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Exciton-Phonon Interactions in Molecular Crystals*

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The interaction of Frankel excitons with optical phonons in molecular crystals is studied by means of a Green's function method in which the use of a canonical transformation allows most of the exciton-phonon interaction to be treated nonperturbatively. The self-energy of the Green's function is then expanded in terms of the intermolecular potential. An expression is obtained for the absorptive part of the dielectric function of the exciton-phonon system. Comparison is made with experiment and also with earlier theories, some of the limitations of which are pointed out.

There are a number of interesting aspects of the theory of molecular crystals, such as the nature of the spectral line shapes and their temperature dependence or the processes of energy transfer and excitation trapping, which are strongly influenced by the coupling of the electronic and vibrational excitations (the exciton-phonon interaction). The conventional exciton theory for the electronic excitations of molecular crystals¹⁻³ is essentially a rigid lattice theory and offers little insight into these matters. In order to understand these and other properties of molecular crystals which arise from or are strongly influenced by this coupling, it is necessary to develop a theory which directly includes the exciton-phonon interaction.⁴

There have already been a number of studies of the present problem⁵⁻¹¹ many of which have involved attempts to treat the entire exciton phonon coupling as a perturbation. Notable among these are the studies involving the calculation of the one exciton Green's function. Suna⁸ and Agranovitch and Konobeev⁹ expand the self-energy of the Green's function in powers of the exciton-phonon coupling, retaining only the lowest-order term. Takeno¹⁰ and Davydov and Nitsovitch⁷ obtain equivalent results by making decoupling approximations to solve the Green's function equations of motion. These methods are all analogs to the standard Green's function treatment of the polaron;¹² however, as we shall see, they are subject to severe limitations when applied to the present problem. This is due, at least in part, to the fact the expansion parameter employed in the perturbation theory is usually quite large. Philpott⁶ and Rashba¹¹ have attempted other nonperturbative approaches to this problem which are quite different from the present analysis.

In this paper we will develop the formal aspects of a theory of exciton-phonon interactions which can be specifically applied to molecular crystals, in which the intermolecular interactions are weak. The theory is based on a Green's function method which is capable of including the results mentioned above, but which also allows us to avoid the major limitations of these earlier theories. We will show how the results of this

calculation can be used to obtain information about the complex dielectric function of the exciton-phonon system and thus about its optical properties.

We consider particularly the interaction of one band of Frenkel excitons with an arbitrary number of bands of optical phonons. Two different types of optical modes are recognized—"high-frequency modes" which arise from the internal vibrations of the molecules and "low-frequency modes" which arise from torsional vibrations or from the relative motions of two molecules in the same unit cell. It is shown that these two types of phonons have quite different effects on the optical spectrum of the solid. Except for a qualitative discussion in Sec. IV, the effects of acoustic phonons are not directly taken into account in this treatment.

The exciton-phonon interaction is assumed to be linear in phonon coordinates, and it is also assumed that we are concerned only with temperatures for which the thermal population of exciton states is negligible. Restricting ourselves to linear terms in the interaction implies that there are no vibrational frequency differences between the ground and excited states. Of course, this is not strictly correct (molecular vibrations can change by as much a 10%-20%); however, the coupling constant for the quadratic terms is usually much smaller than that for the linear terms. We will discuss the effect of the quadratic terms in a future paper. It may be noted that throughout most of the following the phonon band indices are suppressed and, except where doing so might easily lead to confusion [see, e.g., (56)], a one-dimensional notation is employed. This is done only for simplicity, not to imply any assumption as to the dimensionality of the model or the precise number of phonon bands allowed. The model considered is, however, restricted to the case of one molecule per unit cell so that all low-frequency optical modes involved are automatically torsional modes.

The paper is set out as follows. In Sec. I, the Hamiltonian used is defined and the exact diagonalization of this Hamiltonian in two limiting cases is discussed. A unitary transformation is then applied to the Hamiltonian. In Sec. II, the Green's function is defined and an equation for the self-energy is derived. In Sec. III,

the results of Sec. II are compared to previous results. In Sec. IV, the dielectric constant is defined and related to the Green's function. Various approximate forms are derived.

I. PROPERTIES OF THE HAMILTONIAN

The exciton-phonon Hamiltonian may be represented as^{5,8}

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{int}}. \quad (1)$$

In Eq. (1), H_{ex} is defined as

$$H_{\text{ex}} = \sum_n E_0 a_n^\dagger a_n + \sum_{n,n'} J_{n-n'} a_n^\dagger a_{n'}, \quad (2)$$

and represents the Hamiltonian for one band of Frenkel excitons in a perfect rigid crystal. E_0 is the energy of an electronic excitation localized at site n and $J_{n-n'}$ is the resonance interaction between excitations at sites n and n' . For most molecular crystals the maximum value of $J_{n-n'}$ does not exceed a few hundred cm^{-1} , and it is, in fact, often much less. The operators a_n and a_n^\dagger destroy and create an electronic excitation localized at site n . The sum $\sum_{n,n'}$ is over all values of n and n' for which $n \neq n'$. As mentioned earlier, we are employing a one-dimensional notation purely as a matter of convenience; we are not necessarily restricting the analysis to a one-dimensional model.

The free phonon Hamiltonian, H_{ph} , is written as

$$H_{\text{ph}} = \sum_{q,\alpha} \omega_{q,\alpha} b_{q,\alpha}^\dagger b_{q,\alpha}, \quad (3)$$

where $\omega_{q,\alpha}$ is the angular frequency of a phonon of wave vector q , band α ($\hbar=1$). The operators $b_{q,\alpha}$ and $b_{q,\alpha}^\dagger$ are the corresponding destruction and creation operators.

The interaction term, H_{int} , is taken as the first term in a Taylor's series of the exact exciton-phonon interaction in powers of the phonon coordinates. It may be broken into two parts:

$$H_{\text{int}} = H_{\text{int}}' + H_{\text{int}}'', \quad (4)$$

where

$$H_{\text{int}}' = N^{-1/2} \sum_{n,q,\alpha} X_{q,\alpha}^n \omega_{q,\alpha} (b_{q,\alpha} + b_{-q,\alpha}^\dagger) a_n^\dagger a_n, \quad (5)$$

with

$$X_{q,\alpha}^n \omega_{q,\alpha} = N^{-1} e^{iqn} \sum_k f^{(\alpha)}(k, q) = e^{iqn} g_{q,\alpha} \omega_{q,\alpha},$$

and

$$H_{\text{int}}'' = N^{-1/2} \sum_{n,n'} \sum_{q,\alpha} F_{q,\alpha}^{n,n'} a_n^\dagger a_{n'} (b_{q,\alpha}^\dagger + b_{-q,\alpha}), \quad (6)$$

with

$$F_{q,\alpha}^{n,n'} = N^{-1} \sum_k e^{-ikn} \exp[i(k+q)n'] f^{(\alpha)}(k, q),$$

$$f^{(\alpha)}(k, q) = [f^{(\alpha)}(k+q, -q)]^*.$$

H_{int}' describes the interaction of an electronic exci-

tation at site n with optical phonons of wave vector q , band α . The average $\langle g_{q,\alpha} \omega_{q,\alpha} \rangle$, taken over q , is a measure of the energy required to distort a molecule (for high-frequency modes) or to change the orientation of the molecule in the unit cell (for low-frequency modes) from its equilibrium position in the electronic ground state to the equilibrium position in the first electronically excited state. For the high-frequency optical bands information about this parameter can be obtained from molecular spectroscopy, and it is found that often $|\langle g_{q,\alpha} \rangle| \gtrsim 1$. For low-frequency bands the energy involved may be expected to be much less; however, since $\langle \omega_{q,\alpha} \rangle$ is also less in this case, one may still expect that $\langle g_{q,\alpha} \rangle$ is not small.

The term H_{int}'' describes the phonon induced interaction of excitons localized at different lattice sites. $F_{q,\alpha}^{n,n'}$, which measures the strength of this interaction, is small in the case of molecular crystals, for which all intermolecular forces are weak; and for this reason we generally expect

$$| \langle F_{q,\alpha}^{n,n'} \rangle | < | \langle X_{q,\alpha}^n \omega_{q,\alpha} \rangle |,$$

for given α . It should be noted of course that in many cases there is very little direct experimental information available about all of these quantities. The intuitive arguments which have been employed may therefore be quite misleading in certain specific instances; however, it is probably reasonable to expect the conclusions reached to be fairly accurate for the majority of representative molecular crystals. These conclusions concerning the relative sizes of the parameters involved will be useful in understanding the approximations made in later sections.

It is also useful to note that, due to our assumption of a linear exciton-phonon interaction, there are no terms in the Hamiltonian connecting different phonon bands. We may therefore suppress the band index henceforth and consider the problem, initially, of one band of excitons interacting with one band of optical phonons. The generalization of results obtained in this way will be quite straightforward.

The exciton-phonon Hamiltonian may be diagonalized in two limiting cases. The first is when $X = F = 0$, in which case the Hamiltonian can be written as

$$H = \sum_k E_k' a_k^\dagger a_k + \sum_q \omega_q b_q^\dagger b_q, \quad (7)$$

$$a_k = N^{-1/2} \sum_n e^{ikn} a_n, \quad (8a)$$

$$E_k' = E_0 + \sum_{n \neq 0} J_n e^{ikn}. \quad (8b)$$

This corresponds to the limit of zero exciton-phonon interaction. The second case where exact diagonalization is possible is $J = F = 0$ and corresponds to the case of zero intermolecular interaction.⁵ The Hamiltonian can then be diagonalized by the following unitary

transformation:

$$e^{UH}(J=F=0)e^{-U} = \sum_n (E_0 - N^{-1} \sum_q |X_q^n|^2 \omega_q) a_n^+ a_n + \sum_q \omega_q b_q^+ b_q, \quad (9)$$

$$U = N^{-1/2} \sum_{nq} X_q^n a_n^+ a_n (b_q^+ - b_{-q}), \quad (10)$$

where we have assumed that the total exciton density is very small. A useful means of checking the results of any approximate study based on (1) will then be a direct comparison with these two exactly soluble models. The second limit, of course, appears to be of more direct interest in the present case. This will be shown in greater detail in Sec. II of this paper.

In order to formally incorporate these exact results in our approach, we define new operators

$$A_n = \exp(-\hat{C}) a_n \exp(\hat{C});$$

$$B_q = \exp(-\hat{U}) b_q \exp(\hat{U}), \quad (11)$$

where

$$\hat{C} = N^{-1/2} \sum_{n,q} \hat{X}_q^n a_n^+ a_n (b_q^+ - b_{-q}), \quad (12)$$

and \hat{X}_q^n is as yet unspecified [except that we require $\hat{X}_q^n = \exp(inq)f(q)$, and $f(q) = f^*(-q)$]. We will discuss the two useful limits for \hat{X}_q^n . In terms of these new operators, the Hamiltonian may be written as

$$H = \sum_n [E_0 - 2N^{-1} \sum_q \omega_q (X_q^n \hat{X}_{-q}^n - \frac{1}{2} |\hat{X}_q^n|^2)] A_n^+ A_n + \sum_q \omega_q B_q^+ B_q + \sum_{n,n'} J_{n-n'} A_n^+ A_n \theta_n + \theta_{n'} + N^{-1/2} \sum_{n,q} (X_q^n - \hat{X}_q^n) \omega_q \theta_n^+ (B_q^+ + B_{-q}) \theta_n A_n^+ A_n + N^{-1/2} \sum_{n,n'} \sum_q F_q^{nn'} \theta_n^+ (B_q^+ + B_{-q}) \theta_{n'} A_n^+ A_{n'}, \quad (13)$$

where

$$\theta_n = \exp[N^{-1/2} \sum_q \hat{X}_q^n (B_q^+ - B_{-q})].$$

Note that when $\hat{X}_q^n = 0$, the diagonal part of (13) is identical to (7), and when $\hat{X}_q^n = X_q^n$, it becomes identical to (9). Thus, both exactly soluble limits are explicitly included in (13).

The zeroth-order energies of the zero phonon, one phonon, two phonon, etc. states may be calculated using (13) in the limit $\hat{X}_q^n = X_q^n$, which is appropriate in the weak intermolecular coupling case. For example, when the phonon frequencies are independent of wavevector, we find a band of energies for each of the above states, with the bandwidth of each being approximately the total exciton bandwidth (in the limit of zero exciton-phonon interaction) multiplied by a Franck-Condon factor. When the total exciton bandwidth is small compared to a typical optical phonon frequency, this gives a series of narrow, nonoverlapping bands.

For our purposes, it is convenient to add and subtract

in (13) the following expression:

$$\sum_k \tilde{E}_k A_k^+ A_k = \sum_{nn'}' [J_{nn'} \langle \theta_n^+ \theta_{n'} \rangle_0 + N^{-1/2} \sum_q F_q^{nn'} \times \langle \theta_n^+ (B_q^+ + B_{-q}) \theta_{n'} \rangle_0] A_n^+ A_{n'}. \quad (14)$$

Here A_k^+ , A_k are defined in analogy with (8), the average, $\langle \dots \rangle_0$, is over the grand canonical ensemble of the diagonal part of (13), and (we henceforth assume that $kT \ll E_0$)

$$\tilde{E}_k = \sum_{n(n')} \exp[ik(n-n')] \exp[-S(n-n')] \times [J_{n-n'} - N^{-1} \sum_q F_q^{nn'} (\hat{X}_{-q}^n + \hat{X}_{-q}^{n'})], \quad (15)$$

$$S(n) = N^{-1} \sum_q (1 - \cos qn) |\hat{X}_q^n|^2 \coth(\beta \omega_q / 2). \quad (16)$$

In this way, the Hamiltonian can be written

$$H = \sum_k (E_0 + \tilde{E}_k - N^{-1} \sum_q |\hat{X}_q^n|^2 \omega_q) A_k^+ A_k + \sum_q \omega_q B_q^+ B_q + \sum_{kk'} V_{kk'} A_k^+ A_{k'}, \quad (17)$$

$$V_{kk'} = N^{-1} \sum_{nn'} \exp[i(kn - k'n')] \times [J_{n-n'} (\theta_n^+ \theta_{n'} - \langle \theta_n^+ \theta_{n'} \rangle_0) + N^{-1/2} \sum_q F_q^{nn'} \times [\theta_n^+ (B_q^+ + B_{-q}) \theta_{n'} - \langle \theta_n^+ (B_q^+ + B_{-q}) \theta_{n'} \rangle_0] + N^{-3/2} \sum_{nq} \exp[i(k-k')n] (X_q^n - \hat{X}_q^n) \omega_q (B_q^+ + B_{-q})]. \quad (18)$$

We shall see later that this has the effect of making the first order contribution to the self-energy vanish.

II. GREEN'S FUNCTION ANALYSIS

In order to obtain information about the exciton-phonon interaction without explicitly calculating the eigenvalues and eigenfunctions of the system, we will study the one exciton Green's function (which contains phonon operators when $\hat{X}_q^n \neq 0$)

$$\tilde{G}(k; t-t') = -i \langle T \{ A_k(t) A_k^+(t') \} \rangle, \quad (19)$$

where T is the time ordering operator, $A_k(t)$ and $A_k^+(t)$ are in the Heisenberg representation, and $\langle \dots \rangle$ represents a thermal average over the grand canonical ensemble using (17). We may evaluate this expression by use of the functional derivative technique.¹³

To do so, we define the more general function

$$\tilde{G}_S(kk'; t't') = -i \langle T \{ \tilde{S} A_k(t) A_{k'}^+(t') \} \rangle / \langle T \{ \tilde{S} \} \rangle, \quad (20)$$

with

$$\tilde{S} = \exp \left[-i \int_{-\infty}^{+\infty} dt'' \sum_{qq'} \Phi_{qq'}(t'') V_{qq'}(t'') \right]. \quad (21)$$

Here, $\Phi_{qq'}(t)$ is some unspecified test field and $V_{qq'}(t)$ is as defined in (18). Note that this expression reduces to (19) in the limit that $\Phi \rightarrow 0$. The equation of motion

for \tilde{G}_S is

$$[i(\partial/\partial t) - E_k]\tilde{G}_S(kk'; t't') = \delta(t-t')\delta(k-k') - i \sum_{k''} [\langle T\{\tilde{S}V_{kk''}(t)A_{k''}(t)A_{k'}^+(t')\} \rangle / \langle T\{\tilde{S}\} \rangle], \quad (22)$$

where

$$E_k = E_0 + \tilde{E}_k - N^{-1} \sum_q |\hat{X}_q^n|^2 \omega_q.$$

This may be rewritten in terms of the inverse Green's function as

$$\tilde{G}_S^{-1}(kk'; t't') = \tilde{G}_0^{-1}(kk'; t't') + i \sum_{k_1 k_2} \int_{-\infty}^{+\infty} dt_1 \frac{\langle T\{\tilde{S}V_{kk_2}(t)A_{k_2}(t)A_{k_1}^+(t_1)\} \rangle}{\langle T\{\tilde{S}\} \rangle} \times \tilde{G}_S^{-1}(k_1 k'; t't'), \quad (23)$$

where

$$\tilde{G}_0(kk'; t't') = -i \langle T\{A_k(t)A_{k'}^+(t')\} \rangle_0. \quad (24)$$

We may now rewrite the three point function in (23) in terms of a functional derivative.

$$\frac{i \langle T\{\tilde{S}V_{kk_2}(t)A_{k_2}(t)A_{k_1}^+(t_1)\} \rangle}{\langle T\{\tilde{S}\} \rangle} = - \left[\frac{\langle T\{\tilde{S}V_{kk_2}(t)\} \rangle}{\langle T\{\tilde{S}\} \rangle} + i \frac{\delta}{\delta \Phi_{kk_2}(t)} \right] \tilde{G}_S(k_2 k_1; t t_1), \quad (25)$$

and from this we obtain the result that if we define the self-energy of the Green's function as

$$\Sigma_S(kk'; t't') = \tilde{G}_0^{-1}(kk'; t't') - \tilde{G}_S^{-1}(kk'; t't'), \quad (26)$$

then the equation of motion for $\Sigma_S(kk'; t't')$ is

$$\Sigma_S(kk'; t't') = \delta(t-t') \frac{\langle T\{V_{kk'}(t')\tilde{S}\} \rangle}{\langle T\{\tilde{S}\} \rangle} + i \sum_{k_1 k_2} \int_{-\infty}^{+\infty} dt_1 \tilde{G}_S(k_1 k_2; t t_1) \frac{\delta \Sigma_S(k_2 k'; t_1 t')}{\delta \Phi_{kk_1}(t)}. \quad (27)$$

This equation for the self-energy may be solved to arbitrary accuracy by an iterative procedure. To first order we have

$$\Sigma_S^{(1)}(kk'; t't') = \delta(t-t') \langle T\{\tilde{S}V_{kk'}(t')\} \rangle / \langle T\{\tilde{S}\} \rangle. \quad (28a)$$

To second order, we obtain

$$\Sigma_S^{(2)}(kk'; t't') = \Sigma_S^{(1)}(kk'; t't') + \sum_{qq'} \tilde{G}_S(qq'; t't') \times \left\{ \frac{\langle T\{\tilde{S}V_{kq}(t)V_{q'k'}(t')\} \rangle}{\langle T\{\tilde{S}\} \rangle} - \frac{\langle T\{\tilde{S}V_{kq}(t)\} \rangle \langle T\{\tilde{S}V_{q'k'}(t')\} \rangle}{\langle T\{\tilde{S}\} \rangle^2} \right\}. \quad (28b)$$

Let us now allow $\Phi_{qq'}(t) \rightarrow 0$. Recalling our assumption that $E_0/kT \ll 1$, we find for the first-order term

$$\Sigma_S^{(1)}(kk'; t't') \rightarrow \Sigma^{(1)}(k; t-t')\delta(k-k'),$$

$$\Sigma^{(1)}(k, t, -t') = \delta(t-t') \langle V_{kk}(t) \rangle = 0. \quad (29)$$

The second-order term in this limit is

$$\Sigma_S^{(2)}(k, k'; t't') \rightarrow \Sigma^{(2)}(k, t-t')\delta(k-k'),$$

$$\Sigma^{(2)}(k; t-t') = \sum_{k'} \langle T\{V_{kk'}(t)V_{k'k}(t')\} \rangle \tilde{G}(k'; t-t'). \quad (30)$$

Then if we define $\tilde{G}(k\omega)$ as

$$\tilde{G}(k\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} \tilde{G}(kt) dt, \quad (31)$$

and similarly for $\Sigma(k\omega)$, we obtain to the degree of accuracy indicated in (30), and for the temperature of interest

$$\tilde{G}(k\omega) = \left[\omega - E_k - (2\pi)^{-1} \sum_q \int_{-\infty}^{+\infty} \tilde{D}_{k,q}^0(\omega - \omega') \times \tilde{G}(q, \omega') d\omega' \right]^{-1}, \quad (32)$$

and

$$\Sigma(k\omega) = (2\pi)^{-1} \sum_{k'} \int_{-\infty}^{+\infty} \frac{\tilde{D}_{kk'}^0(\omega - \omega') d\omega'}{\omega' - E_{k'} - \Sigma(k'\omega')}. \quad (33)$$

Here $\tilde{D}_{kk'}^0(\omega)$ is the transform of

$$\langle T\{V_{kk'}(t)V_{k'k}(t')\} \rangle_0,$$

defined as in (31). These equations may be solved by iterating further, although it should be noted that it may not be entirely consistent to do so as certain higher order terms have been dropped in deriving (30).

III. ANALYSIS OF RESULTS; COMPARISON WITH EARLIER METHODS

A. $\hat{X}_q^n = 0$

As in Sec. II there are two special cases of interest in examining the above results. The first such case occurs when we set $\hat{X}_q^n = 0$. Then $\theta_n = 1$ so that $a_k = A_k$, and the Green's function has no phonon part [It is then written as $G(k, t)$]. Also in this case we can write (30) as

$$\Sigma^{(2)}(k; t-t') = (2i/N) \sum_q |f(k, q)|^2 \omega_q D_q^0(t'-t) \times G(k+q, t-t'), \quad (34)$$

where $f(kq)$ is defined in (5) and (6), and

$$D_q^0(t) = -i \langle T\{\varphi_q(t)\varphi_{-q}(t')\} \rangle_0, \quad (35)$$

is the usual phonon Green's function, and

$$\varphi_q = (2\omega_q)^{-1/2} (b_q + b_{-q}^+).$$

In this way we obtain for the Green's function

$$G(k\omega) = \left[\omega - E_k - \left(\frac{i}{\pi N} \right) \sum_q |f(k, q)|^2 \omega_q \times \int_{-\infty}^{+\infty} d\omega' D_q^0(\omega') G(k+q, \omega+\omega') \right]^{-1} \quad (36)$$

and for the self-energy

$$\Sigma(k\omega) = \frac{iN^{-1}}{\pi} \sum_q |f(k, q)|^2 \omega_q \times \int_{-\infty}^{+\infty} d\omega' \frac{D_q^0(\omega')}{\omega + \omega' - E_{k+q} - \Sigma(k+q, \omega + \omega')}, \quad (37)$$

where, consistent with our earlier assumptions, $D_q^0(\omega)$ is the Fourier transform of $D_q^0(t)$ in (35).

Equations (36) and (37) are identical to the results of Suna, Davydov, and Nitsovich, and others. They may be further simplified by contour integration on ω' to obtain for example

$$\Sigma(k\omega) = N^{-1} \sum_q |f(k, q)|^2 \times \left(\frac{N_q + 1}{\omega - \omega_q - E_{k+q} - \Sigma(k+q, \omega + \omega_q)} + \frac{N_q}{\omega + \omega_q - E_{k+q} - \Sigma(k+q, \omega + \omega_q)} \right), \quad (38)$$

where N_q is the occupation number of the phonon mode q . A major difficulty with results obtained in this limit is that, as we have seen in Sec. II, they are derived by considering only the lowest-order nonzero term of a perturbation expansion of the self-energy in powers of X_q^n and $F_q^{nn'}/\omega_q$. The factor $F_q^{nn'}/\omega_q$ is expected to be very small, and its higher-order contributions can be neglected; however X_q^n is for many molecular crystals of the order unity or greater, even though its total effect to all orders may be small. It would seem that a result such as (38) will be of limited applicability if it is to be used with confidence.

What is more, it can be shown that even in the limit that $X_q^n \rightarrow 0$, the above results give incorrect predictions of the energy levels of the exciton phonon system. To see this most simply, we consider the special case of (9) with the further simplification that $X_q^n = g \exp(in \cdot q)$ and $\omega_q = \omega$ for all q . In this case, we know that the one exciton energy levels are at $E = E_0 - g^2\omega + n\omega$, $n = 0, 1, 2, \dots$, but from (38) the poles of $G(k\omega)$ occur [to first order in $\Sigma(k\omega)$] at

$$E = E_0 - g^2/(E - \omega - E_0), \quad (39)$$

or

$$E \doteq E_0 - (-1)^n g^2\omega + n\omega, \quad n = 0, 1, \quad (40)$$

in the limit that $g \rightarrow 0$. From this it can be seen that, of the two energy levels which $G(k, \omega)$ is able to predict when approximated in the above manner, one has the wrong energy shift *even in the limit* as $g \rightarrow 0$. It can also be shown¹⁴ that this problem does not immediately vanish when $\Sigma(k, \omega)$ is taken to higher order in g . Indeed, this is a difficulty characteristic of any Green's function calculation in which only finite order perturbation theory is used to obtain the self-energy. The problem is, however, of greater significance when the expansion parameter involved is large, as in the present

example. In Appendix C we derive some analytic results for the exact zero temperature Green's function of this system.

B. $\hat{X}_q^n = X_q^n$

In order to overcome these difficulties we consider the second special case of interest, in which $\hat{X}_q^n = X_q^n$. In this case X_q^n is included in $\Sigma(k, \omega)$ to all orders while the perturbation expansion used is in powers of $F_q^{nn'}/\omega_q$, which can be expected to be quite small for molecular crystals, and powers of $J_n e^{-S(n)}/\omega_q$. For high-frequency optical phonons J_n/ω_q generally is already a small parameter, and the factor $e^{-S(n)}$ only serves to make it smaller. For low-frequency modes J_n/ω_q may be fairly large, although we may nearly always expect $J_n/\omega_q < 10$ and in many cases the ratio is of order unity. However, even in these cases the factor $e^{-S(n)}$ is still generally sufficient to make the expansion parameter small. In a system with m bands of optical phonons $e^{-S(n)}$ has a maximum value at $T = 0$ of $\exp(-m\langle g_{q,\alpha}^2 \rangle)$, where the average is over q and α . If $\langle g_{q,\alpha}^2 \rangle \sim 1$ and if m has its minimum value of $m = 3$ then the factor $e^{-S(n)} \sim 1/10$. What is more, $e^{-S(n)}$ decreases with increasing temperature.

The smallness of these parameters, $F_q^{nn'}/\omega_q$ and $J_n e^{-S(n)}/\omega_q$, appears to be sufficient to justify the truncation used in obtaining (36) and (37) in the case $\hat{X}_q^n = X_q^n$; and it is this method which we propose to use for the study of the exciton-phonon interaction in molecular crystals.

The term $\langle T\{V_{k,k'}(t)V_{k',k}\} \rangle$ is evaluated in Appendix B. For the present we consider only the special case when $F_q^{nn'} = 0$. Then for $t > 0$:

$$\begin{aligned} \langle T\{V_{kq}(t)V_{qk}\} \rangle_0 &= N^{-2} \sum_{nmrs, n \neq m, r \neq s} \exp[ik(n-s) + iq(r-m)] \\ &\times \tilde{J}_{n-m} \tilde{J}_{r-s} [\exp\{-N^{-1} \sum_{q'} |g_{q'}|^2 \\ &\times [\exp(-iq'n) - \exp(-iq'm)] [\exp(iq'r) - \exp(iq's)] \\ &\times [\exp(i\omega_q t) N_{q'} + \exp(-i\omega_q t) (N_{q'} + 1)]\} - 1], \quad (41) \end{aligned}$$

and for $t < 0$ the same result holds with k and q interchanged and t replaced by $-t$ on the right-hand side. Here $\tilde{J}_m = J_m \exp[-S(m)]$, $S(m)$ being defined in (16). As can already be seen, a major difficulty of this approach will be in dealing with $\tilde{D}_{k,k'}^0(\omega)$. It may be necessary to use somewhat more specialized models to obtain results in a closed form, or it may be necessary to use a numerical approach.

IV. DIELECTRIC FUNCTION OF THE MOLECULAR CRYSTAL

In this section we will show how the Green's function (19) may be used to obtain information about the imaginary part of the dielectric function $[\epsilon''(k\omega)]$ and, thus, about the optical properties of the crystal.

As indicated in Sec. III, we will be concerned only with the results of the case $\hat{X}_q^n = X_q^n$.

We may write the function $\epsilon''(k, \omega)$ as

$$\epsilon''(k\omega) = \epsilon''_0(k\omega) - 4\pi\mu_{01}^2 \text{Im}G^R(k, \omega), \quad (42)$$

where for frequencies or energies $\sim E_0$, $\epsilon''_0(k, \omega)$ is a very slowly varying function of ω and $G^R(k\omega)$ is the Fourier transform of the retarded Green's function¹⁵

$$G^R(kt) = -i\Theta(t) \langle [a_k(t), a_k^+] \rangle. \quad (43)$$

In order to relate $G^R(kt)$ to the retarded Green's function corresponding to (19), we must make a decoupling approximation; since $a_k = N^{-1/2} \sum_q \theta_{k-q} A_q$,

$$G^R(kt) \doteq N^{-1} \sum_q \langle \theta_{k-q}(t) \theta_{k-q}^+ \rangle_0 \tilde{G}^R(q, t), \quad (44)$$

where θ_k is the transform of θ_n , defined as in (8) and

$$\tilde{G}^R(kt) = -i\Theta(t) \langle [A_k(t), A_k^+] \rangle. \quad (45)$$

This result is exact if $\tilde{J} = F = 0$ and requires no assumptions about the major part of the exciton phonon interaction.

We will consider first the results obtained if we set $\Sigma(k\omega) = 0$; this is equivalent to neglecting the non-diagonal parts of (17). Then,

$$G^R(kt) = -iN^{-1}\Theta(t)e^{-S} \times \sum_{n,q} \exp[i(k-q)n] \exp[-iE_q t + I_n(t)], \quad (46)$$

with

$$S = N^{-1} \sum_q g_q^2 \coth \beta \omega_q / 2, \quad (47)$$

and

$$I_n(t) = N^{-1} \sum_q g_q^2 e^{iqn} \times [(N_q + 1) \exp(-i\omega_q t) + N_q \exp(i\omega_q t)]. \quad (48)$$

In the case where $I_n(t)$ is not too large, we may expand $\exp[I_n(t)]$ and keep only a few terms:

$$\begin{aligned} \exp\{I_n(t)\} &= 1 + N^{-1} \sum_q g_q^2 e^{iqn} \\ &\times [N_q \exp(i\omega_q t) + (N_q + 1) \exp(-i\omega_q t)] \\ &+ \frac{1}{2} N^{-2} \sum_{q,q'} g_q^2 g_{q'}^2 \exp[i(q+q')n] \\ &\times [N_q N_{q'} \exp(i\omega_q t + i\omega_{q'} t) + N_q (N_{q'} + 1) \\ &\times \exp(i\omega_q t - i\omega_{q'} t) + (N_q + 1) N_{q'} \\ &\times \exp(-i\omega_q t + i\omega_{q'} t) + (N_q + 1) (N_{q'} + 1) \\ &\times \exp(-i\omega_q t - i\omega_{q'} t)] + \dots \end{aligned} \quad (49)$$

This leads to a representation of $G(k, \omega)$ in terms of processes involving successively more phonons. Specifically,

$$\begin{aligned} G^R(k, \omega) &= e^{-S} \{ \zeta(\omega - E_k) + N^{-1} \\ &\times \sum_q g_q^2 [(N_q + 1) \zeta(\omega - E_{k+q} - \omega_q) \\ &+ N_q \zeta(\omega - E_{k+q} + \omega_q)] + \dots \}, \end{aligned} \quad (50)$$

where¹⁶

$$\zeta(x) = (P/x) - i\pi\delta(x). \quad (51)$$

The first peak is the zero phonon line, the second two are sidebands (the second is of course a hot band). If the phonon band is narrow compared to a typical phonon frequency, then these bands do not overlap.

In order to study the form of $\epsilon''(k, \omega)$ in this approximation we may write

$$\text{Im}G^R(k, \omega) = \frac{-e^{-S}}{2N} \sum_{q,n} \exp[i(k-q)n] \int_{-\infty}^{+\infty} dt \exp[i(\omega - E_q)t + I_n(t)]. \quad (52)$$

Considering first the special case where $\omega_q = \omega'$, $g_q = g$,

$$\text{Im}G^R(k, \omega) = \frac{-e^{-S}}{2N} \left\{ 2\pi \sum_q [\delta(\omega - E_k) - \delta(\omega - E_q)] + \sum_q \int_{-\infty}^{+\infty} \exp[i(\omega - E_q)t + I_0(t)] dt \right\}, \quad (53)$$

and using the relation (see Appendix C)

$$\exp[I_0(t)] = \sum_{m=-\infty}^{+\infty} \exp[\frac{1}{2}(m\beta\omega') - im\omega't] \bar{I}_m[g^2 \text{csch} \frac{1}{2}(\beta\omega')], \quad (54)$$

where \bar{I}_m is a modified Bessel function, we obtain

$$\text{Im}G^R(k, \omega) = -\pi e^{-S} \{ \delta(\omega - E_k) + \sum_{m=-\infty}^{+\infty} \exp(\frac{1}{2}m\beta\omega') [\bar{I}_m(g^2 \text{csch} \beta\omega'/2) - \delta_{m,0}] N^{-1} \sum_q \delta(\omega - E_q - m\omega') \}. \quad (55)$$

In the limit as $N \rightarrow \infty$ we may integrate over wave vectors to find

$$\text{Im}G^R(k, \omega) = -\pi e^{-S} [\delta(\omega - E_k) + \sum_{m=-\infty}^{+\infty} \exp(\frac{1}{2}m\beta\omega') \{ \bar{I}_m[g^2 \text{csch} \frac{1}{2}(\beta\omega')] - \delta_{m,0} \} (8\pi^3)^{-1} \int dS_q^{(m)} |\nabla_q E_q|^{-1}]. \quad (56)$$

Here, $S^{(m)}$ is the constant energy surface in the first Brillouin zone defined so that $E_q = \omega - m\omega'$ for all q on $S^{(m)}$.

If ω' is taken to be the frequency of a torsional mode then this result predicts that the absorption spectrum of the solid will consist of a band of sharp, nonoverlapping but closely spaced ($\sim 50 \text{ cm}^{-1}$) peaks, each of which has the same shape as the temperature dependent density of exciton states obtained from (15). The relative intensities of the peaks are such that the band is centered at an energy corresponding to approximately the middle of the free exciton energy band. The intensity decreases slowly at energies above the peak and more rapidly at energies below, exhibiting a shape very similar to that predicted by Urbach's rule.¹⁷ The center of the band does not shift to lower energies as the temperature is increased.

If we consider more than one low-frequency optical phonon mode the over-all shape of the band remains essentially the same; however, the individual peaks begin to merge together and to overlap, thus smoothing out much of the detail exhibited in the simpler example. The acoustic modes, which have not been included at all in this analysis have the effect of smoothing out this fine structure somewhat, so that the experimentally observed absorption band corresponds to the envelope of the band predicted in this theory.

Finally, if we include also the effects of high-frequency optical modes, the absorption band described

above is accompanied by a series of satellite bands, all of which overlap to some extent, both at higher and at lower energies. The satellite bands all exhibit a shape identical to that of the single band obtained above. The spacing of their centers is equal to the frequency of the corresponding vibration ($\sim 500\text{--}1000 \text{ cm}^{-1}$). They decrease slowly in intensity above the main peak and more rapidly below, again obeying an Urbach rule.

These results, as described above, appear to be in good qualitative agreement with most of the experimental evidence available. That the predicted spectrum exhibits much more detail than is experimentally observed can probably be accounted for at least in part by the fact that acoustic phonons have not been included in the theory. That each of the satellite bands has a shape identical to that of the central band in the spectrum (ignoring overlap) also appears to be an oversimplification, which arises from the approximation $\omega_q = \omega'$. Actual calculations, in which an attempt is made to reproduce portions of the observed absorption spectrum, may provide a more definitive method for evaluating these results in detail.

In order to study the general case when g_q and ω_q are no longer constant, we may use the expansion in Eq. (50) to obtain (for $\omega \approx E_k$)

$$\text{Im}G^R(k, \omega) = -\pi e^{-S} [\delta(\omega - E_k) + N^{-2} \sum_{q, q'} \frac{1}{2} (g_q^2 g_{q'}^2) N_q (N_{q'} + 1) \delta(\omega - E_{k+q+q'} + \omega_q - \omega_{q'}) + \dots]. \quad (57)$$

And when the temperature is low enough so that $g_q^4 N_q \ll 1$, we may keep only a few terms to obtain (as $N \rightarrow \infty$)

$$\text{Im}G^R(k, \omega) = -\pi e^{-S} \left[\delta(\omega - E_k) + (2\pi)^{-6} \int dq g_q^2 (N_q + 1) \int_{S(\omega, q)} dS_{q'(\omega, q)} \frac{\frac{1}{2} N_{q'}(\omega, q) g_{q'}^2(\omega, q)}{|\nabla_{q'}(E_{k+q+q'} - \omega_{q'})|_{|q'=q(\omega, q)}} \right]. \quad (58)$$

Here the integral on q is over the entire first Brillouin zone whereas the integral on q' is over the constant energy surface $S(\omega, q)$ for which

$$\omega = E_{k+q+q'}(\omega, q) + \omega_q - \omega_{q'}(\omega, q). \quad (59)$$

A similar analysis can be used to obtain expressions for $\text{Im}G^R(k, \omega)$ valid when $\omega \approx E_k + m\omega'$, $m = \pm 1, 2, \dots$. When $|m|$ becomes very large, however, the overlap between neighboring bands becomes significant and the method breaks down.

Due to their greater complexity, the results obtained in this case (ω_q, g_q not constant) are more difficult to interpret than in the case of vanishing phonon bandwidth. However, preliminary calculations using Eq. (58) to study a few specific models have indicated that if ω_q is a weakly varying function of q then the line shapes obtained do not differ qualitatively from those given by Eq. (56) in the same temperature range.

In order to go further in our analysis, we must now explicitly use the results of Sec. II. From Eq. (44) we can obtain the result (for ω_q, g_q constant)

$$G^R(k, \omega) = e^{-S} \left(\tilde{G}^R(k, \omega) + \sum_{m=-\infty}^{+\infty} \exp(\frac{1}{2} m \beta \omega') [\bar{I}_m(g^2 \coth \frac{1}{2} \beta \omega') - \delta_{m,0}] \int \tilde{G}^R(q, \omega - m\omega') \frac{dq}{(2\pi)^3} \right). \quad (60)$$

And since it can be shown that for the temperatures and energies of interest¹⁵

$$\text{Im}G^R(k, \omega) = \text{Im}G(k, \omega),$$

we obtain

$$\epsilon''(k, \omega) = \epsilon''_0(k, \omega) - 4\pi\mu_{01}^2 e^{-S} [\text{Im}\tilde{G}(k, \omega) + \sum_{m=-\infty}^{+\infty} \exp(m\beta\omega'/2) [\bar{I}_m(g^2 \coth \beta\omega'/2) - \delta_{m,0}] \times \int \text{Im}\tilde{G}(q, \omega - m\omega') dq / (2\pi)^3]. \quad (61)$$

From Eq. (32) we see that

$$\tilde{G}(k, \omega) = [\omega - E_k - \Sigma_r(k, \omega) - i\Sigma_i(k, \omega)]^{-1}, \quad (62)$$

where Σ_r and Σ_i are the real and imaginary part of $\Sigma(k, \omega)$ and hence

$$\text{Im}\tilde{G}(k, \omega) = \Sigma_i(k, \omega) / \{[\omega - E_k - \Sigma_r(k, \omega)]^2 + [\Sigma_i(k, \omega)]^2\}. \quad (63)$$

Using (41) in (63) will give an equation for $\Sigma(k, \omega)$ which is extremely complicated. We expect that numerical computations of simple models will provide insight into the detailed structure of $\epsilon''(k, \omega)$.

V. DISCUSSION

In the present paper, we have shown that the energies and line shapes of the coupled exciton-phonon system could be calculated using Green's function approaches. We have removed the strong coupling by a unitary transformation which produces an exponential dependence of the energies and line shapes on the coupling constant. This indicates that the procedures based on a perturbation expansion in powers of the coupling constant will converge slowly for values of the coupling constant near unity. The formulas we have derived are rather complicated even in second order. It is therefore extremely difficult to go further analytically; however, numerical calculations for simple model systems will be useful.

We have made a number of assumptions in the present work. First, we assumed that a coupling linear in the phonon coordinates is an adequate representation of the physical situation. Some work in the quadratic coupling has shown that interesting and dramatic effects are to be expected when these are included.¹³ We have also worked only within one electronic manifold. Introduction of many bands would further complicate the situation. The assumption was also made that we may neglect the exciton-phonon coupling when averages are taken over phonon variables. The averages then reduce to those of harmonic oscillators in thermal equilibrium. In the same vein, we have neglected the thermal exciton concentration as being

small. Perhaps the most severe approximation is the decoupling approximation used in Eq. (44).

In spite of these approximations, there is hopefully enough in the present analysis to adequately represent the spectra of real molecular crystals. In a future publication, we will apply these results to the calculation of the energy levels and line shapes of simple models of molecular crystals.

APPENDIX A: THERMAL AVERAGES

In this paper, we have repeatedly averaged over the equilibrium distribution of phonons. The basic formula can be written for an ensemble of harmonic oscillators with frequency ω , as¹⁸

$$\langle \exp[i\xi(\gamma_1 b + \gamma_2 b^+)] \rangle = \exp(-\frac{1}{2}\gamma_1\gamma_2\xi^2 \coth\omega\beta/2). \quad (A1)$$

From this, we can find the other averages we need. For example, differentiate (A1) with respect to γ_1 , to find

$$\langle b \exp[i\xi(\gamma_1 b + \gamma_2 b^+)] \rangle = i\xi(N_\omega + 1)\gamma_2 \times \exp[-\frac{1}{2}\gamma_1\gamma_2\xi^2 \coth\omega\beta/2], \quad (A2)$$

where we have used

$$N_\omega = (e^{\beta\omega} - 1)^{-1}, \quad (A3)$$

and

$$\exp[i\xi(\gamma_1 b + \gamma_2 b^+)] = \exp(i\xi\gamma_1 b) \exp(i\xi\gamma_2 b^+) \times \exp(\frac{1}{2}\gamma_1^2\xi_1\gamma_2). \quad (A4)$$

Similarly,

$$\langle b^+ \exp[i\xi(\gamma_1 b + \gamma_2 b^+)] \rangle = i\xi N_\omega \gamma_1 \exp[-\frac{1}{2}\gamma_1\gamma_2\xi^2 \coth\omega\beta/2]. \quad (A5)$$

Other averages can be similarly derived.

APPENDIX B: EVALUATION OF $\langle V_{kq}(t) V_{qk} \rangle$

We may write $\langle V_{kq}(t) V_{qk} \rangle$ as

$$\begin{aligned} \langle V_{kq}(t) V_{qk} \rangle &= N^{-2} \sum_{n,m,r,s} \exp\{i[k(n-s) + q(r-m)]\} (I_1 + I_2 + I_3 + I_4), \\ I_1 &= J_{nm} J_{rs} \langle [\theta_n^+(t) \theta_m(t) - \langle \theta_n^+ \theta_m \rangle] \theta_r^+ \theta_s \rangle, \\ I_2 &= N^{-1/2} J_{nm} \sum_{q'} F_{q',rs} \langle [\theta_n^+(t) \theta_m(t) - \langle \theta_n^+ \theta_m \rangle] \theta_r^+ (b_{q'} + b_{-q'}^+) \theta_s \rangle, \\ I_3 &= N^{-1/2} J_{rs} \sum_{q'} F_{q',nm} \langle \{\theta_n^+(t) [b_{q'}(t) + b_{-q'}^+(t)] \theta_m(t) - \langle \theta_n^+ (b_{q'} + b_{-q'}^+) \theta_m \rangle\} \theta_r^+ \theta_s \rangle, \\ I_4 &= N^{-1} \sum_{q',q''} F_{q',nm} F_{q'',rs} \langle \{\theta_n^+(t) [b_{q'}(t) + b_{-q'}^+(t)] \theta_m(t) - \langle \theta_n^+ (b_{q'} + b_{-q'}^+) \theta_m \rangle\} \theta_r^+ (b_{q''} + b_{-q''}^+) \theta_s \rangle. \end{aligned}$$

It is convenient to define the following function

$$R \equiv \langle \theta_n^+(t) \theta_m(t) \theta_r^+ \theta_s \rangle \\ = \exp[-S(n-m) - S(r-s)] \exp[-N^{-1} \sum_{\sigma} g_{\sigma}^2 \{ (e^{in\sigma} - e^{im\sigma}) (e^{-ir\sigma} - e^{-is\sigma}) N_{\sigma} \exp(i\omega_{\sigma} t) \\ + (e^{-in\sigma} - e^{-im\sigma}) (e^{ir\sigma} - e^{is\sigma}) (N_{\sigma} + 1) \exp(-i\omega_{\sigma} t) \}].$$

Then, we find, on performing the relevant averages:

$$I_1 = J_{n-m} J_{r-s} \{ R - \exp[-S(n-m) - S(r-s)] \}, \\ I_2 = J_{n-m} N^{-1} \sum_{q'} g_{q'} F_{q'} r^s \{ R \{ [\exp(i\omega_{q'} t) N_{q'} - \exp(-i\omega_{q'} t) (N_{q'} + 1)] [\exp(inq') - \exp(imq')] \\ - [\exp(irq') + \exp(isq')] \} - [\exp(irq') + \exp(isq')] \exp[-S(n-m) - S(r-s)] \}, \\ I_3 = N^{-1} J_{r-s} \sum_{q'} g_{q'} F_{q'} n^m \{ R \{ [\exp(-i\omega_{q'} t) (N_{q'} + 1) + \exp(i\omega_{q'} t) N_{q'}] [\exp(irq') - \exp(isq')] \\ - [\exp(inq') + \exp(imq')] \} - [\exp(iq'm) + \exp(iq'n)] \exp[-S(n-m) - S(r-s)] \}, \\ I_4 = N^{-1} \sum_{q, q', q''} F_{q'} n^m F_{q'} r^s \sum_{i=1}^5 A_{q'q''}^{(i)}, \\ A_{q'q''}^{(1)} = N^{-1} (N_{q'} + 1) N_{q''} g_{q'} g_{q''} R \{ [\exp(inq') - \exp(imq')] + [\exp(irq') - \exp(isq')] \exp(i\omega_{q'} t) \} \\ \times \{ [\exp(inq'') - \exp(imq'')] \exp(i\omega_{q''} t) + [\exp(irq'') - \exp(isq'')] \}, \\ A_{q'q''}^{(2)} = -N^{-1} (N_{q'} + 1) (N_{q''} + 1) g_{q'} g_{q''} [1 - \delta(q' + q'')] R \{ [\exp(inq') - \exp(imq')] + \exp(i\omega_{q'} t) \\ \times [\exp(irq') - \exp(isq')] \} \{ [\exp(inq'') - \exp(imq'')] \exp(-i\omega_{q''} t) + [\exp(irq'') - \exp(isq'')] \} \\ + \delta(q' + q'') (N_{q'} + 1) R, \\ A_{q'q''}^{(3)} = -N^{-1} (N_{q'} + 1) N_{q''} g_{q'} g_{q''} (1 - \delta(q' + q'')) R \{ [\exp(inq') - \exp(imq')] + [\exp(irq') - \exp(isq')] \\ \times \exp(i\omega_{q'} t) \} \{ [\exp(inq'') - \exp(imq'')] \exp(-i\omega_{q''} t) + [\exp(irq'') - \exp(isq'')] \} + \delta(q' + q'') N_{q'} R, \\ A_{q'q''}^{(4)} = N^{-1} N_{q'} (N_{q''} + 1) g_{q'} g_{q''} R \{ [\exp(inq') - \exp(imq')] \exp(-i\omega_{q'} t) + [\exp(irq') - \exp(isq')] \} \\ \times \{ [\exp(inq'') - \exp(imq'')] \exp(-i\omega_{q''} t) + [\exp(irq'') - \exp(isq'')] \}, \\ A_{q'q''}^{(5)} = N^{-1} g_{q'} g_{q''} [\exp(iq'n) + \exp(iq'm)] [\exp(iq''r) + \exp(iq''s)] \exp[-S(n-m) - S(r-s)].$$

APPENDIX C: AN EXACT GREEN'S FUNCTION

As an example of the difficulties one may encounter using the Green's function analysis of the exciton-phonon problem without first performing the canonical transformation used in the present paper, let us calculate the Green's function for the exciton-phonon coupling with no intermolecular coupling. The Hamiltonian is given as

$$H = \sum_n E_0 a_n^+ a_n + \sum_{n,q} \omega_q b_q^+ b_q + N^{-1/2} \\ \times \sum_{n,q} g_q \omega_q e^{inq} a_n^+ a_n (b_q^+ + b_{-q}). \quad (C1)$$

We may write this, using the transformation given above,

$$H = \sum_n (E_0 - N^{-1} \sum_q g_q^2 \omega_q) A_n^+ A_n + \sum_q \omega_q B_q^+ B_q \\ = \sum_n \hat{E}_0 A_n^+ A_n + \sum_q \omega_q B_q^+ B_q. \quad (C2)$$

The retarded Green's function may be written

$$G^R(k, t) = -i\theta(t) \langle [a_k^{(t)}, a_k^+] \rangle \quad (C3)$$

or

$$G^R(k, t) = -i\theta(t) N^{-1} \sum_{nn'} \exp[ik(n-n')] \langle [a_n(t), a_{n'}^+] \rangle \quad (C4)$$

We will calculate $\langle [a_n(t), a_n^+] \rangle$. According to (11) and (C2),

$$a_n(t) = A_n(t) \theta_n(t) \\ = \exp(-i\hat{E}_0 t) \exp\{-N^{-1/2} \sum_q r^{inq} g_q \\ \times [B_q^+(t) - B_{-q}(t)]\}. \quad (C5)$$

Also, because (C2) describes noninteracting particles, we have

$$\langle [a_n(t), a_n^+] \rangle = \langle A_n^+ A_n(t) \rangle \langle [\theta_n(t), \theta_n^+] \rangle \\ + \langle [A_n(t), A_n^+] \rangle \langle \theta_n(t) \theta_n^+ \rangle \quad (C6)$$

or

$$\langle [a_n(t), a_n^+] \rangle = \delta_{nn'} \exp(-i\hat{E}_0 t) \{ N_n \langle [\theta_n(t), \theta_n^+] \rangle \\ + \langle \theta_n(t) \theta_n^+ \rangle \}, \quad (C7)$$

where N_n is the average number of excitons at site n . Neglecting $\exp(-\beta\hat{E}_0)$ with respect to 1, we have

$$\langle [a_n(t), a_{n'}^+] \rangle = \delta_{nn'} \exp(-i\hat{E}_0 t) \langle \theta_n(t) \theta_{n'}^+ \rangle. \quad (C8)$$

Using the results of Appendix A,

$$\langle [a_n(t), a_{n'}^+] \rangle = \delta_{nn'} \exp(-i\hat{E}_0 t - S + I_0(t)), \quad (C9)$$

where $I_0(t)$ and S are defined in (48) and (47). Thus,

$$G^R(k, t) = -i\theta(t) \exp[-i\hat{E}_0 t - S + I_0(t)], \quad (C10)$$

and

$$G^R(k, z) = -ie^{-S} \int_0^\infty dt \exp[i(z - \hat{E}_0)t + I_0(t)]. \quad (C11)$$

An illustrative limit is that in which $\omega(q) = \omega$, $g(q) = g$ all q . Then

$$I_0(t) = g^2[(\bar{n}+1) \exp(-i\omega t) + \bar{n} \exp(i\omega t)], \quad (C12)$$

where

$$\bar{n} = (e^{\beta\omega} - 1)^{-1}. \quad (C13)$$

Then, expanding $\exp[I_0(t)]$ and collecting terms,

$$\exp[I_0(t)] = \sum_{m=-\infty}^{+\infty} \exp[\tfrac{1}{2}(m\beta\omega) - im\omega t] \times \bar{I}_m \{ 2g^2[\bar{n}(\bar{n}+1)]^2 \}, \quad (C14)$$

where \bar{I}_m is a modified Bessel function.¹⁹ Finally, we have

$$G(k, z) = \sum_{m=-\infty}^{+\infty} \frac{\exp(m\beta\omega/2) \bar{I}_m[2g^2\bar{n}^{1/2}(\bar{n}+1)^{1/2}]}{z - E_0 - g^2\omega - m\omega}, \quad (C15)$$

$$\{\bar{n}(\bar{n}+1)\}^{1/2} = \tfrac{1}{2} \text{csch} \beta\omega/2. \quad (C16)$$

We see that expanding the denominator in order to find $G(k, z)$ in a power series in g^2 will fail whenever $g^2\omega \geq (z - E_0 - m\omega)$. That is, a series expansion of G in powers of $g^2\omega$ will diverge whenever $z - E_0 - m\omega$ is less than $g^2\omega$. The zeroth-order Green's function has poles at the points $z = E_0 + m\omega$, and the exact Green's function has poles shifted a constant amount down the real axis from these. However the power series expansion of $G(k, z)$ will diverge in the region between the zeroth-order poles and the exact poles. In fact, if

$g^2 \geq 1$, then the power series diverges along the entire real axis, since the circles of divergence now overlap.

In a recent paper,²⁰ Gosar and Choi have used diagrammatic techniques to calculate the Green's function, (C15), and also to consider the case with intermolecular coupling. Their results are similar to our result using the canonical transformation. Our perturbation technique (Sec. II) goes beyond their result.

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