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Triplet States in Mixed Molecular Crystals

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Triplet exciton density of states functions were calculated for crystalline naphthalene and benzene, and the off-diagonal matrix elements of the Green's function were obtained for crystalline naphthalene, using theoretical intermolecular electron-exchange terms. These results were then applied for the study of triplet states in doped molecular crystals, using the one-particle Green's function method. The localized impurity, the impurity pair, and the general impurity problem were considered. The experimental implications of these results concerning the absorption and emission spectra and energy-trapping effects in dilute mixed crystals were considered.

I. INTRODUCTION

The study of triplet states of molecular crystals has been intensively pursued in recent years. The subject naturally divides into two parts: (a) exciton spectroscopy, (b) exciton dynamics. Experimental spectroscopic studies have established the magnitude of the Davydov splitting in the lowest triplet state of crystalline anthracene and naphthalene, which monitor the intermolecular interactions between translationally inequivalent molecules.[1] Zeeman splitting of exciton states determine the sign of these interactions.[2] Studies of triplet exciton dynamics in crystalline anthracene established the isotropy of the diffusion tensor in the *ab* plane of the monoclinic crystal, leading to an estimate of the absolute value of the interaction term between translationally equivalent molecules.[3–6] Theoretical studies[7] of the intermolecular interactions in the lowest triplet state of molecular crystals of aromatic molecules considered the following effects:

(a) Intermolecular electron exchange interactions considered within the framework of the tight-binding approximation lead to a dominating contribution to the exciton band structure, the short-range intermolecular electron terms are of the order of 1–10 cm^{-1}.

(b) The effects of orthogonality corrections between π orbitals centered on different molecules do not exceed 50% of the electron-exchange terms.

(c) The effect of configuration interaction between Davydov neutral exciton states is negligible.

(d) The contribution of configuration mixing with charge-transfer exciton states may enhance the intermolecular interactions by about 50%.

The experimental results[1] for crystalline naphthalene are in excellent agreement with the theoretical results[4,7] in the tight-binding limit calculated using the weak-coupling vibronic scheme. The estimate of the interaction term for translationally equivalent molecules in this system is also consistent with the experimental results of Hanson and Robinson.[1] However, several serious discrepancies between theory and experiment are encountered:

(a) The experiment triplet-exciton diffusion tensor in anthracene is isotropic so that the diffusion coefficients in the *ab* plane and in the *c* direction seems to be about equal.[4–6] Theoretical calculations[4] indicate that the diffusion coefficient in the *ab* plane should be about 2 orders of magnitude higher than in the *c* direction. It is still an open question whether in crystalline anthracene and naphthalene the triplet exciton band structure is dominated by two- (the *ab* plane) or by three-dimensional interactions.

(b) Emission spectra of isotopically substituted benzene crystals[8] led to an estimate of the intermolecular electron-exchange interactions in this system which are appreciably higher than those calculated for this system[9] using the same theoretical methods as for naphthalene and anthracene.

(c) Studies of Zeeman splitting in the first-excited triplet state of naphthalene and of anthracene[2] revealed the surprising feature[2] that, while the intermolecular interactions in the 0–0 band are roughly equal in their absolute values they do differ in their sign, so that the Davydov splittings in the lowest vibronic component of the first triplet state are $-12\ \text{cm}^{-1}$ for naphthalene and $+20\ \text{cm}^{-1}$ for anthracene (the splittings are defined as $E(\perp b)-E(\|b)$. Theoretical calculations[4,7] predict that the intermolecular interactions should be almost equal and the order of energy levels should be identical in these two systems.

Additional complementary information on the intermolecular interactions can be obtained from alternative

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sources which deal with the entire exciton band structure and divert from the classical spectroscopic method based on the determination of the $\mathbf{k}=0$ Davydov components. In this context the optical properties of dilute mixed crystals of isotopically substituted molecules can be related to the exciton density of states in the pure crystal.[10,11] This treatment, based on the one-particle Green's function rests on the implicit assumption that the perturbation induced by isotopic substitution is local. With the availability of theoretical data based on the intermolecular electron-exchange interactions the triplet energy levels of infinitely dilute mixed crystals are now amenable to a theoretical study. Further information concerning the intermolecular interactions can be obtained from the triplet spectra of impurity pairs. Finally, the general impurity problem is of interest in relation to triplet-energy trapping in molecular crystals. In the present work, we present the results of a theoretical study of triplet-energy states in dilute mixed molecular crystals of benzene and of naphthalene.

A unique feature of triplet exciton states is that the bandwidth is extremely narrow. In this context it should be pointed out that the experimental technique based on hot-band spectroscopy[12,13] which proved to be extremely useful in the case of the lowest singlet exciton states of benzene and naphthalene may be of limited utility in monitoring the triplet-exciton band structure. This method utilizes the transition from a vibrational exciton state of the ground state to the exciton band. When the intermolecular interactions are dominated by short-range interactions, the diagonal matrix elements of the crystal energy matrix are approximately equal. This situation of accidental degeneracy leads to the conclusion that the transition moments are approximately equal so that the hot absorption band is proportional to the joint density of state function[14]

$$\sum_{\mathbf{k}}\sum_{j}\delta\{E-[E_j{}^T(\mathbf{k})-E_j{}^V(\mathbf{k})]\},$$

where T and V correspond to the triplet and vibrational energies and j represents the branch of the electronic or the vibrational exciton band so that $E_j{}^T(\mathbf{k})$ and $E_j{}^V(\mathbf{k})$ correspond to the energy dispersion curves in the triplet-exciton band and in the vibrational exciton band, respectively. In the case of singlet exciton states the electronic exciton band width appreciably exceeds the vibrational exciton bandwidth, so that the joint density of states faithfully represents the electronic exciton density of states. In the case of triplet exciton states, the electronic exciton and the ground states vibrational exciton bandwidths are of the same order of magnitude, so that the joint density of states cannot be related in a simple manner to the triplet-exciton band structure. However, the joint density of states will still reflect the critical points in the triplet-exciton density of states.

We hope that the theoretical treatment of the triplet-exciton band structure and of the triplet electronic states in mixed crystals presented herein will stimulate further experimental work concerning the nature of the intermolecular interaction, band structure, and low-temperature triplet-exciton dynamics in molecular crystals.

II. THE GENERAL IMPURITY PROBLEM

A serious difficulty involved in the theoretical treatment of dilute mixed crystals involves the complicated form of the resulting equations for the impurity levels. The simplest case is that of a local perturbation whereupon a single impurity level results which is related to the exciton density of states in the pure crystal via the real part of the diagonal matrix element of the pure-crystal Green's function. Many systems of physical interest provide additional complications as the perturbation is no longer local. The general solution to the problem was in fact provided by the work of Koster and Slater.[15] However, since then, this solution was rederived several times using various techniques such as integral equations theory,[16] second quantization formalism,[17] and the original Koster–Slater approach.[18,19] It will be useful at this stage to present the general equations for the single-impurity case in the tight-binding Frenkel limit using the Green's function method[11] in the form previously applied by us for this problem.[10] The merits of this formulation are twofold: In the first place, the resulting equations are physically transparent and clearly bring up the physical features of the general perturbation problem; furthermore, the resulting equations can be easily handled using matrix methods.

The crystal Hamiltonian containing a single impurity at the site p (the site index refers to both the unit cell and the number of the molecule in this unit cell) is

$$\mathcal{H}=H_p+\sum_i H_i{}^0+\sum_{i>j,(i,j\neq p)} v_{ij}{}^0+\sum_{i\neq p} v_{ip}, \tag{1}$$

or alternatively

$$\mathcal{H}=\mathsf{H}_0+\mathsf{V}. \tag{1a}$$

Where H_p and $H_i{}^0$ refer to the guest and host single molecule Hamiltonian, $v_{ij}{}^0$ are the Coulomb interaction terms between the host molecules i and j, while v_{ip} corresponds to the guest host pair interaction term. H_0 is the Hamiltonian of the pure crystal while V represents the perturbation introduced by the impurity. The mixed-crystal wavefunctions will be displayed in the

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localized excitation representation[10]

$$\Psi=\sum_{l} U(l)\, a_l^f, \tag{2}$$

where a_l^f corresponds to a localized excitation on the site l (including the impurity site) which can be represented as antisymmetrized products of the eigenfunctions φ_i^0 and φ_i^f of H_i^0 and the eigenfunctions ψ_p^0 and ψ_p^f of H_p. The superscripts 0 and f refer to the ground and the excited electronic states, respectively.

Hence we write

$$a_p^f=\mathcal{A}\psi_p^f \prod_{i\neq p} \varphi_i^0 \tag{3}$$

and

$$a_j^f=\mathcal{A}\psi_p^0\varphi_j^f \prod_{j\neq p,\, i\neq j} \varphi_i^0. \tag{3'}$$

The impurity levels are obtained from the general equation

$$\det|\mathbf{1}-\mathsf{G}^0(E)\mathsf{V}|=0, \tag{4}$$

where

$$\mathsf{G}^0(E)=1/(E-\mathsf{H}_0) \tag{5}$$

is the pure-crystal Green's function and V corresponds to the perturbation matrix, both operators are displayed in the localized representation.

The matrix elements of the Green's function are

$$G_{ij}^0(E)=\langle a_i^f \,|\, 1/(E-\mathsf{H}_0) \,|\, a_j^f\rangle \tag{6}$$

and can be represented in the form

$$G_{ij}^0(E)=N^{-1}\sum_{\mathbf{k}}\sum_{\mu}\frac{B_{i\mu}^f(\mathbf{k})B_{j\mu}^f(\mathbf{k})\exp[i\mathbf{k}(\mathbf{R}_i-\mathbf{R}_j)]}{E-E_\mu(\mathbf{k})}, \tag{7}$$

where $E_\mu(\mathbf{k})$ is the dispersion relation for the μth exciton branch ($\mu=1\cdots\sigma$), $\mathbf{k}$ is the exciton wavevector and $B_{i\mu}^f(\mathbf{k})=B_{\alpha\mu}^f(\mathbf{k})$ (where the double i index corresponds to $i\equiv n\alpha$) are the elements of the unitary transformation matrix relating the one-site exciton states to the crystal states in the pure crystal. The Green's function can be expressed in the integral form

$$G_{ij}^0(E-i\epsilon^+)=F_{ij}(E)+i\pi g_{ij}^0(E), \tag{8}$$

where

$$F_{ij}(E)=p\int\frac{g_{ij}^0(E')\,dE'}{E-E'}, \tag{8'}$$

while $g_{ij}^0(E')$ is the weighted density of exciton states matrix. In a crystal characterized by a center of symmetry the diagonal matrix elements correspond to the exciton density of states $g_0(E)=g_{ii}^0(E)$, for all i.

Turning our attention to the perturbation Hamiltonian, we have now to relate the matrix elements of the pure-crystal and the mixed-crystal Hamiltonian. These matrix elements were worked out by Philpott and Craig[19] and are given in the form:

$$\mathfrak{H}_{ij}=\langle a_i^f \,|\, \mathfrak{H} \,|\, a_j^f\rangle=(H_0)_{ij}+\delta_{ij}\delta_{ip}U_0+\delta_{ij}(1-\delta_{ip})d_{pi}$$
$$+(1-\delta_{ij})\delta_{ip}m_{pj}+(1-\delta_{ij})\delta_{jp}m_{pi}, \tag{9}$$

where

$$U_0=\Delta\epsilon_p^f-\Delta\epsilon^f+D_p^f-D^f \tag{9'}$$

corresponds to the change in the molecular excitation energy between the host and the guest. $\Delta\epsilon_p^f$ and $\Delta\epsilon^f$ are the gas-phase excitation energies, while

$$D_p^f=\sum_{i\neq p}\langle|\varphi_i^0|^2 \,|\, v_{ip} \,|\, |\psi_p^f|^2-|\psi_p^0|^2\rangle \tag{10}$$

$$D^f=\sum_{i\neq j}\langle|\varphi_i^0|^2 \,|\, v_{ip}^0 \,|\, |\varphi_j^f|^2-|\varphi_j^0|^2\rangle \tag{10'}$$

correspond to the environmental D terms of the guest molecule in the mixed crystal and of a host molecule in the pure crystal, respectively. We may comment in passing that the expressions displayed in Eqs. (10) and (10′) should be extended to include second-order interactions which give rise to dispersion forces. The matrix elements d_{pi} represent corrections to environmental shifts of the host molecules due to the presence of the guest:

$$d_{pi}=\langle|\psi_p^0|^2 \,|\, v_{pi} \,|\, |\varphi_i^f|^2-|\varphi_i^0|^2\rangle$$
$$-\langle|\varphi_p^0|^2 \,|\, v_{pi}^0 \,|\, |\varphi_i^f|^2-|\varphi_i^0|^2\rangle. \tag{11}$$

Finally, the matrix elements m_{pj} correspond to the change in the intermolecular coupling terms due to the presence of the impurity

$$m_{pj}=\langle\mathcal{A}\psi_p^f\varphi_j^0 \,|\, v_{pj} \,|\, \psi_p^0\varphi_j^f\rangle-\langle\mathcal{A}\varphi_p^f\varphi_j^0 \,|\, v_{pj}^0 \,|\, \varphi_p^0\varphi_j^f\rangle, \tag{12}$$

which correspond to the difference between an off-resonance and a resonance energy-transfer term.

The matrix elements of the perturbation operator V can be displayed in the localized representation in the form

$$\mathsf{V}_{pp}=U_0,$$
$$\mathsf{V}_{pj}=m_{pj};\qquad \mathsf{V}_{ip}=m_{pi},$$
$$\mathsf{V}_{ii}=d_{pi},\qquad i\neq p. \tag{13}$$

The matrix V can be conveniently displayed as a sum of three contributions

$$\mathsf{V}=U_0+\mathsf{m}+\mathsf{d}, \tag{14}$$

where

$$\mathsf{U}_0=\begin{pmatrix} U_0 & 0 & 0 & \cdots \\ 0 & & & \\ 0 & & \bigcirc & \\ 0 & & & \\ \vdots & & & \end{pmatrix} \tag{14a}$$

$$\mathsf{m}=\begin{pmatrix} 0 & m_{01} & m_{02} & \cdots & m_{0i} \\ m_{10} & & & & \\ m_{20} & & \bigcirc & & \\ \vdots & & & & \\ m_{i0} & & & & \end{pmatrix}, \tag{14b}$$

and

$$\mathbf{d}=\begin{pmatrix} 0 & & & & \\ & d_{01} & & \bigcirc & \\ & & d_{02} & & \\ & \bigcirc & & \ddots & \\ & & & & d_{0i} \end{pmatrix}. \qquad (14c)$$

The matrix (14a) corresponds to the local perturbation on the impurity site, (14b) represents the change in the intermolecular coupling terms, while the diagonal matrix (14c) involves the changes in the effective excitation energies of the host molecules induced by the impurity. Now the simplest case is encountered when $\mathbf{m}=\mathbf{d}=0$ and the impurity level is obtained from the relation

$$1-U_0F(E)=0, \qquad (15)$$

where $F(E)=F_{00}(E)$, Eq. (8′) being expressed in terms of the density of exciton states. A further complication is introduced when it is assumed that only $\mathbf{d}=0$ whereupon the energy levels of the mixed crystal are obtained from

$$\det\left|\mathbf{1}-\mathbf{G}^0(E)(\mathbf{U}_0+\mathbf{m})\right|=0. \qquad (16)$$

The order of this determinant is equal to the rank of the matrix $\mathbf{U}_0+\mathbf{m}$. However, in this case Eq. (16) may be reduced by simple manipulations to a 2×2 determinant

$$\begin{vmatrix} 1-\sum_{j\neq p} m_{pj}G_{jp}{}^0(E) & G_{00}{}^0(E) \\ U_0+\sum_{j\neq p}\sum_{j'\neq p} m_{pj}G_{jj'}{}^0(E)m_{j'p} & 1-\sum_{j\neq p} m_{pj}G_{jp}{}^0(E) \end{vmatrix}=0. \qquad (16')$$

This last result was previously derived by Rashba,[16] by Dubovskii and Konobeev,[17] and by Philpott and Craig.[19]

Equation (16) always leads to at least a single (virtual or bound) impurity level. A second bound or virtual level may also appear in this case depending on the magnitude and sign of the m_{pj} terms and on the strength of the local perturbation U_0. This equation was studied by Merrifield[18] and by Body and Ross[20] for the simple case when the m_{pj} terms are proportional to the energy-transfer matrix elements in the pure crystal.

The effect of the diagonal $\mathbf{d}$ matrix on the crystal energy levels is of interest as it brings up some new features of the problem. Consider first the hypothetical case when $\mathbf{m}=0$. The relevant equation is

$$\det\left|\mathbf{1}-\mathbf{G}^0(\mathbf{d}+\mathbf{U}_0)\right|=0. \qquad (17)$$

This determinant is of the order which equals to the rank of the matrix $\mathbf{d}$ plus one. This equation is formally identical with the results for a mixed crystal which contains a number of impurities each characterized by a local perturbation. Let the sites p, p', p'', p''', etc., be occupied by impurity molecules, characterized by the local perturbations U_p, $U_{p'}$, $U_{p''}\cdots$. The perturbation matrix is then

$$\mathbf{V}=\begin{pmatrix} U_p & & & & \\ & U_{p'} & & \bigcirc & \\ & & U_{p''} & & \\ & & & U_{p'''} & \\ & \bigcirc & & & \ddots \end{pmatrix}. \qquad (18)$$

The resulting general energy equation

$$\det\left|\mathbf{1}-\mathbf{G}^0(E)\begin{pmatrix} U_p & & & \\ & U_{p'} & & \\ & & U_{p''} & \\ & & & \ddots \end{pmatrix}\right|=0 \qquad (19)$$

is just equivalent to Eq. (17).

The analysis of impurity pairs previously considered[10,11] can be easily extended to include higher impurity aggregates. The interaction between ν local impurity sites leads at most to ν localized states. A zero-order approximation for any of these levels is given by Eq. (15), e.g., $1-U_pF(E)=0$. However, the proper solutions may involve major corrections to the result of Eq. (15) in view of the contribution of the off-diagonal matrix elements of the Green's function.

Turning back our attention now to Eq. (17) we realize that the single impurity problem which involves both a local perturbation and the change in the d terms will lead, in addition to the single localized state, to an additional manifold of bound or virtual levels (depending on the strength and the signs of the U_0 and of the d_{pj} terms).

The general structure of the equations derived herein clearly reveals that in order to obtain any quantitative information on the energy levels of mixed molecular crystals the diagonal and off-diagonal matrix elements of the Green's function have to be evaluated. These, in turn, are expressed in terms of the matrix elements of the weighted density-of-states function. We shall now demonstrate how these matrix elements can be evaluated for a real system provided that the intermolecular

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interactions are dominated by short-range terms. In this context triplet exciton states are of considerable interest and we shall now proceed to the calculation of the band structure and the off-diagonal elements of the Green's function for the first triplet-exciton state in some organic crystals of aromatic molecules. These data will then be used for calculation of the energy levels of a single impurity and an impurity pair characterized by a local perturbation. Finally, model calculations will be presented for the general impurity problem setting the matrix elements of **d** and **m** as variable parameters.

III. CALCULATION OF THE DENSITY OF TRIPLET EXCITON STATES IN CRYSTALLINE NAPHTHALENE

The energy levels of the pure crystal are obtained by constructing the one site functions

$$\phi_\alpha{}^f(\mathbf{k})=(1/\sqrt{N})\sum_m a_{m\alpha}{}^f\exp(i\mathbf{k}\mathbf{R}_{m\alpha})$$

and diagonalizing the Hamiltonian H_0 in this representation so that the exciton states are

$$\psi_j{}^f(\mathbf{k})=\sum_\alpha B_{\alpha j}{}^f(\mathbf{k})\phi_\alpha{}^f(\mathbf{k}),\qquad j=1\cdots\sigma. \tag{20}$$

The matrix elements of the Hamiltonian take the form

$$\begin{aligned}\mathfrak{L}_{\alpha\beta}(\mathbf{k})&=\langle\phi_\alpha{}^f(\mathbf{k})\mid\mathcal{H}_0\mid\phi_\beta{}^f(\mathbf{k})\rangle\\&=(\Delta\epsilon^f+D^f)\delta_{\alpha\beta}+L_{\alpha\beta}(\mathbf{k}),\end{aligned}$$

where

$$L_{\alpha\beta}(\mathbf{k})=\sum_m I_{n\alpha,m\beta}{}^f\exp[i\mathbf{k}(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})]. \tag{21}$$

In the case of triplet states, the energy transfer matrix elements $I_{n\alpha,m\beta}{}^f$ are given in terms of the intermolecular electron-exchange interactions:

$$I_{n\alpha m\beta}{}^f=K_{n\alpha m\beta}{}^f=\langle(A-1)a_{n\alpha}{}^f a_{m\beta}{}^0\mid V_{n\alpha m\beta}\mid a_{n\alpha}{}^0 a_{m\beta}{}^f\rangle. \tag{22}$$

In Table I we display the electron-exchange terms previously calculated for crystalline naphthalene and anthracene.[7] We have also included in this table the orthogonality corrections arising from π–π intermolecular overlap calculated using the Löwdin symmetric orthogonalization method. The computational procedures were previously described.[7] Our more detailed calculations of these terms presented herein lead to slightly higher overlap corrections than previously reported.[7] We should note the relatively large overlap correction term for the $K_0\frac{1}{2}(a+b)$ interaction in anthracene, while for the case of naphthalene the correction term is small. This may indicate that also the contribution of three and four-center electron-exchange terms, and orthogonality corrections arising from σ–π intermolecular interactions should be more important for the case of anthracene. This may be a reason for the discrepancy between experiment[2] and theory[7] concerning the sign of the $K_0\frac{1}{2}(a+b)$ term in anthracene.

TABLE I. Intermolecular electron-exchange interactions (K) for naphthalene, anthracene, and benzene, and orthogonality corrections (O) for naphthalene and anthracene.

System	Location of molecule	K 10^4 (eV)	O 10^4 (eV)
Naphthalene	b	+4.60	−1.55
	$\frac{1}{2}(a+b)$	−7.35	+0.25
	c	+0.034	−0.0027
Anthracene	b	+4.11	−1.89
	$\frac{1}{2}(a+b)$	−6.88	−3.9
	c	−0.018	−0.0005
Benzene	$\frac{1}{2}(b+c)$	+1.07	···
	$\frac{1}{2}(a+c)$	−0.075	···
	$\frac{1}{2}(a+b)$	+0.055	···
	c	−0.055	···
	a	+0.0068	···

The following comments should be made:

(a) The dominating intermolecular coupling terms are due to the translationally equivalent molecules located at 0, b, 0; 0, $-b$, 0 and the translationally inequivalent molecules located at

$$\tfrac{1}{2}(a+b),0;\quad\tfrac{1}{2}(a-b),0;\quad-\tfrac{1}{2}(a+b),0;\quad\tfrac{1}{2}(-a+b),0.$$

The monoclinic crystal structure ($P_{21/a}$) is characterized by the following symmetry elements (e.g., factor-group elements): E, $\{\sigma_{ac}\mid\pm a/2\}$, $\{c_2(b)\mid\pm b/2\}$ and $\{i\mid 0\}$ whereupon the interactions for the four translationally inequivalent molecules are equal, and so are the interactions for the molecules located along the monoclinic axis b. We shall therefore have to consider just the interaction $\epsilon_b=K_{00,0b}$ and $\epsilon_\tau=K_{00,\frac{1}{2}(a+b)}$ where we have set $\tau=\frac{1}{2}(a+b)$.

(b) The translationally equivalent molecules are related by the symmetry element $\{i\mid 0\}$. The presence of an inversion center implies that $E_j{}^f(\mathbf{k})=E_j{}^f(-\mathbf{k})$. Hence, in general, the interactions have to be evaluated over half of the direct lattice and then the band structure has to be evaluated in half of the reduced zone of the reciprocal lattice. In the present case, only the ϵ_b term has to be considered for translationally equivalent interactions so that it is sufficient to consider the region $0\leq\mathbf{k}\cdot\mathbf{a}\leq\pi$ and $0\leq\mathbf{k}\cdot\mathbf{b}\leq\pi$.

(c) In this system, the dominating interactions are those in the ab plane, so that the problem can be treated as a two-dimensional case. The energies are

$$E_j(\mathbf{k})=E_j(k_a,k_b),\qquad j=1,2. \tag{23}$$

We shall set

$$\mathbf{k}=\mathbf{k}_a+\mathbf{k}_b \tag{24}$$

$$\mathbf{k}_a\cdot\mathbf{a}=2\pi\eta_a;\qquad\mathbf{k}_b\cdot\mathbf{b}=2\pi\eta_b. \tag{24'}$$

TABLE II. Critical points in two-dimensional band structure for naphthalene.

Branch	k_x	k_y	E	Nature of critical point	Energy of critical point 10^4 (eV)
1 (+ branch)	0	0	$\epsilon_1+\epsilon_2$	Saddle point	−19.4
	π	π	$-\epsilon_1$	Saddle point	−8.17
	0	2 arccos $(\epsilon_2/4\epsilon_1)$	$-\epsilon_1-(\epsilon_2^2/8\epsilon_1)$	Minimum	−19.8
2 (− branch)	π	π	$-\epsilon_1$	Saddle point	−8.17
	0	0	$\epsilon_1+\vert\epsilon_2\vert$	Maximum	+36.0

Now we shall define

$$k_x=(\mathbf{k}_a+\mathbf{k}_b)\cdot\mathbf{a}=2\pi\eta_a$$

$$k_y=(\mathbf{k}_a+\mathbf{k}_b)\cdot\mathbf{b}=2\pi\eta_b. \qquad (25)$$

(d) For a crystal characterized by an inversion center, the matrix elements $L_{\alpha\beta}(\mathbf{k})$ [Eq. (21)] are real so that for the *nondiagonal* terms $L_{\alpha\beta}(\mathbf{k})=L_{\beta\alpha}(\mathbf{k})$. As far as the diagonal terms are concerned, one has the general relation $L_{\alpha\alpha}(\mathbf{k})=L_{\beta\beta}(\omega\mathbf{k})$, where ω is an element of the group of the wave vector.[21] In a general case when the group of the wave vector contains only the identity operator, the matrix $\mathfrak{L}$ has to be diagonalized, while only for special directions of the $\mathbf{k}$ vector (e.g., perpendicular to or lying in the symmetry plane of the crystal) the diagonal matrix elements are equal. However, in the present case when the intermolecular coupling is dominated by the short-range interactions ϵ_b and ϵ_τ a case of accidental degeneracy is encountered, and the diagonal terms are equal. This is obvious as from Eq. (21) we can write $L_{11}(\mathbf{k})=L_{22}(\mathbf{k})=2\epsilon_b\cos\mathbf{k}\cdot\mathbf{b}$. Hence the energy-dispersion curves for the exciton branches are just

$$E_1^f(\mathbf{k})=L_{\alpha\alpha}(\mathbf{k})+L_{\alpha\beta}(\mathbf{k})$$

$$E_2^f(\mathbf{k})=L_{\alpha\alpha}(\mathbf{k})-L_{\alpha\beta}(\mathbf{k}), \qquad (26)$$

where we have defined an energy scale where the center of gravity of the exciton band is zero, $\Delta\epsilon^f+D^f=0$. The coefficients in the exciton wavefunction are just

$$B_{\alpha1}(\mathbf{k})=B_{\beta1}(\mathbf{k})=B_{\alpha2}(\mathbf{k})=-B_{\beta2}(\mathbf{k})=1/\surd2, \qquad (27)$$

where the indices 1 and 2 refer to the two exciton branches while α and β refer to the two inequivalent molecules per unit cell.

We now proceed to the calculation of the triplet exciton density of states using the parameters $\epsilon_b=4.6\times10^{-4}$ eV and $\epsilon_\tau=-7.35\times10^{-4}$ eV. In view of the relatively larger overlap corrections for anthracene, and because of the discrepancy between theory[7] and experiment[2] concerning the sign of the ϵ_τ term in this system, our calculations were performed for crystalline naphthalene. The exciton energy dispersion curves are explicitly given by

$$E_{1,2}(\mathbf{k})=2\epsilon_b\cos(\mathbf{k}\cdot\mathbf{b})\pm2\epsilon_\tau\cos\mathbf{k}\cdot\tfrac{1}{2}(a+b)$$

$$\pm2\epsilon_\tau\cos\mathbf{k}\cdot\tfrac{1}{2}(-a+b). \qquad (28)$$

Using the definitions (25) these can be displayed in the form

$$E_1(\mathbf{k})=\epsilon_1\cos k_y+\epsilon_2\cos\tfrac{1}{2}(k_x)\cos\tfrac{1}{2}(k_y)$$

$$E_2(\mathbf{k})=\epsilon_1\cos k_y-\epsilon_2\cos\tfrac{1}{2}(k_x)\cos\tfrac{1}{2}(k_y), \qquad (28')$$

where $\epsilon_1=2\epsilon_b$ and $\epsilon_2=4\epsilon_\tau$. The range of k_x and k_y is $-\pi\leq k_x,\ k_y\leq\pi$. However, for our system we can consider only the range $0\leq k_x,\ k_y\leq\pi$.

General information on the band structure can be obtained by considering the Van Hove-type analytical singularities in the density of state function. Such an analysis does provide quite a complete information without extensive numerical computations. It is also worthwhile to remember that the $F(E)$ functions which determines the energy levels of the localized perturbation problem is also characterized by the same singularities as the density of exciton-states function.[10] In the present two dimensional case, the maximum and minimum points in $g_0(E)$ will be characterized by a step-function discontinuity while the saddle points are characterized by a logarithmic singularity. The singular points are encountered when

$$\nabla_k E_j(\mathbf{k})=0 \qquad (29)$$

so that in our case

$$\partial E_j(\mathbf{k})/\partial k_x=\partial E_j(\mathbf{k})/\partial k_y=0.$$

To determine the nature of the critical point we define

$$E_{yx}=E_{xy}=\partial^2E_j(k)/\partial k_x\partial k_y,$$

$$E_{xx}=\partial^2E_j(k)/\partial k_x^2,$$

$$E_{yy}=\partial^2E_j(\mathbf{k})/\partial k_y^2, \qquad (30)$$

and let

$$\det=\begin{vmatrix}E_{xx} & E_{xy}\\ E_{yx} & E_{yy}\end{vmatrix}. \qquad (30')$$

An extremum is observed when det>0 while a saddle point is encountered provided that det<0.

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[21] A. S. Davydov, Usp. Fiz. Nauk. **82**, 393 (1964) [Sov. Phys.—Usp. **82**, 145 (1964)].

It is now a simple matter to determine the location and the nature of the critical points, and these are displayed in Table II for the two exciton branches. It should be noted that the assignment of the critical points is determined by the signs of the interaction terms.

We now proceed to the direct computations of the exciton density of state. The method we apply is based on considering the number of states characterized by energy less than E which is for the two branches[22]

$$N_j(E)=\frac{1}{4\pi^2}\int_E\int dk_x dk_y, \qquad j=1,2. \qquad (31)$$

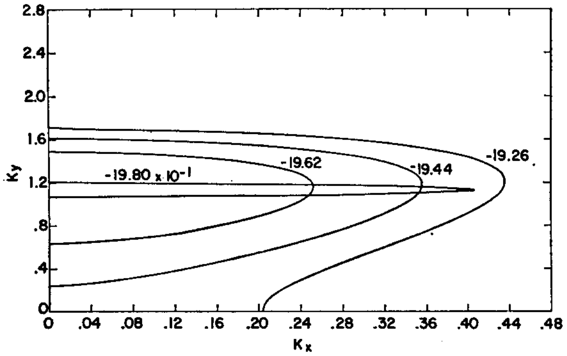

FIG. 1. Constant energy surfaces for the $E_1(\mathbf{k})$ branch of the triplet-exciton band in naphthalene near the bottom of the branch. Energies in 10^{-4} eV. The curve at -19.80×10^{-4} eV has been multiplied by a factor of 10.

The integration extends over all the sets of (k_x, k_y) correspond to a constant energy surface which is less than E. The density of exciton states in the two branches is

$$g_j(E)=\sum_{\mathbf{k}}\delta[E-E_j(\mathbf{k})], \qquad j=1,2 \qquad (32)$$

and can be expressed in the form

$$g_j(E)=\partial N_j/\partial E; \qquad j=1,2. \qquad (33)$$

The total density of states in this band is

$$g_0(E)=\sum_{\mathbf{k}}\sum_{j}|B_{\alpha j}(\mathbf{k})|^2\delta[E-E_j(\mathbf{k})]. \qquad (34)$$

In view of Eq. (27) we get for this simple case

$$g_0(E)=g_1(E)+g_2(E). \qquad (35)$$

We can therefore calculate the total density of states by combining the energy integrals $N_1(E)$ and $N_2(E)$ for the two branches.

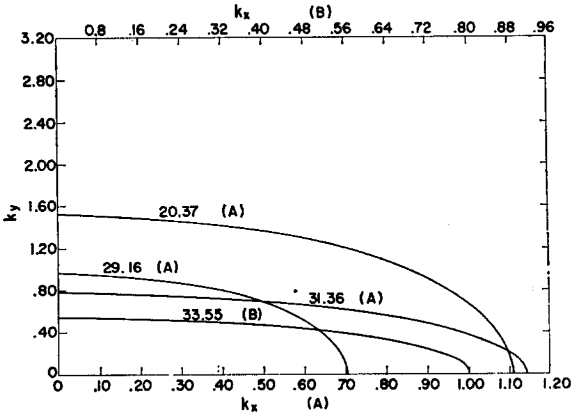

FIG. 2. Constant energy surfaces for the $E_2(\mathbf{k})$ branch of the triplet-exciton band in naphthalene near the top of the branch. Energies in 10^{-4} eV.

Finally, we have to consider the constant energy surfaces. From the dispersion curve $E(k_x, k_y)$ [Eq. (28)] we can obtain the relations $k_x=k_x(E, k_y)$ by simple elimination. Now k_y is varied in the range 0–π for constant E and the corresponding k_x values (in the range 0–π) are computed. A difficulty arises when $k_y=\pi$ which does not give a solution when $E\neq-\epsilon_1$. However, our computations were performed for a small mesh of k_y values (200 points) so that the effect of this mathematical artifact is not noticeable. In Figs. 1 and 2, we present typical constant energy surfaces for the two branches over a small energy range at the bottom of each branch. A general map of constant energy surfaces is displayed in Fig. 3. A schematic representation of typical curves of constant energy is given in Fig. 4. We have to calculate the total number of states in the two branches by evaluating the integrals of the shaded areas in this figure. $g_1(E)$ and $g_2(E)$ are just proportional to the derivations of these areas with respect to the energy. In Fig. 5, we give the total

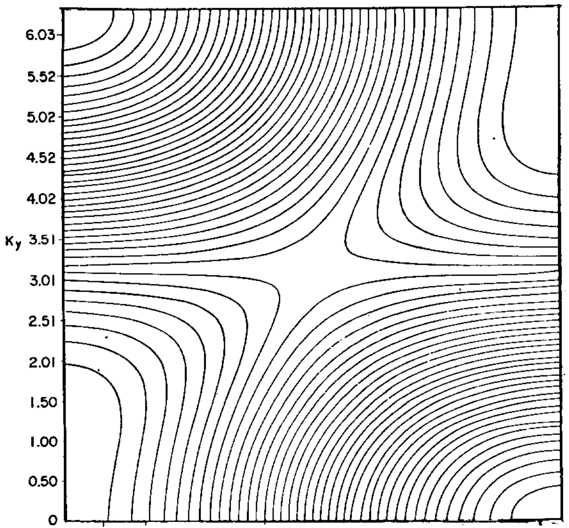

FIG. 3. A general map of constant energy surfaces for the triplet-exciton band in napthalene. The limits of the $\frac{1}{4}$ extended zone are $0\leq k_x\leq 2\pi$ and $0\leq k_y\leq\pi$.

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[22] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Solid State Phys. Suppl. 3, (1963).

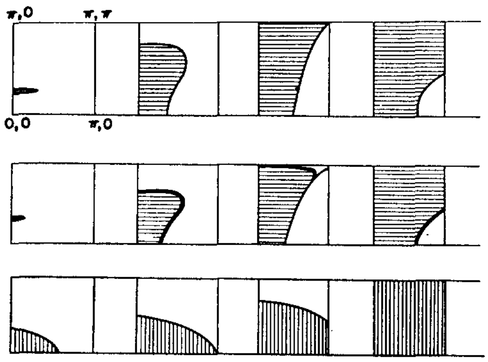

FIG. 4. A schematic representation of constant energy surfaces in the k_xk_y plane for triplet excitons in naphthalene. The four diagrams in the upper line refer to the $E_1(\mathbf{k})$ branch calculated from a two-dimensional model, the diagrams in the middle line correspond to the same branch calculated from a three-dimensional model, while the lower line represents the $\mathbf{E}_2(\mathbf{k})$ branch for a two-dimensional model. To calculate the integral number of states, integration has to be performed over the shaded areas.

number of states $IN=N_1(E)+N_2(E)$ as a function of the energy calculated from 200×200 points in the quarter of the extended Brillouin zone. The resulting density of states obtained from this curve is presented in Fig. 6. The location of the critical points in $g_0(E)$ is consistent with the analysis presented in Table II.

In order to test the adequacy of the two-dimensional model for the density of states, we have performed calculations for a three-dimensional model using the energy-dispersion curve

$$E(k_xk_yk_z)=\epsilon_1\cos k_y+\epsilon_2\cos\tfrac{1}{2}(k_x)\cos\tfrac{1}{2}(k_y)+\epsilon_3\cos k_z, \tag{36}$$

where $2\epsilon_c=\epsilon_3=-0.036\times10^{-4}$ eV.

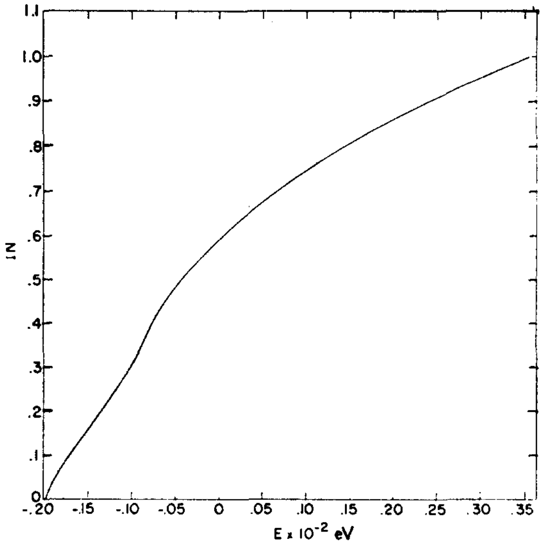

FIG. 5. Total number of states as a function of energy for the triplet-exciton band in naphthalene.

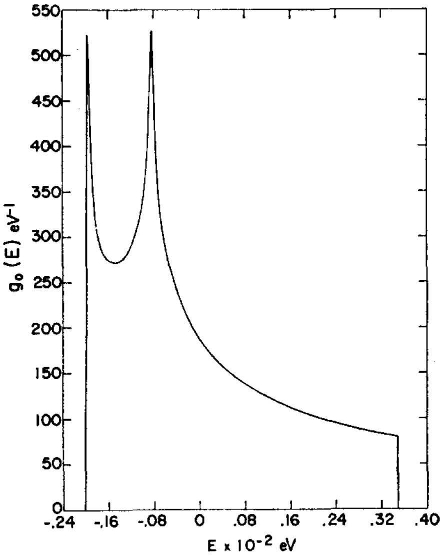

FIG. 6. Density-of-states function for triplet-exciton band in naphthalene calculated from a two-dimensional model.

To count the states up to energy E, a volume integration has been performed over the quarter of the extended zone in the region $0\leq k_x\leq 2\pi$, $0\leq k_y\leq 2\pi$, $0\leq k_z\leq\pi$. Typical schematic curves of constant frequency in the k_xk_y plane (k_z=const) are presented in Fig. 4, these were calculated by setting from Eq. (36) $k_x=k_x(E, k_y, k_z)$. The resulting density of states curve is given in Fig. 7, revealing now the critical points characteristic of a three-dimensional case. However, as the term ϵ_3 is by 2 orders of magnitude smaller than ϵ_1 and ϵ_2, the properties of the pure system and the resulting properties of mixed crystals can be adequately described by the two-dimensional model.

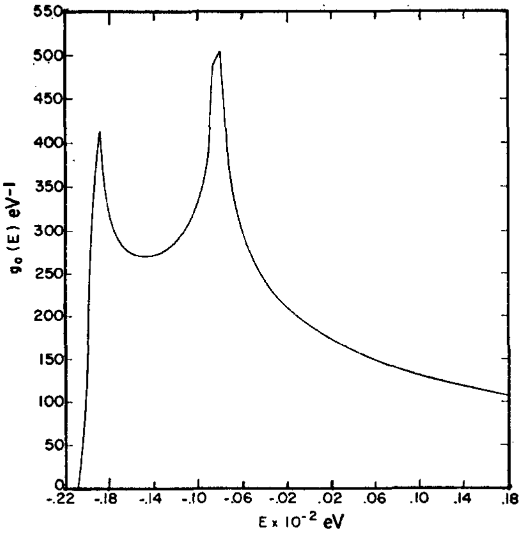

FIG. 7. Density-of-state function for triplet-exciton band in naphthalene calculated from a three-dimensional model.

IV. TRIPLET-EXCITON BAND STRUCTURE IN CRYSTALLINE BENZENE

The benzene crystal is orthorhombic with four molecules per unit cell. The intermolecular electron exchange interactions for the lowest $^3B_{1u}$ exciton state are presented in Table I. The dominant interactions are again short range so that the four exciton branches are

$$\begin{aligned}E_1(\mathbf{k})&=L_{\alpha\alpha}(\mathbf{k})+L_{\alpha\beta}(\mathbf{k})+L_{\alpha\gamma}(\mathbf{k})+L_{\alpha\delta}(\mathbf{k})\\E_2(\mathbf{k})&=L_{\alpha\alpha}(\mathbf{k})+L_{\alpha\beta}(\mathbf{k})-L_{\alpha\gamma}(\mathbf{k})-L_{\alpha\delta}(\mathbf{k})\\E_3(\mathbf{k})&=L_{\alpha\alpha}(\mathbf{k})-L_{\alpha\beta}(\mathbf{k})-L_{\alpha\gamma}(\mathbf{k})+L_{\alpha\delta}(\mathbf{k})\\E_4(\mathbf{k})&=L_{\alpha\alpha}(\mathbf{k})-L_{\alpha\beta}(\mathbf{k})+L_{\alpha\gamma}(\mathbf{k})-L_{\alpha\delta}(\mathbf{k}),\end{aligned}\tag{37}$$

where $\beta=\frac{1}{2}(a+b)$, $\gamma=\frac{1}{2}(b+c)$, and $\delta=\frac{1}{2}(a+c)$.

From the interaction terms presented in Table I, it is apparent that the dominant interaction is that of the reference molecule with the molecule located at $\frac{1}{2}(b+c)$, and the system could have been treated as before on the basis of a two-dimensional model. For the sake of completeness, we have chosen to treat the system as three dimensional including the five interaction terms displayed in Table I. We have to calculate the density of states in the band which consists of four branches. It can be easily realized that if we consider the range of the reciprocal lattice of dimensions of $\frac{1}{4}$ of the extended zone in the region $0\leq k_x\leq 2\pi$, $0\leq k_y\leq 2\pi$ and $0\leq k_z\leq \pi$ and make use of just a single branch [say $E_1(k)$] we shall generate all the energy surfaces corresponding to the four branches. The energy-dispersion curve for this branch is obtained from Eq. (37) in the form

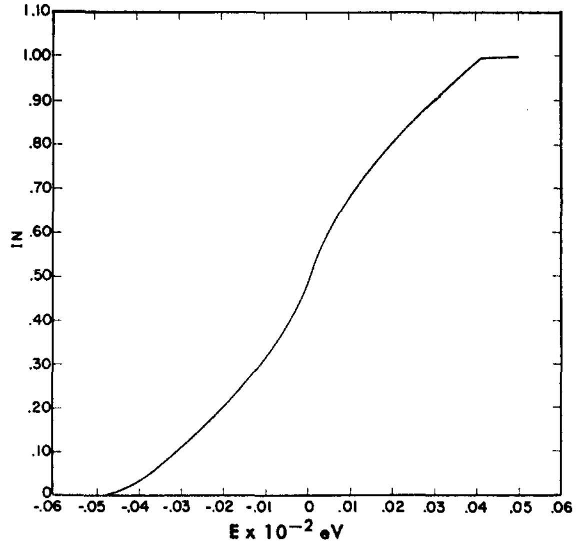

FIG. 9. Total number of states as a function of energy for triplet benzene.

$$E_1(\mathbf{k})=\epsilon_1\cos k_x+\epsilon_2\cos(k_x/2)\cos(k_y/2)+\epsilon_3\cos(k_y/2)\cos(k_z/2)+\epsilon_4\cos(k_x/2)\cos(k_z/2)+\epsilon_5\cos k_z,\tag{38}$$

where

$$\epsilon_1=2\epsilon_a,\quad \epsilon_2=4\epsilon_{(a+b)/2},\quad \epsilon_3=4\epsilon_{(b+c)/2},\quad \epsilon_4=4\epsilon_{(a+c)/2},\quad \epsilon_5=2\epsilon_c.\tag{39}$$

Applying Eq. (39) we can express $k_y=k_y(E_1, k_x, k_z)$ in the form

$$k_y=2\arccos\left(\frac{E_1(k)-\epsilon_1\cos k_x-\epsilon_5\cos k_z-\epsilon_4\cos(k_x/2)\cos(k_z/2)}{\epsilon_2\cos(k_x/2)+\epsilon_3\cos(k_z/2)}\right).\tag{40}$$

In Fig. 8, we display schematically several typical curves of constant energy for several constant values of k_z. Volume integration including all the shaded areas leads to the energy dependence of the number of states up to energy E. These results, given in Fig. 9, were used to calculate the density of states function displayed in Fig. 10.

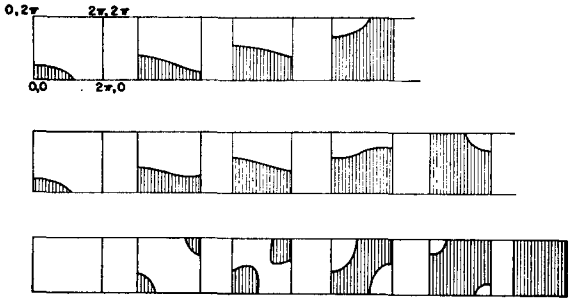

FIG. 8. Schematic representation of constant energy surfaces in the k_xk_y plane for the triplet-exciton band in benzene. Each line corresponds to a constant value of k_z. The calculation of the total number of states was performed by volume integration including the shaded areas for constant E.

We have now to consider the Van Hove analytical singular points in the density of states function. As before, we seek the points for which $\nabla_{\mathbf{k}}E(k_x, k_y, k_z)=0$. Defining again the 3×3 determinant of the second derivatives [Eq. (30a)]. An extremum is encountered when det>0, while when det<0 a saddle point is obtained. In Table III we present the analytical critical points in the triplet-exciton density of states for crystalline benzene.

V. THE LOCALIZED TRIPLET IMPURITY PROBLEM IN CRYSTALLINE NAPHTHALENE AND BENZENE

The energy levels of an impurity characterized by a local perturbation are given from Eq. (15) in the form $1-U_0F(E)=0$ where

$$F(E)=P\int\frac{g_0(E')dE'}{E-E'}.\tag{41}$$

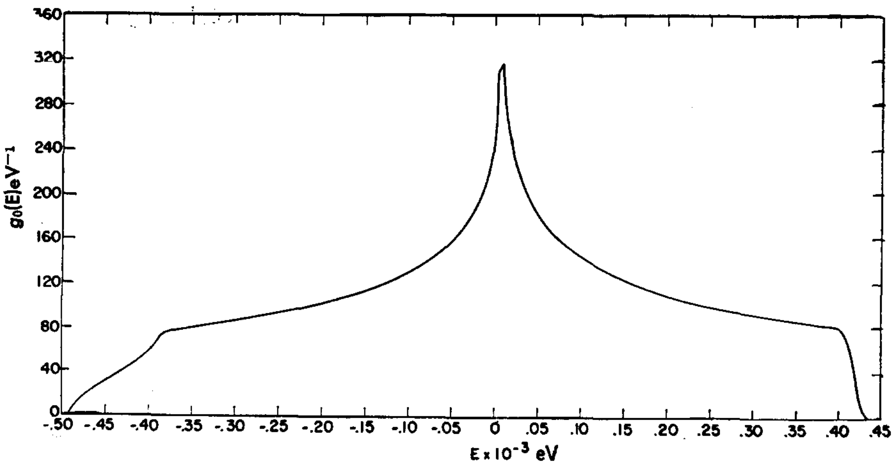

FIG. 10. Triplet-exciton density of states in benzene.

In Figs. 11 and 12 we display the F functions for naphthalene and for benzene calculated from the exciton density of states presented in Secs. III and IV. The F function for naphthalene reveals the features of a two-dimensional system.[10] The extremum points are characterized by logarithmic singularities while the saddle points reveal step discontinuities in the F function. The F function for benzene reveals a square-root critical point at the minimum as expected from a three-dimensional case. The other critical points for this F function are closer to those expected from a three-dimensional model. This is not surprising, in view of the fact that only a single-pair interaction dominates the triplet band structure in benzene.

Turning our attention to the calculation of the energy levels, we should note that the density of state functions and the resulting F functions were calculated using the total electronic interaction. In the weak coupling limit, which is obviously applicable to the cases under consideration, the Green's function has to be expressed in terms of the density of states in the first vibronic band. Our results should be thus modified by the inclusion of a scaling factor for the energy which involves the proper Franck–Condon vibrational overlap factor which for the zero vibrational component in both cases is of the order of 0.3.

Let S be the appropriate Franck–Condon vibrational overlap, and let $g_0^V(\tilde{E})$ be the density of states in the first vibronic band, the new energy scale is now denoted by $\tilde{E}$. Obviously, the following relation holds between the electronic density of states and the vibronic density of states $g_0^V(\tilde{E})=S^{-1}g_0(E)$, where $\tilde{E}=SE$. Hence the following relation is obtained $F^V(\tilde{E})=S^{-1}F(E)$, where $F^V(\tilde{E})$ is now the function (41) calculated for the vibronic band. The solution of Eq. (15) is

$$1-U_0F^V(\tilde{E})=0$$

or alternatively

$$1-U_0/SF(\tilde{E}/S)=0.$$

In Figs. 13 and 14 we present the energy levels for a single impurity. In the case of naphthalene an arbitrary weak perturbation will lead to a bound state, in the case of benzene bound states are observed only for $U_0<-5\times10^{-4}$ eV while virtual states are expected for $U_0\sim-3\times10^{-4}$ eV.

In view of the small triplet-exciton bandwidth, moment expansion methods will be suitable for most perturbation strengths which are of physical interest. As previously demonstrated[10,20,23] the moment expansion of the F function

$$F(E)=\sum_{I=0}^{\infty}\frac{M_{00}^{(I)}}{E^{I+1}}, \tag{42}$$

where

$$M_{00}^{(I)}=\int(E')^Ig_0(E')\,dE' \tag{43}$$

leads to the Nieman Robinson equation[8] in the limit of deep traps

$$E=U_0+(M_{00}^{(2)}/U_0^2)+(M_{00}^{(3)}/U_0^3)+\cdots, \tag{44}$$

TABLE III. Analytical critical points in the triplet exciton density of states function for crystalline benzene.

k_x	k_y	k_z	E (eV)	Nature of critical point
0	2π	0	-4.9×10^{-4}	Minimum
2π	2π	0	-3.85×10^{-4}	Saddle point
2π	1.04π	0.97π	-0.81×10^{-5}	Maximum
π	π	π	$+0.97\times10^{-5}$	Saddle point
0	0.95π	0.97π	1.24×10^{-5}	Minimum
	0	0	4.1×10^{4}	Saddle point
2π	0	0	4.25×10^{-4}	Maximum

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[23] B. Sommer and J. Jortner, J. Chem. Phys. **50**, 822 (1969).

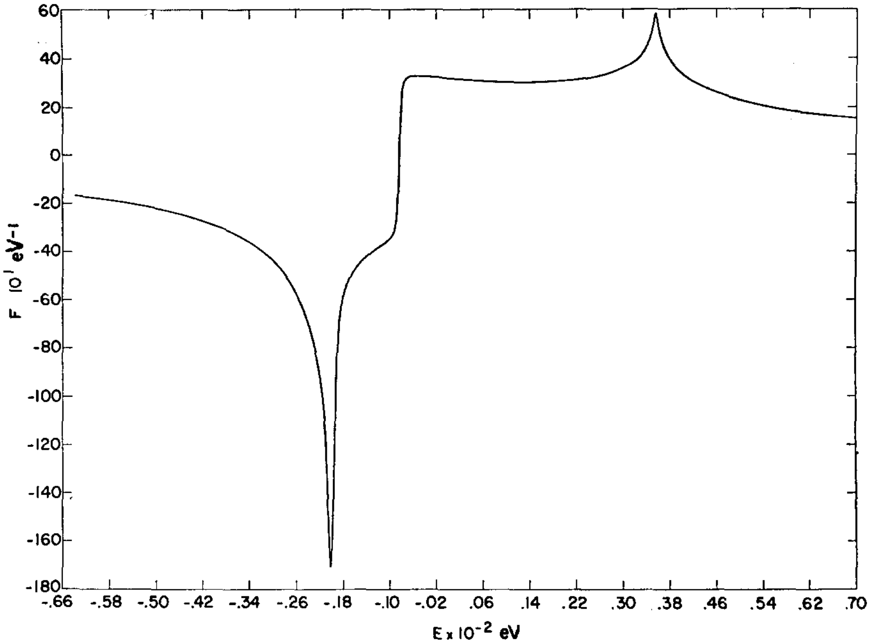

FIG. 11. The $F(E)$ function for the triplet-exciton band in naphthalene.

where the center of gravity of the exciton band has been chosen to be zero, so that $M^{(1)}=0$. Equation (42) is legitimate for deep traps, however, it also works quite well for intermediate trap depths in view of some mathematical artifacts which result from error cancellation. These aspects of the problem have been recently discussed by us.[23] In Table IV, we present the moments of the density-of-states function for naphthalene and benzene, calculated from the data of Figs. 6 and 10. In Table V we present the effect of the exciton band on the impurity levels calculating $E-U_0$ from the exact solution (41) and from the perturbation expansion.

VI. OFF-DIAGONAL MATRIX ELEMENTS OF THE GREEN'S FUNCTION AND THE IMPURITY PAIR PROBLEM

Up to this point our calculations have been relatively simple as they involved only the diagonal matrix elements of the Green's function. We now turn our attention to the interactions between two impurity sites. In this case, the energy levels of the system are determined by both the diagonal and the off-diagonal matrix elements of the Green's function. The simplest example in this case involves two impurities each

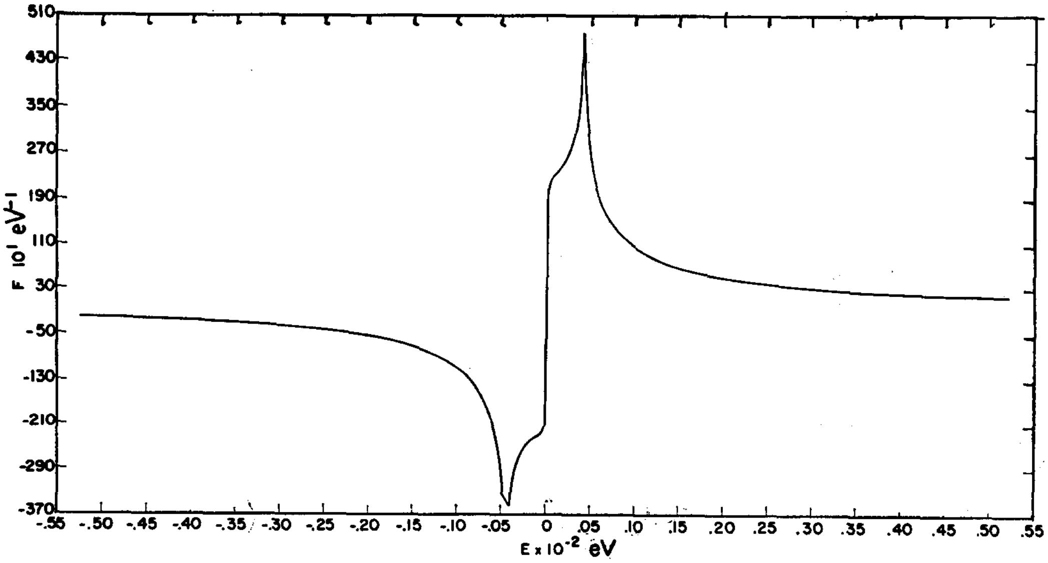

FIG. 12. The $F(E)$ function for the triplet-exciton band in benzene.

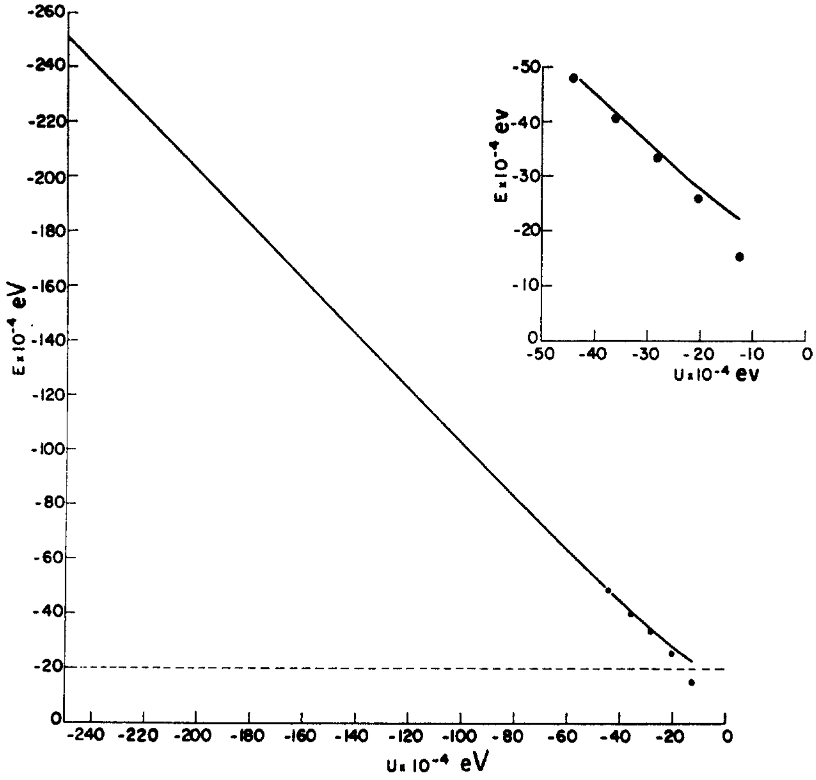

FIG. 13. The localized energy levels of a local impurity in naphthalene. Impurity energy level is given relative to the center of gravity of the exciton band. The solid lines were calculated from Eq. (15). The dots represent the results of the perturbation treatment, which reveals deviation from the exact solution close to the band edge.

characterized by a local perturbation. This problem is of physical interest as it will provide information on the nature of virtual coupling and triplet energy transfer between isotopic impurity molecules. Following our previous discussion it is expected that in the case of the triplet states of an impurity pair, whereupon the intermolecular interactions are of short range, the level splitting will be of the order of the bandwidth.

The diagonal perturbation matrix for the case of the impurity pair (with the impurities located at the sites 0 and l) given by Eq. (18) with $U_0=U_l$. The energy levels are obtained from the equation[24]

$$\begin{vmatrix} 1-U_0F_{00}(E) & -U_0F_{0,l}(E) \\ -U_0F_{0,l}(E) & 1-U_0F_{00}(E) \end{vmatrix} = 0 \qquad (45)$$

TABLE IV. Moments of the density-of-states function for naphthalene and benzene.[a] (The normalization conditions for $g_0(E)$ implies, of course, that $M_{00}^{(0)}=1$.)

System	$M_{00}^{(2)}$ (eV)^2	$M_{00}^{(3)}$ (eV)^3
Naphthalene	2.24×10^{-6}	2.34×10^{-9}
Benzene	4.64×10^{-8}	-9.8×10^{-13}

[a] Zero energy was chosen at the center of gravity of the band, so that $M_{00}^{(1)}=0$.

and the two roots are obtained from the relations

$$U_0^{-1}-F_{00}(E)\pm F_{0,l}(E)=0, \qquad (45')$$

where the real part of the matrix element $G_{0,l}^0(E)$ is related to matrix elements of the weighted density of states function by the relation (8′). The off diagonal elements $g_{n\alpha,m\beta}$ (where $0\equiv n\alpha$ and $l\equiv m\beta$) are

$$g_{n\alpha,m\beta}(E)=N^{-1}\sum_{\mathbf{k}}\sum_{j}\exp[i\mathbf{k}\cdot(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})]$$
$$\times B_{\alpha j}(\mathbf{k})B_{\beta j}^*(\mathbf{k})\delta(E-E_j(\mathbf{k})). \qquad (46)$$

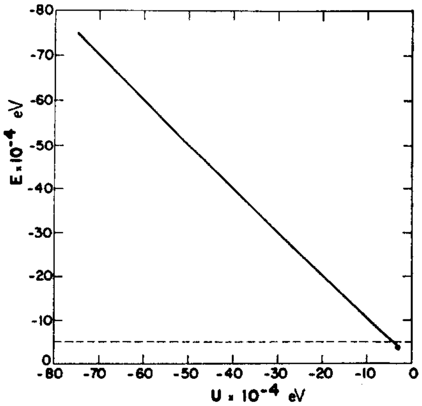

FIG. 14. Localized energy levels of a local impurity in benzene.

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[24] I. M. Lifschitz, Advan. Phys. **13**, 485 (1964).

This equation can now be rewritten in the form

$$g_{n\alpha,m\beta}(E)=N^{-1}\frac{d}{dE}\sum_j\int_E\iint\exp[ik(R_{n\alpha}-R_{m\beta})]$$
$$\times B_{\alpha j}(\mathbf{k})B_{\beta j}{}^*(\mathbf{k})\,dk_x dk_y dk_z. \qquad (47)$$

In view of the relation (27) we can further simplify our result, as the coefficients $B_{\alpha j}(\mathbf{k})$ are independent of the exciton wavevector. As in the calculation of the density of exciton states, we have to calculate the volume integrals in Eq. (47) over constant energies in the Brillouin zone, however, now the integration involves the modulation factor $\exp[i\mathbf{k}\cdot(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})]$.

The numerical calculations of the off-diagonal matrix elements of the Green's function have been performed for the triplet excitons in naphthalene using the energy relation (28). In Figs. 15 and 16 we present typical results for the energy dependence of $g_{n\alpha,m\beta}(E)$ and for the real part of the off-diagonal matrix elements of the Green's function.

To obtain further information on the energy splittings when the perturbation strength exceeds the exciton bandwidth, we shall utilize the moments expansion method.

The off-diagonal matrix elements of the Green's function can be expanded in the form

$$F_{n\alpha,m\beta}(E)=\sum_{l=0}^{\infty}\frac{M_{n\alpha,m\beta}{}^{(l)}}{E^{l+1}}, \qquad (48)$$

where the moments of the off-diagonal matrix elements are:

$$M_{n\alpha,m\beta}{}^{(l)}=\int(E')^l g_{n\alpha,m\beta}(E')\,dE'$$
$$=N^{-1}\sum_{\mathbf{k}}\sum_j[E_j(\mathbf{k})]^l B_{\alpha j}(\mathbf{k})B_{\beta j}(\mathbf{k})$$
$$\times\exp[i\mathbf{k}\cdot(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta}). \qquad (49)$$

Table V. The effect of the exciton band on the energy shifts of the isotopic impurity in naphthalene.[a] Energies E measured relative to the center of gravity of the exciton density of states. $\delta=E-U_0$.

U_0 10^4 eV	δ 10^4 eV Exact solution	δ 10^4 eV Moment expansion three moments
−250	−0.86	−0.86
−202.5	−1.05	−1.05
−155	−1.35	−1.35
−91.7	−2.20	−2.17
−44.2	−4.10	−3.87
−36.3	−4.79	−4.39
−28.3	−5.79	−4.99
−20.4	−7.32	−5.35
−12.5	−10.0	−2.9

[a] Band edge -19.8×10^{-4} eV.

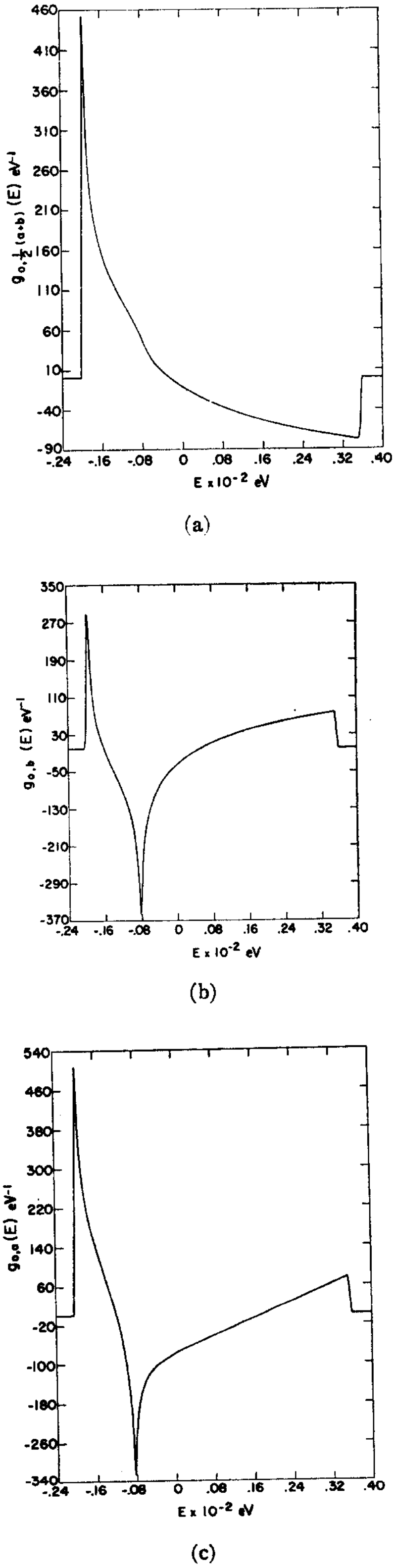


Fig. 15. Off-diagonal matrix elements of the weighted density-of-states function for triplet-exciton band in naphthalene. (a) Second molecule located at τ. (b) Second molecule located at b. (c) Second molecule at a.

Table VI. Moments of the off-diagonal matrix elements of the weighted density-of-state function for the triplet excitons in naphthalene. Moment $M^{(I)}$ is given in units of [(electron volts)^I] $I=1, 2, 3\cdots$.

Location of impurity molecule relative to reference molecule	$M^{(1)}$	$M^{(2)}$	$M^{(3)}$
$\frac{1}{2}(a+b)$	-6.89×10^{-4}	-5.66×10^{-7}	-3.65×10^{-9}
b	4.11×10^{-4}	9.50×10^{-7}	2.55×10^{-9}
a	1.60×10^{-8}	9.51×10^{-7}	1.17×10^{-9}
$(\frac{1}{2}a+\frac{3}{2}b)$	-1.57×10^{-8}	-5.66×10^{-7}	-1.33×10^{-9}

The nature of these moments deserves some further comments. In view of Eq. (27) we can write for the case of triplet states in naphthalene

$$M_{n\alpha,m\alpha}^{(I)}=(1/\sigma N)\sum_{\mathbf{k}}\{[E_1(\mathbf{k})]^I+[E_2(\mathbf{k})]^I\}\times\exp[i\mathbf{k}\cdot(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\alpha})] \quad (49a)$$

$$M_{n\alpha,m\beta}^{(I)}=(1/\sigma N)\sum_{\mathbf{k}}\{[E_1(\mathbf{k})]^I-[E_2(\mathbf{k})]^I\}\times\exp[i\mathbf{k}\cdot(\mathbf{R}_{n\alpha}-\mathbf{R}_{m\beta})]. \quad (49b)$$

Thus in the case when the band structure is dominated by short-range interactions the moments of the off-diagonal weighted density-of-states function can be obtained directly from the energy relation [Eq. (28) for our case]. For triplet states in naphthalene we obtain for $M^{(0)}$, $M^{(1)}$, $M^{(2)}$:

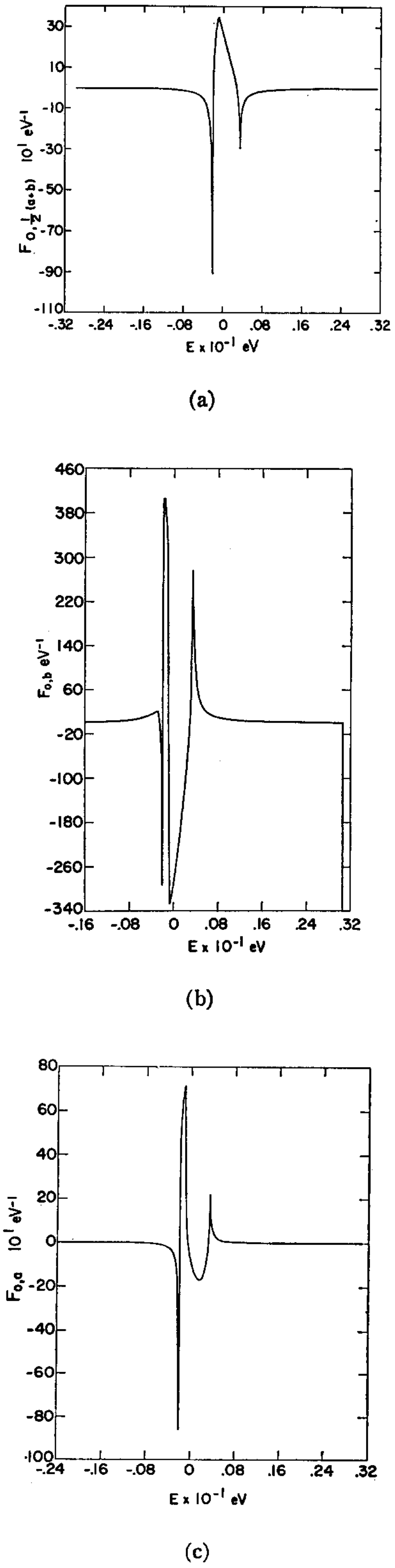
$$M_{n\alpha,m\alpha}^{(0)}=M_{n\alpha,m\beta}^{(0)}=0, \quad (50)$$

$$M_{n\alpha,m\alpha}^{(1)}=\epsilon_b\delta(\mathbf{R}_p+\mathbf{b})+\epsilon_b\delta(\mathbf{R}_p-\mathbf{b}), \quad (50a)$$

$$\begin{aligned}M_{n\alpha,m\beta}^{(1)}=&\epsilon_\tau\delta[\mathbf{R}_p-\tfrac{1}{2}(\mathbf{a}+\mathbf{b})]+\epsilon_\tau\delta[\tfrac{1}{2}(\mathbf{a}+\mathbf{b})-\mathbf{R}_p]\\&+\epsilon_\tau\delta[\mathbf{R}_p-\tfrac{1}{2}(\mathbf{a}-\mathbf{b})]\\&+\epsilon_\tau\delta[\tfrac{1}{2}(\mathbf{a}-\mathbf{b})-\mathbf{R}_p] \qquad \alpha\neq\beta,\end{aligned} \quad (50b)$$

$$\begin{aligned}M_{n\alpha,m\alpha}^{(2)}=&\epsilon_b^2\delta(\mathbf{R}_p-2\mathbf{b})+\epsilon_b^2\delta(2\mathbf{b}-\mathbf{R}_p)\\&+2\epsilon_b^2\delta(\mathbf{R}_p-\mathbf{R}_0)+\epsilon_\tau^2\delta[\mathbf{R}_p-(\mathbf{a}+\mathbf{b})]\\&+\epsilon_\tau^2\delta(\mathbf{a}+\mathbf{b}-\mathbf{R}_p)+4\epsilon_\tau^2\delta(\mathbf{R}_p-\mathbf{R}_0)\\&+2\epsilon_\tau^2\delta(\mathbf{R}_p-\mathbf{a})+2\epsilon_\tau^2\delta(\mathbf{R}_p-\mathbf{b})\\&+2\epsilon_\tau^2\delta(\mathbf{b}-\mathbf{R}_p)+2\epsilon_\tau^2\delta(\mathbf{a}-\mathbf{R}_p),\end{aligned} \quad (50c)$$

$$\begin{aligned}M_{n\alpha,m\beta}^{(2)}=&2\epsilon_b\epsilon_\tau\{\delta[\mathbf{R}_p-(\tfrac{1}{2}\mathbf{a}+\tfrac{3}{2}\mathbf{b})]+\delta(\tfrac{1}{2}\mathbf{a}+\tfrac{3}{2}\mathbf{b}-\mathbf{R}_p)\\&+\delta[\mathbf{R}_p-\tfrac{1}{2}(-a+b)]+\delta[-\tfrac{1}{2}(a-b)-\mathbf{R}_p]\\&+\delta[R_p-\tfrac{1}{2}(\mathbf{a}+\mathbf{b})]+\delta[\tfrac{1}{2}(\mathbf{a}+\mathbf{b})-\mathbf{R}_p]\\&+\delta[\mathbf{R}_p-(-\tfrac{1}{2}\mathbf{a}+\tfrac{3}{2}\mathbf{b})]+\delta(-\tfrac{1}{2}\mathbf{a}+\tfrac{3}{2}\mathbf{b}-\mathbf{R}_p)\}.\end{aligned} \quad (50d)$$



(a)

(b)

(c)

Fig. 16. Real part of the off-diagonal matrix element of the Green's function for the triplet exciton band in naphthalene. (a) Second molecule located at τ. (b) Second molecule located at b. (c) Second molecule located at a.

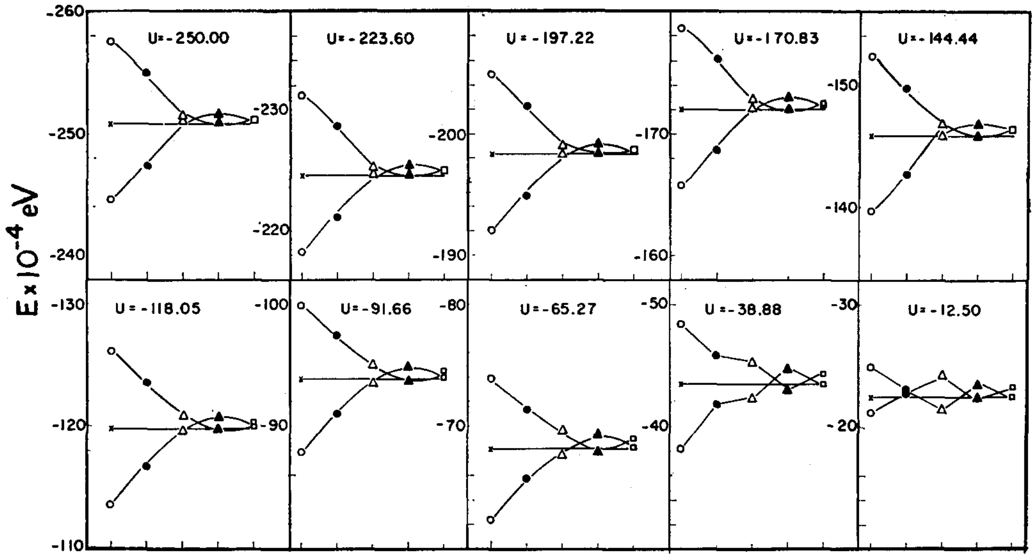


FIG. 17. Schematic representation of the energy levels of an impurity pair in crystalline naphthalene. The strength of the local potential of the impurities, U_0, given in units of 10^{-4} eV. The straight line x—corresponds to the single impurity level. ○ impurity molecules at 0 and at $\frac{1}{2}(a+b)$. ● impurity molecules at 0 and at b. △ impurity molecules at 0 and at a. ▲ impurity molecules at 0 and at $\frac{1}{2}a+\frac{3}{2}b$. ☐ impurity molecules at 0 and at $a+b$. Note the effect of long-range triplet energy transfer for small values of U_0.

These results involve the generalization of the theoretical data of Philpott and Craig[19] for more than a single molecule per unit cell. The zero moments vanish as expected on the basis of the general arguments previously presented.[10,19] The first moments are equal to the pair interactions, while the higher moments are determined by the sums of the products of the intermolecular coupling terms on the lattice sites which connect the impurity molecules.

In Table VI, we present the relevant moments of these off-diagonal matrix elements calculated from the data presented in Fig. 15. The agreement with the results previously obtained for the intermolecular interactions (Table I) is excellent, serving as an adequate accuracy check for our calculations of the off-diagonal matrix elements of the Green's function.

In view of the relation (50) one immediately realizes that in the deep-trap limit the impurity-pair energy levels are just $E=U_0\pm M_{n\alpha,m\beta}^{(1)}$ thus the level splitting is determined by the intermolecular pair interactions, as expected. For shallow traps the general relation (45) has to be applied. In Fig. 17 we present the energy levels of the impurity pair calculated by using the off-diagonal matrix elements of the Green's functions.

These results provide a complete picture for virtual coupling effects between guest molecules. In particular, it is important to notice that in the limit of shallow traps when U_0 is comparable to or smaller than the exciton bandwidth, long-range virtual coupling effects are observed. In this case the splitting between the impurity levels exceeds the intermolecular exciton pair coupling terms.

VII. TRIPLET ENERGY TRAPPING IN DOPED CRYSTALS

Energy trapping phenomena are often encountered by the experimentalist as a real life difficulty. It is quite easy to rationalize energy trapping by an impurity molecule characterized by a negative perturbation ($U_0<0$) when the perturbation strength is sufficient to lead to a bound state outside the band, although even in the simple case of a localized perturbation, the calculation of the trapping cross section is rather tedious.[17] A more interesting case is provided by the general impurity problem and the following questions have to be answered:

(a) What is the effect of the change in the intermolecular coupling terms on the bound impurity state, and under what conditions does an additional state appear outside the band?

(b) What is the effect of the d terms on the appearance of additional energy levels outside the band?

(c) Is it plausible that a general impurity characterized by a positive perturbation strength ($U_0>0$) will result in the appearance of a state located below the band, which may act as an energy trap? A partial answer for problem (a) was provided by Merrifield[18] for a simple model system. In relation to problem (b) Philpott and Craig[19] have pointed out that the inclusion of the diagonal **d** matrix may result in the appearance of states outside the band, (which they assumed to be localized) and have conjectured that the number of these states is equal to the rank of the **d** matrix. Concerning problem (c) it has been experimentally

TABLE VII. Changes in the intermolecular electron-exchange interactions (in electron volts) for substitutional impurities.

Host	Guest	U_0 (eV)	m_{0b} 10^4 eV	$m_{0\frac{1}{2}(a+b)}$ 10^4 eV	$m_{0\frac{1}{2}(-a+b)}$ 10^4 eV
Anthracene	Naphthalene	0.81	−8.16	+14.55	+13.46
Naphthalene	Benzene	1.5	−8.43	+10.12	+5.98

demonstrated by Wolf *et al.*[25] that energy trapping occurs in a doped molecular crystal even when the impurity molecule cannot act as an energy trap. Our motivation for the study of trapping of triplet excitons is twofold. From the experimental point of view, the availability of experimental results makes such a study desirable while from the theoretical point of view the availability of the matrix elements of the weighted density of states function makes it possible to perform model calculations on the energy levels of a general impurity.

To obtain some qualitative information on the order of magnitude of the matrix elements of the matrix $\mathbf{m}$ [Eq. (14b)] we have performed calculations of the intermolecular electron exchange interactions for two model systems: benzene impurity in naphthalene and naphthalene impurity in anthracene. In both cases it was assumed that the guest molecule replaces a host molecule substitutionally so that a center of inversion in the doped crystal is still preserved. From the results displayed in Table VII we conclude that the m_{0j} terms are of the order of the intermolecular electron-exchange interactions in the pure crystal. The order of magnitude of the d_{0i} terms for triplet states can be roughly estimated from the phosphorescence spectra of naphthalene in durene (21 355 cm^{-1}) and naphthalene in deutero naphthalene (21 209 cm^{-1}).[25] Thus the difference between the environment shift D^f terms for the triplet state of naphthalene in these two systems is about 146 cm^{-1}. This result indicates that the individual d_{0i} terms are of the order of 10–50 cm^{-1}, however, their relative signs are unknown.

We have performed model calculations on a general impurity problem in crystalline naphthalene applying the formalism presented in Sec. II and using the off-diagonal elements of the Green's function calculated in Sec. VI. These results are presented in Tables VIII–X. From these data we may conclude that

(a) When the diagonal perturbation strength, U_0, is of the order of the exciton bandwidth, the m_{0j} above may induce the appearance of an additional state outside the band. The two levels thus produced differ in one important respect. While for the impurity level around U_0 (the localized state) the maximum excitation amplitude is located on the impurity molecule (falling off exponentially with the distance from the impurity site), the second state reveals an appreciable spread of the excitation energy around the impurity center. The latter case can be considered as a large radius impurity induced crystal state. It should be noted that when $\mathbf{m}\neq 0$ while $\mathbf{d}=0$ the inversion symmetry for the expansion coefficients around the impurity site is preserved for both levels which appear outside the exciton band.

(b) When U_0 is large the m_{0j} terms alone (i.e., when $\mathbf{d}=0$) cannot induce the appearance of a second level

TABLE VIII. Model calculations for triplet states of an impurity in naphthalene induced by changes in the intermolecular coupling terms. ($\mathbf{m}\neq 0$, $\mathbf{d}=0$).

U_0 10^4 eV	m_{0b} 10^4 eV	$m_{0\frac{1}{2}(a+b)}$ 10^4 eV	$m_{0\frac{1}{2}(-a+b)}$ 10^4 eV	E^{a} 10^4 eV	$U(l)^{b}$	E^{a} 10^4 eV	$U(l)^{b}$
250	−13.75	−25	−25	−24.8	1	266	1
					1.63		-3×10^{-2}
					1.63		-3×10^{-2}
					1.88		-1.2×10^{-1}
					1.88		-1.2×10^{-1}
					1.88		-1.2×10^{-1}
					(2.02)		(-1.2×10^{-1})
250	−13.75	16.25	12.5	251.8		···	···
−150	−25	23.75	31.2	37.2		−165	
50	−25	−25	−25	98.9		−54.4	
50	−21.25	12.5	12.5	62.1		···	···

[a] Energy relative to the center of gravity of the exciton band. Band edges: -19.8×10^{-4} eV, 36×10^{-4} eV.

[b] The expansion coefficients are given in the order $U(0)$, $U(b)$, $U(-b)$, $U[\frac{1}{2}(a+b)]$, $U[-\frac{1}{2}(a+b)]$, $U[\frac{1}{2}(-a+b)]$, $U[\frac{1}{2}(+a-b)$.] These expansion coefficients are evaluated as the eigenvectors of the matrix $|\mathbf{1}-\mathbf{G}^0\mathbf{V}|$ by the elimination method. The last value (given in parentheses) is uncertain due to numerical errors.

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[25] H. Port and H. C. Wolf, in *The Triplet State. Proceedings of an International Symposium American University of Beirut*, A. B. Zahlan, Ed. (Cambridge University Press, London, 1967), p. 393.

TABLE IX. Model calculations for triplet states of an impurity in naphthalene, induced by the changes in level shifts for the host molecules, caused by the guest. ($m=0$, $d\neq 0$).

U_0 (eV)	d_{0b} 10^4 eV	$d_{0(1/2)(a+b)}$ 10^4 eV	$d_{0(1/2)(-a+b)}$ 10^4 eV	E^a 10^4 eV	$U(l)$[b]	E^a 10^4 eV	E^a 10^4 eV	E^a 10^4 eV	E^a 10^4 eV	E^a 10^4 eV
-60×10^{-4}	-25.5	25.5	25.5	40.1		-62.7	···	···	···	···
253×10^{-4}	-25.5	25.5	25.5	···	···	254	···	···	···	···
-60×10^{-4}	12.5	-12.5	-12.5	-21.9		-63.8	···	···	···	···
253×10^{-4}	12.5	-12.5	-12.5	-21.4		253.9	···	···	···	···
-5	12.5	-12.5	-12.5	-21.5			···	···	···	···
1	-100	-100	-100	-111.8	1 2.5×10^3 -1.1×10^3 1.7×10^3 -1.5×10^3 2.2×10^3 (1.3×10^2)	-108.8	-104.9	-97.3	-93.9	-91.2
1	-75	25	-75	-70.4		···	···	···	···	···
1	-75	50	-50	···	···	···	···	···	···	···
1	-75	100	75	···	···	···	···	···	···	···
1	-75	50	50	58.3		···	···	···	···	···
1	-25	-25	-25	-37.8	1 2.4×10^3 -9.6×10^2 1.6×10^3 -1.3×10^3 2.0×10^3 (4.1×10^2)	-36.1	-31.4	-27.2	-20.9	···
1	50	75	-25	···	···	···	···	···	···	···
1	50	75	25	52.6		···	···	···	···	···
1	75	-75	-50	77.5		···	···	···	···	···
1	75	-50	-25	-20.1		···	···	···	···	···

[a] Energy relative to the center of gravity of the exciton band. Band edges: -19.8×10^{-4} eV, 36×10^{-4} eV.

[b] The expansion coefficients are given in the order (see Table VIII) $U(0)$, $U(b)$, $U(-b)$, $U[\frac{1}{2}(a+b)]$, $U[-\frac{1}{2}(a+b)]$, $U[\frac{1}{2}(-a+b)]$, $U[\frac{1}{2}(a-b)]$.

outside the band and only a single localized level appears at about U_0. Thus for the cases considered in Table VII changes of intermolecular terms will not result in the appearance of an X trap.[25]

(c) When the d terms are included, additional states may appear outside the band, even for large values of U_0. The appearance of these states is determined by the absolute size and the relative signs of the d_{0j}. These additional levels correspond to a large-radius impurity-induced excited state. The expansion coefficients for the latter levels do not any more preserve the inversion symmetry around the impurity site.

(d) To ascertain the effect of the m and d terms on the local impurity level around U_0 we notice that the first diagonal term in the determinant (4) is

$$1-G_{00}U_0-\sum_{j\neq 0} m_{0j}G_{0j}.$$

Hence in the case of a deep trap the energy level around U_0 will be affected by the m_{0j} terms and not by the d_{0j} terms. From this result it should not be inferred that environmental shifts do not affect the localized impurity level in the deep-trap limit, as the term U_0 includes also a diagonal contribution of the form $D_p^f-D^f$ [Eq. (9′)]. In the case of a shallow trap, the problem has to be solved exactly and both terms contribute to the energy of the level around U_0.

VIII. CORRELATION WITH EXPERIMENT

The available experimental results on triplet states in mixed molecular crystal were obtained from phosphorescence measurements. We now turn to the analysis of the relevant data:

(a) The low-temperature phosphorescence spectrum of naphthalene h_8 in naphthalene d_8 originates at 21 208.7 cm^{-1}.[25,26] The center of gravity of the triplet

TABLE X. Model calculations for the general impurity problem in naphthalene ($m\neq 0$, $d\neq 0$).

U_0 (eV)	m_{0b} 10^4 eV	$m_{0(1/2)(a+b)}$ 10^4 eV	$m_{0(1/2)(-a+b)}$ 10^4 eV	d_{0b} 10^4 eV	$d_{0(1/2)(a+b)}$ 10^4 eV	$d_{0(1/2)(-a+b)}$ 10^4 eV	E^a 10^4 eV	E^a 10^4 eV	E^a 10^4 eV
250×10^{-4}	-13.75	-25	-25	12.5	-12.5	-12.5	-31.25	-22.6	265.4
250×10^{-4}	-13.75	12.5	12.5	12.5	-12.5	-12.5	-21.5	···	251.3
1	-12.5	12.5	6.25	125	-125	-125	-122.4	···	···

[a] Energy relative to the center of gravity of the exciton band. Band edges: -19.8×10^{-4} eV, 36×10^{-4} eV.

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[26] M. A. El-Sayed, M. T. Wauk, and G. W. Robinson, Mol. Phys. 5, 205 (1962).

Davydov components in crystalline naphthalene h_8 is located at [1] 21 208±2 cm^{-1}. Now assuming that the isotopic substitution is characterized by the local perturbation $U_0=\Delta\epsilon_{\text{guest}}{}^f-\Delta\epsilon_{\text{host}}{}^f$, we can set $U_0=-97$ cm^{-1} estimated from the phosphorescence spectra of naphthalene h_8 and naphthalene d_8 in durene.[25] The impurity level can be estimated from the deep-trap limit [Eq. (44)]

$$E=\Delta\epsilon_{\text{guest}}{}^f-\Delta\epsilon_{\text{host}}{}^f+(M_{00}{}^{(2)}S^2/U_0), \qquad (51)$$

where $M_{00}{}^{(2)}$ is the second moment of the exciton band (calculated without Franck–Condon partition) while $S=0.3$. Using the data of Table IV, one gets that the correction term is negligible, $M_{00}{}^{(2)}S^2/U_0\approx-0.2$ cm^{-1}, so that the center of gravity of the naphthalene exciton band is expected at 21 208.7−0.2=21 208.5 cm^{-1}. From the energy difference between the center of gravity of the Davydov components and the center of gravity of the exciton band the resonance interaction over translationally equivalent molecules, I_{eq}, can be estimated. Hence for triplet naphthalene $I_{\text{eq}}=-0.5\pm2$ cm^{-1}. This result is consistent with the theoretical calculations of electron exchange terms, 4, 7 (see Table I) as one expects from theory that $I_{\text{eq}}=2\epsilon_b S=+1$ cm^{-1}. It should be noted that the U_0 term can also contain a contribution of the order of a few cm^{-1} from the contribution of the term $D_p{}^f-D^f$ [Eq. (9′)],[27] however, the experimental results are not sufficiently accurate to establish this point.

(b) In view of the small triplet-exciton bandwidth in crystalline benzene and naphthalene, the strength of any local perturbation due to hydrogen–deuterium isotopic substitution will exceed the triplet-exciton bandwidth. Thus, for the case of naphthalene triplet band $M_{00}{}^{(2)}S^2\sim15$ cm^{-1}, so that a local perturbation strength $|U_0|>10$ cm^{-1} will lead to $M_{00}{}^{(2)}S^2/|U_0|\leq0.1$ and will thus correspond to a deep-trap limit.[19,20,23] Even for the mildest isotopic substitution which corresponds to the system $C_{10}H_7D/C_{10}H_8$ and $C_{10}D_7H/C_{10}D_8$ (where $|U_0|\sim15$ cm^{-1}) one gets $M_{00}{}^{(2)}S^2/|U_0|\sim1$ cm^{-1}, so that the optical studies will lead to information only concerning the first moment of the exciton density of states, while the information concerning the second moment is on the verge of the experimental error. Extremely interesting information can be obtained from ^{13}C–^{12}C isotopic substitution. As reported by Bernstein Colson and Tint[27] a ^{13}C substitution in benzene leads to a 3-cm^{-1} shift in the excitation energy. Spectroscopic studies of the triplet states of ^{13}C substituted guests in crystalline naphthalene will be of considerable interest, as they will correspond to the shallow and intermediate trap limits and will provide supplementary information on the gross features of the triplet-exciton band structure. It should be noted that in this case the theoretical band structure implies that no virtual scattering states will be observed, as the band structure is dominated by two-dimensional interactions, so that any perturbation will result in a localized state.[10,11,24]

(c) The interpretation of the Nieman and Robinson[8] emission data for deuterated impurities in crystalline benzene imposes a real puzzle. From these data it can be inferred that benzene crystal is the only case where it appears as if the calculation of the intermolecular electron exchange interactions underestimate the triplet-exciton bandwidth by about one to two orders of magnitude. As indicated from the results of Table IV, one expects that $M_{00}{}^{(2)}S\approx3\times10^{-3}$ cm^{-2} so that the correction term in Eq. (51) arising from the effect of the exciton band on the impurity level is negligible in the deep trap limit.[23] The contribution of the changes in the intermolecular coupling terms induced by isotopic substitution are expected to be small (not exceeding 1–2 cm^{-1}) and their contribution to the impurity level will be of the order of $\sum_j m_{0j}M_{0j}{}^{(1)}/U_0$ so that for $U_0\sim50$ cm^{-1} the effect of the m_{0j} thus does not exceed 1 cm^{-1}. The d_{0i} terms in the diagonal matrix d are also expected to have a negligible effect on the energy of the localized state in this case. This conclusion is confirmed by our model calculations. The way out of this difficulty is to consider now Eq. (9′) and note that a diagonal contribution to the perturbation strength U_0, which determines the localized impurity level involves the term $D_p{}^f-D^f$. The D^f term is expected to be quite large (-200 cm^{-1}) so that changes of the order of 5 cm^{-1} in this term induced by isotopic substitution are quite reasonable. Thus it appears that the Nieman–Robinson experiment did not determine the second moment of the triplet-exciton density of states in the triplet state of benzene, but rather monitored isotopic effects on the environmental $D_p{}^f$ term. In the case of a deep trap Eq. (51) should be rewritten (for the case of isotopic substitution) in the form

$$\tilde{E}=\Delta\epsilon_{\text{guest}}{}^f+D_p{}^f+(M_{00}{}^{(2)}S^2/U_0), \qquad (51')$$

when the energy $\tilde{E}$ is now measured relative to the ground state. The last correction term in Eq. (51′) is negligible. This result was previously obtained by Colson.[27] Recently Colson has obtained extensive experimental data on the singlet states of isotopic impurities in crystalline benzene.[27] These results correspond to the deep trap limit, and can be analyzed on the basis of the assumptions that the impurity potential is local.[23] These data provide then an estimate of the first moment of the density of state functions for the singlet-exciton band. However, slight deviations from the simple model were attributed by Colson[27] to the isotopic effect on the D^f term.

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[27] S. D. Colson, J. Chem. Phys. **48**, 3324 (1968).

(d) The observation of the so-called "X traps" in doped crystalline naphthalene[25] can be qualitatively rationalized in terms of the effect of the **d** matrix. A necessary condition for the appearance of a state below the band (when $U_0>0$) is that some of the diagonal d_{0i} terms are negative. As these terms are quite large (in their absolute value), probably exceeding the exciton bandwidth, this situation is plausible. These qualitative arguments indicate that the pair interaction terms leading to solvent shift are responsible for perturbing the exciton states of the host crystal, resulting in the splitting of additional levels outside the band.

To sum up, it should be pointed out that the environmental shift terms of the impurity and those induced by the impurity, which were usually neglected by the spectroscopists as these terms just determine the center of gravity of the exciton band in the pure crystal, are of considerable importance for the understanding of the spectroscopy[27] and energy trapping effects in mixed molecular crystals.

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Density Dependence of Experimental Transport Coefficients of Gases*

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We analyze experimental transport data for several gases as a function of density and temperature. Necessary conditions are proposed to check if the data are consistent with a given density function at fixed temperature. It is found that the theoretically suggested density function, which involves terms logarithmic in the density, satisfies the conditions for the data examined in the temperature and pressure ranges considered. Based on the analyses, first density coefficients of thermal conductivity and viscosity are reported, together with an assessment of their precision, at reduced temperatures up to $T^*\approx 30$.

I. INTRODUCTION

The theoretical description of the density-independent transport coefficients of dilute gases is based on the Chapman–Enskog solution of the Boltzmann equation. The success of this approach has prompted several efforts in recent years to generalize the Boltzmann equation so that the density dependence of the transport coefficients can be taken into account. There are rather special problems, however, which, despite many developments, limit our ability to describe this density dependence quantitatively.

Until recently[1] it was generally assumed that the transport properties of a fluid, such as the thermal-conductivity coefficient λ, and the viscosity coefficient η, could be expanded in a power series in the density ρ. This is an obvious analogy with the power series representation for the density dependence of the thermodynamic properties of a fluid. For example, we have for the equation of state

$$PV=RT+B\rho+C\rho^2+\cdots. \tag{1}$$

Thus one may expect to write

$$\lambda=\lambda_0+\lambda_1\rho+\bar{\lambda}_2\rho^2+\cdots, \tag{2a}$$

$$\eta=\eta_0+\eta_1\rho+\bar{\eta}_2\rho^2+\cdots. \tag{2b}$$

Here λ_0 and η_0 are the Chapman–Enskog zero-density coefficients which depict the effect of binary collisions only, and λ_1, η_1, $\bar{\lambda}_2$, etc., are the density coefficients which account, among others, for the effect of ternary, quadruple, and higher-order collisions. In this article we are especially interested in the coefficients of the linear term, λ_1 and η_1, which are referred to as first density coefficients. For molecules interacting with a repulsive potential, these first density coefficients can be obtained theoretically by solving an integral equation first derived by Choh and Uhlenbeck. Up to this time, the appropriate triple-collision integrals have been

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[1] For a recent survey of the status of the theory we refer to the Boulder *Lectures in Theoretical Physics, Kinetic Theory,* W. E. Brittin, Ed. (Gordon and Breach Science Publishers, Inc., New York, 1967), Vol. 9C.