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THEORY OF VIBRONIC SPECTRA OF MOLECULAR CRYSTALS

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A theory is developed for the vibronic light-absorption spectra of molecular crystals, i.e., of spectra corresponding to simultaneous electronic and intramolecular vibrational excitations (an exciton and a phonon). The basic exciton-phonon interaction mechanism is assumed to be the change $\Delta\nu$ of vibrational frequencies in electronically excited molecules. For not too small $\Delta\nu$ in a crystal energy spectrum the two-particle excitation region is accompanied by a region of one-particle excitations in all or part of $\mathbf{k}$ space, corresponding to the concurrent motions of an exciton and phonon. Formulas are derived for the positions and intensities of absorption bands associated with one-particle excitations as functions of the structure of the exciton and phonon bands and the exciton-phonon coupling parameters. The physical mechanisms are ascertained which predominantly influence the one-particle excitation band structure in different limiting cases. The intensity distribution is derived for a wide-band spectrum corresponding to two-particle excitations.

The theory predicts the possibility of an entire system of crystal impurity bands. When the probability of phonon transfer from site to site is small the different bands can be interpreted as corresponding to exciton quantum states accompanying phonon excitations at different distances from an impurity molecule. A similar structure can also appear in the spectra of pure crystals in a region where several phonons are excited simultaneously with an exciton. Finally, in the current-carrier energy spectra of semiconductors having narrow allowed bands the properties are considered that result from changes of bond strength near excess charges and from the formation of coupled carrier-phonon pairs.

INTRODUCTION

THE general concept of excitons as the lowest electronic excitations in nonmetallic crystals was formulated by Frenkel and by Peierls,[1, 2] along with an approach to an analysis of exciton-phonon interactions. Excitons in molecular and atomic crystals have aroused considerably increased interest following the discovery that the spectra of some organic crystals include multiplets consisting of highly polarized bands (Davydov multiplets[3, 4]). During the last few years the types of exciton excitations have been classified completely and rigorously as a function of the strength of exciton-phonon coupling; a theory has also been developed for the forms of exciton absorption and luminescence bands.[5-8] In all these studies it was assumed, essentially, that an exciton is a purely electronic intramolecular excitation propagating through a crystal, and that phonons represent oscillations corresponding to the external molecular degrees of freedom (translation and rotation). The basic interaction mechanism was the shifting of crystalline oscillator equilibrium positions induced by the presence of excitons. Also considered were changes induced in the energy spectrum of excitons "clothed" with (mainly virtual) phonons, as well as the broadening of absorption and luminescence bands that is caused by phonon emission and absorption accompanying optical electronic transitions.

Some authors have recently extended the foregoing ideas to the interactions between electronic excitations and intramolecular vibrations. Simplification of the pertinent interaction Hamiltonian and new calculating methods have enabled the study of changes in the structure of an exciton band during the "clothing" process[9] and the appearance of new spectral branches,[10] which are being studied most at present in one-dimensional systems[6, 7] and with which [9, 10] we are mainly concerned. We note, incidentally, that some of the results obtained in [9, 10] also apply to interactions between excitons and lattice vibrations.

We shall consider here an entirely different aspect of the interaction between electronic excitations and intramolecular vibrations, governed by the reduction of intramolecular vibrational frequencies in electronically excited molecules. It will be shown that changes of vibrational frequencies lead to a qualitative reorganization of the electronic-vibrational (vibronic) spectra for both pure and impure crystals.

The foregoing effect, whose theory will be developed here, consists essentially in the following. Let us consider one crystalline molecule in a state of electronic-vibrational excitation, and let us study what happens to this excitation. In virtue of translational symmetry it can, of course, be transferred as a whole to a neighboring molecule etc., that is, it can travel along the crystal as an electronic-vibrational exciton. However, another possibility appears. Since there exists some probability that the excited molecule can lose either its purely electronic or its purely vibrational excitation independently, the electronic-vibrational excitation can be decomposed into an electronic and a vibrational exciton that are propagated independently. The outcome of the competition between these two processes is governed by the reduction of vibrational frequencies in electronically excited molecules. The frequency shift $\Delta\nu$ is not too small, being 50–100 cm^{-1} for aromatic molecules; this is of the order of exciton band widths in the corresponding crystals.

The breakup of the electronic-vibrational excitation is associated with a gain $|\Delta\nu|$ of "potential" energy that can compete with the loss of "kinetic" energy that usually accompanies the breakup. Therefore, when $|\Delta\nu|$ is not too small the lower portion of the energy spectrum will comprise a band of states corresponding to the combined propagation of an electronic and a vibrational excitation with the quasimomentum $\mathbf{k}$. The two excitations form a kind of bound state; they move relative to each other within a limited spatial region and remain at a single site during a portion of the time. The absorption bands that are interpreted as being electronic-vibrational in crystal spectra correspond to transitions into quantized states belonging to these bands. Dissociated states lie higher in the energy scale, in the region of two-particle excitations corresponding to independent propagation of the electronic and vibrational excitations. This region corresponds to broad-band absorption, which has not yet been investigated systematically and has evidently not been interpreted properly.

1. HAMILTONIAN OF AN ELECTRONIC-VIBRATIONAL SYSTEM

In the Heitler-London approximation the Hamiltonian of noninteracting electronic excitations and intramolecular vibrations in an ideal crystal can be divided into two terms:

$$H_{00} = \sum_{\mathbf{n}\alpha} [\varepsilon_0 \psi^+_{\mathbf{n}\alpha} \psi_{\mathbf{n}\alpha} + \nu_0 \varphi^+_{\mathbf{n}\alpha} \varphi_{\mathbf{n}\alpha}], \tag{1}$$

$$H_{\mathrm{res}} = \sum_{\mathbf{n}\alpha,\, \mathbf{m}\beta}' [M_{\mathbf{n}\alpha,\, \mathbf{m}\beta} \psi^+_{\mathbf{n}\alpha} \psi_{\mathbf{m}\beta} + \mu_{\mathbf{n}\alpha,\, \mathbf{m}\beta} \varphi^+_{\mathbf{n}\alpha} \varphi_{\mathbf{m}\beta}]. \tag{2}$$

Here $\psi^+_{\mathbf{n}\alpha}$ and $\varphi^+_{\mathbf{n}\alpha}$ are the operators for the creation, at a site $\mathbf{n}\alpha$, of a purely electronic excitation, which will be called an exciton, and of an intramolecular vibration, which will be called a phonon; α is the index of the sublattice containing the molecule, and $\mathbf{n}$ is the index number of this molecule within the sublattice. The coefficients M and μ in (2) are resonance integrals controlling the respective probabilities of excitation transfer from site to site, and are subject to the customary symmetry conditions that make $\mathrm{H}_{\mathrm{res}}$ Hermitian. The operators φ obey the Bose commutation rules, and the operators ψ obey the Pauli rules; φ and ψ also commute among themselves. The primed summation in (2) will always denote $\mathbf{n}\alpha \neq \mathbf{m}\beta$.

The exciton-phonon interaction operator will be given the form

$$H_{int} = H^{(1)}_{int} + H^{(2)}_{int} = \sum_{\mathbf{n}\alpha} \psi^+_{\mathbf{n}\alpha} \psi_{\mathbf{n}\alpha} [a(\varphi^+_{\mathbf{n}\alpha} + \varphi_{\mathbf{n}\alpha}) + b(\varphi^+_{\mathbf{n}\alpha} + \varphi_{\mathbf{n}\alpha})^2] + H^{(2)}_{int} \tag{3}$$

The first term in $\mathrm{H}^{(1)}_{\mathrm{int}}$ represents the shifts of molecular oscillator equilibrium positions, and the second term represents the vibrational frequency shifts, in excited molecules; if a given vibration is incompletely symmetric we have $\alpha = 0$. $\mathrm{H}^{(2)}_{\mathrm{int}}$ includes exciton-phonon interaction terms containing indices of two different sites.

The interaction Hamiltonian (3) is extremely complex. This can be seen from the mere fact that retention of only the first term of $\mathrm{H}^{(1)}_{\mathrm{int}}$ resembles the deformation potential approximation; we shall be interested primarily in the second term of $\mathrm{H}^{(1)}_{\mathrm{int}}$. We therefore introduce an additional limitation by assuming that M, μ, $\Delta\nu$, and the shifts of exciton levels resulting from the "clothing" process—all of which have comparable magnitudes—are considerably smaller than the phonon frequency ν_0.

We temporarily retain in $\mathrm{H}_{\mathrm{int}}$ only the first term of $\mathrm{H}^{(1)}_{\mathrm{int}}$ and make use of the matrix

$$S = -\frac{a}{\nu_0} \sum_{\mathbf{n}\alpha} \psi^+_{\mathbf{n}\alpha} \psi_{\mathbf{n}\alpha} (\varphi_{\mathbf{n}\alpha} - \varphi^+_{\mathbf{n}\alpha}) \tag{4}$$

to perform the canonical transformation

$$(H_{00}+H_{int})\rightarrow \exp(S)(H_{00}+H_{int})\exp(-S)=H_{00}$$
$$-\frac{a^2}{\nu_0}\sum_{\mathbf{n}\alpha}\psi^+_{\mathbf{n}\alpha}\psi_{\mathbf{n}\alpha}. \qquad (5)$$

It follows from (4) and (5) that the effect of H_{int} is then reduced to a renormalization of ϵ_0 by the factor $-a^2/\nu_0$ and to the addition of small corrections $\sim a/\nu_0$ in the transformed operator H_{res}. It can be shown, similarly, that all terms of H_{int} which do not conserve the number of phonons can be excluded with an error of the same order ($\sim \nu_0^{-1}$); we shall henceforth assume that all coefficient renormalizations associated herewith have been performed. We can now understand the governing role of frequency changes in excited molecules. While the first member of H_{int} (usually dominant in the "clothing" effect) is eliminated completely by the canonical transformation, the second member leaves the nondisappearing term

$$b\sum_{\mathbf{n}\alpha}\psi^+_{\mathbf{n}\alpha}\psi_{\mathbf{n}\alpha}(\varphi^+_{\mathbf{n}\alpha}\varphi_{\mathbf{n}\alpha}+\varphi_{\mathbf{n}\alpha}\varphi^+_{\mathbf{n}\alpha}). \qquad (6)$$

We now proceed to write $H^{(2)}_{int}$ as consisting of fourfold products of ψ and φ that conserve the numbers of excitons and phonons and that contain the indices of two different sites. All independent terms of this kind can be represented by

$$H^{(2)}_{int}=\sum_{\mathbf{n}\alpha,\,\mathbf{m}\beta}{}' \{J_{\mathbf{n}\alpha,\,\mathbf{m}\beta}\psi^+_{\mathbf{n}\alpha}\varphi^+_{\mathbf{n}\alpha}\varphi_{\mathbf{m}\beta}\psi_{\mathbf{m}\beta}+K_{\mathbf{n}\alpha,\,\mathbf{m}\beta}\psi^+_{\mathbf{n}\alpha}\varphi^+_{\mathbf{m}\beta}\varphi_{\mathbf{n}\alpha}\psi_{\mathbf{m}\beta}$$
$$+Q_{\mathbf{n}\alpha,\,\mathbf{m}\beta}\psi^+_{\mathbf{n}\alpha}\varphi^+_{\mathbf{m}\beta}\varphi_{\mathbf{m}\beta}\psi_{\mathbf{n}\alpha}+R_{\mathbf{n}\alpha,\,\mathbf{m}\beta}\psi^+_{\mathbf{n}\alpha}(\varphi^+_{\mathbf{n}\alpha}\varphi_{\mathbf{m}\beta}$$
$$+\varphi^+_{\mathbf{m}\beta}\varphi_{\mathbf{n}\alpha})\psi_{\mathbf{n}\alpha}+T_{\mathbf{n}\alpha,\,\mathbf{m}\beta}\varphi^+_{\mathbf{n}\alpha}(\psi^+_{\mathbf{n}\alpha}\psi_{\mathbf{m}\beta}+\psi^+_{\mathbf{m}\beta}\psi_{\mathbf{n}\alpha})\varphi_{\mathbf{n}\alpha}\}. \qquad (7)$$

The first term here represents the transfer of an electronic-vibrational excitation as a whole; the second term represents the exchange of an exciton and phonon between two sites; the third term is a correction of the exciton energy resulting from the presence of a phonon at one of the nearest sites; the fourth and fifth terms are corrections to the resonance integrals of phonons and excitons, respectively.

It will be convenient henceforth to separate the first sum from (7) and to combine it with (6). This is accomplished easily by extending the summation formally to include $\mathbf{n}\alpha = \mathbf{m}\beta$ and employing the definition

$$J_{\mathbf{n}\alpha,\,\mathbf{n}\alpha}=\Delta_\nu. \qquad (8)$$

Transforming to the momentum representation, we have

$$\psi_{\mathbf{n}\alpha}=N^{-1/2}\sum_{\mathbf{k}}\psi_{\mathbf{k}\alpha}e^{i\mathbf{k}\mathbf{n}_\alpha},\quad \varphi_{\mathbf{n}\alpha}=N^{-1/2}\sum_{\mathbf{k}}\varphi_{\mathbf{k}\alpha}e^{i\mathbf{k}\mathbf{n}_\alpha}, \qquad (9)$$

where N is the number of elementary cells in the fundamental volume, and $\mathbf{n}_\alpha$ is the vector coordinate of the $\mathbf{n}\alpha$-th molecule; then

$$H_0=H_{00}+H_{res}=\sum_{\mathbf{k}\alpha\beta}[\varepsilon_{\alpha\beta}(\mathbf{k})\psi_{\mathbf{k}\alpha}{}^+\psi_{\mathbf{k}\beta}+\nu_{\alpha\beta}(\mathbf{k})\varphi_{\mathbf{k}\alpha}{}^+\varphi_{\mathbf{k}\beta}], \qquad (10)$$

where

$$\varepsilon_{\alpha\beta}(\mathbf{k})=\varepsilon_0\delta_{\alpha\beta}+\sum_{\mathbf{n}-\mathbf{m}}M_{\mathbf{n}\alpha,\,\mathbf{m}\beta}e^{-i\mathbf{k}(\mathbf{n}_\alpha-\mathbf{m}_\beta)}, \qquad (11)$$

and $\nu_{\alpha\beta}(\mathbf{k})$ is expressed completely analogously in terms of ν_0 and μ. Furthermore,

$$H_J=\frac{1}{N}\sum_{\mathbf{k}\mathbf{k}_1\mathbf{k}_2\alpha\beta}J_{\alpha\beta}(\mathbf{k})\psi^+_{\mathbf{k}_1\alpha}\varphi^+_{\mathbf{k}-\mathbf{k}_1\alpha}\varphi_{\mathbf{k}-\mathbf{k}_2\beta}\psi_{\mathbf{k}_2\beta}, \qquad (12)$$

where

$$J_{\alpha\beta}(\mathbf{k})=\sum_{\mathbf{n}-\mathbf{m}}J_{\mathbf{n}\alpha,\,\mathbf{m}\beta}e^{-i\mathbf{k}(\mathbf{n}_\alpha-\mathbf{m}_\beta)}. \qquad (13)$$

Finally, the last four terms of (7) are transformed to give

$$H'_{int}=\frac{1}{N}\sum_{\substack{\mathbf{k}\mathbf{k}_1\mathbf{k}_2\\ \alpha\beta}}\{K_{\alpha\beta}(\mathbf{k}_1+\mathbf{k}_2-\mathbf{k})\psi^+_{\mathbf{k}_1\alpha}\varphi^+_{\mathbf{k}-\mathbf{k}_1\beta}\varphi_{\mathbf{k}-\mathbf{k}_2\beta}\psi_{\mathbf{k}_2\beta}$$
$$+Q_{\alpha\beta}(\mathbf{k}_1-\mathbf{k}_2)\psi^+_{\mathbf{k}_1\alpha}\varphi^+_{\mathbf{k}-\mathbf{k}_1\beta}\varphi_{\mathbf{k}-\mathbf{k}_2\beta}\psi_{\mathbf{k}_2\alpha}$$
$$+\psi^+_{\mathbf{k}_1\alpha}[R_{\alpha\beta}(\mathbf{k}-\mathbf{k}_2)\varphi^+_{\mathbf{k}-\mathbf{k}_1\alpha}\varphi_{\mathbf{k}-\mathbf{k}_2\beta}$$
$$+R_{\alpha\beta}(\mathbf{k}_1-\mathbf{k})\varphi^+_{\mathbf{k}-\mathbf{k}_1\beta}\varphi_{\mathbf{k}-\mathbf{k}_2\alpha}]\psi_{\mathbf{k}_2\alpha}$$
$$+\varphi^+_{\mathbf{k}-\mathbf{k}_1\alpha}[T_{\alpha\beta}(\mathbf{k}_2)\psi^+_{\mathbf{k}_1\alpha}\psi_{\mathbf{k}_2\beta}+T_{\alpha\beta}(-\mathbf{k}_1)\psi^+_{\mathbf{k}_1\beta}\psi_{\mathbf{k}_2\alpha}]\varphi_{\mathbf{k}-\mathbf{k}_2\alpha}\}. \qquad (14)$$

All coefficients in (14) are obtained from the corresponding quantities in the coordinate representation by means of sums that differ from (13) only through the absence of terms with $\mathbf{n}\alpha = \mathbf{m}\beta$. The complete exciton-phonon interaction operator is $H_{int} = H_J + H'_{int}$.

2. CONDUCTIVITY TENSOR

We now proceed to derive a formula for the conductivity tensor at absolute zero (T = 0). In some instances we shall use formulas derived by us previously;[11] the numerical designations of these equations will be preceded by the Roman numeral "I."

A general equation for the conductivity tensor is, with $\hbar = 1$,

$$\sigma_{il}(\mathbf{k},\omega)=\pi\omega^{-1}\langle j_i^{+0}(\mathbf{k})\delta(\omega-H)j_l^0(\mathbf{k})\rangle, \qquad (15)$$

where H is the Hamiltonian of the crystal in the absence of electromagnetic fields, and $\mathbf{j}^0(\mathbf{k})$ is a Fourier component of the current density operator, defined by (I.3) and (I.9). Averaging is performed over the ground state of the system, which is assumed to be at zero in the energy scale.

The following comment must be made regarding (15). This equation was derived by assuming that the entire macrofield of the electromagnetic wave (including a longitudinal field generated by unretarded Coulomb interactions) can be regarded as the external field acting on the crystal.[1] In this approach we exclude from (I.36), for the direct Coulomb interaction between particles, the summation over the electrodynamic long wavelength region, replacing it with an interaction through a self-consistent macrofield. The effective Hamiltonians and the energy spectra of the quasiparticles (excitons and phonons) are, of course, entirely different in these two regions, being regularized in the long-wave region and unregularized outside of this region (in the sense of [11]). However, nothing arbitrary appears in the physical results, and all formulas are derived more simply than when the rigorous method of [11] is used.

Using the definition

$$\delta(\omega - H) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty e^{i(\omega - H)t}\, dt, \tag{16}$$

where it is understood that ω contains the positive imaginary part ($\omega \rightarrow \omega + i\delta$), we easily obtain

$$\sigma_{il}(\mathbf{k}, \omega) = \frac{1}{\omega} \operatorname{Re} \int_0^\infty dt e^{i\omega t} \langle \widetilde{j}_i^{+0}(\mathbf{k}, t) \widetilde{j}_l^{0}(\mathbf{k}, 0) \rangle; \ \widetilde{\mathbf{j}}^0(\mathbf{k}, t)$$

$$= e^{iHt} \mathbf{j}^0(\mathbf{k}) e^{-iHt}. \tag{17}$$

Second quantization leads to

$$\mathbf{j}^0(\mathbf{k}) = \frac{1}{\sqrt{vN}} \frac{e}{m} \sum_{\mathbf{n}\alpha} \{ \mathbf{k}_\alpha{}^f e^{-i\mathbf{k}\mathbf{n}_\alpha} \varphi_{\mathbf{n}\alpha} \psi_{\mathbf{n}\alpha} + \mathbf{k}_\alpha{}^{*f} e^{i\mathbf{k}\mathbf{n}_\alpha} \psi^+_{\mathbf{n}\alpha} \varphi^+_{\mathbf{n}\alpha} \}, \tag{18}$$

where $\mathbf{k}_\alpha^f$ are the matrix elements of the quasimomentum for an intramolecular electronic-vibrational transition, and v is the volume of a unit cell. Equation (18) includes only the portion of the operator $\mathbf{j}^0$ that is associated with electronic-vibrational transitions, because all other transitions (such as those that are purely electronic) are not within the frequency region of our present interest.

After substituting (18) into (17), dropping terms equal to zero, and performing some simple transformations, we obtain

$$\hat{\sigma}(\mathbf{k}, \omega) = -\frac{e^2}{v\omega m^2} \operatorname{Im} \hat{F}(\mathbf{k}, \omega), \tag{19}$$

where

$$\hat{F}(\mathbf{k}, \omega) = \sum_{\alpha\beta} F_{\alpha\beta}(\mathbf{k}, \omega) \widehat{\mathbf{k}_\alpha^f \mathbf{k}_\beta{}^{*f}}, \tag{20}$$

$$F_{\alpha\beta}(\mathbf{k}, \omega) = \sum_{\mathbf{n}-\mathbf{m}} \int_{-\infty}^{+\infty} dt F_{\mathbf{n}\alpha, \mathbf{m}\beta}(t - t') \exp\{-i\mathbf{k}(\mathbf{n}_\alpha - \mathbf{m}_\beta)$$

$$+ i\omega(t - t')\}, \tag{21}$$

$$F_{\mathbf{n}\alpha, \mathbf{m}\beta}(t - t') = -i \langle P \widetilde{\psi}_{\mathbf{n}\alpha}(t) \widetilde{\varphi}_{\mathbf{n}\alpha}(t) \widetilde{\varphi}^+_{\mathbf{m}\beta}(t') \widetilde{\psi}^+_{\mathbf{m}\beta}(t') \rangle. \tag{22}$$

Equations (19)–(22) express the conductivity tensor in terms of the exciton-phonon Green's function, which, as is shown especially clearly by (22), represents the propagation of an electronic-vibrational excitation as a whole in a crystal. Equations (21) and (22) are transformed by means of (9) into

$$F_{\alpha\beta}(\mathbf{k}, t - t')$$

$$= -\frac{i}{N} \sum_{\mathbf{k}_1\mathbf{k}_2} \langle P \widetilde{\psi}_{\mathbf{k}_1\alpha}(t) \widetilde{\varphi}_{\mathbf{k}-\mathbf{k}_1\alpha}(t) \widetilde{\varphi}^+_{\mathbf{k}-\mathbf{k}_2\beta}(t') \widetilde{\psi}^+_{\mathbf{k}_2\beta}(t') \rangle, \tag{23}$$

which will be important subsequently.

Equation (19) shows that the segments of the real axis ω where $\hat{F}$ is real correspond to the region of crystal transparency. If isolated poles of $\hat{F}$ are present here, narrow absorption peaks arise. The values of ω corresponding to the poles can be interpreted as the energies of the corresponding quasiparticles.

The spectral representation of $F_{\mathbf{n}\alpha, \mathbf{n}\alpha}$ is

$$F_{\mathbf{n}\alpha, \mathbf{n}\alpha}(\omega) = \sum_\lambda \rho^\lambda_{\mathbf{n}\alpha} / (\omega - E_\lambda), \tag{24}$$

where $\rho_{\mathbf{n}\alpha}$ is the probability that an exciton and a phonon will be localized simultaneously in the quantized state λ at the site $\mathbf{n}\alpha$. The density $\rho^\lambda_{\mathbf{n}\alpha}$, which is easily calculated for isolated poles as the residue of $F_{\mathbf{n}\alpha, \mathbf{n}\alpha}$, is an important physical property that describes the degree of exciton-phonon coupling.

The transition to the interaction representation for the operator H_0 and the calculation of the Green's functions is complicated by the Pauli commutation rules for the operators $\psi_{\mathbf{n}\alpha}$. However, since $H_0 + H_{\text{int}}$ conserves the total number of excitons, when we calculate the Green's functions (22) containing a single exciton-creation operator only a single exciton is present in each intermediate state; therefore the result is entirely unaffected by noncommutativity of $\psi_{\mathbf{n}\alpha}$ and $\psi^+_{\mathbf{n}\alpha}$. Consequently we shall henceforth assume that the exciton operators are of Bose character. The transformation to the interaction representation is then accomplished conventionally, and P products are transformed into T products.

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[1] Different ways of defining the external macrofield (as the total field or its transverse part) were considered in[12-14].

3. GRAPHICAL TECHNIQUE FOR THE GREEN'S FUNCTIONS

The Green's function (23) includes summations over the momenta $\mathbf{k}_1$ and $\mathbf{k}_2$, with consequences that become clearer when we first limit ourselves to crystals having a single molecule in each unit cell. Then

$$H_{int} = \frac{1}{N} \sum_{\mathbf{k}\mathbf{k}_1\mathbf{k}_2} [J(\mathbf{k}) + W(\mathbf{k}|\mathbf{k}_1\mathbf{k}_2) + V_+(\mathbf{k}|\mathbf{k}_2) + V_-(\mathbf{k}|\mathbf{k}_1)]\, \overset{+}{\psi}_{\mathbf{k}_1} \overset{+}{\varphi}_{\mathbf{k}-\mathbf{k}_1} \varphi_{\mathbf{k}-\mathbf{k}_2} \psi_{\mathbf{k}_2}; \tag{25}$$

here the first term was obtained from (12), the second from the first two terms of (14), the third from the third and fifth terms of (14), and the last from the fourth and sixth terms of (14). Since the four coefficients in (25) have different arguments, they lead to terms of entirely different structures in a perturbation series.

We use the definition

$$-i \int_{-\infty}^{+\infty} \langle T\psi_{\mathbf{k}_1}(t)\varphi_{\mathbf{k}-\mathbf{k}_1}(t)\overset{+}{\varphi}_{\mathbf{k}-\mathbf{k}_2}(t')\psi_{\mathbf{k}_2}{}^{+}(t')\rangle\, e^{i\omega(t-t')}\, dt = f_{\mathbf{k}_1}(\mathbf{k}, \omega)\, \delta_{\mathbf{k}_1\mathbf{k}_2}; \tag{26}$$

here $\varphi_{\mathbf{k}}(t)$ and $\psi_{\mathbf{k}}(t)$ are interaction representation operators; therefore the left-hand side of (26) is obviously diagonal with respect to $\mathbf{k}_1$ and $\mathbf{k}_2$. The summation over $\mathbf{k}_1$ in $f_{\mathbf{k}_1}$ gives us the zeroth approximation Green's function $F^{(0)}$.

The first-order correction of the Green's function (23) is

$$\begin{aligned} F_{\alpha\beta}^{(1)}(\mathbf{k}, \omega) &= \frac{1}{N^2} \sum_{\mathbf{k}_1\mathbf{k}_2} f_{\mathbf{k}_1}(\mathbf{k}, \omega)[J(\mathbf{k}) + W(\mathbf{k}|\mathbf{k}_1\mathbf{k}_2) + V_+(\mathbf{k}|\mathbf{k}_2) \\ &\quad + V_-(\mathbf{k}|\mathbf{k}_1)] f_{\mathbf{k}_2}(\mathbf{k}, \omega) = F^{(0)}(\mathbf{k}, \omega) J(\mathbf{k}) F^{(0)}(\mathbf{k}, \omega) \\ &\quad + W^{(0)}(\mathbf{k}, \omega) + F^{(0)}(\mathbf{k}, \omega) V_+^{(0)}(\mathbf{k}, \omega) \\ &\quad + V_-^{(0)}(\mathbf{k}, \omega) F^{(0)}(\mathbf{k}, \omega), \end{aligned} \tag{27}$$

where

$$\begin{aligned} W^{(0)}(\mathbf{k}, \omega) &= \frac{1}{N^2} \sum_{\mathbf{k}_1\mathbf{k}_2} f_{\mathbf{k}_1}(\mathbf{k}, \omega) W(\mathbf{k}|\mathbf{k}_1\mathbf{k}_2) f_{\mathbf{k}_2}(\mathbf{k}, \omega), \\ V_+^{(0)}(\mathbf{k}, \omega) &= \frac{1}{N} \sum_{\mathbf{k}_2} V_+(\mathbf{k}|\mathbf{k}_2) f_{\mathbf{k}_2}(\mathbf{k}, \omega), \\ V_-^{(0)}(\mathbf{k}, \omega) &= \frac{1}{N} \sum_{\mathbf{k}_1} f_{\mathbf{k}_1}(\mathbf{k}, \omega) V_-(\mathbf{k}|\mathbf{k}_1). \end{aligned} \tag{28}$$

Equation (27) shows that the different terms differ greatly in the number of functions $F^{(0)}$ that are derived from the summation. The entire first-approximation correction is represented graphically in Fig. 1a. The rhombus and triangles represent quantities defined by (28). In this latter equation the cofactors in the sums have been written in the same sequence as that in which they would naturally appear in a perturbation-series expansion. In the graphs for each sum a left-hand (or right-hand) vertex indicates that the corresponding product in the sum begins (or ends) with the function f, while a vertical left-hand side of a triangle (or a right-hand side) indicates that the product begins with the coefficient V_+ (or ends with the coefficient V_-). Therefore the $F^{(0)}$ lines are connected to vertical line segments and cannot be connected to the vertices of triangles.

The basic rules for the construction of higher-order graphs are contained in the foregoing. We need only to add the rule that the vertices of the rhombus and triangles can be contiguous with the vertical sides of a rectangle or triangle. For example, Fig. 1b represents the sum of second-order diagrams which terminate at the right in an $F^{(0)}$ line, and which can thus be regarded as corrections to the last diagram of Fig. 1a. The first three graphs of Fig. 1b consist of elements that had already appeared in Fig. 1a; the fourth graph includes a new element corresponding to the analytic expression

$$\frac{1}{N^2} \sum_{\mathbf{k}_1\mathbf{k}_2} f_{\mathbf{k}_1}(\mathbf{k}, \omega) W(\mathbf{k}|\mathbf{k}_1\mathbf{k}_2) f_{\mathbf{k}_2}(\mathbf{k}, \omega) V_-(\mathbf{k}|\mathbf{k}_2). \tag{29}$$

The higher orders will contain new sums including an increasingly large number of summations over $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \ldots$. Therefore, because of the W term in (25) our problem has no exact solution.[2]

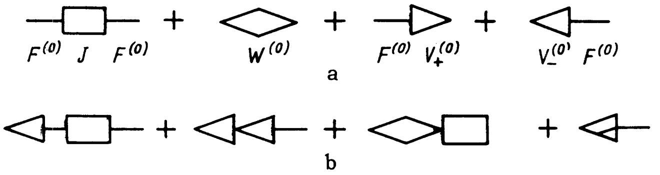

FIG. 1. Perturbation theory corrections of the Green's function: (a) first order; (b) second order.

By means of the aforementioned rules for constructing graphs we easily arrive at the system of equations shown graphically in Fig. 2. The double line represents the complete Green's function $F(\mathbf{k}, \omega)$; the heavy line represents $\mathcal{F}$, which is the sum of all diagrams terminating in $F^{(0)}(\mathbf{k}, \omega)$ lines

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[2] However, an exact solution can be derived in certain special cases. For example, if in W we take into account only an interaction with molecules belonging to a few of the nearest configurational spheres, then sums such as (29) can be factored and the perturbation theory series will contain a finite number of different types of elements. This would be a problem in the theory of degenerate perturbations.[15]

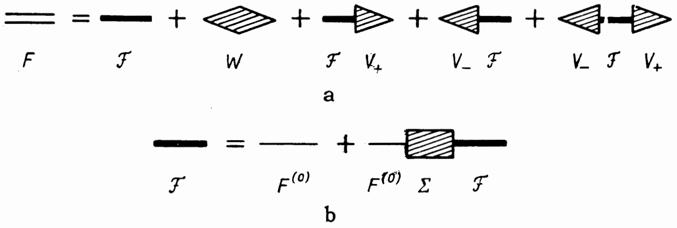

FIG. 2. Graphical system of equations for Green's functions.

on either the left or right; the shaded polygons are the sums of blocks not containing $F^{(0)}$ lines.

Figure 2b shows that

$$\mathcal{F} = \left(\frac{1}{F^{(0)}} - \Sigma\right)^{-1}, \tag{30}$$

and in virtue of Fig. 2a we have

$$F = W + \mathcal{F}(1 + V_-)(1 + V_+) = W + \frac{(1 + V_-)(1 + V_+)}{1/F^{(0)} - \Sigma}. \tag{31}$$

Equation (31) shows that the poles of $\mathcal{F}$ are likewise poles of F with their positions depending on the total irreducible self-energy part $\Sigma(\mathbf{k}, \omega)$.

A similar analysis in the case of a crystal with several molecules per unit cell shows that the graphical system of equations in Fig. 2 remains entirely valid, although all quantities corresponding to different elements of the graphs are now matrices. The indices of the different elements of these matrices are the indices of the molecules in a unit cell; these matrices will be denoted henceforth by $\check{F}$, $\check{\Sigma}$ etc. Equations (30) and (31) for $\check{F}(\mathbf{k}, \omega)$ and $\check{\mathcal{F}}(\mathbf{k}, \omega)$ are then replaced by

$$\check{\mathcal{F}} = \left(\frac{1}{\check{F}^{(0)}} - \check{\Sigma}\right)^{-1},$$

$$\check{F} = \check{W} + (\check{I} + \check{V}_-)\frac{1}{(\check{F}^{(0)})^{-1} - \check{\Sigma}}(\check{I} + \check{V}_+). \tag{32}$$

$\check{F}^{(0)}$ must now be determined explicitly. Let the eigenvectors and eigenvalues of the matrices $\check{\epsilon}(\mathbf{k})$ and $\check{\nu}(\mathbf{k})$ be obtained:

$$\sum_{\beta} \varepsilon_{\alpha\beta}(\mathbf{k}) B_{\beta}^{\lambda}(\mathbf{k}) = \varepsilon_{\lambda}(\mathbf{k}) B_{\alpha}^{\lambda}(\mathbf{k}),$$

$$\sum_{\beta} \nu_{\alpha\beta}(\mathbf{k}) C_{\beta}^{\lambda}(\mathbf{k}) = \nu_{\lambda}(\mathbf{k}) C_{\alpha}^{\lambda}(\mathbf{k}). \tag{33}$$

We then have

$$\psi_{\mathbf{k}\alpha}(t) = \sum_{\lambda\beta} \psi_{\mathbf{k}\beta} B_{\alpha}^{\lambda}(\mathbf{k}) B_{\beta}^{*\lambda}(\mathbf{k}) \exp[-i\varepsilon_{\lambda}(\mathbf{k})t] \tag{34}$$

and $\varphi_{\mathbf{k}\alpha}(t)$ similarly; from (21) and (22) we have

$$F_{\alpha\beta}^{(0)}(\mathbf{k}, \omega) = \frac{1}{N}\sum_{\mathbf{k}_1\lambda\lambda'} \frac{B_{\alpha}^{\lambda}(\mathbf{k}_1) B_{\beta}^{*\lambda}(\mathbf{k}_1) C_{\alpha}^{\lambda'}(\mathbf{k} - \mathbf{k}_1) C_{\beta}^{*\lambda'}(\mathbf{k} - \mathbf{k}_1)}{\omega - \varepsilon_{\lambda}(\mathbf{k}_1) - \nu_{\lambda'}(\mathbf{k} - \mathbf{k}_1)}. \tag{35}$$

4. ENERGY AND ABSORPTION SPECTRA OF A PURE CRYSTAL

We now proceed to analyze the energy spectrum of the system. For simplicity we again begin with a crystal having one molecule in each unit cell. The equation for the poles of the Green's function $\mathcal{F}$ governing the energy spectrum of the system follows from (31) and (35):

$$F^{(0)}(\mathbf{k}, \omega) = \frac{1}{N}\sum_{\mathbf{k}_1} \frac{1}{\omega - \varepsilon(\mathbf{k}_1) - \nu(\mathbf{k} - \mathbf{k}_1)} = \frac{1}{\Sigma(\mathbf{k}, \omega)}. \tag{36}$$

For a fixed value of $\mathbf{k}$ Eq. (36) is the customary equation in the theory of degenerate perturbations for deriving the energy levels of a crystal containing a defect.[15, 16, 11] A special feature remains, however, in that the right-hand member of (36) depends on ω, while the energy spectrum of an unperturbed system is represented by the sum $\Omega(\mathbf{k}, \mathbf{k}_1) = \epsilon(\mathbf{k}_1) + \nu(\mathbf{k} - \mathbf{k}_1)$. It is obvious, first of all, that with $\mathbf{k}$ fixed the roots of (36) will fill the entire variation interval $\mathfrak{S}_{\mathbf{k}}$ of $\Omega(\mathbf{k}, \mathbf{k}_1)$ as a function of $\mathbf{k}_1$. This portion of the spectrum corresponds to states in which the exciton and phonon are not coupled (the region of two-particle excitations). Outside of this interval we can also have isolated roots of $\omega(\mathbf{k})$ corresponding to coupled states in which the exciton and phonon move together (the region of single-particle excitations).

Even when for each fixed value of $\mathbf{k}$ the level $\omega(\mathbf{k})$ lies outside $\mathfrak{S}_{\mathbf{k}}$, the region of $\omega(\mathbf{k})$ values can overlap the total region $\mathfrak{S}$, of two-particle excitations including all intervals $\mathfrak{S}_{\mathbf{k}}$. Since Ω and Σ depend on $\mathbf{k}$, the criterion for isolated roots of $\omega(\mathbf{k})$ can be fulfilled in three-dimensional crystals generally only in a particular region of $\mathbf{k}$ values. Therefore the spectral branch corresponding to single-particle excitations can either be entirely absent, or can exist in the entire Brillouin zone, or can exist only in some part of the Brillouin zone.

We shall consider different limiting cases in order to clarify the roles of different mechanisms of electronic-vibrational exciton motion. Assume that the term $J(\mathbf{k}) \approx \Delta\nu$ is dominant in (25); this is entirely possible since $\Delta\nu$ is the only term in H_{int} that is associated completely with intramolecular interactions; the other terms arise through intermolecular interactions. In the first approxi-

FIG. 3. Self-energy part in first-order perturbation theory.

mation with respect to small terms the self-energy part is the sum of the graphs in Fig. 3, or, in analytic form.

$$\Sigma^{(1)}(\mathbf{k},\omega)=J(\mathbf{k})+\Delta_\nu(V_+^{(0)}(\mathbf{k},\omega)+V_-^{(0)}(\mathbf{k},\omega))+\Delta_\nu^2W^{(0)}(\mathbf{k},\omega). \tag{37}$$

If $|\Delta\nu|$ greatly exceeds the width of the exciton and vibrational bands, the remaining terms of (37) are easily evaluated. Using (28) and the formula for $f_{\mathbf{k}_1}$ as a separate component of the sum in (35), and assuming the absence of the $\mathbf{n}=\mathbf{m}$ term in (13) for $K(\mathbf{k},\omega)$, $Q(\mathbf{k},\omega)$, and $V_\pm(\mathbf{k},\omega)$, it can be shown that

$$K^{(0)}(\mathbf{k},\omega),\ Q^{(0)}(\mathbf{k},\omega)\sim(\omega-\varepsilon_0-\nu_0)^{-4},$$
$$V_\pm^{(0)}(\mathbf{k},\omega)\sim(\omega-\varepsilon_0-\nu_0)^{-2}, \tag{38}$$

so that we may retain only the first term of (37), and

$$F(\mathbf{k},\omega)\approx[\omega-\varepsilon_0-\nu_0-J(\mathbf{k})]^{-1}. \tag{39}$$

This last equation shows that for large $|\Delta\nu|$ the J mechanism of excitation motion is dominant, i.e., the resonance mechanism of the propagation of an electronic-vibrational excitation as a whole.

We now consider the values of $\Delta\nu$ for which single-particle states arise near the edge $\omega_{\lim}$ of the spectrum of two-particle states of width $\Delta\epsilon$, and when the width of the phonon band and all coefficients in (37) except $\Delta\nu$ are sufficiently small. We assume specifically that

$$|\omega(\mathbf{k})-\omega_0|\ll|\omega_0-\omega_{\lim}|\ll\Delta\varepsilon. \tag{40}$$

Here ω_0 is the limiting value of $\omega(\mathbf{k})$ when all the aforementioned small values approach zero. When we use the measure of smallness $\mu(\mathbf{k})=\nu(\mathbf{k})-\nu_0$ the left-hand side of (36) can be expanded in the series

$$F^{(0)}(\mathbf{k},\omega)\approx G(\omega-\nu_0)+\frac{1}{N}\sum_{\mathbf{k}_1}\frac{\mu(\mathbf{k}-\mathbf{k}_1)}{[\omega-\varepsilon(\mathbf{k}_1)-\nu_0]^2},$$
$$G(\omega)=\frac{1}{N}\sum_{\mathbf{k}}\frac{1}{\omega-\varepsilon(\mathbf{k})}. \tag{41}$$

If an extremum of $\epsilon(\mathbf{k})$ is reached at N_{extr} points $\mathbf{k}_i$, then by virtue of (40) we can take μ outside the summation in (41) for $\mathbf{k}=\mathbf{k}_i$; then

$$F^{(0)}(\mathbf{k},\omega)\approx G(\omega-\nu_0)-\frac{1}{N_{\text{extr}}}\sum_i\mu(\mathbf{k}-\mathbf{k}_i)\frac{dG(\omega-\nu_0)}{d\omega}. \tag{42}$$

In the same approximation we can neglect the dependence on ω in $\Sigma(\mathbf{k},\omega)$ and assume $\omega=\omega_{\lim}$;[3)] then $\Sigma=\Delta\nu+\Sigma'(\mathbf{k})$. If ω_0 is determined from the condition $\Delta_\nu G(\omega-\nu_0)=1$ and $F^{(0)}(\mathbf{k},\omega)$ is expanded near ω_0, then (36) is transformed as a result of (42) into

$$\omega(\mathbf{k})=\omega_0+\frac{1}{N_{\text{extr}}}\sum_i\mu(\mathbf{k}-\mathbf{k}_i)+\Sigma'(\mathbf{k})\left[\frac{d}{d\omega_0}\frac{1}{G(\omega_0-\nu_0)}\right]^{-1}. \tag{43}$$

The coefficient of the last term in (43) has a clear physical meaning. Assuming $|V_\pm(\mathbf{k},\omega)|\ll1$ in the present approximation, the probability that an exciton and phonon are localized at a single site in the considered stationary state is calculated using (24), (21), and (31):

$$|a|^2=\left[\frac{d}{d\omega}\frac{1}{G(\omega-\nu_0)}\right]^{-1}. \tag{44}$$

The last term in (43) then becomes $|a|^2\Sigma'(\mathbf{k})$. The frequency dependence of $|a|^2$ depends on the structure of the exciton band. If a quadratic expansion is valid near the points $\mathbf{k}_i$ for $\epsilon(\mathbf{k})$, we then obtain $|a|^2\sim|\omega-\omega_{\lim}|^{1/2}$. The last term in (43) vanishes in the limit and the μ mechanism for the motion of an electronic-vibrational excitation becomes dominant. This mechanism consists in the movement of a phonon among unexcited sites, with the exciton following the phonon adiabatically like a light particle. If $\mathbf{k}_i=0$ the dispersion laws of phonon and electronic-vibrational excitation coincide; for $\mathbf{k}_i\neq0$ they have the more complex relationship (43).

If $\mathbf{k}_i=0$ and $\epsilon(\mathbf{k})$ has a large discontinuity associated with distant interactions, it can be shown similarly[11] that $|a|^2$ either approaches a finite limit or decreases logarithmically; therefore the last term of (43) remains real. We note, incidentally, that even if $|a|^2$ decreases as the square root of $|\omega-\omega_{\lim}|$ in the actual interval its value remains quite large (of the order of several tenths[17]), so that the last term of (43) is practically always real.

We shall now discuss more thoroughly the roles of the different terms in $\Sigma^{(1)}$ [Eq. (37)] from the point of view of their contributions to $\omega(\mathbf{k})$. As in

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[3)] This approximation applies to three-dimensional crystals, to which we confine ourselves here. For one-dimensional systems Σ diverges when $\omega\to\omega_{\lim}$; this case therefore requires a special analysis, which we intend to present in a separate communication along with an investigation of the analytic properties of W and $V_\pm$ for crystals and chains.

the foregoing, we shall consider the case in which the combined probability of all processes associated with phonon propagation is small. This case is very important experimentally, especially for incompletely symmetric vibrations. It is clear from (7) that the Q- and T-terms are unimportant since they are not associated with phonon propagation; their contribution reduces essentially to a correction of $\Delta\nu$. The R-terms, representing corrections of the phonon resonance integrals, are small. The coefficients J and K in (7) are determined by resonance integrals of a single kind and should be comparable in magnitude. Equation (37) can therefore be simplified:

$$\Sigma^{(1)}(\mathbf{k}, \omega) \approx J(\mathbf{k}) + \Delta_\nu^2 K(\mathbf{k}, \omega). \tag{45}$$

It follows from this equation that the resonant exchange K mechanism is just as important as the aforementioned μ and J mechanisms.

From (19), (20), and (24) we obtain a formula for conductivity in a single-particle band:

$$\hat{\sigma}(\mathbf{k}, \omega) = \frac{\pi e^2}{v m \omega^2} |a(\mathbf{k})|^2 \widehat{\mathbf{k}^f \overline{\mathbf{k}^{*f}}} \delta(\omega - \omega(\mathbf{k})). \tag{46}$$

The dependence of absorption intensity in a single-particle band on the separation of the latter from the two-particle excitation spectrum is governed by the aforementioned spectral dependence of $|a|^2$.

We shall now consider crystals having several symmetrically dependent sublattices; we confine ourselves in (20) to $\mathbf{k} \to 0$, which is the most interesting case with respect to optical properties. It follows from symmetry considerations that for $\mathbf{k} \to 0$ all matrices in (32) are diagonalized by a single transformation of the basis; for example, their common eigenvectors can be taken to be $B_\alpha^\lambda(0)$ [see Eq. (33)]. Equation (20) is then transformed into

$$\hat{F}(\omega) = \sum_\lambda F_\lambda(\omega) \widehat{\mathbf{k}_\lambda{}^f \mathbf{k}_\lambda{}^{*f}}, \tag{47}$$

where

$$F_\lambda(\omega) = \sum_{\alpha\beta} B_\alpha{}^{*\lambda} F_{\alpha\beta}(\omega) B_\beta{}^\lambda, \qquad \mathbf{k}_\lambda{}^f = \sum_\alpha B_\alpha{}^\lambda \mathbf{k}_\alpha{}^f, \tag{48}$$

and the $\mathbf{k}_\lambda^f$ vectors are obviously oriented along the symmetry elements of the crystal. With this basis the matrix equation (32) breaks up into a system of independent equations such as (31) with all quantities having the index λ. However, $F_\lambda^{(0)}$ is not given by (36), but by a more complex formula that follows from (35) and (48).

Each isolated root of this system corresponds to a narrow absorption band with polarization determined by the corresponding $\mathbf{k}_\lambda^f$. However, since the equations for different values of λ can differ considerably (which occurs when the probabilities of vibrational-excitation propagation are comparable with the probability of exciton propagation) some of them may have no isolated roots at all. Therefore the electronic-vibrational multiplets may be incomplete, unlike the purely electronic Davydov multiplets,[3] in which the number of bands depends exclusively on the number of molecules σ_c in a unit cell (and on the selection rules).

If the probabilities of all processes associated with phonon propagation can be neglected, then $\nu_\lambda(k) = \nu_0$, $\Sigma_{\alpha\beta} = \Delta_\nu \delta_{\alpha\beta}$, $W = V_\pm = 0$; and it follows from (32) and (35) that

$$F_{\alpha\beta}(\mathbf{k}, \omega) = F(\omega)\delta_{\alpha\beta}, \qquad F(\omega) = \frac{G(\omega - \nu_0)}{1 - \Delta_\nu G(\omega - \nu_0)},$$

$$G(\omega) = \frac{1}{N\sigma_c} \sum_{\mathbf{k}_1\lambda} \frac{1}{\omega - \varepsilon_\lambda(\mathbf{k}_1)}. \tag{49}$$

It can be seen from (20) and (49) that in this case the spectral polarization ratio is independent of frequency. To determine absorption in the two-particle spectrum we write

$$G(\omega - \nu_0) = A(\omega) - iB(\omega), \qquad A(\omega) = \frac{1}{\pi} \int \frac{B(\omega')}{\omega - \omega'} d\omega', \tag{50}$$

and then have, in accordance with (19), (20), and (49),

$$\hat{\sigma}(\omega) = \frac{e^2}{v \omega m^2} \frac{B(\omega)}{[1 - \Delta_\nu A(\omega)]^2 + [\Delta_\nu B(\omega)]^2} \sum_\lambda \widehat{\mathbf{k}_\lambda^f \mathbf{k}_\lambda^{*f}}. \tag{51}$$

Equation (49) shows that $B(\omega)$ is proportional to the density of states in exciton bands and can be determined independently—from the spectrum of $1 \to 0$ transitions,[18] for example (i.e., transitions from ground-state vibrational sublevels to exciton bands). Thus the dispersion relation (50) in conjunction with (51) relates the absorption intensities in the two different spectra.

It was shown at the beginning of Sec. 2 that we determined some physical properties of the system differently for the narrow electrodynamic region (small $\mathbf{k}$) than for the remainder of the Brillouin zone. Therefore the meanings of the quantities appearing in the foregoing formulas must be specified. It is easily understood that in (35) and (49), which contain summations, unregularized quantities can be used in all $\mathbf{k}$ space, (including distant interactions). However, when quantities corresponding to small $\mathbf{k}$ [such as $\omega(\mathbf{k})$ in (46)] are discriminated by the selection rules their regularized values should be used.

5. ABSORPTION SPECTRUM OF IMPURITY CRYSTALS

We shall now consider the electronic-vibrational spectrum of crystals containing extremely small impurity concentrations. We shall confine ourselves, for simplicity, to the case of isotope shift, and shall assume the vanishing of all terms in the Hamiltonian that are associated with phonon propagation. The correction to the Hamiltonian that is associated with an impurity at the site $\mathbf{n}_0\alpha_0$ is given by

$$H_{imp} = \Delta_e \psi^{+}_{\mathbf{n}_0\alpha_0}\psi_{\mathbf{n}_0\alpha_0} + \Delta_v \varphi^{+}_{\mathbf{n}_0\alpha_0}\varphi_{\mathbf{n}_0\alpha_0} + \Delta_{ev}\psi^{+}_{\mathbf{n}_0\alpha_0}\varphi^{+}_{\mathbf{n}_0\alpha_0}\varphi_{\mathbf{n}_0\alpha_0}\psi_{\mathbf{n}_0\alpha_0}, \tag{52}$$

where Δ_e, Δ_v, and Δ_{ev} are the respective corrections of the electronic term, vibrational frequency, and excitation-induced frequency shift. The right-hand member of (19) must be multiplied by the number $\nu N\mathfrak{N}$ of impurity molecules (where ($\mathfrak{N}$ is the concentration); this must be followed by averaging over $\mathbf{n}_0\alpha_0$.

As a consequence of phonon immobility it follows from (22) that

$$\widetilde{F}_{\mathbf{n}\alpha,\mathbf{m}\beta}(t) = \widetilde{F}_{\mathbf{n}\alpha}(t)\,\delta_{\mathbf{n}\alpha,\mathbf{m}\beta}, \quad \widetilde{F}_{\mathbf{n}\alpha} \equiv \widetilde{F}_{\mathbf{n}\alpha,\mathbf{n}\alpha}. \tag{53}$$

In the present section the quantities marked by a tilde pertain to an impure crystal.

If we at first omit the exciton-phonon interaction ($\Delta_v = \Delta_{ev} = 0$), the right-hand side of (22) is factorizable and

$$\widetilde{F}^{(0)}_{\mathbf{n}\alpha}(t) = i\widetilde{G}_{\mathbf{n}\alpha}(t)\,\widetilde{D}_{\mathbf{n}\alpha}(t), \quad \text{or} \quad \widetilde{F}^{(0)}_{\mathbf{n}\alpha}(\omega)$$

$$= i\int\limits_{-\infty}^{+\infty}\frac{d\omega'}{2\pi}\widetilde{G}_{\mathbf{n}\alpha}(\omega-\omega')\,\widetilde{D}_{\mathbf{n}\alpha}(\omega'), \tag{54}$$

where $\widetilde{G}_{\mathbf{n}\alpha}$ and $\widetilde{D}_{\mathbf{n}\alpha}$ are the diagonal elements of the exciton and phonon Green's functions. When we consider the exciton Green's functions ($\check{G}$ and $\check{\widetilde{G}}$) of both a pure and impure crystal and also the perturbation operator $\check{\Delta}_e$ as matrices in the lattice-site representation it is easily shown that

$$\check{\widetilde{G}}(\omega) = \check{G}(\omega) + \check{G}(\omega)\,\check{\Delta}_e\check{G}(\omega)\,/\,[1 - \Delta_e G(\omega)], \tag{55}$$

where $G(\omega)$ is defined by (49). Similarly,

$$\widetilde{D}_{\mathbf{n}\alpha}(\omega) = \omega^{-1}_{\mathbf{n}\alpha}, \quad \omega_{\mathbf{n}\alpha} = \omega - \nu_0 - \Delta_v\delta_{\mathbf{n}\alpha,\mathbf{n}_0\alpha_0}. \tag{56}$$

The substitution of (55) and (56) into (54) determines $\widetilde{F}^{(0)}_{\mathbf{n}\alpha}(\omega)$. At the same time the complete Green's function $\widetilde{F}_{\mathbf{n}\alpha}(\omega)$ is given by

$$\widetilde{F}_{\mathbf{n}\alpha}(\omega) = \widetilde{F}^{(0)}_{\mathbf{n}\alpha}(\omega)\,/\,[1 - \Delta_{\mathbf{n}\alpha}\widetilde{F}^{(0)}_{\mathbf{n}\alpha}(\omega)]; \quad \Delta_{\mathbf{n}\alpha} = \Delta_v + \Delta_{ev}\delta_{\mathbf{n}\alpha,\mathbf{n}_0\alpha_0}, \tag{57}$$

which is analogous to (32). Finally,

$$\widetilde{F}_{\mathbf{n}\alpha}(\omega) = \frac{G(\omega_{\mathbf{n}\alpha}) - \Delta_e[G^2(\omega_{\mathbf{n}\alpha}) - |G_{\mathbf{n}\alpha,\mathbf{n}_0\alpha_0}(\omega_{\mathbf{n}\alpha})|^2]}{[1 - \Delta_e G(\omega_{\mathbf{n}\alpha})][1 - \Delta_{\mathbf{n}\alpha}G(\omega_{\mathbf{n}\alpha})] - \Delta_e\Delta_{\mathbf{n}\alpha}|G_{\mathbf{n}\alpha,\mathbf{n}_0\alpha_0}(\omega_{\mathbf{n}\alpha})|^2}, \tag{58}$$

and it follows from (33) that $\check{G}(\omega)$ is given by

$$G_{\mathbf{n}\alpha,\mathbf{m}\beta}(\omega) = \frac{1}{N}\sum_{\mathbf{k}\lambda}\frac{B^{\lambda}_{\alpha}(\mathbf{k})\,B^{*\lambda}_{\beta}(\mathbf{k})}{\omega - \varepsilon_\lambda(\mathbf{k})}\exp\{i\mathbf{k}(\mathbf{n}_\alpha - \mathbf{m}_\beta)\}. \tag{59}$$

It is easy to grasp the physical meaning of (58) as describing the exciton spectrum when a vibration is localized at a site $\mathbf{n}\alpha$. We obtain the exciton energy spectrum by equating the denominator in (58) to zero:

$$[1 - \Delta_e G(\omega_{\mathbf{n}\alpha})][1 - \Delta_{\mathbf{n}\alpha}G(\omega_{\mathbf{n}\alpha})] = \Delta_e\Delta_{\mathbf{n}\alpha}|G_{\mathbf{n}\alpha,\mathbf{n}_0\alpha_0}(\omega_{\mathbf{n}\alpha})|^2. \tag{60}$$

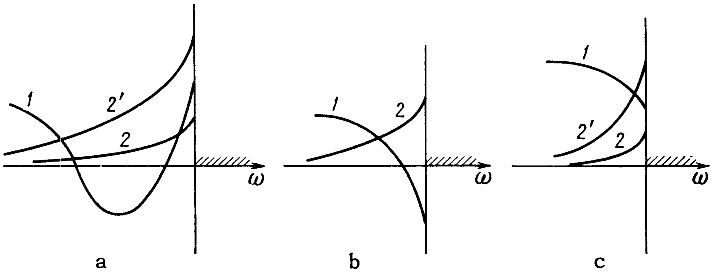
If $\mathbf{n}\alpha = \mathbf{n}_0\alpha_0$, i.e., a phonon is localized in an impurity molecule, then (60) becomes

$$(\Delta_e + \Delta_v + \Delta_{ev})\,G(\omega - \nu_0 - \Delta_v) = 1, \tag{61}$$

which is analogous to Eq. (49) for the poles of $F(\omega)$, and to (I.56) for purely electronic impurity levels.

If $|\mathbf{n} - \mathbf{n}_0| \rightarrow \infty$ the right-hand side of (60) decreases exponentially, and the equation is factorizable. An isolated root of the first bracket in the left-hand member of (60) corresponds to states in which an exciton is localized near an impurity molecule while a vibration is localized in a distant solvent molecule. An isolated root of the second bracket corresponds to states in which an exciton is localized near a phonon at a great distance from an impurity, and thus corresponds to single-particle excitations.

Consider, to begin with, that both brackets have isolated roots. As $|\mathbf{n} - \mathbf{n}_0|$ decreases the two roots are displaced in opposite directions, thus increasing their mutual separation (see Fig. 4a; to



a b c

FIG. 4. Graphs of the left- and right-hand members of Eq. (60) for Δ_e, $\Delta_v < 0$. Curves 1 – left-hand side; curves 2,2′ – possible graphs of right-hand side for different values of $\mathbf{n} - \mathbf{n}_0$. The shaded region pertains to two-particle excitations. a–both factors in the left-hand member of (60) have an isolated root; b–only one of these factors has an isolated root; c–neither factor has an isolated root.

be definite, it is assumed below that Δ_e, $\Delta_v < 0$). Thus, for each value of $\mathbf{n} - \mathbf{n}_0$ we have two discrete levels of the system; the first root will be called the impurity component, and the second root will be called the vibrational component, of the impurity doublet. It follows from (58) that for large $|\mathbf{n} - \mathbf{n}_0|$ the impurity component has exponentially small intensity. With decreasing $|\mathbf{n} - \mathbf{n}_0|$ the right-hand side of (60) increases; then one of the discrete roots approaches the region of two-particle excitations and can disappear by merging with the latter (see curve 2′ in Fig. 4a). In other possible cases one bracket in the left-hand side of (60), or even both brackets, will lack isolated roots; in the first case (60) possesses one isolated root, while in the second case it has one or none (Figs. 4b and 4c).

It follows from (20), (21), (53), and (58) that in the present approximation the polarization ratio is constant over the entire electronic-vibrational spectrum.

All of the mentioned levels form sequences that converge for $|\mathbf{n} - \mathbf{n}_0| \to \infty$. These can be compared with the analogous sequences in [19] for electronic spectra; the latter sequences differ by being of the order $\sim \mathfrak{N}^2$ and result from the formation of pairs of impurity centers, while the sequences in the electronic-vibrational spectrum are of the order $\sim \mathfrak{N}$. It must be mentioned that taking account of a finite phonon propagation rate should affect the spectrum most strongly in the region of large $|\mathbf{n} - \mathbf{n}_0|$.

6. MULTIPHONON SPECTRA

It has been assumed throughout the foregoing treatment that light absorption results in one exciton plus one phonon. However, well-developed vibrational series often are observed in the spectra of molecular crystals. In accordance with the view expounded here the quantum states of such systems are superpositions of states in which an exciton and phonons are propagated differently among lattice sites. A many-body problem thus arises which is, of course, not soluble in the general case, although the principal tendencies are clear from qualitative considerations.

When we limit ourselves to two-phonon states and assume, moreover, that the probability of phonon propagation can be neglected, the problem resembles that of the preceding Section. In addition to states where both phonons are localized at a single site, an infinite set of states arises with separated phonons (at sites $\mathbf{n}\alpha$ and $\mathbf{n}_0\alpha_0$); these states are described by (60) with $\Delta_e = \Delta_{\mathbf{n}\alpha} = \Delta_\nu$ and $\omega_{\mathbf{n}\alpha} = \omega - 2\nu_0$. The energies of these states exceed the energies of states with spatially coincident phonons. The matrix elements for transitions to states with separated phonons are zero so long as the widths of the phonon bands are assumed to be negligibly small, but differ from zero in the next order of magnitude with respect to the ratio between this width and Δ_ν.

The experimental detection of bands corresponding to separate phonons in multiphonon spectra, and of additional bands in impurity spectra (Sec. 5), would stimulate the construction of a more complete theory for these spectra.

7. ENERGY SPECTRA OF SEMICONDUCTORS HAVING A NARROW ALLOWED BAND

The foregoing exposition enables us to consider anew the possible structure of the energy spectrum in semiconductors having a narrow allowed band. Let the width J of the allowed band and the width J_ν of the phonon band be considerably less than the mean frequency ν_0 of optical phonons, which interact most strongly with electrons (J, $J_\nu \ll \nu_0$). The presence of an excess electron or hole at one of the couplings (or sites) changes the strength of the coupling. Therefore the localization of a vibration and excess electric charge at a single coupling results in a gain or loss of energy. This energy H_{int} has the same role as Δ_ν for exciton levels. If H_{int} is comparable with J and J_ν, two-particle states may be accompanied by one-particle states in which an electron and phonon are propagated together. When $H_{\text{int}} < 0$ the one-particle states lie below the two-particle states; the reverse holds for $H_{\text{int}} > 0$. When $J \gg J_\nu$ the effective mass of this formation is considerably greater than the electron effective mass. Thus, above the electron band of width J there may arise current-bearing states corresponding to the concurrent motion of an electron and phonon, with a band width depending on both J and J_ν.

It is interesting to compare this picture with that appearing in polaron theory[20] as a result of "clothing" effects caused mainly by interaction with zero-point vibrations. As was first shown by Pekar in the continuous theory of polarons,[20] and then by several authors for other models (for excitons,[7, 9] small polarons[21] etc.), the "clothing" process changes the effective mass throughout the entire spectrum; the change is appreciable, however, only if $|H_{\text{int}}| \gtrsim \nu_0$. The mechanism discussed here for interaction between an electron and one real phonon alters the spectrum of the system greatly even if $|H_{\text{int}}| \ll \nu_0$ (if only

$|H_{int}| \gtrsim J, J_\nu$). The change does not, of course, extend to the lower portion of the spectrum, where energies lie below ν_0.

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