分子 Exciton 狀態에서의 Stark 效果

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Stark Effect in Molecular Exciton States

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요 약. 제이양자화 형식을 이용하여 분자 exciton 상태에서의 Stark 효과를 설명하는 이론을 전개하였다. 하나의 단위 세포당 두 개이상의 분자를 함유하는 결정에서의 스펙트럼 분리는 Stark효과 뿐만 아니라 Davydov 효과에도 관계 있으므로 이 두 효과를 모두 고려하여 결과에 반영되도록 하였다. 특히 단위세포당 두개의 분자를 함유하는 결정에 있어서의 스펙트럼분리는 외부에서 걸어준 균일한 전기장의 세기에 따라 쌍곡선함수적으로 변한다는 것을 보였으며 이로부터 한 분자의 들뜬 상태에서의 쌍극자모멘트에 관한 정보를 얻을 수 있음을 밝혔다.

ABSTRACT. A formal theory to explain the Stark effect in molecular exciton states is developed using the second-quantization formalism. In this theory not only the Stark effect but also the Davydov effect are explicitly taken into consideration since the observed spectral splitting in the UV spectra for molecular crystals with two or more molecules per unit cell may be the result of combination of the above two effects. Especially for molecular crystals containing two molecules in a unit cell the splitting is shown to be hyperbolically dependent upon the strength of an externally applied, uniform electric field, from which informations regarding the excited state dipole moments of a single molecule may be obtained.

1. INTRODUCTION

The UV absorption spectra of pure molecular crystals, where intermolecular interactions are very weak, show in many respects appearances similar to those of the corresponding solution or gas phase spectra; that is, the absorption bands observed in the solution or gas phase spectra appear in the crystal spectra, too. The effect of intermolecular interactions on the crystal spectra shows up, though not considerable, through the shift of band centers and/or increased (or decreased) band intensities. In particular in molecular crystals which contain two or more molecules in a unit cell the splitting of absorption bands a-

rises, which is not observable in the solution or gas phase spectra. Such spectral splitting are due to the resonance interactions among translationally inequivalent sets of molecules in the crystal and the corresponding phenomeonon is now called "the Davydov splitting" following the name of Russian physicist who first explained the observed spectral splitting theoretically. [1~6]

Measurements and theoretical interpretations of the Davydov splitting are important because they can give us a good deal of insight into the nature of intermolecular interactions in many molecular crystals. Unfortunately, for many molecular crystals the magnitude of Davydov splitting is not quite notable and it is not an easy matter to measure the splitting with sufficient accuracy in actual experiments. A number of molecular crystals (particularly, of aromatic hydrocarbons) have been reported to have the splitting of a few hundred cm^{-1}. [7,8] Most of theoretical calculations of the Davydov splitting for these crystals have been performed using the dipole-dipole approximation and have yielded reasonable results.

On the other hand Hochstrasser and his co-workers[9,10] have recenly published a series of papers regarding the effect of an externally applied, uniform electric field on the absorption spectra of molecular crystals and have suggested a new method of determining the (electric) dipole moment of a single molecule in an electronically excited state. They have shown in somewhat simplified manner that for molecular crystals containing two or more molecules in a unit cell the spectral splitting can be induced by the applied electric field even when the Davydov splitting is not considered to be observable, and such a spectral splitting, which will be referred to as the Stark splitting henceforth, is related to the difference between the dipole moment for the

ground state and that for an electronically excited state the transition to which corresponds to the observed absorption band. Hence, measurements of the Stark splitting can provide a means of estimating the magnitude of dipole moment for a single molecule in an electronically excited state, and Hochstrasser and his co-workers have indeed carried out experiments employing the uniform electric field ranging from 2.0×10^4 to 10.0×10^4 volts/cm. They have reported that an electric field of 7.3×10^4 volts/cm gave a mean Stark splitting of $5.9 \, cm^{-1}$ for benzophenone crystals in the $^1n\pi^*$ state at $4.2°K$. Also, the observed Stark splitting were found to increase linearly with increasing electric field strength and the slopes of thus obtained straight lines were used for estimating the magnitudes of dipole moments for the molecule in various excited states involved in the transitions corresponding to the observed absorption bands. However, strictly speaking, the results obtained by Hochstrasser *et al.* must be said to be applicable only to the case where the Davydov and intermolecular interaction effect are negligible compared to the effect of electric field. Also, in order to obtain theoretically interpretable results one must perform the experiment under the condition that enables the Stark splittings to be observed at the field strength kept as low as possible because too strong field may cause some secondary effects which cannot be handled theroetically very well.

In this paper the effect of an externally applied, uniform electric field on the absorption bands in molecular crystals is investigated theoretically and is generalized so that the method of determining the excited state dipole moment of a molecule proposed by Hochstrasser *et al.* may be applied even to the cases where the Davydov effect is not negligible. The change in intermolecular interaction and the induced polarization due to the presence of an electic field is, how-

ever, assumed to be small and not much attention will be paid to this. [11] In order to formulate the problem mathematically we adopt the molecular exciton theory which has been extensively developed by Davydov, Agranovitch, Craig, and others. [12] Mathematical treatment of the problem described in this paper is apparently similar to that of Agranovitch; [13] however, there is an obvious distinction between the latter and ours since the crystal under consideration here is subject to the influence of an electric field. The theory in this paper is developed with tacit assumption of the rigid lattice and no intramolecular vibration. However, the same formalism can easily be extended to include the vibronic states. [14]

2. Derivation of the Second-Quantized Crystal Hamiltonian

Consider a pure molecular crystal with two or more molecules in a unit cell. In the presence of an externally applied, uniform electric field, ε, the electronic part of the Hamiltonian for such a crystal as described above may be written

$$H = H_0 + V \tag{2-1}$$

where H_0 is the sum of electronic Hamiltonian for individual molecules in the presence of electric field, ε, and V denotes the sum of intermolecular interactions in the crystal. For convenience let us denote the molecular site at the α-th site of n-th cell by the symbol $(n\alpha)$. Then we may rewrite H_0 and V explicitly into

$$H_0 = \sum_{n\alpha} h_{n\alpha} = H_0^{(0)} + H_0^{(1)} \tag{2-2}$$

and

$$V = \frac{1}{2} \sum_{n\alpha, m\beta}'' V_{n\alpha, m\beta} \tag{2-3}$$

where

$$H_0^{(0)} = \sum_{n\alpha} h_{n\alpha}^{(0)} \tag{2-4a}$$

and

$$H_0^{(1)} = -\sum_{n\alpha} \mu_{n\alpha} \cdot \varepsilon \tag{2-4b}$$

In the above expressions $h_{n\alpha}$ and $h_{n\alpha}^{(0)}$ represent the electronic Hamiltonian for an isolated molecule located at the site $(n\alpha)$ in the presence and absence of ε, respectively, $V_{n\alpha, m\beta}$ stands for the intermolecular interaction between the molecule at the site $(n\alpha)$ and that at the site $(m\beta)$, and $\mu_{n\alpha}$ denotes the (electric) dipole moment operator for the molecule at the site $(n\alpha)$. Also, the prime on the summation symbol $\sum_{n\alpha, n\beta}$ means excluding the term for which $n\alpha = m\beta$ from the indicated summation.

Let the eigenfunctions of $h_{n\alpha}$ and $h_{n\alpha}^{(0)}$ be expressed by the functions $\psi_{n\alpha}^f$ and $\varphi_{n\alpha}^f$, respectively, and the corresponding energy eigenvalues by $E_{n\alpha}^f$ and $\epsilon_{n\alpha}^f$. Then we may write

$$h_{n\alpha} \psi_{n\alpha}^f = E_{n\alpha}^f \psi_{n\alpha}^f \tag{2-5}$$

$$h_{n\alpha}^{(0)} \varphi_{n\alpha}^f = \epsilon_{n\alpha}^f \varphi_{n\alpha}^f \tag{2-6}$$

with f representing the appropriate quantum number(s) for an electronic state.

If we designate the creation and annihilation operator for the molecular state $\psi_{n\alpha}^f$ by $a_{n\alpha}^{f+}$ and $a_{n\alpha}^f$, respectively, we may rewrite the Hamiltonian (2-1) in terms of $a_{n\alpha}^{f+}$ and $a_{n\alpha}^f$ as follows: [15]

$$\begin{aligned} H = &\sum_{n\alpha} \sum_f E_{n\alpha}^f a_{n\alpha}^{f+} a_{n\alpha}^f \\ &+ \frac{1}{2} \sum_{n\alpha, m\beta}' \sum_{\substack{f,f' \\ g,g'}} V_{n\alpha, m\beta}(fg; f'g') \, a_{n\alpha}^{f+} a_{m\beta}^{g+} \\ &\times a_{m\beta}^{g'} a_{n\alpha}^{f'} \end{aligned} \tag{2-7}$$

where [16]

$$V_{n\alpha, m\beta}(fg; f'g') = \int \psi_{n\alpha}^{f*} \psi_{m\beta}^{g*} V_{n\alpha, m\beta} \psi_{n\alpha}^{f'} \psi_{m\beta}^{g'} d\tau$$

-exchange terms. $\tag{2-8}$

The operators $a_{n\alpha}^{f+}$ and $a_{n\alpha}^f$ are known to be the so-called "Pauli operators" and satisfy the following commutation relations:

$[a_{n\alpha}^f, a_{m\beta}^{g+}] = 0$ unless $f = g$ and $n\alpha = m\beta$,

$[a_{n\alpha}^f, a_{m\beta}^g] = [a_{n\alpha}^{f+}, a_{m\beta}^{g+}] = 0$,

and

$$[a_{n\alpha}^f, a_{n\alpha}^{f+}]_+ = 1 \qquad (2\text{-}9)$$

They are known also to satisfy the following important sum rules:

$$\sum_f a_{n\alpha}^{f+} a_{n\alpha}^f = 1 \qquad (2\text{-}10a)$$

and

$$\sum_{n\alpha} \sum_f a_{n\alpha}^{f+} a_{n\alpha}^f = \sigma N, \qquad (2\text{-}10b)$$

where N is the number of unit cells in the crystal and σ denotes the number of molecules contained in a unit cell.

In the molecular exciton theory we use the (localized) electronic exciton creation and annihilation operator, $B_{n\alpha}^{f+}$ and $B_{n\alpha}^f$, instead of $a_{n\alpha}^{f+}$ and $a_{n\alpha}^f$. According to Agranovitch $B_{n\alpha}^{f+}$ and $B_{n\alpha}^f$ can be defined in terms of $a_{n\alpha}^{f+}$ and $a_{n\alpha}^f$ as follows:

$$B_{n\alpha}^{f+} = a_{n\alpha}^{f+} a_{n\alpha}^0 \quad \text{and} \quad B_{n\alpha}^f = a_{n\alpha}^{0+} a_{n\alpha}^f, \qquad (2\text{-}11)$$

where the superscript 0 represents the electronic ground state and f the excited state. The occupation numbers for the state f and 0, $N_{n\alpha}(f)$ and $N_{n\alpha}(0)$, respectively, are given by

$$N_{n\alpha}(f) = a_{n\alpha}^{f+} a_{n\alpha}^f \quad \text{and} \quad N_{n\alpha}(0) = a_{n\alpha}^{0+} a_{n\alpha}^0 \qquad (2\text{-}12)$$

It is obvious that $N_{n\alpha}(f)$ and $N_{n\alpha}(0)$ are equal to either 1 or 0, and if $N_{n\alpha}(f) = 1$, $N_{n\alpha}(f')$ for some other state f' is zero. Hence, it is always true that

$$N_{n\alpha}(f) \ N_{n\alpha}(0) = 0$$

for the state f other than the ground state. Therefore,

$$\begin{aligned} B_{n\alpha}^{f+} B_{n\alpha}^f &= a_{n\alpha}^{f+} a_{n\alpha}^0 a_{n\alpha}^{0+} a_{n\alpha}^f \\ &= N_{n\alpha}(f) \ (1 - N_{n\alpha}(0)) \\ &= N_{n\alpha}(f) \\ &= a_{n\alpha}^{f+} a_{n\alpha}^f \qquad (2\text{-}14) \end{aligned}$$

Accordingly, $B_{n\alpha}^{f+}$ and $B_{n\alpha}^f$ also satisfy the sum

rules

$$\sum_f B_{n\alpha}^{f+} B_{n\alpha}^f = 1 \qquad (2\text{-}15a)$$

and

$$\sum_{n\alpha} \sum_f B_{n\alpha}^{f+} B_{n\alpha}^f = \sigma N.$$

It can also be shown that the statistical considerations[17] lead us to the conclusion that $B_{n\alpha}^{f+}$ and $B_{n\alpha}^f$ approximately satisfy the following commutation rules:

$$[B_{n\alpha}^f, B_{n\alpha}^{f+}] = 1, \qquad (2\text{-}16a)$$

$$[B_{n\alpha}^f, B_{\beta m}^g] = [B_{n\alpha}^{f+}, B_{m\beta}^{g+}] = 0, \qquad (2\text{-}16b)$$

and

$$[B_{n\alpha}^f, B_{m\beta}^{g+}] = 0 \quad \text{unless } n\alpha = m\beta \text{ and } f = g. \qquad (2\text{-}16c)$$

That is, in this sense $B_{n\alpha}^{f+}$ and $B_{n\alpha}^f$ are the Bose operators. In Appendix I it is shown that the Hamiltonian (2-7) may berewritten in terms of $B_{n\alpha}^f$ and $B_{n\alpha}^f$ into the following form:

$$\begin{aligned} H = E_0 &+ \sum_{n\alpha} \sum_{f(\neq 0)} \Delta_{n\alpha}^f B_{n\alpha}^{f+} B_{n\alpha}^f \\ &+ \frac{1}{2} \sum_{n\alpha, m\beta}{}' \sum_{\substack{f, f' \\ (\neq 0)}} V_{n\alpha, m\beta}(f0; 0f') (B_{n\alpha}^{f+} + B_{n\alpha}^f) \\ &\qquad\qquad \times (B_{m\beta}^{f'+} + B_{m\beta}^{f'}) \qquad (2\text{-}17) \end{aligned}$$

where

$E_0 =$ electronic ground state energy for the entire crystal in the presence of electric field,

$$= \sum_{n\alpha} \left\{ E_{n\alpha}^0 + \frac{1}{2} \sum_{m\beta}{}' V_{n\alpha, m\beta} \ (00; 00) \right\} \qquad (2\text{-}18)$$

and

$$\begin{aligned} \Delta_{n\alpha}^f = \ & \{E_{n\alpha}^f - E_{n\alpha}^0\} \\ & + \sum_{m\beta}{}' \{V_{n\alpha, m\beta}(f0; f0) - V_{n\alpha, m\beta}(00; 00)\}. \qquad (2\text{-}19) \end{aligned}$$

The second part in the expression (2-19) may be regarded as the change in van der Waals interactions for the crystal on electronic excitation of a single molecule in the presence of an electric field. The apparent form of the derived

crystal Hamiltonian (2-17) may seem to resemble those used by other people, [18] but unlike the latter the effect of an electric field is implicitly incorporated into the expression (2-17) since we are working on the basis of $\phi_{n\alpha}^f$ representation, not on the $\varphi_{n\alpha}^f$ representation.

3. Diagonalization of the Crystal Hamiltonian

In order to find the energy eigenvalues for elementary excitation we have to diagonalize the Hamiltonian (2-17). To do so, we adopt the Tyablikov's method of diagonalization of Hamiltonian of the quadratic form[19,20] and proceed as follows. Suppose that by a canonical transformation the Hamiltonian can be converted into the following form in terms of a set of new Bose operators ξ_μ^+ and ξ_μ:

$$H = \phi_0 + \sum_\mu E_\mu \xi_\mu^+ \xi_\mu. \tag{3-1}$$

Then, the equations of motion for the operators ξ_μ^+ and ξ_μ may be written in the form

$$\frac{d}{dt} \xi_\mu^+ = i[H, \xi_\mu^+] = iE_\mu \xi_\mu^+ \tag{3-2a}$$

and

$$\frac{d}{dt} \xi_\mu = i[H, \xi_\mu] = -iE_\mu \xi_\mu \tag{3-2b}$$

where we have made use of the following properties of ξ_μ^+ and ξ_μ:

$$[\xi_\mu, \xi_{\mu'}^+] = \delta_{\mu\mu'} = \begin{cases} 1 & \text{for } \mu = \mu' \\ 0 & \text{otherwise} \end{cases} \tag{3-3a}$$

and

$$[\xi_\mu, \xi_{\mu'}] = [\xi_\mu^+, \xi_{\mu'}^+] = 0. \tag{3-3b}$$

Now, we assume that $B_{n\alpha}^{f\pm}$ and $B_{n\alpha}^f$ can be written in terms ξ_μ^+ and ξ_μ as follows:

$$B_{n\alpha}^{f+} = \sum_\mu \{u_\mu^*(n\alpha, f)\xi_\mu^+ + v_\mu(n\alpha, f)\xi_\mu\} \tag{3-4a}$$

and

$$B_{n\alpha}^f = \sum_\mu \{u_\mu(n\alpha, f)\xi_\mu + v_\mu^*(n\alpha, f)\xi_\mu^+\} \tag{3-4b}$$

Using the Hamiltonian (2-17), one can obtain the equations of motion for the operator $B_{n\alpha}^{f+}$ in the following form:

$$\frac{d}{dt} B_{n\alpha}^{f+} = i[H, B_{n\alpha}^{f+}] = i\{\Delta_{n\alpha}^f B_{n\alpha}^{f+} + \sum_{m\beta}' \sum_{f'(\neq 0)} V_{n\alpha, m\beta}(f0; 0f')(B_{m\beta}^{f'+} + B_{m\beta}^{f'})\} \tag{3-5}$$

Substitution of (3-4a) into Eq. (3-5) and use of Eqs. (3-2a) and (3-2b) yield

$$\sum_\mu \{E_\mu u_\mu^*(n\alpha, f)\xi_\mu^+ - E_\mu v_\mu(n\alpha, f)\xi_\mu\}$$
$$= \sum_\mu \{\xi_\mu^+ [\Delta_{n\alpha}^f u_\mu^*(n\alpha, f)$$
$$+ \sum_{m\beta}' \sum_{f'(\neq 0)} V_{n\alpha, m\beta}(f0; 0f')(u_\mu^*(m\beta, f')$$
$$+ v_\mu^*(m\beta, f'))] + \xi_\mu[\Delta_{n\alpha}^f v_\mu(n\alpha, f)$$
$$+ \sum_{m\beta}' \sum_{f'(\neq 0)} V_{n\alpha, m\beta}(f0; 0f')(u_\mu(m\beta, f')$$
$$+ v_\mu(m\beta, f'))]\}. \tag{3-6}$$

since ξ_μ and ξ_μ^+ are linearly independent of each other, coefficients of these operators in Eq. (3-6) should identically vanishing for all μ. Thus we obtain

$$(E_\mu - \Delta_{n\alpha}^f) u_\mu(n\alpha, f) = -(E_\mu + \Delta_{n\alpha}^f)v_\mu(n\alpha, f)$$
$$= \sum_{m\beta}' \sum_{f'(\neq 0)} V_{n\alpha, m\beta}(f0; 0f')[u_\mu(m\beta, f')$$
$$+ v_\mu(m\beta, f')]. \tag{3-7}$$

We impose the following normalization condition on the solutions $u_\mu(\alpha n, f)$ and $v_\mu(n\alpha, f)$

$$\sum_{n\alpha} \sum_{f(\neq 0)} \{u_\mu(n\alpha, f)u_\mu^*(n\alpha, f) - v_\mu(n\alpha, f) v_\mu^*(n\alpha, f)\} = 1. \tag{3-8}$$

Then Eq. (3-7) along with (3-8) uniquely determines the solutions $u_\mu(n\alpha, f)$ and $v_\mu(n\alpha, f)$. Also, substituting (3-4a) and (3-4b) into (2-16a) through (2-16c) and making use of the relations (3-3a) and (3-3b) we can obtain another important orthonormality conditions:

$$\sum_\mu \{u_\mu(n\alpha,)u_\mu^*(m\beta, f') - v_\mu(n\alpha, f) v_\mu^*(m\beta, f')\} = \delta_{nm}\delta_{\alpha\beta}\delta_{ff'} \tag{3-9a}$$

and

$$\sum_\mu \{u_\mu(n\alpha,\ f)v_\mu^*(m\beta,f') - v_\mu^*(n\alpha,f)$$

$$\times u_\mu(m\beta,\ f')\} = 0. \qquad (3\text{-}9b)$$

In Appendix II we derive some other useful orthogonality relations for $u_\mu(n\alpha,f)$ and $v_\mu(n\alpha,f)$ and it will be shown that the eigenvalues for Eq. (3-7), E_μ, are real and positive.

For simplicity, let

$$\tilde u_\mu(n\alpha,f) \equiv u_\mu(n\alpha,f) + v_\mu(n\alpha,f).$$

We may rewrite Eq. (3-7) into the following form:

$$v_\mu(n\alpha,\ f) = -\frac{E_\mu - \Delta_{n\alpha}^f}{E_\mu + \Delta_{n\alpha}^f}\ u_\mu(n\alpha,f). \quad (3\text{-}10)$$

It then follows from the definition of $\tilde u_\mu(n\alpha,f)$ and Eq. (3-7) that

$$\tilde u_\mu(n\alpha,\ f) = \left(1 - \frac{E_\mu - \Delta_{n\alpha}^f}{E_\mu + \Delta_{n\alpha}^f}\right)u_\mu(n\alpha,f)$$

$$= -\frac{2\Delta_{n\alpha}^f}{E_\mu + \Delta_{n\alpha}^f}u_\mu(n\alpha,f)$$

or

$$u_\mu(n\alpha,f) = -\frac{E_\mu + \Delta_{n\alpha}^f}{2\Delta_{n\alpha}^f}\ \tilde u_\mu(n\alpha,f). \qquad (3\text{-}11)$$

Substituting (3-11) into (3-7), we obtain

$$(E_\mu^2 - \Delta_{n\alpha}^{f2})\tilde u_\mu(n\alpha,f)$$
$$= 2\Delta_{n\alpha}^f \sum_{m\beta} \sum_{f'(\neq 0)} V_{n\alpha,m\beta}\ (f0;\ 0f')\ \tilde u_\mu(m\beta,f') \qquad (3\text{-}12)$$

In Appendix III it is shown that if the relationship (3-7) [or (3-12)] holds, then the Hamiltonian (2-17) is diagonalized into the following form:

$$H = E_0 - \sum_\mu E_\mu \left(\sum_{n\alpha} \sum_{f(=0)} |v_\mu(n\alpha,f)|^2\right)$$
$$+ \sum_\mu E_\mu \xi_\mu^+ \xi_\mu \qquad (3\text{-}13)$$

4. Determination of the Excitation Energy E_μ.

In order to determine the elementary excitation (that is, molecular exciton in the presence of an electric field) energy, E_μ, we must solve Eq. (3-12) with respect to the coefficients $\tilde u_\mu(n\alpha,f)$. Since translational symmetry of the crystal remains intact despite the presence of a uniform

electric field ε, we look for the solution of the following form:

$$\tilde u_\mu(n\alpha,f) = (N\sigma)^{-1/2}\tilde u_k^\alpha(\mu,f)\ \exp(ik\cdot r_{n\alpha}), \qquad (4\text{-}1)$$

where k is the appropriate wave vector and $r_{n\alpha}$ is the position vector for the site $(n\alpha)$ with respect to an arbitrarily chosen origin.

Subsitution of (4-1) into (3-12) gives us

$$(E_\mu^2 - \Delta_{n\alpha}^{f2})\tilde u_k^\alpha(\mu,f)$$
$$= 2\Delta_{n\alpha}^f \sum_{m\beta}' \sum_{f'(\neq 0)} V_{n\alpha,m\beta}\ (f0;\ 0f')e^{ik\cdot(r_{m\beta}-r_{n\alpha})}$$
$$\times \tilde u_k^\beta(\mu,f'). \qquad (4\text{-}2)$$

It is difficult to obtain the solutions by solving Eq. (4-2) directly because the factor $V_{n\alpha,m\beta}(f0;0f')$ interconnects two different (molecular) electronic states f and f'. However, in order to predict the position of a band center we may restrict ourselves to the case for which $f=f'$. In other words, to a good aproximation we may exclude all other terms except the term representing the intermolecular resonance interaction, $V_{n\alpha,m\beta}(f0;0f)$. Then, Eq. (4-2) is further simplified to

$$(E_\mu^2 - \Delta_{n\alpha}^{f2})\tilde u_k^\alpha(\mu,f)$$
$$= 2\Delta_{n\alpha}^f \sum_{m\beta}' V_{n\alpha,m\beta}(f0;0f)e^{ik\cdot(r_{m\beta}-r_{n\alpha})}$$
$$\times \tilde u_k^\beta(\mu,f). \qquad (4\text{-}3)$$

In molecular crystals where intermolecular interactions are weak energies for the exciton states are not much different from those for the corresponding electronic states of a single molecule in the crystal, and therefore one may replace the term $(E_\mu^2 - \Delta_{n\alpha}^{f2})$ by $2\Delta_{n\alpha}^f(E_\mu - \Delta_{n\alpha}^f)$. Hence

$$(E_\mu - \Delta_{n\alpha}^f)\tilde u_k^\alpha(\mu,f)$$
$$= \sum_{m\beta}'\ V_{n\alpha,m\beta}(0;0\ f)e^{ik\cdot(r_{m\beta}-r_{n\alpha})}\tilde u_k^\beta(\mu,f). \qquad (4\text{-}4)$$

The approximation we have just adopted is equivalent to the so-called Heitler-London approximation. [21] For convenience, let us introduce two

quantities called the equivalent sum and the inequivalent sum designated by $L_{aa}^{f}(k)$ and $L_{a\beta}^{f}(k)$, respectively, which are defined as below:

$$L_{aa}^{f}(k) = \sum_{m(\neq n)} V_{na,ma}(f0;0f)e^{ik\cdot(r_{ma}-r_{na})}$$

(4-5a)

and

$$L_{a\beta}^{f}(k) = \sum_{m} V_{na,m\beta}(f0;0f)e^{ik\cdot(r_{m\beta}-r_{na})}$$ (4-5b)

Since E_{na}^{f}, ϵ_{na}^{f}, $\varDelta_{na}^{f}$, $L_{aa}^{f}(k)$, and $L_{a\beta}^{f}(k)$ are independent of the index n which represents a particular unit cell, we may drop such index from the above-mentioned quantities without any ambiguity. Thus Eq. (4-4) may be reexpressed in terms of (4-5a) and (4-5b) as follows:

$$[E_{\mu}-\varDelta_{a}^{f}-L_{aa}^{f}(k)]\,\tilde{u}_{k}^{a}(\mu,f)$$
$$=\sum_{\beta(\neq a)} L_{a\beta}^{f}(k)\tilde{u}_{k}^{\beta}(\mu,f). \quad (\alpha=1,\,2,\,\cdots\cdots\sigma)$$

(4-6)

E_{μ} can be determined by solving the secular equation

$$\det[\{E_{\mu}-\varDelta_{a}^{f}-L_{aa}^{f}(k)\}\,\delta_{\alpha\beta}-L_{a\beta}^{f}(k)]=0$$
$$(\alpha=1,\,2,\cdots\sigma;\,\beta=1,\,2,\cdots\sigma) \qquad (4-7)$$

Eq. (4-7), in general, yields σ solutions for E_{μ}, which correspond to energy levels of the σ exciton bands in the presence of an electric field. The oscillator strength of the photon induced transition from the ground state to the state of E_{μ} is

$$F_Q(\mu)=\frac{2mE_{\mu}}{\hbar^2 e^2}|\sum_{na}\sum_{f(\neq 0)}(e_Q\cdot\mu_{na}^{f0})$$
$$\times\tilde{u}_{\mu}(na,f)e^{-iQ\cdot r_{na}}|^2 \qquad (4-8)$$

where Q is the propagation vector of the photon, e_Q the polarization vector of the photon and $\mu_{na}^{f0}=\int\phi_{na}^{f*}\,\mu_{na}\phi_{na}^{0}d\tau$ is the transition dipole. [22]

Actual application of Eq. (4-6) to molecular crystals requires knowledge of the crystal structure data as well as experimental conditions such as the polarization plane and direction of propagation vector of the light wave used, and we

cannot go further beyond this stage. However, for illustration of the theory developed thus far let us consider the case where two molecules are contained in a unit cell. In this case the secular equation (4-7) becomes

$$\begin{vmatrix} E_{\mu}-\varDelta_{a}^{f}-L_{aa}^{f}(k) & -L_{a\beta}^{f}(k) \\ -L_{\beta a}^{f}(k) & E_{\mu}-\varDelta_{\beta}^{f}-L_{\beta\beta}^{f}(k) \end{vmatrix}=0.$$

(4-9)

The two solutions for E_{μ} of the above equation are given by

$$E_f^{\pm}(k)=\frac{1}{2}[\varDelta_a^f+\varDelta_\beta^f+L_{aa}^f(k)+L_{\beta\beta}^f(k)]$$
$$\pm\frac{1}{2}[\{\varDelta_a^f-\varDelta_\beta^f+L_{aa}^f(k)-L_{\beta\beta}^f(k)\}^2$$
$$+4|L_{a\beta}^f(k)|^2]^{1/2}. \qquad (4-10)$$

where we have noted the relation

$$L_{\beta a}^{f}(k)=L_{a\beta}^{f}(k)^*.$$

The solutions represented by (4-10) give two exciton bands originating from the f-th electronic state of an isolated molecule.

5. Stark Effect and Davydov Splitting

In order to discuss the Davydov splitting and the Stark effect in molecular crystals let us consider the case where two molecules are contained in a unit cell. The two energy levels given by (4-10) would be degenerate if it were not for either intermolecular interaction or an externally applied electric field or both, and the absorption line corresponding to the transitions to such levels (from the crystal ground state) would constitute a singlet. However, in actual crystal spectra the would-be singlet will appear as a doublet due to the presence of afore-mentioned intermolecular interaction and an electric field, and such spectral splitting can in turn be used to estimate the effect of intermolecular interactions and/or an externally applied field. One of the difficult problems here is that an externally applied field itself may influence indirectly the inter-

molecular interactions via reorientation of permanent dipole moments and induced polarization and thus affected intermolecular interactions themselves can in turn alter the strength of field actually "felt" by molecules. This is the kind of difficulty which is essential to all the many body problems and must be treated in a self-consistent manner. In order to avoid such a difficulty we take only the direct interaction between the molecular dipole moment and an external field into consideration in this paper assuming intuitively that effect of the field on intermolecular interactions, particularly for weak transitions in molecular crystals, may be ignored. However in a paper subsequent to this we intend to develop a method of estimating the magnitude of such effect for the crystals where intermolecular interactions are of appreciable magnitude.

Taking the difference of two energy levels given by (4-10), we may write

$$\Delta E_f(k) \equiv E_f{}^+(k) - E_f{}^-(k)$$
$$= [\{\Delta_\alpha^f - \Delta_\beta^f + L_{\alpha\alpha}^f(k) - L_{\beta\beta}^f(k)\}^2$$
$$+ 4|L_{\alpha\beta}^f(k)|^2]^{1/2}. \qquad (5\text{-}1)$$

In the exciton spectroscopy the selection rule is $k=Q$,[23] where Q is the propagation vector of incident electromagnetic wave. Since in the region of electromagnetic spectrum which we are concerned with here $|Q| \approx 0$,[24] we may represent the selection rule by $|k|=0$. However, when using such selection rule, one must be careful because $L_{\alpha\alpha}^f(k)$ and $L_{\beta\beta}^f(k)$ are nonanalytic in the vicinity of $k=0$.[25,26] In other words there is no unique exciton band defined at $k=0$, the center of Brillouin zone. If we, however, specify the direction of k near $k=0$, we can get out of this trouble. For an arbitrary direction of k (or Q) $L_{\alpha\alpha}^f(k)$ is not in general equal to $L_{\beta\beta}^f(k)$, and Eq. (5-1) cannot be further simplified and comparison of an experimentally measured splitting with theoretically calculated one

will become a complicated matter. However, if we choose the direction of incident light wave such that its propagation vector be either parallel or perpendicular to the plane of symmetry of the crystal, it may be shown that[26]

$$L_{\alpha\alpha}^f(k) = L_{\beta\beta}^f(k).$$

Under these conditions the spectral splitting is given by

$$\Delta E_f(0) = [(\Delta_\alpha^f - \Delta_\beta^f)^2 + 4|L_{\alpha\beta}^f(0)|^2]^{1/2}. \qquad (5\text{-}2)$$

Since the change in the van der Waals energy [the second part of Eq. (2-19)] has been assumed to be affected very little by the presence of an external field ε, we may approximate $\Delta_\alpha^f - \Delta_\beta^f$ by $(E_\alpha^f - E_\alpha^0) - (E_\beta^f - E_\beta^0)$ and the latter can be estimated using the perturbation theory.

Application of the first-order perturbation theory to Eqs. (2-5) and (2-6) gives us

$$E_\alpha^f - E_\alpha^0 \cong (\epsilon_\alpha^f - \epsilon_\alpha^0) - \Delta\mu_\alpha^f \cdot \varepsilon \qquad (5\text{-}3a)$$

and

$$E_\beta^f - E_\beta^0 \cong (\epsilon_\beta^f - \epsilon_\beta^0) - \Delta\mu_\beta^f \cdot \varepsilon \qquad (5\text{-}3b)$$

where

$$\Delta\mu_\alpha^f \equiv \mu_{\alpha f}^{(0)} - \mu_{\alpha 0}^{(0)}$$
$$= \int \varphi_\alpha^{f*} \mu_\alpha \varphi_\alpha^f d\tau - \int \varphi_\alpha^{0*} \mu_\alpha \varphi_\alpha^0 d\tau \qquad (5\text{-}4a)$$

and

$$\Delta\mu_\beta^f \equiv \mu_{\beta f}^{(0)} - \mu_{\beta 0}^{(0)}$$
$$= \int \varphi_\beta^{f*} \mu_\beta \varphi_\beta^f d\tau - \int \varphi_\beta^{0*} \mu_\beta \varphi_\beta^0 d\tau. \qquad (5\text{-}4b)$$

$\Delta\mu_\alpha^f$ represents the vectorial difference between the dipole moment for the f-th (excited) state and that for the ground state in the molecule with orientation α and $\Delta\mu_\beta^f$ means the same thing for the molecule with orientation β.

For pure molecular crystals $\epsilon_\alpha^f = \epsilon_\beta^f$, $\epsilon_\alpha^0 = \epsilon_\beta^0$, and $|\Delta\mu_\alpha^f| = |\Delta\mu_\beta^f| \equiv \Delta\mu^f$ since all the molecules in the crystal are of the same kind. Hence

$$\Delta_\alpha^f - \Delta_\beta^f \approx - (\Delta\mu_\alpha^f - \Delta\mu_\beta^f) \cdot \varepsilon$$

$$= \Delta\mu^f (\cos \theta_\beta - \cos \theta_\alpha)\varepsilon \qquad (5\text{-}5)$$

where θ_α and θ_β are angles which $\Delta\mu_\alpha^f$ and $\Delta\mu_\beta^f$ make with the electric field ε, respectively. If the molecular and crystal structure and the direction of ε relative to the crystal axes are known one can calculate the term $(\cos \theta_\beta - \cos \theta_\alpha)$. Substituting (5-5) into Eq. (5-2), we obtain the following expression representing the observed spectral splitting:

$$\Delta E_f(0) = [\{\Delta\mu^f (\cos \theta_\beta - \cos \theta_\alpha)\varepsilon\}^2$$
$$+ 4|L_{\alpha\beta}^f(0)|^2]^{1/2} \qquad (5\text{-}6)$$

If we measure the spectral splittings for various strengths and directions of ε while the propagation vector of incident light wave is made to be either parallel or perpendicular to the plane of symmetry of the crystal, we can obtain the values for $\Delta\mu^f$. If we plot $\Delta E_f(0)$ against $\Delta\mu^f (\cos \theta_\beta - \cos \theta_\alpha)\varepsilon$, we will obtain a hyperbolic curve as shown in the *Fig.* 1 provided that ε is not too large.

In the limit that $\varepsilon = 0$ we obtain $2|L_{\alpha\beta}^f(0)|$ for $\Delta E_f(0)$, which is the well-known Davydov splitting. On the other hand if the Davydov splitting $2|L_{\alpha\beta}^f(0)|$ is negligibly small, Eq. (5-6) reduces to the relation used by Hochstrasser *et al.* Thus our formula for the spectral splitting
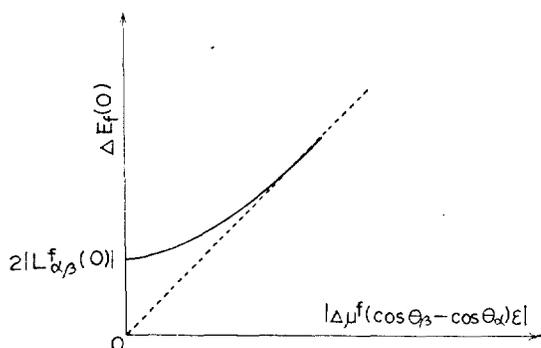

Fig. 1. Plot of $\Delta E_f(0)$ against $|\Delta\mu^f (\cos \theta_\beta - \cos \theta_\alpha \varepsilon|$ (not drawn to scale. The slope of asymptotic line for the hyperbola is 1.)

[Eq. (5-6)] can be considered to represent the combined effect of external field and intermolecular resonance interactions correctly. Though the type of experiment described here has yet to be performed, the results obtained by Hochstrasser and Lin[27] provide some evidences that the formula (5-6) is indeed reasonable.

6. Conclusions and Discussions

We have developed here a theory to explain the Stark effect in molecular exciton states for the crystals containing two or more molecules in a unit cell to the extent that the theory can be applied to the case where the Davydov splitting is not negligible compared to the Stark splitting under the assumption that the externally applied electric field is low enough for the change in intermolecular interactions to be ignored. The result derived for the crystals containing two molecules in a unit cell correctly shows the combined effect of both electric field and intermolecular resonance interactions, and this in turn can be used to estimate the values for vectorial difference between the dipole moment for the excited state and that for the ground state. There are two important points we have to mention in connection with the experiment described here. The first is that the measured quantity $\Delta\mu^f$ itself is not necessarily equal to the difference between the magnitude of excited state dipole moment and that of the ground state dipole moment since $\Delta\mu^f$ is merely the magnitude of vectorial difference between these two dipole moments. Only when the direction of molecular dipole moment remains unchanged on electronic excitation, we can regard $\Delta\mu^f$ as the difference between the magnitude of excited state dipole moment and that of the ground state dipole moment. The second is that in the experiment described here the absolute sign for $\Delta\mu^f$ cannot be determined. In order to determine the magnitude of dipole

moment for an excited state one must obtain the additional information from some other sources regarding whether the magnitude of dipole moment increases or decreases on electronic excitation in a molecule. There are some indications that the magnitude of dipole moment in molecules is likely to decrease on electronic excitation.[23,29] The theory developed here can easily be extended to the case where there are more than two molecules except that the calculations involved are more complicated than in the case of two molecules per unit cell. The observed spectral splitting plotted against the applied field strength is expected to show a hyperbolic curve provided that the Davydov splitting is not negligibly small and the applied field is not too strong. If we can identify the factor group to which the unit cell of the crystal under consideration does belong, the actual calculation will be greatly facilitated. Since we did not take into consideration the electron spins and interactions between them, the theory developed here may be applied only to the case of excited singlet states. Regarding extension of the theory to triplet states we intend to publish elsewhere.

Appendix I

By making use of the various properties of operators $a_{n\alpha}^{f+}$, $a_{n\alpha}^{f}$, $B_{n\alpha}^{f-}$, and $B_{n\alpha}^{f}$ the first term in the Hamiltonian(2-7) may be rewritten as follows:

$$
\begin{aligned}
&\sum_{n\alpha}\sum_{f} E_n^f\ a_{n\alpha}^{f+}\ a_{n\alpha}^{f} \\
&= \sum_{n\alpha} E_{n\alpha}^0\ a_{n\alpha}^{0+}\ a_{n\alpha}^0 + \sum_{n\alpha}\sum_{f(\neq 0)} E_{n\alpha}^f\ a_{n\alpha}^{f+}\ a_{n\alpha}^f \\
&= \sum_{n\alpha} E_{n\alpha}^0 (1-\sum_{f'\neq 0} a_{n\alpha}^{f'+}\ a_{n\alpha}^{f'}) + \sum_{n\alpha}\sum_{f(\neq 0)} E_{n\alpha}^f\ a_{n\alpha}^{f+}\ a_{n\alpha}^{f} \\
&= \sum_{n\alpha} E_{n\alpha}^0 + \sum_{n\alpha}\sum_{f(\neq 0)} (E_{n\alpha}^f - E_{n\alpha}^0)\ a_{n\alpha}^{f+}\ a_{n\alpha}^{f} \\
&= \sum_{n\alpha} E_{n\alpha}^0 + \sum_{n\alpha}\sum_{f(\neq 0)} (E_{n\alpha}^f - E_{n\alpha}^0) B_{n\alpha}^{f+}\ B_{n\alpha}^{f}. \quad (AI-1)
\end{aligned}
$$

Since the concentration of excited molecules is very low, we may ignore the interaction between two excited molecules. Thus among the second term in the Hamiltonian (2-7) we are

left only with terms involving $V_{n\alpha,m\beta}(f0;f'0)$. $V_{n\alpha,m\beta}(00;ff')$, $V_{n\alpha,m\beta}(f0;0f')$ and $V_{n\alpha,m\beta}(0f;f'0)$.

In this approximation the second term of the Hamiltonian (2-7) may be shown to take the form

$$
\begin{aligned}
&\frac{1}{2}\sum_{n\alpha,m\beta} V_{n\alpha m\beta}(00;00)a_{n\alpha}^{0-}\ a_{m\beta}^{0+}\ a_{n\alpha}^0\ a_{m\beta}^0 \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f(\neq 0)} V_{n\alpha,m\beta}(f0;f0)\ a_{n\alpha}^{f+}\ a_{m\beta}^{0+}\ a_{n\alpha}^f\ a_{m\beta}^0 \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f(\neq 0)} V_{n\alpha,m\beta}(0f;0f)\ a_{n\alpha}^{0+}\ a_{m\beta}^{f+}\ a_{n\alpha}^0\ a_{m\beta}^f \\
&+\frac{1}{2}\sum_{f(\neq 0)f(\neq 0)}'\sum\sum V_{n\alpha,m\beta}(ff';00)a_{n\alpha}^{f+}a_{m\beta}^{f'+}\ a_{n\alpha}^0\ a_{m\beta}^0 \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f(\neq 0)f'(\neq 0)}\sum V_{n\alpha,m\beta}(00;ff')a_{n\alpha}^{0+}\ a_{m\beta}^{0+}\ a_{n\alpha}^f\ a_{m\beta}^{f'} \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f(\neq 0)f'(\neq 0)}\sum V_{n\alpha,m\beta}(f0;0f')a_{n\alpha}^{f+}\ a_{m\beta}^{0+}\ a_{n\alpha}^0\ a_{m\beta}^{f'} \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}\sum_{f'(\neq 0)f(\neq 0)}\sum V_{n\alpha,m\beta}(0f;f'0)a_{n\alpha}^{0+}\ a_{m\beta}^{f+}\ a_{n\alpha}^{f'}\ a_{m\beta}^0 \\
&\hspace{8cm}(AI-2)
\end{aligned}
$$

We may rewrite (AI-2) in terms of $B_{n\alpha}^{f+}$ and $B_{n\alpha}^f$ as follows:

$$
\begin{aligned}
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\ V_{\alpha,m}(00;00)(1-\sum_{f(\neq 0)} B_{n\alpha}^{f+}B_{n\alpha}^f) \\
&\hspace{3cm}\times(1-\sum_{f'(\neq 0)} B_{m\beta}^{f'+}B_{m\beta}^{f'}) \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f(\neq 1)} V_{n\alpha,m\beta}(f0;f0)B_{n\alpha}^{f+}B_{n\alpha}^f \\
&\hspace{3cm}\times(1-\sum_{f'(\neq 0)} B_{m\beta}^{f'+}\ B_{m\beta}^{f'}) \\
&+\frac{1}{2}\sum_{n\alpha,m}'\sum_{f(\neq 0)} V_{n\alpha,m\beta}(0f;0f) \\
&\hspace{3cm}\times(1-\sum_{f'(\neq 0)} B_{n\alpha}^{f'+}B_{n\alpha}^{f'})B_{m\alpha}^{f+}\ B_{m\beta}^f \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f'(\neq 0)} V_{n\alpha,m\beta}(ff';00)\ B_{n\alpha}^{f+}\ B_{m\beta}^{f'} \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(00;ff')B_{n\alpha}^{f+}\ B_{m\beta}^{f'} \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(f0;0f')B_{n\alpha}^{f+}\ B_{m\beta}^{f'} \\
&+\frac{1}{2}\sum_{n\alpha,m\beta}\sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(0f;f'0)\ B_{n\alpha}^f\ B_{m\beta}^{f'+}.
\end{aligned}
$$

Terms involving the operators $B_{n\alpha}^{f+}\ B_{m\beta}^f B_{m\beta}^{f'-}B_{m\beta}^{f'}$, etc. are ignored since these terms represent the exciton-exciton collision terms which are of little importance when the concentration of excited molecules is low as in our case.

Assuming the states $\psi_{n\alpha}^f$'s are nondegenerate, we may take $\psi_{n\alpha}^f$ as real functions. Then

$$
V_{n\alpha,m\beta}(f0;f0) = \int |\psi_{n\alpha}^f|^2|\psi_{m\beta}^0|^2\ V_{n\alpha,m\beta}\ d\tau
$$

—exchange terms,

$$V_{n\alpha,m\beta}(ff';00) = V_{n\alpha,m\beta}(00;ff')$$
$$= V_{n\alpha,m\beta}(0f';f0) = V_{n\alpha,m\beta}(f0;0f'), \text{ etc.}$$

Hence the second term of the Hamiltonian(2-7) may be simplified to

$$\frac{1}{2}\sum_{n\alpha,m\beta} V_{n\alpha,m\beta}(00;00)$$
$$-\sum_{n\alpha,m\beta}'\sum_{f(\neq0)} V_{n\alpha,m\beta}(00;00) \; B_{n\alpha}^{f-}B_{n\alpha}^{f}$$
$$+\sum_{n\alpha,m\beta}'\sum_{f(\neq0)} V_{n\alpha,m\beta}(f0;f0) \; B_{n\alpha}^{f+} \; B_{n\alpha}^{f}$$
$$+\frac{1}{2}\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq0)} V_{n\alpha,m\beta}(f0;0f')(B_{n\alpha}^{f+}+B_{n\alpha}^{f})$$
$$\times (B_{m\beta}^{f'-}+B_{m\beta}^{f'}). \qquad (AI-3)$$

Collecting (AI-1) and (AI-3), we obtain the Hamiltonian (2-17).

Appendix II

First we prove that the eigenvalues of Eq. (3-7) are real and positive. From the normalization condition (3-8) we have

$$E_\mu = E_\mu \sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f) u_\mu{}^*(n\alpha,f)$$
$$-v_\mu(n\alpha,f)v_\mu{}^*(n\alpha,f)\}$$
$$=\sum_{n\alpha}\sum_{f(\neq0)} \{\varDelta_{n\alpha}^f|u_\mu(n\alpha,f)|^2+\varDelta_{n\alpha}^f|v_\mu(n\alpha,f)|^2\}$$
$$+\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq0)} V_{n\alpha,m\beta}(f0;0f')\tilde{u}_\mu^*(n\alpha,f)$$
$$\tilde{u}_\mu(m\beta,f'), \qquad (AII-1)$$

where we have used Eq. (3-7). Since the right-hand side of (AII-1) is real, E_μ is also real. Also, as shown by Tyablikov,[20] substitutions $(u,v)\rightarrow(v'^*, u'^*)$ and $E\rightarrow -E'$ in Eq. (3-7) will yield another set of equations with eigenvalues $E'_\mu = -E_\mu$; however, the normalization condition in this case should be written as

$$\sum_{n\alpha}\sum_{f(\neq0)} \{u'_\mu(fn\alpha,)u_\mu'^*(n\alpha,f)$$
$$-v'_\mu(n\alpha,f) \; v_\mu'^*(n\alpha,f)\} = -\delta_{\mu\mu'}.$$

Hence, the selection of the solutions corresponding to $E>0$ and the normalization condition (3-8) automatically excludes the solutions with $E<0$.

Now we prove that

$$\sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f)u_{\mu'}^*(n\alpha,f)$$
$$-v_\mu(n\alpha,f)v_{\mu'}^*(n\alpha,f)\} = \delta_{\mu\mu'} \qquad (AII-2)$$

and

$$\sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f)v_{\mu'}(n\alpha,f)$$
$$-v_\mu(n\alpha,f) \; u_{\mu'}(n\alpha,f)\} = 0. \qquad (AII-3)$$

From (3-7)

$$E_\mu \sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f)u_{\mu'}^*(n\alpha,f)$$
$$-v_\mu(n\alpha,f)v_{\mu'}^*(n\alpha,f)\}$$
$$=\sum_{n\alpha}\sum_{f(\neq0)}\varDelta_{n\alpha}^f\{u_\mu(n\alpha,f)u_{\mu'}^*(n\alpha,f)$$
$$+v_\mu(n\alpha,f)v_{\mu'}^*(n\alpha,f)\}+\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq0)}$$
$$V_{n\alpha,m\beta}(f0;0f')\tilde{u}_\mu(m\beta,f')\tilde{u}_{\mu'}^*(n\alpha,f). \qquad (AII-4)$$

Interchanging μ and μ' and complex-conjugating in (AII-4), we have

$$E_\mu \sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f)u_{\mu'}^*(n\alpha,f) -v_\mu(n\alpha,f)$$
$$v_{\mu'}^*(n\alpha,f)\} =\sum_{n\alpha}\sum_{f(\neq0)}\varDelta_{n\alpha}^f\{u_\mu(n\alpha,f)u_{\mu'}^*(n\alpha,f)$$
$$+v_\mu(n\alpha,f)v_{\mu'}^*(n\alpha,f)\}+\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq0)}$$
$$V_{n\alpha,m\beta}(f0;0f')\tilde{u}_{\mu'}^*(m\beta,f')\tilde{u}_\mu(n\alpha,f). \qquad (AII-5)$$

Subtracting (AII-5) from (AII-4), we obtain

$$(E_\mu-E_{\mu'})\sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f)u_{\mu'}^*(n\alpha,f)$$
$$-v_\mu(n\alpha,f)v_{\mu'}^*(n\alpha,f)\} = 0 \qquad (AII-6)$$

On the other hand from (3-7) we may write another identity as follows:

$$E_\mu \sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f)v_{\mu'}(n\alpha,f)$$
$$-v_\mu(n\alpha,f)u_{\mu'}(n\alpha,f)\} =\sum_{n\alpha}\sum_{f(\neq0)}\varDelta_{n\alpha}^f\{u_\mu(n\alpha,f)$$
$$v_{\mu'}(n\alpha,f) +v_\mu(n\alpha,f)u_{\mu'}(n\alpha,f)\}$$
$$+\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq0)} V_{n\alpha,m\beta}(f0;0f')\tilde{u}_\mu(m\beta,f')$$
$$\tilde{u}_\mu(n\alpha,f). \qquad (AII-7)$$

Interchanging μ and μ', we obtain

$$-E_{\mu'} \sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f) \; v_{\mu'}(n\alpha,f)-v_\mu(n\alpha,f)$$
$$u_{\mu'}(n\alpha,f) =\sum_{n\alpha}\sum_{f(\neq0)}\varDelta_{n\alpha}^f\{u_\mu(n\alpha,f)v_{\mu'}(n\alpha,f)$$
$$+v_\mu(n\alpha,f)u_{\mu'}(n\alpha,f)\}+\sum_{n\alpha,m\beta}'\sum_{f,f'(\neq0)}$$
$$V_{n\alpha,m\beta}(f0;0f')\tilde{u}_{\mu'}(m\beta,f')\tilde{u}_\mu(n\alpha,f). \qquad (AII-7),$$

Subtracting (AII-8) from (AII-7), we have

$$(E_\mu-E_{\mu'})\sum_{n\alpha}\sum_{f(\neq0)} \{u_\mu(n\alpha,f)v_{\mu'}(n\alpha,f)$$
$$-v_\mu(n\alpha,f)u_{\mu'}(n\alpha,f)\} = 0 \qquad (AII-9)$$

Eqs. (AII-6) and (AII-9) prove (AII-2) and (AII-3), respectively.

Appendix III

By direct substitution of (3-4a) and (3-4b) into (2-17) and use of the commutation rules (3-3a) and (3-3b) we obtain

$$H = E_0 + \sum_{\mu,\mu'} A_{\mu\mu'} \xi_\mu^+ \xi_{\mu'} + \sum_{\mu,\mu'} B_{\mu\mu'} \xi_\mu \xi_{\mu'}$$
$$+ \sum_{\mu,\mu'} C_{\mu\mu'} \xi_\mu^+ \xi_{\mu'}^+ + \sum_{\mu,\mu'} D_{\mu\mu'} \xi_\mu \xi_{\mu'}, \qquad (AIII-1)$$

where

$$A_{\mu\mu'} = \sum_{n\alpha} \sum_{f(\neq 0)} \Delta_{n\alpha}^f u_\mu^*(n\alpha, f) u_{\mu'}(n\alpha, f)$$
$$- \frac{1}{2} \sum_{n\alpha,m\beta}' \sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(f0;0f') \tilde{u}_\mu^*(n\alpha, f)$$
$$\tilde{u}_{\mu'}(m\beta, f'),$$

$$B_{\mu\mu'} = \sum_{n\alpha} \sum_{f(\neq 0)} \Delta_{n\alpha}^f v_\mu(n\alpha, f) v_{\mu'}^*(n\alpha, f)$$
$$+ \frac{1}{2} \sum_{n\alpha,m\beta}' \sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(f0;0f') \tilde{u}_\mu(n\alpha, f)$$
$$\tilde{u}_{\mu'}^*(m\beta, f'),$$

$$C_{\mu\mu'} = \sum_{n\alpha} \sum_{f(\neq 0)} \Delta_{n\alpha}^f u_\mu^*(n\alpha, f) v_{\mu'}^*(n\alpha, f)$$
$$+ \frac{1}{2} \sum_{n\alpha,m\beta}' \sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(f0;0f') \tilde{u}_\mu^*(n\alpha, f)$$
$$\tilde{u}_{\mu'}^*(m\beta, f'),$$

and

$$D_{\mu\mu'} = \sum_{n\alpha} \sum_{f(\neq 0)} \Delta_{n\alpha}^f u_\mu(n\alpha, f) v_\mu(n\alpha, f)$$
$$+ \frac{1}{2} \sum_{n\alpha,m\beta}' \sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(f0;0f') \tilde{u}_{\mu'}(n\alpha, f)$$
$$\tilde{u}_\mu(m\beta, f').$$

Using Eq. (AII-7), we can easily confirm that

$$C_{\mu\mu'} = -C_{\mu'\mu}, \quad C_{\mu\mu} = 0$$
$$D_{\mu\mu'} = -D_{\mu'\mu}, \quad D_{\mu\mu} = 0.$$

Hence, terms involving $\xi_\mu^+ \xi_{\mu'}^+$ and $\xi_\mu \xi_{\mu'}$ vanish. Moreover

$$\sum_{\mu,\mu'} A_{\mu\mu'} \xi_\mu^+ \xi_{\mu'} + \sum_{\mu,\mu'} B_{\mu\mu'} \xi_\mu \xi_{\mu'}^+$$
$$= \sum_{\mu,\mu'} A_{\mu\mu'} \xi_\mu^+ \xi_{\mu'} + \sum_{\mu,\mu'} B_{\mu\mu'}(\delta_{\mu\mu'} + \xi_\mu^+ \xi_\mu)$$
$$= \sum_{\mu,\mu'} (A_{\mu\mu'} + B_{\mu'\mu}) \xi_\mu^+ \xi_{\mu'} + \sum_\mu B_{\mu\mu}$$

Since from (AII-4)

$$A_{\mu\mu'} + B_{\mu'\mu}$$
$$= \sum_{n\alpha} \sum_{f(\neq 0)} \Delta_{n\alpha}^f \{u_\mu^*(n\alpha, f) u_{\mu'}(n\alpha, f)$$
$$+ v_\mu^*(n\alpha, f)) v_{\mu'}(n\alpha, f)\}$$
$$+ \sum_{n\alpha,m\beta}' \sum_{f,f'(\neq 0)} V_{n\alpha,m\beta}(f0;0f') \tilde{u}_\mu^*(n\alpha, f)$$
$$\tilde{u}_{\mu'}(m\beta, f') = E_\mu \delta_{\mu\mu'}$$

and from (III-9a)

$$\sum_\mu \tilde{u}_\mu(n\alpha, f) \tilde{u}_\mu^*(m\beta, f')$$
$$= \sum_\mu \{u_\mu(n\alpha, f) + v_\mu(n\alpha, f)\} \{u_\mu^*(m\beta, f')$$
$$+ v_\mu^*(m\beta, f')\}$$
$$= 2 \sum_\mu v_\mu(n\alpha, f) v_\mu^*(m\beta, f')$$
$$+ 2 \sum_\mu v_\mu(n\alpha, f) u_\mu^*(m\beta, f')$$
$$= 2 \sum_\mu \tilde{u}_\mu^*(m\beta, f') v_\mu(n\alpha, f)$$

we have

$$\sum_{\mu,\mu'} A_{\mu\mu'} \xi_\mu^+ \xi_{\mu'} + \sum_{\mu,\mu'} B_{\mu\mu'} \xi_\mu \xi_{\mu'}^+$$
$$= \sum_\mu E_\mu \xi_\mu^+ \xi_\mu - \sum_\mu E_\mu (\sum_{n\alpha} \sum_{f(\neq 0)} |v_\mu(n\alpha, f)|^2).$$

Thus the diagonalized form of the Hamiltonian (3-13) has been justified.

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