kk} have the form of hopping rates.

Both Γ_{kk} and γ_{kk} are obtained from quantities[12]

$$W_{kk';qs} = \int_0^\infty d\tau \{ \langle V_{sk'} V_{kq}(\tau) \rangle \exp[i(E_s - E_{k'})\tau] + \langle V_{sk'}(\tau) V_{kq} \rangle \exp[-i(E_k - E_q)\tau] \} ; \tag{2.4}$$

the single angle brackets denote an average over phonon states, $V_{kq}(\tau) = e^{iH_{\mathrm{ph}}\tau} V_{kq} e^{-iH_{\mathrm{ph}}\tau}$, and $\mathbf{s} = \mathbf{k}' - \mathbf{k} + \mathbf{q}$. The scattering rates are given by

$$\Gamma_{kk} = N^{-1} \sum_q W_{qq;kk} , \tag{2.5}$$

and the hopping rates are given by

$$\gamma_{kk} = \left(\frac{1}{2} \frac{d^2}{dk^2} - \frac{d^2}{dK^2} \right) \mathrm{Re}\, N^{-1} \sum_q W_{q,q+K;k,k+K} \Big|_{K=0} \tag{2.6}$$

(or various equivalent forms[6,12]). Derivation of the diffusion coefficient thus requires evaluation of the correlation functions $\langle V_{sk'} V_{kq}(\tau) \rangle$, of the integrals in Eq. (2.4), of the sums in Eqs. (2.5) and (2.6), and of the thermal average in Eq. (2.3).

III. UNTRANSFORMED COUPLING

A. General results

If the electron–phonon coupling is sufficiently weak, the last term in Eq. (2.1) can be treated as a perturbation. Then in Eq. (2.2) the operator V_{kq} is given by

$$V_{kq} = g_{k-q} \omega_{k-q} (b_{k-q} + b_{-k+q}^{+}) . \tag{3.1}$$

The required correlation functions are of the form

$$\langle V_{k+K,q+K} V_{qk}(\tau) \rangle = |g_{k-q}|^2 \omega_{k-q}^2 \times [(n_{k-q}+1) e^{-i\omega_{k-q}\tau} + n_{k-q} e^{i\omega_{k-q}\tau}] , \tag{3.2}$$

where we have used the results $g_{-q} = g_q^*$ and $\omega_{-q} = \omega_q$. In Eq. (3.2) n_{k-q} is the thermal equilibrium number of phonons in mode $k-q$, given by

$$n_{k-q} = n(\omega_{k-q}) = (e^{\beta\omega_{k-q}} - 1)^{-1} , \tag{3.3}$$

where $\beta = 1/k_B T$, with k_B the Boltzmann constant. Substitution of Eq. (3.2) in Eq. (2.4) yields integrals leading to δ functions:

$$W_{q,q+K;k,k+K} = \pi |g_{k-q}|^2 \omega_{k-q}^2 \times \{ (n_{k-q}+1)[\delta(E_{k+K} - E_{q+K} - \omega_{k-q}) + \delta(E_k - E_q - \omega_{k-q})] + n_{k-q}[\delta(E_{k+K} - E_{q+K} + \omega_{k-q}) + \delta(E_k - E_q + \omega_{k-q})] \} . \tag{3.4}$$

The scattering rates are then obtained as

$$\Gamma_{kk} = 2\pi N^{-1} \sum_q |g_q|^2 \omega_q^2 [(n_q+1)\delta(E_{k-q} - E_k + \omega_q) + n_q \delta(E_{k-q} - E_k - \omega_q)] . \tag{3.5}$$

At this level of approximation, there is no scattering unless the excitation bandwidth B is wider than some phonon energy so that single-phonon processes are energetically feasible. The hopping rates are obtained by substituting Eq. (3.4) in Eq. (2.6) and changing the summation variable to $\mathbf{k} - \mathbf{q}$:

$$\gamma_{kk} = \left(\frac{1}{2} \frac{d^2}{dk^2} - \frac{d^2}{dK^2} \right) \pi N^{-1} \sum_q |g_q|^2 \omega_q^2 \times \{ (n_q+1)[\delta(E_{k+K} - E_{k-q+K} - \omega_q) + \delta(E_k - E_{k-q} - \omega_q)] + n_q[\delta(E_{k+K} - E_{k-q+K} + \omega_q) + \delta(E_k - E_{k-q} + \omega_q)] \}_{K=0} . \tag{3.6}$$

In the limit K = 0, both terms in a given square bracket have the same derivative with respect to k, which equals the derivative of the first term with respect to K. Hence γ_{kk} is zero; with weak electron–phonon coupling there is no hopping, as expected, and the diffusion coefficient is given by the standard band expression involving the scattering rates Γ_{kk}.

B. Optical phonons

For a narrow optical phonon band we can set $g_q = g$, $\omega_q = \omega$, and $n_q = n$ for all q. The scattering rates are then

$$\Gamma_{kk}^{\mathrm{op}} = 2\pi g^2 \omega^2 [(n+1) N_{\mathrm{ex}}(E_k - \omega) + n N_{\mathrm{ex}}(E_k + \omega)] , \tag{3.7}$$

where $N_{\mathrm{ex}}(E)$ is the excitation density of states. In general the resulting diffusion coefficient is difficult to obtain except by numerical means. However, for wide parabolic excitation bands such that $B \gg \omega$, we can set

$$\Gamma_{kk}^{\mathrm{op}} \approx 2\pi g^2 \omega^2 (2n+1) N_{\mathrm{ex}}(E_k) , \tag{3.8}$$

$$v_k^2 = 2E_k / m^* \tag{3.9}$$

where m^* is the effective mass. Conventional procedures[13] then lead to

$$D/a^2=\frac{[2\pi k_BT/(m^*)^5]^{1/2}}{g^2\omega^2(2n+1)}\ , \qquad (3.10)$$

where a is the intermolecular distance. Since $m^*\sim 1/B$, then $D\sim B^{5/2}/\omega^2$. The mobility $\mu=e\beta D$ varies as $T^{-1/2}$ at low temperatures such that $k_BT\ll\omega$, changing eventually to $T^{-3/2}$ when $k_B\gg\omega$.

C. Acoustic phonons

We assume that acoustic phonons can be adequately described by a Debye spectrum, cutoff frequency ω_D, and that the electron–phonon coupling is given by the deformation potential approximation

$$g_q=(A/\omega_q)^{1/2}\ . \qquad (3.11)$$

The scattering rate is then

$$\Gamma^{\rm ac}_{kk}=2\pi AN^{-1}\sum_q\omega_q[(n_q+1)\delta(E_{k-q}-E_k+\omega_q)+n_q\delta(E_{k-q}-E_k-\omega_q)]\ . \qquad (3.12)$$

Further formal results can be obtained by defining the joint density of states at total wave vector k by

$$\rho_k(E,\omega)=N^{-1}\sum_q\delta(\omega-\omega_q)\delta(E-E_{k-q})\ , \qquad (3.13)$$

which satisfies

$$N^{-1}\sum_k\rho_k(E,\omega)=N_{\rm ph}(\omega)N_{\rm ex}(E)\ , \qquad (3.14)$$

where $N_{\rm ph}(\omega)$ is the phonon density of states. Using Eq. (3.13) in Eq. (3.12) we obtain

$$\Gamma^{\rm ac}_{kk}=2\pi A\int dE\int d\omega\,\rho_k(E,\omega)\omega\times\{[n(\omega)+1]\delta(E-E_k+\omega)+n(\omega)\delta(E-E_k-\omega)\}\ . \qquad (3.15)$$

In some limits, results can be obtained more directly. In the conventional semiconductor limit $B\gg k_BT\gg\omega_D$, we have $n_q\approx k_BT/\omega_q\gg1$, and $|E_{k-q}-E_k|\gg|\omega_q|$ except for a few sets of wave vectors. These results yield

$$\Gamma^{\rm ac}_{kk}=4\pi Ak_BTN_{\rm ex}(E_k)\ , \qquad (3.16)$$

$$D/a^2=[\pi/k_BT(m^*)^5]^{1/2}/A\ , \qquad (3.17)$$

so that $D\sim B^{5/2}/A\sim B^{3/2}$ if we assume A is proportional to B. Equation (3.17) gives the standard $T^{-3/2}$ temperature dependence for the mobility.[13]

In molecular crystals one may also require the limit $k_BT\gg\omega_D\gg B$. Then in Eq. (3.12) nonzero contributions arise only for frequencies $\omega_q\le B$. Taking on average $|E_{k-q}-E_k|\approx\frac{1}{2}B$ yields for all k,

$$\Gamma^{\rm ac}\approx 4\pi Ak_BTN_{\rm ph}(\tfrac{1}{2}B)\ , \qquad (3.18)$$

where for a Debye spectrum $N_{\rm ph}(\omega)=3\omega^2/\omega_D^3$. Taking similarly $\langle v_k^2\rangle\approx(\frac{1}{2}Ba)^2$, we obtain

$$D/a^2=\omega_D^3/12\pi Ak_BT\ , \qquad (3.19)$$

so that $D\sim\omega_D^3/A\sim\omega_D^3/B$ (with the previous assumption $A\propto B$) and the mobility varies as T^{-2}. The narrow excitation band in this limit greatly reduces the number of allowed one-phonon scattering processes, so that the diffusion coefficient may be large, as the ratio ω_D/B indicates.

Finally, in the limit $k_BT\gg\omega_D$, the scattering rates are given by Eq. (3.16) but the thermal averages in D have to be taken over a narrow excitation band. We take $v_k^2\sim(\frac{1}{2}Ba)^2$ and $N_{\rm ex}(E_k)\sim 1/B$, obtaining

$$D/a^2=B^3/(16\pi Ak_BT)\ , \qquad (3.20)$$

so that the mobility varies as T^{-2}. This result accords with the narrow excitation band treatments of Glarum[14] and Friedman.[15]

IV. TRANSFORMED COUPLING

A. Transformation

The transformation of the Hamiltonian (2.1) which yields a weak residual excitation–phonon coupling even when the g_q are large has been discussed several times.[4–7,16,17] It produces a uniform shift in the excitation energy levels and a displacement in the equilibrium position of the phonons corresponding to the formation of a polaron. Since the transfer interactions J_{nm} compete with this tendency to form a localized state, the optimum transformation should be determined variationally.[6,17] However, for present purposes we use the full clothing transformation which is exact for $J=0$ and yields the correct untransformed results for large J and weak coupling. The results are qualitatively similar to those which would be obtained with the full variational transformation, but are simplified by the absence of the temperature-dependent variational parameters.

After the transformation, the excitation part of the Hamiltonian (2.2) is

$$H_{\rm ex}=\sum_k\left(\epsilon-N^{-1}\sum_q\omega_q|g_q|^2+\sum_h\tilde{J}_hE^{i\mathbf{k}\cdot\mathbf{R}_h}\right)a_k^+a_k\ , \qquad (4.1)$$

where $\mathbf{R}_h$ is a lattice vector and

$$\tilde{J}_h\equiv J_{n+h,n}\langle\theta^+_{n+h}\theta_n\rangle\ , \qquad (4.2)$$

$$\theta_n\equiv\exp\left[N^{1/2}\sum_q(g_q^n)^*(b_q^+-b_{-q})\right], \qquad (4.3)$$

$$\langle\theta^+_{n+h}\theta_n\rangle=\exp\left[-N^{-1}\sum_q(2n_q+1)|g_q|^2(1-\cos\mathbf{q}\cdot\mathbf{R}_h)\right]. \qquad (4.4)$$

The phonon part is

$$H_{\rm ph}=\sum_q\omega_q(b_q^+b_q+\tfrac{1}{2})\ . \qquad (4.5)$$

The residual coupling is described by the operators

$$V_{kq}=N^{-1/2}\sum_{n,h}J_he^{i\mathbf{k}\cdot\mathbf{R}_h}e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{R}_n}(\theta^+_{n+h}\theta_n-\langle\theta^+_{n+h}\theta_n\rangle)\ . \qquad (4.6)$$

The excitation part and the coupling are temperature dependent through the thermal averages in Eqs. (4.2) and (4.6); this partition of the Hamiltonian ensures the correct thermal equilibrium behavior.

B. Correlation functions

To simplify the treatment of the correlation functions, we assume that the phonons belong to a narrow optical band and ignore any anisotropy. We neglect any terms which are exactly zero for zero phonon bandwidth[4] and retain only terms corresponding to sites h which are nearest neighbors of the origin. Then we obtain

$$\langle V_{k+K,q+K}(\tau)V_{qk}\rangle=\sum_h \tilde{J}_h^2\{[\gamma_1(\tau)-2\gamma_2(\tau)]\,e^{i\mathbf{K}\cdot\mathbf{R}_h}$$
$$+[\gamma_4(\tau)-2\gamma_3(\tau)]\exp[i(\mathbf{k}+\mathbf{q}+\mathbf{K})\cdot\mathbf{R}_h]\}$$
$$+\gamma_2(\tau)(E_qE_{q+K}+E_kE_{k+K})+\gamma_3(\tau)(E_kE_{q+K}+E_{k+K}E_q), \quad (4.7)$$

where E_k is the bracketed quantity in Eq. (4.1) and

$$\gamma_1(\tau)=e^{G(\tau)}-1, \qquad \gamma_2(\tau)=e^{(1/2)G(\tau)}-1\ ,$$
$$\gamma_3(\tau)=e^{-(1/2)G(\tau)}-1, \qquad \gamma_4(\tau)=e^{-G(\tau)}-1\ , \quad (4.8)$$

with

$$G(\tau)=2N^{-1}\sum_q |g_q|^2[n_q e^{i\omega_q\tau}+(n_q+1)\,e^{-i\omega_q\tau}]\ . \quad (4.9)$$

As in Sec. III.B, we take $g_q=g$ and $n_q=n$ for all q, but if we take $\omega_q=\omega$ the correlation functions do not decay to zero as normally required in the limit $\tau\to\infty$. Instead, we put

$$G(\tau)=2g^2A(\tau)[n\,e^{i\omega\tau}+(n+1)\,e^{-i\omega\tau}]\ , \quad (4.10)$$

where $A(\tau)$ is the Fourier transform of the phonon density of states $N_{\rm ph}(\omega)$. Here, $A(\tau)$ decays to zero as $\tau\to\infty$, so making the correlation functions decay to zero. These decays in turn determine the form of the quantities $W_{q,q+K;k,k+K}$ through their effect on the integration in Eq. (2.4).

For the integration it is convenient to rewrite $G(\tau)$ as[4,6]

$$G(\tau)=4g^2[n(n+1)]^{1/2}A(\tau)$$
$$\times\{\exp[i\omega(\tau+\tfrac{1}{2}i\beta)]+\exp[-i\omega(\tau+\tfrac{1}{2}i\beta)]\}\ . \quad (4.11)$$

Then the $\gamma(\tau)$ are simply related to the generating function for the modified Bessel functions, so that for example

$$\gamma_1(\tau)=\sum_{m=-\infty}^{+\infty}\exp[im\omega(\tau+\tfrac{1}{2}i\beta)]\{I_m[yA(\tau)]-\delta_{m0}\}\ , \quad (4.12)$$

where

$$y=4g^2[n(n+1)]^{1/2}\ . \quad (4.13)$$

This form can be used in deriving the results for untransformed coupling from those for transformed coupling (see Sec. V), but in general the factor $A(\tau)$ in the argument of the Bessel functions makes analytical integration difficult. However, since the decay of the $\gamma(\tau)$ is produced by the decay of $A(\tau)$, which is determined by the phonon bandwidth Δ, it should be possible to find some simpler approximate form which gives the decay of $\gamma(\tau)$ in terms of Δ.

For analytical convenience we use the Gaussian form

$$A(\tau)=\exp(-\Delta^2\tau^2/4)\ , \quad (4.14)$$

where $\Delta\ll\omega$, so that the band is narrow. The integration is facilitated by changing the variable to $z=\tau+\frac{1}{2}\beta i$, when $A(\tau)\approx A(z)$ provided $\beta\Delta\ll 1$. This limit, implying uniform excitation across the phonon band, will be assumed throughout the remainder of this paper. We can then write

$$\gamma_1(z)=\exp[y\cos\omega z\exp(-\Delta^2z^2/4)]-1\ . \quad (4.15)$$

This has turning values near $\omega z=l\pi$, and lies below the function

$$\exp[y\exp(-\Delta^2z^2/4)]-1\ . \quad (4.16)$$

Because $\Delta\ll\omega$ and $\beta\Delta\ll 1$, this function shows an almost exponential decay which we write as $\exp(-\Gamma^2\tau^2/4)$. From the half-width at half-maximum we find that to a good approximation we can set

$$\Gamma=\Delta \quad (y\le 1)\ , \quad (4.17)$$
$$\Gamma=\Delta y^{1/2} \quad (y>1)\ . \quad (4.18)$$

Our form for the correlation function is then

$$\gamma_1(z)\approx[\exp(y\cos\omega z)-1]\exp(-\Gamma^2z^2/4)\ , \quad (4.19)$$

with analogous forms for the other $\gamma_i(z)$. These forms can now be expanded,

$$\gamma_1(z)=\exp(-\Gamma^2z^2/4)\sum_{m=-\infty}^{+\infty}e^{im\omega z}[I_m(y)-\delta_{m0}]\ , \quad (4.20)$$

with a more tractable dependence on z [compare to (4.12)].

For large y (strong coupling, high temperature), $I_m(y)\sim e^y/(2\pi y)^{1/2}$, so that $\gamma_1\gg 2\gamma_2$ in Eq. (4.7). In γ_4 and γ_3 the corresponding argument is $-y$, so that the terms in the Bessel series alternate in sign, but again $\gamma_4\gg 2\gamma_3$. We therefore neglect γ_2 and γ_3 as before,[4,6] except in deriving the untransformed limit of the transformed results, which implies small y.

C. Scattering and hopping rates

With the foregoing assumptions, we have

$$W_{q,q+K;k,k+K}=\int_0^\infty d\tau\{\exp[i(E_{q+K}-E_{k+K})\tau]+e^{i(E_q-E_k)\tau}\}\sum_h\tilde{J}_h^2\{\gamma_1(\tau)\,e^{i\mathbf{K}\cdot\mathbf{R}_h}+\gamma_4(\tau)\exp[i(\mathbf{q}+\mathbf{k}+\mathbf{K})\cdot R_h]\}\ , \quad (4.21)$$

which can be written as

$$W_{q,q+K;k,k+K}=\int_0^\infty d\tau\{\exp[i(E_{q+K}-E_{k+K})\tau]+e^{i(E_q-E_k)\tau}\}e^{-\Gamma^2\tau^2/4}\sum_{m=-\infty}^{+\infty}e^{im\omega\tau}\,e^{-(1/2)m\beta\omega}[I_m(y)-\delta_{m0}]$$
$$\times\sum_h\tilde{J}_h^2\{e^{i\mathbf{K}\cdot\mathbf{R}_h}+(-1)^m\exp[i(\mathbf{q}+\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_h\}\ . \quad (4.22)$$

Only the real part of this expression is required, and this depends on the integral

$$\int_0^\infty d\tau\cos a\tau\,e^{-\Gamma^2\tau^2/4}=(\pi^{1/2}/\Gamma)\,e^{-a^2/\Gamma^2} \quad (4.23)$$

so that

$$W_{q,q+K;k,k+K}=(\pi^{1/2}/\Gamma)\sum_{m=-\infty}^{+\infty}e^{-(1/2)m\beta\omega}[I_m(y)-\delta_{m0}]\{\exp[-(E_{q+K}-E_{k+K}+m\omega)^2/\Gamma^2]+\exp[-(E_q-E_k+m\omega)^2/\Gamma^2]\}$$
$$\times\left(\sum_h\tilde{J}_h^2\{e^{i\mathbf{K}\cdot\mathbf{R}_h}+(-1)^m\exp[i(\mathbf{q}+\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_h]\}\right). \qquad (4.24)$$

(The lattice is assume to have inversion symmetry, which makes the last factor real.)

The terms with $m>0$ represent m-phonon absorption processes and those with $m<0$ represent m-phonon emission. For simplicity in what follows we shall assume that the excitation bandwidth $\tilde{B}$ is less than ω, so that only zero-phonon processes make any significant contribution in Eq. (4.24). (Note that this condition depends on the temperature-dependent renormalized bandwidth, which for strong coupling is much less than the bare bandwidth.) Thus we take

$$W_{q,q+K;k,k+K}=\frac{\pi^{1/2}}{\Gamma}[I_0(y)-1]\{\exp[-(E_{q+K}-E_{k+K})^2/\Gamma^2]+\exp[-(E_q-E_k)^2/\Gamma^2]\}\left(\sum_h\tilde{J}_h^2\{e^{i\mathbf{K}\cdot\mathbf{R}_h}+\exp[i(\mathbf{q}+\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_h]\}\right). \qquad (4.25)$$

Both Γ_{kk} and γ_{kk} can be obtained from the sum of this quantity over q. We perform this sum by transforming to an integral over the excitation density of states, again taken for analytical convenience to be Gaussian:

$$N_{ex}(E)=e^{-E^2/\tilde{B}^2}/(\pi^{1/2}\tilde{B})\ . \qquad (4.26)$$

In Eq. (4.25), the term in $\exp[i(\mathbf{q}+\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_h]$ is difficult to deal with, when $W_{q,q+k;k,k+K}$ is summed over $\mathbf{q}$. In order to make it a function of energy, we note that when this term is multiplied by a factor even in $\mathbf{q}$ (such as a function of E_q), then when summed over q,

$$\sum_h J_h^2\exp[i(\mathbf{q}+\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_h]=\sum_h J_h^2\cos\mathbf{q}\cdot\mathbf{R}_h\cos(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_h\simeq\tfrac{1}{2}E_{\mathbf{q}}E_{\mathbf{k}+\mathbf{K}}\ , \qquad (4.27)$$

where the last form is exact for a one-dimension near-neighbor system, and has the correct average in three dimensions. A similar form is easily derived when the factor is even in $q+K$, by changing the summation over q to be over $\mathbf{q}+\mathbf{K}$. Then

$$N^{-1}\sum_q W_{q,q+K;k,k+K}=[I_0(y)-1](1/\Gamma\tilde{B})\int_{-\infty}^{+\infty}e^{-E^2/B^2}\Big[\exp[-(E-E_{k+K})^2/\Gamma^2]\Big(\sum_h\tilde{J}_h^2e^{i\mathbf{K}\cdot\mathbf{R}_h}+EE_k\Big)$$
$$+\exp[-(E-E_k)^2/\Gamma^2]\Big(\sum_h\tilde{J}_h^2e^{i\mathbf{K}\cdot\mathbf{R}_h}+EE_{k+K}\Big)\Big]\ . \qquad (4.28)$$

The required integrals are

$$\int_{-\infty}^{+\infty}\exp[-(p^2x^2\pm2qx)]\,dx=(\pi^{1/2}/p)\,e^{q^2/p^2}\ , \qquad (4.29)$$

$$\int_{-\infty}^{+\infty}x\exp[-(p^2x^2\pm2qx)]\,dx=(q^2/p^2)(\pi^{1/2}/p)\,e^{q^2/p^2}\ , \qquad (4.30)$$

leading to

$$N^{-1}\sum_q W_{q,q+K;k,k+K}=\{[I_0(y)-1]\,\pi^{1/2}(\tilde{B}^2+\Gamma^2)^{-1/2}\}\{\exp[-E_{k+K}^2/(B^2+\Gamma^2)]+\exp[-E_k^2/(B^2+\Gamma^2)]\}$$
$$\times\left[\sum_h J_h^2e^{i\mathbf{K}\cdot\mathbf{R}_h}+E_kE_{k+K}\left(1+\frac{\Gamma^2}{\tilde{B}^2}\right)^{-1}\right]\ . \qquad (4.31)$$

This expression contains no assumptions about the relative magnitudes of Γ and $\tilde{B}$, which enter symmetrically except in the last term, arising from the assumption (4.27).

The scattering rates are obtained by setting $\mathbf{K}=0$. Then

$$\Gamma_{kk}=\{2\pi^{1/2}[I_0(y)-1](\tilde{B}^2+\Gamma^2)^{-1/2}\}\exp[-E_k^2/(\tilde{B}^2+\Gamma^2)]\Big[\sum_h\tilde{J}_h^2+E_k^2(1+\Gamma^2/\tilde{B}^2)^{-1}\Big]\ . \qquad (4.32)$$

The last term moves the maximum scattering rate away from the center of the band (taken to be $E_k=0$), but is negligible when $\Gamma\gg\tilde{B}$ and is never large even when $\Gamma\ll\tilde{B}$ is because of the exponential. We therefore omit this term for algebraic convenience and write

$$\Gamma_{kk}=\frac{2\pi^{1/2}[I_0(y)-1]z\tilde{J}^2}{(\tilde{B}^2+\Gamma^2)^{1/2}}\exp[-E_k^2/(\tilde{B}^2+\Gamma^2)], \qquad (4.33)$$

where z is the number of nearest neighbors of any site and $\tilde{J}$ is an average transfer integral.

In the calculation of the hopping rates, a number of terms cancel, because the Gaussian functions in Eq. (4.31) each have the same k derivative as the first Gaussian has derivative in the limit $\kappa=0$. The first derivative of $e^{i\kappa\cdot\mathbf{R}_h}$ with respect to κ yields an odd function of h, which is zero by symmetry. The remaining terms give

$$\gamma_{kk}=\frac{2\pi^{1/2}[I_0(y)-1]}{(\tilde{B}^2+\Gamma^2)^{1/2}}\exp[-E_k^2/(\tilde{B}^2+\Gamma^2)]$$

$$\times\left(\sum_h \tilde{J}_h^2 R_h^2+\frac{v_k^2}{1+\Gamma^2/B^2}-\frac{2E_k^2 v_k^2}{(\tilde{B}^2+\Gamma^2)(1+\Gamma^2/\tilde{B}^2)}\right) \quad . \tag{4.34}$$

Here the term in $E_k^2 v_k^2$ is never large, by the previous arguments. The term in v_k^2 increases the scattering significantly near the center of the band when $\Gamma \ll \tilde{B}$, but has no important qualitative effect. We therefore omit both terms for simplicitly, and write

$$\gamma_{kk}=\frac{2\pi^{1/2}[I_0(y)-1]\,z\tilde{J}^2 a^2}{(\tilde{B}^2+\Gamma^2)^{1/2}}\exp[-E_k^2/(B^2+\Gamma^2)] \tag{4.35}$$

$$=a^2\Gamma_{kk}\ , \tag{4.36}$$

where a is an average intermolecular distance. The result (4.36) should be qualitatively correct in many models, and offers a useful way of estimating γ_{kk} from Γ_{kk}, which is easier to calculate.

D. Diffusion coefficient

With Eq. (4.36), the diffusion coefficient becomes

$$D=\langle\langle v_k^2/\Gamma_{kk}+a^2\Gamma_{kk}\rangle\rangle\ . \tag{4.37}$$

We evaluate the thermal average over excitation states by integrating over the density of states (4.26), setting

$$v_k^2 \approx \tfrac{1}{4}a^2\tilde{B}^2 e^{-E_k^2/\tilde{B}^2}\ . \tag{4.38}$$

Then

$$D/a^2=Q^{-1}\int_{-\infty}^{+\infty} dE\, e^{-\beta E} e^{-E^2/\tilde{B}^2}$$

$$\times\left(\frac{\tilde{B}^2 e^{-E^2/\tilde{B}^2}}{4\Gamma_0\exp[-E^2/(\tilde{B}^2+\Gamma^2)]}+\Gamma_0\exp[-E^2/(\tilde{B}^2+\Gamma^2)]\right), \tag{4.39}$$

where

$$Q=\int_{-\infty}^{+\infty} dE\, e^{-\beta E} e^{-E^2/\tilde{B}^2}\ , \tag{4.40}$$

$$\Gamma_0=\frac{2\pi^{1/2}[I_0(y)-1]\,z\tilde{J}^2}{(\tilde{B}^2+\Gamma^2)^{1/2}}\ . \tag{4.41}$$

The integrations are evaluated using Eq. (4.29), and after simplification yield

$$D/a^2=\frac{\tilde{B}^2}{4\Gamma_0}\left(\frac{\tilde{B}^2+\Gamma^2}{\tilde{B}^2+2\Gamma^2}\right)^{1/2}\exp[-\beta^2\tilde{B}^2\Gamma^2/4(\tilde{B}^2+2\Gamma^2)]$$

$$+\Gamma_0\left(\frac{\tilde{B}^2+\Gamma^2}{2\tilde{B}^2+\Gamma^2}\right)^{1/2}\exp[-\beta^2\tilde{B}^4/4(2\tilde{B}^2+\Gamma^2)]\ . \tag{4.42}$$

Substituting for Γ_0 from Eq. (4.41) with the assumption $2z\tilde{J}^2 \approx \frac{1}{4}\tilde{B}^2$, and noting also that the first exponent is always less than $\beta^2\Gamma^2/4$ which we have assumed to be much less than unity, we obtain

$$D/a^2=\frac{1}{\pi^{1/2}[I_0(y)-1]}\,\frac{(\tilde{B}^2+\Gamma^2)}{(\tilde{B}^2+2\Gamma^2)^{1/2}}+\tfrac{1}{4}\pi^{1/2}[I_0(y)-1]$$

$$\times\frac{\tilde{B}^2}{(2\tilde{B}^2+\Gamma^2)^{1/2}}\exp[-\tfrac{1}{4}\beta^2\tilde{B}^2/(2\tilde{B}^2+\Gamma^2)]\ . \tag{4.43}$$

Although the derivation of this expression has used a number of simplifying assumptions, there are none about the relative sizes of $\tilde{B}$ and Γ.

The first term in Eq. (4.43) represents the band contribution, which falls with increasing temperature owing to the increase in $I_0(y)$ through n in Eq. (4.13). The corresponding decrease in $\tilde{B}$ via Eqs. (4.2) and (4.4) contributes to the fall in this contribution unless $\Gamma \gg \tilde{B}$. The second term in Eq. (4.43) represents the hopping contribution, which increases with increasing temperature through $I_0(y)$ and the exponential factor. However, once $\tilde{B}$ becomes much less than Γ, the exponential factor becomes constant, and the decrease in $\tilde{B}^2$ outweighs the increase in $I_0(y)$, so that eventually the second term also decreases with increasing temperature. The occurrence of this decrease is discussed in more detail below.

In the limit $\Gamma \gg \tilde{B}$ assumed in most previous work, Eq. (4.43) reduces to

$$D/a^2=\frac{\Gamma}{(2\pi)^{1/2}[I_0(y)-1]}+\frac{\pi^{1/2}[I_0(y)-1]\tilde{B}^2}{4\Gamma}\ . \tag{4.44}$$

This is essentially of the form derived earlier.[4] We note that in Eq. (4.44) Γ, or equivalently Δ, cannot tend to zero (which would make D infinite), because the equation is valid only for $\Gamma \gg \tilde{B}$. On the other hand, $\tilde{B}$ can tend to zero, in which case only the band term remains. As the velocities v_k^2 in Eq. (4.37) tend to zero, so do the scattering rates Γ_{kk}; both factors vary as $\tilde{B}^2$, so that their ratio tends to a constant.

At sufficiently high temperatures, y becomes large, so that $I_0(y)-1$ can be replaced by its asymptotic value $e^y/(2\pi y)^{1/2}$, while $\Gamma=\Delta y^{1/2}$. The hopping term in Eq. (4.44) then dominates, and can be written as

$$D/a^2=\left(\frac{B^2}{8\Delta g^2 2^{1/2}}\right)\sinh\frac{\beta\omega}{2}\exp\left(-2g^2\tanh\frac{\beta\omega}{4}\right)\ . \tag{4.45}$$

This agrees exactly with Gosar's result for a Gaussian density of states,[18] and the temperature dependence is similar to that of Holstein's result[19] except that he obtains the square root of the hyperbolic sine factor. When $\beta\omega \ll 1$, the hyperbolic functions can be replaced by their arguments, leaving the temperature dependence of D as

$$D \sim \tfrac{1}{2}\beta\omega\, e^{-g^2\beta\omega/2}\ . \tag{4.46}$$

For $g^2\beta\omega \ll 1$, the exponential tends to a constant value and D becomes proportional to β, thus decreasing with increasing temperature as noted above. However, for $g^2 \gg 1$ it is possible to have $\beta\omega \ll 1$ so that Eq. (4.46) holds, but $g^2\beta\omega \sim 1$ so that the exponential dominates the temperature dependence. This gives the activated behavior usually regarded as typical of hopping transport but actually appropriate only to very strong excitation-phonon coupling (for example, Holstein's much-reproduced illustration[19] uses $g^2=10$, a value thought appropriate in transition metal oxide systems).

In the opposite limit $B \gg \Gamma$, we obtain the new result

$$D/a^2=\frac{\tilde{B}}{\pi^{1/2}[I_0(y)-1]}+\frac{(\pi/2)^{1/2}}{4}[I_0(y)-1]\tilde{B}\,e^{-\beta^2\tilde{B}^2/8}. \tag{4.47}$$

Here Γ does not occur and so can tend to zero, being already assumed much smaller than B. If then B tends to zero, the diffusion coefficient vanishes, as expected. Vibrational dispersion (nonzero Δ) is therefore not essential to obtain diffusion motion and finite transport coefficients in this limit, but to show this has required a sufficiently general theory. In the language of time-dependent perturbation theory,[20] for $\Gamma \gg \tilde{B}$ the dense manifold of final states is described by $N_{\rm ph}(\omega)$ but for $\tilde{B} \gg \Gamma$ it is described by $N_{\rm ex}(E)$, as in Eqs. (3.18) and (3.16).

At temperatures high enough to make $y > 1$, Γ increases with increasing temperature through the factor $y^{1/2}$ in Eq. (4.18), while B decreases through its dependence on J given by Eq. (4.4). Thus, at some temperature B always falls sufficiently far below Γ to make Eq. (4.44) supersede Eq. (4.47). However, the weaker the coupling g and the wider the excitation band, the more likely this temperature is to exceed the crystal melting temperature.

The behavior of the diffusion coefficient as a function of temperature is illustrated for various values of the parameters in Figs. 1–5. The curves are obtained from the full expression (4.43). All energies are expressed as multiples of the phonon frequency ω, and the diffusion coefficient is expressed as a multiple of ωa^2. For typical values $\omega \approx 100$ cm^{-1} and $a^2 = 50$ Å^2, ωa^2 corresponds to 1.5×10^{-4} cm^2 s^{-1}. The phonon bandwidth Δ is fixed at 0.1ω (say, 10 cm^{-1}). In order to satisfy the condition $\beta\Delta \ll 1$, $1/\beta\omega$ is restricted to values greater than 0.2. To exclude unphysically high temperatures, $1/\beta\omega$ is restricted to values less than 5, corresponding

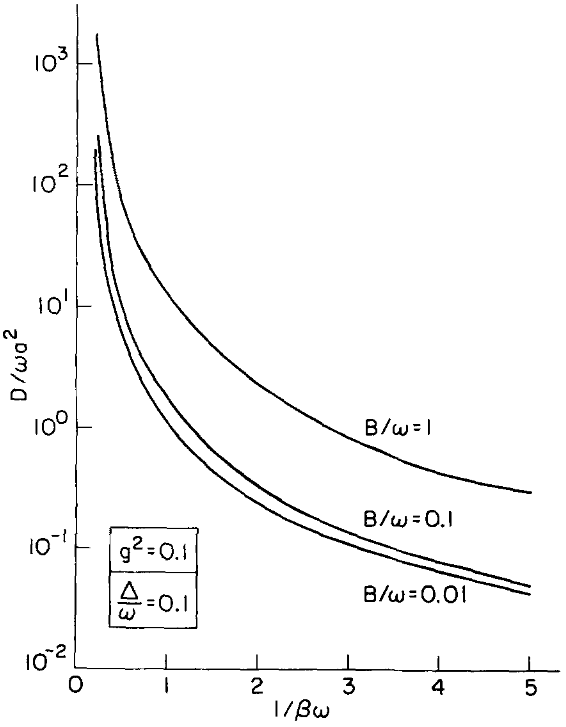

FIG. 1. The reduced diffusion coefficient $D/\omega a^2$ as a function of the reduced temperature $1/\beta\omega$ for different values of the reduced electronic bandwidth B/ω. The electron–phonon coupling strength satisfies $g^2 = 0.1$ (very weak coupling).

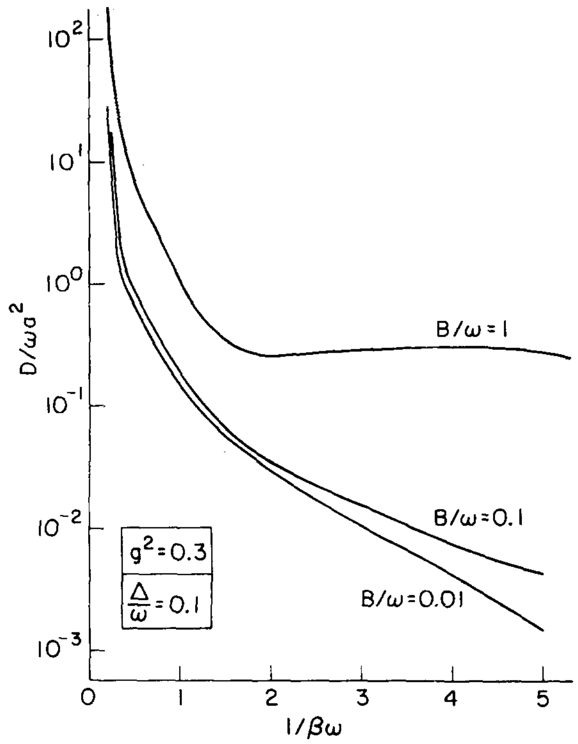

FIG. 2. As Fig. 1, but with $g^2 = 0.3$ (weak coupling).

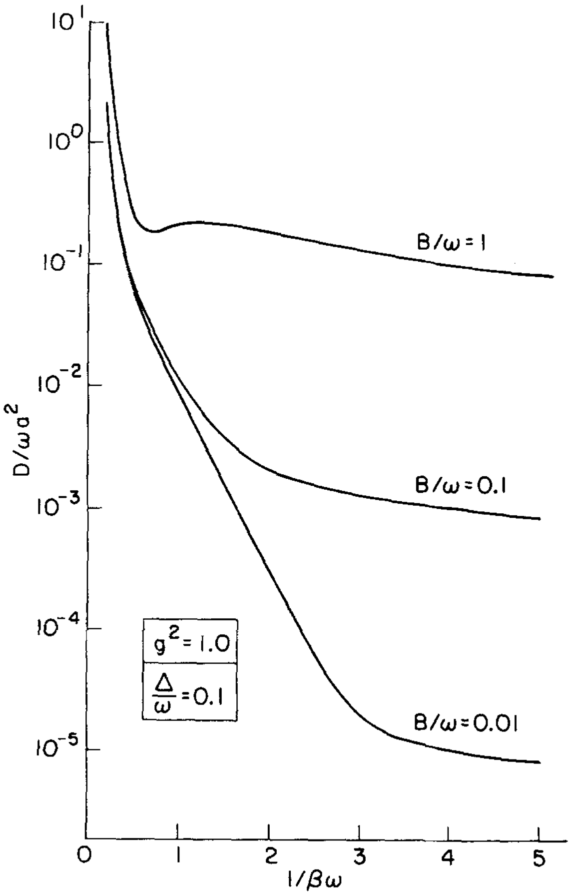

FIG. 3. As Fig. 1, but with $g^2 = 1$ (medium coupling).

to a crystal melting temperature of roughly 750 K for $\omega = 100\ \mathrm{cm}^{-1}$. The drift mobility is obtained as a multiple of ea^2/h by multiplying $D/\omega a^2$ by $\beta\omega$; for the parameter values above, ea^2/h corresponds to $1.2\ \mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$.

The various shapes of curve in Figs. 1–5 result from two effects. The first is that as g^2 increases the band term decreases more rapidly with temperature and the hopping term increases more rapidly, while the second is that as B/ω decreases, the relative importance of the hopping term decreases. For *very weak coupling* ($g^2 = 0.1$; Fig. 1), the hopping term is still increasing steadily at $1/\beta\omega = 5$; for $B/\omega = 1$, the hopping and band terms are then roughly equal, but for the smaller values of B/ω, the band term becomes almost independent of B, as in Eq. (4.44), and the hopping term makes a negligible contribution. For *weak coupling* ($g^2 = 0.3$; Fig. 2), the hopping term increases more rapidly and has started to decrease at $1/\omega\beta = 5$; for $B/\omega = 1$, the hopping term succeeds in producing a weak broad maximum in D, while for the smaller values of B/ω, the reduced importance of the hopping term means that it succeeds only in raising the curve for $B/\omega = 0.1$ farther above that for $B/\omega = 0.01$ than for very weak coupling. For *medium coupling* ($g^2 = 1$; Fig. 3), the hopping term has a sharper and narrower maximum which is reflected in the curve for $B/\omega = 1$; for the smaller values of B/ω, D still decreases monotonically, but the more rapid decrease of the band term means that the hopping term dominates at the highest temperatures. For *strong coupling* ($g^2 = 3$; Fig. 4), these features are accentuated, with the maximum in the hopping term now sharp enough to produce maxima in D for $B/\omega = 1$ and 0.1 and a weak change of curvature for $B/\omega = 0.01$. Finally, for *very strong coupling* ($g^2 = 10$; Fig. 5), there are marked minima in D for all three values of B/ω, with a rapidly increasing D at higher temperatures which is just levelling out at $1/\beta\omega = 5$; as noted above, only in this case is there any sizable region of activated behavior.

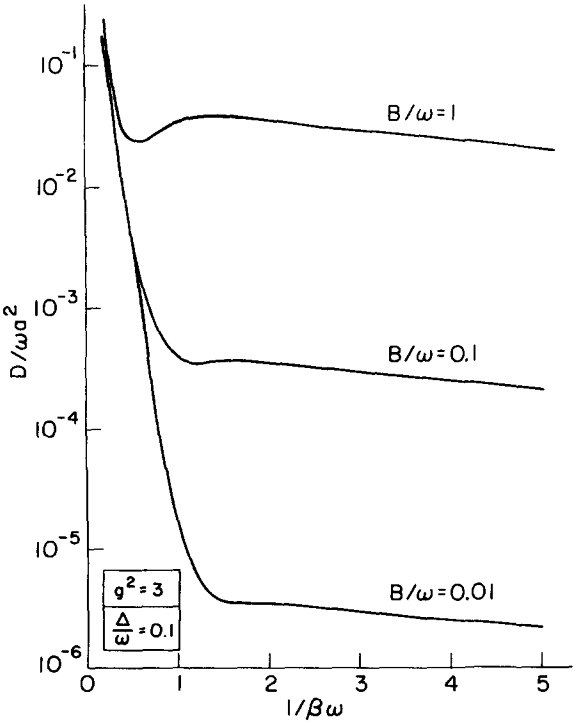

FIG. 4. As Fig. 1, but with $g^2 = 3$ (strong coupling).

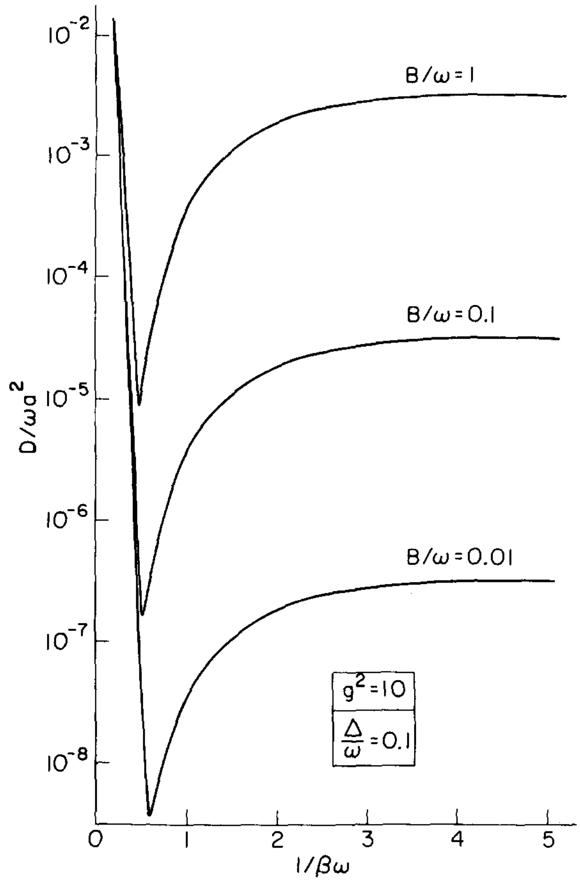

FIG. 5. As Fig. 1, but with $g^2 = 10$ (very strong coupling).

The effect of changing phonon bandwidth Δ, not shown in the figures, can be deduced from Eq. (4.43). Reducing Γ by reducing Δ always reduces the band term; it has opposing effects on the two factors in the hopping term, but always increases their product if $\beta B < 2$. Once $\tilde{B}$ falls well below Γ, the diffusion coefficient is given by Eq. (4.44), and decreasing Δ is clearly seen to increase the relative importance of hopping.

V. RELATION BETWEEN TRANSFORMED AND UNTRANSFORMED COUPLING

A. Principles

In the present treatment, it is necessary to use transformed coupling if the parameter g is large enough and the temperature is high enough, but is is sufficient to use untransformed coupling if g is small enough and the temperature is low enough. One might also hope to recover the results for untransformed coupling from those for transformed coupling in the limit $g \to 0$ and $n \to 0$. However, it is by no means obvious that this hope is realized, since the untransformed coupling is treated with the perturbation (3.1) depending on $g\omega$, whereas the transformed coupling is treated with the perturbation (4.6) depending on J as well as g and ω. This difference stems from the use of the bare and clothed excitation representations in the two cases.

Nevertheless, two different representations may still give the same expressions for an observable such as the diffusion coefficient.

As far as we know, the equivalence of the two treatments when the coupling is weak has not previously been demonstrated. For untransformed coupling, there is no scattering in lowest order unless $B > \omega$ for some of the phonon modes in question when one-phonon processes are possible. For transformed coupling, zero-phonon processes are always possible even when $B \ll \Gamma \ll \omega$, which is the usual assumption. Thus the two treatments have been applied in opposite limits which could not be related. In the present work we have shown how transformed coupling can also be applied to the limit $B \gg \omega \gg \Gamma$, and we are therefore able to demonstrate its equivalence to untransformed coupling for small g and n.

We consider only optical phonons, as in Sec. IV, in the limit $B > \omega$ as required for untransformed coupling. In this limit the diffusion coefficient is independent of Γ or Δ, as shown by Eq. (4.45), so that we can set $\Delta = 0$. Then for untransformed coupling the scattering rates are given by Eq. (3.7). We show that the same scattering rates follow for transformed coupling for small g.

B. Scattering rates

The results for transformed coupling in Sec. IV assume in several places that the coupling is strong and that $B < \omega$. In order to recover the weak-coupling limit, it is necessary to relax these assumptions.

The general expression for the correlation functions is Eq. (4.7), involving the quantities $\gamma_i(\tau)$ which depend on the function $G(\tau)$ through Eq. (4.8). For strong coupling, γ_2 and γ_3 can be neglected compared with γ_1 and γ_4. However, for weak coupling $G(\tau)$ is small in magnitude, and then

$$\gamma_2 = \tfrac{1}{2}\gamma_1 = \tfrac{1}{2}G(\tau) , \tag{5.1}$$

$$\gamma_3 = \tfrac{1}{2}\gamma_4 = -\tfrac{1}{2}G(\tau) . \tag{5.2}$$

Using $\Delta = 0$ so that $A(\tau) = 1$ in Eq. (4.10) for $G(\tau)$, we obtain the correlation functions

$$\langle V_{k+K,q+K}(\tau) V_{qk} \rangle = g^2 [n e^{i\omega\tau} + (n+1) e^{-i\omega\tau}] \times (E_k - E_q)(E_{k+K} - E_{q+K}) . \tag{5.3}$$

To lowest order in g, $\tilde{J}_h = J_h$, by Eq. (4.4), so that the transformed energies E_k in Eq. (5.3) are equal to the untransformed energies.

For the scattering rates, we set $\kappa = 0$ in Eq. (5.3) to obtain

$$\Gamma_{kk} = 2\pi N^{-1} g^2 \sum_q (E_k - E_q)^2 \times [n\delta(E_k - E_q + \omega) + (n+1)\delta(E_k - E_q - \omega)] , \tag{5.4}$$

$$\Gamma_{kk} = 2\pi g^2 \omega^2 N^{-1} \sum_q [n\delta(E_k - E_q + \omega) + (n+1)\delta(E_k - E_q - \omega)]. \tag{5.5}$$

Here the delta functions make the transformed perturbation, giving scattering rates varying like J^2, yield scattering rates varying like ω^2 as for the untransformed perturbation. Finally, Eq. (5.5) gives

$$\Gamma_{kk} = 2\pi g^2 \omega^2 [n N_{ex}(E_k + \omega) + (n+1) N_{ex}(E_k - \omega)] , \tag{5.6}$$

in agreement with Γ_{kk} given for untransformed coupling by Eq. (3.7).

The equivalence of the scattering rates can also be shown from the Bessel function series for $\gamma_1(\tau)$ and its analogues, Eq. (4.12), with $A(\tau) = 1$. For strong coupling and $B < \omega$, only the term $m = 0$ is retained, proportional to $I_0(y) - 1$, but for $B > \omega$ terms for higher m are retained. For weak coupling (small y), $I_0(y) - 1$ varies as $\frac{1}{4} y^2 \sim g^4$, whereas $I_1(y)$ varies as $\frac{1}{2} y \sim g^2$, so that in this limit the term in $I_1(y)$ is dominant, provided always that $B > \omega$. [Note that the transformed coupling also yields the weak coupling limit for $B < \omega$, which in this case is the $I_0(y) - 1$ term; the transformed coupling must be treated to higher order to yield this limit.]

C. Hopping rates

The hopping rates are obtained from Eq. (5.3), which yields an expression resembling Eq. (3.6):

$$\gamma_{kk} = \left(\frac{1}{2}\frac{d^2}{dk^2} - \frac{d^2}{dK^2}\right) \pi g^2 N^{-1} \sum_q (E_k - E_{k-q})(E_{k+K} - E_{q+K}) \{ n [\delta(E_{k+K} - E_{k-q+K} + \omega) + \delta(E_k - E_{k-q} + \omega)] + (n+1) [\delta(E_{k+K} - E_{k-q+K} - \omega) + \delta(E_k - E_{k-q} - \omega)] \}_{K=0} , \tag{5.7}$$

$$\gamma_{kk} = \left(\frac{1}{2}\frac{d^2}{dk^2} - \frac{d^2}{dK^2}\right) \pi g^2 \omega N^{-1} \sum_q \{ (E_k - E_{k-q}) [(n+1)\delta(E_{k+K} - E_{k-q+K} - \omega) - n\delta(E_{k+K} - E_{k-q+K} + \omega)] + (E_{k+K} - E_{k-q+K}) [(n+1)\delta(E_k - E_{k-q} - \omega) - n\delta(E_k - E_{k-q} + \omega)] \}_{K=0} . \tag{5.8}$$

By arguments like those following Eq. (3.6), it follows that terms involving either an energy difference and the second derivative of a delta function or a delta function and the second derivative of an energy difference yield zero net contribution in the limit $K = 0$. The only terms which contribute involve first derivatives of the energy difference with respect to k, but in this limit the energy difference becomes ω, independent of k, so that its derivative is zero, when $K = 0$. Thus the hopping rates are zero, as deduced for untransformed coupling.

In Sec. IV.C we suggested that in many models it might be adequate to set $\gamma_{kk} \approx a^2 \Gamma_{kk}$, as in Eq. (4.36). For weak coupling this is seen to be untrue, since (to order g^2) $\gamma_{kk} = 0$ and $\Gamma_{kk} \sim g^2$. However, even if γ_{kk} were taken as $a^2 \Gamma_{kk}$, this would have negligible effect on the diffusion coefficient because the hopping term would then vary as g^2, a factor g^4 smaller than the band term, which varies as $1/\Gamma_{kk} \sim g^{-2}$.

VI. DISCUSSION

In this paper we have shown how electronic transport in molecular crystals can be treated much more generally than hitherto. The present treatment avoids (i) the assumption that vibrational relaxation is fast compared with excitation transfer ($\Gamma \gg \tilde{B}$, as usually assumed in polaron and exciton transport theories), and (ii) the assumption that the excitation–phonon coupling is weak ($g\omega n \ll B$, as usually assumed in conventional semconductor transport theories). In particular, such a generalization is necessary to treat charge-carrier transport in aromatic hydrocarbon crystals. In these systems, the carrier bandwidths are of the order of 1000 cm^{-1} compared with phonon bandwidths of no more than a few tens of cm^{-1}, but the electron–phonon coupling need not be weak. This feature has also been recognized in recent specialized theories of carrier transport in anthracene and naphthalene,[21] and different regimes of exciton–phonon coupling have been discussed.[22]

However, most of the detailed results in this paper have been derived under simplifying assumptions to permit easier algebraic and numerical analysis. Only local linear excitation–phonon coupling has been treated, and anisotropy has been ignored. The fully clothed transformation given by Eqs. (4.1)–(4.3) has been used rather than the proper variational transformation[6,17] which requires separate numerical evaluation (although this could readily be incorporated once evaluated). The excitation and phonon densities of states in Sec. IV have been taken as Gaussian, and the parameters have been chosen to satisfy $\beta\Delta \ll 1$ and $B/\omega < 1$.

With these restrictions on the validity of the final results in Sec. IV, it is not appropriate to attempt a quantitative fit to the behavior of any specific substance, especially for charge carriers. In any case, information on the parameter values is rather sparse. Adequate phonon dispersion curves and densities of states are fairly readily available or obtainable by calculations, but there are rather few exciton and charge-carrier band structures available, and these are mostly several years old and hence do not incorporate recent advances in quantum chemistry. The different types of electron–phonon coupling have been identified, but there are few attempts to deduce accurate coupling parameters. Exceptions are the use of semiempirical calculations to obtain couplings to molecular vibrations[23] and the analysis of spectra to obtain exciton–phonon couplings.[24,25] However, even though a quantitative fit to experiment is inappropriate, we can indicate how the qualitative features of our results may relate to experimental data. We consider only charge-carrier mobilities, which have been measured as a function of temperature for enough substances to begin to reveal some kind of pattern.

Schein[26] has emphasized the tendency for mobilities in molecular crystals to lie in the range 0.1–10 $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ and to vary with temperature as T^{-n} with typically $0 < n < 2$. Most of the crystals studied are aromatics and heteroaromatics for which relatively wide carrier bands are expected. Figures 1–5 show that although the curves generally give lower mobilities as the electron–phonon coupling strength g increases (compare the labeling of the axes), this trend is least marked for the widest bands with $B/\omega = 1$. Mobilities in the required range are obtained at $1/\beta\omega = 2$ (room temperature if $\omega = 100\ \mathrm{cm}^{-1}$) for $g^2 = 0.1–1$. The curves also show that the diffusion coefficient for $B/\omega = 1$ depends only weakly on temperature for much of the range shown, except for very weak and very strong coupling. Since the mobility contains the extra factor T^{-1}, these dependences imply a variation T^{-n} with n close to 1, noticeably different from the standard narrow-band result T^{-2} but in qualitative agreement with the observed trend.

It has been remarked[27] that the smallest mobilities tend to show an activated behavior, intermediate ones the weak temperature dependence just discussed, and larger ones a more rapid decrease like T^{-n} with $n = 2.5–3$. As noted in Sec. IV, activated behavior requires very strong electron–phonon coupling, but it is not obvious why this might be present in the very low mobility crystals studied, electrons in orthorhombic sulphur[28] and β-nitrogen[29] and holes in γ-oxygen.[29] At the opposite extreme, the hole and electron mobilities in the *ab* plane of durene vary as $T^{-2.5}$, attaining values as high as 50 $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ below 150 K and falling to 5 and 8 $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$, respectively, at room temperature.[30] Durene has the same crystal structure as anthracene, but the peripheral methyl groups might be expected to reduce the carrier bandwidths in the *ab* plane. However, in the present treatment a smaller bandwidth does not necessarily imply a smaller mobility if the electron-phonon coupling is weaker too. Weaker coupling also implies a wider region in which band motion dominates with its rather strong temperature dependence. Thus the behavior of durene could be explained in terms of particularly weak coupling, but any microscopic reason for such weak coupling remains to be found.

The present model is therefore able to interpret the observed rough correlation between the magnitude of carrier mobilities and their temperature dependence consistently as a dependence of both quantities on the electron–phonon coupling strength. This interpretation appears physically reasonable, but the omission of nonlocal coupling from the model should be borne in mind. Such coupling is central to theories[21,31] of the almost temperature-independent electron mobilities in the c' direction of anthracene and naththalene and their deuterated forms and of the rapid increase in the mobility for naphthalene and deuteronaphthalene at low temperatures.[32,33] The present methods can be extended to treat nonlocal coupling and also strong anisotropy, which appears to play a major role in anthracene and naphthalene.[21]

The problem with the theory of electronic transport in molecular crystals has been to deduce the transport, given a model Hamiltonian containing what one considers to be the essential physical interactions. Since several interactions may be comparable in size, simple perturbative methods fail. The method[12] adopted here yields a rather direct solution to the problem. Given the clothing transformation, one has then to evaluate the correlation functions, which can be regarded as the central factors in the transport theory. The transport coefficients are then evaluated by integration and summations which can be performed numerically if necessary. This more automatic approach to transport theory should stimulate the realistic evaluation of the necessary parameters.

ACKNOWLEDGMENTS

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