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## Dispersive Contribution to the Cohesive Energy of an Optically Active Crystal

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The second-quantization method of Hopfield and Mahan for the calculation of the van der Waals energies in solids is extended to the case where the molecules of the solid are optically active. The crystal energy of cohesion is computed by taking the difference of the zero-point energies of the crystal with and without the intermolecular interactions and is written in terms of an integral of a response function at imaginary frequencies. A part of the energy is shown to be proportional to the optical rotatory strengths of the molecules. The leading term that discriminates between enantiomeric interactions is the same as that obtained by summation of the two-body potential found by Craig, Power, and Thirunamachandran. Finally, this discriminating energy is expressed as an integral over the optical rotation angles at imaginary frequencies.

### I. INTRODUCTION

In a recent paper, Craig, Power, and Thirunamachandran<sup>1</sup> have investigated the interactions between optically active molecules in crystals using the perturbation method. They showed that the interaction between one dextro- and another dextro-molecule is different from a dextro- and a laevo-molecule. This difference arises in part from the fact that transitions from the ground to excited states are both electrically and magnetically allowed. Thus the energy expression includes electric as well as magnetic dipolar coupling terms.

In the present paper, we supplement the earlier work by adopting an alternative viewpoint following Hopfield<sup>2</sup> and Mahan.<sup>3</sup>

The low-energy excited states of a molecular crystal are called exciton states and the existence of such states has been demonstrated experimentally for a number of systems. For such crystals the dispersion forces form an important contribution to the binding energy and it was pointed out by Hopfield that the dispersion energy may be interpreted as the decrease in zero-point energy of excitons due to dipolar interactions. This viewpoint was further developed by Mahan, who obtained an ex-

pression for the zero-point energy in a closed form. In this paper, we extend his approach to interactions in optically active crystals. Optical activity in a crystal may either arise because of a dissymmetric packing as in silica or the molecules themselves may be intrinsically dissymmetric. We confine our attention to the latter class.

## II. THEORY

### A. Hamiltonian and Two-Body Potential

Let us consider a crystal with one molecule per unit cell. In the dipole-dipole approximation for the intermolecular coupling, the total Hamiltonian is given by

$$H = \sum_{\vec{L}} H_{\vec{L}} + \frac{1}{2} \sum_{\vec{L} \neq \vec{L}'} \mu_{\vec{L}}^{\vec{L}} \phi_{ij}(\vec{L} - \vec{L}') \mu_{\vec{L}'}^{\vec{L}'} + \frac{1}{2} \sum_{\vec{L} \neq \vec{L}'} m_{\vec{L}}^{\vec{L}} \phi_{ij}(\vec{L} - \vec{L}') m_{\vec{L}'}^{\vec{L}'}, \quad (2.1)$$

where

$$\phi_{ij}(\vec{R}) = (\delta_{ij} - 3\hat{R}_i\hat{R}_j)/R^3.$$

$H_{\vec{L}}$  is the Hamiltonian for the free molecule at lattice site  $\vec{L}$ ;  $\vec{\mu}^{\vec{L}}$  and  $\vec{m}^{\vec{L}}$  are electric and magnetic dipole moment operators defined by

$$\vec{\mu}^{\vec{L}} = e \sum_{\vec{n}} \vec{r}_{\vec{n}}^{\vec{L}}, \quad \vec{m}^{\vec{L}} = (e/2mc) \sum_{\vec{n}} \vec{r}_{\vec{n}}^{\vec{L}} \times \vec{p}_{\vec{n}}^{\vec{L}}. \quad (2.2)$$

In (2.2), the summation is over the optical electrons of the molecule at lattice site  $\vec{L}$ . We emphasize that the essential difference between the models for dielectric crystals and optically active crystals is the presence of the additional magnetic dipole coupling term in (2.1). With a Hamiltonian similar to (2.1) for two molecules as the starting point in our previous paper,<sup>1</sup> the intermolecular energy was deduced using second-order perturbation theory. The resulting dispersion potential between two molecules ( $a$ ) and ( $b$ ) included a term (2.3) discriminating between enantiomers:

$$V_{\text{disc-disp}}(R) = \frac{-2[\cos\gamma - 3\cos\theta(a)\cos\theta(b)]}{R^6(E_{n(a)} + E_{n(b)})} \times \text{Re}[c^{||,||}R^{||}(a)R^{||}(b) + c^{||,\perp}R^{||}(a)R^{\perp}(b) + c^{\perp,||}R^{\perp}(a)R^{||}(b) + c^{\perp,\perp}R^{\perp}(a)R^{\perp}(b)], \quad (2.3)$$

where

$$R^{||} = \vec{\mu} \cdot \vec{m} = \mu m \cos\alpha, \quad R^{\perp} = |\vec{\mu} \times \vec{m}| = \mu m \sin\alpha$$

are related to optical rotatory strengths of the molecules and the  $c$ 's are geometrical factors depending on the orientations of the molecule in the crystal.  $\Theta(a)$  and  $\Theta(b)$  are the polar angles of the electric moments and  $\gamma$  is the angle between the transition-moment vectors;  $\alpha$  is the angle between  $\vec{\mu}$  and  $\vec{m}$ . The energy (2.3) is in addition to the two-molecule van der Waals energy arising from the electric dipole energy which is given by

$$V_{\text{disp}}(R) = - \frac{\mu_i^{n(a)} \mu_j^{n(a)} \mu_k^{n(b)} \mu_l^{n(b)}}{R^6(E_{n(a)} + E_{n(b)})} c_{ijkl}. \quad (2.4)$$

A term similar to (2.4) but involving magnetic transition moments also occurs. It is very small and will be neglected in our treatment. In Eqs. (2.3) and (2.4),  $E_{n(a)}$  and  $E_{n(b)}$  are the transition energies for transitions from the ground state to dipole accessible states  $n(a)$  and  $n(b)$ . To obtain the total energy, (2.3) and (2.4) have to be summed over  $n(a)$  and  $n(b)$ , noting that the geometrical factors  $c$  are level dependent. Finally, the total crystal energy obtained in this way by second-order perturbation theory is

$$U_{\text{cryst}}^{(2)} = -\frac{1}{2} \sum_{\substack{n(\vec{L}), n(\vec{L}') \\ \vec{L} \neq \vec{L}'}} [V_{\text{disp}}(\vec{L} - \vec{L}') + V_{\text{disc-disp}}(\vec{L} - \vec{L}')]. \quad (2.5)$$

In the boson-exciton model of Hopfield,<sup>2</sup> the Hamiltonian (2.1) can be completely diagonalized and we obtain the exact energy in the form of an integral. This form for the energy gives (2.5) as the leading term in a perturbation expansion of the integrand. This is demonstrated in Sec. III. In the remainder of this section, we derive the integral expression for the total energy.

### B. SECOND-QUANTIZATION AND EIGENVALUE EQUATION

Following Hopfield, we rewrite (2.1) in terms of creation and annihilation operators  $b_{\vec{k}n}^{\dagger}$ ,  $b_{\vec{k}n}$  for excitons. The collective exciton states behave as bosons if only a small number of states are excited. Thus the  $b$  operators obey the commutation rules

$$[b_{\vec{k}n}, b_{\vec{k}'n'}^{\dagger}] = \delta_{\vec{k}\vec{k}'} \delta_{nn'}, \quad (2.6a)$$

$$[b_{\vec{k}n}, b_{\vec{k}'n'}] = 0. \quad (2.6b)$$

$H$  is now written explicitly as

$$H = \sum_{\vec{k}, n} \hbar\omega_n b_{\vec{k}n}^{\dagger} b_{\vec{k}n} + \frac{1}{2} \sum_{\substack{n, n' \\ \vec{k}}} [b_{\vec{k}n} b_{-\vec{k}n'} \langle 0 | \mu^i | n \rangle \langle 0 | \mu^j | n' \rangle + \langle 0 | m^i | n \rangle \langle 0 | m^j | n' \rangle] + b_{\vec{k}n}^{\dagger} b_{-\vec{k}n'} \langle n | \mu^i | 0 \rangle \langle n' | \mu^j | 0 \rangle + \langle n | m^i | 0 \rangle \langle n' | m^j | 0 \rangle + b_{\vec{k}n}^{\dagger} b_{\vec{k}n'}^{\dagger} \langle 0 | \mu^i | n \rangle \langle n' | \mu^j | 0 \rangle + \langle 0 | m^i | n \rangle \langle n' | m^j | 0 \rangle + b_{\vec{k}n}^{\dagger} b_{\vec{k}n'}^{\dagger} \langle n | \mu^i | 0 \rangle \langle 0 | \mu^j | n' \rangle + \langle n | m^i | 0 \rangle \langle 0 | m^j | n' \rangle] T_{ij}(\vec{k}), \quad (2.7)$$

where

$$T_{ij}(\vec{k}) = \sum_{\Gamma \neq 0} e^{i\vec{k} \cdot \vec{\Gamma}} (\delta_{ij} - 3\hat{L}_i \hat{L}_j) / L^3.$$

Since the molecules are identical, their common spectra are simply labeled  $\omega_n$ , and the matrix elements  $\langle 0 | \mu^i | n \rangle$ ,  $\langle 0 | m^i | n \rangle$  are independent of lattice site. The Hamiltonian (2.7) may be rewritten as

$$\begin{aligned} H = & \sum_{\vec{k}, n} \hbar \omega_n b_{\vec{k}n}^\dagger b_{\vec{k}n} \\ & + \sum_{\substack{n, n' \\ \vec{k}}} \hbar A_{\vec{k}nn'} (b_{\vec{k}n} b_{-\vec{k}n'} + b_{\vec{k}n}^\dagger b_{-\vec{k}n'}^\dagger) \\ & + \sum_{\substack{n, n' \\ \vec{k}}} \hbar C_{\vec{k}nn'} (b_{\vec{k}n} b_{\vec{k}n'}^\dagger + b_{\vec{k}n}^\dagger b_{\vec{k}n'}), \end{aligned} \quad (2.8)$$

where

$$\begin{aligned} A_{\vec{k}nn'} = & \frac{1}{2} (\langle 0 | \mu^i | n \rangle \langle 0 | \mu^j | n' \rangle \\ & + \langle 0 | m^i | n \rangle \langle 0 | m^j | n' \rangle) T_{ij}(\vec{k}) / \hbar, \\ C_{\vec{k}nn'} = & \frac{1}{2} (\langle 0 | \mu^i | n \rangle + \langle 0 | \mu^j | n' \rangle \\ & + \langle n | m^i | 0 \rangle + \langle 0 | m^j | n' \rangle) T_{ij}(\vec{k}) / \hbar. \end{aligned} \quad (2.9)$$

Without loss of generality we may choose wave functions so that the electric and magnetic transition dipole matrix elements are real and imaginary, respectively. With such a choice it follows that

$$\begin{aligned} E_{nn'}(\vec{k}) = & A_{\vec{k}nn'} + C_{\vec{k}nn'} \\ = & \langle 0 | \mu^i | n \rangle \langle 0 | \mu^j | n' \rangle T_{ij}(\vec{k}) / \hbar, \\ M_{nn'}(\vec{k}) = & C_{\vec{k}nn'} - A_{\vec{k}nn'} \\ = & -\langle 0 | m^i | n \rangle \langle 0 | m^j | n' \rangle T_{ij}(\vec{k}) / \hbar. \end{aligned} \quad (2.10)$$

We note that  $A = C$ , i. e.,  $M = 0$ , corresponds to Mahan's case of dielectric.<sup>3</sup> A complete diagonalization of (2.7) is possible even if  $A \neq C$ , and the diagonalized Hamiltonian may be written as

$$\frac{1}{2} \sum_{\lambda, \vec{k}} \hbar \omega_\lambda (\vec{k}) (B_{\vec{k}\lambda}^\dagger B_{\vec{k}\lambda} + B_{\vec{k}\lambda} B_{\vec{k}\lambda}^\dagger) - \frac{1}{2} \sum_{n, \vec{k}} \hbar \omega_n, \quad (2.11)$$

where  $B_{\vec{k}\lambda}$ ,  $B_{\vec{k}\lambda}^\dagger$  are boson operators linearly dependent on the  $b_{\vec{k}n}$ ,  $b_{-\vec{k}n}^\dagger$  and  $b_{\vec{k}n}^\dagger$ ,  $b_{-\vec{k}n}$ , respectively, using a Bogolyubov-type transformation. This is defined by

$$\begin{aligned} B_{\vec{k}\lambda} = & \frac{1}{2} \sum_n (D_{\lambda n} + F_{\lambda n}) b_{\vec{k}n} + \frac{1}{2} \sum_n (F_{\lambda n} - D_{\lambda n}) b_{-\vec{k}n}^\dagger, \\ B_{\vec{k}\lambda}^\dagger = & \frac{1}{2} \sum_n (D_{\lambda n} + F_{\lambda n}) b_{\vec{k}n}^\dagger + \frac{1}{2} \sum_n (F_{\lambda n} - D_{\lambda n}) b_{-\vec{k}n}, \end{aligned} \quad (2.12)$$

where the matrices  $D$  and  $F$ , both real, have to be suitably chosen to diagonalize (2.8) and also to en-

sure that the  $B$ 's obey the commutation relations

$$[B_{\vec{k}\lambda}, B_{\vec{k}'\lambda'}^\dagger] = \delta_{\vec{k}\vec{k}'} \delta_{\lambda\lambda'}, \quad (2.13a)$$

$$[B_{\vec{k}\lambda}, B_{\vec{k}'\lambda'}] = 0. \quad (2.13b)$$

The substitution of (2.12) into (2.11) leads to an eigenvalue equation for the  $\omega_\lambda(\vec{k})$ 's, which are the frequencies of the boson modes with operators  $B_{\vec{k}\lambda}$ . To demonstrate the result of the transformation (2.12) we give the results of substitution of (2.12) both in the commutation relations (2.13) and in the Hamiltonian (2.11). First, using (2.13a) with  $\vec{k} = \vec{k}'$ , we find

$$\frac{1}{2} \sum_n (D_{\lambda n} F_{\lambda n} + F_{\lambda n} D_{\lambda n}) = \delta_{\lambda\lambda'}. \quad (2.14)$$

Second, using (2.13b) with  $\vec{k} = -\vec{k}'$ , we get

$$\frac{1}{2} \sum_n (D_{\lambda n} F_{\lambda n} - F_{\lambda n} D_{\lambda n}) = 0. \quad (2.15)$$

Adding (2.14) to (2.15), we obtain

$$\sum_n D_{\lambda n} F_{\lambda n} = \delta_{\lambda\lambda'}. \quad (2.16)$$

We now follow the transformation (2.12) on the Hamiltonian. The Hamiltonians (2.8) and (2.11) are equivalent; so on substituting (2.12) into (2.11) and equating the coefficients of the  $b$  operator products we obtain

$$\sum_\lambda \omega_\lambda D_{\lambda n} D_{\lambda n'} = \delta_{nn'} \omega_n + 2M_{nn'}(\vec{k}), \quad (2.17)$$

$$\sum_\lambda \omega_\lambda F_{\lambda n} F_{\lambda n'} = \delta_{nn'} \omega_n + 2E_{nn'}(\vec{k}). \quad (2.18)$$

The relationship (2.16) enables us to reduce (2.17) and (2.18) to linear equations in  $F$ 's and  $D$ 's. In particular, multiplying (2.17) by  $F_{\lambda'n'}$  and summing over  $n'$ , we find

$$\sum_\lambda \omega_\lambda D_{\lambda n} \delta_{\lambda\lambda'} = \omega_n F_{\lambda'n} + 2 \sum_{n'} F_{\lambda'n'} M_{nn'}(\vec{k}),$$

which reduces to

$$D_{\lambda n} = \frac{\omega_n}{\omega_\lambda} F_{\lambda n} + \frac{2}{\omega_\lambda} \sum_{n'} F_{\lambda n'} M_{nn'}(\vec{k}). \quad (2.19)$$

Similarly, (2.18) yields

$$F_{\lambda n} = \frac{\omega_n}{\omega_\lambda} D_{\lambda n} + \frac{2}{\omega_\lambda} \sum_{n'} D_{\lambda n'} E_{nn'}(\vec{k}). \quad (2.20)$$

It is instructive to note the symmetry in the relationships (2.19) and (2.20), which is not apparent in the case of a dielectric where  $M_{nn'} = 0$ . In the dielectric calculation  $D_{\lambda n}$  and  $F_{\lambda n}$  are multiples of each other. Finally, to obtain the eigenvalue equation for  $\omega_\lambda$  we eliminate  $F_{\lambda n}$  between (2.19) and (2.20). This gives

$$(\omega_\lambda^2 - \omega_n^2) D_{\lambda n} = 2 \sum_{n'} D_{\lambda n'} W_{nn'}(\vec{k}), \quad (2.21)$$

where

$$W_{nn'}(\vec{k}) = \omega_n E_{n'n}(\vec{k}) + \omega_{n'} M_{nn'}(\vec{k})$$

$$+ 2 \sum_{n''} E_{n''n'}(\vec{k}) M_{nn''}(\vec{k}) .$$

Equation (2.21) may be rearranged to the form

$$\sum_n \left( \delta_{nn'} + \frac{2 W_{nn'}(\vec{k})}{\omega_n^2 - \omega_{\lambda'}^2} \right) D_{\lambda n'} = 0 . \quad (2.22)$$

An alternative derivation of the eigenvalue equation (2.22) is possible using the Heisenberg equations of motion for the boson operators  $b_{\vec{k}n}$  and  $B_{\vec{k}\lambda}$ .

### C. Crystal Energy

From (2.11) the total crystal energy is given as

$$\sum_{\vec{k}} \left[ \sum_{\lambda} \frac{1}{2} \hbar \omega_{\lambda}(\vec{k}) - \sum_n \frac{1}{2} \hbar \omega_n \right] . \quad (2.23)$$

This is the sum over the  $\vec{k}$  modes of the difference between the zero-point energy of the coupled exciton modes of frequency  $\omega_{\lambda}$  and the uncoupled exciton modes of frequency  $\omega_n$ . The frequencies  $\omega_n$  are considered as given, while  $\omega_{\lambda}$  are determined by the eigenvalue equation (2.22). To evaluate (2.23) we use a contour integral method analogous to that of Maradudin, Montroll, and Weiss<sup>4</sup> in lattice vibration calculations. If  $D_{\lambda n'}$  is considered as a column vector labeled by  $n'$ , then (2.22) is equivalent to

$$[I_{nn'} + R_{nn'}(\vec{k}, \omega_{\lambda})] D_{\lambda n'} = 0 , \quad (2.24)$$

where  $I$  is the unit matrix and

$$R_{nn'}(\vec{k}, \omega) = 2 W_{nn'}(\vec{k}) / (\omega_n^2 - \omega^2) . \quad (2.25)$$

Equation (2.24) has a nontrivial solution if and only if

$$\det[I_{nn'} + R_{nn'}(\vec{k}, \omega_{\lambda})] = 0 , \quad (2.26)$$

and the roots of

$$\Delta(\vec{k}, \omega) = \det[I_{nn'} + R_{nn'}(\vec{k}, \omega)] = 0 \quad (2.27)$$

are the eigenfrequencies  $\omega_{\lambda}$ .  $\Delta(\vec{k}, \omega)$  has poles at  $\omega = \omega_n$  and zeros at  $\omega = \omega_{\lambda}$ . We now consider the contour integral

$$\frac{1}{2\pi i} \int_C \phi(z) \frac{df(z)}{dz} \frac{1}{f(z)} dz = \sum_a \phi(a) - \sum_b \phi(b) , \quad (2.28)$$

where  $a$ 's and  $b$ 's are zeros and poles, respectively, of  $f(z)$  inside  $C$  and  $\phi(z)$  is analytic inside and on  $C$ . This is applied to the function  $\phi(z) = z$  and  $f(z) = \Delta(\vec{k}, z)$ , and  $C$  is the infinite semicircle in the right half-plane  $\omega_n > 0$ ,  $\omega_{\lambda} > 0$ . Then, we have

$$\sum_{\lambda} \omega_{\lambda} - \sum_n \omega_n = \frac{1}{2\pi i} \int_C z \frac{d\Delta(\vec{k}, z)}{dz} \frac{1}{\Delta(\vec{k}, z)} dz$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} \ln \Delta(\vec{k}, iy) dy \quad (2.29)$$

if the contribution over the large semicircle vanishes. Now, we have

$$\ln \det(I + R) = \text{Tr} \ln(I + R) , \quad (2.30)$$

and so the crystal energy is

$$\mathcal{E}_{\text{cryst}} = \sum_{\vec{k}} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} \text{Tr} \ln[I + R(\vec{k}, iy)] dy . \quad (2.31)$$

In the straightforward case of only one level ( $n$ ) being active, (2.31) reduces to

$$\mathcal{E}_{\text{cryst}} = \sum_{\vec{k}} \frac{1}{2} \hbar [ (2W_{nn} + \omega_n^2)^{1/2} - \omega_n ] . \quad (2.32)$$

### III. APPROXIMATE ENERGY BY PERTURBATION THEORY

In nonpolar molecular crystals the binding energies are small and a perturbation approach to the evaluation of Eq. (2.31) for the crystal energy is appropriate. This is independent of the number of levels involved since all matrix elements are small. Therefore, the  $R$  matrix can be taken to be small compared with  $I$ , and we may expand  $\ln(I + R)$  to any desired order. Retaining terms up to second order in  $R$ , we get

$$\begin{aligned} \mathcal{E}_{\text{cryst}} &\approx \sum_{\vec{k}} \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} \text{Tr} (R - \frac{1}{2} R^2) dy \\ &= \frac{\hbar}{2\pi} \sum_{\vec{k}} \int_{-\infty}^{\infty} \left( \sum_n \frac{W_{nn}(\vec{k})}{\omega_n^2 + y^2} \right. \\ &\quad \left. - \sum_{n, n'} \frac{W_{nn'}(\vec{k}) W_{n'n}(\vec{k})}{(\omega_n^2 + y^2)(\omega_{n'}^2 + y^2)} \right) dy . \end{aligned} \quad (3.1)$$

Integrating over  $y$  and using

$$\int_{-\infty}^{\infty} \frac{dy}{(\omega_n^2 + y^2)(\omega_{n'}^2 + y^2)} = \frac{\pi}{(\omega_n + \omega_{n'})\omega_n\omega_{n'}} ,$$

when  $\omega_n, \omega_{n'} > 0$ , we have

$$\mathcal{E}_{\text{cryst}} = \frac{\hbar}{2} \sum_{\vec{k}} \left( \sum_n \frac{W_{nn}(\vec{k})}{\omega_n} - \sum_{n, n'} \frac{W_{nn'}(\vec{k}) W_{n'n}(\vec{k})}{\omega_n \omega_{n'} (\omega_n + \omega_{n'})} \right) . \quad (3.2)$$

Substituting for  $W_{nn}$ , in terms of the matrix elements  $E$  and  $M$ , as in Eqs. (2.21) and (2.22), we find

$$\mathcal{E}_{\text{cryst}} = \frac{\hbar}{2} \sum_{\vec{k}} \left( \sum_{n, n'} \frac{2}{\omega_n} E_{nn'}(\vec{k}) M_{nn'}(\vec{k}) - \sum_{n, n'} \frac{[\omega_n E_{n'n}(\vec{k}) + \omega_{n'} M_{nn'}(\vec{k})][\omega_n E_{nn'}(\vec{k}) + \omega_{n'} M_{n'n}(\vec{k})]}{\omega_n \omega_{n'} (\omega_n + \omega_{n'})} \right) . \quad (3.3)$$

To obtain (3.3) we have used the fact that

$$\sum_{\vec{k}} E_{nn}(\vec{k}) = \sum_{\vec{k}} M_{nn}(\vec{k}) = 0,$$

thus accounting for the absence of the terms linear in  $E$  and  $M$ ; we have also neglected terms of fifth or higher order in the matrix elements. The expression for the crystal energy (3.3) divides naturally into three parts:

$$\begin{aligned} \mathcal{E}_{\text{cryst}} = & -\frac{\hbar}{2} \sum_{\vec{k}} \sum_{n,n'} \frac{E_{n'n}(\vec{k}) E_{nn'}(\vec{k})}{\omega_n + \omega_{n'}} \\ & -\frac{\hbar}{2} \sum_{\vec{k}} \sum_{n,n'} \frac{M_{nn'}(\vec{k}) M_{n'n}(\vec{k})}{\omega_n + \omega_{n'}} \\ & + \hbar \sum_{\vec{k}} \sum_{n,n'} \frac{E_{nn'}(\vec{k}) M_{n'n}(\vec{k})}{\omega_n + \omega_{n'}}. \end{aligned} \quad (3.4)$$

The first term gives the electrostatic dispersion energy of the crystal and, as shown by Mahan,<sup>3</sup> is the sum of the two-molecule van der Waals energy over all pairs in the crystal. The second term in (3.4) is an analogous term due to magnetic polarization and will always be very small compared with the electric energy. Our interest lies in the third term of (3.4), which depends on both the electric and magnetic dipole matrix elements of the constituent molecules. It is easy to express this contribution to the energy in terms of a sum over pairs of molecules of a two-molecule interaction involving the optical rotatory pseudotensor  $R_{ij}^0 = \langle 0 | \mu_i | n \rangle \langle n | m_j | 0 \rangle$ , whose trace is the optical rotatory strength of the molecule. The  $\vec{k}$  sum can be performed for this term exactly as for the term involving polarizability. We have

$$\begin{aligned} \sum_{\vec{k}} T_{ij}(\vec{k}) T_{\sigma\tau}(\vec{k}) \\ = \sum_{\vec{L}, \vec{L}', \vec{k}} e^{i\vec{k} \cdot (\vec{L} - \vec{L}')} \frac{(\delta_{ij} - 3\hat{L}_i \hat{L}_j)(\delta_{\sigma\tau} - 3\hat{L}'_\sigma \hat{L}'_\tau)}{L^3 L'^3} \end{aligned}$$

$$= N \sum_{\vec{L} \neq 0} \frac{(\delta_{ij} - 3\hat{L}_i \hat{L}_j)(\delta_{\sigma\tau} - 3\hat{L}'_\sigma \hat{L}'_\tau)}{L^6}, \quad (3.5)$$

where  $N$  is the total number of molecules in the crystal.

Thus we have

$$\begin{aligned} \hbar \sum_{n,n'} \sum_{\vec{k}} \frac{E_{nn'}(\vec{k}) M_{n'n}(\vec{k})}{\omega_n + \omega_{n'}} \\ = -N \sum_{n,n'} \sum_{\vec{L} \neq 0} \frac{\langle 0 | \mu^i | n \rangle \langle 0 | \mu^j | n \rangle \langle n | m^\sigma | 0 \rangle \langle n' | m^\tau | 0 \rangle}{\hbar \omega_n + \hbar \omega_{n'}} \\ \times \frac{(\delta_{ij} - 3\hat{L}_i \hat{L}_j)(\delta_{\sigma\tau} - 3\hat{L}'_\sigma \hat{L}'_\tau)}{L^6}. \end{aligned} \quad (3.6)$$

This is the same as that which would be obtained by summing over the two-molecule potential  $V(R)_{\text{disc-disp}}$  as given by Craig, Power, and Thirunamachandran,<sup>1</sup> quoted in (2.3).

It is possible to relate the energy to an integral over imaginary frequency of an optical rotatory-angle tensor  $\theta_{i\sigma}(\omega)$ . If we define

$$\theta_{i\sigma}(\omega) = \frac{8\pi}{3} \sum_n \frac{\langle 0 | \mu^i | n \rangle \langle n | m^\sigma | 0 \rangle}{\omega_n^2 - \omega^2} \frac{\omega^2}{\hbar c} \quad (3.7)$$

to be the specific rotation-angle tensor in  $\text{rad cm}^2$  at circular frequency  $\omega$ , then (3.6) can be written

$$\begin{aligned} -\frac{9}{32} \frac{N}{\pi^3} \sum_{\vec{L} \neq 0} \int_0^\infty \frac{\theta_{i\sigma}(iy) \theta_{j\tau}(iy)}{y^2} dy \\ \times (\delta_{ij} - 3\hat{L}_i \hat{L}_j)(\delta_{\sigma\tau} - 3\hat{L}'_\sigma \hat{L}'_\tau) / L^6 \\ = -\frac{3}{(2\pi)^3} N \frac{G_{ij\sigma\tau}}{R^6} \int_0^\infty \frac{\theta_{i\sigma}(iy) \theta_{j\tau}(iy)}{y^2} dy, \end{aligned} \quad (3.8)$$

where  $G_{ij\sigma\tau} R^6$  is the lattice sum (3.9),

$$\frac{3}{4} \sum_{\vec{L} \neq 0} \frac{(\delta_{ij} - 3\hat{L}_i \hat{L}_j)(\delta_{\sigma\tau} - 3\hat{L}'_\sigma \hat{L}'_\tau)}{L^6}. \quad (3.9)$$

<sup>1</sup>D. P. Craig, E. A. Power, and T. Thirunamachandran, Chem. Phys. Letters 6, 211 (1970); Proc. Roy. Soc. (London) A322, 165 (1971).

<sup>2</sup>J. J. Hopfield, Phys. Rev. 112, 1555 (1958).

<sup>3</sup>G. D. Mahan, J. Chem. Phys. 43, 1569 (1965).

<sup>4</sup>A. A. Maradudin, E. W. Montroll, and G. W. Weiss, Solid State Phys. Suppl. 3, 138 (1963).