

Energy Bands of the Frenkel Excitons in Complex Crystal Lattices and the Effect of Medium on Exciton Energies

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0-99 Energy Bands of the Frenkel Excitons in Complex Crystal Lattices and the Effect of Medium on Exciton Energies

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Abstract

The Frenkel excitons in crystal lattices containing several kinds of atoms (or molecules) per unit cell are investigated theoretically in the representation of second quantization. The crystal Hamiltonian is expressed as the sum of the quadratic terms in the Bose operators suitable for describing the creation and annihilation of electronic excitations of an atom. The procedure for diagonalizing the crystal Hamiltonian and the method of calculating the energy bands of excitons are shown in detail. The result obtained corresponds to the generalization of the existing theory for Frenkel's excitons. By making use of this result, the microscopic theory for dielectric constant tensor of crystal is developed on the assumption of long-wavelength excitons. Finally the Frenkel excitons in a medium instead of vacuum are discussed from a microscopic point of view and it is found that the effective dipole-dipole interaction between the atoms responsible for excitons is expressible in terms of the dielectric constant tensor of the medium obtained from the microscopic theory.

§ 1. Introduction

Existing theory of Frenkel's exciton is applicable to crystals consisting of the same kind of atoms (or molecules).^{1,2,3)} Molecular crystals such as the crystalline anthracene, naphthalene and so on are appropriate for the application of the theory. Ionic crystals contain at least two different kinds of atoms forming their own lattices, i.e., the sublattices, each of which is composed of the same kind of atoms. In discussing the exciton in one sublattice by the existing theory, it is usual to regard all other sublattices as the medium having a dielectric constant.^{3,4,5)} However this procedure is only phenomenological, so that the development of the exciton theory taking account of all the Coulomb interactions between sublattices from a microscopic point of view is desirable.

In this paper the Frenkel excitons in crystal lattices containing several kinds of atoms per unit cell are investigated theoretically in the representation of second quantization. In this representation, the creation and annihilation of electronic excitations of an atom are described by the corresponding operators satisfying the commutation relations for bosons, and the crystal Hamiltonian including all the Coulomb interactions between atoms is expressed as a sum of the quadratic terms in these operators. The procedure for diagonalizing the crystal Hamiltonian and the method for calculating the energy bands of excitons are shown in the main part of § 2. The remaining part of this section deals with the transition dipole moments of excitons and the macroscopic polarization and electric field which arise from the distribution of the transition dipole moments. By making use of the results obtained in § 2, the general expression for the dielectric constant tensor of the crystal due to the presence of exciton states is derived in § 3 on the assumption that the wavelengths of excitons are very long as compared with a lattice constant.

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When one considers the case where the atoms participating in excitons are in a medium, the role played by the medium becomes a subject of discussion. The usual approach to this problem is the macroscopic one making use of the dielectric constant of the medium, i.e., the various quantities in vacuum, for example, the Coulomb interaction energy and the transition dipole moment of exciton defined in vacuum, are changed to the corresponding ones in the medium with the help of the dielectric constant.^{3,4,5)} The validity of this approach has to be examined by the microscopic theory. In § 4, the effect of the medium on exciton energies is discussed from a microscopic point of view and the expression for the effective dipole-dipole interaction between atoms in the medium is derived by making use of the results obtained in the preceding sections.

§ 2. Exciton States and Corresponding Energies

Consider a crystal consisting of several kinds of atoms (or molecules) called A, B, \dots . There are σ_J identical atoms of $J (J=A, B, \dots)$ in the unit cell. The equilibrium position vector of the l th unit cell relative to an origin at some atom is denoted by $\mathbf{r}(l)$ and the locations of σ_J identical atoms within the unit cell are described by the vectors $\mathbf{r}(\lambda_J)$ where λ_J takes the values $1, 2, \dots, \sigma_J$. Thus the position vector of the λ_J th atom in the l th unit cell is given by $\mathbf{r}(l\lambda_J) = \mathbf{r}(l) + \mathbf{r}(\lambda_J)$.

It is assumed that the electronic wave functions and the corresponding energies of isolated atoms are known. For simplicity we shall deal with the case where the electronic states of isolated atoms do not have degeneracy and hence the wave functions are real. The wave functions are classified according to the irreducible representations of the local group, i.e., the symmetry group of the lattice site occupied by the atom. The σ_J identical atoms have the same local group. Let f_J be the quantum number of each excited state of the atom J . The corresponding wave function of the λ_J th atom in the l th unit cell is denoted by $\varphi(l\lambda_J f_J)$. The ground state is represented by $f_J=0$.

In the following discussion, λ_J and f_J appear frequently in pair, so that we shall denote the set (λ_J, f_J) by ρ_J which takes the values $1, 2, \dots, \sigma_J n_J$ where n_J is the number of excited states taken into account. Furthermore the notations λ, f and ρ not having the subscript J will be used when the discussion covers all the atoms of A, B, \dots in the unit cell. In this case, λ takes the $\sum_J \sigma_J$ values, f the n_A or n_B or \dots values according as the atom concerned, and ρ the $\sum_J \sigma_J n_J$ values.

In order to treat the problem in the representation of second quantization, we introduced the creation and annihilation operators of atomic excitation: the operator $B^+(l\rho)(B(l\rho))$ creates (destroys) the excitation f of the atom at the lattice side $l\lambda$. If the expectation value of $B^+(l\rho)B(l\rho)$ is considerably smaller than unity, these operators satisfy the commutation relations for bosons,^{1,2)} i.e.,

$$[B(l\rho), B^+(l'\rho')] = \delta_{ll'} \delta_{\rho\rho'}. \quad (2.1)$$

According to the procedure given by Agranovich,³⁾ the excitation-energy operator H for the total system is written down, up to the quadratic terms in $B^+(l\rho)$, and $B(l\rho)$, as

$$H = \sum_{l\rho} \Delta(\rho) B^+(l\rho) B(l\rho) + \frac{1}{2} \sum'_{l\rho, l'\rho'} M(l\rho, l'\rho') [B(l\rho) + B^+(l\rho)] [B(l'\rho') + B^+(l'\rho')], \quad (2.2)$$

where $\Delta(\rho)$ is the energy difference between the excited and ground states of an isolated atom, and the real quantity M is defined by

$$M(l\rho, l'\rho') = \int \varphi(l\lambda f) \varphi(l'\lambda' 0) V(l\lambda, l'\lambda') \varphi(l\lambda 0) \varphi(l'\lambda' f') d\tau, \quad (2.3)$$

which is the matrix element of the Coulomb interaction $V(l\lambda, l'\lambda')$ between the atoms $l\lambda$ and $l'\lambda'$ and has the property

$$M(l'\rho', l\rho) = M(l\rho, l'\rho'). \quad (2.4)$$

The prime on the summation in the second term of eq. (2.2) indicates that the term with $l=l'$ has to be excluded when $\lambda=\lambda'$.

The unitary transformation taking account of translation symmetry is

$$B(l\rho) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} B(\rho, \mathbf{k}) \exp[i\mathbf{k} \cdot \mathbf{r}(l\rho)], \quad (2.5)$$

where N is the total number of unit cells in the crystal and \mathbf{k} is the wave vector, the inverse transformation of eq. (2.5) being given by $B(\rho, \mathbf{k}) = N^{-1/2} \sum_l B(l\rho) \exp[-i\mathbf{k} \cdot \mathbf{r}(l\lambda)]$. When we substitute eq. (2.5) into eq. (2.1), we see that the operators $B(\rho, \mathbf{k})$ satisfy the commutation relations

$$[B(\rho, \mathbf{k}), B^+(\rho', \mathbf{k}')] = \delta_{\rho\rho'} \delta_{\mathbf{k}\mathbf{k}'}. \quad (2.6)$$

By means of the transformation (2.5), the Hamiltonian (2.2) is rewritten as

$$H = \sum_{\mathbf{k}} \sum_{\rho} A(\rho) B^+(\rho, \mathbf{k}) B(\rho, \mathbf{k}) + \frac{1}{2} \sum_{\mathbf{k}} \sum_{\rho\rho'} M(\rho\rho', \mathbf{k}) [B(\rho, -\mathbf{k}) + B^+(\rho, \mathbf{k})] [B(\rho', \mathbf{k}) + B^+(\rho', -\mathbf{k})], \quad (2.7)$$

where $M(\rho\rho', \mathbf{k})$ is defined by

$$M(\rho\rho', \mathbf{k}) = \sum_l' M(l\rho, 0\rho') \exp\{-i\mathbf{k} \cdot [\mathbf{r}(l\lambda) - \mathbf{r}(\lambda')]\}, \quad (2.8)$$

and has the relations

$$M(\rho'\rho, \mathbf{k}) = M^*(\rho\rho', \mathbf{k}) = M(\rho\rho', -\mathbf{k}), \quad (2.9)$$

as seen from eqs. (2.4) and (2.8). The prime on the summation of eq. (2.8) means excluding the term with $l=0$ when $\lambda=\lambda'$.

The Hamiltonian (2.7) can be diagonalized in terms of new Bose operators B_{μ} and B_{μ}^+ defined by

$$B(\rho, \mathbf{k}) = \sum_{\mu} [B_{\mu}(\mathbf{k}) u_{\mu}(\rho, \mathbf{k}) + B_{\mu}^+(-\mathbf{k}) v_{\mu}^*(\rho, -\mathbf{k})]. \quad (2.10)$$

The commutation relations for B_{μ} and B_{μ}^+ are

$$[B_{\mu}(\mathbf{k}), B_{\mu'}^+(\mathbf{k}')] = \delta_{\mu\mu'} \delta_{\mathbf{k}\mathbf{k}'}, \quad (2.11)$$

and, in order that the transformation (2.10) be canonical, the amplitude function u_{μ} and v_{μ} must satisfy the relations

$$\left. \begin{aligned} \sum_{\rho} [u_{\mu}(\rho, \mathbf{k}) u_{\mu'}^*(\rho, \mathbf{k}) - v_{\mu}(\rho, \mathbf{k}) v_{\mu'}^*(\rho, \mathbf{k})] &= \delta_{\mu\mu'}, \\ \sum_{\rho} [u_{\mu}(\rho, \mathbf{k}) v_{\mu'}(\rho, -\mathbf{k}) - v_{\mu}(\rho, \mathbf{k}) u_{\mu'}(\rho, -\mathbf{k})] &= 0, \end{aligned} \right\} \quad (2.12)$$

$$\left. \begin{aligned} \sum_{\mu} [u_{\mu}(\rho, \mathbf{k}) u_{\mu'}^*(\rho', \mathbf{k}) - v_{\mu}^*(\rho, -\mathbf{k}) v_{\mu'}(\rho', -\mathbf{k})] &= \delta_{\rho\rho'}, \\ \sum_{\mu} [u_{\mu}(\rho, \mathbf{k}) v_{\mu'}^*(\rho', \mathbf{k}) - v_{\mu}^*(\rho, -\mathbf{k}) u_{\mu'}(\rho', -\mathbf{k})] &= 0. \end{aligned} \right\} \quad (2.13)$$

With the help of eq. (2.12), the inverse transformation of eq. (2.10) is given by

$$B_{\mu}(\mathbf{k}) = \sum_{\rho} [B(\rho, \mathbf{k}) u_{\mu}^*(\rho, \mathbf{k}) - B^+(\rho, -\mathbf{k}) v_{\mu}^*(\rho, \mathbf{k})]. \quad (2.14)$$

Substituting the transformation (2.10) into eq. (2.7) and using eq. (2.9), we see that the Hamiltonian

has the diagonal from

$$H = \sum_{\mathbf{k}} \sum_{\mu} E_{\mu}(\mathbf{k}) B_{\mu}^{\dagger}(\mathbf{k}) B_{\mu}(\mathbf{k}), \quad (2.15)$$

if the amplitude functions u_{μ} and v_{μ} satisfy the system of equations

$$\begin{aligned} [E_{\mu}(\mathbf{k}) - \Delta(\rho)] u_{\mu}(\rho, \mathbf{k}) &= -[E_{\mu}(\mathbf{k}) + \Delta(\rho)] v_{\mu}(\rho, \mathbf{k}) \\ &= \sum_{\rho'} M(\rho\rho', \mathbf{k}) [u_{\mu}(\rho', \mathbf{k}) + v_{\mu}(\rho', \mathbf{k})]. \end{aligned} \quad (2.16)$$

The functions $E_{\mu}(\mathbf{k})$ are the possible exciton energies and μ specifies the exciton band.

To simplify the system of equations (2.16), we introduce the new amplitude function ξ_{μ} defined by

$$\xi_{\mu}(\rho, \mathbf{k}) = [u_{\mu}(\rho, \mathbf{k}) + v_{\mu}(\rho, \mathbf{k})] / \sqrt{\Delta(\rho)}, \quad (2.17)$$

in terms of which u_{μ} and v_{μ} are expressed as

$$\left. \begin{aligned} u_{\mu}(\rho, \mathbf{k}) &= \frac{E_{\mu}(\mathbf{k}) + \Delta(\rho)}{2\sqrt{\Delta(\rho)}} \xi_{\mu}(\rho, \mathbf{k}), \\ v_{\mu}(\rho, \mathbf{k}) &= \frac{\Delta(\rho) - E_{\mu}(\mathbf{k})}{2\sqrt{\Delta(\rho)}} \xi_{\mu}(\rho, \mathbf{k}), \end{aligned} \right\} \quad (2.18)$$

from the first equation of eq. (2.16), and the second equation of eq. (2.16) is written as

$$[E_{\mu}^2(\mathbf{k}) - \Delta^2(\rho)] \xi_{\mu}(\rho, \mathbf{k}) = \sum_{\rho'} L(\rho\rho', \mathbf{k}) \xi_{\mu}(\rho', \mathbf{k}), \quad (2.19)$$

where

$$L(\rho\rho', \mathbf{k}) = 2\sqrt{\Delta(\rho)\Delta(\rho')} M(\rho\rho', \mathbf{k}). \quad (2.20)$$

It is comprehensible to represent eq. (2.19) in the matrix form. Let $\xi_{\mu}(\mathbf{k})$ be the column vector whose $\sum_{\rho} \sigma_{\rho} n_{\rho}$ components are $\{\xi_{\mu}(\rho, \mathbf{k})\}$ at given \mathbf{k} . Then eq. (2.19) can be expressed as

$$\mathcal{L}(\mathbf{k}) \xi_{\mu}(\mathbf{k}) = E_{\mu}^2(\mathbf{k}) \xi_{\mu}(\mathbf{k}), \quad (2.21)$$

where $\mathcal{L}(\mathbf{k})$ is the $(\sum_{\rho} \sigma_{\rho} n_{\rho}) \times (\sum_{\rho} \sigma_{\rho} n_{\rho})$ matrix whose rows and columns are labeled by ρ :

$$\mathcal{L}_{\rho\rho'}(\mathbf{k}) = \Delta^2(\rho) \delta_{\rho\rho'} + L(\rho\rho', \mathbf{k}). \quad (2.22)$$

The matrix $\mathcal{L}(\mathbf{k})$ written in the partitioned form is

$$\mathcal{L}(\mathbf{k}) = \begin{pmatrix} \mathcal{L}^A(\mathbf{k}) & \mathcal{L}^{AB}(\mathbf{k}) & \cdot \\ \mathcal{L}^{BA}(\mathbf{k}) & \mathcal{L}^B(\mathbf{k}) & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix} \quad (2.23)$$

where $\mathcal{L}^J(\mathbf{k})$ is the $\sigma_{J} n_{J} \times \sigma_{J} n_{J}$ matrix, $\mathcal{L}^{JJ'}(\mathbf{k})$ the $\sigma_{J} n_{J} \times \sigma_{J'} n_{J'}$ matrix and $\mathcal{L}^{J'J}(\mathbf{k})$ the transposed matrix of $\mathcal{L}^{JJ'}(\mathbf{k})$, whose elements are

$$\left. \begin{aligned} \mathcal{L}_{\rho\rho'}^{JJ'}(\mathbf{k}) &= [\Delta^2(\rho_J) \delta_{\rho_J \rho'_J} + L(\rho_J \rho'_J, \mathbf{k})] \delta_{\rho_J \rho'_J} \delta_{\rho'_J \rho_J}, \\ \mathcal{L}_{\rho\rho'}^{J'J}(\mathbf{k}) &= L(\rho_J \rho'_J, \mathbf{k}) \delta_{\rho_J \rho'_J} \delta_{\rho'_J \rho_J} \quad (J \neq J'). \end{aligned} \right\} \quad (2.24)$$

It follows from eqs. (2.9), (2.20) and (2.21) that the matrix $\mathcal{L}(\mathbf{k})$ at a given \mathbf{k} is Hermitian and the squared exciton energies $E_{\mu}^2(\mathbf{k})$ are given by the eigenvalues of the matrix $\mathcal{L}(\mathbf{k})$.

If we replace \mathbf{k} by $-\mathbf{k}$ in eq. (2.21), take the complex conjugate of the resulting equation, and make use of eq. (2.9), we obtain the result that

$$\mathcal{L}(\mathbf{k}) \xi_{\mu}^*(-\mathbf{k}) = E_{\mu}^2(-\mathbf{k}) \xi_{\mu}^*(-\mathbf{k}). \quad (2.25)$$

From eqs. (2.21) and (2.25) we see that the set of squared energies $\{E_{\mu}^2(-\mathbf{k})\}$ and the set of squared

energies $\{E_\mu^2(\mathbf{k})\}$ are eigenvalues of the same matrix $\mathcal{L}(\mathbf{k})$. We therefore obtain

$$E_\mu(-\mathbf{k}) = E_\mu(\mathbf{k}), \quad (2.26)$$

for positive E_μ . Equations (2.21), (2.25) and (2.26) show that $\xi_{\mu^*}^*(-\mathbf{k})$ satisfies the same equation as $\xi_\mu(\mathbf{k})$, which implies that

$$\xi_{\mu^*}^*(-\mathbf{k}) = \xi_\mu(\mathbf{k}), \quad (2.27)$$

apart from an unimportant phase factor.

Substituting eq. (2.18) into eqs. (2.12) and (2.13), and making use of eqs. (2.26) and (2.27), we obtain

$$\sum_\rho \sqrt{E_\mu(\mathbf{k})E_{\mu'}(\mathbf{k})} \xi_\mu(\rho, \mathbf{k}) \xi_{\mu'}^*(\rho, \mathbf{k}) = \delta_{\mu\mu'}, \quad (2.28)$$

$$\sum_\mu E_\mu(\mathbf{k}) \xi_\mu(\rho, \mathbf{k}) \xi_{\mu'}^*(\rho', \mathbf{k}) = \delta_{\rho\rho'}. \quad (2.29)$$

These are the orthonormal and complete conditions on the functions $\sqrt{E_\mu(\mathbf{k})} \xi_\mu(\rho, \mathbf{k})$. The state with one exciton of the type $\mu\mathbf{k}$ can be calculated by solving the system of equations (2.19) under the conditions mentioned above.

In the theory of Frenkel's exciton, it is usually assumed that the electron orbits of an atom are well localized near its nucleus. Therefore the Coulomb interaction between atoms is expanded into a series in inverse powers of the distance between the centers of atoms. The individual terms of the series correspond to the multipole-multipole interactions of various orders. The leading term gives the crystal field due to point charges, the effect of which has already been taken into account in the quantity $\mathcal{A}(\rho)$. If the electric dipole moment arising from an intra-atomic transition differs from zero, the first term of this series contributing to $L(\rho\rho', \mathbf{k})$ corresponds to the dipole-dipole interaction. We shall retain only this term.

In this approximation, $L(\rho\rho', \mathbf{k})$ can be written as the sum of the macroscopic part $L_M(\rho\rho', \mathbf{k})$ and the structure-dependent part $L_S(\rho\rho', \mathbf{k})$:^{6,7)}

$$L(\rho\rho', \mathbf{k}) = L_M(\rho\rho', \mathbf{k}) + L_S(\rho\rho', \mathbf{k}), \quad (2.30)$$

with the definitions of

$$L_M(\rho\rho', \mathbf{k}) = \frac{8\pi}{v} \sqrt{\mathcal{A}(\rho)\mathcal{A}(\rho')} \frac{\mathbf{k} \cdot \mathbf{p}(\rho) \mathbf{k} \cdot \mathbf{p}(\rho')}{k^2}, \quad (2.31)$$

$$L_S(\rho\rho', \mathbf{k}) = \frac{8\pi}{v} \sqrt{\mathcal{A}(\rho)\mathcal{A}(\rho')} \mathbf{p}(\rho) \cdot \hat{F}(\lambda\lambda', \mathbf{k}) \cdot \mathbf{p}(\rho'), \quad (2.32)$$

where v is the volume of a unit cell and

$$\mathbf{p}(\rho) = \int \varphi(\lambda\lambda 0) \mathbf{p} \varphi(\lambda\lambda') d\tau, \quad (2.33)$$

is the matrix element of the electric dipole moment \mathbf{p} for electrons of the atom λ . The tensor \hat{F} is symmetric and its components $\Gamma_{ij}(i, j = x, y, z)$ satisfy

$$\Gamma_{ji}(\lambda\lambda', \mathbf{k}) = \Gamma_{ij}(\lambda\lambda', \mathbf{k}). \quad (2.34)$$

In addition we have the relations

$$\hat{F}(\lambda\lambda, \mathbf{k}) = \hat{F}^*(\lambda\lambda', \mathbf{k}) = \hat{F}(\lambda\lambda', -\mathbf{k}). \quad (2.35)$$

The explicit expression for \hat{F} is given in ref. 7 ($D^{\lambda\lambda'}(\lambda\lambda'|\mathbf{k})$ in ref. 7 is identical with $4\pi\Gamma_{ij}(\lambda\lambda', -\mathbf{k})/v$).

The matrix element of electric dipole moment for the transition to an exciton state can be calculated as follows. In the representation of second quantization, the dipole moment operator of the atom at the lattice site $l\lambda$ is written as

$$\mathbf{p}^{\text{op}}(l\lambda) = \sum_{\rho} \mathbf{p}(\rho) [B(l\rho) + B^+(l\rho)]. \quad (2.36)$$

The Fourier component of this operator is given by

$$\begin{aligned} \mathbf{p}^{\text{op}}(\lambda, \mathbf{k}) &= \frac{1}{\sqrt{N}} \sum_l \mathbf{p}^{\text{op}}(l\lambda) \exp[-i\mathbf{k} \cdot \mathbf{r}(l\lambda)] \\ &= \sum_{\rho} \sqrt{\Delta(\rho)} \mathbf{p}(\rho) [B_{\mu}(\mathbf{k}) \xi_{\mu}(\rho, \mathbf{k}) + B_{\mu}^*(-\mathbf{k}) \xi_{\mu}^*(\rho, -\mathbf{k})], \end{aligned} \quad (2.37)$$

where eqs. (2.5), (2.10) and (2.17) have been used. The wave function of the $\mu\mathbf{k}$ exciton state, $|\mu\mathbf{k}\rangle$, is obtained from the wave function of the crystal ground state, $|0\rangle$, by the rule $|\mu\mathbf{k}\rangle = B_{\mu}^+(\mathbf{k})|0\rangle$. It follows from this that the matrix element of $\mathbf{p}^{\text{op}}(\lambda, \mathbf{q})$ is given by

$$\langle 0 | \mathbf{p}^{\text{op}}(\lambda, \mathbf{q}) | \mu\mathbf{k} \rangle = \delta_{\mathbf{q}\mathbf{k}} \mathbf{p}_{\mu}(\lambda, \mathbf{k}), \quad (2.38)$$

where

$$\mathbf{p}_{\mu}(\lambda, \mathbf{k}) = \sum_{\rho} \sqrt{\Delta(\rho)} \xi_{\mu}(\rho, \mathbf{k}) \mathbf{p}(\rho). \quad (2.39)$$

Consequently

$$\mathbf{P}_{\mu}(\mathbf{k}) = \sum_{\lambda} \mathbf{p}_{\mu}(\lambda, \mathbf{k}) = \sum_{\rho} \sqrt{\Delta(\rho)} \xi_{\mu}(\rho, \mathbf{k}) \mathbf{p}(\rho), \quad (2.40)$$

is the matrix element of the electric dipole moments for all the atoms in the unit cell constructed with the wave functions of the crystal ground state and the exciton state of the type $\mu\mathbf{k}$.

Finally we derive the expressions for the macroscopic polarization and the corresponding macroscopic electric field which arise from the distribution of transition dipole moments with \mathbf{k} satisfying

$$|\mathbf{k}|a \ll 1, \quad (2.41)$$

where a is a lattice constant. The microscopic polarization density $\mathbf{P}^{\text{op}}(\mathbf{r})$ is written, from eqs. (2.36) and (2.37), as

$$\begin{aligned} \mathbf{P}^{\text{op}}(\mathbf{r}) &= \sum_{\lambda} \mathbf{p}^{\text{op}}(l\lambda) \delta[\mathbf{r} - \mathbf{r}(l\lambda)] \\ &= \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} \sum_{\lambda} \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{p}^{\text{op}}(\lambda, \mathbf{k}) \sum_l \delta[\mathbf{r} - \mathbf{r}(l\lambda)]. \end{aligned} \quad (2.42)$$

Since the sum over l is a function which has the periodicity of crystal lattice, it can be expanded as

$$\sum_l \delta[\mathbf{r} - \mathbf{r}(l\lambda)] = \frac{1}{v} \sum_{\mathbf{g}} \exp\{i\mathbf{g} \cdot [\mathbf{r} - \mathbf{r}(\lambda)]\}, \quad (2.43)$$

where \mathbf{g} are the reciprocal lattice vectors.

The macroscopic polarization operator $\mathbf{P}^{\text{op}}(\mathbf{r})$ is defined as the average of $\mathbf{P}^{\text{op}}(\mathbf{r})$ over the volume of a unit cell, i.e., $\mathbf{P}^{\text{op}} = v^{-1} \int_{\text{cell}} \mathbf{P}^{\text{op}}(\mathbf{r} + \mathbf{r}') d\mathbf{r}'$. For small \mathbf{k} satisfying eq. (2.41), only the term with $\mathbf{g} = 0$ gives the nonvanishing contribution to this average, and hence we obtain the result that the Fourier component of $\mathbf{P}^{\text{op}}(\mathbf{r})$ is given by

$$\mathbf{P}^{\text{op}}(\mathbf{k}) = \frac{1}{v} \sum_{\lambda} \mathbf{p}^{\text{op}}(\lambda, \mathbf{k}). \quad (2.44)$$

It follows from eqs. (2.38), (2.40) and (2.44) that the macroscopic polarization $\mathbf{P}_\mu(\mathbf{k})$ produced by the $\mu\mathbf{k}$ exciton is written as

$$\mathbf{P}_\mu(\mathbf{k}) = \frac{1}{v} \mathbf{P}_\mu(\mathbf{k}), \quad (2.45)$$

which is just the transition dipole moment per unit volume.

If we split $\mathbf{P}_\mu(\mathbf{k})$ into two parts $\mathbf{P}_\mu^{\parallel}(\mathbf{k})$ and $\mathbf{P}_\mu^{\perp}(\mathbf{k})$ respectively parallel and perpendicular to \mathbf{k} , the Maxwell equation in the absence of free charges is written as $\mathbf{k} \cdot [\bar{\mathbf{E}}_\mu(\mathbf{k}) + 4\pi\mathbf{P}_\mu^{\parallel}(\mathbf{k})] = 0$ where $\bar{\mathbf{E}}_\mu(\mathbf{k})$ is the macroscopic electric field in the system. Since $\bar{\mathbf{E}}_\mu(\mathbf{k})$ satisfies $\mathbf{k} \times \bar{\mathbf{E}}_\mu(\mathbf{k}) = 0$ if the retardation effect is ignored (the light velocity being taken to be infinite), we have the relation that $\mathbf{k} \times [\bar{\mathbf{E}}_\mu(\mathbf{k}) + 4\pi\mathbf{P}_\mu^{\parallel}(\mathbf{k})] = 0$. Thus the vector $\bar{\mathbf{E}}_\mu(\mathbf{k}) + 4\pi\mathbf{P}_\mu^{\parallel}(\mathbf{k})$ itself must vanish identically and so

$$\bar{\mathbf{E}}_\mu(\mathbf{k}) = -4\pi\mathbf{P}_\mu^{\parallel}(\mathbf{k}) = -4\pi\mathbf{k}\mathbf{k} \cdot \mathbf{P}_\mu(\mathbf{k})k^{-2}. \quad (2.46)$$

§3. Dielectric Constant Tensor Due to the Presence of Exciton States

Substituting eq. (2.30) into eq. (2.19), we obtain the system of equations for an energy E

$$\sum_{\rho'} \{ [E^2 - \Delta^2(\rho)] \delta_{\rho\rho'} - L_S(\rho\rho', \mathbf{k}) \} \xi(\rho', \mathbf{k}) = \sum_{\rho'} L_M(\rho\rho', \mathbf{k}) \xi(\rho', \mathbf{k}). \quad (3.1)$$

By use of eq. (2.31), the right hand side of eq. (3.1) can be written as

$$\sum_{\rho'} L_M(\rho\rho', \mathbf{k}) \xi(\rho', \mathbf{k}) = -2\sqrt{\Delta(\rho)} \mathbf{p}(\rho) \cdot \bar{\mathbf{E}}(\mathbf{k}), \quad (3.2)$$

where

$$\bar{\mathbf{E}}(\mathbf{k}) = -4\pi\mathbf{k}\mathbf{k} \cdot \mathbf{P}(\mathbf{k})k^{-2}, \quad (3.3)$$

is the macroscopic electric field produced by the macroscopic polarization $\mathbf{P}(\mathbf{k})$, as shown in eq. (2.46). The macroscopic polarization is taken as

$$\mathbf{P}(\mathbf{k}) = \frac{1}{v} \sum_{\rho} \sqrt{\Delta(\rho)} \xi(\rho, \mathbf{k}) \mathbf{p}(\rho), \quad (3.4)$$

according to eqs. (2.45) and (2.40). In this section we consider only the long-wavelength excitons for \mathbf{k} satisfying the condition (2.41).

If we use the Green function $G(\rho\rho', E, \mathbf{k})$ satisfying

$$\sum_{\rho''} \{ [E^2 - \Delta^2(\rho)] \delta_{\rho\rho''} - L_S(\rho\rho'', \mathbf{k}) \} G(\rho'\rho'', E, \mathbf{k}) = \delta_{\rho\rho'}, \quad (3.5)$$

we can solve eq. (3.1) for $\xi(\rho, \mathbf{k})$ to obtain

$$\xi(\rho, \mathbf{k}) = -2 \sum_{\rho'} G(\rho\rho', E, \mathbf{k}) \sqrt{\Delta(\rho')} \mathbf{p}(\rho') \cdot \bar{\mathbf{E}}(\mathbf{k}). \quad (3.6)$$

Substitution of this solution into eq. (3.4) leads to

$$\mathbf{P}(\mathbf{k}) = \frac{1}{4\pi} [\hat{\epsilon}(E, \mathbf{k}) - \hat{1}] \cdot \bar{\mathbf{E}}(\mathbf{k}), \quad (3.7)$$

where $\hat{1}$ is the unit dyadic and $\hat{\epsilon}$ is the dielectric constant tensor given by

$$\hat{\epsilon}(E, \mathbf{k}) = \hat{1} - \frac{8\pi}{v} \sum_{\rho\rho'} \sqrt{\Delta(\rho)\Delta(\rho')} G(\rho\rho', E, \mathbf{k}) \mathbf{p}(\rho) \mathbf{p}(\rho'). \quad (3.8)$$

The components of $\hat{1}$ and the dyad $\mathbf{p}(\rho)\mathbf{p}(\rho')$ are respectively δ_{ij} and $p_i(\rho)p_j(\rho')$.

It is seen from eq. (3.5) that the Green function can be expressed in terms of mechanical excitons

which correspond to the solutions of eq. (2.19) ignoring the contribution due to $L_M(\rho\rho', \mathbf{k})$. Denoting the energy and the amplitude function for the mechanical exciton of the type $m\mathbf{k}$ by $E_m(\mathbf{k})$ and $\eta_m(\rho, \mathbf{k})$, respectively, we have the system of equations

$$\sum_{\rho'} \{ [E_m^2(\mathbf{k}) - \Delta^2(\rho)] \delta_{\rho\rho'} - L_S(\rho\rho', \mathbf{k}) \} \eta_m(\rho', \mathbf{k}) = 0, \quad (3.9)$$

with the orthonormal and complete conditions on $\eta_m(\rho, \mathbf{k})$

$$\sum_{\rho} \sqrt{E_m(\mathbf{k}) E_{m'}(\mathbf{k})} \eta_m(\rho, \mathbf{k}) \eta_{m'}^*(\rho, \mathbf{k}) = \delta_{mm'}, \quad (3.10)$$

$$\sum_m E_m(\mathbf{k}) \eta_m(\rho, \mathbf{k}) \eta_m^*(\rho', \mathbf{k}) = \delta_{\rho\rho'}, \quad (3.11)$$

corresponding to eqs. (2.28) and (2.29). In addition we have the properties

$$E_m(-\mathbf{k}) = E_m(\mathbf{k}), \quad (3.12)$$

and

$$\eta_m^*(\rho, -\mathbf{k}) = \eta_m(\rho, \mathbf{k}), \quad (3.13)$$

which can be obtained from a similar discussion to that given in deriving eqs. (2.26) and (2.27).

The fact that the function $\sqrt{E_m(\mathbf{k})} \eta_m(\rho, \mathbf{k})$ are orthonormal and complete allows us to expand the Green function in the form of $G(\rho\rho', E, \mathbf{k}) = \sum_{mm'} [E_m(\mathbf{k}) E_{m'}(\mathbf{k})]^{1/2} \eta_m(\rho, \mathbf{k}) \eta_{m'}(\rho', \mathbf{k}) g_{mm'}(E, \mathbf{k})$. Substituting this expansion into eq. (3.5) and using eqs. (3.9) and (3.10), we find that the expansion coefficient is given by $g_{mm'}(E, \mathbf{k}) = \delta_{mm'} / [E^2 - E_m^2(\mathbf{k})]$ and hence

$$G(\rho\rho', E, \mathbf{k}) = \sum_m \frac{E_m(\mathbf{k}) \eta_m(\rho, \mathbf{k}) \eta_m^*(\rho', \mathbf{k})}{E^2 - E_m^2(\mathbf{k})}. \quad (3.14)$$

Accordingly, eq. (3.8) is written as

$$\hat{\varepsilon}(E, \mathbf{k}) = \hat{1} - \frac{8\pi}{v} \sum_m \frac{E_m(\mathbf{k})}{E^2 - E_m^2(\mathbf{k})} \mathbf{P}_m(\mathbf{k}) \mathbf{P}_m(\mathbf{k}), \quad (3.15)$$

where

$$\mathbf{P}_m(\mathbf{k}) = \sum_{\rho} \sqrt{\Delta(\rho)} \eta_m(\rho, \mathbf{k}) \mathbf{p}(\rho), \quad (3.16)$$

is the matrix element of the electric dipole moment for the unit cell constructed with the wave functions of the crystal ground state and the mechanical exciton state. From eqs. (3.12), (3.13), (3.15) and (3.16), we obtain the relations between the components ε_{ij} of $\hat{\varepsilon}$ written as

$$\varepsilon_{ji}(E, \mathbf{k}) = \varepsilon_{ij}^*(E, \mathbf{k}) = \varepsilon_{ij}(E, -\mathbf{k}). \quad (3.17)$$

The expression (3.15) is the generalized form of the existing formula for $\hat{\varepsilon}^{2,6)}$ which holds for crystals containing the same kind of atoms in the unit cell.

Since we are dealing with Coulomb excitons determined from the full expression of eq. (2.19) instead of the expression omitting $L_M(\rho\rho', \mathbf{k})$, we shall rewrite eq. (3.15) in terms of Coulomb excitons. The Green function \tilde{G} corresponding to eq. (2.19) is written as

$$\tilde{G}(\rho\rho', E, \mathbf{k}) = \{ [E^2 - \Delta^2(\rho)] I - \mathcal{L}_S(\mathbf{k}) - \mathcal{L}_M(\mathbf{k}) \}^{-1}_{\rho\rho'}, \quad (3.18)$$

where I is unit matrix, and $\mathcal{L}_S(\mathbf{k})$ and $\mathcal{L}_M(\mathbf{k})$ are the matrices whose elements are $L_S(\rho\rho', \mathbf{k})$ and $L_M(\rho\rho', \mathbf{k})$. The well-known formula for matrices leads to

$$\begin{aligned} \{ [E^2 - \Delta^2(\rho)] I - \mathcal{L}_S(\mathbf{k}) - \mathcal{L}_M(\mathbf{k}) \}^{-1}_{\rho\rho'} &= \{ [E^2 - \Delta^2(\rho)] I - \mathcal{L}_S(\mathbf{k}) \}^{-1}_{\rho\rho'} \\ &+ \sum_{\rho''\rho'''} \{ [E^2 - \Delta^2(\rho)] I - \mathcal{L}_S(\mathbf{k}) \}^{-1}_{\rho\rho''} \{ \mathcal{L}_M(\mathbf{k}) \}_{\rho''\rho'''} \{ [E^2 - \Delta^2(\rho)] I - \mathcal{L}_S(\mathbf{k}) - \mathcal{L}_M(\mathbf{k}) \}^{-1}_{\rho'''\rho'}. \end{aligned}$$

which is transformed into the relation between the Green function for the Coulomb and mechanical excitons as follows:

$$\begin{aligned} \tilde{G}(\rho\rho', E, \mathbf{k}) &= G(\rho\rho', E, \mathbf{k}) \\ &+ \frac{8\pi}{v k^2} \sum_{\rho''\rho'''} G(\rho\rho'', E, \mathbf{k}) \sqrt{\Delta(\rho'')\Delta(\rho''')} \mathbf{k} \cdot \mathbf{p}(\rho'') \mathbf{k} \cdot \mathbf{p}(\rho''') \tilde{G}(\rho''\rho''', E, \mathbf{k}), \end{aligned} \quad (3.19)$$

where eqs. (2.31) and (3.18) have been used.

Multiplying both sides of eq. (3.19) by $(8\pi/v)\sqrt{\Delta(\rho)\Delta(\rho')}\mathbf{p}(\rho)\mathbf{p}(\rho')$, taking the sum over all $\rho\rho'$, and using the expression for $\hat{\varepsilon}$ given by eq. (3.8), we obtain

$$\hat{F}(E, \mathbf{k}) = \hat{1} - \hat{\varepsilon}(E, \mathbf{k}) + [\hat{1} - \hat{\varepsilon}(E, \mathbf{k})] \cdot \mathbf{k} \mathbf{k} \cdot \hat{F}(E, \mathbf{k}) k^{-2}, \quad (3.20)$$

where the tensor $\hat{F}(E, \mathbf{k})$ is defined as

$$\hat{F}(E, \mathbf{k}) = \frac{8\pi}{v} \sum_{\rho\rho'} \sqrt{\Delta(\rho)\Delta(\rho')} \tilde{G}(\rho\rho', E, \mathbf{k}) \mathbf{p}(\rho) \mathbf{p}(\rho'). \quad (3.21)$$

From eq. (3.20), we obtained that $\mathbf{k} \cdot \hat{F} = \mathbf{k} \cdot (\hat{1} - \hat{\varepsilon}) k^2 / (\mathbf{k} \cdot \hat{\varepsilon} \cdot \mathbf{k})$, which is substituted into the right hand side of eq. (3.20) to give

$$\hat{F}(E, \mathbf{k}) = \hat{1} - \hat{\varepsilon}(E, \mathbf{k}) + \frac{[\hat{1} - \hat{\varepsilon}(E, \mathbf{k})] \cdot \mathbf{k} \mathbf{k} \cdot [\hat{1} - \hat{\varepsilon}(E, \mathbf{k})]}{\mathbf{k} \cdot \hat{\varepsilon}(E, \mathbf{k}) \cdot \mathbf{k}}. \quad (3.22)$$

If we use eqs. (2.19), (2.28) and (3.18), we can express the Green function \tilde{G} as the bilinear expansion

$$\tilde{G}(\rho\rho', E, \mathbf{k}) = \sum_{\mu} \frac{E_{\mu}(\mathbf{k}) \xi_{\mu}(\rho, \mathbf{k}) \xi_{\mu}^*(\rho', \mathbf{k})}{E^2 - E_{\mu}^2(\mathbf{k})}, \quad (3.23)$$

in a similar way to that used in deriving eq. (3.14). Substituting this expression into eq. (3.21) and using eq. (2.40), we find from eq. (3.22) the desired relation between the transition dipole moment and the dielectric constant tensor written in terms of Coulomb excitons as follows:

$$\begin{aligned} & \frac{8\pi}{v} \sum_{\mu} \frac{E_{\mu}(\mathbf{k})}{E^2 - E_{\mu}(\mathbf{k})} \mathbf{P}_{\mu}(\mathbf{k}) \mathbf{P}_{\mu}^*(\mathbf{k}) \\ &= \hat{1} - \hat{\varepsilon}(E, \mathbf{k}) + \frac{[\hat{1} - \hat{\varepsilon}(E, \mathbf{k})] \cdot \mathbf{k} \mathbf{k} \cdot [\hat{1} - \hat{\varepsilon}(E, \mathbf{k})]}{\mathbf{k} \cdot \hat{\varepsilon}(E, \mathbf{k}) \cdot \mathbf{k}}, \end{aligned} \quad (3.24)$$

where $\mathbf{P}_{\mu}(\mathbf{k})$ is given by eq. (2.40). It should be noted that the formulae (3.15) and (3.24) are applicable to any isolated system if the condition (2.41) is satisfied.

§ 4. Effective Dipole-Dipole Interaction

We divide all the atoms in crystal into two systems, the system A consisting of the σ_A atoms of A and the system R consisting of all other atoms which can be regarded as the "medium" for excitons in the system A if the condition (2.41) for long wavelength is satisfied. Let $\xi_{\mu}^A(\mathbf{k})$ and $\xi_{\mu}^R(\mathbf{k})$ be the column vectors whose components are respectively $\{\xi_{\mu}(\rho_A, \mathbf{k})\}$ and $\{\xi_{\mu}(\rho_R, \mathbf{k})\}$, where ρ_A takes the σ_{ANA} values and ρ_R the $\sum_{J(\neq A)} \sigma_{JNJ}$ values. The column vector $\xi_{\mu}(\mathbf{k})$ and the matrix $\mathcal{L}(\mathbf{k})$ of eq. (2.21) for the total system are written as

$$\xi_{\mu}(\mathbf{k}) = \begin{bmatrix} \xi_{\mu}^A(\mathbf{k}) \\ \xi_{\mu}^R(\mathbf{k}) \end{bmatrix} \quad (4.1)$$

$$\mathcal{L}(\mathbf{k}) = \begin{bmatrix} \mathcal{L}^A(\mathbf{k}) & \mathcal{L}^{AR}(\mathbf{k}) \\ \mathcal{L}^{RA}(\mathbf{k}) & \mathcal{L}^R(\mathbf{k}) \end{bmatrix} \quad (4.2)$$

where the elements of $\mathcal{L}^A(\mathbf{k})$ are given by eq. (2.24), and those of $\mathcal{L}^R(\mathbf{k})$ and $\mathcal{L}^{AR}(\mathbf{k})$ ($\mathcal{L}^{RA}(\mathbf{k})$ being the transposed matrix of $\mathcal{L}^{AR}(\mathbf{k})$) are

$$\left. \begin{aligned} \mathcal{L}^R_{\rho\rho'}(\mathbf{k}) &= [\Delta^2(\rho_R)\delta_{\rho_R\rho'_R} + L(\rho_R\rho'_R, \mathbf{k})]\delta_{\rho\rho_R}\delta_{\rho'\rho'_R}, \\ \mathcal{L}^{AR}_{\rho\rho'}(\mathbf{k}) &= L(\rho_A\rho_R, \mathbf{k})\delta_{\rho\rho_A}\delta_{\rho'\rho_R}. \end{aligned} \right\} \quad (4.3)$$

Substituting eqs. (4.1) and (4.2) into eq. (2.21), we obtain the pair of equations

$$\mathcal{L}^A(\mathbf{k})\xi_{\mu^A}(\mathbf{k}) + \mathcal{L}^{AR}(\mathbf{k})\xi_{\mu^R}(\mathbf{k}) = E_{\mu^2}(\mathbf{k})\xi_{\mu^A}(\mathbf{k}), \quad (4.4)$$

$$\mathcal{L}^{RA}(\mathbf{k})\xi_{\mu^A}(\mathbf{k}) + \mathcal{L}^R(\mathbf{k})\xi_{\mu^R}(\mathbf{k}) = E_{\mu^2}(\mathbf{k})\xi_{\mu^R}(\mathbf{k}). \quad (4.5)$$

The solutions of eq. (4.5) for $\xi_{\mu^R}(\mathbf{k})$ is given by

$$\xi_{\mu^R}(\mathbf{k}) = G^R(E_{\mu}, \mathbf{k})\mathcal{L}^{RA}(\mathbf{k})\xi_{\mu^A}(\mathbf{k}), \quad (4.6)$$

where G^R is the Green function matrix defined by $G^R(E_{\mu}, \mathbf{k}) = [E_{\mu^2}(\mathbf{k})I - \mathcal{L}^R(\mathbf{k})]^{-1}$, whose elements $G(\rho_R\rho'_R, E_{\mu}, \mathbf{k})$ satisfy

$$\sum_{\rho'_R} \{ [E_{\mu^2}(\mathbf{k}) - \Delta^2(\rho_R)]\delta_{\rho_R\rho'_R} - L(\rho_R\rho'_R, \mathbf{k}) \} G(\rho'_R\rho''_R, E_{\mu}, \mathbf{k}) = \delta_{\rho_R\rho''_R}. \quad (4.7)$$

Substitution of eq. (4.6) into eq. (4.4) yields the following equation for the system A :

$$[\mathcal{L}^A(\mathbf{k}) + \mathcal{L}^{AR}(\mathbf{k})G^R(E_{\mu}, \mathbf{k})\mathcal{L}^{RA}(\mathbf{k})]\xi_{\mu^A}(\mathbf{k}) = E_{\mu^2}(\mathbf{k})\xi_{\mu^A}(\mathbf{k}), \quad (4.8)$$

or, by use of eqs. (2.24) and (4.3),

$$\sum_{\rho'_A} [\Delta^2(\rho_A)\delta_{\rho_A\rho'_A} + L^{\text{eff}}(\rho_A\rho'_A, E_{\mu}, \mathbf{k})]\xi_{\mu}(\rho'_A, \mathbf{k}) = E_{\mu^2}(\mathbf{k})\xi_{\mu}(\rho_A, \mathbf{k}), \quad (4.8a)$$

where

$$L^{\text{eff}}(\rho_A\rho'_A, E_{\mu}, \mathbf{k}) = L(\rho_A\rho'_A, \mathbf{k}) + \sum_{\rho_R\rho'_R} L(\rho_A\rho_R, \mathbf{k})G(\rho_R\rho'_R, E_{\mu}, \mathbf{k})L(\rho'_R\rho'_A, \mathbf{k}), \quad (4.9)$$

is the Fourier component of the effective interaction between atoms in the system A ; the first term is the interaction energy in vacuum and the second term is the contribution to the interaction energy due to the medium.

Now consider the Coulomb excitons in the system R taken to be isolated from the system A by assuming $\mathcal{L}^{AR}(\mathbf{k})$ to be the null matrix. The energy and the amplitude function of the ν exciton in this system are denoted by $E_{\nu}(\mathbf{k})$ and $\zeta_{\nu}(\rho_R, \mathbf{k})$, respectively, where ν specifies the exciton band. These quantities satisfy the following system of equations

$$\sum_{\rho'_R} \{ [E_{\nu^2}(\mathbf{k}) - \Delta^2(\rho_R)]\delta_{\rho_R\rho'_R} - L(\rho_R\rho'_R, \mathbf{k}) \} \zeta_{\nu}(\rho'_R, \mathbf{k}) = 0, \quad (4.10)$$

with the conditions of

$$\sum_{\rho_R} \sqrt{E_{\nu}(\mathbf{k})E_{\nu'}(\mathbf{k})} \zeta_{\nu}(\rho_R, \mathbf{k})\zeta_{\nu'}^*(\rho_R, \mathbf{k}) = \delta_{\nu\nu'}, \quad (4.11)$$

$$\sum_{\rho_R} E_{\nu}(\mathbf{k})\zeta_{\nu}(\rho_R, \mathbf{k})\zeta_{\nu'}^*(\rho'_R, \mathbf{k}) = \delta_{\rho_R\rho'_R}, \quad (4.12)$$

which correspond to eqs. (2.19), (2.28) and (2.29) for the total system. It is easy to show from the above equations that the Green function satisfying eq. (4.7) can be expressed as the bilinear expansion

$$G(\rho_R\rho'_R, E_{\mu}, \mathbf{k}) = \sum_{\nu} \frac{E_{\nu}(\mathbf{k})\zeta_{\nu}(\rho_R, \mathbf{k})\zeta_{\nu}^*(\rho'_R, \mathbf{k})}{E_{\mu^2}(\mathbf{k}) - E_{\nu^2}(\mathbf{k})}. \quad (4.13)$$

Substituting eq. (4.13) into the second term of eq. (4.9) and using the expressions (2.30)~(2.32)

in the dipole approximation, we obtain

$$\begin{aligned}
 & \sum_{\rho_R \rho'_R} L(\rho_A \rho_R, \mathbf{k}) G(\rho_R \rho'_R, E_\mu, \mathbf{k}) L(\rho'_R \rho'_A, \mathbf{k}) / \frac{8\pi}{v} \sqrt{\Delta(\rho_A) \Delta(\rho'_A)} \\
 &= \mathbf{k} \cdot \mathbf{p}(\rho_A) \mathbf{k} \cdot \mathbf{p}(\rho'_A) k^{-2} \frac{8\pi}{v} \sum_{\nu} \frac{E_\nu(\mathbf{k}) k^{-2}}{E_\mu^2(\mathbf{k}) - E_\nu^2(\mathbf{k})} |\mathbf{k} \cdot \mathbf{P}_\nu(\mathbf{k})|^2 \\
 &+ \mathbf{k} \cdot \mathbf{p}(\rho'_A) \frac{8\pi}{v} \sum_{\nu} \sum_{\lambda_R} \frac{E_\nu(\mathbf{k}) k^{-2}}{E_\mu^2(\mathbf{k}) - E_\nu^2(\mathbf{k})} \mathbf{p}(\rho_A) \cdot \hat{\Gamma}(\lambda_A \lambda_R, \mathbf{k}) \cdot \mathbf{p}_\nu(\lambda_R, \mathbf{k}) \mathbf{P}_\nu^*(\mathbf{k}) \cdot \mathbf{k} \\
 &+ \mathbf{k} \mathbf{p} \cdot (\rho_A) \frac{8\pi}{v} \sum_{\nu} \sum_{\lambda_R} \frac{E_\nu(\mathbf{k}) k^{-2}}{E_\mu^2(\mathbf{k}) - E_\nu^2(\mathbf{k})} \mathbf{k} \cdot \mathbf{P}_\nu(\mathbf{k}) \mathbf{p}_\nu^*(\lambda_R, \mathbf{k}) \cdot \hat{\Gamma}(\lambda_R \lambda'_A, \mathbf{k}) \cdot \mathbf{p}(\rho'_A) \\
 &+ \frac{8\pi}{v} \sum_{\nu} \sum_{\lambda_R \lambda'_R} \frac{E_\nu(\mathbf{k})}{E_\mu^2(\mathbf{k}) - E_\nu^2(\mathbf{k})} \mathbf{p}(\rho_A) \cdot \hat{\Gamma}(\lambda_A \lambda_R, \mathbf{k}) \cdot \mathbf{p}_\nu(\lambda_R, \mathbf{k}) \mathbf{p}_\nu^*(\lambda'_R, \mathbf{k}) \cdot \hat{\Gamma}(\lambda'_R \lambda'_A, \mathbf{k}) \cdot \mathbf{p}(\rho'_A),
 \end{aligned} \tag{4.14}$$

where λ_R takes the $\sum_{J(\neq A), \sigma_J}$ values and

$$\mathbf{P}_\nu(\mathbf{k}) = \sum_{\lambda_R} \mathbf{p}_\nu(\lambda_R, \mathbf{k}) = \sum_{\rho_R} \sqrt{\Delta(\rho_R)} \zeta_\nu(\rho_R, \mathbf{k}) \mathbf{p}(\rho_R), \tag{4.15}$$

is the transition dipole moment for all the atoms of the system R in the unit cell.

We assume that the dipole moments $\mathbf{p}(\lambda_R, \mathbf{k})$ are independent of λ_R , which may be realized in many crystals for long-wavelength excitons satisfied by the conditions (2.41). In this case we have

$$\sum_{\lambda_R} \hat{\Gamma}(\lambda_A \lambda_R, \mathbf{k}) \cdot \mathbf{p}_\nu(\lambda_R, \mathbf{k}) = \hat{\Gamma}(\lambda_A R, \mathbf{k}) \cdot \mathbf{P}_\nu(\mathbf{k}), \tag{4.16}$$

where

$$\hat{\Gamma}(\lambda_A R, \mathbf{k}) = \sum_{\lambda_R} \hat{\Gamma}(\lambda_A \lambda_R, \mathbf{k}) / \sum_{J(\neq A)} \sigma_J. \tag{4.17}$$

By substituting eq. (4.16) into eq. (4.14), we see that the sum over ν in each term can be expressed in terms of the dielectric constant tensor $\hat{\varepsilon}^R$ for the isolated system R . Indeed, according to eq. (3.24), we obtain the relations

$$\begin{aligned}
 & \frac{8\pi}{v} \sum_{\nu} \frac{E_\nu(\mathbf{k})}{E_\mu^2(\mathbf{k}) - E_\nu^2(\mathbf{k})} \mathbf{P}_\nu(\mathbf{k}) \mathbf{P}_\nu^*(\mathbf{k}) \\
 &= \hat{1} - \hat{\varepsilon}^R(E_\mu, \mathbf{k}) + \frac{[\hat{1} - \hat{\varepsilon}(E_\mu, \mathbf{k})] \cdot \mathbf{k} \mathbf{k} \cdot [\hat{1} - \hat{\varepsilon}^R(E_\mu, \mathbf{k})]}{\mathbf{k} \cdot \hat{\varepsilon}^R(E_\mu, \mathbf{k}) \cdot \mathbf{k}},
 \end{aligned} \tag{4.18}$$

$$\frac{8\pi}{v} \sum_{\nu} \frac{E_\nu(\mathbf{k}) k^{-2}}{E_\mu^2(\mathbf{k}) - E_\nu^2(\mathbf{k})} \mathbf{P}_\nu(\mathbf{k}) \mathbf{P}_\nu^*(\mathbf{k}) \cdot \mathbf{k} = \frac{[\hat{1} - \hat{\varepsilon}^R(E_\mu, \mathbf{k})] \cdot \mathbf{k}}{\mathbf{k} \cdot \hat{\varepsilon}^R(E_\mu, \mathbf{k}) \cdot \mathbf{k}}, \tag{4.19}$$

$$\frac{8\pi}{v} \sum_{\nu} \frac{E_\nu(\mathbf{k}) k^{-2}}{E_\mu^2(\mathbf{k}) - E_\nu^2(\mathbf{k})} |\mathbf{k} \cdot \mathbf{P}_\nu(\mathbf{k})|^2 = \frac{k^2}{\mathbf{k} \cdot \hat{\varepsilon}^R(E_\mu, \mathbf{k}) \cdot \mathbf{k}} - 1. \tag{4.20}$$

Making use of eqs. (4.14), (4.16) and (4.18)~(4.20), and ignoring the dependence of $\hat{\varepsilon}^R$ and $\hat{\Gamma}$ on \mathbf{k} because of the condition (2.41), we find that eq. (4.9) in the dipole approximation, i.e., the Fourier component of the effective dipole-dipole interaction can be written as

$$L^{\text{eff}}(\rho_A \rho'_A, E_\mu^0, \mathbf{k}) = L_M^{\text{eff}}(\rho_A \rho'_A, E_\mu^0, \mathbf{k}) + L_S^{\text{eff}}(\rho_A \rho'_A, E_\mu^0), \tag{4.21}$$

where E_μ^0 means $E_\mu(\mathbf{k})$ at $\mathbf{k}=0$ and

$$L_M^{\text{eff}}(\rho_A \rho'_A, E_\mu^0, \mathbf{k}) = \frac{8\pi}{v} \sqrt{\Delta(\rho_A) \Delta(\rho'_A)} \frac{\mathbf{k} \cdot \mathbf{p}^{\text{eff}}(\rho_A, E_\mu^0) \mathbf{k} \cdot \mathbf{p}^{\text{eff}}(\rho'_A, E_\mu^0)}{\mathbf{k} \cdot \hat{\varepsilon}^R(E_\mu^0, 0) \cdot \mathbf{k}} \tag{4.22}$$

$$L_S^{\text{eff}}(\rho_A \rho'_A, E_\mu^0) = \frac{8\pi}{v} \sqrt{\Delta(\rho_A) \Delta(\rho'_A)} \mathbf{p}(\rho_A) \cdot \hat{\Gamma}^{\text{eff}}(\lambda_A \lambda'_A, E_\mu^0) \cdot \mathbf{p}(\rho'_A), \tag{4.23}$$

with the definitions of

$$\mathbf{p}^{\text{eff}}(\rho_A, E_{\mu^0}) = \{\hat{1} + [\hat{1} - \hat{\varepsilon}^R(E_{\mu^0}, 0) \cdot \hat{F}(R\lambda_A, 0)]\} \cdot \mathbf{p}(\rho_A), \quad (4.24)$$

$$\hat{F}^{\text{eff}}(\lambda_A \rho'_A, E_{\mu^0}) = \hat{F}(\lambda_A \rho'_A, 0) + \hat{F}(\lambda_A R, 0) \cdot [\hat{1} - \hat{\varepsilon}(E_{\mu^0}, 0)] \cdot \hat{F}(R\lambda'_A, 0). \quad (4.25)$$

Note that the components of $\hat{\varepsilon}^R$ and \hat{F} at $\mathbf{k}=0$ are real, as seen from eqs. (2.35) and 3.17).

The expressions (4.22) and (4.23) should be compared with $L_M(\rho_A \rho'_A, \mathbf{k})$ and $L_S(\rho_A \rho'_A, 0)$ in vacuum given by eqs. (2.31) and (2.32). We consider cubic crystals with the dielectric constant tensor of $\hat{\varepsilon}^R(E_{\mu^0}, 0) = \varepsilon^R(E_{\mu^0}) \hat{1}$. Since the tensor $\hat{F}(\lambda\lambda', 0)$ is given by $-(1/3)\hat{1}$ for lattice sites λ and λ' possessing at least tetrahedral symmetry⁶⁾, eq. (4.24) is written as $\mathbf{p}^{\text{eff}}(\rho_A, E_{\mu^0}) = \mathbf{p}(\rho_A) [\varepsilon^R(E_{\mu^0}) + 2]/3$ and so the macroscopic part (4.22) is given by

$$L_M^{\text{eff}}(\rho_A \rho'_A, E_{\mu^0}, \mathbf{k}) = \frac{1}{\varepsilon^R(E_{\mu^0})} \left[\frac{\varepsilon^R(E_{\mu^0}) + 2}{3} \right]^2 L_M(\rho_A \rho'_A, \mathbf{k}). \quad (4.26)$$

The existence of $\varepsilon^R(E_{\mu^0})$ in the denominator reflects the Coulomb law in the medium. The expression (4.26) agrees with the results obtained from the macroscopic theory^{2,3,4)}. In the same way we obtain

$$L_S^{\text{eff}}(\rho_A \rho'_A, E_{\mu^0}) = \frac{\varepsilon^R(E_{\mu^0}) + 2}{3} L_S(\rho_A \rho'_A, 0), \quad (4.27)$$

which does not correspond to the result from the macroscopic theory by reason of the fact that L_S^{eff} and L_S are essentially of the microscopic character.

If the interaction energies between atom are very small as compared with the one-atom excitation energy $\mathcal{A}(\rho_A)$ (this is the usual case for Frenkel's excitons), we may replace E_{μ^0} in eqs. (4.21) ~ (4.25) by \mathcal{A} , a typical value of $\mathcal{A}(\rho_A)$, with the result that eq. (4.21) is independent of the exciton energies to be solved. Thus, from eq. (4.8a), we can obtain the exciton energies of the system A by diagonalizing the $\sigma_{An_A} \times \sigma_{An_A}$ matrix constructed from $\hat{F}^{\text{eff}}(\rho_A \rho'_A, \mathcal{A}, \mathbf{k})$, if the components of the tensors $\hat{\varepsilon}^R(\mathcal{A}, 0)$ and $\hat{F}(\lambda\lambda', 0)$ are known. We emphasize here that the formula for $\hat{F}(\lambda\lambda', \mathbf{k})$ given in ref. 7 is very useful for numerical calculations.

The formulae derived in this paper will be utilized for analyzing the experimental data of lead halides which contain four lead ions and eight halogen ions per unit cell. The result will be reported elsewhere.

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