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Polariton Modes of Molecular Crystals and Helical Polymers*†

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The exciton modes of a molecular crystal are expressed in a second-quantized form by a model Hamiltonian which may be exactly diagonalized by the Bogoljubov canonical transformation. The formal connection between theories based upon one-electron functions and theories based upon one-molecule functions is demonstrated. The exciton-photon interaction is formulated, and the exponential term in the interaction coefficient is retained. The polariton modes of the molecular crystal are found by a Bogoljubov canonical transformation of the total exciton-photon Hamiltonian. The secular equation for those polariton modes which represent electromagnetic waves propagating in a dispersive medium is solved, and a general refractive index is defined. The general refractive index is used for the formulation of the optical dispersion and optical activity of the molecular crystal entirely in terms of molecular moments, molecular energies, and intermolecular interactions. Since the intermolecular interaction is not treated as a perturbation, this theory correctly represents the intensities of crystal transitions which arise from even the weakest molecular transitions. The helical polymer is considered as a special case of the molecular crystal. A major term in the optical rotation of the helical polymer follows directly from the correct dipole selection rules. Use of periodic boundary conditions for the formulation of the optical rotation of the helical polymer is shown to be valid.

I. INTRODUCTION

PROTEINS and DNA, biopolymers of great biological importance, have helical structure; therefore, there has been great interest recently among physicists and chemists in the electronic properties of helical polymers. Much work has been done with the perturbation treatment[1–3] of exciton states of helical polymers, and more recently with nonperturbational treatments.[4–6] In this paper, the helical polymer is considered as a special case of a molecular crystal. A theory of the exciton modes of a molecular crystal and the interaction of the exciton modes with photons is developed and applied to the helical polymer.

Agronovitch[7] and Fukutome[8,9] represent the exciton modes of the molecular crystal by a second-quantized formalism. The exact electron Hamiltonian for the molecular crystal is approximated by a model Hamiltonian which may be exactly diagonalized by the Bogoljubov[10] canonical transformation. Agronovitch bases the exciton representation on the states of an isolated molecule; Fukutome uses a set of one-electron functions as a basis.

In this paper, the Frenkel,[11] or tight-binding exciton modes of a molecular crystal are discussed in the second-quantization formalism. Hartree-Fock (HF) molecular orbitals of a single molecule are used as a basis for the model Hamiltonian.

The interaction of the molecular crystal with light is represented by an exciton-photon Hamiltonian. Hopfield[12] has shown that an exciton-photon Hamiltonian of this form may be exactly diagonalized by the Bogoljubov canonical transformation; the normal modes of the exciton-photon Hamiltonian are called polaritons. Agronovitch[7] has solved the secular equation for those polariton modes which represent electromagnetic waves propagating in a dispersive medium, and has expressed the refractive index of the crystal in terms of exciton dipole moments and exciton energies.

In this paper, the exponential term is retained in the exciton-photon coupling. The solution of the secular equation for the photonlike modes is used to define a general refractive index for the molecular crystal. This refractive index expresses the optical dispersion and optical activity of the crystal. The Hermitian eigenvalue problem for the crystal excitons is used to formulate the crystal optical properties entirely in terms of the molecular dipole moments, molecular energies, and the intermolecular interaction; it is not necessary to solve the exciton eigenvalue problem. The form of the optical dispersion and optical activity relations are identical for the one-electron and one-molecule representations. The one-molecule representation may be used to express the optical properties of the crystal in terms of observable monomer properties; the one-electron representation may be used to express the optical properties of the crystal in terms of a computed basis set.

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Since the intermolecular interaction has not been treated as a perturbation, the theory presented here is still valid when simple perturbation theory fails. Crystal transitions which are related to very weak or forbidden molecular transitions are accurately represented by the relations derived here.

The helical polymer is considered as a special case of the molecular crystal; the optical dispersion and optical activity of the helical polymer are expressed in terms of the monomer energies, monomer moments, and the interaction between monomers. The helix term in the optical rotation, a term which is due to the helical geometry, follows directly from the use of the correct dipole selection rules with the correct expression for optical rotation. The validity of the use of periodic boundary conditions is demonstrated, and the reason for the failure of Moffitt's theory[1] to include the helix term in the optical rotation is discussed.

II. CRYSTAL EXCITONS

The model molecular crystal, which is discussed here, has one molecule per unit cell; therefore, each molecule is labeled by a lattice vector $\mathbf{l}$.

Only Frenkel excitons are discussed here. The extension of this formalism to Wannier excitons[13] has been discussed by the author[14] through the use of Wannier functions, and by Fukutome[9] through the use of Löwdin[15] orbitals.

The basis set for describing the Frenkel exciton modes of a molecular crystal is the set of HF molecular orbitals of a single molecule which is situated in the time-averaged potential field of the crystal; this basis set is divided into hole states $\{\phi_{\mathbf{l}\alpha}\}$, and electron states $\{\phi_{\mathbf{l}\mu}\}$. The basis functions are assumed to be real. The model Hamiltonian is

$$H=E_H+\sum_{\mathbf{l},A} W_A B_{\mathbf{l}A}{}^\dagger B_{\mathbf{l}A}+\sum_{\mathbf{l},\mathbf{m}}\sum_{A,B} U_{\mathbf{lm}}(AB)B_{\mathbf{l}A}{}^\dagger B_{\mathbf{m}B}$$

$$+\tfrac{1}{2}\Big[\sum_{\mathbf{l},\mathbf{m}}U_{\mathbf{lm}}(AB)B_{\mathbf{l}A}{}^\dagger B_{\mathbf{m}B}{}^\dagger+\text{H.c.}\Big], \qquad (1)$$

where

$$U_{\mathbf{lm}}(AB)=\int d^3r\int d^3r'\phi_{\mathbf{l}\mu}{}^*(\mathbf{r})\phi_{\mathbf{m}\nu}{}^*(\mathbf{r}')$$

$$\times U(\mathbf{r}',\mathbf{r})\phi_{\mathbf{m}\beta}(\mathbf{r}')\phi_{\mathbf{l}\alpha}(\mathbf{r}).$$

E_H is the N-electron HF ground-state energy and W_A is the energy of an electron-hole pair. The exciton operator $B_{\mathbf{l}A}$ has boson commutator relations.

The model Hamiltonian, Eq. (1), may be rewritten as

$$H=\sum_{\mathbf{l}} H_{\mathbf{l}}+\sum_{\mathbf{l}\neq\mathbf{m}} V_{\mathbf{lm}}. \qquad (2)$$

The one-molecule Hamiltonian $H_{\mathbf{l}}$ may be diagonalized by means of the Bogoljubov canonical transformation. A new set of exciton operators is defined as

$$B_{\mathbf{l}f}=\sum_A\,[c_{Af}B_{\mathbf{l}A}-d_{Af}B_{\mathbf{l}A}{}^\dagger]. \qquad (3)$$

The diagonalization condition is

$$[H_{\mathbf{l}},B_{\mathbf{l}f}{}^\dagger]=\Delta_f B_{\mathbf{l}f}{}^\dagger. \qquad (4)$$

This diagonalization procedure represents the mixing of different one-electron states to form one-molecule states for a molecule in the field of the crystal; this procedure is similar to the configuration interaction method commonly used in molecular-orbital theory.

The model Hamiltonian, Eq. (1), may now be expressed in terms of the one-molecule exciton operators as

$$H=\epsilon_0+\sum \Delta_f B_{\mathbf{l}f}{}^\dagger B_{\mathbf{l}f}+\sum_{\mathbf{l}\neq\mathbf{m}} V_{\mathbf{lm}}(f,g)B_{\mathbf{l}f}{}^\dagger B_{\mathbf{m}g}$$

$$+\tfrac{1}{2}\sum_{\mathbf{l}\neq\mathbf{m}}\,[V_{\mathbf{lm}}(f,g)B_{\mathbf{l}f}{}^\dagger B_{\mathbf{m}g}{}^\dagger+\text{H.c.}], \qquad (5)$$

where

$$\epsilon_0=E_H-N\sum_{Af}\Delta_f\, d_{Af}{}^2$$

and

$$V_{\mathbf{lm}}(f,g)=\sum_{AB} V_{\mathbf{lm}}(AB)(c_{Af}+d_{Af})(c_{Bg}+d_{Bg}).$$

This Hamiltonian is formally identical to that used by Agronovitch.[7] The diagonalization of the one-molecule Hamiltonian, $H_{\mathbf{l}}$, has transformed the model Hamiltonian from one-electron representation to one-molecule representation. Agronovitch[7] uses the exact states of the isolated molecule as his basis; the present theory uses functions for the molecule in the average crystal field, but with only part of the intramolecular correlation interaction included.

The one-molecule exciton operators $B_{\mathbf{l}f}$ may be combined to form crystal exciton operators with Bloch symmetry. The model Hamiltonian then may be expressed as

$$H=\epsilon_0+\sum \Delta_f B_f{}^\dagger(\mathbf{k})B_f(\mathbf{k})+\sum \Gamma_{fg}(\mathbf{k})B_f{}^\dagger(\mathbf{k})B_g(\mathbf{k})$$

$$+\tfrac{1}{2}\sum\,[\Gamma_{fg}(\mathbf{k})B_f{}^\dagger(\mathbf{k})B_g{}^\dagger(-\mathbf{k})+\text{H.c.}], \qquad (6)$$

where

$$B_f(\mathbf{k})=N^{-1/2}\sum_{\mathbf{l}} e^{-i\mathbf{k}\cdot\mathbf{l}}B_{\mathbf{l}f},$$

$$\Gamma_{fg}(\mathbf{k})=\sum_{\mathbf{h}}{}'\, V_{\mathbf{l},\mathbf{l}+\mathbf{h}}(f,g)e^{i\mathbf{k}\cdot\mathbf{h}},$$

and N is the number of molecules in the crystal.

This Hamiltonian is diagonalized by defining exciton operators which are dressed with the exciton-exciton interaction:

$$B_\rho(\mathbf{k})=\sum_f\,[\mathbf{u}_{f\rho}{}^*(\mathbf{k})B_f(\mathbf{k})-\mathbf{v}_{f\rho}{}^*(\mathbf{k})B_f{}^\dagger(-\mathbf{k})]. \qquad (7)$$

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The diagonalization condition is

$$[H,B_\rho^\dagger(\mathbf{k})]=E_\rho(\mathbf{k})B_\rho^\dagger(\mathbf{k}). \tag{8}$$

Fukutome[8] has shown that the diagonalization condition may be expressed in matrix form as an Hermitian eigenvalue problem

$$[\Delta^2+2\Delta^{1/2}\Gamma(\mathbf{k})\Delta^{1/2}]\boldsymbol{\omega}(\mathbf{k})=\boldsymbol{\omega}(\mathbf{k})\mathbf{E}^2(\mathbf{k}), \tag{9}$$

where $\boldsymbol{\omega}(\mathbf{k})$ is a unitary matrix defined as

$$\boldsymbol{\omega}(\mathbf{k})=\Delta^{1/2}[\mathbf{u}(\mathbf{k})-\mathbf{v}(\mathbf{k})]\mathbf{E}^{-1/2}(\mathbf{k}). \tag{10}$$

The crystal exciton eigenvalue equation, Eq. (9), represents the formal description of crystal exciton modes in terms of the one-molecule basis. A description of the crystal excitons in terms of the one-electron basis is found by diagonalizing the model Hamiltonian, Eq. (1), directly; the Hermitian eigenvalue equation for the one-electron basis is formally identical to Eq. (9). Fukutome[8] uses a one-electron basis, and Agronovitch[7] uses a one-molecule basis; the present theory establishes the connection between these two theories.

III. EXCITON-PHOTON INTERACTION

In this section the interaction of electromagnetic radiation with a molecular crystal is discussed in an exciton-photon formalism similar to that used by Hopfield[12] and by Agronovitch.[7]

The exciton-photon Hamiltonian is expressed in the radiation gauge as

$$\begin{aligned}H={}&E_0+\sum_{\rho,\mathbf{k}} E_\rho(\mathbf{k})B_\rho^\dagger(\mathbf{k})B_\rho(\mathbf{k})\\&+\sum_{\mathbf{q},\lambda} \hbar\omega_q a_\lambda^\dagger(\mathbf{q})a_\lambda(\mathbf{q})+\sum \Gamma_{\rho\mathbf{k}}^\lambda(\mathbf{q})[a_\lambda^\dagger(-\mathbf{q})+a_\lambda(\mathbf{q})]\\&\times[B_\rho^\dagger(\mathbf{k})-B_\rho(-\mathbf{k})]+\sum \tfrac{1}{2}\hbar\omega_q\left(\frac{\omega_0}{\omega_q}\right)^2\\&\times[a_\lambda^\dagger(\mathbf{q})a_\lambda(\mathbf{q})+a_\lambda^\dagger(\mathbf{q})a_\lambda^\dagger(-\mathbf{q})+\text{H.c.}],\end{aligned} \tag{11}$$

where $a_\lambda^\dagger(\mathbf{q})$ is a photon creation operator. The interaction coefficients are defined as

$$T_{\rho k}^\lambda(\mathbf{q})=(2\pi\hbar/\omega_q V)^{1/2}\mathbf{J}_{\rho\mathbf{k}}(\mathbf{q})\cdot\hat{\epsilon}_\lambda(\mathbf{q}), \tag{12}$$

and

$$\omega_0=(4e^2\pi N/mV)^{1/2},$$

where V is the crystal volume. The crystal current vector, $\mathbf{J}_{\rho\mathbf{k}}(\mathbf{q})$ is defined in terms of the molecular current operator in the one-molecule basis, $\mathbf{J}_{f\mathbf{l}}(\mathbf{q})$, as

$$\mathbf{J}_{\rho\mathbf{k}}(\mathbf{q})=\sum_{\mathbf{l}}\frac{e^{-i\mathbf{k}\cdot\mathbf{l}}}{N^{1/2}}\{\sum_f [u_{f\rho}^*(\mathbf{k})-v_{f\rho}^*(\mathbf{k})]\mathbf{J}_{f\mathbf{l}}(\mathbf{q})\}. \tag{13}$$

The molecular current operator is expressed in the one-electron basis as

$$\mathbf{J}_{f\mathbf{l}}(\mathbf{q})=\sum_A [c_{Af}-d_{Af}]\mathbf{J}_{A\mathbf{l}}(\mathbf{q}),$$

where

$$\mathbf{J}_{A\mathbf{l}}(\mathbf{q})=\int d^3\mathbf{r}\,\phi_{\mathbf{l}\mu}(\mathbf{r})[-(e/m)e^{i\mathbf{q}\cdot\mathbf{r}}(\hbar/i)\boldsymbol{\nabla}]\phi_{\mathbf{l}\alpha}(\mathbf{r}).$$

For a simple crystal or linear polymer, the lattice summation in Eq. (13) may be carried out:

$$\mathbf{J}_{\rho\mathbf{k}}(\mathbf{q})=\{N^{1/2}\sum_f [u_{f\rho}^*(\mathbf{k})-v_{f\rho}(\mathbf{k})]\mathbf{J}_f(\mathbf{q})\}\delta_{\mathbf{k},\mathbf{q}}, \tag{14}$$

where $\mathbf{J}_f(\mathbf{q})$ is the current matrix for the molecule with $\mathbf{l}=0$. For the helical polymer, this simple relationship does not hold[16,17]; the special case of the helical polymer is discussed in Sec. IV.

The exciton-photon Hamiltonian may be simplified as

$$\begin{aligned}H={}&E_0+\sum_{\mathbf{q}}\Big\{\sum_\rho E_\rho(\mathbf{q})B_\rho^\dagger(\mathbf{q})B_\rho(\mathbf{q})+\sum_\lambda \hbar\omega_q a_\lambda^\dagger(\mathbf{q})a_\lambda(\mathbf{q})\\&+\sum_{\lambda\rho}\Gamma_\rho^\lambda(\mathbf{q})[a_\lambda^\dagger(-\mathbf{q})+a_\lambda(\mathbf{q})][B_\rho^\dagger(\mathbf{q})-B_\rho(-\mathbf{q})]\\&+\sum_\lambda \tfrac{1}{2}\hbar\omega_q\left(\frac{\omega_0}{\omega_q}\right)^2[a_\lambda^\dagger(\mathbf{q})a_\lambda(\mathbf{q})+a_\lambda^\dagger(\mathbf{q})a_\lambda^\dagger(\mathbf{q})+\text{H.c.}]\Big\},\end{aligned} \tag{15}$$

where $T_{\rho\mathbf{q}}^\lambda(\mathbf{q})$ has been rewritten as $T_\rho^\lambda(\mathbf{q})$.

The Bogoljubov canonical transformation is used to diagonalize the exciton-photon Hamiltonian of Eq. (15). A new set of boson operators is defined as

$$\begin{aligned}\xi_i(\mathbf{q})={}&\sum_\rho [\mu_{i\rho}^*(\mathbf{q})B_\rho(\mathbf{q})-\nu_{i\rho}^*(\mathbf{q})B_\rho^\dagger(-\mathbf{q})]\\&+\sum_\lambda [u_{i\lambda}^*(\mathbf{q})a_\lambda(\mathbf{q})-v_{i\lambda}(\mathbf{q})a_\lambda^\dagger(-\mathbf{q})].\end{aligned} \tag{16}$$

The diagonalization condition is

$$[H,\xi_i^\dagger(\mathbf{q})]=\mathcal{E}_i(\mathbf{q})\xi_i^\dagger(\mathbf{q}). \tag{17}$$

The normal modes, represented by the $\xi_i^\dagger(\mathbf{q})$ operators, have been called "polaritons" by Hopfield.[12] Only the photonlike polariton modes are considered here; these are modes which represent electromagnetic waves propagating in a dispersive medium.

With the use of Eq. (17), the equations which describe the photonlike polariton modes are found to be

$$\begin{aligned}&[\mathcal{E}_i^2(\mathbf{q})-\hbar^2\omega_q^2-\hbar^2\omega_0^2]u_{i\lambda}(\mathbf{q})\\&\qquad=2\mathcal{E}_i^2(\mathbf{q})\sum_{\lambda'} g_i^{\lambda\lambda'}(\mathbf{q})u_{i\lambda'}(\mathbf{q}),\end{aligned} \tag{18}$$

where

$$g_i^{\lambda\lambda'}(\mathbf{q})=\sum_\rho\frac{2E_\rho(\mathbf{q})T_\rho^{\lambda*}(\mathbf{q})T_\rho^{\lambda'}(\mathbf{q})}{[\mathcal{E}_i^2(\mathbf{q})-E_\rho^2(\mathbf{q})]}\frac{\hbar\omega_q}{\mathcal{E}_i^2(\mathbf{q})}. \tag{19}$$

These two coupled equations represent the coupling between two polarizations of the photon field and the exciton field. The secular equation (18) is diagonalized

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[16] A. W. Luehrmann and F. M. Loxsom, J. Chem. Phys. (to be published).

[17] W. Rhodes, J. Chem. Phys. 37, 2433 (1962).

by choosing the photon polarizations in order that

$$g_i^{\lambda_1\lambda_2}(\mathbf{q})=0. \tag{20}$$

The energies of these modes are

$$\mathcal{E}_i^2(\mathbf{q})=(\hbar^2\omega_q^2+\hbar\omega_0^2)/[1-2g_i^{\lambda_i\lambda_i}(\mathbf{q})], \tag{21}$$

where $i=1, 2$. Equation (21) expresses the energies of the photonlike modes, and Eq. (20) determines their polarizations; therefore, the description of these modes is complete.

The refractive index for light propagating through a dispersive medium is defined as

$$n_i(\mathbf{q})=\hbar\omega_q/\mathcal{E}_i(\mathbf{q}); \tag{22}$$

therefore, the refractive index for the photonlike polariton modes is

$$n_i^2(\mathbf{q})=\frac{1-2g_i^{\lambda_i\lambda_i}}{1+(\omega_0/\omega_q)^2}. \tag{23}$$

The general refractive index, Eq. (23), expresses the optical dispersion of the molecular crystal. Because the exponential term is included in the interaction coefficient, the general refractive index may be used also to express the optical rotatory dispersion of molecular crystals.

IV. OPTICAL DISPERSION

If only the dipole coupling term in the interaction vector is retained, and the oscillator strength sum rule holds, then Eq. (23) may be approximated as

$$n_i^2(\mathbf{q})=1+4\pi\alpha_i^{\lambda_i\lambda_i}(\mathbf{q}). \tag{24}$$

The crystal polarizability tensor is defined as

$$\boldsymbol{\alpha}_i(\mathbf{q})=\frac{2}{V}\sum_\rho\left(\frac{E_\rho(\mathbf{q})\mathbf{P}_\rho^*(\mathbf{q})\mathbf{P}_\rho(\mathbf{q})}{E_\rho^2(\mathbf{q})-\mathcal{E}_i^2(\mathbf{q})}\right), \tag{25}$$

where $\mathbf{P}_\rho(\mathbf{q})$ is the crystal dipole moment vector. The normal-mode polarizations are defined by Eq. (20). Equation (25) may be expressed in matrix form as

$$\boldsymbol{\alpha}_i(\mathbf{q})=(2/V)\{\mathbf{P}^\dagger(\mathbf{q})\mathbf{E}(\mathbf{q})[\mathbf{E}^2(\mathbf{q})-\boldsymbol{\mathcal{E}}_i^2(\mathbf{q})]^{-1}\mathbf{P}(\mathbf{q})\}. \tag{26}$$

An equation similar to Eq. (14) relates the crystal dipole moment to the molecular dipole moment:

$$\mathbf{P}_\rho(\mathbf{q})=N^{1/2}\sum_f[u_{f\rho}^*(\mathbf{q})+v_{f\rho}^*(\mathbf{q})]\mathbf{P}_f(\mathbf{q}),$$

or, in matrix form,

$$\mathbf{P}(\mathbf{q})=N^{1/2}[\mathbf{u}^\dagger(\mathbf{q})+\mathbf{v}^\dagger(\mathbf{q})]\mathbf{P}_0. \tag{27}$$

With the aid of Eqs. (9) and (10), this relation is expressed in terms of the $\boldsymbol{\omega}(\mathbf{q})$ matrix as

$$\mathbf{P}(\mathbf{q})=N^{1/2}\mathbf{E}^{-1/2}(\mathbf{q})\boldsymbol{\omega}^\dagger(\mathbf{q})\boldsymbol{\Delta}^{1/2}\mathbf{P}_0. \tag{28}$$

If Eq. (28) is substituted into Eq. (26), then the crystal polarizability becomes

$$\boldsymbol{\alpha}_i(\mathbf{q})=(2N/V)\mathbf{P}_0^\dagger\boldsymbol{\Delta}[\boldsymbol{\Delta}^2+2\boldsymbol{\Gamma}(\mathbf{q})\boldsymbol{\Delta}-\boldsymbol{\mathcal{E}}_i^2(q)]^{-1}\mathbf{P}_0. \tag{29}$$

This equation expresses the crystal polarizability in terms of molecular energies, molecular dipole moments, and the intermolecular interaction. It is not necessary to solve any eigenvalue problem. Equation (29) is identical in form whether expressed in terms of the one-electron basis or in terms of the one-molecule basis. The one-electron basis is appropriate for a calculation of the crystal optical dispersion in terms of a computed basis set; the one-molecule basis is appropriate for a calculation in terms of experimentally observable molecular quantities. A complex polarizability may be defined by introducing a decay factor matrix into the denominator of Eq. (29).

For weak exciton-photon interaction, $\mathcal{E}_i^2(\mathbf{q})$ may be approximated as $(\hbar\omega_q)^2$ in Eq. (29); the resultant expression is similar to that found by Rhodes *et al.*[4,18] by the use of linear response theory.

The oscillator strength sum rule holds for the crystal excitons if it holds for the molecular functions. The sum of the crystal oscillator strengths is

$$\textstyle\sum_\rho \mathbf{F}_\rho(\mathbf{k})=(2m/e^2\hbar^2N)\mathbf{P}^\dagger(\mathbf{k})\mathbf{E}(\mathbf{k})\mathbf{P}(\mathbf{k}).$$

With the aid of Eq. (28) it is easy to see that

$$\mathbf{P}^\dagger(\mathbf{k})\mathbf{E}(\mathbf{k})\mathbf{P}(\mathbf{k})=N\mathbf{P}_0^\dagger\Delta\mathbf{P}_0,$$

therefore,

$$\sum_\rho\mathbf{F}_\rho(\mathbf{k})=\sum_f\mathbf{f}_f=\sum_A\mathbf{f}_A.$$

V. OPTICAL ROTATION

The formalism which was developed in the previous sections is applied here to optical rotation. For light propagating in the $\hat{\epsilon}_3$ direction, the polarization directions for left and right circularly polarized light are

$$\hat{\epsilon}_l=(1/\sqrt{2})[\hat{\epsilon}_1+i\hat{\epsilon}_2],$$

and

$$\hat{\epsilon}_r=(1/\sqrt{2})[\hat{\epsilon}_1-i\hat{\epsilon}_2].$$

The condition that l and r are the polarization directions, Eq. (20), implies that

$$g_i^{11}(\mathbf{q})=g_i^{22}(\mathbf{q})$$

and

$$\mathrm{Re}[g_i^{12}(\mathbf{q})]=0.$$

Optical rotation is defined as

$$\phi=\tfrac{1}{2}q(n_l-n_r), \tag{30}$$

and the refractive index is defined by Eq. (24); therefore

$$\phi_3(q)=(q/\bar{n})\ \mathrm{Im}[g^{12}(q)], \tag{31}$$

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[18] W. Rhodes and M. Chase, Rev. Mod. Phys. **39**, 348 (1967).

where

$$\bar{n}=\tfrac{1}{2}(n_\rho+n_r),$$

and $(\omega_0/\omega_q)^2$ has been neglected. The optical rotation is expressed in terms of the current vector by means of Eqs. (12) and (19):

$$\phi_3(q)=-\frac{4\pi\bar{n}}{c\omega_q V}\sum_\rho \operatorname{Im}\left(\frac{E_\rho[\mathbf{J}_\rho{}^*(q)\cdot\hat{\epsilon}_1][\mathbf{J}_\rho(\mathbf{q})\cdot\hat{\epsilon}_2]}{E_\rho{}^2(q)-\mathcal{E}^2(q)}\right),\quad(32)$$

where

$$\mathcal{E}(q)=\hbar\omega_q/\bar{n}.$$

Equation (32) represents the extension to crystals and polymers of a formula for the optical rotation of molecules which Stephen[19] derived by a field theoretic scattering formalism.

The current vector in Eq. (32) may be expanded in a multipole series; if only terms to first order in the crystal magnetic moment vector $\mathbf{M}_\rho(\mathbf{q})$ are retained and the rotational strength sum rule holds, the optical rotation is approximated as

$$\phi_3(q)=\operatorname{Im}\{\hat{\epsilon}_1\cdot\mathbf{\Phi}_3(q)\cdot\hat{\epsilon}_1+\hat{\epsilon}_2\cdot\mathbf{\Phi}_3(q)\cdot\hat{\epsilon}_2\},\qquad(33)$$

where the crystal optical rotation tensor is defined as

$$\Phi_3(q)=\left(\frac{4\pi N}{\hbar cv}\bar{n}\right)\mathcal{E}^2(q)\sum_\rho\frac{\mathbf{P}_\rho(q)\mathbf{M}_\rho(q)}{E_\rho{}^2(q)-\mathcal{E}^2(q)}.\qquad(34)$$

Since the dipole contribution to the refractive index is the same for the left and right circular polarizations, there is no term in Eq. (34) involving only dipole coupling. Equation (33) represents the extension to crystals and polymers of a formula for the optical rotation which Rosenfeld[20] derived by a semiclassical perturbation theory. Equation (34) may be written in matrix form as

$$\mathbf{\Phi}_3(\mathbf{q})=\left[\frac{4\pi N}{\hbar cv}\bar{n}\mathcal{E}^2(\mathbf{q})\right]\mathbf{P}^\dagger(q)[\mathbf{E}^2(q)-\boldsymbol{\mathcal{E}}^2(q)]^{-1}\mathbf{M}(q).\quad(35)$$

The crystal magnetic dipole vector is related to the molecular magnetic dipole vector by a relation similar to Eq. (32):

$$\mathbf{M}(\mathbf{q})=N^{1/2}\mathbf{E}^{1/2}(\mathbf{q})\boldsymbol{\omega}^\dagger(\mathbf{q})\mathbf{\Delta}^{-1/2}\mathbf{M}_0.\qquad(36)$$

With the use of Eqs. (9), (28), and (36), the crystal optical rotation tensor is expressed entirely in terms of the molecular moments, the molecular energies, and the intermolecular energies as

$$\Phi_3(q)=\left(\frac{4\pi N}{\hbar cv}\bar{n}\right)\mathcal{E}^2(q)\mathbf{P}_0{}^\dagger \times[\mathbf{\Delta}^2+2\mathbf{\Delta}\mathbf{\Gamma}(q)-\boldsymbol{\mathcal{E}}^2(q)]^{-1}\mathbf{M}_0.\qquad(37)$$

Equation (37) is identical in form whether expressed in terms of the one-molecule basis or the one-electron basis. A complex optical rotatory power may be defined by introducing a decay factor matrix into the denominator of Eq. (37).

The rotational strength sum rule holds for the crystal modes, if it holds for the molecular basis. The sum of the crystal rotational strengths is

$$\sum_\rho \mathbf{R}_\rho(\mathbf{k})=(1/N)\mathbf{P}^\dagger(\mathbf{k})\mathbf{M}(\mathbf{k}),$$

with the aid of Eqs. (28) and (36), it is easy to see that

$$\mathbf{P}^\dagger(k)\mathbf{M}(k)=N\mathbf{P}_0{}^\dagger\mathbf{M}_0,$$

therefore,

$$\sum_\rho \mathbf{R}_\rho(k)=\sum_f \mathbf{R}_f=\sum_A \mathbf{R}_A.$$

Equations (29) and (37) are the main results for the simple crystal and linear polymer; these relations explicitly express the crystal quantities in terms of molecular quantities without the need to solve the exciton eigenvalue problem.

VI. HELICAL POLYMER

In this section the polariton description of molecular crystal optical properties is applied to a simple model for the helical polymer. Discussions of the optical properties of the helical polymer by the use of linear response theory may be found in recent papers by Ando[5] and by Rhodes *et al.*[4,18,21]

The model helical polymer which is discussed here is composed of identical monomer units; each monomer unit is related to every other monomer by a screw operation $\{C_z(\Delta\phi)|\Delta t\}^n$. The basic screw operation is a rotation of $\Delta\phi$ about the helix axis (the z axis), followed by a nonprimitive translation Δt along the helix axis. If periodic boundary conditions are assumed, the set of screw operations is a group of symmetry operations for the helical polymer. The eigenstates of the helical polymer Hamiltonian transform according to one of the irreducible representations of the group of screw operations. More detailed discussions of the symmetry and group theory properties of the helical polymer are found in papers by Rhodes[17] and by Luehrmann and Loxsom.[16]

Because of the screw symmetry of the helical polymer, the summation relation of Eq. (14) does not hold for the helical polymer. The correct summation for the dipole moment is

$$\mathbf{P}_{\rho\mathrm{k}}(\mathbf{q})=\mathbf{P}_\rho(\mathbf{k})[\hat{\epsilon}_-\hat{\epsilon}_+\delta_{k,q_z+S}+\hat{\epsilon}_+\hat{\epsilon}_-\delta_{k,q_z-S}+\hat{\epsilon}_z\hat{\epsilon}_z\delta_{k,q_z}],\quad(38)$$

where $\mathbf{P}_\rho(k)$ is defined in Eq. (28), $S=\Delta\phi/\Delta t$, and

$$\hat{\epsilon}_\pm=(1/\sqrt{2})(\hat{\epsilon}_x\pm i\hat{\epsilon}_y).$$

Polymer transitions from the ground state to an exciton state with $k=q_z\pm S$ are polarized perpendicular to the helix axis; transitions to states with $k=q_z$ are polarized parallel to the helix axis.

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[19] J. Stephen, Proc. Cambridge Phil. Soc. **54**, 81 (1958).

[20] L. Rosenfeld, Z. Physik **52**, 161 (1928).

[21] W. Rhodes and F. M. Loxsom (unpublished).

The expressions for the polarizability of the helical polymer are very similar to Eq. (29). The helix selection rules mean that there are different values of k in the interaction matrix $\Gamma(k)$ for different polarizations.

For light propagating parallel to the helix axis, the normal-mode polarizations are left and right circular; only the transitions with $k=q\pm S$ are allowed. The small q value may be neglected for optical dispersion; therefore, the helical polymer polarizability is

$$\boldsymbol{\alpha}(q,S)=(2N/V)\mathbf{P}_0{}^{\dagger}\boldsymbol{\Delta}[\boldsymbol{\Delta}^2+2\boldsymbol{\Gamma}(S)\boldsymbol{\Delta}-\boldsymbol{\mathcal{E}}^2(q)]^{-1}\mathbf{P}_0. \quad (39)$$

For light propagating along the x axis of the helix, the normal-mode polarizations are along the z and y axes. Only the transitions with $k=0$ are allowed for the z polarization, and only transitions with $k=S$ are allowed for the x polarization. The polymer polarizability for the z-polarization direction is

$$\boldsymbol{\alpha}(q,0)=(2N/V)\mathbf{P}_0{}^{\dagger}\boldsymbol{\Delta}[\boldsymbol{\Delta}^2+2\boldsymbol{\Gamma}(0)\boldsymbol{\Delta}-\boldsymbol{\mathcal{E}}^2(q)]^{-1}\mathbf{P}_0. \quad (40)$$

If the Rosenfeld formula, Eq. (34), is applied to the helical polymer, the optical rotation is similar in form to Eq. (37). For light propagating parallel to the helix axis, the optical rotation is

$$\phi_z(q)=2\,\mathrm{Im}\{\hat{\epsilon}_-\cdot\boldsymbol{\Phi}(q,S)\cdot\hat{\epsilon}_+\}, \quad (41)$$

where

$$\boldsymbol{\Phi}(q,k)=[(4\pi N/\hbar cv)\bar{n}]\mathcal{E}^2(q)\mathbf{P}_0{}^{\dagger}\times[\boldsymbol{\Delta}^2+2\boldsymbol{\Delta}\boldsymbol{\Gamma}(k)-\boldsymbol{\mathcal{E}}^2(q)]^{-1}\mathbf{M}_0. \quad (42)$$

For light propagating perpendicular to the helix axis, there is a term proportional to ρ, the radial displacement of the center of a monomer from the helix axis[22]; the term is due to the shift of the magnetic dipole from the helix axis to the monomer center. For light propagating perpendicular to the helix, the optical rotation is

$$\phi_\perp(q)=\mathrm{Im}\{\hat{\epsilon}_+\cdot\boldsymbol{\Phi}(q,S)\cdot\hat{\epsilon}_-\}+\mathrm{Im}\{\hat{\epsilon}_z\cdot\boldsymbol{\Phi}(q,0)\cdot\hat{\epsilon}_z\}$$
$$+\frac{2\pi\bar{n}}{\hbar^2c^2}\mathcal{E}^2(q)\,\mathrm{Im}\{(\boldsymbol{\varrho}\cdot\hat{\epsilon}_-)\hat{\epsilon}_+\cdot[\boldsymbol{\alpha}(q,0)-\boldsymbol{\alpha}(q,S)]\cdot\hat{\epsilon}_z\}, \quad (43)$$

where $\boldsymbol{\Phi}(q,k)$ is defined in Eq. (44), and $\boldsymbol{\alpha}(q,k)$ is defined by Eqs. (39) and (40).

There is an additional term in the optical rotation of the helical polymer which is not indicated in the expressions for the linear systems. The reduction of Eq. (32) to (33) is not valid for the helical polymer, because the term which involves only dipole coupling is not zero. This additional term is called the helix term, or the exciton term. In two recent papers,[22,23] the author has shown that this term arises solely from the helical symmetry, and is not an effect of a particular theoretical model.

Consider the case of light propagating along the helix axis. The modes with $k=q+S$ and $k=q-S$ are polarized left and right, respectively. The dipole part of the refractive index is different for left and right polarizations because of the k dependence of the interaction matrix $\Gamma(k)$. Optical rotation is proportional to the difference between the polarizabilities for left and right polarizations; therefore, the helix term in the optical rotation is

$$\phi_h(q)=\left(\frac{2\pi\mathcal{E}^2}{\hbar^2c^2}\bar{n}\right)\frac{1}{2q}\hat{\epsilon}_+\cdot[\boldsymbol{\alpha}(q,\,S+q)-\boldsymbol{\alpha}(q,\,S-q)]\cdot\hat{\epsilon}_-. \quad (44)$$

Equation (44) may be approximated as a derivative:

$$\phi_h(q)=\left(\frac{2\pi}{\hbar^2c^2}\bar{n}\right)\mathcal{E}^2(q)\frac{\partial}{\partial k}[\hat{\epsilon}_+\cdot\boldsymbol{\alpha}(q,k)\cdot\hat{\epsilon}_-]\bigg|_S. \quad (45)$$

For light propagating perpendicular to the helix axis, Eq. (45) gives a zero value for the helix term; therefore, for a randomly oriented solution of helical polymers, the helix term is one-third of that in Eq. (45).

Moffitt,[1] in a classic paper, used simple exciton theory to describe the optical rotation of the helical polymer. Moffitt, Fitts, and Kirkwood[24] criticized the early Moffitt theory because the helix term in the optical rotation was omitted; this missing helix term was found only by abandoning periodic boundary conditions. However, it has been shown here that by using Eq. (32) rather than Eq. (33), the helix term is retained for a periodic model of the helix. Moffitt used Eq. (33), the Rosenfeld formula for optical rotation; therefore, he naturally omitted the helix term in the optical rotation. The use of periodic boundary conditions is quite valid if Eq. (32), Stephen's formula, is used to describe the optical rotation of the helical polymer.

VII. DISCUSSION

A nonperturbational theory of the exciton modes of a molecular crystal has been used to describe optical dispersion and optical activity. The optical properties of the crystal are expressed in terms of molecular moments, molecular energies, and the intermolecular interaction; it is not necessary to solve the exciton eigenvalue equation.

The model Hamiltonian is appropriate for weakly interacting molecules; however, since the model Hamiltonian is diagonalized exactly, the theory developed here may be useful for strong intermolecular interaction. For weakly interacting molecules, this theory is preferable to a perturbation treatment. For weakly allowed or forbidden transitions, first-order perturbation treatments are inadequate for a description of the crystal optical properties; it is necessary to include higher-order terms in the perturbation expansion. The nonperturbational theory accurately represents intensities of crystal transitions which arise from weakly allowed or forbidden molecular transitions.

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[22] F. M. Loxsom, J. Chem. Phys. **51**, 4899 (1969).

[23] F. M. Loxsom, Int. J. Quantum Chem., Symposium No. 3, Interscience (1969).

[24] W. Moffitt, D. Fitts, and J. G. Kirkwood, Proc. Natl. Acad. Soc. (U. S.) **43**, 723 (1957).

The form of the crystal polarizability and optical rotation tensors, Eqs. (29) and (37), are the same for both the one-molecule and one-electron basis sets. The one-electron basis set, which has been discussed here, has the average crystal field included in its defining equation. If the crystal field is approximated in the same way as the correlation interaction has been, then a set of molecular orbitals for an isolated molecule may be used as a basis for expressing Eqs. (29) and (37); the crystal-field interaction is included in the interaction matrix. The set of molecular orbitals represents the simplest computed basis set for a calculation of the optical properties of a molecular crystal or polymer.

The approximation of the intermolecular interaction as a dipole-dipole coupling is represented by

$$\Gamma(\mathbf{q})=\mathbf{P}_0\cdot\mathbf{d}(\mathbf{q})\cdot\mathbf{P}_0{}^{\dagger},$$

where

$$\mathbf{d}(\mathbf{q})=\sum_{\mathbf{h}}\mathbf{d}(\mathbf{h})e^{i\mathbf{q}\cdot\mathbf{h}},$$

and $\mathbf{d}(\mathbf{h})$ is the dipole interaction tensor between molecules separated by $\mathbf{h}$. Rhodes *et al.*[4,18] have shown that, with the use of the dipole approximation, the crystal polarizability may be expressed in terms of the molecular polarizability; the crystal optical rotation may be expressed in terms of the molecular optical rotation tensor also.

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Selection Rules for Anharmonic Interactions of Nearest Neighbors in Crystals with the Zinc Blende or Diamond Structure

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Selection rules are derived for multiple-phonon processes which are dominated by anharmonic interactions between nearest-neighbor lattice particles. These nearest-neighbor selection rules (NSR) are different from and supplementary to the usual group-theoretical selection rules. NSR for wave vectors at X or L are expressed in Born's (NSRB) and in Keating's (NSRK) formalism. The NSRB refer to anharmonic two-particle interactions; the NSRK allow interactions between two or more particles. The applicability of the NSR to various multiple-phonon processes—with emphasis on infrared two-phonon absorption—is investigated and the results of some relevant model calculations are given. Practical rules for further applications are proposed.

1. INTRODUCTION

We shall present a new type of selection rules for multiple-phonon interactions in crystals of the zinc-blende or diamond structure. These rules supplement the usual group-theoretical selection rules, and specify conditions under which anharmonic interactions between nearest-neighbor particles vanish.

Selection rules are commonly formulated for simple interaction expressions. If such an expression approximates a real interaction sufficiently well, then a forbidden (approximate) interaction will correspond to a real process of weak intensity. Infrared multiple-phonon absorption, for example, if forbidden by the group-theoretical selection rules (GSR) in the electric dipole approximation,[1] is extremely weak for all cases of practical interest.

The nearest-neighbor selection rules (NSR) to be derived here[2] are based on certain assumptions referring to the form of the anharmonic interactions and the magnitudes of the harmonic amplitudes. These assumptions, and the neglect of the contributions of higher-order neighbors to the anharmonicities, represent approximations to the situation in real materials. From our present state of knowledge we can suggest where and to what degree these approximations should be satisfied, but the validity of these approximations is not as well established as that for the GSR. If an interaction is forbidden by the NSR and the related real process is found

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[1] J. L. Birman, Phys. Rev. **131**, 1489 (1963).

[2] Some of the material of the present paper is discussed in greater detail in the following Foundational Research Projects Quarterly Reports: Naval Ordnance Laboratory Corona Report No. 688, p. 35, 1966 (unpublished); No. 705, p. 37, 1966 (unpublished); and No. 715, p. 39, 1967 (unpublished); Naval Ordnance Laboratory, Corona, California, and Naval Weapons Center Corona Laboratories Report No. TP 756, p. 9, 1968 (unpublished). These publications, hereafter referred to as N1, N2, N3, and N4, respectively, are available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151, where they are listed as AD-645980, AD-651544, AD-655889, and AD-830635.