has a decided advantage since it requires less computer storage and is faster. The results should be essentially the same as found with the linear variation method.

It would be of some interest to compare the time behavior of quantum wave packets and corresponding classical probability density functions for this system, as was done previously for anharmonic oscillators having one degree of freedom.[6] We investigated this possibility, and concluded that the classical calculation would be prohibitively expensive since the classical trajectories of each of the systems in the ensemble would each have to be computed by numerical integration of the equations of motion.

Finally, we make an often neglected point aptly illustrated by our calculations and brought out by the referee. In treating multidimensional problems as direct products of one- (or lower) dimensional problems, it is very important to remove all possible off-diagonal terms of the Hamiltonian in one (or lower) dimension before forming the direct product representation. This is very important for exact calculations and is often not done in vibrational calculations.

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Electronic States of Mixed Molecular Crystals

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In this paper we consider the energy levels of dilute mixed crystals in the weak vibronic coupling limit using the one-particle Green's-function method. The perturbation Hamiltonian is treated explicitly with reference to impurity molecules differing from the host molecules by isotopic substitution. The general equations derived for the energy levels, for excitation amplitudes, and for the optical properties of the mixed crystal are expressed in terms of the weighted density-of-states function of the pure crystal. This treatment emphasizes the relation between the density of exciton states in the pure crystal and the optical properties of mixed crystals. The nature of bound and virtual impurity states are considered, and new experiments using the impurity-induced electronic-absorption method are suggested.

I. INTRODUCTION

The energy spectra of elementary excitations in pure crystals are characterized by some simplifying features arising from the translational symmetry of the crystal lattice, which implies the existence and conservation of the crystal quasimomentum $\hbar\mathbf{k}$, so that the energy spectrum is determined by a dispersion relation $E(\mathbf{k})$. The quantum states corresponding to the elementary excitation can then be described by modulated plane waves characterized by a wave vector $\mathbf{k}$. The studies of the theory of vibrational and electronic states of ideal ordered solids rest on the one-particle approximation. Well-known examples are Bloch states in metals, phonons in solids, spin waves in ferromagnetic crystals, and exciton states in molecular crystals. The problem of the electronic structure of disordered systems is much more complicated, as in the absence of translational symmetry the crystal quasimomentum does not appear as a good quantum number. The first example for the application of perturbation techniques for the study of the energy spectrum of a perturbed solid is found in Rayleigh's work[1] on the shifts in normal-mode frequencies of such a system. Since then a vast amount of work has been performed on the effect of impurities and disorder on lattice vibrations.[2–5] In view of the correspondence between the theory of lattice vibrations and the tight-binding approximation in the quantum theory of solids, it is obvious that the same technique can be applied for the study of the electronic states of solids. Koster and Slater[6–8] studied the effect of impurities on the electronic states in a crystal, making use of a Green's-function method, this approach being further extended for the case of electron traps[9–12] and dirty superconductors.[13] Studies on spin waves in perturbed systems were carried out using similar methods.[14,15]

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In the present work we consider the effect of impurities on the electronic spectra of molecular crystals of organic molecules. It is well known that these systems can be adequately described in terms of the extreme tight-binding Frenkel exciton model.[16,17] Such studies are of interest because of the following reasons:

(a) They provide information about the relationship between the energy levels of a single molecule and the crystal states which is complementary to that obtained from the study of the spectra of pure crystals. These studies will lead to further information concerning intermolecular interactions in excited states.

(b) These studies are of interest as they provide information on the band structure of exciton bands. This information is not obtained from optical studies of pure crystals at low temperatures,[16,17] where the optical absorption from the ground state is restricted by the quasimomentum selection rules.

(c) Energy-trapping effects, which are of interest in the interpretation of energy-transfer phenomena in biological systems, require the understanding of impurity levels.

(d) Some cooperative excitation effects in molecular crystals, where two excitations on adjacent molecules are initiated by a single photon absorption, can be understood on the basis of the theory of impurity states.[18,19]

(e) Perhaps the most interesting problem in this field involves the joint theoretical and experimental study of heavily doped molecular crystals, to determine whether the Davydov splitting of the molecular energy levels arises primarily from symmetry relations or can arise from resonance coupling between randomly distributed molecules.[20,21] This problem is of general interest in the understanding of the electronic structure of disordered systems.

What is the experimental evidence for guest–host interactions in molecular crystals? Exciton-trapping effects have been known for a long time. In these studies, the fluorescence emission induced by light absorbed by the host occurs preferentially from the guest molecule, whenever its lowest electronic state lies lower than the lowest host level. Recently, direct spectroscopic evidence has been obtained for guest–host interactions in mixed crystals. From electron spin resonance studies of triplet states of guest molecules in molecular crystals,[22] it can be inferred that the guest-molecule orientation is the same as that of the host molecule, so that the guest molecule just displaces the host molecule. The polarization ratios and the intensity enhancement factors for the tetracene–anthracene system[23–24] provide evidence for off-resonance intermolecular interactions. Extremely interesting studies were performed on isotopically mixed crystals. The experimental studies of the phosphorescence of dilute mixed crystals of benzene–deuterobenzene[25] and naphthalene–deuteronaphthalene[26] provide evidence for the role of intramolecular electron-exchange interactions in the triplet exciton state. Extensive studies have been performed, yielding a clear picture of intermolecular interactions in singlet exciton states in mixed crystals of naphthalene and deuteronaphthalene and benzene–deuterobenzene,[20,27–29] studied over a wide concentration range. Fluorescence spectra of dilute isotopically mixed crystals[30] provide further evidence for the delocalization of the excitation energy in the vicinity of the impurity center.

Some theoretical studies of impurity states in molecular crystals have included the examination of idealized situations such as one-dimensional crystals[31–32] and crystals with only nearest-neighbor interactions.[33] Perturbation techniques at various degrees of sophistication have also been applied.[34–40] Koster and Slater's work[6–8] on the theory of the energy levels of an excess electron in impure crystals is of immediate relevance for the study of the energy levels of mixed crystals, and was used by Merrifield,[31] by Philpott and Craig,[38–40] and by Ross and Body.[36]

Two limiting cases for guest–host interactions can be immediately distinguished.[32] In a pure crystal, the

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energy levels corresponding to a given molecular transition are spread into a band, the total bandwidth being determined by the intermolecular coupling. In dilute mixed crystals, the perturbation of the host energy levels by the impurity is expected to be negligibly small. If the host exciton bandwidth is small or comparable to the energy difference between the transitions of the guest and the host molecules, we are considering the case of shallow traps, where the localized excitations involving the guest and host molecules are nearly degenerate and the host band structure has to be taken into account. On the other hand, if the exciton bandwidth is small compared to the host–guest energy separation, we have to consider the limiting case of deep traps, where only pairwise guest–host interactions need be considered.

In the present paper, the theory of the excited states of isotopically mixed crystals is presented, based on the single-particle Green's function for the excited state of the mixed crystal, which is related to the Green's function for the pure crystal.[9–11] The latter is expressed in terms of the density of states in the exciton band of the pure crystal. A similar approach has been previously applied for the study of electron traps in solids[9–13] and the effect of impurities on phonon states[3,4,9] and spin waves.[14,15]

Frenkel exciton states in molecular crystals were extensively studied during the last 20 years.[16,17] However, most of the studies of the optical properties concentrated on $\mathbf{k}=0$ exciton states in an attempt to understand the Davydov splittings and the polarization components in the optical spectrum. The understanding of exciton dynamics in molecular crystals requires rather detailed information concerning the whole exciton band structure. Some experimental information concerning the exciton band structure can be obtained from hot-band spectroscopy, that is, transitions from a vibrational exciton band to an electronic exciton band,[41,42] and from electronic–vibrational cooperative excitations.[18,19] The present study makes it possible to derive theoretical and empirical data for the density of states in the exciton band from the optical properties of mixed crystals.

II. THE ELECTRONIC STATES OF PURE CRYSTALS

In what follows, we shall briefly consider the conventional theory of Frenkel exciton states within the framework of the tight-binding Heitler–London approximation. The excited states of the crystal are represented by the eigenvalues of the Hamiltonian operator:

$$\mathcal{H}_0=H_0-E_0, \tag{2.1}$$

where

$$H_0=\sum_{n=1}^{N}\sum_{\alpha=1}^{\sigma}H_{n\alpha}^0+\sum_{n\alpha<m\beta}V_{n\alpha m\beta} \tag{2.2}$$

is the Hamiltonian of a rigid crystal consisting of $N\sigma$ molecules with σ molecules per unit cell and E_0 is the crystal ground-state energy in first order. The zero-order crystal states representing a localized excitation on the molecule $n\alpha$ are represented in terms of an antisymmetrized product of the eigenfunctions $\varphi_{n\alpha}^f$ of the free-molecule Hamiltonian $H_{n\alpha}^0$:

$$a_{n\alpha}^f=\mathcal{A}\varphi_{n\alpha}^f\prod_{m\beta\neq n\alpha}\varphi_{m\beta}^0. \tag{2.3}$$

It is assumed that the localized excitation functions are orthogonal:

$$\langle a_{n\alpha}^f \mid a_{n'\alpha'}^{f'}\rangle=\delta_{nn'}\delta_{\alpha\alpha'}\delta_{ff'}. \tag{2.4}$$

Considering a single exciton band, the crystal wavefunctions are represented in terms of the coefficients $B_{\alpha j}^f(\mathbf{k})$ which are the elements of the unitary transformation matrix from the one-site exciton states $\varphi_\alpha^f(\mathbf{k})$ to the crystal states $\psi_j^f(\mathbf{k})$:

$$\psi_j^f(\mathbf{k})=\sum_{\alpha=1}^{\sigma}B_{\alpha j}^f(\mathbf{k})\phi_\alpha^f(\mathbf{k})$$

$$=(N)^{-1/2}\sum_{n=1}^{N}\sum_{\alpha=1}^{\sigma}B_{\alpha j}^f(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{R}_{n\alpha})a_{n\alpha}^f, \tag{2.5}$$

where $j=1\cdots\sigma$ corresponds to the σ branches of the exciton band. The crystal states $E_j^f(\mathbf{k})$ for a single electronic configuration are obtained by the diagonalization of the energy matrix:

$$\langle\phi_\alpha^f(\mathbf{k})\mid\mathcal{H}_0\mid\phi_\beta^f(\mathbf{k})\rangle=(\Delta E^f+D^f)\delta_{\alpha\beta}+\mathfrak{L}_{\alpha\beta}^{ff}(\mathbf{k}) \tag{2.6}$$

for each $\mathbf{k}$. Here ΔE^f is the free-molecule excitation energy, D^f the first-order environmental shift. The matrix $\|\mathfrak{L}\|$ is determined by the exciton transfer integrals and can be represented in the general form

$$\mathfrak{L}_{\alpha\beta}^{ff'}(\mathbf{k})=\sum_n\left[\int\mathcal{A}\varphi_{n\alpha}^0\varphi_{m\beta}^fV_{n\alpha m\beta}\varphi_{n\alpha}^{f'}\varphi_{m\beta}^0d\tau\right]$$

$$\times\exp[i\mathbf{k}\cdot(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})]. \tag{2.7}$$

The first-order theory has to be extended to take into account crystal-field-induced mixing[43,44] between exciton states derived from different electronic configurations. This effect is of importance for exciton states characterized by a moderately large bandwidth (i.e., the first singlet exciton states of naphthalene[44] and of anthracene[43,45]). When the exciton band structure is dominated by small intermolecular electron-

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exchange interactions[46] (as is the case for triplet states of aromatic hydrocarbons), the effects of crystal-field mixing are negligible. To proceed, the tight-binding Hamiltonian [Eq. (1)] has to be diagonalized in the basis set $\psi_j^f(\mathbf{k})$ or, alternatively, in $\phi_\alpha^f(\mathbf{k})$, where now $\{f\}$ refers to all the excited molecular states. The pure-crystal wavefunctions, which are characterized by the band quantum number μ and the wavevector $\mathbf{k}$, can be displayed in the form

$$\psi_\mu(\mathbf{k})=\sum_j\sum_f c_{jf}{}^\mu(\mathbf{k})\psi_j{}^f(\mathbf{k})=\sum_\alpha\sum_f b_{\alpha f}{}^\mu(\mathbf{k})\phi_\alpha{}^f(\mathbf{k}). \tag{2.8}$$

The relation between the expansion coefficients in Eq. (2.8) is

$$C_{jf}{}^\mu(\mathbf{k})=\sum_\alpha b_{\alpha f}{}^\mu(\mathbf{k})[B_{\alpha j}{}^f(\mathbf{k})]^*. \tag{2.9}$$

The crystal energy levels $E_\mu(\mathbf{k})$ can be obtained by diagonalization of the energy matrix

$$\langle\psi_j{}^f(\mathbf{k})\mid\mathcal{H}_0\mid\psi_{j'}{}^{f'}(\mathbf{k})\rangle=\sum_\beta\sum_\alpha B_{\alpha j}{}^f(\mathbf{k})B_{\beta j'}{}^{f'}(\mathbf{k})\times\langle\phi_\alpha{}^f(\mathbf{k})\mid\mathcal{H}_0\mid\phi_\beta{}^{f'}(\mathbf{k})\rangle, \tag{2.10}$$

where

$$\langle\phi_\alpha{}^f(\mathbf{k})\mid\mathcal{H}_0\mid\phi_\beta{}^{f'}(\mathbf{k})\rangle=(\Delta E^f+D^f)\delta_{ff'}\delta_{\alpha\beta}+\sum_m\langle\varphi_{n\alpha}{}^f\varphi_{n\alpha}{}^{f'}\mid V_{n\alpha m\beta}\mid\varphi_{m\beta}{}^0\varphi_{m\beta}{}^0\rangle(1-\delta_{ff'})+\mathcal{L}_{\alpha\beta}{}^{ff'}(\mathbf{k}). \tag{2.11}$$

Several comments should be made at this point:

(a) For a crystal characterized by a center of symmetry the energy matrix is real, so that the expansion coefficients can be chosen as real.[16]

(b) For the case of a single electronic configuration, the diagonal matrix elements $\mathcal{L}_{\alpha\alpha}{}^{ff}(\mathbf{k})$ are equal for all values of α, only for the special directions of the $\mathbf{k}$ vector perpendicular to or lying in a symmetry plane of the crystal. Only then $|B_{\alpha j}{}^f|^2=\text{const}$, independent of $\mathbf{k}$. In other cases, a complete solution of Eq. (2.6) is necessary.[16]

(c) When crystal-field mixing is taken into account, the energy matrix (2.10) can be simplified only for the special directions of the $\mathbf{k}$ vector mentioned above. Only in this case the energy matrix will be diagonal in the branch index j. This simple case was previously considered in the calculation of crystal-field mixing for $\mathbf{k}=0$ exciton states.

III. THE DENSITY OF STATES AND THE GREEN'S FUNCTION

We shall now approach the problem of the density of states of a molecular crystal by considering a general formalism which is applicable for both the pure and the mixed crystal. Let $\mathcal{H}$ be the crystal Hamiltonian characterized by eigenvalues E_κ and eigenfunctions ψ_κ. The crystal wavefunctions are expanded in terms of the localized excitations functions $a_{n\alpha}{}^f$ of the pure crystal:

$$\psi_\kappa=(N)^{-1/2}\sum_n\sum_\alpha\sum_f U_\kappa(n\alpha f)a_{n\alpha}{}^f. \tag{3.1}$$

The expansion coefficients form a unitary matrix,

$$(1/N)\sum_n\sum_\alpha\sum_f U_\kappa{}^*(n\alpha f)U_{\kappa'}(n\alpha f)=\delta_{\kappa\kappa'}, \tag{3.2}$$

$$(1/N)\sum_\kappa U_\kappa{}^*(n\alpha f)U_\kappa(n'\alpha'f')=\delta_{nn'}\delta_{\alpha\alpha'}\delta_{ff'}. \tag{3.3}$$

We introduce now a Green's function $\mathbf{G}(E)$ for the pure crystal defined by the symbolic equation

$$\mathbf{G}(E)=(E-\mathcal{H})^{-1}. \tag{3.4}$$

This expression is conveniently expressed using the localized excitation representation:

$$\sum_{n''\alpha''f''}[E\delta_{nn''}\delta_{\alpha\alpha''}\delta_{ff''}-(\mathcal{H})_{n\alpha f,n''\alpha''f''}]\times G_{n''\alpha''f'',n'\alpha'f'}(E)=\delta_{nn'}\delta_{\alpha\alpha'}\delta_{ff'}. \tag{3.5}$$

Applying the orthogonality relations (3.2) and (3.3), the Green's function in the localized representation can be displayed in the form

$$G_{n\alpha f,n'\alpha'f'}(E)=\sum_\kappa[U_\kappa{}^*(n\alpha f)U_\kappa(n'\alpha'f')/(E-E_\kappa)]. \tag{3.6}$$

Following Gooding and Moser,[11] we introduce a weighted density-of-states function for the crystal states:

$$g_{n\alpha f,n'\alpha'f'}(E)=(1/N)\sum_\kappa U_\kappa{}^*(n\alpha f)U_\kappa(n'\alpha'f')\delta(E-E_\kappa). \tag{3.7}$$

From the orthogonality relation (3.3) which ensures the closure property of the basis functions, one gets

$$\int g_{n\alpha f,n'\alpha'f'}(E)dE=\delta_{nn'}\delta_{\alpha\alpha'}\delta_{ff'}. \tag{3.8}$$

The density of states in the energy spectrum per one molecule is given by

$$g(E)=(N\sigma)^{-1}\sum_\kappa\delta(E-E_\kappa). \tag{3.9}$$

From Eqs. (3.2) and (3.7) it immediately follows that

$$g(E)=(N\sigma)^{-1}\sum_n\sum_\alpha\sum_f g_{n\alpha f,n\alpha f}(E)=(N\sigma)^{-1}\,\mathrm{Trg}(E). \tag{3.10}$$

The Green's function (3.6) can now be expressed in the integral form

$$G_{n\alpha f,n'\alpha'f'}(E)=\int_{-\infty}^{\infty}\frac{g_{n\alpha f,n'\alpha'f'}(E')dE'}{E-E'}. \tag{3.11}$$

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The general relationship between the density of states and the Green's function can be readily established by considering the Green's function with an imaginary argument $\mathbf{G}(E-i\epsilon^{+})$, where $\epsilon^{+}>0$, i.e., $\epsilon^{+}\rightarrow 0$. The application of the well-known symbolic identity

$$(E-E'-i\epsilon^{+})^{-1}=P(E-E')^{-1}+i\pi\delta(E-E') \qquad (3.12)$$

leads to the separation of the matrix elements of the Green's function into real and imaginary parts:

$$G_{n\alpha f,n'\alpha' f'}(E-i\epsilon^{+})=F_{n\alpha f,n'\alpha' f'}(E)+i\pi g_{n\alpha f,n'\alpha' f'}, \qquad (3.13)$$

where

$$F_{n\alpha f,n'\alpha' f'}(E)=P\int\frac{g_{n\alpha f,n'\alpha' f'}(E')dE'}{E-E'}, \qquad (3.14)$$

whereupon the general relation between the density of states and the Green's function is

$$g(E)=(\pi N\sigma)^{-1}\operatorname{Im}\operatorname{Tr}\mathbf{G}(E-i\epsilon^{+}). \qquad (3.15)$$

Turning our attention to the case of a pure crystal, we set

$$U_{k\mu}(n\alpha f)=b_{\alpha f}{}^{\mu}(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{R}_{n\alpha}), \qquad (3.16)$$

and the Green's function is then given by

$$G^{0}{}_{n\alpha f,n'\alpha' f'}(E)=N^{-1}\times\sum_{\mathbf{k}}\sum_{\mu}\frac{[b_{\alpha f}{}^{\mu}(\mathbf{k})]^{*}[b_{\alpha' f'}{}^{\mu}(\mathbf{k})]\exp[i\mathbf{k}\cdot(\mathbf{R}_{n'\alpha'}-\mathbf{R}_{n\alpha})]}{E-E_{\mu}(\mathbf{k})}, \qquad (3.17)$$

while the weighted density of exciton states is

$$g^{0}{}_{n\alpha f,n'\alpha' f'}(E)=N^{-1}\sum_{\mathbf{k}}\sum_{\mu}[b_{\alpha f}{}^{\mu}(\mathbf{k})]^{*}[b_{\alpha' f'}{}^{\mu}(\mathbf{k})]\times\exp[i\mathbf{k}\cdot(\mathbf{R}_{n'\alpha'}-\mathbf{R}_{n\alpha})]\times\delta[E-E_{\mu}(\mathbf{k})]. \qquad (3.18)$$

The density of exciton states is now given by

$$g_{0}(E)=(N\sigma)^{-1}\sum_{\mathbf{k}}\sum_{\mu}\delta[E-E_{\mu}(\mathbf{k})]=\mathrm{Tr}\mathbf{g}^{0}(E). \qquad (3.19)$$

A comment concerning the diagonal matrix elements of the $\mathbf{g}^{0}(E)$ matrix for the pure crystal is in order. These are given in the form

$$g^{0}{}_{n\alpha f,n\alpha f}(E)=N^{-1}\sum_{\mu}\sum_{\mathbf{k}}|b_{\alpha f}{}^{\mu}(\mathbf{k})|^{2}\delta[E-E_{\mu}(\mathbf{k})]. \qquad (3.18')$$

If the molecules in the unit cell are crystallographically inequivalent, nothing can be done, and it is necessary to know both the b's and the energy levels. If, however, the molecules of the unit cell can be mapped one to another by factor-group operations, these expressions may be simplified. In this case one may group together the wave vectors $\mathbf{k}'$, $\mathbf{k}''$, $\cdots$ in the "star" of $\mathbf{k}$ obtained by transforming $\mathbf{k}$ by the factor-group operations; the corresponding energies $E_{\mu}(k)$, $E_{\mu}(\mathbf{k}')$, $E_{\mu}(\mathbf{k}'')$ $\cdots$ are equal for each μ. We denote $\alpha'\alpha''\cdots$ the sites to which α is sent by the factor group operation. Therefore we can write

$$\begin{aligned}g^{0}{}_{n\alpha f,n\alpha f}(E)&=N^{-1}\sum_{\mu}\sum_{\mathbf{k}}(|b_{\alpha f}{}^{\mu}(\mathbf{k})|^{2}+|b_{\alpha f}{}^{\mu}(\mathbf{k}')|^{2}+|b_{\alpha f}{}^{\mu}(k'')|^{2}+\cdots)\delta[E-E_{\mu}(\mathbf{k})]\\&=N^{-1}\sum_{\mu}\sum_{\{\mathbf{k}\}}(|b_{\alpha f}{}^{\mu}(\mathbf{k})|^{2}+|b_{\alpha' f}{}^{\mu}(\mathbf{k})|^{2}+|b_{\alpha'' f}{}^{\mu}(\mathbf{k})|^{2}+\cdots)\times\delta[E-E_{\mu}(\mathbf{k})],\end{aligned} \qquad (3.18'')$$

where $\{\mathbf{k}\}$ represents the summation taking one wave vector from each "star." Now using the normalization condition (19), we obtain

$$\sum_{f}g^{0}{}_{n\alpha f,n\alpha f}(E)=N^{-1}\sum_{\mu}\sum_{\mathbf{k}}\delta[E-E_{\mu}(\mathbf{k})]. \qquad (3.20)$$

Hence, for the pure crystal all the diagonal sums over the excited states are independent of the site indices. In the special case under consideration the density of states can be expressed from the knowledge of the matrix elements of $\mathbf{g}^{0}(E)$ for a single site.

The normalization condition for the density of states function is directly obtained from Eq. (3.8) in the form

$$\int g_{0}(E)dE=f, \qquad (3.21)$$

where f in Eq. (3.21) stands for the number of exciton bands.

IV. THE ELECTRONIC STATES OF MIXED MOLECULAR CRYSTALS

We shall consider now the effect of substitutional impurities on the excited states of a molecular crystal. The physical situation which is of the greatest interest for the study of shallow traps in molecular crystals prevails when the guest and host molecules differ in isotopic substitution. In this case the perturbation potential can be described in terms of a localized perturbation. Small differences in intermolecular coupling terms arising from nuclear displacements in the two isotopic molecules can be neglected, so that the local perturbation strength will correspond to the differences between the excitation energies of the isolated molecule. One can adopt a general perturbation scheme and expand the mixed-crystal wavefunctions in terms of the electronic states of the pure crystal [Eq. (3.1)].

Let H be the perturbed lattice Hamiltonian. Now define a Hamiltonian $\mathcal{H}=H-\tilde{E}_{0}$ relative to the ground-state energy $\tilde{E}_{0}$ of the perturbed system, the mixed-crystal wavefunctions ψ_{κ} [Eq. (3.1)] corresponding to eigenvalues E_{κ}. The perturbation due to the impurities is defined by $V=\mathcal{H}-\mathcal{H}_{0}$.

To proceed with the generalized perturbation treat-

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ment we now consider the perturbation operator V in the localized representation. The matrix $\mathbf{V}$ is of rank ν, where ν is equal to the number of perturbed sites (i.e., number of impurities times number of sites over which the perturbation is extended) multiplied by number of bands under consideration. In order to establish a relationship between the states of the mixed and the pure crystal we shall make use of the operator identity

$$\mathbf{G}(E)=\mathbf{G}^0(E)+\mathbf{G}^0(E)\mathbf{V}\mathbf{G}(E). \qquad (4.1)$$

Now defining $(\mathbf{I}-\mathbf{G}^0\mathbf{V})^{-1}$ as the inverse of the matrix $[\mathbf{I}-\mathbf{G}^0(E)\mathbf{V}]$, we write

$$\mathbf{G}(E)=[\mathbf{I}-\mathbf{G}^0(E)\mathbf{V}]^{-1}\mathbf{G}^0(E) \qquad (4.2)$$

or, alternatively,

$$\mathbf{G}(E)=\mathbf{G}^0(E)+\mathbf{G}^0(E)\mathbf{V}[\mathbf{I}-\mathbf{G}^0(E)\mathbf{V}]^{-1}\mathbf{G}^0(E). \qquad (4.3)$$

These are the general expressions for the mixed-crystal Green's functions in terms of the pure-crystal Green's function. The matrix elements of the reciprocal matrix in Eq. (*h*.2) can be expressed in terms of the complementary minors $C_{n\alpha f,n'\alpha' f'}$ of the matrix $[\mathbf{I}-\mathbf{G}^0(E)\mathbf{V}]$:

$$\{[\mathbf{I}-\mathbf{G}^0(E)\mathbf{V}]^{-1}\}_{n\alpha f,n'\alpha' f'}=C_{n'\alpha' f',n\alpha f}/D(E), \qquad (4.4)$$

where

$$C_{n\alpha f,n'\alpha' f'}=(\pm 1)\ \mathrm{minor}[(\mathbf{I}-\mathbf{G}^0\mathbf{V})]_{n\alpha f,n'\alpha' f'} \qquad (4.5)$$

and

$$D(E)=\det|\mathbf{I}-\mathbf{G}^0(E)\mathbf{V}|. \qquad (4.6)$$

It is now apparent that $\mathbf{G}(E)$ has poles at the unperturbed energies and at the energy E, where $D(E)$ is singular, so that the perturbed energy levels of interest are obtained from the simple relation

$$D(E)=0. \qquad (4.7)$$

Since the matrix $\mathbf{V}$ is of rank ν, the structure of the matrix $(\mathbf{I}-\mathbf{G}^0\mathbf{V})$ is characterized by $\nu\times\nu$ filled rows and columns followed by diagonal terms of unity, and the other elements being zero. Thus the determinant $D(E)$ has dimension of $\nu\times\nu$. This general result was first established in the work of Koster and Slater.[6] To proceed, we shall derive the general expression for the density of states of the mixed crystal. From Eqs. (4.3) and (4.4) we obtain

$$\begin{aligned} Tr\mathbf{G}(E)&=\mathrm{Tr}\mathbf{G}^0(E)\\ &+\sum_{n\alpha f}\sum_{n'\alpha' f'}\sum_{n''\alpha'' f''}\sum_{n'''\alpha''' f'''}G^0{}_{n\alpha f,n'\alpha' f'}V_{n'\alpha' f',n''\alpha'' f''}\\ &\times C_{n'''\alpha''' f''',n''\alpha'' f''}G^0{}_{n'''\alpha''' f''',n\alpha f} \qquad (4.8)\end{aligned}$$

Now making use of the algebraic identities

$$\sum_{n\alpha f}G^0{}_{n\alpha f,n'\alpha' f'}G^0{}_{n'''\alpha''' f''',n\alpha f}=-(d/dE)G^0{}_{n'''\alpha''' f''',n'\alpha' f'} \qquad (4.9)$$

and

$$D(E)=\sum_{n'\alpha' f'}(\mathbf{I}-\mathbf{G}^0\mathbf{V})_{n\alpha f,n'\alpha' f'}C_{n\alpha f,n'\alpha' f'}, \qquad (4.10)$$

one obtains

$$\begin{aligned}&\sum_{n\alpha f}\sum_{n'\alpha' f'}\sum_{n''\alpha'' f''}\sum_{n'''\alpha''' f'''}G^0{}_{n\alpha f,n'\alpha' f'}V_{n'\alpha' f',n''\alpha'' f''}\\ &\times C_{n'''\alpha''' f''',n''\alpha'' f''}G^0{}_{n'''\alpha''' f''',n\alpha f}=(dD/dE). \qquad (4.11)\end{aligned}$$

From Eqs. (4.8)–(4.11) the general expression for the perturbed density of states is obtained:

$$g(E)=g_0(E)+(\pi N\sigma)^{-1}\,\mathrm{Im}(d/dE)\ \ln D(E-i\epsilon^+). \qquad (4.12)$$

Three comments should be made at this point: (a) The general result (4.12) is a direct consequence of Dyson's equation. (b) The general perturbation expansion should in principle include all exciton bands. (c) The correction term is of the order of $(1/N\sigma)$. The general relations thus derived can now be applied for the study of electronic states of mixed crystals.

V. THE WEAK VIBRONIC COUPLING LIMIT

In order to study the effects isotopic impurities have on the excited states of molecular crystals, the rigid-lattice approximation has to be relaxed so that the effect of intramolecular vibrations has to be considered. The effect of shallow traps can be studied in the vicinity of the first exciton band. The first exciton bands of typical molecular crystals of organic molecules arising from singlet excitation are characterized by Davydov splittings[16,17] (and therefore exciton bandwidths) of the order of 50–500 cm^{-1}, while triplet exciton bandwidths are of the order [46] of 1–50 cm^{-1}; thus in all these cases of interest the separation between intramolecular vibrational levels exceeds the exciton bandwidth. It is well known that when the intermolecular interactions are small compared to the intramolecular electronic–vibrational coupling, then the vibrational intramolecular interactions are diagonalized before the intermolecular interaction terms. In this weak vibronic coupling limit the molecular vibronic functions form the basis for the diagonalization of the crystal Hamiltonian.

The perturbation Hamiltonian for the isotopically doped crystal will be displayed in the form

$$V=\mathcal{H}-\mathcal{H}_0=(H-H_0)-(\tilde{E}-E_0), \qquad (5.1)$$

where $\tilde{E}$ and E_0 correspond to the ground-state energies of the mixed crystal and of the pure crystal, respectively.

The orthogonal molecular wavefunctions are taken in the harmonic approximation

$$\varphi^f(q,Q)=\varphi^{mr}(q,Q)=\varphi^m(q)\chi^{mr}(Q), \qquad (5.2)$$

where q and Q refer to the electronic and nuclear coordinates, respectively, while m and r label the elec-

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tronic state and the vibrational state, respectively. φ^m and χ^{mr} represent the electronic and vibrational wavefunction of a single molecule.

The molecular perturbation terms arise from the changes in nuclear kinetic energy and have the simple form[38]

$$H-H_0=-\tfrac{1}{2}\sum_i\sum_{\{p\}}[(1/M_1)-(1/M_2)](\partial^2/\partial Q_{ip}{}^2)$$
$$=\sum_{\{p\}}t_p, \qquad (5.3)$$

where $\{p\}$ represents the sites occupied by the guest molecules, while i runs over all the coordinates of the substituted nuclei.

The molecular ground-state wavefunction of a guest molecule can be represented in the form

$$\tilde{\varphi}^{00}=\varphi^0(q)\tilde{\chi}^{00}(Q). \qquad (5.4)$$

The electronic wavefunction is unaffected by isotopic substitution, while the vibrational wavefunction $\tilde{\chi}^{00}(Q)$ can be expanded in terms of the vibrational wavefunctions of the host molecules $\chi^{0i}(Q)$:

$$\tilde{\chi}^{00}(Q)=\sum_i \alpha_{0i}\chi^{0i}(Q). \qquad (5.5)$$

Defining the matrix elements between vibrational states by

$$\omega_{ij}=\langle\chi^{0i}\mid t\mid\chi^{0j}\rangle \qquad (5.6)$$

and neglecting anharmonicity effects, the molecular energy levels are obtained from the secular equation:

$$\begin{vmatrix} \epsilon^{00}+\omega_{00}-\tilde{\epsilon} & 0 & \omega_{02} & \cdots \\ 0 & \epsilon^{01}+\omega_{11}-\tilde{\epsilon} & 0 & \cdots \\ \omega_{02} & 0 & \epsilon^{02}+\omega_{22}-\tilde{\epsilon} & \cdots \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \end{vmatrix}=0. \qquad (5.7)$$

Assuming that the off-diagonal vibronic matrix elements are smaller than the energy separation between vibronic levels,[47] the first-order ground-state energy is

$$\tilde{\epsilon}^{00}=\epsilon^{00}+\omega_{00}. \qquad (5.8)$$

In a similar way, for a molecular excited state of the guest molecule we set

$$\tilde{\varphi}^f=\tilde{\varphi}^{r\mu}=\varphi^r(q)\chi^{r\mu}(Q). \qquad (5.9)$$

The first-order correction to the vibronic level $r\mu$ is

$$v_{\mu\mu}=\langle\chi^{r\mu}\mid\hat{t}\mid\chi^{r\mu}\rangle=\tilde{\epsilon}^{r\mu}-\epsilon^{r\mu}. \qquad (5.10)$$

Hence the difference in the 0–0 excitation energy between the guest and the host molecules is

$$U_0=v_{00}-\omega_{00}. \qquad (5.11)$$

From Eqs. (5.3) and (5.11) we define the perturbation operator

$$V=\sum_{\{p\}}(t_p-\omega_{00}). \qquad (5.12)$$

Now limiting our attention to vibronic bands constructed from a single electronic state, we shall expand the crystal wavefunction in terms of the pure crystal states:

$$\psi_r=\sum_l\sum_\mu U_r(l,\mu)a_l{}^{r\mu}, \qquad (5.13)$$

where $l\equiv n\alpha$ is the site index. The matrix elements of V are

$$\langle a_l{}^{r\mu}\mid V\mid a_{l'}{}^{r\mu'}\rangle=\sum_{\{p\}}\delta_{lp}\delta_{l'p}[v_{\mu\mu'}-\omega_{00}\delta_{\mu\mu'}]. \qquad (5.14)$$

Thus the perturbation operator is local, being diagonal in the site index. However, the scrambling of vibronic states is rather awkward. Provided that the off-diagonal matrix elements of the perturbation operator are relatively small compared to the diagonal terms (this is just the approximation we have used in the derivation of the first-order correction to the molecular energies), the perturbation operator in the localized representation is just

$$\langle a_l{}^{r\mu}\mid V\mid a_{l'}{}^{r\mu'}\rangle=\sum_{\{p\}}\delta_{lp}\delta_{l'p}\delta_{\mu\mu'}[v_{\mu\mu'}-\omega_{00}]. \qquad (5.15)$$

In the work of Philpott and Craig,[38] second-order corrections to the excited state (but not the ground-state) energy of the vibronic states were included, leading essentially to the same result.

To demonstrate the simplicity of this result, we notice that for the case of a single impurity

$$\det\mid\mathbf{I}-\mathbf{G}^0\mathbf{V}\mid=[1-G_{00,00}(E)(v_{00}-\omega_{00})]$$
$$\times[1-G_{01,01}(E)(v_{11}-\omega_{00})]\times\cdots, \qquad (5.16)$$

where

$$G_{0\mu,0\mu}(E)=\int\frac{g^0{}_{0\mu,0\mu}(E')\,dE'}{E-E'}, \qquad (5.17)$$

$g^0{}_{0\mu,0\mu}$ being the density of states in the μth vibronic band. Thus the localized state of interest is obtained from the equation

$$1-G_{00,00}(E)(v_{00}-\omega_{00})=1-G_{00,00}(E)U_0=0. \qquad (5.18)$$

From this discussion we conclude that, provided the off-diagonal matrix elements of the nuclear kinetic-energy operator are small, the isotopic substitution can be considered as a localized perturbation. The Green's function in the weak coupling case has to be expressed in terms of the density of states in the first vibronic band. The latter is related to the exciton band structure, where all the electronic coupling terms are

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[47] For the case of a one-dimensional oscillator the first-order correction term is $\omega_{00}=[(M_1-M_2)/2M_2](\tfrac{1}{2}\hbar\nu_0)$, where $\hbar\nu_0$ is the oscillator frequency, while the exact solution will yield the energy correction $\{[(M_1)^{1/2}-(M_2)^{1/2}]/(M_2)^{1/2}\}(\tfrac{1}{2}\hbar\nu_0)$; setting $M_1/M_2=\tfrac{1}{2}$, we get $\omega_{00}=0.25(\tfrac{1}{2}\hbar\nu_0)$, while the exact solution is $0.29(\tfrac{1}{2}\hbar\nu_0)$. Hence the off-diagonal matrix elements are of the order of $0.1\omega_{00}$.

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modified by the proper Franck–Condon vibrational overlap factors.

VI. THE LOCALIZED PERTURBATION PROBLEM

We shall now consider the simplest case of a molecular crystal in the weak-coupling approximation perturbed by the introduction of a single isotopic molecule at the lattice site 0α. Considering a single electronic configuration, the perturbation operator in the localized representation is displayed in the simple form

$$V_{n\alpha,m\beta}=U_0\delta_{n0}\delta_{m0}\delta_{\alpha\beta}. \qquad (6.1)$$

The perturbed energy levels are obtained from the relation (4.7),

$$D(E)=1-U_0G_0(E)=0, \qquad (6.2)$$

where

$$G_0(E)=G^0{}_{0\alpha,0\alpha}(E).$$

It is of considerable interest to consider now the expression for the density of states of the perturbed system. Using Eq. (4.12) we obtain

$$g(E)=g_0(E)+(\pi N\sigma)^{-1}\,\mathrm{Im}(d/dE)\,\ln[1-U_0G_0(E-i\epsilon^+)]. \qquad (6.3)$$

Using Eqs. (3.13) and (3.20) we separate the Green's function for the pure crystal into real and imaginary parts

$$G_0(E-i\epsilon^+)=F(E)+i\pi g_0(E), \qquad (6.4)$$

$$F(E)=P\int\frac{g_0(E')dE'}{E-E'}, \qquad (6.5)$$

and now $g_0(E)$ represents the density of states in the lowest exciton vibronic band. By substitution of Eq. (6.4) into Eq. (6.3) one gets

$$g(E)=g_0(E)-(N\sigma)^{-1}\times\frac{U_0{}^2F'(E)g_0(E)+U_0[1-U_0F(E)]g_0'(E)}{[1-U_0F(E)]^2+[\pi U_0g_0(E)]^2}, \qquad (6.6)$$

where

$$F'(E)=dF/dE; \qquad g_0'(E)=dg_0/dE.$$

The correction to the density of states induced by the presence of the impurity molecule is characterized by a maximum in the vicinity of the energy $E=E_r$, where $1-U_0F(E_r)=0$. This result is of course consistent with Eq. (6.2). It is now easy to demonstrate that the correction term exhibits an approximate Lorentzian shape. Expanding the function $F(E)$ around $E=E_r$ in a power series

$$F(E)=F(E_r)+(E-E_r)F'(E_r)+\cdots \qquad (6.7)$$

and substituting in Eq. (6.6), we get

$$g(E)=g_0(E)+(\pi N\sigma)^{-1}\{\Gamma_0(E)/[(E-E_r)^2+\Gamma_0(E)^2]\}, \qquad (6.8)$$

where the energy dependent bandwidth is given by

$$\Gamma_0(E)=-\pi g_0(E)/F'(E_r); \qquad (6.9)$$

provided that $\Gamma_0(E)$ varies slowly with the energy at the vicinity of E_r (which is the case when E_r is sufficiently removed from critical points in the band), the line shape is expected to be an asymmetric Lorentzian. As the resonance energy is determined by the strength U_0 of the local perturbation, we can distinguish three cases of physical interest:

(a) For limiting small values of $|U_0|$ (i.e., $|U_0|<|U_c|$) there will be no solution for the energy equation (6.2), and the change in the density of states is a monotonic function of the energy in the range of the unperturbed band. This case is encountered only when the exciton band structure is determined by three-dimensional interactions.

(b) For intermediate values of $|U_0|$ the resonance energy is located within the energy range of the unperturbed exciton band. In this case a virtual scattering state is observed, being characterized by a width of $\sim\Gamma_0(E_r)$. Again this case is only encountered in practice in the three-dimensional model.

(c) For sufficiently large values of $|U_0|$, E_r will be located outside the unperturbed band. In this case the correction to the density of states outside the band reduces to a delta function, since

$$\pi^{-1}\lim_{\epsilon\to 0}[\epsilon/(x^2+\epsilon^2)]=\delta(x),$$

so that outside the band

$$g(E)=(N\sigma)^{-1}\delta(E-E_r). \qquad (6.10)$$

A single state is then separated from the top or from the bottom of the exciton band, depending on the sign of U_0.

In Fig. 1 we display the general form of the density of states and the F function for a typical three-dimensional case. The $g_0(E)$ function presented herein provides a zero-order approximation for the density of states in the first singlet exciton band of crystalline naphthalene, being approximated by the shape of the "hot" 1→0 band in this system.[16] The bandwidth was chosen to be 210 cm^{-1}. The typical shape of the F function which is derived from the empirical data does not reveal some analytic singularities, which are complementary to the Van Hove analytic singularities in the density-of-states function. These will be discussed in Sec. VII. However, these singular points are of minor importance for the impurity level split from the band. The F function reveals the critical values U_c and the critical values U_+ and U_- of the perturbation parameter leading to bound states above and below the band, respectively. Localized states are expected to occur when $|U_0|>|U_-|$ for a negative perturbation and when $|U_C|>|U_+|$ for a positive perturbation. It will

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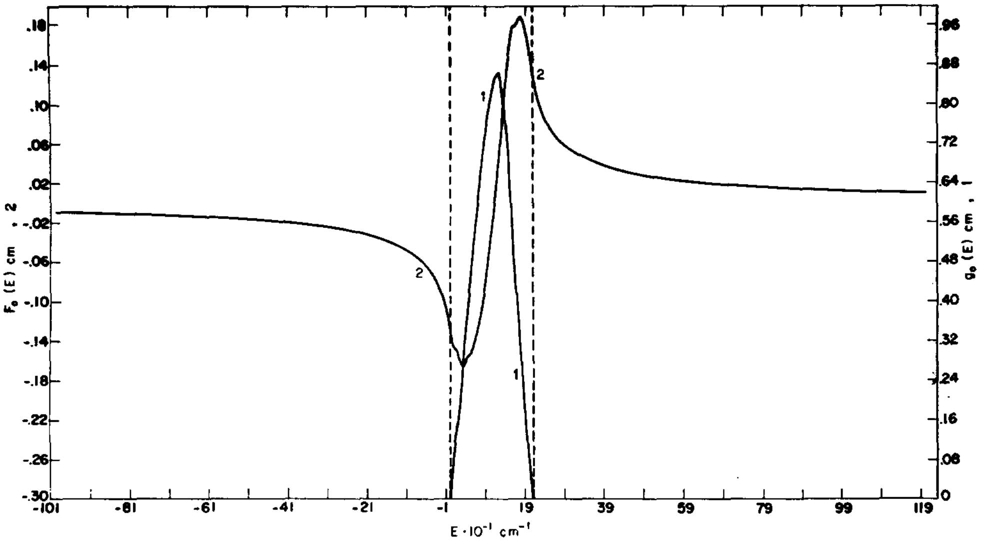

FIG. 1. The pure-crystal density-of-states function (curve 1) and the $F(E)$ function for a three-dimensional case (see text). The maximum and minimum values of $F(E)$ correspond to $(U_c^+)^{-1}$ and $(U_c^-)^{-1}$, respectively, where U_c^+ and U_c^- correspond to the limiting strengths of the perturbation ($|U_0|<U_c^+$ or $|U_c^-|$) for which no solution of the energy equation can be found. The intersections of the dashed lines (which correspond to the band edges) with $F(E)$ yield the values of U_+ and U_-. Virtual states will be observed when $|U_c^-|<|U_0|<|U_-|$ (for $U_0<0$) or when $U_c^+<U_0<U_+$ (for $U_0>0$). Bound states will occur when $|U_0|>|U_-|$, ($U_0<0$) or $U_0>U_+$, ($U_0>0$).

be demonstrated in Sec. VII that for the one-dimensional and the two-dimensional cases $U_c=\infty$ and $U_+=U_-=0$, so that localized states are observed for an arbitrarily small strength of the perturbation. In the three-dimensional case when $|U_0|$ exceeds the critical values U_+ or U_-, the intersection of $1/U_0$ with the F curve leads then to two solutions, one corresponding to a bound state E_r outside the band while the second corresponds to an antiresonance E_{ar} within the band. This is easily demonstrated by noting that the condition for observing a resonance is $\Gamma_0>0$, so that $F'<0$, which is the case outside the band, while for the case of an antiresonance, $\Gamma_0<0$, so that $F'>0$. Using similar arguments for the case of a virtual level, a resonance is observed in the region where $F'<0$ followed by an antiresonance in the range where $F'>0$.

We have thus demonstrated that each bound impurity state outside the band or a virtual state within the band is accompanied by an antiresonance within the band. These antiresonances compensate for the appearance of a localized or a virtual level in another region of the energy spectrum. As the total number of states in the system is invariant, and not affected by the perturbation, it is thus apparent that the increase in the density of states due to the formation of a bound or of a virtual state should be accompanied by an antiresonance.

Using the above-mentioned density of states function for the pure crystal, we have calculated the energies E_r and the changes in the density of states for the dilute mixed crystal. These results are displayed in Figs. 2 and 3.

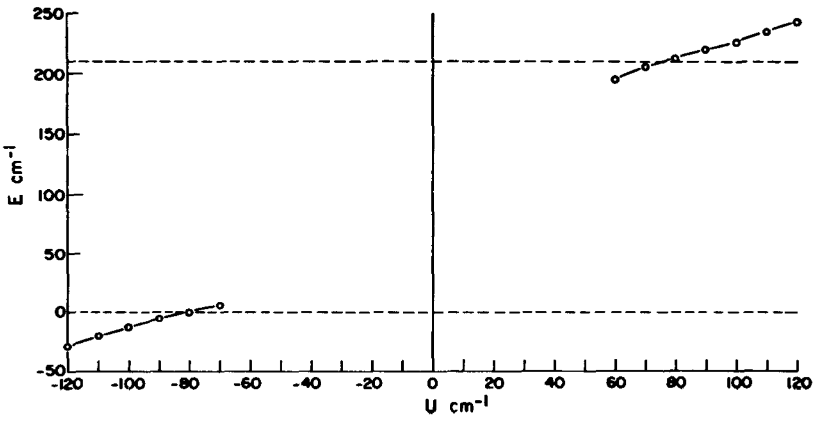

FIG. 2. The dependence of the energy of a bound or virtual impurity state on the strength, U_0, of the local perturbation calculated for the unperturbed exciton band structure presented in Fig. 1. The dashed curves represent the band edges. Note that for this model, $U_+=75$ cm^{-1} while $U_-=-80$ cm^{-1}. Virtual states are observed in the region $U_0=-70$–-80 cm^{-1} and $U_0=60$–75 cm^{-1}.

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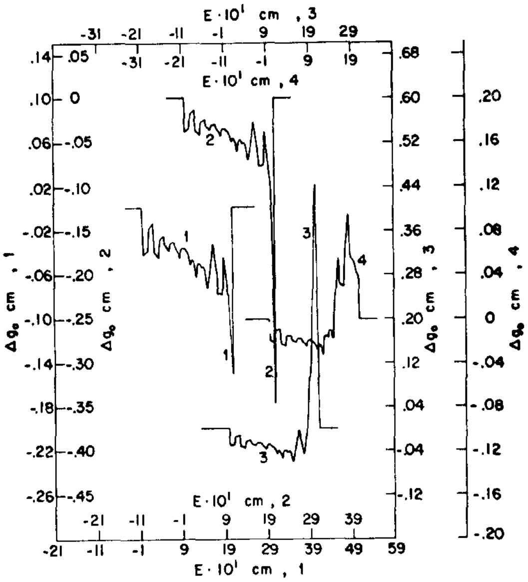

FIG. 3. The change in the density-of-states functions in the region of the exciton band induced by a local perturbation, calculated from the band structure of Fig. 1. Curve 1: $U_0=+120$ cm^{-1}. Curve 2: $U_0=+90$ cm^{-1}. Curve 3: $U_0=+60$ cm^{-1}. Curve 4: $U_0=+30$ cm^{-1}. Curves 1 and 2 correspond to bound states. Curve 3 represents a virtual state, while Curve 4 corresponds to the limit of a very weak perturbation where no solutions to Eq. (6.2) are available.

VII. DIMENSIONALITY CRITERION FOR THE APPEARANCE OF LOCALIZED STATES

Following the discussion of the general rules for the appearance of bound and virtual states, we shall now consider some general rules for the appearance of localized states in one-, two-, and three-dimensional systems. In the case of Frenkel exciton states, one- and two-dimensional systems are of real physical interest. Thus exciton states in polymers are governed by interactions in one dimension, while in some other cases, such as triplet states of aromatic hydrocarbons, the intermolecular interactions are determined by intermolecular interactions in two dimensions.

The general rules for the splitting of the localized state from the edge of the exciton band can be derived from the study of the behavior of the function F near the critical analytical points in the exciton band. To bring up our physical understanding of this treatment and to introduce some definitions and notation we shall first consider the derivation of the nonanalytic contribution to the density of states near the critical point using the method of Fourier transforms of generalized functions.[2,48]

Consider a single exciton band consisting of $j=1\cdots\sigma$ branches. The density of states can be written as

$$g_0(E)=\sum_{\mathbf{k}}\sum_j\delta[E-E_j(\mathbf{k})].$$

Using the delta-function expansion

$$\delta(x)=(2\pi)^{-1}\int_{-\infty}^{\infty}d\alpha e^{i\alpha x}$$

and the integral representation for the summation over the Brillouin zone

$$N^{-1}\sum_{\mathbf{k}}\rightarrow\frac{v_0}{(2\pi)^l}\int d^3\mathbf{k},$$

where v_a is the volume of the unit cell, the density of states can be displayed in the form

$$g_0(E)=(2\pi)^{-1}\int_{-\infty}^{\infty}d\alpha e^{-i\alpha E}f(\alpha),\qquad(7.1)$$

where

$$f(\alpha)=\sum_j f_j(\alpha)\qquad(7.2)$$

and

$$f_j(\alpha)=\frac{v_a}{(2\pi)^l\sigma}\int d^3\mathbf{k}\exp[iE_j(\mathbf{k})\alpha],\qquad(7.3)$$

where $l=1$ for the one-dimensional case, $l=2$ for the two-dimensional case, and $l=3$ for the three-dimensional case.

The singularities in $g_0(E)$ are determined by the behavior of $f(\alpha)$ for large values of α, this contribution being determined from the region where $\nabla_{\mathbf{k}}E_j(\mathbf{k})=0$. Around these Van Hove singular points the exciton energy can be expanded in power series

$$E_j(\mathbf{k})=E_j^c+\sum_{\nu,\nu'=1}^{l}\beta_{\nu\nu'}(k_\nu-k_\nu^c)(k_{\nu'}-k_{\nu'}^c).\qquad(7.4)$$

Linear transformation of the coordinate systems in the $\mathbf{k}$ space leads to the results

$$\sum_{\nu,\nu'}\beta_{\nu\nu'}(k_\nu-k_\nu^c)(k_{\nu'}-k_{\nu'}^c)=\sum_{i=1}^{l}\gamma_i\varphi_i^2,\qquad(7.5)$$

where $\gamma_i=+1$ or $\gamma_i=-1$. The number of the negative γ_i values is referred to as the index of the critical point. The nonanalytic contribution to the density of states $g_0^c(E)$ can be displayed in the form

$$g_0^c(E)=(2\pi)^{-1}\sum_j\int d\alpha\exp[-i(E-E_j^c)\alpha]f_j^c(\alpha),\qquad(7.6)$$

where

$$f_j(\alpha)^c=\frac{Av_a}{(2\pi)^l\sigma}\iiint d\varphi_1d\varphi_2d\varphi_3\exp(i\alpha\sum_i\gamma_i\varphi_i^2).\qquad(7.7)$$

A is the Jacobian of the transformation from the set of coordinates $\{(k_\nu-k_\nu^c)\}$ to $\{\varphi_i\}$. The integral in Eq. (7.7) is now separable, being reduced to the product of

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[48] M. J. Lighthill, *An Introduction to Fourier Analysis and Generalized Functions* (Cambridge University Press, London, 1958).

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three integrals, each being given by

$$\int d\varphi_i \exp(i\alpha\gamma_i\varphi_i)^2 = (\pi/|\alpha|)^{1/2} \exp[\tfrac{1}{4}(i\pi\gamma_i)\ \mathrm{sgn}\alpha], \tag{7.8}$$

where $\mathrm{sgn}\alpha = 1$ for $\alpha > 0$ and $\mathrm{sgn}\alpha = -1$ for $\alpha < 0$. Hence for the l-dimensional case

$$f_j^c(\alpha) = \frac{Av_a}{(2\pi)^l\sigma} \frac{\pi^{l/2}}{|\alpha|^{l/2}} \exp[\tfrac{1}{4}(i\pi)\ \mathrm{sgn}\alpha \sum_{i=1}^{l} \gamma_i]. \tag{7.9}$$

Making use of the Fourier transforms of generalized functions, the well-known expression for the density of states near the analytical critical points is obtained.[2]

We shall now demonstrate that the function F is characterized by the same types of critical points as the density-of-states function. Considering again a single exciton band, we write

$$F(E) = P \int \frac{g_0(E')dE'}{E-E'} = (N\sigma)^{-1} \sum_{\mathbf{k}} \sum_j [E - E_j(\mathbf{k})]^{-1}. \tag{7.10}$$

Following the arguments applied for the derivation of Eq. (3.20), we notice that the second equality holds for all crystals where the molecules in the unit cell can be transformed into each other by one of the factor-group operations. Finally we write

$$F(E) = \frac{v_a}{(2\pi)^l\sigma} \sum_j P \int \frac{d^3\mathbf{k}}{E - E_j(\mathbf{k})}. \tag{7.10$'$}$$

Using the expression for Chaucy's principal part

$$Px^{-1} = -\mathrm{Im} \lim_{\delta \to 0^+} \int_0^\infty d\alpha e^{-ix\alpha} e^{-\delta\alpha}, \tag{7.11}$$

we write

$$F(E) = -\mathrm{Im} \int_0^\infty d\alpha e^{-iE\alpha} f(\alpha), \tag{7.12}$$

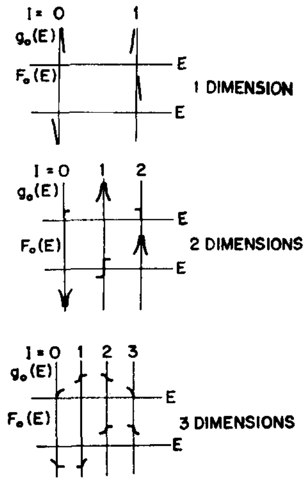

FIG. 4. A schematic representation of Van Hove type critical analytical points in the density-of-states function and in the F function for one-, two-, and three-dimensional systems.

where $f(\alpha)$ is given by Eqs. (7.2) and (7.3), so that the same function $f(\alpha)$ determines the behavior of both the density of states and of the F function. As before, the behavior of $f(\alpha)$ for large values of α determines the behavior of F near the critical points. The contribution to F will be split to an analytic term and a nonanalytic part F^c. Using Eqs. (7.12), (7.3), and (7.7), we can write

$$F^c(E) = -\mathrm{Im} \sum_j \int_0^\infty d\alpha \exp[-i(E - E_j^c)\alpha] f_j^c(\alpha), \tag{7.13}$$

where $f_j^c(\alpha)$ is given by Eq. (7.5). Finally making use of Heaviside's step function $h(\alpha)$[48] [defined by $h(\alpha) = 0$ for $\alpha < 0$ and $h(\alpha) = 1$ for $\alpha > 0$], we write

$$F^c(E) = -\mathrm{Im} \sum_j \int_{-\infty}^\infty d\alpha h(\alpha) \times \exp[-i(E - E_j^c)\alpha] f_j^c(\alpha). \tag{7.14}$$

Making use of the Fourier transforms of generalized functions as displayed by Lighthill,[48] the following results are obtained for the behavior of the F function near the critical points:

For one dimension,

$I = 0$ (minimum):

$$F^c(E) \propto -|E - E_c|^{-1/2} h(E_c - E);$$

$I = 1$ (maximum):

$$F^c(E) \propto |E - E_c|^{-1/2} h(E - E_c). \tag{7.15a}$$

For two dimensions,

$I = 0$ (minimum):

$$F^c(E) \propto -\ln|E - E_c|;$$

$I = 1$ (saddle point):

$$F^c(E) \propto \mathrm{sgn}(E - E_c);$$

$I = 2$ (maximum):

$$F^c(E) \propto \ln|E - E_c|. \tag{7.15b}$$

For three dimensions,

$I = 0$ (minimum):

$$F^c(E) \propto |E - E_c|^{1/2} h(E_c - E);$$

$I = 1$ (saddle point S_1):

$$F^c(E) \propto |E - E_c|^{1/2} h(E - E_c);$$

$I = 2$ (saddle point S_2):

$$F^c(E) \propto -|E - E_c|^{1/2} h(E_c - E);$$

$I = 3$ (maximum):

$$F^c(E) \propto -|E - E_c|^{1/2} h(E - E_c). \tag{7.15c}$$

Thus the singularities in the F function are of the

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same form as the Van Hove analytic singularities in the density of states. These results are displayed in Fig. 4.

We can now demonstrate that the Lifschitz rules[9] for the behavior of the localized state energy near the band edge arise from the singularity of the F function at the edge. Let E_c^0 be the energy corresponding to the band edge and let the localized state near the exciton band edge be characterized by the energy $E_c^0-\Delta E$ $(\Delta E>0)$. The strength of the perturbation $\bar{U}_0$ which gives rise to this localized state is now determined from Eq. (7.15) in the following way:

For the one-dimensional case,

$$\alpha\,|\,\Delta E\,|^{-1/2}=1/\bar{U}_0. \tag{7.16a}$$

For the two-dimensional case,

$$-\beta\ln|\,\Delta E\,|=1/\bar{U}_0. \tag{7.16b}$$

For the three-dimensional case,

$$\gamma\,|\,\Delta E\,|^{1/2}=1/\bar{U}_0, \tag{7.16c}$$

where α, β, and γ are constants determined by the structure of the unit cell. Thus we obtain:

One dimension,

$$\Delta E=\alpha^2\bar{U}_0^2. \tag{7.17a}$$

Two dimensions,

$$\Delta E=\exp(-1/\beta\bar{U}_0). \tag{7.17b}$$

Three dimensions,

$$\Delta E=1/\gamma^2\bar{U}_0^2. \tag{7.17c}$$

Thus for the one- and two-dimensional cases any arbitrary small perturbation will lead to a bound state. This is a direct consequence from the divergence of the F integral near the band edge. In the case of a one-dimensional perturbation the localized state will depart from the band edge quadratically in $\bar{U}_0$, while in the case of the two-dimensional perturbation the localized state will depart exponentially in $-1/\bar{U}_0$. Virtual states can be observed when three-dimensional intermolecular interactions determine the band structure.

VIII. IMPURITY PAIRS

The discussion of the single impurity state in a molecular crystal is only applicable for limiting small impurity concentrations of the order of $1/\sigma N$, when the interaction between different impurity sites can be neglected. Such interactions are of considerable interest in the study of energy migration between traps. These virtual coupling effects between guest molecules have been previously considered by McConnel[49] for electron transfer, and by Robinson *et al.*[25] and by Craig[32,38] for the case of electronic excitation transfer. The interaction between two impurity sites, which are characterized by a sufficiently large trap depth, to yield localized states will lead to two energy levels below or above the band, the splitting of the levels being determined by the off-diagonal matrix elements of the density-of-states matrix, which in turn is determined by the intermolecular interactions. In the case of isotopically substituted molecules such studies will provide an extremely useful information on the nature of the intermolecular interactions which determine the exciton bandwidth. In the case of short-range (electron-exchange or charge-transfer) interactions, the splitting of the energy levels of the impurity pair is expected to be of the order of the Davydov splitting. On the other hand, when the intermolecular interactions are dominated by long-range dipole–dipole coupling, the splitting between these localized states is expected to be appreciably smaller than the Davydov splitting in the pure crystal. We are not aware of any direct spectroscopic study of the impurity-pair splitting in the case of electronic spectra of molecular crystals. The study of the infrared spectra of HCl/DCl mixed crystals[50] provides an example for the information which can be obtained for impurity coupling in the case of deep traps.

Consider now an impurity pair, with the identical isotopically substituted molecules being located at sites $0=0\alpha$ and $l=m\beta$. Considering again a single exciton band, the determinant $D(E)$ takes the form

$$D(E-i\epsilon^+)=\begin{vmatrix}1-U_0G_{0,0}(E-i\epsilon^+) & -U_0G_{0,l}(E-i\epsilon^+)\\ -U_0G_{l,0}(E-i\epsilon^+) & 1-U_0G_{l,l}(E-i\epsilon^+)\end{vmatrix}, \tag{8.1}$$

where the off-diagonal matrix elements are given by Eq. (3.13). The imaginary part of the determinant leads to damping of the virtual states. The condition for the formation of a pair of localized states is given by

$$\begin{vmatrix}1-U_0F_{0,0}(E) & -U_0F_{0,l}(E)\\ -U_0F_{0,l}(E) & 1-U_0F_{0,0}(E)\end{vmatrix}=0. \tag{8.2}$$

To derive a first-order approximation to the splitting of the energy levels, we write for the solutions of Eq. (8.2)

$$E=E_r+\tilde{E}', \tag{8.3}$$

where E_r is the solution for the single impurity problem satisfying Eq. (5.18). Power expansion of $F_{0,0}$ and of $F_{0,l}$ around E_r, retaining the first-order terms in E', leads to the results

$$\tilde{E}'=F_{0,l}(E_r)/[F_{0,0}'(E_r)-F_{0,l}'(E_r)] \tag{8.4a}$$

and

$$\tilde{E}'=-F_{0,l}(E_r)/[F_{0,0}'(E_r)+F_{0,l}'(E_r)]. \tag{8.4b}$$

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[49] H. McConnel, J. Chem. Phys. **35**, 508 (1961).

[50] G. L. Hiebert and D. F. Hornig, J. Chem. Phys. **20**, 919 (1952).

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For large separations of the impurity centers, $F_{0,l}(E)$ decays exponentially with the separation $\mathbf{R}_0-\mathbf{R}_l$, and in this limiting case the splitting is symmetrical around E_r, so that

$$E\rightarrow E_r\pm F_{0,l}(E_r)/F_{0,0}'(E_r). \tag{8.5}$$

IX. MOMENTS EXPANSION METHOD

The general expressions derived herein are applicable for any strength of the perturbation. When the strength of the perturbation considerably exceeds the bandwidth, the general expressions reduce to simple perturbation expressions. This was pointed out by Philpott and Craig.[38] Such perturbation expressions were previously applied by Robinson and Nieman[25] for the interpretation of the quasiresonance shifts of isotopic guest molecules. We shall now demonstrate how the perturbation expressions for the limit of deep traps are related to the moments of the density-of-states function.

The function $F_{0\alpha,0\alpha}(E)$ for E values which are appreciably larger than the energies E' within the exciton band can be expanded in the form

$$F_{0\alpha,0\alpha}(E)=E^{-1}\sum_{I=0}^{\infty}\frac{m_{0\alpha,0\alpha}{}^{(I)}}{E^I}, \tag{9.1}$$

where $m_{0\alpha,0\alpha}{}^{(I)}$ is the ith moment of the exciton density-of-states function:

$$m_{0\alpha,0\alpha}{}^{(I)}=\int g_{0\alpha,0\alpha}(E')(E')^I dE'. \tag{9.2}$$

The closure relation (3.8) implies that $m_{0\alpha,0\alpha}{}^{(0)}=1$. For a crystal where the molecules in the unit cell can be interchanged by factor-group operations, we can write $g_{0\alpha,0\alpha}=g_0(E)$ and

$$m_{0\alpha,0\alpha}{}^{(I)}=N^{-1}\sum_j\sum_{\mathbf{k}}[E_j(\mathbf{k})]^I. \tag{9.3}$$

For the limit of a deep trap, Eqs. (8.1) and (8.2) lead to

$$E=U_0+m_{0\alpha,0\alpha}{}^{(1)}+[m_{0\alpha,0\alpha}{}^{(2)}-(m_{0\alpha,0\alpha}{}^{(1)})^2]/U_0+\cdots, \tag{9.4}$$

resulting in the ordinary perturbation expression.

For the case of deep traps the off-diagonal term takes the limiting form

$$F_{0\alpha,m\beta}(E)=E^{-1}\sum_{I=0}^{\infty}\frac{m_{0\alpha,m\beta}{}^{(I)}}{E^I}, \tag{9.5}$$

where the moments of the off-diagonal matrix element are

$$\begin{aligned}m_{0\alpha,m\beta}{}^{(I)}&=\int(E')^I g_{0\alpha,m\beta}(E')dE'\\&=N^{-1}\sum_{\mathbf{k}}\sum_j[E_j(\mathbf{k})]^I B_{\alpha j}(\mathbf{k})B_{\beta j}{}^*(\mathbf{k})\\&\qquad\times\exp[i\mathbf{k}\cdot(\mathbf{R}_{0\alpha}-\mathbf{R}_{m\beta})].\end{aligned} \tag{9.6}$$

From Eq. (3.8) it follows that $m_{0\alpha,m\beta}{}^{(0)}=0$, so that for large E values $F_{0\alpha,m\beta}(E)\rightarrow m_{0\alpha,m\beta}{}^{(1)}/E^2$. For deep traps, the splitting of the energy levels for the impurity pair can now be obtained from Eq. (8.5) by setting $F'_{0\alpha,0\alpha}(E)\approx-1/E^2$, so that the energy levels are $E\approx U_0\pm m_{0\alpha,m\beta}{}^{(1)}$, the limiting splitting being determined by the first moment of the off-diagonal matrix element.

X. ESTIMATES OF EXCITON BANDWIDTHS

For the case of an intermediate trap depth, when the strength of the perturbation is comparable to the exciton bandwidth, some useful information can be obtained by considering the energy shifts of isotopic impurities. Consider a case of a negative perturbation $U_0<0$, so that the localized state is located at the energy $-|\Delta E|$ below the exciton lowest band edge. Let us approximate the exciton density of states by a simple step function of width Δ; then Eq. (6.2) leads to the simple relation

$$|\Delta E|/(|\Delta E|+\Delta)=\exp(-\Delta/|U_0|). \tag{10.1}$$

This relation is expected to hold when $|U_0|\sim\Delta$. As the available information concerning exciton bandwidths is rather meager, such estimates are of interest. The experimental results of Sheka[20] are available for the C_8D_{10} impurity in C_8H_{10}. The $k=0$ component is located at the bottom of the band.[16] From these data one gets $\Delta E=-44$ cm^{-1}, while $U_0=-115$ cm^{-1}.[19,39] From Eq. (10.1) one gets $\Delta=190$ cm^{-1} for the width of the first singlet exciton band in crystalline naphthalene. This result is in good agreement with the experimental data based on hot-band spectra and an electronic–vibrational cooperative excitation in crystalline naphthalene, which lead to an estimate of 150–200 cm^{-1} for the bandwidth.[19] In the case of C_6H_6 impurity in C_6D_6 $U_0=-200$ cm^{-1}, as inferred by Broude.[51] Nieman and Robinson[25] observed the impurity band of C_6H_6 at 37.853 cm^{-1}. The first Davydov component of crystalline C_6H_6 is located at 37.803 cm^{-1},[50] corresponding to the bottom of the singlet exciton band as inferred from the emission data of Vatulev *et al.*[52] The bottom of the exciton band in C_6D_6 is reported to be located at 38 024 cm^{-1}, although this result is not certain in view of the presence of C_6D_5H impurity in the sample. Using these data, $\Delta E=-171$ cm^{-1} and Eq. (10.1) yields $\Delta=80$ cm^{-1}. This estimate indicates that the Au Davydov component in crystalline benzene (C_6H_6), which is symmetry forbidden, is expected to be located at energy lower than $37\,805+80=37\,885$ cm^{-1}, that is about 40 cm^{-1} above the C polarized component. The present treatment of the "quasiresonance shifts"[25] in Robinson's terminology is self-con-

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[51] V. L. Broude, Usp. Fiz. Nauk. **79**, 577 (1961) [Sov. Phys.—Usp. **4**, 584 (1962)].

[52] V. N. Vatulev, N. I. Sheremet, and T. M. Shpak, Opt. Spectrosc. **12**, 315 (1963).

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sistent and more general than the previous perturbation expansions applied by Nieman and Robinson.

XI. EXPANSION COEFFICIENTS

We shall now turn our attention to the expansion coefficients $U_\kappa(n\alpha)$ which determine to what extent the electronic excitation is localized on the impurity site. For a weak local perturbation (relative to the exciton bandwidth) appreciable delocalization of the electronic excitation around the impurity center occurs, so that the localized states of the mixed crystal can be considered as quasidelocalized excited states. These expansion coefficients were used by Craig and Philpott[38–40] for the study of optical transition strengths. For the case of a system consisting of a single impurity at the site 0α (or rather a dilute mixed crystal), the amplitude of the expansion coefficient $U_\kappa(0\alpha)$ is amenable to direct experimental observation by the study of the fluorescence spectrum of the mixed crystal.[30] Complementary experimental information concerning this expansion coefficient can be obtained from the cooperative electronic–vibrational excitations in the pure crystal.[18,19]

Consider a crystal with the impurity molecules localized at the lattice sites $\{p\}$ (where the impurity sites are $p\equiv m\beta$); the wavefunction in the localized basis set is given in the form $\psi=\sum_l U(l)a_l$ (where all the lattice sites are denoted by $l\equiv n\alpha$). The wavefunction can be displayed in the homogeneous Fredholm representation:

$$\psi=G^0V\psi, \tag{11.1}$$

where again $G=(E-\mathcal{H}_0)^{-1}$. Using the orthogonality relation (2.4), the following equation immediately results for the expansion coefficients:

$$\sum_l U(l)\delta_{l'l}=\sum_l \langle a_{l'}\mid G^0V\mid a_l\rangle U(l). \tag{11.2}$$

Using the localized representation for the perturbation operator [Eq. (5.15)], one gets the general result

$$U(l')=U_0\sum_{\{p\}}G_{l',p}{}^0(E)\,U(p). \tag{11.3}$$

This equation provides a starting point for the theoretical studies of heavily doped crystals.

Considering again low impurity concentration limit, for the case of a single impurity at the site $p=0$, Eq. (11.3) reduces to the well-known result

$$U(l')=U_0G_{l',0}{}^0(E)\,U(0).$$

The normalization condition (3.2) and the algebraic identity (4.9) lead to the result

$$\begin{aligned}1=\sum_{l'}\mid U(l')\mid^2&=U_0{}^2\mid U(0)\mid^2\sum_{l'}\mid G_{l',0}{}^0(E)\mid^2\\&=U_0{}^2\mid U(0)\mid^2[-(d/dE)G_{00}{}^0(E)],\end{aligned} \tag{11.4}$$

so that for a localized impurity state

$$U(0)=[U_0\mid -F'(E_r)\mid^{1/2}]^{-1} \tag{11.5}$$

and

$$U(l')=G_{0,l'}{}^0(E_r)/\mid -F'(E_r)\mid^{1/2}. \tag{11.6}$$

In the limit of a deep trap we can apply the moments expansion method, which leads to the results $U(0)\rightarrow 1$ and $U(l')\rightarrow m_{0,l'}{}^{(1)}/U_0$, in agreement with perturbation theory.

It is interesting to point out that the step-function approximation employed in Sec. X for the estimate of the exciton bandwidth provides also useful semiquantitative information concerning the expansion coefficients. In this approximation we can write

$$F(E)=\Delta^{-1}\ln[\mid\Delta E\mid/(\mid\Delta E\mid+\Delta)], \tag{11.7}$$

so that

$$F'(E_r)=[\mid\Delta E\mid(\mid\Delta E\mid+\Delta)]^{-1} \tag{11.8}$$

and

$$\mid U(0)\mid^2=\mid\Delta E\mid(\mid\Delta E\mid+\Delta)/U_0{}^2.$$

For the case of C_8H_{10} impurity in C_8D_{10}, $U_0=-115$ cm^{-1} and $\Delta E=-44$ sm^{-1}[20]; using $\Delta=190$ cm^{-1}, we calculate $\mid U(0)\mid^2=0.89$, in excellent agreement with the experimental value[30] $\mid U(0)\mid^2=0.9$ obtained from the emission spectrum of the mixed crystal. For the C_8H_{10} impurity in β-$C_{10}H_4D_4$, $U_0=-78$ cm^{-1}[19,39] and $\Delta E=19$ cm^{-1},[20] leading to $\mid U(0)\mid^2=0.61$, which is consistent with the experimental value[30] of $\mid U(0)\mid^2=0.5$. Similar data for the mixed benzene crystals will be of considerable interest, as they will provide complementary information concerning the exciton bandwidth in crystalline benzene.

XII. OPTICAL PROPERTIES

The theoretical study of mixed molecular crystals originated in Rashba's work on the polarization ratio for shallow traps. Craig and Philpott[38–40] and Ross[36] calculated the transition moments for optical excitation using the expansion coefficients for the impurity states. In order to consider both localized and virtual impurity states on the same footing, it is useful to treat the optical properties of dilute mixed crystals by considering the susceptibility tensor $\|S_{\lambda\nu}\|$ induced by the electromagnetic-field perturbation, which can be displayed in the form[53–55]

$$S_{\lambda\nu}(E)=\langle\psi_0\mid\mu_\lambda \mathrm{G}(E-i\epsilon^+)\mu_\nu\mid\psi_0\rangle, \tag{12.1}$$

where ψ_0 is the ground-state wavefunction and μ_λ ($\lambda=1$, 2, 3) corresponds to the components of the electric dipole operator $\boldsymbol{\mu}$. The dipole strength per unit energy[38]

$$d(E)=\sum_\kappa\mid\langle\psi_0\mid\boldsymbol{\mu}\mid\psi_\kappa\rangle\mid^2\delta(E-E_\kappa) \tag{12.2}$$

will be given by

$$d(E)=\pi^{-1}\,\mathrm{Im}\sum_\lambda S_{\lambda\lambda}(E)=\pi^{-1}\,\mathrm{Im\,Tr}\mathbf{S}. \tag{12.3}$$

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Considering a single exciton band and making use of the localized representation, we write

$$d(E)=\pi^{-1}\,\mathrm{Im}\sum_n\sum_m\sum_\alpha\sum_\beta \boldsymbol{\mu}_\alpha \times\langle a_{n\alpha}{}^f\,|\,\hat{G}(E-i\epsilon^+)\,|\,a_{m\beta}{}^f\rangle\boldsymbol{\mu}_\beta. \quad (12.4)$$

The one-molecule transition moments are

$$\boldsymbol{\mu}\alpha=\langle\psi_0\,|\,\boldsymbol{\mu}\,|\,a_{n\alpha}{}^f\rangle \quad\text{and}\quad \mu_\beta=\langle\psi_0\,|\,\boldsymbol{\mu}\,|\,a_{m\beta}{}^f\rangle.$$

Considering a crystal with an impurity molecule at the site 0γ, the Green's function is obtained from Eq. (4.3) in the form

$$G_{n\alpha,m\beta}(E)=G^0{}_{n\alpha,m\beta}(E) +[U_0G^0{}_{n\alpha,0\gamma}(E)G^0{}_{0\gamma,m\beta}(E)]/[1-U_0G^0{}_{0\gamma,0\gamma}(E)]. \quad (12.5)$$

We thus get

$$d(E)=d^0(E)+\pi^{-1}\,\mathrm{Im}\sum_n\sum_m\sum_\alpha\sum_\beta \boldsymbol{\mu}_\alpha \times\{U_0/[1-U_0G_0(E-i\epsilon^+)]\}G^0{}_{n\alpha,0\gamma}(E-i\epsilon^+) \times G^0{}_{0\gamma,m\beta}(E-i\epsilon^+)\,\boldsymbol{\mu}_\beta, \quad (12.6)$$

where the dipole strength for the pure crystal is just

$$d^0(E)=\pi^{-1}\,\mathrm{Im}\sum_n\sum_m\sum_\alpha\sum_\beta \boldsymbol{\mu}_\alpha G^0{}_{n\alpha,m\beta}(E-i\epsilon^+)\,\boldsymbol{\mu}_\beta. \quad (12.7)$$

Making use of the general relation (3.13) which leads to the sum rules

$$\sum_n g^0{}_{n\alpha,m\beta}(E)=\sum_j B_{\alpha j}(0)B_{\beta j}(0)\delta[E-E_j(0)] \quad (12.8)$$

and

$$\sum_n F_{n\alpha,m\beta}(E)=\sum_j B_{\alpha j}(0)B_{\beta j}(0)/[E-E_j(0)], \quad (12.9)$$

we immediately obtain the well-known result

$$d^0(E)=N\sum_j \mathbf{M}(j)\cdot\mathbf{M}(j)\delta[E-E_j(0)], \quad (12.10)$$

where the transition moments for the pure crystal (for each exciton branch) are

$$\mathbf{M}(j)=\sum_\alpha \boldsymbol{\mu}_\alpha B_{\alpha j}(0). \quad (12.11)$$

Turning our attention to Eq. (12.6), we can make use of Eqs. (12.8) and (12.9) so that the second term in (12.6) can be represented as a product of a line-shape function $L(E)$ and a term $T(E)$ determined by the transition moments and the $\mathbf{k}=0$ energy levels of the unperturbed crystal,

$$d(E)=d^0(E)+L(E)T(E), \quad (12.12)$$

where

$$T(E)=\sum_j \mathbf{M}(j)/[E-E_j(0)] \times\sum_{j'}\mathbf{M}(j')/[E-E_{j'}(0)] \quad (12.13)$$

and

$$L(E)=\frac{g_0(E)U_0{}^2}{[1-U_0F(E)]^2+\pi^2U_0{}^2g_0(E)^2}. \quad (12.14)$$

Making use of the simple power expansion (6.7), we get the line function in the form of an asymmetric Lorentzian:

$$L(E)=\frac{g_0(E_r)-(E-E_r)g_0'(E_r)}{(E-E_r)^2[F'(E_r)]^2U_0{}^2+[\pi g_0(E_r)U_0]^2}. \quad (12.15)$$

Using the definition (6.9) we get

$$L(E)=\frac{|\,\Gamma_0(E)\,|}{|\,F'(E_r)\,|\,[(E-E_r)^2+\Gamma_0(E)^2]}. \quad (12.16)$$

For the case of a localized impurity state the line-shape function outside the band reduces to a delta function, and one obtains in that region

$$d(E)=[T(E)/\,|\,F'(E_r)\,|\,]\delta(E-E_r). \quad (12.17)$$

This leads immediately to the Rasba result[34,35] for the anomalous polarization ratio $P(i/j)$:

$$[P(i/j)]_{\text{guest}} =[P(i/j)]_{\text{host}}\{[E_r-E_j(0)]/[E_r-E_i(0)]\}^2. \quad (12.18)$$

The absolute intensity of the intense components of the adsorption band will be determined by $\{F'(E_r)[E_r-E_1(0)]^2\}^{-1}$, where $E_1(0)$ is the energy of the $\mathbf{k}=0$ component of the pure crystal which is closest-lying to the band edge $E_c{}^0$. From the general relation (7.15) for the three-dimensional case, $F'(E_r)\propto|\,E_r-E_c{}^0\,|^{-1/2}$, so that the absolute intensity is proportional to $(E_r-E_c{}^0)^{1/2}[E_r-E_1(0)]^{-2}$. If the $\mathbf{k}=0$ state is located at the bottom of the band, which is the case for the first singlet exciton bands of naphthalene and of benzene, the band intensity for impurity states localized below the band ($U_0<0$) are expected to diverge as $[E_r-E_1(0)]^{-3/2}$ when E_r approaches the band edge. On the other hand, when $E_1(0)\neq E_c{}^0$, the intensity will decrease when $E_r\rightarrow E_c{}^0$.

What further information concerning the exciton band structure can be obtained from the optical data? From the experimental point of view we notice that the Davydov components at $\mathbf{k}=0$ are narrow (relative to the bandwidth) at low temperatures. Hence the background absorption induced by the impurity can be in principle detected experimentally. From the theoretical point of view, comparing our result for the line-shape function with the data of Goodings and Moser,[11] we notice that $L(E)$ is determined by the diagonal matrix element of the perturbed density-of-states function.

In the case of a relative strong $|\,U_0\,|$ when a localized state is formed, the line-shape function will also have a nonvanishing contribution in the region of the unperturbed exciton band. For a simple density-of-states

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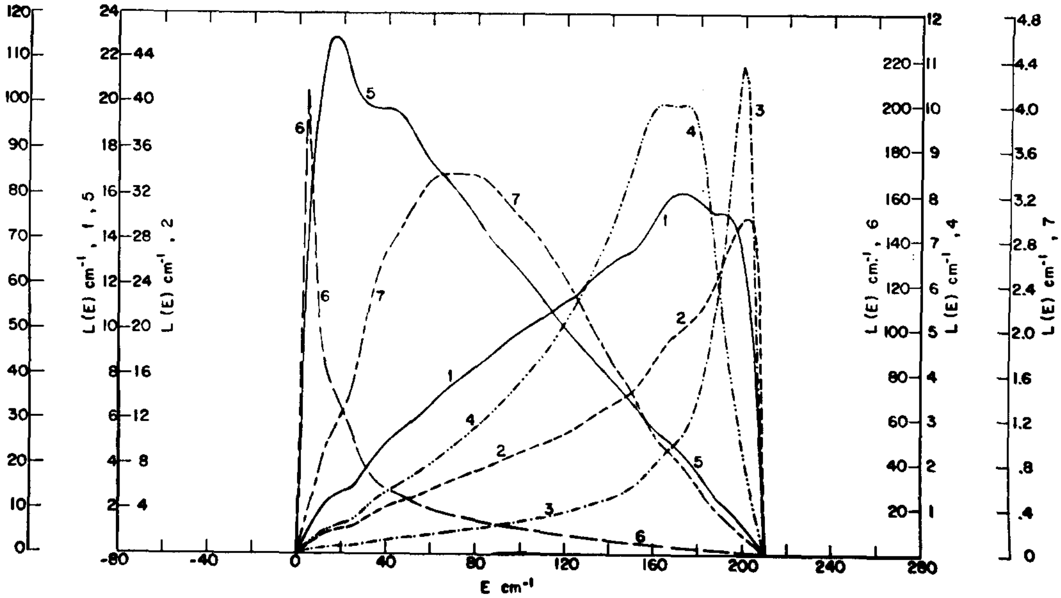

FIG. 5. The line-shape function calculated from the band structure displayed in Figure 1. Curve 1: $U_0 = +120$ cm^{-1}. Curve 2: $U_0 = +90$ cm^{-1}. Curve 3: $U_0 = +60$ cm^{-1}. Curve 4: $U_0 = +30$ cm^{-1}. Curve 5: $U_0 = -120$ cm^{-1}. Curve 6: $U_0 = -70$ cm^{-1}. Curve 7: $U_0 = -20$ cm^{-1}. From the analysis of Fig. 3, we notice that Curves 1, 2, and 5 correspond to bound states, and yield a large contribution to $L(E)$ throughout the whole region of the exciton band. Curves 3 and 6 correspond to virtual state, leading to an appreciable contribution to $L(E)$ only near the band edges. Curve 4 and 7 correspond to extremely small perturbation, which leads to $L(E)$ functions which are quite close to the shape of $g_0(E)$.

function, as that displayed in Fig. 1, this contribution will be characterized by a continuous background with a broad Lorentzian superimposed on it at the energy E_{ar}, corresponding to the antiresonance in the density of states, as demonstrated in Sec. IV. The Lorentzian will be located in this case near the center of the band, and will be appreciably attenuated, due to a large $\Gamma_0(E)$ factor in the region where the density of states is high.

In the case of an extremely weak perturbation, so that $|U_0| < |U_c|$, the line-shape function will be a monotonous function of the energy throughout the whole range of the unperturbed band, being roughly proportional to the density of states. As the absolute intensity depends on the factor $1/[E-E_j(0)]^2$, it is expected that the impurity absorption will be manifested in broadening of the wings of the Davydov components accompanied by a strongly polarized background absorption. In this case and in the case of bound impurity states, a careful experimental study (using photoelectric detection methods) of the line shape of the Davydov components and of the background absorption will be a difficult but interesting task.

Finally, we consider the case of a virtual state lying close to the band edge within the band. The line shape will again be a Lorentzian superimposed on a continuous background. However, in this case, the line will be fairly narrow as the attenuation is minimum near the band edge. The intensity will be high in one polarization direction because of the contribution of the energy denominator $[E-E_j(0)]^{-2}$. Such state is definitely amenable to experimental observation. In Figs. 5 and 6, we have displayed the expected behavior of the line-shape function and the absorption coefficient based on the simple band model also employed in Fig. 1. We have chosen the positions of the Davydov components to be located at the bottom of the band and 150 cm^{-1} above it. These results demonstrate the applicability of the impurity-induced electronic-absorption method to monitor the exciton band structure.

XIII. DISCUSSION

The present paper considers the problem of dilute isotopically mixed molecular crystals from a unified point of view using the one-particle Green's-function method. The basic relations used are based on the connection between the density of states of the perturbed and the pure crystal, and the general dispersion relation connecting the real and the imaginary parts of the one-particle Green's function. This unified approach previously used for phonon states, electron traps, magnetic impurities, and spin waves can be also applied for the study of Frenkel exciton states in the weak vibronic coupling limit.

The general structure of the equations determining the energy levels and optical properties of dilute mixed molecular crystals implies how these properties are re-

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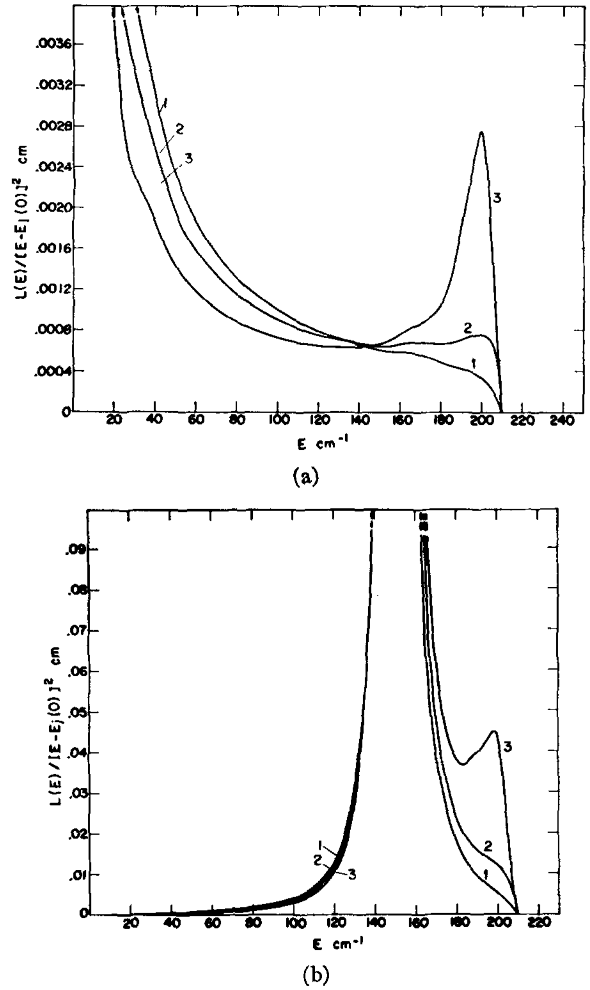
lated to the density of states in the exciton band in the pure crystal. In future papers we shall demonstrate how theoretical and empirical information about the density of states in singlet and triplet exciton bands of crystals of organic molecules and of polymers can be utilized for the understanding of the electronic states of mixed crystals and of energy trapping effects in these systems. Contrary to what was often stated before,[56] the diagonal and off-diagonal matrix elements of the Green's function can be calculated for real systems, so that the general relations obtained herein are of current physical interest.



(a)

(b)

FIG. 6. Impurity-induced electronic absorption in molecular crystals. The unperturbed exciton density of states is taken from Fig. 1. Two Davydov components in the pure crystal are assumed to be located at $E_1(0)=0$ cm^{-1} and $E_2(0)=150$ cm^{-1}. The exciton bandwidth is $\Delta=210$ cm^{-1}. Curve 1: $U_0=+120$ cm^{-1}. Curve 2: $U_0=+90$ cm^{-1}. Curve 3: $U_0=+60$ cm^{-1}. (a) The absorption function $L(E)/[E-E_1(0)]^2$ for one polarization direction. (b) The absorption function $L(E)/[E-E_2(0)]^2$ for the second polarization direction. Note that in the case of localized states (Curves 1 and 2) continuous absorption is induced throughout the whole exciton-band region. For the case of a virtual state (Curve 3) a resonance is observed near the band edge.

What are the experimental implications of the present treatment? In the case of deep traps, the energy shifts can be treated by perturbation theory and will lead to complementary information concerning the intermolecular interactions,[25] similar information will be obtained from the study of impurity pairs in the deep-trap limit. When the perturbation strength is of the order of the exciton bandwidth, the energy shifts provide a useful information concerning the exciton bandwidth. Finally, for even weaker perturbation, virtual states can be optically observed. Experimental studies of impurity-induced electronic absorption, similar to current work on far-infrared induced absorption,[3-5] in the range of the exciton band will be of considerable interest. The information obtained from hot-bands spectroscopy[41,42] is fraught with difficulties, as these experiments have to be performed at relatively high temperatures (100°K) when phonon broadening is appreciable. On the other hand, the impurity-induced electronic-absorption method is free from these difficulties.

In the present work we have assumed that the exciton band structure is unaffected in the dilute mixed crystal. This approximation is justified in view of Lifschitz' optical model,[9] which shows that the energy shift is expected to be $\Delta E_b=CU_0U_-/(U_-+U_0)$, $(U_0<0)$, where C is the impurity concentration. For a typical case like naphthalene we set $U_-=-50$ cm^{-1}; then for $C=0.05$ and $U_-=-115$ cm^{-1} the energy shift is $\Delta E_b \approx 1.5$ cm^{-1}. In this context it is worthwhile to point out that the correction to the density of states is expected to be singular near any Van Hove critical point in the band. The correction of the order of C contains both the derivatives of g_0 and of F which diverge at these points [see Eq. (6.6)]. A way out of this difficulty is to apply the Lifschitz method,[9] expanding the integral number of states in a power series in C. Such a treatment leads to a general power expansion of the density of states in terms of the impurity concentration, consisting of divergent terms, which, however, can be summed up at the critical points, leading to a uniform shift of the order of ΔE_b in the density of states.

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[56] R. G. Body and I. G. Ross, Australian J. Chem. 19, 1 (1966).

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