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present calculations is at least as good as obtained with the assumptions of Singh *et al.* The results are of course somewhat sensitive to the potential parameters used, but the present experimental uncertainty is too large to justify any definite conclusions. For instance, if the preaveraged potential parameters for NH_3 obtained⁸ from viscosity are used ($\epsilon_0/k=340^\circ\text{K}$, $\sigma_0=3.13 \text{ \AA}$, $\delta=0.7$), the values of $RT\alpha/b_0$ in Table II are changed to -2.72 and -2.50 , respectively.

IV. CONCLUDING REMARKS

The treatment of Stogryn and Hirschfelder makes several approximations which are valid only for (12-6) potentials, such as Eq. (12). Singh *et al.* assume that such approximations are also valid for their potential. Values of α are very sensitive to the parameter ratios given by Eq. (12), for instance. Since the averaged

potential preserves the (12-6) form, no new assumptions are necessary, and since its use is relatively simple, it could also be extended for any type of angular-dependent potential.

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Exciton Migration in Molecular Crystals*

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The migration of Frenkel excitons in molecular crystals is studied theoretically, starting from the microscopic equations of motion for the exciton density. The migration process is found to be diffusionlike on a long time scale for all temperatures as long as the exciton-phonon coupling is present. If there is no exciton-phonon coupling, the migration is wavelike. A discussion of the relevant time scales for the wavelike (coherent) process and the diffusion (incoherent) process is given. Several different approximation techniques, based on the cumulant expansion, projection operator, and functional derivative methods, are shown to be mathematically equivalent as applied to this problem.

I. INTRODUCTION

The migration of Frenkel excitons in molecular crystals has been the subject of investigation in recent years.¹ In those cases studied over a wide temperature, the exciton mobility has been found experimentally to have a rather involved temperature dependence, decreasing rapidly at first as the temperature increases from 0°K then becoming constant and finally exhibiting a very gradual increase with temperature, usually in the range $200\text{--}400^\circ\text{K}$. It has also been established that the exciton density may be fitted to a macroscopic diffusion equation in the high temperature region and that, under these conditions, the exciton migration is probably best regarded as a form of random walk. Such observations, of course, relate only to the macroscopic properties of inevitably impure and imperfectly crystalline substances. The fundamental processes involved in this energy transport are still not well understood theoretically.

A number of theoretical approaches to this problem

have already been reported.² Many of these investigations are limited by the assumption of a specific model for the migration process. In a more general treatment, Haken and Strobl³ have introduced a stochastic model for the exciton Hamiltonian which leads to an exact solution and which describes, in different limits, both coherent and incoherent (hopping) motion. Perhaps even more informative, however, has been the perturbation-theoretic approach adopted by several authors⁴ in the study of both exciton and polaron migration. Beginning with a model Hamiltonian, ordinary time dependent perturbation theory is used to obtain a formal expression for the probability of an exciton moving between two different lattice sites. It is found that the terms in this expression corresponding to coherent motion, in which an exciton moves without disturbing the thermal equilibrium of the lattice, decrease in importance with increasing temperature while the terms corresponding to incoherent motion, in which exciton migration is always accompanied by a change in the thermal phonon dis-

tribution, increase in importance as the temperature is raised. Unfortunately, the perturbation theory diverges in practice and one is ultimately forced to treat these two forms of motion separately by adopting a model of purely coherent migration in the low temperature limit and a hopping model in the limit of high temperatures. Even in this approach the coherent motion has been treated phenomenologically as a diffusion process, although, as we shall see, it is actually quite different in nature; and the incoherent motion has typically been treated in a manner which is inappropriate for the high temperature range where this form of exciton transport is apparently most significant.

In order to overcome these difficulties and to improve upon the theoretical basis of our understanding of these processes, we present in this article an approach to the exciton migration problem which is not subject to the limitations of perturbation theory, in its usual form, and which *does not require the assumption of a specific model for the migration process*. The paper is set out as follows. In Sec. II we describe a model exciton-phonon Hamiltonian which is identical to that discussed in an earlier article⁵ on the optical properties of molecular crystals. We also obtain at this point a formal expression for the microscopic exciton density, the evaluation of which will form the basis of our analysis. In Sec. III we use the cumulant expansion techniques of Kubo⁶ to obtain an approximate solution to the equations of motion for exciton density. In Sec. IV the dependence of this solution upon the details of the phonon dispersion relation is discussed, and in Sec. V the results of this analysis are applied to the problem of exciton migration. Section VI contains a discussion of some of the assumptions involved in our approach and some further conclusions which may be drawn regarding the relationship between the present study and earlier investigations of this problem. In a series of appendices it is shown that our results may also be obtained in a more general form through a number of other common approximation techniques.

II. FORMULATION OF THE PROBLEM

We will consider a model system with one band of Frenkel excitons and several bands of optical phonons. The model Hamiltonian, which has been discussed at length in an earlier article,⁵ may be written as

$$\mathcal{H} = \mathcal{H}_{\text{ex}} + \mathcal{H}_{\text{ph}} + \mathcal{H}', \quad (1)$$

where

$$\mathcal{H}_{\text{ex}} = \sum_k \epsilon(k) a_k^+ a_k, \quad (2)$$

$$\mathcal{H}_{\text{ph}} = \sum_{\lambda\alpha} \omega_{\lambda\alpha} b_{\lambda\alpha}^+ b_{\lambda\alpha}, \quad (3)$$

and

$$\mathcal{H}' = N^{-1/2} \sum_{k,\lambda,\alpha} f(k,\lambda)^{(\alpha)} a_{k+\lambda}^+ a_k (b_{\lambda\alpha} + b_{-\lambda\alpha}^+). \quad (4)$$

Here a_k^+ , a_k are the creation and annihilation operators

for an exciton of wave vectors \mathbf{k} . Similarly, $b_{\lambda,\alpha}^+$ and $b_{\lambda,\alpha}$ create and destroy, respectively, a phonon of wave vector λ in band α . Both the exciton and phonon operators are assumed to satisfy Bose-Einstein commutation relations. For notational convenience we will drop the phonon band indices throughout most of the following and will discuss at a later point the generalization of our results to systems with several bands of optical phonons (a qualitative discussion of the effects of acoustic phonons is given in Sec. V).

For optical phonons in molecular crystals the exciton-phonon interaction term, \mathcal{H}' , cannot generally be treated as a small perturbation. On the other hand, the dispersion of $\epsilon(k)$, the free exciton energy, is usually very small due to the weak intermolecular forces. We may take advantage of this fact by introducing a new set of operators (we assume periodic boundary conditions for the crystal):

$$A_n = e^{-S} N^{-1/2} \sum_k \exp(-ikn) a_k e^S = e^{-S} a_n e^S \quad (5)$$

and

$$B_\lambda = e^{-S} b_\lambda e^S, \quad (6)$$

where

$$S = N^{-1/2} \sum_{n,\lambda} X_\lambda^n a_n^+ a_n (b_{\lambda^+} - b_{-\lambda}) \quad (7)$$

and

$$X_\lambda^n = N^{-1} \exp(i\lambda n) \sum_k [f(k, \lambda) / \omega_\lambda] = \exp(i\lambda n) C_\lambda. \quad (8)$$

In terms of these new operators, we may write

$$\begin{aligned} \mathcal{H} = & \sum_n (E_0 - N^{-1} \sum_\lambda |X_\lambda^n|^2 \omega_\lambda) A_n^+ A_n + \sum_\lambda \omega_\lambda B_\lambda^+ B_\lambda \\ & + \sum_{nm} J_{n-m} A_n^+ A_m \theta_n + \theta_m \\ & + N^{-1/2} \sum_{\substack{nm\lambda \\ n \neq m}} F_{\lambda}^{nm} \theta_n^+ (B_\lambda^+ + B_{-\lambda}) \theta_m A_n^+ A_m, \end{aligned} \quad (9)$$

where

$$\theta_n = \exp[-N^{-1/2} \sum_\lambda X_\lambda^n (B_\lambda^+ - B_{-\lambda})], \quad (10)$$

$$\epsilon(k) = E_0 + \sum_{n \neq 0} e^{ikn} J_n, \quad (11)$$

and

$$F_{\lambda}^{nm} = N^{-1} \sum_k e^{-ikn} \exp[i(k+\lambda)m] f(k, \lambda), \quad n \neq m. \quad (12)$$

In obtaining Eq. (9) we have restricted ourselves to the space of states with total exciton number zero or one. This is a reasonable approach to the study of processes which occur at low exciton densities in real crystals. Because of this restriction the exciton statistics are no longer a factor, and our model becomes formally identical to the small polaron model used to study electron migration in insulators.⁴

It is this representation of the exciton-phonon Hamiltonian which will form the basis of our approach. The operators A_n^+ , A_n create and destroy at lattice site n an excitation described as a "clothed" exciton, i.e., an electronic excitation accompanied by a vibrational distortion which changes the center of nuclear motion of the crystal from that of the ground state vibrational potential to that of the excited state potential. This new excitation is stationary with respect to the major part of the exciton-phonon interaction. In this representation both the third and fourth terms on the right-hand side of Eq. (9) are nondiagonal and may, in some manner, be treated as perturbations. In the following analysis, however, we will only deal explicitly with the third term. The fourth term, which describes a vibrationally induced interaction between different lattice sites, has little effect if the intermolecular forces are weak, and will be neglected in the present study. We have also neglected exciton-phonon interaction terms which are quadratic in the phonon operators.^{4c} Some of these terms can be included in an analogous fashion to the linear terms and will lead to slightly different Franck-Condon factors. Because optical mode frequency shifts on excitation are usually small in molecular crystals of benzene, etc., these terms also lead to very small effects in the limit of weak intermolecular interactions and will be neglected.

We may then write the Hamiltonian in the clothed exciton representation as

$$\mathcal{H} = \sum_k \tilde{\epsilon}(k) A_k^+ A_k + \sum_\lambda \omega_\lambda B_\lambda^+ B_\lambda + \sum_{k,k'} V_{kk'} A_k^+ A_{k'}, \quad (13)$$

where

$$A_k = N^{-1/2} \sum_n \exp(ikn) A_n, \quad (14)$$

$$\tilde{\epsilon}(k) = E_0 - N^{-1} \sum_\lambda |X_\lambda^n|^2 \omega_\lambda + \sum_{n \neq 0} \exp(ikn) J_n \langle \theta_{n+m} + \theta_m \rangle, \quad (15)$$

and

$$V_{kk'} = N^{-1} \sum_{\substack{n,m \\ n \neq m}} \exp(ikn) \times \exp(-ik'm) J_{n-m} (\theta_n + \theta_m - \langle \theta_n + \theta_m \rangle). \quad (16)$$

The angle brackets around the phonon operators denote an average with respect to the thermal free phonon ensemble ($\mathcal{H}_{\text{ph}} = \sum_\lambda \omega_\lambda B_\lambda^+ B_\lambda$). In this form the major part of both the exciton-phonon interaction and the intermolecular electronic interaction are included in the diagonal part of the Hamiltonian. The terms $\{V_{kk'}\}$, which correspond to fluctuations of the exciton bandwidth about its value in the equilibrium free phonon ensemble, must still be treated as a perturbation in this representation; however, it will be possible to do this in a manner which entirely avoids

the divergences encountered in ordinary perturbation theory.

The object of principal interest to us will be the microscopic exciton density. More specifically, if one knows that an exciton has been created by an optical transition at time t_2 and lattice site m in a crystal which was initially at thermal equilibrium, then we wish to know the probability of finding an exciton at any lattice site m' at any later time t_1 . This probability is just the microscopic exciton density and will be denoted $P_n(t)$ ($n = m' - m$; $t = t_1 - t_2$).

To calculate $P_n(t)$, we must first discuss the nature of the species which is moving through the crystal. Clearly, if the exciting quantum of light is equal in energy to the clothed exciton energy, then the transport will be initiated by that species. However if the crystal is illuminated by a broad source, then by the Franck-Condon principle the most likely state to which the crystal is excited is that due to a vertical excitation. The crystal becomes excited without any change in its vibrational motion, which is therefore determined by the ground state potential and the temperature. This is precisely the kind of electronic excitation which is created by the operator a_m^+ defined in Eq. (5). However, this type of excitation will rapidly (in times like 10^{-12} sec⁷) exchange phonons with the bath via the exciton-phonon interaction, and thereby reaching vibrational equilibrium with the potential of the excited state, thus becoming clothed. Thus, the species which is migrating (at least on a long time scale) through the crystal is the clothed exciton; hence in order to discuss the nature of energy transfer, the microscopic exciton density is taken to be

$$P_n(t) = \langle A_0 A_n^+(t) A_n(t) A_0^+ \rangle, \quad (17)$$

where the operators $A_n(t)$ and $A_n^+(t)$ are in the Heisenberg representation and the bracket represents a thermal average over the canonical ensemble. We have also taken $m=0$ and $t_2=0$ for convenience. It is this expression which we will attempt to calculate in order to learn about the process of energy transport in molecular crystals.

III. APPROXIMATION TECHNIQUES

In this section we will consider a method for obtaining an approximation to the exciton density which is based upon a truncated cumulant expansion of the time evolution operator as it appears in $P_n(t)$. Whenever $kT = \beta^{-1} \ll E_0$, we may write Eq. (17) as

$$P_n(t) = \langle 0 | A_0 \langle A_n^+(t) A_n(t) \rangle A_0^+ | 0 \rangle, \quad (18)$$

where the inner angle brackets again denote a thermal phonon average and the ket vector $|0\rangle$ represents the electronic and vibrational ground state of our model system. If we define an operator superscript "x"⁶ so

that for any two operators A, B

$$A^*B \equiv [A, B] \equiv AB - BA, \tag{19}$$

then we may write

$$\langle A_n^+(t) A_n(t) \rangle = \langle \exp(iH^*t) \rangle A_n^+ A_n, \tag{20}$$

and if

$$3\mathcal{C}_0 = \sum_k \tilde{\epsilon}(k) A_k^+ A_k + \sum_\lambda \omega_\lambda B_\lambda^+ B_\lambda$$

and

$$V = \sum_{k,k'} V_{kk'} A_k^+ A_{k'} \\ = \sum_{n,m} J_{n-m} (\theta_n^+ \theta_m - \langle \theta_n^+ \theta_m \rangle) A_n^+ A_m, \tag{21}$$

we get the result

$$\langle A_n^+(t) A_n(t) \rangle = \left\langle \exp_T \left(i \int_0^t V^*(\tau) d\tau \right) \right\rangle \\ \times \exp \left[i t \sum_k \tilde{\epsilon}(k) (A_k^+ A_k)^* \right] A_n^+ A_n, \tag{22}$$

where $V^*(\tau)$ is in the interaction representation with respect to H_0 and where the subscript “ T ” means that all products of such operators are to be time ordered with latest times appearing to the left.

We may represent the first exponential in (22) by a cumulant expansion⁶

$$\left\langle \exp_T \left(i \int_0^t V^*(\tau) d\tau \right) \right\rangle = \exp \left[\sum_{n=1}^{\infty} K_n^*(t) (n!)^{-1} \right]. \tag{23}$$

The first few terms in this expansion are

$$K_1^*(t) = i \int_0^t \langle V^*(\tau) \rangle d\tau = 0, \\ K_2^*(t) = - \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle V^*(\tau_1) V^*(\tau_2) \rangle. \tag{24}$$

Since we are able to treat V as a small perturbation, we will retain in the cumulant expansion only terms up to order V^2 . This yields

$$\left\langle \exp \left(i \int_0^t V^*(\tau) d\tau \right) \right\rangle \cong \exp \left[\frac{1}{2} K_2^*(t) \right]. \tag{25}$$

For the set of functions $[G_{n,m}(t)]$, defined as

$$G_{n,m}(t) = \langle 0 | A_0 \langle A_n^+(t) A_m(t) \rangle A_0^+ | 0 \rangle, \tag{26}$$

we may differentiate with respect to time and obtain the equation of motion at this level of approximation

$$dG_{nm}(t)/dt = i \sum_p [\tilde{J}_{n-p} G_{pm}(t) - \tilde{J}_{p-m} G_{np}(t)] \\ - \int_0^t d\tau \sum_{rspq} \tilde{J}_{r-s} \tilde{J}_{p-q} [g_{rspq}(\tau) - 1] \\ \times [U_{psnq}(\tau) G_{rm}(t) + U_{pmrq}(\tau) G_{ns}(t)] \\ - \sum_{rspq} \{ \tilde{J}_{m-s} \tilde{J}_{p-q} [g_{mspq}(\tau) - 1] U_{prnq}(\tau) G_{rs}(t) \\ + \tilde{J}_{r-n} \tilde{J}_{p-q} [g_{rnpq}(\tau) - 1] U_{pmsq}(\tau) G_{rs}(t) \}, \tag{27}$$

where $U_{rspq}(t) = [\exp(-i5\mathcal{C}_0 t)]_{rs} [\exp(i5\mathcal{C}_0 t)]_{pq}$,

$$\tilde{J}_n = J_n \langle \theta_n^+ \theta_m \rangle \\ = J_n \exp[-N^{-1} \sum_\lambda |X_\lambda|^2 (1 - \cos \lambda t) \coth(\beta \omega_\lambda / 2)] \tag{28}$$

and

$$g_{nmpq}(t) = \langle \theta_n^+(t) \theta_m(t) \theta_p^+ \theta_q \rangle / \langle \theta_n^+ \theta_m \rangle \langle \theta_p^+ \theta_q \rangle \\ = \exp \left\{ -N^{-1} \sum_\lambda C_\lambda^2 [(e^{i n \lambda} - e^{i m \lambda}) (e^{-i p \lambda} - e^{-i q \lambda}) N_\lambda \right. \\ \times \exp(i \omega_\lambda t) + (e^{-i n \lambda} - e^{-i m \lambda}) (e^{i p \lambda} - e^{i q \lambda}) (N_\lambda + 1) \\ \left. \times \exp(-i \omega_\lambda t) \right\}, \tag{29}$$

$$N_\lambda = [\exp(\beta \omega_\lambda) - 1]^{-1}. \tag{30}$$

The mathematical details involved in obtaining Eqs. (28) and (29) are discussed elsewhere.⁵ We have in (27) a closed set of integro-differential equations for the functions $\{G_{n,m}(t)\}$, the solution of which would yield (for $n=m$) an expression for $P_n(t)$. As we shall see in Appendices A and B an identical set of equations may be obtained from considerations based upon either a projection operator⁸ or functional derivative technique.⁹

In order to proceed, we make the weak coupling approximation; that is, we assume that $g_{nmpq}(t-\tau) - 1$ decays so quickly that we may effectively replace $U_{rspq}(\tau)$ by $\delta_{rs} \delta_{pq}$ to find:

$$dG_{nm}(t)/dt = i \sum_p [\tilde{J}_{n-p} G_{pm}(t) - \tilde{J}_{m-p} G_{np}(t)] \\ - \sum_{pr} [\tilde{J}_{r-p} \tilde{J}_{p-n} \gamma_{rppn}(t) G_{rm}(t) \\ + \tilde{J}_{p-r} \tilde{J}_{m-p} \gamma_{prmp}(t) G_{nr}(t) - \tilde{J}_{m-r} \tilde{J}_{p-n} \gamma_{mrpn}(t) G_{pr}(t) \\ - \tilde{J}_{p-n} \tilde{J}_{m-r} \gamma_{pnmr}(t) G_{pr}(t)], \tag{31}$$

where

$$\gamma_{nmpq}(t) = \int_0^t d\tau [g_{nmpq}(t-\tau) - 1]. \tag{32}$$

The validity of this approximation will be discussed later. We will now examine the factors $\gamma_{nmpq}(t)$.

In the Einstein approximation ($\omega_\lambda = \omega$), a limit which is surely closely approached by real molecular crystals, $\gamma_{n,m,p,q}(t) = 0$ except in the following cases:

- (a) both $n=q$ and $m=p$, $\gamma_{n,m,m,n}(t) = \gamma_1(t)$;
- (b) either $n=q$ or $m=p$, $\gamma_{n,m,p,n}(t) = \gamma_2(t)$;
- (c) either $n=p$ or $m=q$, $\gamma_{n,m,n,q}(t) = \gamma_3(t)$;
- (d) both $n=p$ and $m=q$, $\gamma_{n,m,n,m}(t) = \gamma_4(t)$. (33)

Of these $\gamma_1(t)$ and $\gamma_4(t)$ give the largest contribution, and within our approximations (see later) these two are equal. Retaining only terms of this kind, and making the nearest neighbor approximation, we find

(where $\tilde{J}_n = \delta_{n,\pm 1}\tilde{J}$),

$$\begin{aligned} d\mathcal{G}_{nm}(t)/dt &= i\tilde{J}[\mathcal{G}_{n+1,m}(t) + \mathcal{G}_{n-1,m}(t) - \mathcal{G}_{n,m+1}(t) - \mathcal{G}_{n,m-1}(t)] \\ &- 2\tilde{J}^2\gamma_1(t)[2\mathcal{G}_{nm}(t) - \mathcal{G}_{n+1,m+1}(t)\delta_{nm} - \mathcal{G}_{n-1,m-1}(t)\delta_{nm} \\ &\quad - \delta_{n,m+1}\mathcal{G}_{mn} - \delta_{n,m-1}\mathcal{G}_{mn}]. \end{aligned} \quad (34)$$

Note that in the limit in which $T=0$, $\gamma_1=0$, and we find:

$$\mathcal{G}_{nm}^{(0)}(t) = I_n(2i\tilde{J}t)I_m(-2i\tilde{J}t), \quad (35)$$

where I_m is a modified Bessel function. This agrees with Merrifield.^{2b} We find:

$$\begin{aligned} \langle R^2(t) \rangle^{(0)} &\equiv a^2 \sum_{n=-\infty}^{\infty} n^2 P_n^{(0)}(t) = a^2 \sum_{n=-\infty}^{\infty} n^2 \mathcal{G}_{nn}^{(0)}(t) = 2\tilde{J}^2 t^2 a^2, \end{aligned} \quad (36)$$

where a is the lattice constant. Thus, in this limit, the transport is not diffusion like, but coherent and wave-like.

Also, in the limit in which \tilde{J} can be neglected with respect to $\tilde{J}^2\gamma_1(t)$ (extremely high temperature), we find

$$\mathcal{G}_{nn}^{(\infty)}(t) = I_n \left[4\tilde{J}^2 \int_0^t \gamma_1(\tau) d\tau \right] \exp \left[-4\tilde{J}^2 \int_0^t \gamma_1(\tau) d\tau \right] \quad (37)$$

and

$$\langle R^2(t) \rangle^\infty = 4\tilde{J}^2 a^2 \int_0^t \gamma_1(\tau) d\tau. \quad (38)$$

We will show in Sec. IV that $\gamma_1(t)$ reaches its asymptotic value for t small compared to exciton lifetimes, and thus,

$$\langle R^2(t) \rangle^\infty = 4\tilde{J}^2 a^2 t \gamma_1(\infty) \quad (39)$$

so that this process is diffusionlike with diffusion coefficient $D = 2\tilde{J}^2 a^2 \gamma_1(\infty)$.

In the general case, we will be interested in the solution of Eq. (34) for long times and general T . We may then replace $\gamma_1(t)$ by $\gamma_1(\infty)$. We also introduce new functions $G_{nm}(t) = \exp[4\tilde{J}^2 t \gamma_1(\infty)] \mathcal{G}_{nm}(t)$. Then using the fact that the Hamiltonian conserves k , we can write

$$G_{nm}(t) = \sum_K e^{iK n} g_{n-m}^K(t), \quad (40)$$

where $g_{n-m}^K(t)$ depends on $n-m$ only (we are of course considering the one dimensional case here). We find that the equation of motion of the $g_q^K(t)$ to be

$$\begin{aligned} \dot{g}_q^K(t) &= i\tilde{J}[(e^{iK}-1)g_{q+1}^K(t) + (e^{-iK}-1)g_{q-1}^K(t)] \\ &+ 4\tilde{J}^2\gamma_1(\infty)\delta_{q,0}\cos K g_0^K(t) + 2\tilde{J}^2\gamma_1(\infty) \\ &\times [\delta_{q,1}e^{-iK}g_{-1}^K(t) + \delta_{q,-1}e^{iK}g_1^K(t)]. \end{aligned} \quad (41)$$

From this we can directly derive an equation for $\langle R^2(t) \rangle = \sum_n \mathcal{G}_{nn}(t) n^2 a^2$ (see Appendix C for details).

$$\langle R^2(t) \rangle = a^2 [(2\alpha + 4\tilde{J}^2/3\alpha)t + (4\tilde{J}^2/9\alpha^2)(e^{-3\alpha t} - 1)], \quad (42)$$

where we have written

$$\alpha = 2\tilde{J}^2\gamma_1(\infty). \quad (43)$$

At very low temperatures, such that α is very small and for times such that αt is also small, we find

$$\langle R^2(t) \rangle = a^2(2\alpha t + 2\tilde{J}^2 t^2) \cong 2\tilde{J}^2 a^2 t^2, \quad (44)$$

while for high temperatures, such that \tilde{J} is small and α large, we find

$$\langle R^2(t) \rangle = 2\alpha t a^2. \quad (45)$$

These results agree with Eq. (36) and Eq. (38). Note, also that at very small t , such that $\gamma_1(t)$ is small (i.e., $t \ll 10^{-12}$ sec, see Sec. IV), we again find

$$\langle R^2(t) \rangle = 2\tilde{J}^2 t^2 a^2 + O(t^3). \quad (46)$$

Finally, at very large t , we find:

$$\lim_{t \rightarrow \infty} \langle R^2(t) \rangle / t = (\frac{4}{3}\tilde{J}^2/\alpha + 2\alpha) a^2. \quad (47)$$

Thus, the diffusion coefficient is given by

$$D = (\frac{2}{3}\tilde{J}^2/\alpha + \alpha) a^2. \quad (48)$$

In the next section, we discuss the evaluation of $\gamma_1(\infty)$.

IV. MODELS OF PHONON DISPERSION

The function $\gamma_1(t)$ defined in (36) depends significantly upon the dispersion of the phonon bands. We will consider the details of this relationship in this section before proceeding to the discussion of exciton transport phenomena in Sec. V. We may write that

$$\begin{aligned} \gamma_1(t) &\cong \int_0^t d\tau \{ \exp\{-2N^{-1} \sum_{\lambda,\alpha} C_{\lambda\alpha}^2 \\ &\times [N_{\lambda\alpha} \exp(i\omega_{\lambda\alpha}\tau) + (N_{\lambda\alpha} + 1) \exp(-i\omega_{\lambda\alpha}\tau)]\} - 1 \}, \end{aligned} \quad (49)$$

where α is a phonon band index. The major dispersion is in $\omega_{\lambda,\alpha}$ so that if the temperature is not too low we may take $C_{\lambda,\alpha}^2 \approx C_\alpha^2$ and $N_{\lambda,\alpha} \approx N_\alpha$ to obtain (as $N \rightarrow \infty$)

$$\begin{aligned} \gamma_1(t) &= \int_0^t d\tau \{ \prod_\alpha \exp[-2C_\alpha^2 N_\alpha A_\alpha(\tau) \exp(i\omega_\alpha^0\tau) \\ &+ (-2C_\alpha^2)(N_\alpha + 1)A_\alpha^*(\tau) \exp(-i\omega_\alpha^0\tau)] - 1 \}, \end{aligned} \quad (50)$$

where

$$\begin{aligned} A_\alpha(t) &= \frac{1}{2\pi} \int_{-\pi}^{+\pi} d\lambda \exp[i(\omega_{\lambda\alpha} - \omega_\alpha^0)t] \\ &= \int_{-\infty}^{\infty} d\omega \rho^\alpha(\omega) e^{i\omega t}. \end{aligned} \quad (51)$$

Here ω_α^0 is the center of the band, $\rho^{(\alpha)}(\omega)$ is the density

of phonon states in the band, and $\omega = \omega_{\lambda, \alpha} - \omega_{\alpha}^0$. We may also note that, since we are ultimately to be concerned only with the long time behavior of $\gamma_1(t)$, the purely oscillatory terms in the integrand of (50) may be dropped to obtain, in the absence of degeneracies,

$$\gamma_1(t) = \int_0^t d\tau \left(\prod_{\alpha} I_0 \{ 2C_{\alpha}^2 [N_{\alpha}(N_{\alpha}+1)]^{1/2} | A_{\alpha}(\tau) | \} - 1 \right) \quad (52)$$

where $I_0(x)$ is a modified Bessel function. Note, at this level of approximation, $\gamma_1 = \gamma_4$.

Let us now consider a few specific models of phonon dispersion. The first model is that of a Lorentzian density of states

$$\rho^{(1)}(\omega) = [(\Delta/\pi)/(\Delta^2 + \omega^2)], \quad (53)$$

and from (51) we obtain

$$A^{(1)}(\tau) = e^{-\Delta\tau}. \quad (54)$$

Here Δ is the phonon band width, and we may generally expect Δ to be 1 to 10 cm^{-1} for optical phonons in molecular crystals. We will consider also the case of a Gaussian density of phonon states

$$\rho^{(2)}(\omega) = (1/\Delta\pi^{1/2}) \exp(-\omega^2/\Delta^2) \quad (55)$$

which yields

$$A^{(2)}(\tau) = \exp(-\Delta^2\tau^2/4). \quad (56)$$

We may note at this point that whenever t is of the order of a typical exciton lifetime or greater the quantity Δt is a very large number and $e^{-\Delta t}$ or $\exp[-(\Delta t/2)^2]$ is correspondingly very small. The integrand in Eq. (52) becomes very small for $\tau \gg 10^{-11}$ sec ($\Delta = 1-10 \text{ cm}^{-1}$) as long as T is not too high and we may therefore extend the upper limit of the integral to infinity. In this way we obtain, for a Lorentzian density of phonon states,

$$\gamma_1^{(1)}(\infty) = \sum_{\{l_{\alpha}\}} \prod_{\alpha} \{ [4C_{\alpha}^4 N_{\alpha}(N_{\alpha}+1)]^{l_{\alpha}} / (l_{\alpha}!)^2 \} \times (1/2 \sum_{\alpha} l_{\alpha} \Delta_{\alpha}), \quad (57)$$

and in the case when only one phonon band is strongly coupled with the exciton band, this is essentially

$$\gamma_1^{(1)}(\infty) = (2\Delta)^{-1} \sum_{l=1}^{\infty} \frac{[4C^4 N(N+1)]^l}{l(l!)^2} \quad (58)$$

or

$$\gamma_1^{(1)}(\infty) = \Delta^{-1} \left[\int_0^z \left[\frac{I_0(x) - 1}{x} \right] dx \right] \quad (58')$$

with

$$z = 2C^2 \text{csch} \frac{1}{2} \beta \omega^0.$$

Using the asymptotic form of the integral¹⁰ we find

$$\gamma_1^{(1)}(\infty) \cong (0.4/\Delta) (e^z/z^{3/2}). \quad (58'')$$

The corresponding expression to Eq. (58) for the case

of a Gaussian density of states is just

$$\gamma_1^{(2)}(\infty) = \frac{(\pi/2)^{1/2}}{\Delta} \sum_{l=1}^{\infty} \frac{[4C^4 N(N+1)]^l}{l^{1/2}(l!)^2}. \quad (59)$$

It will be interesting to consider briefly one further model of phonon dispersion, which is specified by

$$\omega(k) = \omega_0 + \Delta \cos k.$$

This occurs in the nearest-neighbor approximation, taken to first order in (Δ/ω_0) . The density of states in this case is highly singular at the zone boundaries. It is essentially this model of phonon dispersion which is considered exclusively by Holstein and others.⁴ We may show that

$$A(\tau) = \int_0^{\Delta\tau} \mathcal{J}_0(\Delta\tau) \quad (60)$$

$\mathcal{J}_0(x)$ being a Bessel function, and we have, at low temperatures,

$$\gamma_1(\infty) = \left[4C^4 N(N+1) \int_0^{\infty} \mathcal{J}_0^2(\Delta t) dt \right]. \quad (61)$$

The integral in (61) is closely related to a form which has been previously evaluated approximately by the method of steepest descents.^{4a} However, it can be seen here that this integral diverges and that this model of phonon dispersion is apparently pathological when studied by these methods.

V. APPLICATION TO EXCITON TRANSPORT

Most theoretical and experimental approaches to the problem of exciton migration in molecular crystals have involved the assumption that the exciton motion is macroscopically a diffusion process. This has been shown experimentally to be the case for triplet excitons at room temperature. In most approaches, however, the experimental diffusion lengths and diffusion coefficients are measured only indirectly through techniques which do not test this basic assumption. Similarly, most theoretical studies of this problem provide formal expressions for the diffusion coefficient for a particular model of exciton migration without directly confirming that the migration process in question is actually diffusion like.

Using the results of Sec. III and IV, we may now discuss the transport of excitons in molecular crystals. From Eq. (48), the long time behavior is diffusive with a diffusion coefficient consisting of two terms, one of which (J^2/α) decreases with temperature and the other of which (α) increases with temperature and then decreases. In Table I, we have calculated D as a function of temperature for a typical set of parameter values in molecular crystals. In this calculation, we have assumed that only one band is strongly coupled. Addition of more bands with weak coupling does not change the qualitative behavior. The qualitative agreement with experiment is good.

Since the exciton will move in the crystal for a time equal to its lifetime, some interesting effects may be possible. For example, at very low temperatures, such that $\alpha\tau$ (where τ is the exciton lifetime) is small, the behavior of the migration should be very different from the long time or high temperature behavior. In this case, we find that the transport has a large component of coherent or wavelike behavior. For our simple calculation in Table I and $\tau = 10^{-7}$ sec, we find this behavior for $\beta\omega_0 > 15$. For a optical phonons of 500 cm^{-1} , this corresponds to $T < 40^\circ\text{K}$. However, at such low temperatures, trapping effects will be very important. Notice also that if the exciton phonon coupling is very weak (C_α very small), α will be small and the same result will occur.

It is important to note that as $T \rightarrow 0$, the expression (52) for $\gamma_1(\infty)$ gets smaller and our result for D gets large without limit. This result would be modified had we included exciton-acoustic-phonon interactions. Since the acoustic bands contain states whose frequencies vanish as the phonon wave vector goes to zero, then exciton-acoustic-phonon scattering processes can occur (even at $T=0$) which do not evolve in a purely oscillatory manner in time and hence may contribute to $\gamma_1(\infty)$. These processes can be included within the present formalism with little difficulty. The strength of the exciton-phonon coupling is much less for acoustic modes than for optical modes; thus, the effect of acoustic modes may be neglected except at very low T . At these low temperatures, the interaction of excitons with impurities and imperfections are extremely important.

Finally, we can look at the very high temperature results. In this case, $\gamma_1(\infty)$ can be approximated as in Eq. (58''), and we find

$$D \propto a^2 \exp(-2C^2 \tanh\beta\omega_0/4) (2C^2 \text{csch}\beta\omega_0/2)^{-3/2} \quad (62)$$

which is similar to Holstein.^{4a}

VI. CONCLUSIONS

In this study we have presented a discussion of the transport properties of excitons in molecular crystals. Using a simple model Hamiltonian for the exciton-phonon system, we derived an expression for the probability of excitation transport valid to second order in the fluctuation of the intermolecular interaction about its thermal average. The result is also exact in the limit of zero exciton-phonon interaction. The expression exhibits the characteristics of coherent motion at very low temperatures and weak exciton-phonon coupling and that of incoherent motion at high temperatures and strong coupling.

In addition to the restriction of our model to small fluctuations in the intermolecular coupling, we have assumed the phonon bands to be narrow. This assumption may be relaxed; however, the resulting expressions are difficult to evaluate in the simplest cases. We have

TABLE I. Diffusion coefficient for $\tilde{J}(T=0) = 1 \text{ cm}^{-1}$, $a = 5 \text{ \AA}$, $\Delta = 1 \text{ cm}^{-1}$, $c = 2$.

$\beta\omega_0$ ^a	$D = \frac{2}{3} \tilde{J}^2 a^2 \alpha^{-1} + \alpha a^2$ $\frac{2}{3} \tilde{J}^2 a^2 \alpha^{-1} (\text{cm}^2/\text{sec})$	$\alpha a^2 (\text{cm}^2/\text{sec})$
10	3.2×10^{-2}	0.75×10^{-7}
6	3.7×10^{-4}	0.6×10^{-6}
5	1.1×10^{-4}	0.2×10^{-4}
4	0.4×10^{-4}	0.4×10^{-4}
3	1.0×10^{-5}	0.8×10^{-4}
2	2.2×10^{-6}	0.9×10^{-4}
1.5	1.3×10^{-7}	1.7×10^{-4}
1.2	1.2×10^{-8}	1.9×10^{-4}
1.0	1.0×10^{-9}	2.4×10^{-4}

^a $\beta = (kT)^{-1}$.

also neglected quadratic terms^{4c} in the exciton-phonon coupling and acoustic mode coupling [which is usually weak, and thus our procedure may be inappropriate since then J_{nm} will not be small compared to $f(k, \lambda)$]. Some of these terms will give rise to local scattering effects (terms analagous to $\gamma_{mmmm}(t)$ in Eq. 33), which are absent in our model. Haken and Reineker^{3b} have treated the case in which the local scattering dominates the scattering. We have also neglected the terms F_{λ}^{nm} in Eq. (9). All of these approximations are justified in the limit that the temperature dependence of the Franck-Condon factors are the major cause of the exciton-phonon scattering. As we have argued, this should be true in the moderate to high temperature region for the organic molecular crystals such as naphthalene and anthracene. Finally, we have assumed a one-dimensional solid in many of our results. This makes the algebra extremely simple, and its extension to higher dimensions is straightforward but tedious. In a future publication, we intend to apply these results to the problem of exciton migration in impure crystals.

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APPENDIX A: FUNCTIONAL DERIVATIVE APPROACH⁹

Let us define the function $\tilde{G}_{ij}(t)$, element of $\mathbf{G}(t)$, as

$$\tilde{G}_{ij}(t) \equiv \langle \tilde{S} \rangle^{-1} \langle A_0 A_i^+(t) \tilde{S} A_j(t) A_0^+ \rangle, \quad (A1)$$

where all operators are in the Heisenberg representation, and

$$\tilde{S} = \exp_T \left(-i \int_{-\infty}^{+\infty} \sum_{nm} U_{nm}(t) C_{mn}(t) dt \right) \quad (A2)$$

and

$$V(t) = e^{iHt} V e^{-iHt} \equiv \sum_{\substack{nm \\ n \neq m}} C_{nm}(t) A_n^+(t) A_m(t). \quad (\text{A3})$$

The set $\{U_{n,m}(t')\}$ is some continuous function set with respect to which we may take functional derivatives of $\tilde{G}(t)$.

The equation of motion of $\tilde{G}_{ij}(t)$ is

$$i[d\tilde{G}_{ij}(t)/dt] = - \sum_n [A_0 C_{ni}(t) A_n^+(t) \tilde{S} A_i(t) A_0^+ - \langle A_0 A_i^+(t) \tilde{S} C_{jn}(t) A_j(t) A_0^+ \rangle] \langle \tilde{S} \rangle^{-1}. \quad (\text{A4})$$

The higher-order functions on the right-hand side of (A4) may be expressed as functional derivatives of $\tilde{G}_{l,m}(t)$.

$$\begin{aligned} \sum_l \frac{\delta \tilde{G}_{ij}(t)}{\delta U_{il}(t')} &\equiv (\mathbf{\Delta}(t') \mathbf{G}(t))_{ij} \\ &= -i \langle \tilde{S} \rangle^{-1} \sum_l \langle A_0 C_{li}(t') A_l^+(t) \tilde{S} A_j(t) A_0^+ \rangle \\ &\quad + i \sum_l \tilde{G}_{lj}(t) \frac{\langle C_{li}(t') \tilde{S} \rangle}{\langle \tilde{S} \rangle}, \quad (\text{A5}) \end{aligned}$$

$$\begin{aligned} \sum_l \frac{\delta \tilde{G}_{il}(t)}{\delta U_{ij}(t')} &\equiv (\mathbf{G}(t) \mathbf{\Delta}(t'))_{ij} \\ &= -i \langle \tilde{S} \rangle \sum_l \langle A_0 A_i^+(t) S A_l(t) C_{jl}(t') A_0^+ \rangle \\ &\quad + i \sum_l \tilde{G}_{il}(t) \frac{\langle C_{lj}(t') \tilde{S} \rangle}{\langle \tilde{S} \rangle}. \quad (\text{A6}) \end{aligned}$$

Thus we may write (A4) as

$$i[d\mathbf{G}(t)/dt] = -i \mathbf{\Delta}^\times(t) \mathbf{G}(t) - \langle \mathbf{C}^\times(t) \rangle \mathbf{G}(t), \quad (\text{A7})$$

where

$$\langle \mathbf{C}(t) \rangle_{ij} \equiv \langle C(t)_{ji} \tilde{S} \rangle / \langle \tilde{S} \rangle \quad (\text{A8})$$

and the superscript "x" is to be interpreted as in (19).

Integrating (A7) over t yields

$$\mathbf{G}(t) = - \int_0^t \{ \mathbf{\Delta}^\times(t'') + i \langle \mathbf{C}^\times(t'') \rangle \} \mathbf{G}(t'') dt'' + \mathbf{G}(t=0), \quad (\text{A9})$$

and substitution of this expression into the first term on the right-hand side of (A7) allows us to write, in the limit as $\{U_{ij}(t'') \rightarrow 0\}$ and $\tilde{S} \rightarrow 1$,

$$i\mathbf{G}(t) = - \lim_{\{U\} \rightarrow 0} \left[\int_0^t dt' \mathbf{\Delta}^\times(t) \langle \mathbf{C}^\times(t') \rangle \mathbf{G}(t') + \langle \mathbf{C}^\times(t) \rangle \tilde{\mathbf{G}}(t) \right] \quad (\text{A10})$$

in obtaining (A10) we have dropped terms of order V^3 , or CA^2 , in keeping with our assumption that V may be treated as a small perturbation. The matrix $\mathbf{G}(t) = \lim(\tilde{S} \rightarrow 1) \tilde{\mathbf{G}}(t)$. If we replace $\tilde{\mathbf{G}}(t)$ on the right-hand side of (A10) by $\mathbf{G}(t)$, an approximation which is also

correct to order V^2 , we finally obtain

$$i\tilde{\mathbf{G}}(t) = -[\tilde{\mathbf{J}}^\times]^\times \mathbf{G}(t) - \lim_{s \rightarrow 1} \int_0^t dt' \mathbf{\Delta}^\times(t) \langle \mathbf{C}^\times(t') \rangle \mathbf{G}(t'), \quad (\text{A11})$$

where

$$[\tilde{\mathbf{J}}^\times]_{ij} = \tilde{J}_{ji}. \quad (\text{A12})$$

Upon taking the indicated functional derivatives, (A11) may be rewritten in component form and in the weak coupling limit it becomes identical to Eq. (31).

APPENDIX B: PROJECTION OPERATOR TECHNIQUE⁸

Let us define a projection operator P such that for any general operator \mathcal{O}

$$\mathcal{O}\mathcal{O} = \langle \mathcal{O} \rangle. \quad (\text{B1})$$

Then, if $N_0(t) = A_0^+(t) A_0(t) = e^{iHt} A_0^+ A_0 e^{-iHt}$, we may define

$$N_0^{(1)}(t) = \mathcal{O} N_0(t), \quad N_0^{(2)}(t) = (1 - \mathcal{O}) N_0(t). \quad (\text{B2})$$

Since $N_0^{(2)}(t=0) = 0$, we find that

$$\begin{aligned} \dot{N}_0^{(1)}(t) &= i\mathcal{O} L N_0^{(1)}(t) \\ &- \mathcal{O} L \int_0^t ds \exp[is(1 - \mathcal{O})L] (1 - \mathcal{O}) L N_0^{(1)}(t-s), \quad (\text{B3}) \end{aligned}$$

where $L = H^\times$ is the Liouville operator.

Using the properties of the projection operator, we may show that

$$(1 - \mathcal{O}) L \mathcal{O} = V^\times \mathcal{O} = L_1 \mathcal{O}, \quad (\text{B4})$$

$$\mathcal{O} L (1 - \mathcal{O}) = \mathcal{O} V^\times = \mathcal{O} L_1, \quad (\text{B5})$$

where V is the nondiagonal part of H in (13) and where we have defined L_1 as the Liouville operator for the fluctuation of the intermolecular coupling about its thermal average. With these identities we find

$$\begin{aligned} \dot{N}_0^{(1)}(t) &= i\mathcal{O} L N_0^{(1)}(t) \\ &- \mathcal{O} L_1 \int_0^t ds \exp[is(1 - \mathcal{O})L] L_1 N_0^{(1)}(t-s). \quad (\text{B6}) \end{aligned}$$

The first term on the right corresponds to coherent or wavelike exciton motion, while the second term contains the exciton-phonon coupling and is rigorously second order in V . If we drop from the exponential all terms of order V and higher we may find, upon taking matrix elements in the basis $\{|n\rangle = A_n^+ |0\rangle\}$, that the equation of motion for $\mathcal{G}_{n,m}(t) = \langle n | N_0^{(1)}(t) | m \rangle$ becomes identical to Eq. (31) when the weak coupling limit is taken.

It should be pointed out that another projection operator commonly used in similar problems is a product of P and D , the operator which takes the diagonal element (in the exciton site representation in our case). If this projection operator is used, an equation may be derived for the number operator

which is similar to but not identical to (B6). The interesting point about this equation is that while the solutions for high temperature are identical to those of (B6) for that limit, at low temperatures, the solutions to the new equation are not equal to those of (B6), but are quite different and exhibit incorrect features (e.g., *negative probabilities*). This behavior is due to the fact that $DV=0$, and hence using this projector implicitly takes H' (not V) as the perturbation. The moral is clear: be careful to choose the correct projection operator for the problem.

APPENDIX C

In this section we will derive Eq. (42) from Eq. (41). First, we introduce new functions

$$h_q^K(t) = e^{iKq/2} g_q^K(t). \tag{C1}$$

The equations of motion of these functions become

$$\begin{aligned} \dot{h}_q^K(t) &= 2J \sin(K/2) [h_{q-1}^K(t) - h_{q+1}^K(t)] \\ &+ 2\alpha \cos K \delta_{q,0} h_0^K(t) + \alpha [\delta_{q,1} h_{-1}^K(t) + \delta_{q,-1} h_1^K(t)]. \end{aligned} \tag{C2}$$

From the definition of the functions h_q^K , we can see that the mean square displacement $\langle R^2(t) \rangle$ is given by

$$\langle R^2(t) \rangle = - \lim_{K \rightarrow 0} \{ e^{-2\alpha t} N [\partial^2 h_0^K(t) / \partial K^2] \} a^2. \tag{C3}$$

Thus, we need only solve for h_0^K in order to find the mean square displacement and the diffusion constant. Defining $f^K(t) = h_1^K(t) - h_{-1}^K(t)$, we find that we can write the equations of motion for h_0^K and f^K in integral equation form.

$$\begin{aligned} h_0^K(t) &= N^{-1} J_0(\beta t) + 2\alpha \cos K \int_0^t d\tau J_0[\beta(t-\tau)] h_0^K(\tau) \\ &+ \alpha \int_0^t d\tau J_1[\beta(t-\tau)] f^K(\tau), \end{aligned} \tag{C4}$$

$$\begin{aligned} f^K(t) &= 2N^{-1} J_1(\beta t) + 4\alpha \cos K \int_0^t d\tau J_1[\beta(t-\tau)] h_0^K(\tau) \\ &+ \alpha \int_0^t d\tau \{ J_2[\beta(t-\tau)] - J_0[\beta(t-\tau)] \} f^K(\tau), \end{aligned} \tag{C5}$$

where $\beta = 4\tilde{J} \sin K/2$, and J_n is the usual Bessel function. Then, taking the second derivative with respect to K of (C4) and the first derivative of (C5), allowing $K \rightarrow 0$, and defining

$$x(t) = \lim_{K \rightarrow 0} (\partial f^K(t) / \partial K), \tag{C6}$$

$$y(t) = - \lim_{K \rightarrow 0} [N (\partial^2 h_0^K / \partial K^2)] \tag{C7}$$

we find,

$$x(t) = \frac{2\tilde{J}t}{N} - 4\alpha\tilde{J} \int_0^t d\tau (t-\tau) h_0^0(\tau) - 2\alpha \int_0^t x(\tau) d\tau, \tag{C8}$$

$$\begin{aligned} y(t) &= -2\tilde{J}^2 t^2 - 2\alpha \int_0^t \{ N h_0^0(\tau) + 2N\tilde{J}^2 (t-\tau)^2 h_0^0(\tau) \\ &- y(\tau) \} d\tau + \alpha\tilde{J}N \int_0^t (t-\tau) x(\tau). \end{aligned} \tag{C9}$$

The solution of these equations for $\langle R^2(t) \rangle / a^2 = e^{-2\alpha t} y(t)$ is

$$\langle R^2(t) \rangle / a^2 = (2\alpha + 4\tilde{J}^2/3\alpha)t + (4\tilde{J}^2/9\alpha^2)(e^{-3\alpha t} - 1). \tag{C10}$$

We should point out here that the equation for the density matrix proposed by Avakian *et al.*^{2c} can also be manipulated this way to give (in their notation) for near-neighbor interactions

$$\langle R^2(t) \rangle / a^2 = \{ 2\beta^2 t / \Gamma - [\beta^2 (1 - e^{-2\Gamma t}) / \Gamma^2] \} a^2,$$

so that

$$D = a^2 \beta^2 / \Gamma,$$

where Γ is the inverse of the relaxation time.

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