

Green's Function Approach to Exciton-Phonon Interactions*

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The system of a tightly bound exciton which is weakly coupled to phonons is treated by means of many-body Green's functions. Relevance of the formalism for the calculation of absorption and emission spectra, quasiparticle properties, lattice distortion, and exciton propagation is established. A variational technique is found useful for deriving formal relationships. Evaluations are carried out for an approximate Hamiltonian representing excitons in a one-dimensional lattice; both Einstein-model phonons and one-dimensional acoustic phonons are investigated. Approximations include a one-phonon approximation and, for many-phonon processes, the replacement of the exciton-phonon vertex function Γ by unity. The relation of these approximations to perturbation theory is assessed in specific cases. Finite-temperature calculations performed apply to excitons whose energies are large compared to κT . Among the results is the conclusion that the interacting exciton is not merely "renormalized"; instead, as in the case of electron-phonon interactions, the spectrum of excitations includes many diverse quasiparticle modes and other complex structure.

INTRODUCTION

GROUNDWORK for the treatment of exciton-phonon interactions was already laid in the pioneering works of Frenkel¹ and of Peierls.² Frenkel and Peierls recognized the fundamental role played by the effects of phonons on excitons in the absorption of light by solids; they even foresaw the possibility of the (self-) trapping of excitons as one such effect. With the advance of experimental techniques since the time of these papers, the scope of questions pertaining to the exciton-phonon problem has increased considerably. One would like to know in detail what phonons do to the structure of absorption and emission spectra, to the propagation of energy in a crystal, and to many other processes in which excitons are involved. Nevertheless, work in this area has remained relatively scant and a good understanding of phonon effects has not yet been reached.

Hope for significant progress in this field is offered by the development, in recent years, of certain many-body techniques which have been successfully applied to other areas of solid-state physics. In the present work, use is made of one such technique: The exciton-phonon problem is formulated in terms of many-body Green's functions.^{3,4} In principle, this method can be used to calculate all relevant properties; so far, we have found it mainly convenient for computing spectral shapes and quasiparticle properties. Calculations of spectral shapes have been made by a number of authors⁵⁻⁷ who em-

ployed a form of perturbation theory which is equivalent to the Green's function method insofar as perturbation converges. Our calculations on simple physical models indicate that it is not unusual for perturbation theory to fail in the most interesting regions of the spectra; one advantage of the Green's function formalism is that it is specifically designed to circumvent such nonconvergence difficulties. In any case, the formalism can be regarded as an improved language for talking about a many-body system; it makes for conceptual simplicity and ease of generalization to calculations of many diverse properties of the system.

In the first section of the present paper, formal developments are presented: The Green's functions are defined and some of their properties reviewed; expressions relating the Green's functions to several topics of interest in the exciton-phonon problem are given. The formalism is then applied to specific simple models in the second part of the paper.

FORMALISM

The Exciton-Phonon System

We describe the exciton-phonon system by the model Hamiltonian

$$H = \sum_k \omega(k) a_k^* a_k + \sum_q \nu(q) b_q^* b_q + N^{-1/2} \sum_{k,q} f(k,q) a_{k+q}^* a_k \varphi_q, \quad (1)$$

where

$$\varphi_q \equiv [2M\nu(q)]^{-1/2} [b_q + b_{-q}^*]. \quad (2)$$

In this expression, a_k^* is the creation operator for an exciton of wave vector k , while b_q^* creates a phonon of wave vector q . The lattice is thought of as consisting of N identical molecules each having a mass M . Units are such that $\hbar=1$. A one-dimensional notation is employed, although the use of three dimensions at this stage would be an inessential complication; specific calculations are eventually confined to one-dimensional models in any case. With the lattice constant taken as

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¹ J. Frenkel, *Phys. Rev.* **37**, 17 and 1276 (1931); *Physik. Z. Sowjetunion* **9**, 158 (1936).

² R. Peierls, *Ann. Physik* **13**, 905 (1932).

³ V. Galitskii and A. Midgal, *Zh. Eksperim. i Teor. Fiz.* **34**, 139 (1958) [English transl.: *Soviet Phys.—JETP* **7**, 96 (1958)].

⁴ P. C. Martin and J. Schwinger, *Phys. Rev.* **115**, 1342 (1959).

⁵ A. S. Davydov and E. I. Rashba, *Ukr. Fiz. Zh.* **2**, 226 (1957).

⁶ Y. Toyozawa, *Progr. Theoret. Phys. (Kyoto)* **20**, 53 (1958); Technical Report, Ser. A, No. 79, Institute for Solid State Physics, University of Tokyo (1963) (to be published in *Progr. Theoret. Phys.*).

⁷ J. J. Hopfield, *Phys. Chem. Solids* **22**, 63 (1961).

the unit of length, the allowed values of the one-dimensional wave vectors are $2\pi j/N$, $j=0, 1, 2, \dots, N-1$. The subscript $k+q$ appearing in the interaction term must be interpreted modulo 2π . Spin is also neglected; in effect, we are dealing with singlet excitons.

The tightly bound or Frenkel model of the exciton is used, so that the operators a_k^* can be expressed as

$$a_k^* = N^{-1/2} \sum_n \exp(-ikn) a_n^*, \quad (3)$$

where a_n^* , when acting on the ground state of the crystal, produces a state in which only the n th molecule is excited. The assumption of tight binding also allows us to restrict attention to a single exciton band, assumed nondegenerate.

In the Hamiltonian (1), terms describing direct conversion of excitons into phonons (and vice versa) have been omitted; this omission is justified if the phonon energies $\nu(q)$ are small compared to the exciton energies $\omega(k)$ provided, of course, that the coupling $f(k, q)$ is not excessive. Other terms, of higher order in exciton and/or phonon operators, have been left out for the sake of simplicity; no formal justification can be supplied for this procedure. As a consequence of these omissions, the Hamiltonian conserves exciton number. The exciton operators are taken to satisfy Bose commutation rules. Although this assumption is not clear-cut in a one-dimensional lattice,⁸ we shall not be interested in problems involving more than one exciton, and our results are independent of the commutation rules employed.

The Hamiltonian (1) is recognized as having the same form as the Hamiltonian ordinarily used to describe electron-phonon interactions, except that electrons are fermions. Thus, our formalism will be substantially equivalent to the formalism used in Green's function treatments of the electron-phonon system.⁹⁻¹¹

Green's Functions Defined

The following definitions of the exciton and phonon Green's functions, respectively, are adopted:

$$G_{kp}(t, t') = -i \langle T \{ a_k(t) a_p^*(t') \} \rangle, \quad (4)$$

$$D_{qr}(t, t') = -i \langle T \{ \varphi_q(t) \varphi_{-r}(t') \} \rangle. \quad (5)$$

The operators appearing in (4) and (5) are expressed in the Heisenberg picture and are ordered by the symbol T such that time arguments increase towards the left. The brackets denote an ensemble average

$$\langle Q \rangle \equiv \text{Tr} \{ \rho Q \}, \quad (6)$$

where ρ is an appropriate density matrix.

⁸ D. B. Chesnut and A. Suna, *J. Chem. Phys.* **39**, 146 (1963).

⁹ A. B. Migdal, *Zh. Eksperim. i Teor. Fiz.* **34**, 1438 (1958) [English transl.: *Soviet Phys.—JETP* **7**, 996 (1958).]

¹⁰ S. Engelsberg and J. R. Schrieffer, *Phys. Rev.* **131**, 993 (1963).

¹¹ R. D. Puff and G. D. Whitfield, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd Ltd., Edinburgh, 1963), pp. 171-190.

The space-time translational invariance of the Hamiltonian (1) allows writing the Green's function (4) in the form

$$G_{kp}(t, t') = \delta_{kp} G_k(t-t') \quad (7)$$

(provided the chosen ρ does not destroy this invariance) and makes it convenient to work with the Fourier transform of the Green's function, defined as

$$G(k_0, k) = \int_{-\infty}^{\infty} dt \exp(ik_0 t) G_k(t) \quad (8)$$

(similarly for the phonon Green's function).

Zero-Exciton-Temperature Approximation

The formalism is considerably simplified if we make the assumption

$$\omega(k) \gg \kappa T \equiv 1/\beta \quad (9)$$

and, consequently, if we perform the ensemble averages only over no-exciton states. In these states, the exciton-phonon interaction vanishes, and the grand canonical density matrix becomes, in effect,

$$\rho = \exp(-\beta H_{\text{ph}}) / \text{Tr}[\exp(-\beta H_{\text{ph}})],$$

$$H_{\text{ph}} \equiv \sum_q \nu(q) b_q^* b_q. \quad (10)$$

It is true that the density matrix (10) is, in fact, exact for the exciton-conserving Hamiltonian (1) and for a no-exciton ensemble. This statement has only formal significance, however, as for the macroscopic times necessary to establish thermal equilibrium in a real crystal, the otherwise negligible exciton-phonon conversion terms must come into play. None of the finite-temperature results presented below are, in general, applicable to low-lying excitons where (9) might not hold.

With the ensemble (10), the Green's function formalism will be only slightly modified from the usual zero-temperature treatment,³ and it will not be necessary to introduce imaginary-time Green's functions.⁴ We call this the zero-exciton-temperature approximation because all the temperature effects originate in the thermal distribution (10) of phonons alone; the thermal generation of excitons is neglected, so that the lattice is at absolute zero so far as excitons are concerned. Within the zero-exciton-temperature approximation, the problem is formally essentially identical to the polaron problem of a single electron, in an otherwise empty conduction band, interacting with phonons. The Green's function formalism for this problem has been discussed by Puff and Whitfield.¹¹ We collect here some resulting properties of the Green's functions for future reference.

The phonon Green's function (4) is exactly that of

noninteracting phonons.

$$D(k_0, k) = M^{-1} \left\{ \frac{(1+n_k)}{[k_0^2 - \nu(k)^2 + i0^+]} - \frac{n_k}{[k_0^2 - \nu(k)^2 - i0^+]} \right\}, \quad (11)$$

$$n_k \equiv 1 / [\exp(\beta\nu(k)) - 1]. \quad (12)$$

[The symbol 0^+ denotes a positive, real infinitesimal. We have assumed $\nu(k) = \nu(-k)$.]

The exciton Green's function $G(k_0, k)$, viewed as a function of the complex variable k_0 , is characterized in this scheme by being analytic in the entire half-plane above the real axis. We shall also be interested in the related quantities $G^>(k_0, k)$ and $G^<(k_0, k)$, which, for the full grand canonical ensemble and for a complete, exciton-nonconserving Hamiltonian are given by

$$G^>(k_0, k) = \sum_{r,s} W_s |\langle s | a_k | r \rangle|^2 2\pi\delta(k_0 - E_r + E_s) \quad (13)$$

and

$$G^<(k_0, k) = \sum_{r,s} W_r |\langle s | a_k | r \rangle|^2 2\pi\delta(k_0 - E_r + E_s), \quad (14)$$

and are related by

$$G^>(k_0, k) = \exp(\beta k_0) G^<(k_0, k). \quad (15)$$

Here, r and s label stationary states of the system and

$$W_s \equiv \exp(-\beta E_s) / \sum_r \exp(-\beta E_r). \quad (16)$$

In the zero exciton temperature limit, $G^<$ vanishes and $G^>$ is related to G by

$$G^>(k_0, k) = -2 \operatorname{Im} G(k_0, k). \quad (17)$$

We shall nevertheless have occasion to calculate $G^<$ in its more physically accurate form (14). This will be done by using the relation (15), with $G^>$ computed in the zero-exciton-temperature approximation by means of (17). This procedure should give $G^<$ to a good approximation, provided $\exp(\beta k_0) \gg 1$; within the restriction (9), this will be the case for values of k_0 in the most interesting range of energies, that corresponding to one or more excitons.

Variational Method

A convenient way of generating arbitrarily complicated Green's functions and the equations of motion satisfied by them is the variational approach of Schwinger.¹² With a few minor generalizations, the zero-temperature variational formalism can be made to apply to finite temperatures in the zero-exciton-temperature limit.

We employ the variational technique by first adding to the Hamiltonian H the "source term"

$$H_s = \sum_q J_q(t) \varphi_q, \quad (18)$$

and then performing variations on the functions $J_q(t)$, in the end setting these equal to zero.

In order to achieve a compact definition of the ensemble average of an operator when sources are present, we make use of the interaction-picture S matrix for time development of the system governed by the interaction Hamiltonian (18).

$$S \equiv U(\infty, -\infty) \equiv T \left\{ \exp -i \int_{-\infty}^{\infty} dt H_s(t) \right\}, \quad (19)$$

$$H_s(t) = \sum_q J_q(t) \exp(iHt) \varphi_q \exp(-iHt) \quad (20)$$

(the symbol T orders the operators following a power series expansion of the exponential). A definition of the ensemble average which reduces to the definition (6) when sources are removed (then $S=1$) is

$$\langle Q(t) \rangle = \operatorname{Tr} \{ \rho T[SQ(t)] \} / \operatorname{Tr} \{ \rho S \}. \quad (21)$$

With the definition (21), the customary result is obtained for the functional derivative of a time-ordered product of j operators:

$$\begin{aligned} \delta / \delta J_q(t') \langle T \{ Q_1(t_1) Q_2(t_2) \cdots Q_j(t_j) \} \rangle \\ = -i \langle T \{ Q_1(t_1) \cdots Q_j(t_j) \varphi_q(t') \} \rangle \\ + i \langle T \{ Q_1(t_1) \cdots Q_j(t_j) \} \rangle \langle \varphi_q(t') \rangle. \end{aligned} \quad (22)$$

With the aid of (22), the equation of motion for G becomes a single differential-functional-differential equation:

$$\begin{aligned} i\partial / \partial t G_{kp}(t, t') = \delta_{kp} \delta(t-t') + \omega(k) G_{kp}(t, t') \\ + N^{-1/2} \sum_q f(k-q, q) \{ \langle \varphi_q(t) \rangle G_{k-q,p}(t, t') \\ + i\delta / \delta J_q(t) G_{k-q,p}(t, t') \}. \end{aligned} \quad (23)$$

To completely specify the solution of (23), an initial condition must be stated. It is sufficient instead to give the initial condition on the noninteracting exciton Green's function $G_{kp}^0(t, t')$; the provision is only that the coupling be weak enough so that perturbation theory for the full Green's function converges in some finite region in the k_0 plane. The condition on G^0 is the same as that on G :

$$\begin{aligned} G_{kp}^0(t+0^+, t) = \langle a_k(t) a_p^*(t) \rangle, \\ G_{kp}^0(t-0^+, t) = \langle a_p^*(t) a_k(t) \rangle. \end{aligned} \quad (24)$$

Note that the ensemble averages in (24) must be computed according to the prescription (21); thus the expressions (24) may in general contain dependence on the functions $J_q(t)$.

Equation (23) can then be converted to an infinite nest of integral equations,¹³ of which the leading equation is the Dyson equation:

$$G(k_0, k) = G_0(k_0, k) + G_0(k_0, k) \Sigma(k_0, k) G(k_0, k). \quad (25)$$

¹² J. Schwinger, Proc. Natl. Acad. Sci. U.S.A. 37, 452 (1951).

¹³ See Ref. 10, Appendix A, for details.

G_0 is the noninteracting exciton Green's function, and the exciton self-energy function Σ is defined as

$$\Sigma(k_0, k) = i \int (dq_0/2\pi) \sum_q |f(k, q)|^2 G(k_0 + q_0, k + q) \times D(q_0, q) \Gamma(k_0, q_0; k, q). \quad (26)$$

The quantity Γ (the exciton-phonon vertex function) satisfies a more complicated equation; within the variational framework, Γ is formally defined as

$$\Gamma_{k_p; q}(t, t'; t'') = -N^{1/2} f(p, q)^{-1} \times [\delta / \delta \langle \varphi_q(t'') \rangle] G_{k_p}^{-1}(t, t'), \quad (27)$$

where the inverse of G is defined by

$$\sum_q \int_{-\infty}^{\infty} dt'' G_{k_q}^{-1}(t, t'') G_{q_p}(t'', t') = \delta_{k_p} \delta(t - t'). \quad (28)$$

The $\Gamma(k_0, q_0; k, q)$ appearing in (26) results after sources are turned off (then $p = k - q$) and the time-dependent Γ is transformed with respect to two independent time differences. One is led naturally to the hierarchy of integral equations satisfied by G , D , Γ , and other more complicated functions.¹³

Formal Approximations

The definition (27) for the vertex function Γ leads ordinarily (when ground-state expectation values, not general ensemble averages, are used) to the fact that, in the limit of vanishing coupling, $\Gamma(k_0, q_0; k, q)$ approaches the value unity.¹³ It is this feature which makes the definition (27) of Γ useful and which allows an approximate termination of the infinite nest of equations.

If Γ indeed approaches the value unity as the coupling $f(p, q)$ is made to vanish, then, according to (27), all variational derivatives of G must also vanish in this limit—i.e., the noninteracting exciton Green's function G_0 must be independent of the source functions $J_q(t)$. The only source dependence of G_0 lies in the initial conditions (24); it is readily verified that these initial conditions are independent of the phonon sources only if the density matrix ρ can be written as a product of factors each involving only exciton or only phonon

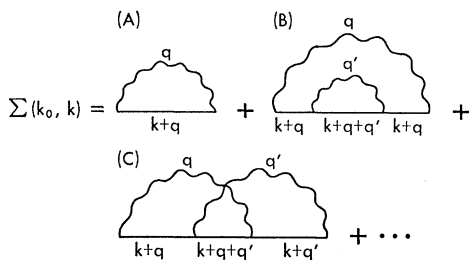


FIG. 1. Perturbation series for the self-energy. The three lowest order terms are shown. G_0 is denoted by a straight line, D by a wiggly one. Labels denote arguments (energy variables such as k_0 are suppressed).

operators. It can be shown that this factorizability of the density matrix is also necessary if it is to be at all possible to express the Green's function as a perturbation series involving only noninteracting exciton Green's functions. Since the exact grand canonical density matrix does not satisfy the factorizability criterion, the present formalism bogs down for lack of any effective approximation procedures; one is forced to resort to the imaginary-time Green's functions.⁴

The zero-exciton-temperature density matrix (10), on the other hand, is trivially factorizable. Thus, $\Gamma = 1$ in lowest order, and the usual perturbation series applies. This perturbation series is generated by solving the set of integral equations iteratively, beginning with $G = G_0$ and $\Gamma = 1$. The first few terms in the series for the self-energy are represented in Fig. 1.

We shall not concern ourselves with an accurate evaluation of the vertex function Γ but shall, in fact, terminate the set of integral equations by setting $\Gamma = 1$ in Eq. (26). In terms of the perturbation series for the self-energy, this " $\Gamma = 1$ approximation" involves leaving out all diagrams in which two phonon lines "cross," as in diagram (C) of Fig. 1. When the product $|f(k, q)|^2 D(q_0, q)$ is regarded as an effective, retarded exciton-exciton interaction, the $\Gamma = 1$ approximation can be identified with the time-dependent Hartree-Fock approximation.¹¹

We shall frequently use an approximation which is even more severe than $\Gamma = 1$. In the "one-phonon approximation" we retain for the self-energy only diagram (A) of Fig. 1. The validity of both the $\Gamma = 1$ and the one-phonon approximation is discussed in the course of specific evaluations.

Absorption and Emission Spectra

The formalism introduced will now be related to several topics of physical interest. Probably the most important of these topics, from the point of view of experiments, is the effect of phonons on the absorption and emission spectra of a crystal. The connection with Green's functions is immediate if the expression (13) for $G^>(E, k)$ is compared with the standard perturbation theory (Born approximation) result for the probability of absorption of a photon of energy^{6,7} E :

$$W_{\text{abs}}(E) = (2\pi/\hbar) (|\xi|^2/E) N^{-1} \times \sum_{r,s} W_r |\langle r | a_{k=E/c} | s \rangle|^2 \delta(E + E_r - E_s). \quad (29)$$

Here $|\xi|^2/E$ represents the exciton-photon coupling; r, s , and W_r have the same meaning as in Eqs. (13)–(16). The value $k = E/c$ is essentially zero (in units of the reciprocal lattice vector) for light in the visible range. Thus

$$W_{\text{abs}}(E) = (\text{const}/E) G^>(E, 0) = (-2 \text{const}/E) \text{Im} G(E, 0). \quad (30)$$

The factor $1/E$ in the energy dependence of the ab-

sorption probability does not have an appreciable effect on the shape of the absorption curve in the range of exciton energies; all the interesting structure is given by $G^>(E,0)$ alone.

Similarly $G^<(E,0)$, Eq. (14), is proportional to the emission probability for a photon of energy E . With the interpretation of $G^>$ and $G^<$ as the absorption and emission probabilities, respectively, the relation (15) is seen to be nothing but the familiar statement of detailed balance for a system in thermal equilibrium. Because of this relation, and because G is simply related to $G^>$, a knowledge of the one-particle exciton Green's function G is equivalent to an immediate knowledge of the detailed shapes of both absorption and of emission spectra.

Quasiparticle Properties

The determination of quasiparticle properties from the Green's function $G(k_0, k)$ is a common procedure in the applications of the Green's function formalism.^{3,4} Quasiparticles can usually be identified with the poles of $G(k_0, k)$ in the complex k_0 plane; the real part of such a pole gives the energy, the imaginary part the lifetime of the quasiparticle, while the residue of $G(k_0, k)$ at the pole is a measure of the relative probability for exciting the mode in question. For example, one might be able to recognize a "trapped-exciton" mode by the characteristics usually associated with such an exciton: large effective mass and a short lifetime. A quasiparticle description of the spectrum of excitations has considerable intuitive value; however, as we shall see in the examples below, such a description is sometimes inaccurate and hardly ever complete.

Lattice Displacement

The idea that an exciton may produce around it a distortion of the lattice is as old as the idea of the exciton itself.¹ Although no attempts seem to have been made at an experimental determination of such a distortion, it is at least in principle an important consequence of the exciton-phonon interaction.

The pattern of lattice displacements produced by an initially localized exciton is formally the simplest quantity associated with lattice displacements and is probably also closest to being experimentally tangible. The operator representing the displacement of the n th lattice point is

$$r_n = N^{-1/2} \sum_q \exp(iqn) \varphi_q. \quad (31)$$

If an exciton is created at the n th lattice site at time $t=0$, the resulting displacements at distances m from this site, as a function of time, are

$$\begin{aligned} S_m(t) &= \langle a_n(0) r_{n+m}(t) a_n^*(0) \rangle \\ &= N^{-3/2} \sum_{k,p} \exp[i(p-k)m] \\ &\quad \times \langle a_p(0) \varphi_{k-p}(t) a_k^*(0) \rangle. \end{aligned} \quad (32)$$

The correlation function which appears in the second line of (32) is related to the three-point function

$$\begin{aligned} \langle T \{ a_p(t_1) \varphi_{k-p}(t_2) a_k^*(t_3) \} \rangle \\ = \delta / \delta J_{k-p}(t_2) G_{pk}(t_1, t_3) |_{J_q(t)=0}. \end{aligned} \quad (33)$$

In fact, $\langle a_p(0) \varphi_{k-p}(t) a_k^*(0) \rangle$ is the analytic continuation of (33), from the piece corresponding to $t_1 > t_2 > t_3$, to $t_1 = t_3 = 0$, $t_2 = t$. As is suggested by the functional derivative expression for (33), this three-point function is in turn readily expressed in terms of the quantities G , D , and Γ , in a fashion quite analogous to the procedure used in deriving Dyson's equation.

We do not present this rather lengthy calculation but merely give the final result. Within the $\Gamma=1$ approximation, we find that the q -wave vector component of the displacement $S_m(t)$,

$$S_q(t) = N^{-1/2} \sum_m e^{-iqm} S_m(t), \quad (34)$$

is the solution of

$$\begin{aligned} \partial^2 S_q(t) / \partial t^2 + \nu(q)^2 S_q(t) \\ = (NM)^{-1} \sum_k f(k, q) G_{k+q}^*(t) G_k(t) \end{aligned} \quad (35)$$

(for $T=0$).

Equation (35) has a clear-cut physical interpretation: The mode $S_q(t)$ which in the absence of excitons oscillates with frequency $\nu(q)$ is driven by the term on the right of Eq. (35); the resemblance of this driving term to the exciton-phonon interaction term in the Hamiltonian (1) is not too surprising. The calculation of $S_m(t)$ from the time-dependent exciton Green's function is, from (35), straightforward, though not as direct as the computation of spectra and of quasiparticle properties.

Though formally and conceptually simple, the exciton-phonon correlation expressed by means of (32) tends to lead to a rather obscure and complex pattern of displacements. A simpler and more intuitive displacement configuration shows up only in formally more complicated exciton-phonon correlation functions. The five-point function,

$$\begin{aligned} S_m^k(t) &= N \langle a_k(0) a_n^*(t) a_n(t) r_{n+m}(t) a_k^*(0) \rangle \\ &= N^{-1/2} \sum_{p,q} \langle a_k(0) a_{p+q}^*(t) a_p(t) \varphi_q(t) a_k^*(0) \rangle \\ &\quad \times \exp(iqm), \end{aligned} \quad (36)$$

describes the lattice displacement, a distance m from the exciton, which results after a plane-wave exciton of wave-vector k is created at time $t=0$. To get at this five-point function approximately, we proceed as follows: The time-ordered five-point Green's function, from which (36) can be obtained by analytic continuation, can be written [see Eq. (22)] as a functional derivative of a four-point function which involves only exciton operators (up to terms which vanish when sources are removed). This four-point function is then approximated by neglecting correlations between

excitons.

$$\begin{aligned} & \langle T\{a_k(t_1)a_{p+q}^*(t_2)a_p(t_3)a_k^*(t_4)\} \rangle \\ & \approx \langle T\{a_k(t_1)a_k^*(t_4)\} \rangle \langle T\{a_{p+q}^*(t_2)a_p(t_3)\} \rangle \\ & + \langle T\{a_k(t_1)a_{p+q}^*(t_2)\} \rangle \langle T\{a_p(t_3)a_k^*(t_4)\} \rangle. \end{aligned} \quad (37)$$

The noncorrelation approximation (37) is consistent with $\Gamma=1$ in the present context. Upon performing the functional differentiation of (37), we obtain products of exciton Green's functions with three-point functions of the type (33). The end result of the subsequent analytic continuations is (for $\Gamma=1$)

$$\begin{aligned} S_m^k(t) &= \text{Re}\{N^{-1} \sum_q f(k,q)M^{-1\nu}(q)^{-1} \\ & \times \exp(-iqm)G_k^>(t)^* \int_{-\infty}^{\infty} (dx/2\pi) \exp(-ixt) \\ & \times G(x,k)[(1+n_q)G(x-\nu(q), k+q) \\ & + n_q G(x+\nu(q), k+q)]\}. \end{aligned} \quad (38)$$

Exciton Propagation

In order to understand the effect of phonons on the experimentally important area of energy transport via excitons, it is necessary to calculate the spatial propagation of an interacting exciton. The formal description for the propagation of an exciton is somewhat cumbersome. The probability that an exciton, created at $t=0$ on the n th lattice site, is found m sites away at a time t , is given by

$$P_m(t) = \langle a_n(0)a_{n+m}^*(t)a_{n+m}(t)a_n^*(0) \rangle. \quad (39)$$

It is no longer consistent to break this four-point function up by means of the noncorrelation approximation (37), essentially because an additional functional differentiation with respect to phonon sources is not involved now. Instead, at zero temperature, we split (39) up by introducing a sum over a complete set of intermediate states between the operators $a_{n+m}^*(t)$ and $a_{n+m}(t)$. Taking for the complete set of no-exciton states the set of free-phonon states, we may write (39) as the sum

$$P_m(t) = \sum_{j=0}^{\infty} P_m^j(t), \quad (40)$$

where j denotes the number of phonons in the intermediate state, i.e.,

$$\begin{aligned} P_m^0(t) &= |G_{m+n,n}^>(t)|^2; \\ P_m^1(t) &= \sum_q |\langle b_q(0)a_{m+n}(t)a_n^*(0) \rangle|^2; \\ P_m^2(t) &= (2!)^{-1} \sum_{q,q'} |\langle b_q(0)b_{q'}(0)a_{m+n}(t)a_n^*(0) \rangle|^2; \end{aligned} \quad (41)$$

etc. Note that the space-time exciton Green's function directly describes exciton propagation in a rigid lattice ($P_m=P_m^0$); it has been used for this purpose by

Merrifield.¹⁴ The one-phonon correction involves a three-point function which can be related to the exciton Green's function as before ($\Gamma=1$, $T=0$).

$$\begin{aligned} \langle b_q(0)a_{m+n}(t)a_n^*(0) \rangle &= [M\nu(q)]^{-1/2}N^{-3/2} \\ & \times \sum_p f^*(p,q) \exp(ipm) \int_{-\infty}^{\infty} (dx/2\pi) \\ & \times \exp(-ixt)G(x,p+q)G^*(x+\nu(q),p). \end{aligned} \quad (42)$$

No attempt has been made to evaluate the higher phonon terms in $P_m(t)$.

APPLICATIONS

Physical Models

In the models to which our formalism will now be applied, we shall restrict ourselves to a one-dimensional lattice with tightly bound excitons whose propagation takes place by a nearest-neighbor interaction. The exciton energy $\omega(k)$ then has the form

$$\omega(k) = \epsilon - 2\omega \cos k, \quad (43)$$

where ϵ is the energy of the excited state for an isolated molecule, while $-\omega$ is the matrix element of the exciton Hamiltonian which connects nearest neighbors (we assume $\omega > 0$ without loss of generality; if the correct ω is negative, one only has to replace k by $\pi-k$ everywhere).

Einstein-model phonons [$\nu(q)=\nu$, independent of q] will be dealt with most extensively; for these phonons, the coupling $f(k,q)$ will also be replaced by a constant. Our Einstein model is identical with the model employed by Merrifield in a description of the interactions between excitons and vibrational excitons¹⁵; our method of dealing with this model is entirely different, however.

Several calculations are performed with the longitudinal (acoustic) phonons that arise in a one-dimensional chain of identical molecules. These phonons have the dispersion law

$$\nu(q) = \nu |\sin \frac{1}{2}q|, \quad (44)$$

while the coupling has for nearest-neighbor interactions the form

$$f(k,q) = \gamma \sin^2 \frac{1}{2}q + i\eta \sin \frac{1}{2}q \cos(k + \frac{1}{2}q). \quad (45)$$

The term involving γ is a sort of deformation potential of the exciton; the η term arises from the change in the transfer matrix element ω when the lattice is strained.

One-Phonon Einstein Model

The q_0 integration in the expression (26) for the exciton self-energy function can be performed explicitly after Γ is set equal to unity and after the expression (11)

¹⁴ R. E. Merrifield, J. Chem. Phys. **28**, 647 (1958).

¹⁵ R. E. Merrifield, J. Chem. Phys. **40**, 445 (1964).

is substituted for the phonon Green's function D . The integration is done by closing the contour of integration above and making use of the fact that the only singularities of the integrand in the upper half q_0 plane are the poles of D , whose locations are known [see (11)]. For zero temperature ($n_q=0$) the result is

$$\Sigma(k_0, k) = -\sum_q |f(k, q)|^2 [2MN\nu(q)]^{-1} \times G(k_0 - \nu(q), k + q). \quad (46)$$

In the one-phonon approximation, the noninteracting exciton Green's function

$$G_0(k_0, k) = 1/(k_0 - \epsilon + 2\omega \cos k + i0^+) \quad (47)$$

is used to approximate the Green's function appearing in (46). If now, in the limit of large N , the sum in (46) is converted to an integral, this integral can be carried out explicitly in the Einstein model.

$$\begin{aligned} \Sigma(k_0, k) &= -f^2/(4\pi M\nu) \int_{-\pi}^{\pi} dq G_0(k_0 - \nu, k + q) \\ &= (f^2/2M\nu)/[(k_0 - \epsilon - \nu + i0^+)^2 - 4\omega^2]^{1/2}. \end{aligned} \quad (48)$$

The branch of the square root in (48) must be chosen so that the imaginary part of $\Sigma(k_0, k)$ is negative for real values of k_0 .

The self-energy (48) is pure imaginary for real k_0 in the range $\epsilon - 2\omega + \nu < k_0 < \epsilon + 2\omega + \nu$, which is just the range of energies of one phonon together with one exciton. Outside this range, the imaginary part of Σ is infinitesimal. The finite imaginary part of Σ gives rise

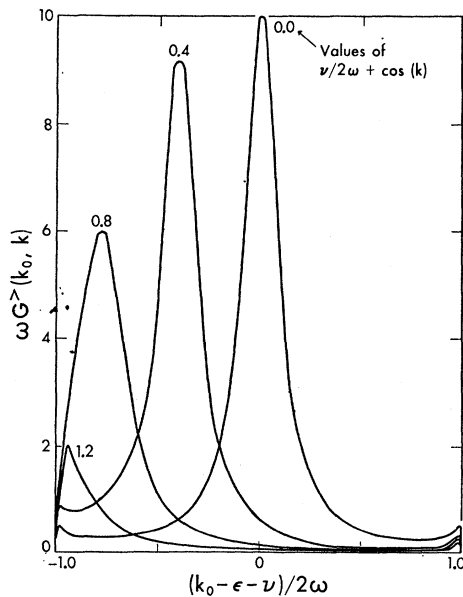


FIG. 2. $G^-(k_0, k)$ in the one-phonon Einstein model. The coupling constant $f^2/8M\nu\omega^2$ is taken as 0.1. Only the continuum portion is displayed. For negative values of the parameter $\nu/2\omega + \cos k$, the spectra are mirror images of the ones shown, reflected about $k_0 - \epsilon - \nu = 0$.

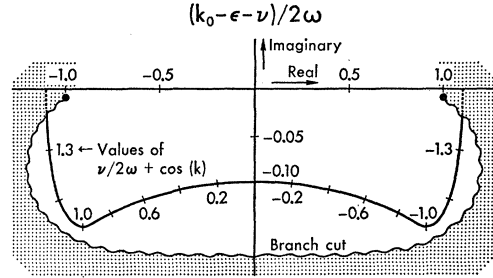


FIG. 3. Path of the complex pole of $G(k_0, k)$ in the one-phonon Einstein model. The coupling is the same as in Fig. 2.

to a continuum in the density of states $G^>(k_0, k)$, for the range of energies indicated; this continuum is illustrated in Fig. 2. There is a broad peak at about the unperturbed exciton energy, except when the latter approaches a continuum edge. This quasiparticle peak can indeed be associated with a pole of the Green's function; this pole occurs on only one of the two Riemann sheets of G —the branch cut must be judiciously deformed, as is done in Fig. 3, to display this pole. Near the continuum edges, the correspondence between the main peak and the pole of G becomes vague. As the unperturbed exciton energy is shifted outside the continuum, this pole eventually touches the real axis in the “unphysical” sheet (as distinguished from the “physical” sheet on whose real axis $G^>$ is evaluated) and splits into two real poles; this behavior seems to have no physical significance whatever.

The peculiar peaks near the continuum edges are not associated with any poles of the Green's function; their physical origin is unclear. Similar edge peaks were also found by Engelsberg and Schrieffer for the case of electrons interacting with phonons.¹⁰

Outside the range of energies corresponding to the continuum, $G^>(k_0, k)$ (it is proportional to the imaginary part of G) can only have delta-function peaks; these are located at poles of G , which now lie infinitesimally below the (physical) real axis. There are two such delta-function peaks, indicating undamped modes of the system in the present approximation. They occur just outside the edges of the continuum, except when the unperturbed exciton energy $\omega(k)$ lies outside the continuum; in the latter case, one of the peaks lies near the energy $\omega(k)$.

The existence of a stable mode of excitation above the continuum is physically unreasonable and indeed is a consequence of the one-phonon approximation. When many-phonon processes are included (see below), the continuum, in fact, extends to infinite energies; what in the one-phonon approximation is the upper stable mode becomes a broad peak in the density of states with a slightly shifted energy. The lower cutoff of the continuum as well as the stability of the lower mode are, on the other hand, real effects in a one-dimensional crystal and persist in the many-phonon treatment.

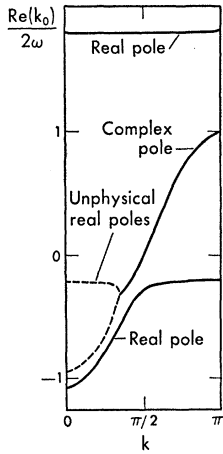


FIG. 4. Band structure in the one-phonon Einstein model. The real parts of the locations of the various poles are shown for $\nu/2\omega=0.8$; coupling is the same as in Fig. 2.

The positions of the three peaks in $G^>(k_0, k)$ (the real part of the corresponding pole for the broad peak) are shown in the band diagram of Fig. 4. The residues of G at these poles are shown in Fig. 5; these give the areas under the sharp peaks exactly and the area under the broad peak approximately (except near the continuum edges). Note that the peak lying nearest the unperturbed exciton energy has the greatest area, so long as it is isolated from the other two. The areas under the peaks give the relative probabilities for exciting the corresponding quasiparticle modes. Only when the mode nearest the unperturbed exciton energy is clearly dominant is one justified to speak of it as a “dressed exciton”—in general, one has to concede the existence of several quasiparticle branches. It should be added that none of the modes which arise in the one-phonon

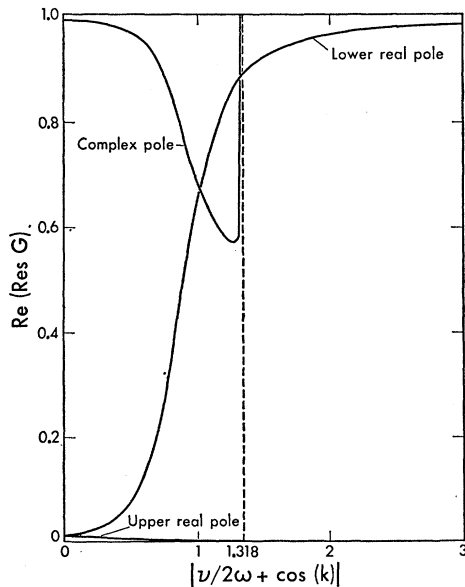


FIG. 5. Real parts of residues of $G(k_0, k)$. Coupling is the same as in Fig. 2.

approximation can be identified with a trapped exciton; such an exciton must by definition be accompanied by a severe lattice distortion, i.e., many phonons.

One-Phonon Acoustic Model

With the one-dimensional acoustic phonons (44) and the appropriate interaction (45), it is no longer possible to find an explicit expression for even the one-phonon self-energy. We have made numerical evaluations of this self-energy for various choices of the parameters ν , γ , and η ; only a brief description of the results of these calculations is presented.

The qualitative features of the spectrum of excitations are for the acoustic phonons quite similar to those for Einstein-model phonons. There is a continuum,

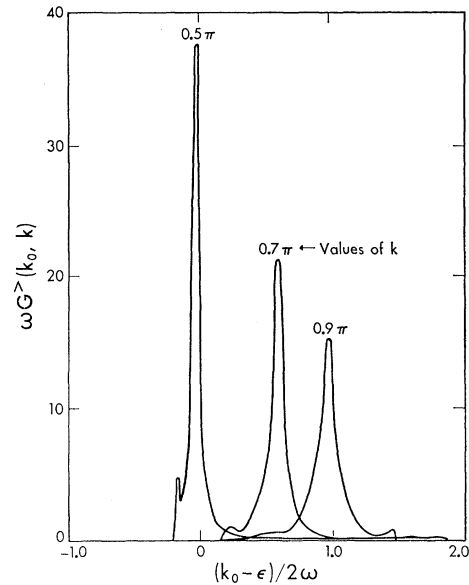


FIG. 6. $G^>(k_0, k)$ in the one-phonon acoustic model. The maximum phonon energy ν is taken as $\nu/2\omega=1.4$; the coupling constants are $\gamma^2/8M\nu\omega^2=\eta^2/8M\nu\omega^2=0.1$.

although its location now depends on the wave vector k ; the continuum features a dominant broad peak and, frequently, edge peaks. Two delta-function peaks also occur, usually just outside the continuum. The edge peaks are occasionally quite prominent. Another qualitative feature distinguishing the spectrum from that of the Einstein model is that the main continuum peak may become quite sharp; correspondingly, the associated pole of the Green's function approaches the real axis in the physical sheet. A typical density of states $G^>(k_0, k)$ is shown in Fig. 6.

A typical band diagram giving the locations of the three poles is presented in Fig. 7. The way in which the undamped modes imitate the phonon dispersion (44) is striking and suggests that the flat portions of the corresponding curves in Fig. 4 are similarly a consequence of the flatness of the Einstein-model phonons. It looks

as though these modes can be interpreted as bound states of an exciton with one phonon, where the total momentum k is shared so as to extremize the total energy. In particular, the lower mode, whose stability is real, minimizes this total energy. This mode can be expected to be a prominent feature of the absorption spectrum at low temperatures; its observation would, in effect, lead to a determination of the phonon dispersion law. Therefore, it is of interest to digress briefly from the one-dimensional model in order to estimate the continuum edge structure in real three-dimensional crystals.

Continuum Edge in Three Dimensions

The pole of the Green's function just below the continuum edge is a consequence of the fact that the self-energy is singular at this edge. The singularity will always be present in a one-dimensional model, as is clear from the following. In the one-phonon approximation, the edge occurs at the minimum (with respect to q) of the energy $\omega(k+q)+\nu(q)$; except at special and isolated points, we may expand this energy about its minimum as

$$E(k,q) \equiv \omega(k+q) + \nu(q) = E(k,q_0) + C(k)(q-q_0)^2 + \dots \quad (49)$$

Writing $x_0 \equiv k_0 - E(k,q_0)$, $x \equiv q - q_0$, the one-phonon self-energy has near the continuum edge the form

$$\Sigma(x_0, k) = \text{const} \int dx / [x_0 - C(k)x^2 + i0^+] \sim \text{const}' (-x_0)^{-1/2}. \quad (50)$$

Similarly, $\Sigma(x_0, \mathbf{k})$ behaves as $\ln(x_0)$ in two dimensions (cf. Ref. 1—there, the continuum edge extends over a surface, so that the resulting problem is essentially a two-dimensional one). In three dimensions, however, the self-energy is no longer singular at the edge. The real part of Σ does, however, have a peak there, and the height of this peak determines whether or not a pole will occur. Unfortunately, this height depends on the entire energy band and not just the region near the minimum of $E(\mathbf{k}, \mathbf{q})$. The above properties can be seen with the aid of a simple mock calculation which assumes a cylindrical Brillouin zone, exact quadratic dependence of the energy about its minimum, and a momentum-independent coupling.

$$\Sigma(x_0) \sim \lambda \int_0^R r dr \int_0^Z dz / (x_0 - ar^2 - bz^2 + i0^+);$$

$$\Sigma(0) \sim (\lambda Z/2a) F([aR^2/bZ^2]^{1/2}), \quad (51)$$

where

$$F(u) \equiv \ln(1+u^2) + 2u \operatorname{arccot}(u).$$

The peak value $\Sigma(0)$ is seen to depend on the extreme values of the energy, aR^2 and bZ^2 ; $\Sigma(0)$ is large only when the ratio of these energies is large or small, i.e.,

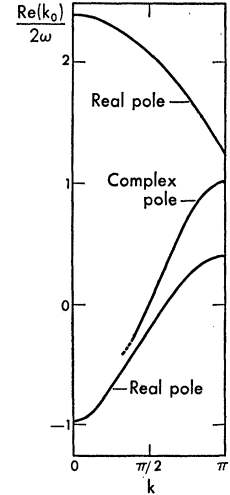


FIG. 7. Band structure in the one-phonon acoustic model. Values of ν and the coupling constants are the same as in Fig. 6.

when the crystal is predominantly one- or two-dimensional. In the general case, a pole of the Green's function occurs near the continuum edge only when the unperturbed exciton energy $\omega(\mathbf{k})$ is also near this edge; this pole continues along the edge until $\omega(\mathbf{k})$ exceeds the edge energy by $\Sigma(0)$. Evaluations of the integral (51) show that the peculiar continuum edge peak is always associated with a pole near the edge; when the pole merges into the continuum, the edge peak also disappears.

Remarks on the One-Phonon Approximation

The one-phonon approximation for the exciton self-energy corresponds identically to the perturbative method used by several authors to calculate absorption spectra.⁵⁻⁷ Toyozawa⁸ confines attention to the shape of a single peak and thus misses the possibility of additional structure introduced by the interaction with the phonons. Some of this additional structure is treated in a general way by Davydov and Rashba⁵; however, these authors in effect neglect the real part of the self-energy. This is a serious omission; for example, in our one-dimensional calculation, this real part gave rise to the poles near the continuum edge; in a two-dimensional calculation (as in Ref. 1), the real part of Σ leads to structure in the continuum region as well.

Still, the results of the last two sections could have been obtained without the mention of Green's functions. We have many reasons for presenting these calculations as a part of a Green's function treatment of exciton-phonon interactions. For one, it will be shown shortly (at least for the Einstein model) that, although the one-phonon approximation describes the one-phonon structure of the spectra reasonably well, the description breaks down if one attempts to improve it by going to higher order in the perturbation series. The intrinsically nonperturbative Green's function formalism provides a means for assessing the validity of results obtained from perturbation theory. By being part of the general

formalism, the one-phonon calculations can, moreover, be applied towards properties of the system other than the absorption spectrum: We have already discussed quasiparticle properties; we can also make use of our formal expressions relating the exciton Green's function to lattice displacements and to exciton propagation.

Multiphonon Einstein Model

In the Einstein model the sum (or integral) in (46) can be evaluated even if the full exciton Green's function is retained. It is easy to show that $\Sigma(k_0, k)$, as given by this approximate ($\Gamma=1$) expression, does not depend on the wave vector k . The result of the q integration is then a difference equation for $\Sigma(k_0)$.

$$\Sigma(k_0) = (f^2/2M\nu) / \{ [k_0 - \epsilon - \nu - \Sigma(k_0 - \nu)]^2 - 4\omega^2 \}^{1/2}. \quad (52)$$

An interesting special case of (52) occurs if ν is allowed to approach zero in (52), while the coupling $\lambda^2 = f^2/2M\nu$ is kept constant. Then (52) becomes simply a quartic equation for Σ . There is only one pole of the exciton Green's function; it occurs at precisely

$$k_0 = \epsilon - 2\omega \cos k - i\lambda^2 / |2\omega \sin k|. \quad (53)$$

This example provides an illustration of the breakdown of the usual quasiparticle description: Although the imaginary part of the pole diverges as k approaches the band-edge values 0 or π , the corresponding peak in the density of states, shown in Fig. 8, shows no unusually large broadening. Also, the real part of the pole (53) does not give the position of the peak very accurately, especially near the band edges. Note that

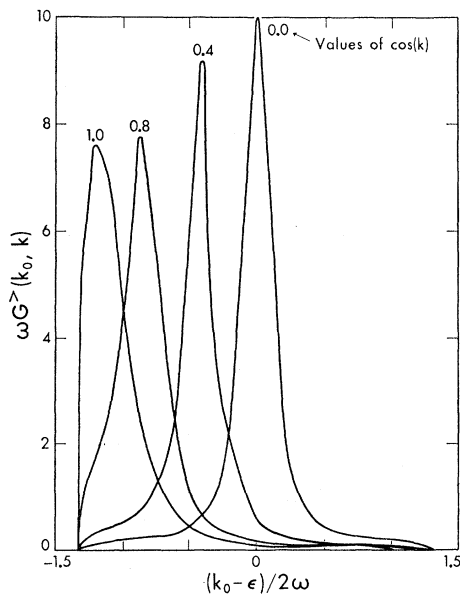


FIG. 8. $G^>(k_0, k)$ for zero-energy phonons. The coupling $\lambda^2/4\omega^2$ is taken as 0.1. Curves for $\cos k < 0$, not shown, are reflections (about 0) of the curves for $|\cos k|$.

$G^>(k_0, 0)$, as shown in Fig. 8 ($\cos k = 1$), constitutes a theoretical prediction of the zero-temperature absorption-line shape for an exciton interacting with very-low-energy quanta, e.g., rotational states of the molecules.

For finite values of ν , (52) can be solved iteratively, starting with $\Sigma(k_0) = 0$. As this has to be done numerically, it is not much more difficult to do the calculation for finite temperatures; for finite temperatures, the equation to be solved is the second-order difference equation

$$\Sigma(k_0) = (1+n)F(k_0 - \nu) + nF(k_0 + \nu), \quad (54)$$

where

$$F(x) \equiv (f^2/2M\nu) / \{ [x - \epsilon - \Sigma(x)]^2 - 4\omega^2 \}^{1/2},$$

and

$$n \equiv 1 / (\exp \beta \nu - 1).$$

Although the solution of (54) cannot be given in closed form, some of its properties can be examined directly. Thus, we find that $\Sigma(k_0)$ has singularities in the vicinity of the points $\epsilon \pm 2\omega + j\nu$, $j = 1, 2, 3, \dots$ and, for nonzero temperatures, also $j = -1, -2, -3, \dots$. Physically, these energies correspond to the production (or absorption) of 1, 2, 3, \dots phonons together with the exciton; we expect structure in the spectrum near these energies. Some density-of-states plots calculated for band-edge values of the wave vector (corresponding to optical absorption spectra for excitons of positive or of negative effective mass) are shown in Figs. 9 and 10. The corresponding emission spectra, obtained by using the relation (15), are presented in Figs. 11 and 12.

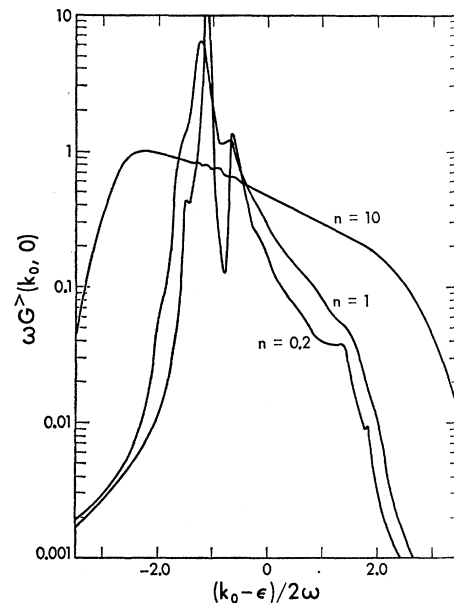


FIG. 9. Absorption spectrum for positive mass exciton. The temperature is indicated by $n \equiv 1 / (\exp \beta \nu - 1)$. The Einstein phonon energy is taken as $\nu/2\omega = 0.4$. The coupling constant is $f^2/8M\nu\omega^2 = 0.1$.

We do not seriously expect Figs. 9-12 to be capable of being subjected to a meaningful experimental test. These results are presented merely to illustrate the sort of detailed description of spectra that the Green's function technique can generate. One can see broadening and shifting of various peaks with the temperature; unfortunately this approach does not lead to any understanding of the physical origin of such behavior.

Perturbation Theory (Einstein Model)

The iterative solution of (52), when expanded in powers of f^2 , agrees term for term with the partial, $\Gamma=1$, perturbation series for Σ . But such an expansion is obviously not valid near the singularities of Σ ; correspondingly then, perturbation theory must also break down. This difficulty can be seen explicitly in the fourth-order perturbation term $\Sigma_{(B)}$ [diagram (B) of Fig. 1]:

$$\Sigma_{(B)}(k_0, k) = - (f^2/2M\nu)^2 (k_0 - \epsilon - \nu) \times [(k_0 - \epsilon - \nu)^2 - 4\omega^2]^{-3/2} \times [(k_0 - \epsilon - 2\nu)^2 - 4\omega^2]^{-1/2}. \quad (55)$$

This term is to be added to the second-order term ($\Sigma_{(A)}$), given in (48). Now according to (52), the singularities of Σ are, in general, expected to be of the order of inverse square roots. The second-order term $\Sigma_{(A)}$ indeed shows a one-phonon ($k_0 \approx \epsilon \pm 2\omega + \nu$) singularity of this nature, but the fourth-order correction $\Sigma_{(B)}$ overcomes this singularity by diverging as the $-3/2$ power. Moreover, the addition of $\Sigma_{(B)}$ to $\Sigma_{(A)}$ can (and does) lead to the wrong sign of the imaginary part of Σ at the pole of G that lies near the one-phonon singularity of Σ . This pole is actually shifted above the real axis, in contradiction to our assumption concerning poles of G . Increasingly worse one-phonon singularities are added, the farther out one goes in the perturbation series. On the other hand, the behavior of $\Sigma_{(B)}$ near the two-phonon singularity is reasonable and is only affected adversely if a higher order term is added. It appears that the behavior near the j th-phonon singularity is described well by $2j$ th-order perturbation; in

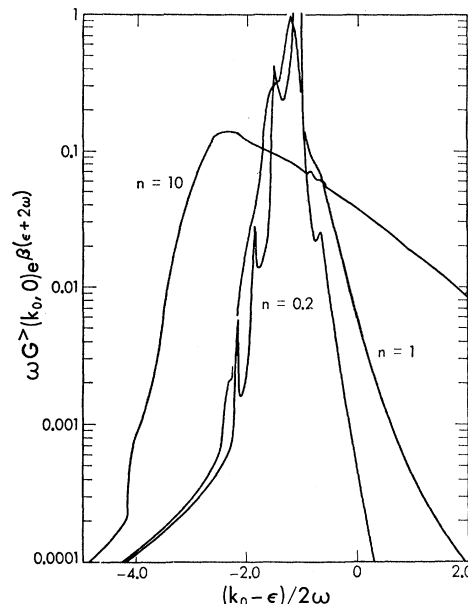


FIG. 11. Emission spectrum for positive mass exciton. Parameters are as in Fig. 9.

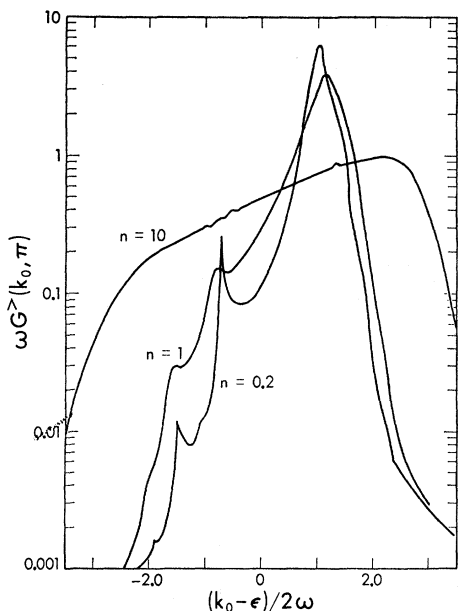


FIG. 10. Absorption spectrum for negative mass exciton. Parameters are as in Fig. 9.

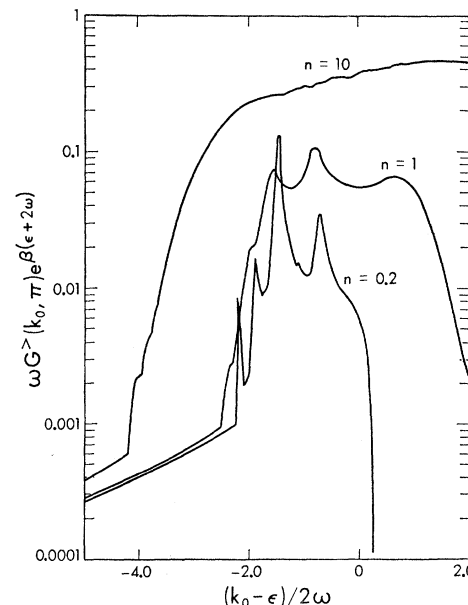


FIG. 12. Emission spectrum for negative mass exciton. Parameters are as in Fig. 9.

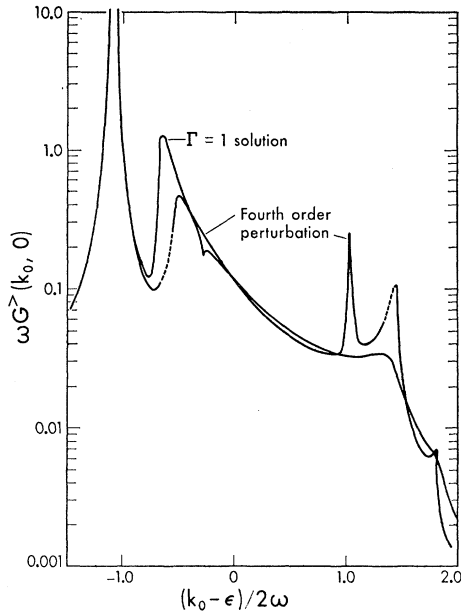


FIG. 13. Comparison of perturbation theory with the $\Gamma=1$ approximation ($T=0$). The parameters are as in Fig. 9. Dashed portions in the perturbation curve are sketched for regions where the perturbation result is grossly in error; these sketched portions are not based on any calculation. The large peak near $(k_0 - \epsilon)/2\omega = -1$ is a delta function which has been given an artificial width of 0.02ω .

particular, our use of the one-phonon approximation as part of a nonperturbative treatment seems to be vindicated, at least so far as it applied to one-phonon effects.

It might be thought that the trouble at the one-phonon singularity is canceled in fourth order by the "line-crossing" term which is left out in the $\Gamma=1$ approximation. An evaluation of this term [$\Sigma_{(C)}$: diagram (C) in Fig. 1] for the Einstein model leads, however, to a one-phonon singularity which is of different order from the singularity in $\Sigma_{(B)}$. Explicitly,

$$\begin{aligned} \Sigma_{(C)}(k_0, k) = & - (f^2/2M\nu)^2 [4\omega^2 - h(k_0)^2] \\ & \times [4\omega^2 - 4\omega h(k_0) \cos k + h(k_0)^2]^{-1} \\ & \times [(k_0 - \epsilon - \nu)^2 - 4\omega^2]^{-1} \\ & \times [(k_0 - \epsilon - 2\nu)^2 - 4\omega^2]^{-1/2}, \end{aligned}$$

where

$$\begin{aligned} h(k_0) \equiv & \{k_0 - \epsilon - \nu + [(k_0 - \epsilon - \nu)^2 - 4\omega^2]^{1/2}\}^2 \\ & \times \{k_0 - \epsilon - 2\nu + [(k_0 - \epsilon - 2\nu)^2 - 4\omega^2]^{1/2}\}. \quad (56) \end{aligned}$$

Although the expression (56) for the line-crossing term does support our contention that fourth-order perturbation is not valid for a description of one-phonon effects, this expression also points to weaknesses of the $\Gamma=1$ approximation, insofar as two-phonon effects are accurately described by fourth-order perturbation theory. We can in no way argue that the $\Sigma_{(C)}$ is small compared to $\Sigma_{(B)}$ retained in the $\Gamma=1$ approximation. What is more, the $\Sigma_{(C)}$ has two additional singularities

for values of k_0 satisfying

$$h(k_0) = \exp(\pm ik). \quad (57)$$

These may lead to new poles of G , with corresponding additional two-phonon structure in the density of states G . A typical absorption spectrum, calculated first within the $\Gamma=1$ approximation, then in fourth-order perturbation, is shown in Fig. 13. An additional sharp peak arising from the line-crossing term is clearly visible. Evidently, an approximation better than $\Gamma=1$ is required for an accurate description of two-phonon effects, accurate insofar as the Hamiltonian (1) is used. It would, however, be physically unwarranted to attempt such a more accurate calculation without, at the same time, adding to the Hamiltonian interaction terms which are quadratic in the displacement operators.

Lattice Distortion

Of the two expressions (32) and (36), descriptive of the lattice distortion produced by an exciton, the pattern of displacements (32) is by far the easiest to evaluate. Unfortunately, little can be learned from the results of such a calculation. In the Einstein model, the spreading exciton leaves behind it a wake of displacements which continue to oscillate without diminishing amplitude, since no coupling exists between the independent oscillators representing phonons. The displacements are thus only an indication of the exciton's past history. With acoustic phonons, there is a different sort of difficulty—it turns out that the pattern of displacements is entirely dominated by a strong distortion pulse which is produced initially and which spreads essentially independently of the exciton.

The evaluation of (36), via the expression (38), is difficult in even the simplest model. The task becomes reasonable if we approximate the Green's functions which appear in (38) by free-exciton Green's functions; not only does this procedure lead to an immediate evaluation of the x integral, it also allows the system to reach a steady state in the limit $t \rightarrow \infty$. In effect, we are then calculating the lattice displacement accompanying an exciton that is forcibly kept in free-exciton-like motion. The result depends on whether or not the unperturbed exciton energy $\epsilon - 2\omega \cos k$ exceeds the continuum threshold $\epsilon - 2\omega + \nu$. Below this threshold, at $T=0$, we obtain a localized, exponentially decreasing distortion surrounding the exciton.

$$\begin{aligned} S_m^k(t) = & - (f/2M\nu) [(v + 2\omega \cos k)^2 - 4\omega^2]^{-1/2} \\ & \times [r^{|m|} \cos(km + 2\omega t \cos k)], \quad (58) \end{aligned}$$

where

$$\begin{aligned} r \equiv & \nu/2\omega + \cos k - [(\nu/2\omega + \cos k)^2 - 1]^{1/2}, \\ & |\nu + 2\omega \cos k| > 2\omega, \end{aligned}$$

and

$$2\omega t \gg 1.$$

A distortion pattern having the same form for $k=0$

was also found by Merrifield.¹⁵ The divergence in the displacement which occurs when the continuum threshold is approached is a consequence of our forcing the exciton to propagate as though it were free.

Within the continuum, when the production of real phonons becomes possible, we obtain a nonlocalized distortion pattern due to the presence of as many phonons as are needed to maintain the "free" motion of the exciton.

$$S_m^k(t) = (f/2M\nu)[4\omega^2 - (\nu + 2\omega \cos k)^2]^{-1/2} \times \{\sin[(k - q_0)m + 2\omega t \cos k]\}, \quad (59)$$

where

$$|\nu + 2\omega \cos k| < 2\omega, \\ 2\omega t \gg 1,$$

and

$$q_0 \equiv \arccos(\nu/2\omega + \cos k).$$

It is simple enough to generalize $S_m^k(t)$ to finite temperatures; in addition to (58) and (59), which are to be multiplied by $1+n$, there is a contribution, proportional to n , of the phonons in the ensemble. For momenta such that $|2\omega \cos k - \nu| < 2\omega$, in particular near $k=0$, these phonons lead to an additional background of the type (59). When $|2\omega \cos k - \nu| > 2\omega$ (the upper portion of the energy band), a pattern with a shape like (59) appears; it is due to the fact that in this energy range the background phonons cannot be absorbed.

Exciton Propagation

If nontrivial results describing exciton propagation are to be obtained, it is not possible to make approximations such as those of the last section. We are faced with the full analytic structure of the Green's function in evaluating the necessary transforms and momentum sums. This structure is, as we saw, quite complicated in even the one-phonon Einstein model. We have calculated $P_m^0(t)$ and $P_m^1(t)$ in this model, by means of a laborious numerical evaluation. The root-mean-square exciton displacement so calculated is presented in Fig. 14. It appears that, although the no-phonon contribution to this displacement eventually slacks off, the one-phonon correction just makes up for it in a way such that the net rate of exciton propagation is essentially unaffected. This interesting result is most likely a consequence of the severe physical assumptions in-

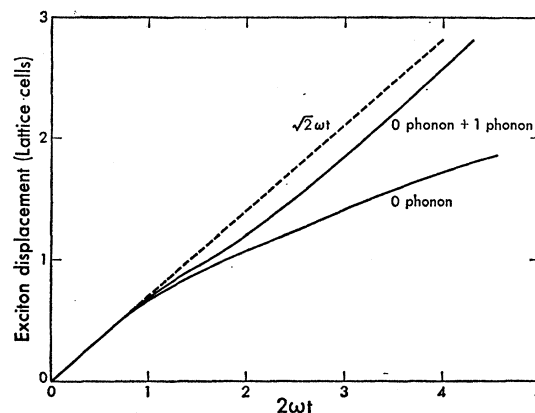


FIG. 14. Root-mean-square exciton displacement. The dashed line represents the rms displacement for a noninteracting exciton. Values of parameters used: $\nu/2\omega=0.4$; $f^2/8M\nu\omega^2=0.1$.

herent in the Einstein model: Both the phonons and the exciton-phonon interaction are confined to individual lattice sites in this model.

Concluding Remarks

In this work we have tried to explore the usefulness of the Green's function technique for calculating general features of the interacting exciton-phonon system. Although we have reservations concerning some of our approximations, we have indicated ways in which Green's functions can be convenient for computing properties such as spectral shapes and quasiparticle characteristics. Perhaps the greatest virtue of the formalism, in particular of the variational procedure, is the ease with which purely formal expressions can be derived; it is not always easy to perform specific evaluations of such formal expressions.

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