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Variational approach to exciton transport in molecular crystals^{a)}

David R. Yarkony and Robert Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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The variational results for the free energy of an interacting exciton phonon system are used to derive expressions for the scattering rate and diffusion constant of an exciton in such a system. These expressions are applicable to both wide and narrow band cases, and includes the possibility of an abrupt transition from wide band (free) exciton to narrow band (localized) exciton. Some comments are made on the possibility of observing this transition by thermal modulation spectroscopy.

I. INTRODUCTION

In an earlier paper (to be referred to as Paper I),¹ the free energy of an exciton interacting with phonons (in the approximation of linear exciton-phonon coupling) was considered. Using a unitary transformation containing variational parameters, the free energy of the system was minimized. It was found that the properties of the quasiparticle, consisting of the exciton and its tightly bound phonon cloud, were temperature dependent. In particular, the number of phonons bound to the exciton, n_{ph} , is a function of temperature in a way that depends significantly on the exciton bandwidth and exciton-phonon coupling energy. For sufficiently large bandwidths, n_{ph} changes *abruptly* at some temperature; this abrupt change is due to there being two minima in the free energy functional (for sufficiently large bandwidth). In the present paper, we consider the relationship between these changes in exciton structure and exciton transport. Using the usual projection operator formalism,² the equation of motion of the exciton density matrix is derived. Since we will be concerned with the possibility of an abrupt change in transport properties, this equation must be sufficiently general to apply to both large bandwidth and small bandwidth cases; this means the earlier results³⁻⁵ must be extended, and that the results will apply to small polaron motion as well.⁶⁻⁸

In Sec. II, the molecular crystal Hamiltonian is defined; in Sec. III, the equation of motion for the exciton density is derived; and in Sec. IV discussed in detail in the momentum space representation. In Sec. V, the diffusion coefficient and scattering times for the exciton are discussed in a way which does not involve either a narrow exciton band or a high temperature approximation. The contributions of both bandlike and hopping terms to the diffusion coefficient are considered. In Sec. VI we comment on the connection between the formalisms and ideas presented herein and a theory of the thermal modulation spectroscopy, reserving for a future publication a more complete analysis.

II. THE HAMILTONIAN

We will consider a molecular crystal Hamiltonian with linear exciton-phonon coupling. This model has been examined previously by many authors and, in par-

ticular, has been used by Grover and Silbey³ to discuss exciton transport in the narrow band, fully dressed exciton regime and by Rackovsky and Silbey³ to consider energy transfer between two molecules embedded in a lattice. The Hamiltonian is given in second quantized form as

$$H = H_{ex} + H_{ph} + H_{int}, \quad (2.1)$$

where

$$H_{ph} = \sum_q \omega_q (b_q^\dagger b_q + \frac{1}{2}) \quad (2.2)$$

and (in exciton site space)

$$H_{ex} = \sum_n E_0 a_n^\dagger a_n + \sum_{n,m} J_{nm} a_n^\dagger a_m \quad (2.3)$$

and

$$H_{int} = N^{-1/2} \sum_{n,q} \omega_q C_q^n (b_{-q} + b_q^\dagger) a_n^\dagger a_n. \quad (2.4)$$

Here H_{ex} is the Hamiltonian for a single band of Frenkel excitons in a perfect rigid crystal with E_0 the electronic excitation energy of a single molecule and $J_{n,m}$ being the usual resonance transfer integral between molecules at site n and site m . H_{ph} is the harmonic phonon Hamiltonian with ω_q being the frequency of the normal mode of wave vector q . The operators $a_n (a_n^\dagger)$ destroy (create) a n excitation on site n , while $b_q (b_q^\dagger)$ destroy (create) a phonon of wave vector q . The interaction term represents the linear coupling of an electronic excitation at site n with phonons of wave vector q . Translational symmetry requires that J_{nm} be a function of $\mathbf{R}_n - \mathbf{R}_m$ only and that $C_q^n = C_q e^{i\mathbf{q} \cdot \mathbf{R}_n}$, where $C_q = C_q^*$.

The transformation to the *partially* dressed exciton representation¹ is given by e^{-u} with

$$u = -N^{-1/2} \sum_{n,q} g_q^n (b_{-q} - b_q^\dagger) a_n^\dagger a_n, \quad (2.5)$$

$$g_q^n = g_q \exp(i\mathbf{q} \cdot \mathbf{R}_n).$$

The parameters g_q^n are chosen to minimize the free energy, as in Paper I. In the transformed representation, $\tilde{H} = e^u H e^{-u}$

$$\begin{aligned} &= \sum_n \bar{E} a_n^\dagger a_n + \sum_q (b_q^\dagger b_q + \frac{1}{2}) \omega_q + \sum_{n,m} J(n-m) \theta_n^\dagger \theta_m a_n^\dagger a_m \\ &+ N^{-1/2} \sum_{n,q} \omega_q (C_q^n - g_q^n) (b_q + b_q^\dagger) a_n^\dagger a_n, \end{aligned} \quad (2.6)$$

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where

$$a_n^* \theta_n^* = e^{-u} a_n^* e^{-u} = \exp\left(-N^{1/2} \sum_q g_q^n (b_{-q} - b_q^*)\right) a_n^* \quad (2.7)$$

and

$$\bar{E} = E_0 - N^{-1} \sum_q (2C_q g_q^* - g_{-q} g_q) \quad (2.8)$$

Note that if $J_{nm} \equiv 0$, then setting $g_q^n = C_q^n$ diagonalizes H . The representation in which $g_q^n = C_q^n$ will be referred to as the (fully) dressed exciton representation. This Hamiltonian is now partitioned as

$$\tilde{H} = H^0 + V, \quad (2.9)$$

where

$$H^0 = H_{\text{ex}}^0 + H_{\text{ph}} \quad (2.10)$$

$$H_{\text{ex}}^0 = \sum_n \bar{E} a_n^* a_n + \sum_{n,m}' J_{nm} \langle \theta_n^* \theta_m \rangle_L a_n^* a_m \quad (2.11)$$

and

$$V = \sum_{n,m}' J(n-m) (\theta_n^* \theta_m - \langle \theta_n^* \theta_m \rangle_L) a_n^* a_m + N^{-1/2} \sum_{n,q} f_q^n (b_{-q} + b_q^*) a_n a_n \equiv V_1 + V_2, \quad (2.12)$$

where

$$f_q^n = \omega_q (C_q^n - g_q^n) = f_q e^{i\mathbf{q} \cdot \mathbf{R}_n} \quad (2.13)$$

and

$$\langle \theta_n^* \theta_m \rangle_L = \exp - \left[N^{-1} \sum_q g_q^2 (1 - \cos \mathbf{q} \cdot \mathbf{R}_{nm}) (2\bar{n}_q + 1) \right] \quad (2.14)$$

being the thermal average over a canonical ensemble of phonons of the operator $\theta_n^* \theta_m$. Note that following Paper I we have partitioned H so that $\langle V \rangle_L = 0$. Also observe that from I, f_q^n , H^0 , and V are temperature dependent through the temperature dependence of g_q .

Finally, if the transformation to exciton states of wave vector k is made by defining

$$a_{\mathbf{k}} = N^{-1/2} \sum_n e^{i\mathbf{k} \cdot \mathbf{R}_n} a_n, \quad (2.15)$$

then

$$H_{\text{ex}}^0 = \sum_{\mathbf{k}} (\bar{E} + \hat{J}(k)) a_{\mathbf{k}}^* a_{\mathbf{k}} \equiv \sum_{\mathbf{k}} \epsilon(\mathbf{k}) a_{\mathbf{k}}^* a_{\mathbf{k}}, \quad (2.16)$$

$$V = N^{-1} \sum_{\substack{n,m \\ \mathbf{k}, \mathbf{k}'}} J(n-m) (\theta_n^* \theta_m - \langle \theta_n^* \theta_m \rangle_L) e^{i\mathbf{k} \cdot \mathbf{R}_{nm}} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_m} a_{\mathbf{k}}^* a_{\mathbf{k}'} + N^{-1/2} \sum_{\mathbf{k}, \mathbf{q}} f_{\mathbf{q}} (b_{-\mathbf{q}} + b_{\mathbf{q}}^*) a_{\mathbf{k}}^* a_{\mathbf{k}+\mathbf{q}} \quad (2.17a)$$

$$\equiv V_1 + V_2, \quad (2.17b)$$

and where

$$\hat{J}(\mathbf{k}) = \sum_{\mathbf{h}} e^{i\mathbf{k} \cdot \mathbf{R}_h} \tilde{J}(\mathbf{h}), \quad (2.18)$$

$$\tilde{J}(\mathbf{h}) = \langle \theta_n \theta_m \rangle_L J_{nm} \quad \text{for } \mathbf{R}_n - \mathbf{R}_m = \mathbf{R}_h. \quad (2.19)$$

We will refer to H given by Eqs. (2.9)–(2.11) and 2.12 as the direct space representation and that given by Eqs.

(2.9), (2.10), (2.16), and (2.17) as the momentum space representation.

Note that we can add to Eq. (2.14) or (2.12a) additional terms which represent different exciton–phonon interactions. For example, if a term linear in phonon coordinate, but not site diagonal in exciton space is added to V , such as

$$V^1 = \sum_{n,m} F_{nm}^q \omega_q (b_q + b_{-q}^*) a_n^* a_m \quad (2.20)$$

then after the unitary transformation, this becomes

$$e^u V^1 e^{-u} = \sum_{n,m} F_{nm}^q \omega_q [(b_q + b_{-q}^*) - g_q^n] \theta_n^* \theta_m a_n^* a_m. \quad (2.21)$$

This when averaged can be added to H_{ex}^0 [Eq. (2.11)] to define a new \tilde{J}_{nm} while the fluctuating part can be added to the first term in Eq. (2.12). This increases the labor in what follows, but does not change the qualitative features of the results. We will not consider this type of interaction further, except to say that it is easily handled by the methods of this paper.

Another kind of exciton phonon interaction term which may be important is quadratic in phonon variables:

$$V' = \sum_{n,q,q'} G_{q,q'}^n a_n^* a_n (b_q + b_{-q}^*) (b_{q'} + b_{-q'}^*). \quad (2.22)$$

This introduces qualitatively new features into the problem^{9,10} which will be treated in another paper.⁹ However, if we assume that the phonon band which is most strongly coupled linearly [i. e., in Eq. (2.4)] and that which is most strongly coupled quadratically [Eq. (2.22)] are different, then the unitary transformation does not affect V' . It will then lead to another term in exciton scattering rate⁹ (the “local” term in Haken’s language⁵) which can easily be incorporated into the equation for the diffusion coefficient.

III. THE MICROSCOPIC EXCITON DENSITY

In this section, we determine the equation of motion of the microscopic exciton density defined in the following way. We assume that at time $t=0$, the exciton is in a partially clothed state given by the parameters g_q of the last section and the lattice is in a canonical ensemble at temperature T . The process (excitation plus subsequent vibrational relaxation to the optimal clothed state) by which this is achieved is not considered herein, although the Hamiltonian is general enough to describe it. Certainly, for long times, the species which migrates is expected to be the one described by the g_q . The required exciton density is thus given by the formal solution to the following problem: if at the initial time, $t=0$, a partially clothed exciton is created in state i , $A_i^* |0\rangle \equiv e^u a_i^* e^{-u} |0\rangle$ (for u as defined above), in a thermal bath of phonons, what is the probability $[P_{f,i}(t)]$ that at time t the exciton is in state f regardless of the state of the lattice. Note that we have not specified the nature of the initial state i ; it may be a site state, or a momentum state, or a wave packet. We find that

$$P_{f,i}(t) = \text{Tr}_L \langle 0 | A_f e^{-iHt} A_i^* |0\rangle \rho_L \langle 0 | A_i e^{iHt} A_f^* |0\rangle \quad (3.1a)$$

$$= \text{Tr}_L \langle 0 | a_f e^{-i\tilde{H}t} a_i^* |0\rangle \rho_L \langle 0 | a_i e^{i\tilde{H}t} a_f^* |0\rangle \quad (3.1b)$$

$$= \langle 0 | a_f \text{Tr}_L (e^{-i\tilde{H}t} \rho_i e^{i\tilde{H}t}) a_f^\dagger | 0 \rangle \tag{3.1c}$$

$$= \langle 0 | a_f \text{Tr}_L \rho_i(t) a_f^\dagger | 0 \rangle, \tag{3.1d}$$

where Tr_L denotes the trace over phonon states, $|0\rangle$ is the exciton vacuum state (ground electronic state) and

$$\rho_i(t) = e^{-i\tilde{H}t} \rho_i e^{i\tilde{H}t}, \tag{3.2}$$

$$\rho_i = a_i^\dagger | 0 \rangle \rho_L \langle 0 | a_i, \tag{3.3}$$

$$\rho_L = e^{-\beta H_{ph}} / Q, \tag{3.4}$$

$$Q = \text{Tr}_L e^{-\beta H_{ph}}. \tag{3.5}$$

Thus, $P_{fi}(t)$ has the form of the diagonal matrix element of a time evolved density operator ρ_i which depends on the initial state of the system. Note that $P_{fi}(t)$ is also given by

$$P_{fi}(t) = \langle 0 | a_i \langle e^{i\tilde{H}t} a_f^\dagger a_f e^{-i\tilde{H}t} \rangle_L a_i^\dagger | 0 \rangle. \tag{3.6}$$

The equation of motion for $P_{fi}(t)$ is now obtained from the projection operator formalism. Using this method,³ we find the time derivative of

$$\rho^{(1)}(t) \equiv \rho_L \text{Tr}_L \rho_i(t) \equiv \pi \rho_i(t) \tag{3.7}$$

to be

$$\begin{aligned} \dot{\rho}^{(1)}(t) &= -i\pi \mathcal{L}^0 \rho^{(1)}(t) - \pi \mathcal{L}' \\ &\times \int_0^t d\tau e^{-i(1-\tau)\mathcal{L}\tau} (1-\pi) \mathcal{L} \rho^{(1)}(t-\tau). \end{aligned} \tag{3.8}$$

The Liouville operator $\mathcal{L} = \mathcal{L}^0 + \mathcal{L}'$ is defined by

$$\mathcal{L}A \equiv [H, A] = [H^0, A] + [V, A] \equiv \mathcal{L}^0 A + \mathcal{L}' A. \tag{3.9}$$

Equation (3.8) is exact to all orders in V and corresponding difficult to evaluate. A tractable result can be obtained by taking the second term in Eq. (3.8) to second order in V , then

$$\dot{\rho}^{(1)}(t) = -i\pi \mathcal{L}^0 \rho^{(1)}(t) - \pi \mathcal{L}' \int_0^t e^{-i\mathcal{L}^0\tau} \mathcal{L}' \rho^{(1)}(t-\tau) d\tau. \tag{3.10}$$

Note that in the above equations the fact the excitation is created in state i must be incorporated as an initial condition. It does not affect the form of Eq. (3.8) or (3.10). This observation will prove to be of considerable value later in relating the direct space and momentum space formulations. Taking matrix elements of $\rho^{(1)}(t)$ in exciton (although not necessarily direct or momentum) space gives

$$\begin{aligned} \dot{S}_{p_1 p_2}(t) &= -i \sum_q [(H_{\mathbf{q}\mathbf{x}}^0)_{p_1 \mathbf{q}} S_{\mathbf{q} p_2}(t) - S_{p_1 \mathbf{q}}(t) (H_{\mathbf{q}\mathbf{x}}^0)_{\mathbf{q} p_2}] + \sum_{\mathbf{q}\mathbf{r}\mathbf{s}\mathbf{x}} \int_0^t d\tau \{ [\langle V_{\mathbf{s}\mathbf{x}}(-\tau) V_{p_1 \mathbf{q}} \rangle_L U_{\mathbf{q}\mathbf{r}\mathbf{x} p_2}(\tau) \\ &+ \langle V_{x p_2} V_{\mathbf{q}\mathbf{r}}(-\tau) \rangle_L U_{p_1 \mathbf{q}\mathbf{s}\mathbf{x}}(\tau) S_{\mathbf{r}\mathbf{s}}(t-\tau) - [\langle V_{p_1 \mathbf{q}} V_{\mathbf{r}\mathbf{s}}(-\tau) \rangle_L U_{\mathbf{q}\mathbf{r}\mathbf{x} p_2}(\tau) S_{\mathbf{s}\mathbf{x}}(t-\tau) + \langle V_{\mathbf{r}\mathbf{s}}(-\tau) V_{x p_2} \rangle_L U_{p_1 \mathbf{q}\mathbf{s}\mathbf{x}}(\tau) S_{\mathbf{q}\mathbf{r}}(t-\tau)] \}, \end{aligned} \tag{3.11}$$

where

$$\rho_L S(t) = \rho^{(1)}(t), \tag{3.12}$$

$$V_{\mathbf{s}\mathbf{x}}(\tau) = e^{iH_{ph}\tau} V_{\mathbf{s}\mathbf{x}} e^{-iH_{ph}\tau}, \tag{3.13}$$

$$U_{\mathbf{q}\mathbf{r}\mathbf{s}\mathbf{x}}(\tau) \equiv (e^{-iH_{\mathbf{q}\mathbf{x}}^0\tau})_{\mathbf{q}\mathbf{r}} (e^{iH_{\mathbf{q}\mathbf{x}}^0\tau})_{\mathbf{s}\mathbf{x}}. \tag{3.14}$$

Equation (3.11) is the desired result. $P_{f,i}(t)$ is obtained from its solution for $p_1 = p_2 = f$ with $S_{\mathbf{k}_j}(0) = \delta_{\mathbf{k}_j} \delta_{i_j}$ as the initial condition.

IV. EXCITON DENSITY IN MOMENTUM SPACE

In this section, we evaluate the equation of motion for the exciton density [Eq. (3.11)] in a momentum (\mathbf{k}) space representation. This representation is particularly useful since H conserves total wavevector and $H^{(0)}$ is diagonal. Equation (3.11) becomes

$$\begin{aligned} \dot{S}_{\mathbf{k}_1 \mathbf{k}_2}(t) &= -i[\epsilon(\mathbf{k}_1) - \epsilon(\mathbf{k}_2)] S_{\mathbf{k}_1 \mathbf{k}_2}(t) + \sum_{\mathbf{q}} \int_0^t d\tau S_{\mathbf{q}\mathbf{s}}(t-\tau) \{ \langle V_{\mathbf{s}\mathbf{k}_2} V_{\mathbf{k}_1 \mathbf{q}}(\tau) \rangle_L U_{\mathbf{q}\mathbf{k}_2}(\tau) + U_{\mathbf{k}_1 \mathbf{s}}(\tau) \langle V_{\mathbf{s}\mathbf{k}_2}(\tau) V_{\mathbf{k}_1 \mathbf{q}} \rangle_L \} \\ &- \sum_{\mathbf{q}} \int_0^t d\tau S_{\mathbf{k}_1 \mathbf{k}_2}(t-\tau) U_{\mathbf{k}_1 \mathbf{k}_2}(\tau) \{ \langle V_{\mathbf{k}_1 \mathbf{q}}(\tau) V_{\mathbf{q}\mathbf{k}_1} \rangle_L U_{\mathbf{q}\mathbf{k}_1}(\tau) + \langle V_{\mathbf{k}_2 \mathbf{q}} V_{\mathbf{q}\mathbf{k}_2}(\tau) \rangle_L U_{\mathbf{k}_2 \mathbf{q}}(\tau) \}, \end{aligned} \tag{4.1}$$

where $\mathbf{s} = \mathbf{k}_2 - \mathbf{k}_1 + \mathbf{q}$ and $U_{\mathbf{k}_1 \mathbf{k}_2}(\tau) = e^{-i[\epsilon(\mathbf{k}_1) - \epsilon(\mathbf{k}_2)]\tau}$. In the interaction representation, defined by

$$S_{\mathbf{k}_1 \mathbf{k}_2}^I(t) = e^{i[\epsilon(\mathbf{k}_1) - \epsilon(\mathbf{k}_2)]t} S_{\mathbf{k}_1 \mathbf{k}_2}(t), \tag{4.2}$$

the equation becomes

$$\begin{aligned} \dot{S}_{\mathbf{k}_1 \mathbf{k}_2}^I(t) &= -\sum_{\mathbf{q}} \int_0^t d\tau S_{\mathbf{q}\mathbf{s}}^I(t-\tau) \{ \langle V_{\mathbf{k}_1 \mathbf{q}}(\tau) V_{\mathbf{q}\mathbf{k}_1} \rangle_L U_{\mathbf{q}\mathbf{k}_1}(\tau) + \langle V_{\mathbf{k}_2 \mathbf{q}} V_{\mathbf{q}\mathbf{k}_2}(\tau) \rangle_L U_{\mathbf{k}_2 \mathbf{q}}(\tau) \} \\ &+ \sum_{\mathbf{q}} S_{\mathbf{q}\mathbf{s}}^I(t-\tau) [U_{\mathbf{q}\mathbf{s}}(t-\tau) U_{\mathbf{k}_2 \mathbf{k}_1}(t-\tau)] \{ \langle V_{\mathbf{s}\mathbf{k}_2} V_{\mathbf{k}_1 \mathbf{q}}(\tau) \rangle_L U_{\mathbf{q}\mathbf{k}_1}(\tau) + \langle V_{\mathbf{s}\mathbf{k}_2}(\tau) V_{\mathbf{k}_1 \mathbf{q}} \rangle_L U_{\mathbf{k}_2 \mathbf{q}}(\tau) \} \end{aligned} \tag{4.3}$$

The diagonal elements of S (or S^I) satisfy a particularly simple equation, called the generalized master equation:

$$\dot{S}_{\mathbf{k}\mathbf{k}}(t) = -\sum_{\mathbf{q}} \int_0^t d\tau S_{\mathbf{k}\mathbf{k}}(t-\tau) w_{\mathbf{q}\mathbf{k}}(\tau) + \sum_{\mathbf{q}} \int_0^t d\tau S_{\mathbf{q}\mathbf{q}}(t-\tau) w_{\mathbf{k}\mathbf{q}}(\tau), \tag{4.4}$$

where

$$w_{\mathbf{qk}}(\tau) = \langle V_{\mathbf{kq}} V_{\mathbf{qk}}(\tau) \rangle_L U_{\mathbf{kq}}(\tau) + \langle V_{\mathbf{kq}}(\tau) V_{\mathbf{qk}} \rangle_L U_{\mathbf{qk}}(\tau) = 2 \operatorname{Re} \langle V_{\mathbf{kq}} V_{\mathbf{qk}}(\tau) \rangle_L U_{\mathbf{kq}}(\tau). \quad (4.5)$$

In the usual weak coupling limit, Eqs. (4.3) or (4.4) are manipulated by replacing $S_{\mathbf{kk}}(t - \tau)$ by $S_{\mathbf{kk}}(t)$ on the right-hand side and taking the upper limit on the integral to infinity, so that the Eq. (4.3) becomes

$$\begin{aligned} \dot{S}_{\mathbf{k}_1 \mathbf{k}_2}^I(t) &= -S_{\mathbf{k}_1 \mathbf{k}_2}^I(t) \sum_{\mathbf{q}} \int_0^\infty d\tau [\langle V_{\mathbf{k}_1 \mathbf{q}}(\tau) V_{\mathbf{qk}_1} \rangle_L U_{\mathbf{qk}_1}(\tau) + \langle V_{\mathbf{k}_2 \mathbf{q}} V_{\mathbf{qk}_2}(\tau) \rangle_L U_{\mathbf{k}_2 \mathbf{q}}(\tau)] \\ &\quad + \sum_{\mathbf{q}} S_{\mathbf{qk}}^I(t) U_{\mathbf{qk}}(t) U_{\mathbf{k}_2 \mathbf{k}_1}(t) \int_0^\infty d\tau [\langle V_{\mathbf{qk}_2} V_{\mathbf{k}_1 \mathbf{q}}(\tau) \rangle_L U_{\mathbf{qk}_2}(\tau) + \langle V_{\mathbf{qk}_2}(\tau) V_{\mathbf{k}_1 \mathbf{q}} \rangle_L U_{\mathbf{k}_1 \mathbf{q}}(\tau)] \\ &\equiv -S_{\mathbf{k}_1 \mathbf{k}_2}^I(t) \Gamma_{\mathbf{k}_1 \mathbf{k}_2} + \sum_{\mathbf{q}} S_{\mathbf{qk}}^I(t) U_{\mathbf{qk}}(t) U_{\mathbf{k}_2 \mathbf{k}_1}(t) W_{\mathbf{k}_1 \mathbf{k}_2; \mathbf{qk}}, \end{aligned} \quad (4.6)$$

where we have used the fact that $U_{\mathbf{qk}}(t - \tau) = U_{\mathbf{qk}}(t) U_{\mathbf{qk}}(\tau)$. In the same limit, we find the generalized master equation (4.4) has become a Pauli master equation:

$$\dot{S}_{\mathbf{kk}}(t) = - \sum_{\mathbf{q}} W_{\mathbf{qk}} S_{\mathbf{kk}}(t) + \sum_{\mathbf{q}} W_{\mathbf{kq}} S_{\mathbf{qk}}(t), \quad (4.7)$$

where

$$W_{\mathbf{qk}} = \int_0^\infty w_{\mathbf{qk}}(\tau) d\tau = \int_0^\infty 2 \operatorname{Re} \langle V_{\mathbf{kq}} V_{\mathbf{qk}}(\tau) \rangle e^{i[\epsilon(\mathbf{k}) - \epsilon(\mathbf{q})]\tau} = W_{\mathbf{kq}} e^{-\beta[\epsilon(\mathbf{q}) - \epsilon(\mathbf{k})]} \quad (4.8)$$

using the canonical average and the properties of the Fourier transform. This is just the principle of detailed balance. In this limit, then, the probability of finding an exciton in a state \mathbf{k} at infinite time (regardless of lattice state) will be given by the Boltzmann equilibrium form (where radiative processes have been neglected)

$$S_{\mathbf{kk}}(\infty) = e^{-\beta \epsilon(\mathbf{k})} / \sum_{\mathbf{q}} e^{-\beta \epsilon(\mathbf{q})}. \quad (4.9)$$

The terms $W_{\mathbf{qk}}$ can be interpreted as the rate of scattering from state \mathbf{k} to state \mathbf{q} (more precisely, $W_{\mathbf{qk}}$ is the probability per unit time that an exciton in state \mathbf{k} will be scattered by the phonons into state \mathbf{q}); thus, the scattering time from state \mathbf{k} to state \mathbf{q} is given by $\tau_{\mathbf{qk}} = W_{\mathbf{qk}}^{-1}$. In addition the term $\sum_{\mathbf{q}} W_{\mathbf{qk}}$ can be interpreted as the total rate of scattering from state \mathbf{k} .

The first term in Eq. (4.6) can also be interpreted in a simple manner. One easily finds that

$$\operatorname{Im} \sum_{\mathbf{q}} \int_0^\infty d\tau \{ \langle V_{\mathbf{k}_1 \mathbf{q}}(\tau) V_{\mathbf{qk}_1} \rangle_L U_{\mathbf{qk}_1}(\tau) + \langle V_{\mathbf{k}_2 \mathbf{q}} V_{\mathbf{qk}_2}(\tau) \rangle_L U_{\mathbf{k}_2 \mathbf{q}}(\tau) \} \equiv \delta \epsilon^{(2)}(\mathbf{k}_1) - \delta \epsilon^{(2)}(\mathbf{k}_2), \quad (4.10)$$

where $\delta \epsilon^{(2)}(\mathbf{k}_1)$ is the thermal average of the second order perturbation correction to $\epsilon(\mathbf{k}_1)$. (Note that the thermally averaged first order contribution is zero.) Since the structure of this term is the same as the first term on the right in Eq. (4.1), we will see that this represents a correction to the bandlike motion of the excitons. Using (4.10) in (4.6) and transforming back to the original representation, we find, in the weak coupling limit,

$$\begin{aligned} \dot{S}_{\mathbf{k}_1 \mathbf{k}_2}(t) &= -i[\epsilon^{(2)}(\mathbf{k}_1) - \epsilon^{(2)}(\mathbf{k}_2)] S_{\mathbf{k}_1 \mathbf{k}_2}(t) - S_{\mathbf{k}_1 \mathbf{k}_2}(t) \sum_{\mathbf{q}} \operatorname{Re} \int_0^\infty d\tau \{ \langle V_{\mathbf{k}_1 \mathbf{q}} V_{\mathbf{qk}_1}(\tau) \rangle_L U_{\mathbf{qk}_1}(\tau) + \langle V_{\mathbf{k}_2 \mathbf{q}} V_{\mathbf{qk}_2}(\tau) \rangle_L U_{\mathbf{k}_2 \mathbf{q}}(\tau) \} \\ &\quad + \sum_{\mathbf{q}} S_{\mathbf{qk}}(t) \int_0^\infty d\tau \{ \langle V_{\mathbf{qk}_2} V_{\mathbf{k}_1 \mathbf{q}}(\tau) \rangle_L U_{\mathbf{qk}_2}(\tau) + \langle V_{\mathbf{qk}_2}(\tau) V_{\mathbf{k}_1 \mathbf{q}} \rangle_L U_{\mathbf{k}_1 \mathbf{q}}(\tau) \}, \end{aligned} \quad (4.11)$$

where $\epsilon^{(2)}(\mathbf{k}_1) = \epsilon(\mathbf{k}_1) + \delta \epsilon^{(2)}(\mathbf{k}_1)$. Equation (4.11) and its diagonal form, Eq. (4.7) will be used to compute diffusion coefficients. Note that Eq. (4.11) has a "coherent" part (represented by the first term on the right) and a scattering or "incoherent" part; however, in order to analyze the motion of the excitons on *very* short time scales, the weak coupling limit (i.e., "Markovian" approximation) should be abandoned. In this paper, we will be concerned with long time measurements which give diffusion constants and the like.

We now turn to the specific form of the correlation functions in Eq. (4.11) for the Hamiltonian of Sec. II. In Appendix A, we show (within the narrow phonon band approximation)

$$\begin{aligned} \langle V_{\mathbf{qk}_2}(\tau) V_{\mathbf{k}_1 \mathbf{q}} \rangle_L &= \delta(\mathbf{s} - \mathbf{k}_2 + \mathbf{k}_1 - \mathbf{q}) N^{-1} \left\{ \sum_{\mathbf{h}} \bar{J}_{\mathbf{h}}^2 \gamma_{\mathbf{h}}^{(1)}(\tau) e^{i(\mathbf{k}_2 - \mathbf{k}_1) \cdot \mathbf{R}_{\mathbf{h}}} \right. \\ &\quad \left. + \sum_{\mathbf{h}} \bar{J}_{\mathbf{h}}^2 \gamma_{\mathbf{h}}^{(4)}(\tau) e^{i(\mathbf{k}_1 + \mathbf{s}) \cdot \mathbf{R}_{\mathbf{h}}} + f_{\mathbf{k}_2 - \mathbf{s}} g_{\mathbf{s} - \mathbf{k}_2} \bar{\lambda}_{\mathbf{k}_2 - \mathbf{s}}^-(\tau) [\epsilon(\mathbf{k}_1) + \epsilon(\mathbf{k}_2) - \epsilon(\mathbf{q}) - \epsilon(\mathbf{s})] + |f_{\mathbf{k}_2 - \mathbf{s}}|^2 \lambda_{\mathbf{k}_2 - \mathbf{s}}^+(\tau) \right\}, \end{aligned} \quad (4.12)$$

where the definitions of symbols not previously encountered are found in Appendix A. The first terms in the bracket in (4.12) are the contribution from the terms in V representing the fluctuations \mathbf{s} in J_{n-m} (the "clothing" of the exciton) while the other terms arise from the incomplete clothing which is a feature of the variational procedure. At sufficiently high temperature, the exciton becomes fully clothed¹ so that $f=0$, and only the first terms in the bracket contribute. The theory then reduces to the earlier one of Grover and Silbey. At low temperatures, $f_{\mathbf{k}}$ is

not zero so that all terms in (4.12) have to be considered. Note also that the time dependence of the bracketed terms in (4.12) is fundamentally different from the other terms. In fact, the terms proportional to f and $|f|^2$ do not decay in time at this level of approximation (while the terms in brackets do, owing to phonon dispersion), since the functions $\lambda^*(\tau)$ are purely oscillatory. Thus, without further coarse graining² the kernels in the original equation of motion [Eq. (4.3), for example] do not decay and the usual arguments leading to the weak coupling limit equations [Eq. (4.6)] would not hold. (Note, however, that the transition probabilities in the weak coupling limit, $W_{\mathbf{k}\mathbf{k}}$, are just what one gets from the usual Fermi golden rule formula with this perturbation.) In the present case, we will only be concerned with diffusion coefficients and total transition rates, which are coarse grained quantities; thus, the oscillatory behavior of $\lambda^*(\tau)$ will not give any problem.

V. EXCITON SCATTERING TIMES AND DIFFUSION CONSTANTS

The total scattering rate $\Gamma_{\mathbf{k}\mathbf{k}}$ out of state \mathbf{k} is given from Eq. (4.11) as

$$\Gamma_{\mathbf{k}\mathbf{k}} = \sum_{\mathbf{q}} \text{Re} \int_0^{\infty} d\tau \{ \langle V_{\mathbf{k}\mathbf{q}}(\tau) V_{\mathbf{q}\mathbf{k}} \rangle_L U_{\mathbf{k}\mathbf{k}}(\tau) + \langle V_{\mathbf{k}\mathbf{q}} V_{\mathbf{q}\mathbf{k}}(\tau) \rangle_L U_{\mathbf{k}\mathbf{k}}(\tau) \}. \quad (5.1)$$

Using the results of Appendix A, Eq. (4.12), and the definition of $U_{\mathbf{q}\mathbf{k}}(\tau)$, we find

$$\begin{aligned} \Gamma_{\mathbf{k}\mathbf{k}} &= 2\pi N^{-1} \sum_{\mathbf{q}} |f_{\mathbf{q}}|^2 \{ (\bar{n}_{\mathbf{q}} + 1) \delta[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) - \omega_{\mathbf{q}}] + \bar{n}_{\mathbf{q}} \delta[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) + \omega_{\mathbf{q}}] \} + 2\pi N^{-1} 2 \\ &\times \sum_{\mathbf{q}} f_{\mathbf{q}} g_{\mathbf{q}} \omega_{\mathbf{q}} \{ (\bar{n}_{\mathbf{q}} + 1) \delta[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) - \omega_{\mathbf{q}}] + \bar{n}_{\mathbf{q}} \delta[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) + \omega_{\mathbf{q}}] \} + 2N^{-1} \\ &\times \sum_{\mathbf{q}} \text{Re} \int_0^{\infty} d\tau e^{-i[\epsilon(\mathbf{q}) - \epsilon(\mathbf{k})]\tau} \left\{ \sum_{\mathbf{h}} J_{\mathbf{h}}^2 (\gamma_{\mathbf{h}}^{(1)}(\tau) + e^{i(\mathbf{k} + \mathbf{q}) \cdot \mathbf{R}_{\mathbf{h}}} \gamma_{\mathbf{h}}^{(4)}(\tau)) \right\} \equiv \Gamma_{\mathbf{k}\mathbf{k}}^{(1)} + \Gamma_{\mathbf{k}\mathbf{k}}^{(2)}. \end{aligned} \quad (5.2)$$

Noting that, from Eq. (2.12), $f_{\mathbf{q}} = (C_{\mathbf{q}} - g_{\mathbf{q}})\omega_{\mathbf{q}}$, we find that the first two terms add to give

$$\begin{aligned} \Gamma_{\mathbf{k}\mathbf{k}}^{(1)} &= 2\pi N^{-1} \sum_{\mathbf{q}} (C_{\mathbf{q}}^2 - g_{\mathbf{q}}^2) \omega_{\mathbf{q}}^2 [(\bar{n}_{\mathbf{q}} + 1) \delta(\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) - \omega_{\mathbf{q}}) \\ &+ \bar{n}_{\mathbf{q}} \delta(\epsilon(\mathbf{k}) - \epsilon(\mathbf{k} - \mathbf{q}) + \omega_{\mathbf{q}})], \end{aligned} \quad (5.3)$$

which for a narrow optical phonon band becomes

$$\Gamma_{\mathbf{k}\mathbf{k}}^{(1)} \cong 2\pi (C^2 - g^2) \omega^2 [(\bar{n}_0 + 1) N(\epsilon(\mathbf{k}) - \omega_0) + \bar{n}_0 N(\epsilon(\mathbf{k}) + \omega_0)], \quad (5.4)$$

where $N(\epsilon)$ is the exciton density of states at $\epsilon - \bar{E}$ and $n_0 = e^{-\beta\omega_0}/(1 - e^{-\beta\omega_0})$, ω_0 the optical phonon frequency. Note for a narrow exciton band (bandwidth less than ω_0), this term is zero reflecting the fact that one phonon processes do not contribute in this case. Also, for $\epsilon(\mathbf{k})$ at the bottom of the band, $N(\epsilon(\mathbf{k}) - \omega_0) = 0$, so that at low temperatures there is less scattering at the bottom of the exciton band than at the top. The remaining terms in Eq. (5.2) are more difficult to evaluate since the time dependence of the integrand is so complicated. In Appendix B, a detailed discussion of this term is given; we merely present the final result for $\Gamma_{\mathbf{k}\mathbf{k}}^{(2)}$ here, for the various cases.

For wide exciton bands (bandwidths a few times ω_0), $\Gamma_{\mathbf{k}\mathbf{k}}^{(2)}$ is relatively small at low temperatures since $g/c \ll 1$ and given approximately by [see Eq. (B16)]

$$\begin{aligned} \Gamma_{\mathbf{k}\mathbf{k}}^{(2)} &\cong \frac{Z\bar{J}^2}{\omega_b} \sum_{l=0}^{\infty} S_l(\mathbf{k}; g^2) N(\epsilon_{\mathbf{k}} - l\omega_0) \\ &+ 2\pi Z\bar{J}^2 g^2 e^{-\beta\omega_0} N(\epsilon_{\mathbf{k}} + \omega_0), \end{aligned}$$

where we have defined $S_l(\mathbf{k}; g^2)$ in Appendix B, and we have assumed a nearest neighbor model for convenience with z the number of neighbors. At high temperatures, the exciton phonon coupling is large, the clothed bandwidth becomes small, and

$$\Gamma_{\mathbf{k}\mathbf{k}}^{(2)} = \frac{2Z\bar{J}^2 e^y}{\omega_b \sqrt{2\pi y^3}},$$

where

$$y = 4g^2 \bar{n}_0^{1/2} (\bar{n}_0 + 1)^{1/2}.$$

Therefore, for a wide exciton band, the scattering rate for state near the bottom of the band is small and dependent on \mathbf{k} at low temperatures, and large and independent of \mathbf{k} at high temperatures. There is a possibility of an abrupt transition from weak to strong scattering as T increases.¹

For narrow exciton bands, there is a smooth increase in the scattering rate as T increases and, the scattering is largely independent of \mathbf{k} . No abrupt transition occurs.

Table I shows the variation of $\Gamma_{\mathbf{k}\mathbf{k}}$ (at the bottom of the exciton band) vs temperature for a wide band ($J/\omega_0 = 2$) strongly coupled ($c = 2$) case and a narrow band ($J/\omega_0 = \frac{1}{2}$), weakly coupled ($c = \frac{1}{2}$) case.

B. Diffusion coefficients

The diffusion coefficient D can be found by solving the equations of motion for $R^2(t) \equiv \sum_{\mathbf{n}} n^2 \rho_{\mathbf{n}\mathbf{n}}(t)$ at long time, assuming that the initial state is localized on site $\mathbf{n} = 0$. When this is done, D consists of a number of terms, some representing bandlike motion and others representing hoppinglike motion. Neglecting some small terms, we find [see Eq. (4.6)]

$$\begin{aligned} D &= 2 \sum_{\mathbf{k}} v_{\mathbf{k}}^2 \rho_{\mathbf{k}\mathbf{k}}^e (\gamma_0 + \Gamma_{\mathbf{k}\mathbf{k}})^{-1} \\ &+ \sum_{\mathbf{k}} \rho_{\mathbf{k}\mathbf{k}}^e \left[\text{Re} \left[\frac{d^2 \sum_{\mathbf{q}} W_{\mathbf{q}, \mathbf{q} + \mathbf{k}; \mathbf{k}, \mathbf{k} + \mathbf{q}}}{dk^2} \right]_{\mathbf{k}=0} - \left[\frac{d^2 \Gamma_{\mathbf{k}, \mathbf{k} + \mathbf{k}}}{dk^2} \right]_{\mathbf{k}=0} \right], \end{aligned}$$

where $\rho_{\mathbf{k}\mathbf{k}}^e$ is the equilibrium (Boltzmann) distribution of

TABLE I. Calculation of Γ_{kk} for the bottom of the exciton band using Eqs. (5.4)–(5.6). The exciton density of states is taken to be

$$N(\epsilon) = \frac{2}{\pi z^2 \tilde{J}^2} [z^2 \tilde{J}^2 - \epsilon^2]^{1/2}, \quad |\epsilon| \leq z \tilde{J}.$$

kT/ω_0	Γ/ω_0
(1) $J/\omega_0 = 0.5, c = 0.5^a$	
0.5	0.182
1.0	0.704
2.0	0.891
(2) $J/\omega_0 = 2.0, c = 2.0, (\omega_b/\omega_0) = 0.01^b$	
< 0.5	$4.3\bar{n}_0$
0.5	0.05
1.0	0.14
2.0	0.33

^aFor $kT/\omega_0 \geq 2.2$, the one phonon processes drop out because of energy non-conservation, and multiple phonon processes dominate. This causes a dip in Γ .

^bFor $kT/\omega_0 < 0.5$, the one phonon processes dominate, while above 0.5 (the transition temperature) the exciton bandwidth is very small and multiple phonon processes dominate.

exciton states $[\exp(-\beta E_k)/\sum_k \exp(-\beta E_k)]$ and \mathbf{v}_k is the velocity of the exciton in state \mathbf{k} ($\mathbf{v}_k \equiv \nabla_{\mathbf{k}} E_k$).

At high temperature, where $\Gamma_{kk} \rightarrow \Gamma$ (independent of k and large) and \mathbf{v}_k becomes small due to the decrease in the exciton bandwidth, $D - \Gamma$, the hopping term. At low temperatures, only the states at the bottom of the band will be populated, so Γ_{kk} is small, so $D - 2\sum_k V_k^2 \rho_{kk} (\gamma_0 + \Gamma_{kk})^{-1}$ (the bandlike term). In addition, we have inserted a term, γ_0 , representing the contribution to the scattering rate from quadratic phonon-exciton scattering and local fluctuations (see the discussion at the end of Sec. II).

If the exciton band is wide and the coupling strong, so that an abrupt transition from “free” to “localized” state can occur as T increases, then the motion switches abruptly from bandlike to hopping (and from a relatively large to a small D).

VI. CONNECTION TO THERMAL MODULATION SPECTROSCOPY

In this section we consider the temperature dependence of the spectral line shape function for the linear exciton-phonon Hamiltonian described in Sec. II. As a consequence of the simplicity of this Hamiltonian, the results of the discussion will be elementary in nature. The intent is simply to establish the connection between the formalism of this work and a theory of the thermal modulation spectrum of molecular crystals.¹⁰ A more complete discussion, employing a Hamiltonian which includes quadratic exciton phonon coupling, will be the subject of a future publication.

We consider a single vertical (Franck-Condon) excitation in a perfect crystal at temperature T in its electronic ground state. The spectral line shape function for this system is given in the long wavelength approximation by

$$\hat{I}(\omega) = \frac{\mu^2}{2\pi} \int_{-\infty}^{+\infty} dt e^{-i\omega t} I(t) = \frac{\mu^2}{\pi} \text{Re} \int_0^{\infty} dt e^{-i\omega t} I(t), \quad (6.1)$$

$$I(t) = \sum_{j,j'} \langle 0 | \langle A_j e^{i\tilde{H}t} A_{j'}^\dagger e^{-i\tilde{H}t} | 0 \rangle, \quad (6.2)$$

where μ is the transition dipole moment. Transforming to k -exciton space and using the decoupling approximation of Abram-Silbey,³ Eq. (6.2) reduces to

$$I(t) = \sum_{\mathbf{k}, \mathbf{h}} \mathcal{D}_{\mathbf{h}}(t) \mathcal{G}_{\mathbf{k}}(t) e^{-i\mathbf{k} \cdot \mathbf{R}_{\mathbf{h}}}, \quad (6.3)$$

where the phonon correlation function $\mathcal{D}_{\mathbf{h}}(t)$ is given by

$$\mathcal{D}_{\mathbf{h}}(t) = \langle \theta_j \theta_{j+\mathbf{h}}^\dagger(t) \rangle_L = X(T) \exp N^{-1} \sum_{\mathbf{q}} g_{\mathbf{q}}^2 (\cos \mathbf{q} \cdot \mathbf{R}_{\mathbf{h}}) \times [e^{i\omega_{\mathbf{q}} t} (\bar{n}_{\mathbf{q}} + 1) + e^{-i\omega_{\mathbf{q}} t} \bar{n}_{\mathbf{q}}], \quad (6.4)$$

and the exciton correlation function $\mathcal{G}_{\mathbf{k}}(t)$ is given by

$$\mathcal{G}_{\mathbf{k}}(t) = \langle 0 | a_{\mathbf{k}} \langle e^{i\tilde{H}t} a_{\mathbf{k}}^\dagger e^{-i\tilde{H}t} \rangle_L | 0 \rangle, \quad (6.5)$$

with the Debye-Waller factor $X(T)$ being

$$X(T) = \exp \left[-N^{-1} \sum_{\mathbf{q}} g_{\mathbf{q}}^2 (2\bar{n}_{\mathbf{q}} + 1) \right]. \quad (6.6)$$

Using the projector operator formalism $\mathcal{G}_{\mathbf{k}}(t)$ is found to have (to second order in V) the following simple time dependence

$$\dot{\mathcal{G}}_{\mathbf{k}}(t) = i\epsilon(\mathbf{k}) \mathcal{G}_{\mathbf{k}}(t) - \int_0^t \sum_{\mathbf{q}} \langle V_{k\mathbf{q}} V_{q\mathbf{k}}(t-\tau) \rangle e^{i\epsilon(\mathbf{q})\tau} \mathcal{G}_{\mathbf{k}}(t-\tau), \quad (6.7)$$

which in the interaction representation [defined by $\mathcal{G}_{\mathbf{k}}^I(t) e^{i\epsilon(\mathbf{k})t} = \mathcal{G}_{\mathbf{k}}(t)$] becomes

$$\dot{\mathcal{G}}_{\mathbf{k}}^I(t) = - \int_0^t \sum_{\mathbf{q}} \langle V_{k\mathbf{q}} V_{q\mathbf{k}}(\tau) \rangle_L e^{i[\epsilon(\mathbf{q}) - \epsilon(\mathbf{k})]\tau} \mathcal{G}_{\mathbf{k}}^I(t-\tau). \quad (6.8)$$

As discussed in Sec. IV, we can deconvolute Eq. (6.8) [not Eq. (6.7)] to give (in the original representation)

$$\dot{\mathcal{G}}_{\mathbf{k}}(t) = [i\epsilon^{(2)}(\mathbf{k}) - \Gamma_{\mathbf{k}\mathbf{k}}] \mathcal{G}_{\mathbf{k}}(t), \quad (6.9)$$

so that

$$\mathcal{G}_{\mathbf{k}}(t) = e^{[i\epsilon^{(2)}(\mathbf{k}) - \Gamma_{\mathbf{k}\mathbf{k}}]t}. \quad (6.10)$$

From this equation we see that the line shape function will involve the exciton energy correct to second order.

We next compare the thermal modulation spectrum for two antipodal extremes of our simple Hamiltonian (i) the narrow exciton-narrow phonon band, and (ii) the wide exciton-narrow phonon band, approximations. (The narrow phonon band or Einstein approximation is employed as computational convenience which should not alter the conclusions of this discussion in any essential manner.)

From Eqs. (6.1), (6.3), (6.10), and (6.4) (for Einstein phonons) we find

$$\frac{\hat{I}(\omega)}{NX(T)} = \int d\epsilon N(\epsilon) \left\{ \sum_{l=-\infty}^{\infty} I_l \left(g^2 \operatorname{csch} \frac{\beta\omega_0}{2} \right) e^{\beta l \omega_0/2} \right. \\ \left. \times L(\epsilon, \omega, l) + L(\epsilon, \omega, 0) \delta(\epsilon - \epsilon^*) - L(\epsilon, \omega, 0) \right\}, \quad (6.11)$$

where

$$\epsilon^* = \epsilon(\mathbf{k} = 0), \\ L(\epsilon, \omega, l) = \frac{\Gamma(\epsilon, T)}{(\omega - \epsilon + l\omega_0)^2 + \Gamma^2(\epsilon, T)}, \quad (6.12)$$

and $\Gamma(\epsilon, T)$ is the temperature dependent scattering rate of an exciton of energy, ϵ . We concentrate our analysis on the zero phonon line (zpl) whose spectrum is found by setting $l=0$ in Eq. (6.11):

$$\frac{\hat{I}_{zpl}(\omega)}{NX(T)} = \int d\epsilon N(\epsilon) \left[\left\{ I_0 \left(g^2 \operatorname{csch} \frac{\beta\omega_0}{2} \right) - 1 \right\} L(\epsilon, \omega, 0) \right. \\ \left. + L(\epsilon, \omega, 0) \delta(\epsilon - \epsilon^*) \right]. \quad (6.13)$$

We can further simplify the analysis by considering a case in which the sudden dressing of the exciton (for case ii) occurs at low temperature (around $T = T_c$) so that $I_0(g^2 \operatorname{csch} \frac{1}{2}\beta\omega_0) \approx 1$. For example, from l we might choose $c=2$ and for case (i) $|J|/\omega < \frac{1}{2}$ while for case (ii) $|J|/\omega \geq 2$. Then Eq. (6.13) reduces to (making the Γ dependence of L explicit):

$$\frac{\hat{I}_{zpl}(\omega)}{X(T)} = N(\epsilon^*) L(\epsilon^*, \omega, \Gamma^*); \quad \Gamma^* \equiv \Gamma(\epsilon^*, T), \quad (6.14)$$

while for the tms , we have

$$\hat{I}_{zpl}^{tms}(\omega) \equiv \int_T^{T+\Delta T} \left\{ \frac{d}{dT} \hat{I}_{zpl}(\omega) \right\} dT = \frac{d}{dT} \hat{I}_{zpl}(\omega) \Big|_{T=T^*} \Delta T, \\ T \leq T^* \leq T + \Delta T, \quad (6.15)$$

and for the purposes of this discussion T , T^* , and $T + \Delta T$ are assumed to lie in a neighborhood of T_c .

Using Eq. (6.6)

$$\frac{d\hat{I}_{zpl}(\omega)}{dT} = -\alpha(T) \hat{I}_{zpl}(\omega) + \dot{X}(T) \frac{d}{dT} \{L(\epsilon^*, \omega, \Gamma^*) N(\epsilon^*)\} \\ \equiv \Delta \hat{I}_{zpl}(\omega), \quad (6.16)$$

where

$$\alpha(T) = g^2 \bar{n}_0 (\bar{n}_0 + 1) \omega_0 \beta^2 k_B. \quad (6.17)$$

Evaluation of the second term in Eq. (6.16) is simplified by neglecting changes in $N(\epsilon^*)$ with temperature and considering only the explicit temperature dependence of $\Gamma(\epsilon^*, T)$. When this is done the final expression of becomes (neglecting second order corrections to ϵ):

$$\Delta \hat{I}_{zpl}(\omega) = -a \hat{I}_{zpl}(\omega) + b \hat{D}_{zpl}(\omega), \quad (6.18)$$

where

$$\hat{D}_{zpl}(\omega) = \frac{2(\epsilon^* - \omega)}{(\epsilon^* - \omega)^2 + \Gamma^2(\epsilon^*, T)} \quad (6.19)$$

and

$$a = \alpha(T) + \frac{d \ln \Gamma(T)}{dT} \equiv a_1 + a_2, \quad (6.20)$$

$$b = \alpha(T) z \tilde{J} + 2\omega_0 f \frac{dg}{dT} \equiv b_1 + b_2. \quad (6.21)$$

Here a_1 and b_1 correspond to the effects of changes in the Debye-Waller factor and changes in ϵ resulting from "band narrowing" respectively while a_2 and b_2 correspond in turn to those effects which are a consequence of the temperature dependence of $\Gamma_{k=0}$ and the temperature dependent energy shift in ϵ . Note that $a > 0$ since $d \ln \Gamma / dT > 0$ while b has the sign of \tilde{J} , since $dg/dT > 0$.

In the narrow exciton band case $a = a_1$ and $b = b_1$, so that $\hat{I}_{zpl}^{tms}(\omega)$ consists of an inverted direct absorption line plus a small derivative line. A similar result is obtained in the wide exciton band case with modified intensities since here the full expressions for a and b must be used. The significant difference between the two cases will be the broadening and red shift (of both the direct and derivative line) observed in case (ii). These changes are a consequence of Eq. (6.15) in conjunction with the effects discussed with regard to a_2 and b_2 .

VII. CONCLUSIONS

In the present paper, we have discussed the effect of an abrupt change in the exciton phonon scattering on the transport properties of the exciton. The abrupt change is brought about by a sudden narrowing of the exciton band due to the localized state becoming lower in energy than the delocalized state. We have relied upon our previous variational results, which showed that there are two minima in the free energy surface of a wide band exciton. As T is increased, the localized state becomes more stable than the delocalized state; we have assumed that the exciton always chooses to be in the more stable state and have neglected fluctuations and the thermal population of the less stable state. Such effects may be important in some cases.

In the present paper, we found, as expected, that the abrupt change (in the wide band case) in the nature of the exciton state is also evidenced in the scattering rate, Γ_{kk} , and the diffusion constant. The exciton goes from being a wave, scattered intermittently by phonons, to a localized state (quasibound to its lattice position) which moves by phonon assisted hopping. In this way, the analogy to the small polaron theories of Toyozawa⁷ and Emin⁸ is evident. One problem with the present treatment in the wide band case should be pointed out. For temperatures such that the simple variational treatment predicts that all k states should prefer to be delocalized, the scattering rate, Γ_{kk} , of states near the middle and top of the band may still be large (much larger than that of states at the bottom of the band). This indicates that these states may not be adequately described by our simple variational method.

In the case that the exciton band is not wide enough to exhibit the abrupt transition, but is still wider than the phonon frequency, another simple effect can take place. As T increases, the exciton band width will decrease

until one phonon processes become impossible and then multiphonon processes dominate. This may give rise to a significant change in Γ_{kk} as this scattering channel disappears.

There is another interesting manifestation of the scattering in the wide band case: the band narrowing factor, $\exp\{-\sum_{\mathbf{q}} g_{\mathbf{q}}^2 \coth(\beta\omega_{\mathbf{q}}/2)\}$, is a complicated function of temperature, since $g_{\mathbf{q}}$ is. For the simple model of a one-dimensional exciton band with nearest neighbor interactions, the variational theory predicts that this factor depends much less strongly on T than $\coth\beta\omega_{\mathbf{q}}/2$ it-

self. This suggests that the band narrowing will be almost independent of temperature until the abrupt change to a localized state takes place. In the narrow band case, this is not true.

This paper has been solely concerned with linear phonon-exciton coupling; as such it leaves out important terms⁹ which we tried to include phenomenologically by including a γ_0 (local fluctuations) in the diffusion coefficient. However, a more complete theory will have to include linear and quadratic terms and more than one phonon band.

APPENDIX A

From the definition of $V(t)$, Eq. (2.17) and Eq. (3.13), we will evaluate the correlation function $\langle V_{\mathbf{k}_2}(t)V_{\mathbf{k}_1}(t) \rangle_L$.

$$\langle V_{\mathbf{k}_2}(t)V_{\mathbf{k}_1}(t) \rangle_L = \langle [V_1(t)]_{\mathbf{k}_2}[V_1]_{\mathbf{k}_1} \rangle_L + \langle [V_2(t)]_{\mathbf{k}_2}[V_2]_{\mathbf{k}_1} \rangle_L + \langle [V_1(t)]_{\mathbf{k}_2}[V_2]_{\mathbf{k}_1} \rangle_L + \langle [V_2(t)]_{\mathbf{k}_2}[V_1]_{\mathbf{k}_1} \rangle_L \quad (A1)$$

Now,

$$\begin{aligned} \langle [V_2(t)]_{\mathbf{k}_2}[V_2]_{\mathbf{k}_1} \rangle_L &= f_{\mathbf{k}_2-\mathbf{s}} f_{\mathbf{q}-\mathbf{k}_1} \langle (b_{\mathbf{s}-\mathbf{k}_2}(t) + b_{\mathbf{k}_2-\mathbf{s}}^*(t))(b_{\mathbf{q}-\mathbf{k}_1} + b_{\mathbf{k}_1-\mathbf{q}}^*) \rangle_L \\ &= \delta(\mathbf{s} - \mathbf{k}_2 + \mathbf{q} - \mathbf{k}_1) |f_{\mathbf{k}_2-\mathbf{s}}|^2 [(\bar{n}_{\mathbf{k}_2-\mathbf{s}} + 1) e^{-i\omega_{\mathbf{k}_2-\mathbf{s}}t} + \bar{n}_{\mathbf{k}_2-\mathbf{s}} e^{i\omega_{\mathbf{k}_2-\mathbf{s}}t}], \end{aligned} \quad (A2)$$

where $\bar{n}_{\mathbf{q}} = (e^{\beta\omega_{\mathbf{q}}} - 1)^{-1}$;

$$\langle [V_1(t)]_{\mathbf{k}_2}[V_1]_{\mathbf{k}_1} \rangle_L = N^{-2} \sum_{\substack{\mathbf{n}, \mathbf{m} \\ \mathbf{n}' = \mathbf{m}'}} J_{\mathbf{n}\mathbf{m}} J_{\mathbf{n}'\mathbf{m}'} e^{i\mathbf{s} \cdot \mathbf{R}_{\mathbf{n}\mathbf{m}}} e^{i\mathbf{k}_1 \cdot \mathbf{R}_{\mathbf{n}'\mathbf{m}'}} e^{i(\mathbf{s}-\mathbf{k}_2) \cdot \mathbf{R}_{\mathbf{m}}} e^{i(\mathbf{k}_1-\mathbf{q}) \cdot \mathbf{R}_{\mathbf{m}'}} \langle [\theta_{\mathbf{n}}^*(t)\theta_{\mathbf{m}}(t) - \langle \theta_{\mathbf{n}}^* \theta_{\mathbf{m}} \rangle][\theta_{\mathbf{n}'}^* \theta_{\mathbf{m}'} - \langle \theta_{\mathbf{n}'}^* \theta_{\mathbf{m}'} \rangle] \rangle_L \quad (A3)$$

For a narrow phonon band, the largest terms are for (1) $n = m'$, $m = n'$; (2) $n = n'$, $m \neq m'$; (3) $n \neq n'$, $m = m'$; (4) $n = n'$, $m = m'$. As before,³ we keep only terms (1) and (4). Using standard techniques,^{3,4} we find

$$\langle [V_1(t)]_{\mathbf{k}_2}[V_1]_{\mathbf{k}_1} \rangle_L = \delta(\mathbf{s} - \mathbf{k}_2 + \mathbf{k}_1 - \mathbf{q}) N^{-1} \sum_{\mathbf{h}} \tilde{J}_{\mathbf{h}}^2 [e^{i(\mathbf{k}_2-\mathbf{k}_1) \cdot \mathbf{R}_{\mathbf{h}}} \gamma_{\mathbf{h}}^{(1)}(t) + e^{i(\mathbf{k}_1-\mathbf{q}) \cdot \mathbf{R}_{\mathbf{h}}} \gamma_{\mathbf{h}}^{(4)}(t)], \quad (A4)$$

where (note the tilde over the $J_{\mathbf{h}}$!)

$$\gamma_{\mathbf{h}}^{(1)}(t) = -1 + \exp 2N^{-1} \sum_{\mathbf{q}} g_{\mathbf{q}}^2 (1 - \cos \mathbf{q} \cdot \mathbf{R}_{\mathbf{h}}) [(\bar{n}_{\mathbf{q}} + 1) e^{-i\omega_{\mathbf{q}}t} + \bar{n}_{\mathbf{q}} e^{i\omega_{\mathbf{q}}t}], \quad (A5)$$

and in $\gamma_{\mathbf{h}}^{(4)}(t)$, the exponent is the negative of that in $\gamma_{\mathbf{h}}^{(1)}(t)$. Finally,

$$\begin{aligned} \langle [V_2(t)]_{\mathbf{k}_2}[V_1]_{\mathbf{k}_1} \rangle_L &= N^{-1} \sum_{\mathbf{n}\mathbf{m}} J_{\mathbf{n}\mathbf{m}} e^{i\mathbf{k}_1 \cdot \mathbf{R}_{\mathbf{n}\mathbf{m}}} e^{i(\mathbf{k}_1-\mathbf{q}) \cdot \mathbf{R}_{\mathbf{m}}} f_{\mathbf{k}_2-\mathbf{s}} \langle (b_{\mathbf{s}-\mathbf{k}_2}(t) + b_{\mathbf{k}_2-\mathbf{s}}^*(t))(\theta_{\mathbf{n}}^* \theta_{\mathbf{m}} - \langle \theta_{\mathbf{n}}^* \theta_{\mathbf{m}} \rangle) \rangle_L \\ &= \delta(\mathbf{s} - \mathbf{k}_2 + \mathbf{k}_1 - \mathbf{q}) f_{\mathbf{k}_2-\mathbf{s}} g_{\mathbf{k}_2-\mathbf{s}} [\epsilon(\mathbf{q}) - \epsilon(\mathbf{k}_1)] [(\bar{n}_{\mathbf{s}-\mathbf{k}_2} + 1) e^{-i\omega_{\mathbf{s}-\mathbf{k}_2}t} - \bar{n}_{\mathbf{s}-\mathbf{k}_2} e^{i\omega_{\mathbf{s}-\mathbf{k}_2}t}]. \end{aligned} \quad (A6)$$

We define

$$\lambda_{\mathbf{q}}^{\pm}(t) = (\bar{n}_{\mathbf{q}} + 1) e^{-i\omega_{\mathbf{q}}t} \pm \bar{n}_{\mathbf{q}} e^{i\omega_{\mathbf{q}}t} \quad (A7)$$

Substitution of these formulas into Eq. (A1) gives Eq. (4.12).

APPENDIX B

We will evaluate the terms in Eq. (5.2) arising from the unitary transformation of H and resulting in fluctuations of J_{nm} . These are written as

$$\begin{aligned} \Gamma_{\mathbf{k}\mathbf{k}}^{(2)} &= 2N^{-1} \sum_{\mathbf{q}} \text{Re} \int_0^{\infty} dt e^{-i[\epsilon(\mathbf{q}) - \epsilon(\mathbf{k})]t} \\ &\quad \times \sum_{\mathbf{h}} \tilde{J}_{\mathbf{h}}^2 [\gamma_{\mathbf{h}}^{(1)}(t) + \gamma_{\mathbf{h}}^{(4)}(t) \cos(\mathbf{k} + \mathbf{q}) \cdot \mathbf{R}_{\mathbf{h}}], \end{aligned} \quad (B1)$$

with (see Appendix A)

$$\gamma_{\mathbf{h}}^{(1)}(t) = \exp \left\{ 2N^{-1} \sum_{\lambda} g_{\lambda}^2 (1 - \cos \lambda \cdot \mathbf{R}_{\mathbf{h}}) \right.$$

$$\left. \times [(\bar{n}_{\lambda} + 1) e^{-i\omega_{\lambda}t} + \bar{n}_{\lambda} e^{i\omega_{\lambda}t}] \right\} - 1. \quad (B2)$$

The form of $\gamma_{\mathbf{h}}^{(4)}(t)$ is the same as that of $\gamma_{\mathbf{h}}^{(1)}(t)$ except for an overall sign in the exponent. For an Einstein phonon band of frequency ω_0 ,

$$\gamma_{\mathbf{h}}^{(1)}(t) = \exp \{ 2g^2 [(\bar{n}_0 + 1) e^{-i\omega_0t} + \bar{n}_0 e^{i\omega_0t}] - 1 \}, \quad (B3)$$

independent of \mathbf{h} , where $\bar{n}_0 = (e^{\beta\omega_0} - 1)^{-1}$. For an optical phonon band whose width, Δ , is 1-10 cm^{-1} or a small fraction of ω_0 , we expect Eq. (B2) to resemble Eq. (B3). In order to reduce Eq. (B2) to a simple form, Grover and Silbey chose a Lorentzian density of phonon states.

In contrast, Emin⁸ has used a nearest neighbor dispersion law for the phonons,

$$\omega_{\lambda} = \omega_0 + \omega_b (\cos q_x + \cos q_y + \cos q_z); \quad (\text{B4})$$

however, the final results are essentially the same. By substituting Eq. (B4) into Eq. (B2), replacing g_{λ}^2 by g^2 , and \bar{n}_{λ} by \bar{n}_0 (both expected to be good for narrow bands, $\omega_b/\omega_0 \ll 1$), we find

$$\gamma_h^{(1)}(t) = \exp \{ 2g^2 A(t) [(\bar{n}_0 + 1) e^{-i\omega_0 t - i\phi(t)} + \bar{n}_0 e^{i\omega_0 t + i\phi(t)}] - 1 \}, \quad (\text{B5})$$

where

$$A(t) = J_0^2(\omega_b t) \{ J_0^2(\omega_b t) + J_1^2(\omega_b t) \}^{1/2}, \quad (\text{B6})$$

$$\phi(t) = -\arctan \{ J_1(\omega_b t) / J_0(\omega_b t) \}, \quad (\text{B7})$$

where $J_n(\omega_b t)$ is the n th order Bessel function, and h is a nearest neighbor of the origin. Using the generating function for modified Bessel functions (and dropping the subscript h),

$$\gamma^{(1)}(t) = \sum_{l=-\infty}^{+\infty} e^{\beta l \omega_0 / 2} e^{-i l \omega_0 t + \phi(t)} [I_l(\gamma A(t)) - \delta_{l0}], \quad (\text{B8})$$

with

$$y = 4g^2 \bar{n}_0^{1/2} (\bar{n}_0 + 1)^{1/2} \equiv 2g^2 \operatorname{csch} \frac{\beta \omega_0}{2}. \quad (\text{B9})$$

The term $\gamma^{(4)}(t)$ will have a $(-1)^l$ in the sum. If instead of the dispersion law, Eq. (B4), we had substituted a Lorentzian density of states of width $6\omega_b$, $A(t)$ would be $\exp(-3\omega_b t)$, while for a Gaussian density of states of width $6\omega_b$, $A(t) \propto \exp(-9\omega_b^2 t^2)$, and $\phi(t) = 0$ for both.

When the form of $\gamma^{(1)}$ is put into the equation for $\Gamma_{kk}^{(2)}$, integrals of the following type arise:

$$F_l(U) = \int_0^{\infty} dt \cos[(u + l\omega_0)t + \phi(t)] \times e^{\beta l \omega_0 / 2} [I_l(\gamma A(t)) - \delta_{l0}]. \quad (\text{B10})$$

where $u = \epsilon(q) - \epsilon(k)$. The term $I_l - \delta_{l0}$ decays to zero in a time scale $\sim \omega_b^{-1}$; since the cos term oscillates on a time scale $\sim (u + l\omega_0)^{-1} \ll \omega_b^{-1}$, $F_l(u)$ will be very small unless $(u + l\omega_0)$ is less than or equal to the phonon bandwidth ($\sim 6\omega_b$). If $(u + l\omega_0) \gg \omega_b$ then $F_l(u)$ will be proportional to $\omega_b^2 / (u + l\omega_0)^3$ as can be seen immediately by breaking the integral in (B10) into a sum of integrals [$t = \tau + 2\pi n / (u + l\omega_0)$]:

$$F_l(u) \cong \sum_{n=0}^{\infty} \int_0^{2\pi / (u + l\omega_0)} d\tau \cos(u + l\omega_0)\tau e^{\beta l \omega_0 / 2} \times \left\{ I_l \left(\gamma A \left(\tau + \frac{2\pi n}{u + l\omega_0} \right) \right) - \delta_{l0} \right\} \cong \sum_{n=0}^{\infty} \int_0^{2\pi / (u + l\omega_0)} d\tau \cos(u + l\omega_0)\tau \times e^{\beta l \omega_0 / 2} e^{-3\omega_b \tau} \{ I_l(\gamma A_n) - \delta_{l0} \} = \frac{2\pi (3\omega_b)^2}{(u + l\omega_0)^3} e^{\beta l \omega_0 / 2} \sum_{n=0}^{\infty} \{ I_l(\gamma A_n) - \delta_{l0} \}, \quad (\text{B11})$$

where $A_n = A[2\pi n / (\Omega + l\omega_0)]$, and we have assumed, for simplicity, that the decay of $A(t)$ is exponential. In the limit that $u + l\omega_0 \approx 0$, we have

$$F_l(u) = \int_0^{\infty} dt e^{\beta l \omega_0 / 2} \{ I_l(\gamma A(t)) - \delta_{l0} \} \equiv F_l^R(u). \quad (\text{B12})$$

By substituting these results into Eq. (B1), we find

$$\Gamma_{kk}^{(2)} \cong 2N^{-1} \sum_{\mathbf{q}} \sum_{\mathbf{h}} \bar{J}_{\mathbf{h}}^2 \sum_{l=-\infty}^{+\infty} \{ 1 + (-1)^l \cos(\mathbf{k} + \mathbf{q}) \cdot \mathbf{R}_{\mathbf{h}} \} \times F_l^R(\epsilon_{\mathbf{q}} - \epsilon_{\mathbf{k}}) \Delta(\epsilon_{\mathbf{q}} - \epsilon_{\mathbf{k}} + l\omega_0), \quad (\text{B13})$$

where

$$\Delta(x) = \begin{cases} 1 & |x| < \omega_b \\ 0 & \text{otherwise} \end{cases}.$$

If, again for simplicity, a nearest neighbor model is assumed, we find (z is the number of nearest neighbors)

$$\Gamma_{kk}^{(2)} \cong 2N^{-1} \sum_{\mathbf{q}} \sum_{l=-\infty}^{+\infty} \{ z \bar{J}^2 + \epsilon_{\mathbf{k}} \epsilon_{\mathbf{q}} (-1)^l \} \times F_l^R(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{q}}) \Delta(\epsilon_{\mathbf{q}} - \epsilon_{\mathbf{k}} + l\omega_0). \quad (\text{B14})$$

At low temperatures, y [see Eq. (B9)] is small due to n_0 (note that g will also be relatively small for wide bands at low T),

$$F_l^R \approx \int_0^{\infty} dt e^{\beta l \omega_0 / 2} \frac{[\frac{1}{2} \gamma A(t)]^{|l|}}{|l|!} \approx \frac{(2g^2)^{|l|}}{|l|!} \frac{e^{\beta \omega_0 / 2 (l-|l|)}}{(1 - e^{-\beta \omega_0})^{|l|}} \int_0^{\infty} A^{|l|}(t) dt, \quad l \neq 0 = \frac{(2g^2)^{|l|}}{|l|!} \frac{e^{(l/2)\beta \omega_0 (l-|l|)}}{(1 - e^{-\beta \omega_0})^{|l|}} \frac{1}{|l| (3\omega_b)}, \quad (\text{B15})$$

and

$$F_0^R \cong \frac{2g^4}{3\omega_b} n_0(n_0 + 1).$$

Thus, at low T ,

$$\Gamma_{kk}^{(2)} \cong \sum_{l=1}^{\infty} 4N(\epsilon_{\mathbf{k}} - l\omega_0)(n_0 + 1)^l [z \bar{J}^2 + (-1)^l \epsilon_{\mathbf{k}}(\epsilon_{\mathbf{k}} - l\omega_0)] \frac{(2g^2)^l}{l!} + 8g^2 N(\epsilon_{\mathbf{k}} + \omega_0) n_0 [z \bar{J}^2 - \epsilon_{\mathbf{k}}(\epsilon_{\mathbf{k}} + \omega_0)] + 16g^4 N(\epsilon_{\mathbf{k}}) [z \bar{J}^2 + \epsilon_{\mathbf{k}}^2] n_0(n_0 + 1) + O(g^6) = \sum_{l=1}^{\infty} z \bar{J}^2 S_l(\mathbf{k}; g^2) N(\epsilon_{\mathbf{k}} - l\omega_0) + 8g^2 N(\epsilon_{\mathbf{k}} + \omega_0) n_0 [z \bar{J}^2 - \epsilon_{\mathbf{k}}(\epsilon_{\mathbf{k}} + \omega_0)] + 16g^4 N(\epsilon_{\mathbf{k}}) [z \bar{J}^2 + \epsilon_{\mathbf{k}}^2] n_0(n_0 + 1). \quad (\text{B16})$$

At high T , the exciton bandwidth becomes smaller than ω_0 , so that only the $l=0$ term in Eq. (B14) remains, and

$$\Gamma_{\mathbf{k}\mathbf{k}}^{(2)} \cong 2 \int d\epsilon N(\epsilon) [z\tilde{J}^2 + \epsilon\epsilon_{\mathbf{k}}] F_0(\epsilon - \epsilon_{\mathbf{k}})$$

if the exciton bandwidth is *smaller* than the phonon bandwidth, we have

$$\begin{aligned} \Gamma_{\mathbf{k}\mathbf{k}}^{(2)} &\cong 2z\tilde{J}^2 F_0^R \\ &= \frac{2z\tilde{J}^2}{\omega_b} \int_0^\infty d(\omega_b t) [I_0(yA(t)) - 1] \\ &= \frac{2z\tilde{J}^2}{3\omega_b} \int_0^y dx \frac{I_0(x) - 1}{x} \quad \text{if } A(t) = e^{-3\omega_b t} \\ &\cong \frac{2z\tilde{J}^2}{3\omega_b} \frac{e^y}{(2\pi y^3)^{1/2}} \quad \text{for large } y \\ &\cong \frac{2z\tilde{J}^2}{3\omega_b} \frac{y^2}{8} \quad \text{for small } y. \end{aligned} \tag{B17}$$

If the exciton bandwidth is *larger* than the phonon bandwidth, we have

$$\begin{aligned} \Gamma_{\mathbf{k}\mathbf{k}}^{(2)} &\cong 2 \int_{\epsilon_{\mathbf{k}}-3\omega_b}^{\epsilon_{\mathbf{k}}+3\omega_b} d\epsilon N(\epsilon) [z\tilde{J}^2 + \epsilon\epsilon_{\mathbf{k}}] F_0^R(\epsilon - \epsilon_{\mathbf{k}}) \\ &\cong 2N(\epsilon_{\mathbf{k}}) [z\tilde{J}^2 + \epsilon_{\mathbf{k}}^2] 6\omega_b F_0^R \\ &= 4N(\epsilon_{\mathbf{k}}) [z\tilde{J}^2 + \epsilon_{\mathbf{k}}^2] \frac{e^y}{(2\pi y^3)^{1/2}} \quad \text{for large } y \\ &= 4N(\epsilon_{\mathbf{k}}) [z\tilde{J}^2 + \epsilon_{\mathbf{k}}^2] \frac{y^2}{8} \quad \text{for small } y. \end{aligned} \tag{B18}$$

If, for this case, $N(\epsilon_{\mathbf{k}}) = 0$ (e. g., at the top or bottom of the band) we have to be more careful of the integral. For the bottom of the band we have

$$\begin{aligned} \Gamma_{\mathbf{k}\mathbf{k}}^{(2)} &\cong 2 \int_{\epsilon_{\mathbf{k}}}^{\epsilon_{\mathbf{k}}+3\omega_b} d\epsilon N(\epsilon) [z\tilde{J}^2 + \epsilon_{\mathbf{k}}^2] F_0(\epsilon - \epsilon_{\mathbf{k}}) \\ &\cong 2[z\tilde{J}^2 + \epsilon_{\mathbf{k}}^2] N\left(\epsilon_{\mathbf{k}} + \frac{3\omega_b}{2}\right) F_0^R(3\omega_b) \end{aligned}$$

$$\begin{aligned} &\approx 2[z\tilde{J}^2 + \epsilon_{\mathbf{k}}^2] N\left(\epsilon_{\mathbf{k}} + \frac{3\omega_b}{2}\right) y^2/8 \quad \text{for small } y \\ &\approx 2[z\tilde{J}^2 + \epsilon_{\mathbf{k}}^2] N\left(\epsilon_{\mathbf{k}} + \frac{3\omega_b}{2}\right) \frac{e^y}{(2\pi y^3)^{1/2}} \quad \text{for large } y. \end{aligned}$$

APPENDIX C

There are some typographical errors in Ref. 1, specifically in Eqs. (5.3) and (5.5) as well as some numerical errors in Table II. In Eq. (5.3), J should be replaced by \tilde{J} . In Eq. (5.4) $|J|e^{-J^2}$ should be replaced by $|\tilde{J}|$ in the argument of the Bessel functions and by $|\tilde{J}| \cosh\beta\omega_p/2$ in the term multiplying the Bessel functions. In addition, the last column of Table II, labeled f_{min} , should be replaced by 0.275, 0.830, 1.38, 2.000, 0.300, 0.950, 1.50, 2.0, 0.088, 0.175, 0.370, 2.0, 2.1, 2.5, 0.060, 0.125, 0.200, 1.75, 2.00, 0.040, 0.080, 1.48, 0.135, 2.0.

The conclusions of the article are unaffected.

- ¹D. R. Yarkony and R. Silbey, *J. Chem. Phys.* **65**, 1042 (1976).
- ²R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Britten, B. W. Downs, and J. Downs (Interscience, New York, 1961), Vol. III.
- ³M. Grover and R. Silbey, *J. Chem. Phys.* **54**, 4843 (1971); S. Rackovsky and R. Silbey, *Mol. Phys.* **25**, 61 (1973); I. Abram and R. Silbey, *J. Chem. Phys.* **63**, 2317 (1975).
- ⁴V. M. Kenkre and R. Knox, *Phys. Rev. B* **9**, 5279 (1974); V. M. Kenkre, *Phys. Rev. B* **11**, 1741 (1975); **12**, 2150 (1975); V. M. Kenkre and T. Rahman, *Phys. Lett. A* **50**, 170 (1974).
- ⁵H. Haken and G. Strobl, *Z. Phys.* **262**, 135 (1973); H. Haken and P. Reinecker, *Z. Phys.* **249**, 253 (1972); **250**, 300 (1972).
- ⁶T. Holstein, *Ann. Phys. (N. Y.)* **8**, 325 (1959).
- ⁷K. Cho and Y. Toyozawa, *J. Phys. Soc. Japan* **30**, 1555 (1971); H. Sumi, *J. Phys. Soc. (Japan)* **32**, 616 (1972).
- ⁸D. Emin, *Adv. Phys.* **22**, 57 (1973); D. Emin, *Adv. Phys.* **24**, 305 (1975); E. Gorham-Bergeron and D. Emin, *Phys. Rev. B* **15**, 3667 (1977).
- ⁹R. W. Munn and R. Silbey (unpublished work).
- ¹⁰B. H. Loo, A. H. Francis, and K. W. Hipps, *J. Chem. Phys.* **65**, 5068 (1977) and references therein.