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Charge-Transfer Interaction in Linear Chain Molecular Crystals

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The charge-transfer interaction is investigated theoretically for linear chain systems in molecular crystals. The charge-transfer excitation energy is shown to diverge in crystals by the usual configuration interaction method considering only one-molecule excitation. In order to overcome this difficulty, the second quantized Hamiltonian is solved with the Bose approximation for the charge-transfer exciton. Consequently, reasonable results are obtained for the stabilization of the ground state due to the contribution of many virtual excitons, for the electric dipole moment of the ground state, and for the transition moment of a charge-transfer excitation. The results correspond well to those by Mulliken's theory for an electron donor-acceptor pair. The second quantization model is also applied in the extended form to crystals of charge-transfer complexes and ionic radicals of complex stoichiometry. The lower excited states in these crystals are understood as the coupled ones of the one-site and two-site charge-transfer configurations.

Concerning the crystals of charge-transfer (abbreviated hereafter to CT) complexes and radical ion salts, the geometrical structures and also the electrical, magnetic and optical properties have been studied by many authors from the experimental point of view.[1-5] Consequently, some interesting phenomena have been found in relation with their electronic structures. For example, radical salt crystals such as (Quinolinium)$^+$(Tetracyano-*p*-quinodimethan)$_2^-$ and (*N*-Methylphenazinium)$^+$(Tetracyano-*p*-quinodimethan)$^-$ exhibit a large electrical conductivity up to $10^2\,\mho\,\mathrm{cm}^{-1}$.[3a,3c] Furthermore, some of radical salt crystals are known to show in the infrared region strong absorption bands characteristic of the interaction between electron donor and acceptor.[6-9] In contrast to a plenty of experimental studies, there are only a few literatures[10] about the theory of electronic structures of these crystals.

Concerning usual molecular crystals[11-15] as well as CT complex crystals, the CT interaction plays an important role in their electronic processes. For example, the absorption bands ascribed to no intramolecular excitations were found for the α-form crystals of perylene and 9,10-dichloroanthracene and were assigned reasonably to the CT band.[14,15]

Under these circumstances, we undertake to develop the theory in the second quantization form on the electronic structures of molecular crystals and also of crystals of CT complexes and radical ion salts. We propose a model Hamiltonian appropriate to the case where the Coulomb energy

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1) For reviews of CT complexes, see R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962), and G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin (1961).

2) a) C. J. Fritchie, Jr., and P. Arthur, Jr., *Acta Crystallogr.*, **21**, 139 (1966). b) A. W. Hanson, *ibid.*, **B24**, 768 (1968). c) D. S. Brown, S. C. Wallwork and A. Wilson, *ibid.*, **17**, 168 (1964). d) H. Matsuda, K. Osaki and I. Nitta, This Bulletin, **31**, 611 (1958).

3) a) W. J. Siemons, P. E. Bierstedt and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963). b) Y. Matsunaga, *ibid.*, **42**, 1982 (1965). c) L. R. Melby, *Can. J. Chem.*, **43**, 1448 (1965).

4) a) K. Nakamoto, *J. Amer. Chem. Soc.*, **74**, 1739 (1952). b) S. K. Lawer, R. M. Hochstrasser and C. Reid, *Mol. Phys.*, **4**, 162 (1961). c) J. Tanaka and K. Yoshihara, This Bulletin, **38**, 739 (1965). d) H. Kuroda, T. Kunii, S. Hiroma and H. Akamatu, *J. Mol. Spectry.*, **22**, 60 (1967). e) T. Amano, H. Kuroda and H. Akamatu, This Bulletin, **41**, 83 (1968). f) T. Sakata and S. Nagakura, *ibid.*, **42**, 1497 (1969). g) J. Tanaka and M. Mizuno, *ibid.*, **42**, 1841 (1969).

5) a) R. C. Hughes and Z. G. Soos, *J. Chem. Phsy.*, **48**, 1066 (1968). b) K. Siratori and T. Kondow, *J. Phys. Soc. Japan*, **27**, 301 (1969). c) R. G. Kepler, *J. Chem. Phys.*, **39**, 3528 (1963). d) D. B. Chesnut and P. Arthur, Jr., *ibid.*, **36**, 2969 (1962).

6) T. Kondow, K. Siratori and H. Inokuchi, *J. Phys. Soc. Japan*, **21**, 824 (1966).

7) T. Kondow, K. Siratori and H. Inokuchi, *ibid.*, **23**, 98 (1967).

8) Y. Iida, This Bulletin, **42**, 71 (1969).

9) Y. Iida, *ibid.*, **42**, 637 (1969).

10) J. I. Krugler, C. G. Montgomery and H. M. McConnell, *J. Chem. Phys.*, **41**, 2421 (1964).

11) L. E. Lyons, *J. Chem. Soc.*, **1957**, 5001.

12) J. Tanaka, *Progr. Theoret. Phys.* (Kyoto), Suppl. **12**, 183 (1959).

13) Sang-Il Choi, J. Jortner, S. A. Rice and R. Silbey, *J. Chem. Phys.*, **41**, 3294 (1964).

14) J. Tanaka, This Bulletin, **36**, 1237 (1963).

15) J. Tanaka and M. Shibata, *ibid.*, **41**, 34 (1968).

is larger than the transfer energy and discuss the CT electronic state. At first, the basic theory of the CT interaction in molecular crystals is presented. Thereafter the problem of some CT complexes and ionic radical crystals of complex stoichiometry, for example Et_3NH^+(Tetracyano-*p*-quinodimethan)$_2^-$ crystals, is treated by applying the basic theory in the extended form.

Theoretical

Wave Functions and Energy Levels. We consider a linear chain system consisting of N identical radicals or molecules and also that consisting of alternatively located N electron donors and N electron acceptors. In the former case, each component acts as both donor and acceptor. In the latter case, however, the electron donor and acceptor can be distinguished explicitly from each other. Furthermore, in these crystals the component molecules and radicals are assumed to be equally spaced. In actuality, the X-ray crystal analysis data show that there exists one-dimensional equivalent interaction along a chain in most of these crystals.[2a–d]

We can represent the ground configuration as $\psi(0,0)$ and one site CT configuration as $\psi(\pm 1,j)$ in which an electron on the jth site component transfers to the nearest neighbors.[*1] Here + and − show the direction of electron migration. The numbering of j is made for identical molecules or radicals in the case of molecular or radical crystals, and for electron donors and for electron acceptors separately in the case of CT complexes.

Keeping the above-mentioned facts in mind, we construct the wave functions of crystals. In the case of usual molecular crystals and of weak CT complex crystals, the ground configurations $\psi(0,0)$ is singlet, and there are possibilities of singlet and triplet for the CT configurations. By considering only the highest occupied and lowest vacant orbitals, the wave functions of the ground and CT configurations can be represented by the following equations for usual molecular crystals:

$$\psi(0,0) = |\phi_1{}^0(1)\bar{\phi}_1{}^0(2)\cdots\phi_j{}^0(2j-1)\bar{\phi}_j{}^0(2j)\cdots \phi_N{}^0(2N-1)\bar{\phi}_N{}^0(2N)|\ \text{(singlet)} \tag{1}$$

$$\psi(m,j) = \frac{1}{\sqrt{2}}\{|\phi_1{}^0(1)\bar{\phi}_1{}^0(2)\cdots\phi_j{}^0(2j-1)\bar{\phi}^v_{j+m}(2j)\cdots \phi_N{}^0(2N-1)\bar{\phi}_N{}^0(2N)| \pm |\phi_1{}^0(1)\bar{\phi}_1{}^0(2)\cdots \bar{\phi}^v_{j+m}(2j-1)\bar{\phi}_j{}^0(2j)\cdots\phi_N{}^0(2N-1)\bar{\phi}_N{}^0(2N)|\} \tag{2}$$

where $m=\pm 1$ (+ and − correspond to the singlet and triplet states, respectively), $\phi_j{}^0$ is the highest occupied molecular orbital of the jth site component, and suffix v signifies the lowest vacant molecular orbital. They are orthonormalized like Wannier orbitals. The wave function for the CT configuration which satisfies the translational symmetry of crystals can be written as follows:

$$\Psi(m,k) = \frac{1}{\sqrt{N}}\sum_j e^{ikj}\,\psi(m,j),\quad m = 1,\,-1 \tag{3}$$

where $\boldsymbol{k}=2\pi/N\boldsymbol{j}$ ($j=1, 2, \cdots, N$) from the cyclic boundary condition and the unit length is taken to be equal to the distance between the neighbouring molecules for usual molecular crystals and that between the neighbouring donor (acceptor) molecules for CT complexes.

The above-mentioned two CT configurations $\Psi(1,k)$ and $\Psi(-1,k)$ mix with each other, and consequently the following two energy levels can be obtained.

$$\begin{aligned} \omega_{k+} &= \omega + \sum_{\substack{l\\ l\neq 0}} e^{-ikl}\,U_1(|\boldsymbol{l}|) + |\sum_l e^{-ikl}\,U_2(\boldsymbol{l})|\cdot\tau \\ \omega_{k-} &= \omega + \sum_{\substack{l\\ l\neq 0}} e^{-ikl}\,U_1(|\boldsymbol{l}|) - |\sum_l e^{-ikl}\,U_2(\boldsymbol{l})|\cdot\tau \end{aligned} \tag{4}$$

where

$$\begin{aligned} &U_1(|\boldsymbol{j}\text{-}\boldsymbol{j}'|) = <\psi(m,j)|\boldsymbol{H}|\psi(m,j')> \\ &U_2(\boldsymbol{j}\text{-}\boldsymbol{j}') = <\psi(1,j)|\boldsymbol{H}|\psi(-1,j')> \\ &\omega = <\psi(m,j)|\boldsymbol{H}|\psi(m,j)>;\quad m=1,\,-1 \\ &U_2(\boldsymbol{l})\neq U_2(-\boldsymbol{l}) \end{aligned} \tag{5}$$

and

$$\tau = \frac{\sum_l U_2(\boldsymbol{l})}{|\sum_l U_2(\boldsymbol{l})|}$$

The corresponding wave functions are

$$\Psi(1,k,\nu) = \frac{1}{\sqrt{2N}}\sum_j e^{ikj}\{\psi(1,j) + \nu e^{i\theta_k} \times\psi(-1,j)\} \tag{6}$$

where

$$e^{i\theta_k} = \frac{\sum_l e^{ikl}U_2(\boldsymbol{l})}{|\sum_l e^{ikl}U_2(\boldsymbol{l})|}\cdot\tau \tag{7}$$

and $\nu=\pm$.

The interaction between the ground configuration and the one site CT configuration with the spin multiplicity of singlet is rather large and can not be disregarded. For the evaluation of the matrix element necessary for the calculation of the interaction, the following two cases can be considered, when there is a center of symmetry of the point group between the neighbouring two molecules (or radicals).

Case A) When

$$<\psi(1,j)|\boldsymbol{H}|\psi(0,0)> = <\psi(-1,j)|\boldsymbol{H}|\psi(0,0)>$$

the matrix element is

$$<\Psi(1,k,\nu)|\boldsymbol{H}|\psi(0,0)> = \sqrt{2N}\ \beta\delta_{k0}\delta_{\nu+} \tag{8}$$

Case B) When

[*1] In the case of CT complexes, $\psi(\pm 1,j)$ represents the configuration in which an electron on the jth donor molecule transfers to the nearest neighbouring acceptor molecule.

$$<\Psi(1,j)|\boldsymbol{H}|\phi(0,0)> = -<\phi(-1,j)|\boldsymbol{H}|\phi(0,0)>,$$

the matrix element is

$$<\Psi(1,k,\nu)|\boldsymbol{H}|\phi(0,0)> = \sqrt{2N}\,\beta\delta_{k0}\delta_{\nu-} \tag{9}$$

where

$$\beta = <\phi(1,j)|\boldsymbol{H}|\phi(0,0)>$$

The quantity β corresponds to the transfer energy which determines the band width in the band model. As is seen in Eqs. (8) and (9), the only CT configurations of $k=0$, $\nu=+$ and $k=0$, $\nu=-$ mix with the ground configuration for cases A and B, respectively. Hereafter we consider only case A, since the similar discussion can be applied to case B. By taking the configuration interaction between the ground and CT configurations into account on the assumption of neglecting the contribution from the excited configurations in which many molecules are excited simultaneously in a crystal, the energy eigen values for the system can be obtained as follows:

$$E = \frac{\varepsilon_{0+}}{2} \pm \frac{1}{2}\sqrt{\varepsilon_{0+}{}^2+8N\beta^2} \tag{10}$$

where

$$\varepsilon_{k\nu} = \omega_{k\nu} - <\phi(0,0)|\boldsymbol{H}|\phi(0,0)>$$

Therefore the excitation energy between these states is

$$E_{\text{exc.}} = \sqrt{\varepsilon_{0+}{}^2+8N\beta^2}$$

The obtained excitation energy depends on N and diverges with its increase.

$$E_{\text{exc.}} \to \infty \quad (N \to \infty)$$

This divergence arises from disregarding the configurations in which two or more than two molecules are excited simultaneously in a crystal. In the present paper, we undertake to overcome this difficulty by adopting second quantization formalism.

In the case of radical crystals and of strong CT complex crystals, each component has open shell structure and $S=1/2$. Since it is difficult to handle explicity the spin multiplicity of each electronic state of the crystal, we neglect the electron spin for simplicitly in these cases and represent the wave functions of the ground and CT configurations by the simple product of appropriate orbitals $\phi_j{}^0$'s. Then we can obtain the conclusion that the transition energy diverges with the increasing N also for this case.

Hamiltonian and the Bose Approximation. From the above discussion we can write a model Hamiltonian in the following second quantization form.[16]

$$\boldsymbol{H} = \boldsymbol{H}_1 + \boldsymbol{H}_2 + \boldsymbol{H}_3 \tag{12}$$

$$\boldsymbol{H}_1 = \sum_{j,\sigma}\varepsilon\, a^+_{j\sigma}a_{j\sigma} \tag{13}$$

$$\begin{aligned}\boldsymbol{H}_2 = {} & \frac{1}{2}\sum_{\substack{j\cdot j'\\ \sigma,\sigma'\\ (j\sigma)\neq(j'\sigma')}} U(j'\sigma',0;0,j\sigma)(a^+_{j'\sigma'}a_{j\sigma}+a^+_{j\sigma}a_{j'\sigma'}) \\ & + \frac{1}{2}\sum_{\substack{j\cdot j'\\ \sigma,\sigma'\\ (j\sigma)\neq(j'\sigma')}} U(j'\sigma',j\sigma;0,0)(a^+_{j'\sigma'}a^+_{j\sigma}+a_{j\sigma}a_{j'\sigma'})\end{aligned} \tag{14}$$

$$\boldsymbol{H}_3 = \sum_{j,\sigma}\beta(a^+_{j\sigma}+a_{j\sigma}) \tag{15}$$

Here $a^+_{j\sigma}$ and $a_{j\sigma}$ are the creation and annihilation operators for an excitation which transfers an electron on the jth site, by one site, to $\sigma(\sigma=+,-)$ direction.

Hamiltonian $\boldsymbol{H}_1$ corresponds to the diagonal matrix element of $(j\sigma)$ excitation and $\varepsilon=<\phi(m,j)\cdot|\boldsymbol{H}|\phi(m,j)>-<\phi(0,0)|\boldsymbol{H}|\phi(0,0)>$; $m=1,-1$.

The first term of $\boldsymbol{H}_2$ signifies the process of the excitation transfer in which an excitation $(j\sigma)$ transfers to that of $(j'\sigma')$ and its inverse process. The coefficient $U(j'\sigma',\ 0;0,j\sigma)$ is the corresponding matrix element, satisfying the relations $U(j'\sigma,\ 0;0,\ j\sigma)=U_1(|j-j'|)$ and $U(j'-,\ 0;0,j+)=U_2(j-j')$. The second term of H_2 signifies the pair creation and the pair annihilation of two excitations $(j\sigma)$ and $(j'\sigma')$, $U(j'\sigma',j\sigma;0{,}0)$ being its matrix element. The matrix elements $U(j'\sigma',\ 0;0,\ j\sigma)$ and $U(j'\sigma',\ j\sigma;\ 0{,}0)$ are considered to be small compared with the diagonal matrix element ε, since these quantities are proportional to the square of the intermolecular overlap integral.

Hamiltonian $\boldsymbol{H}_3$ represents the interaction between configurations which differ in the excitation number by one from each other and the interaction energy corresponds to the transfer (or resonance) energy β. This term represents the CT interaction.

Considering the diagonalization of the Hamiltonian $\boldsymbol{H}$, we disregard the second term of $\boldsymbol{H}_2$ for simplicity, since this term may give negligibly small influence when ε is large compared with $U(j'\sigma',\ j\sigma;\ 0{,}0)$.

We difine new operators which create and annihilate a one site CT exciton corresponding to Eq. (6).

$$b_{k+} = \frac{1}{\sqrt{2N}}\sum_k \mathrm{e}^{-ikj}(a_{j+}+\mathrm{e}^{-i\theta_k}a_{j-})$$

$$b_{k-} = \frac{1}{\sqrt{2N}}\sum_j \mathrm{e}^{-ikj}(a_{j+}-\mathrm{e}^{-i\theta_k}a_{j-}) \tag{16}$$

The inverse transformation is,

$$a_{j+} = \frac{1}{\sqrt{2N}}\sum_k \mathrm{e}^{ikj}(b_{k+}+b_{k-})$$

$$a_{j-} = \frac{1}{\sqrt{2N}}\sum_k \mathrm{e}^{ikj+i\theta_k}(b_{k+}-b_{k-}) \tag{17}$$

Operators $a^+_{j\sigma}$ and $a_{j\sigma}$ are essentially the Pauli operators.[10,16] However, we assume both $a^+_{j\sigma}$ and $a_{j\sigma}$ to be the Bose operators as usually done. Then $b^+_{k\nu}$ and $b_{k\nu}$ $(\nu=+,-)$ are also the Bose operators as can be shown easily. In this approximation the Hamiltonian can be diagonalized by the fol-

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[16] V. M. Agranovich, *J. Exptl. Theoret. Phys.* (U.S.S.R.), **37**, 430 (1959).

lowing procedures. From Eq. (16),

$$\sum_{j,\sigma}\varepsilon\, a^{+}_{j\sigma}a_{j\sigma}=\sum_{k,\nu}\varepsilon\, b^{+}_{k\nu}b_{k\nu}$$

$$\frac{1}{2}\sum_{\substack{j\cdot j'\\ \sigma,\sigma \\ (j\sigma)\neq(j'\sigma')}}U(j'\sigma',0;0,j\sigma)(a^{+}_{j'\sigma'}a_{j\sigma}+a^{+}_{j\sigma}a_{j'\sigma'})$$

$$=\sum_{k}\sum_{l}\mathrm{e}^{-ikl}U_1(|\boldsymbol{l}|)(b^{+}_{k+}b_{k+}+b^{+}_{k-}b_{k-})$$

$$+\sum_{k}|\sum_{l}\mathrm{e}^{-ikl}U_2(\boldsymbol{l})|(b^{+}_{k+}b_{k+}-b^{+}_{k}-b_{k-})$$

$$\sum_{j,\sigma}\beta(a^{+}_{j\sigma}+a_{j\sigma})=\sqrt{2N}\beta(b^{+}_{0+}+b_{0+}) \tag{18}$$

Therefore,

$$\boldsymbol{H}=\sum_{k,\nu}\varepsilon_{k\nu}b^{+}_{k\nu}b_{k\nu}+\sqrt{2N}\beta(b^{+}_{0+}+b_{0+}) \tag{19}$$

Furthermore, by introducing new Bose operators[17)]

$$c_{0+}=b_{0+}+\frac{\sqrt{2N}\beta}{\varepsilon_{0+}} \tag{20}$$

$$c_{k\nu}=b_{k\nu}\qquad \text{expcept for } (k=0,\nu=+)$$

the Hamiltonian can be diagonalized as follows:

$$\boldsymbol{H}=\sum\varepsilon_{k\nu}c^{+}_{k\nu}c_{k\nu}-2N\frac{\beta^2}{\varepsilon_{0+}} \tag{21}$$

Next we construct wave functions represented by the original representations which are applied prior to the diagonalization. For the ground state $|0\rangle$

$$|0\rangle=\sum_{n=0}^{\infty}\alpha_n|n\rangle_{\mathrm{o}} \tag{22}$$

where $|n\rangle_{\mathrm{o}}$ is the wave function of the original representation in which the number of virtual excitations of $(k=0,\ \nu=+)$ is n and no other excitation exists and suffix o means the original representation. Coefficient α_n can be obtained from

$$c_{0+}|0\rangle=0 \tag{23}$$

$$\sum_{n}\alpha_n^2=1\ \text{(normalization condition)} \tag{24}$$

The final result is

$$\alpha_n=\frac{(-\gamma)^n}{\sqrt{n!}}\mathrm{e}^{-\frac{1}{2}\gamma^2}\qquad (N\to\infty) \tag{25}$$

where

$$\gamma=\sqrt{2N}\frac{\beta}{\varepsilon_{0+}}$$

Extention of the Theory to Complex Radical Salt Crystals. As a model for complex radical salt, we take a closed linear chain of $2N$ acceptors (A) in which N excess electrons exist. The crystals of tetracyano-*p*-quinodimethan with various donor cations fit into this model. We take the above-mentioned localized model and neglect electron spin for simplicity. There are two ground configurations with excess electrons at odd and even number sites. They are represented by $\phi^{\mathrm{o}}(0,0)$ and $\phi^{\mathrm{e}}(0,0)$, respectively. The off diagonal matrix element between them is zero. Therefore the ground state is doubly degenerate unless there is an asymmetry concerning the locations of the cations. Hereafter we assume that N excess electrons locate at odd-number molecular sites even when the degeneracy is not removed. Then we can take $\phi^{\mathrm{o}}(0,0)$ as the ground configuration of the system.

The CT configuration in which an electron on $(2j-1)$-th site migrates by m sites in the + (or −) direction is represented by $\phi^{\mathrm{o}}(m,\ 2j-1)$ (or $\phi^{\mathrm{o}}(-m,\ 2j-1)$), $m=1$ and 2 being assumed in the present paper. The excitation process corresponding to $m=1$ and 2 can be represented schematicaly by $\cdots\mathrm{AA^{-}AA^{-}}\cdots\rightarrow\cdots\mathrm{AAA^{-}A^{-}}\cdots$ and by $\cdots\mathrm{A^{-}AA^{-}A}\cdots\rightarrow\cdots\mathrm{AAA^{=}A}\cdots$, respectively. Therefore these two kinds of excitations are different from each other in their characters.

By replacing $\phi(m,j)$ in Eq. (3) by $\phi^{\mathrm{o}}(m,\ 2j-1)$, we can construct the wave function $\Psi^{\mathrm{o}}(m,k)$ for the m site CT configuration which satisfies the translational symmetry of the crystal.[*2] Furthermore, combining $\Psi^{\mathrm{o}}(m,k)$'s corresponding to charge transfer in the + and − directions, we can obtain

$$\Psi^{\mathrm{o}}(m,k,\nu)=\frac{1}{\sqrt{2N}}\sum_{j}\mathrm{e}^{ikj}\{\phi^{\mathrm{o}}(m,2j-1)$$

$$+\nu\phi^{\mathrm{o}}(-m,2j-1)\} \tag{26}$$

where $\nu=+,-$. We neglected for simplicity the small terms which correspond to $U_1(|\boldsymbol{l}|)$ and $U_2(\boldsymbol{l})$ of Eq. (7). As in the case of usual molecular crystals and of crystals of CT complexes mentioned in the preceding chapter, the excitation energy calculated for complex radical salt crystals by this single excitation model diverges for $k=0$ and $\nu=+$.

The second quantization Hamiltonian may be written as

$$\boldsymbol{H}=\sum_{j,\sigma}\varepsilon a^{+}_{j\sigma}a_{j\sigma}+\sum_{j,\sigma}(\varepsilon+\Delta)\,b^{+}_{j\sigma}b_{j\sigma}$$

$$+\sum_{j,\sigma}\beta\,(b^{+}_{j\sigma}a_{j\sigma}+a^{+}_{j\sigma}b_{j\sigma})+\sum_{j,\sigma}\beta\,(a^{+}_{j\sigma}+a_{j\sigma}) \tag{27}$$

where ε, $\varepsilon+\Delta$ and β are defined as

$$\varepsilon=\langle\phi^{\mathrm{o}}(m,2j-1)|\boldsymbol{H}|\phi^{\mathrm{o}}(m,2j-1)\rangle$$

$$-\langle\phi^{\mathrm{o}}(0,0)|\boldsymbol{H}|\phi^{\mathrm{o}}(0,0)\rangle\quad\text{for } m=\pm1,$$

$$\varepsilon+\Delta=\langle\phi^{\mathrm{o}}(m,2j-1)|\boldsymbol{H}|\phi^{\mathrm{o}}(m,2j-1)\rangle$$

$$-\langle\phi^{\mathrm{o}}(0,0)|\boldsymbol{H}|\phi^{\mathrm{o}}(0,0)\rangle\quad\text{for } m=\pm2$$

$$\beta=\langle\phi^{\mathrm{o}}(2,2j-1)|\boldsymbol{H}|\phi^{\mathrm{o}}(1,2j-1)\rangle$$

$$=\langle\phi^{\mathrm{o}}(1,2j-1)|\boldsymbol{H}|\phi^{\mathrm{o}}(0,0)\rangle$$

$$\langle\phi^{\mathrm{o}}(2,2j-1)|\boldsymbol{H}|\phi^{\mathrm{o}}(0,0)\rangle=0\ \text{(assumed)}$$

Operators $a^{+}_{j\sigma}$ and $a_{j\sigma}$ are the creation and the annihilation ones for an excitation which transfers an electron at $(2j-1)$th site, by one site, in the $\sigma(\sigma=+,-)$ direction. Operators $b^{+}_{j\sigma}$ and $b_{j\sigma}$ are the creation and the annihilation operators for an excitation which transfers an electron at the $(2j-1)$-

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17) D. B. Chesnut, *Mol. Cryst.*, **1**, 351 (1966).

[*2] By electron-phonon interaction the unit spacing of the crystal is twice that of the crystal without N excess electrons even if the chain is regular.

th site, by two sites, in the σ direction. The first and the second terms of Eq. (27) correspond to the diagonal matrix elements. The third terms represent the interactions between the one site CT configurations and the two site ones. The fourth terms represent the interaction between the ground configuration and the one site CT configurations. The usual Pauli commutation relations hold for the one-site and two-site CT operators. The one-site CT operators $a^+_{j\sigma}$ and $a_{j\sigma}$ commute with the two-sites ones $b^+_{j\sigma}$ and $b_{j\sigma}$, since the wave functions of the former are orthogonal to those of the latter when molecular orbitals in a crystal are orthonormalized.

The symmetry of translation is brought into the theory by transforming $a^+_{j\sigma}$, $a_{j\sigma}$, $b^+_{j\sigma}$ and $b_{j\sigma}$ to the wave operators $A_{k\nu}$ and $B_{k\nu}$;

$$A_{k+} = \frac{1}{\sqrt{2N}} \sum_{j=1}^{N} e^{-ikj}(a_{j+} + a_{j-})$$

$$A_{k-} = \frac{1}{\sqrt{2N}} \sum_{j=1}^{N} e^{-ikj}(a_{j+} - a_{j-}) \tag{28}$$

The operators $B_{k\nu}$ are defined in the same form as $A_{k\nu}$.

By the aid of the inverse transformation of Eq. (28), Eq. (27) is transformed as follows:

$$\boldsymbol{H} = \sum_{k,\nu} \varepsilon A^+{}_{k\nu} A_{k\nu} + \sum_{k,\nu} (\varepsilon + \Delta) B^+_{k\nu} B_{k\nu} + \sum_{k,\nu} \beta\, (A^+_{k\nu} B_{k\nu} + B^+_{k\nu} A_{k\nu}) + \sqrt{2N}\,\beta\, (A_{0+} + A_{0+}) \tag{29}$$

By assuming $a^+_{j\sigma}$, $a_{j\sigma}$, $b^+_{j\sigma}$ and $b_{j\sigma}$ to be the Bose operators as in the preceding section, the Hamiltonian can be diagonalized by the following transformation to new boson operators $C^+_{k\nu}$, $C_{k\nu}$, $D^+_{k\nu}$ and $D_{k\nu}$. The new operators are

$$\begin{aligned} C_{k\nu} &= u_{k\nu} A_{k\nu} + v_{k\nu} B_{k\nu} \\ D_{k\nu} &= u'_{k\nu} A_{k\nu} + v'_{k\nu} B_{k\nu} \end{aligned} \tag{30}$$

for the k, ν states except for the $k=0$, $\nu=+$ state. For the $k=0$, $\nu=+$ state they are

$$\begin{aligned} C_{0+} &= u_{0+} A_{0+} + v_{0+} B_{0+} + w \\ D_{0+} &= u'_{0+} A_{0+} + v'_{0+} B_{0+} + w' \end{aligned} \tag{31}$$

Here it may be assumed in general that coefficients $u_{k\nu}$, $v_{k\nu}$ $u'_{k\nu}$ and $v'_{k\nu}$ to be real.

The transformation is canonical when

$$\begin{aligned} & u^2_{k\nu} + v^2_{k\nu} = 1, \\ & u'^2_{k\nu} + v'^2_{k\nu} = 1, \quad u_{k\nu} u'_{k\nu} + v_{k\nu} v'_{k\nu} = 0 \\ & \text{for all } k,\nu \end{aligned} \tag{32}$$

Eq. (32) can be solved and the coefficients are represented by parameter $\chi_{k\nu}$ as follows:

$$\begin{aligned} & u_{k\nu} = -\sin\chi_{k\nu}, \quad v_k = \cos\chi_{k\nu} \\ & u'_{k\nu} = \cos\chi_{k\nu}, \quad v'_{k\nu} = \sin\chi_{k\nu}; \\ & -\frac{\pi}{2} \leq \chi_{k\nu} < \frac{\pi}{2} \end{aligned} \tag{33}$$

where we neglect the trivial phase factor.

The parameter $\chi_{k\nu}$ is determined by the diagonalization of Hamiltonian. The Hamiltonian of Eq. (29) is reduced to the following diagonal forms:

$$\begin{aligned} [\boldsymbol{H}, C_{k\nu}] &= -E_{k\nu} C_{k\nu} \\ [\boldsymbol{H}, D_{k\nu}] &= -E'_{k\nu} D_{k\nu} \end{aligned} \tag{34}$$

From Eqs. (30), (31) and (34)

$$\begin{aligned} & (\varepsilon - E_{k\nu}) u_{k\nu} + \beta\, v_{k\nu} = 0 \\ & \beta u_{k\nu} + (\varepsilon + \Delta - E_{k\nu}) v_{k\nu} = 0 \\ & (\varepsilon - E'_{k\nu}) u'_{k\nu} + \beta\, v'_{k\nu} = 0 \\ & \beta\, u'_{k\nu} + (\varepsilon + \Delta - E'_{k\nu}) v'_{k\nu} = 0 \end{aligned} \tag{35}$$

for all the k, ν. In particular, for the case of $k=0$, $\nu=+$

$$\sqrt{2N}\,\beta\, u_{0+} = E_{0+}\, w, \quad \sqrt{2N}\,\beta\, u'_{0+} = E'_{0+}\, w' \tag{36}$$

The solutions of Eq. (35) are

$$\begin{aligned} E_{k\nu} &= \varepsilon + \frac{\Delta}{2} - \frac{1}{2}\sqrt{\Delta^2 + 4\beta^2} \\ E'_{k\nu} &= \varepsilon + \frac{\Delta}{2} + \frac{1}{2}\sqrt{\Delta^2 + 4\beta^2} \end{aligned} \tag{37}$$

where we tentatively assume $E_{k\nu} < E'_{k\nu}$. The energies $E_{k\nu}$ and $E'_{k\nu}$ and therefore also $u_{k\nu}$, $v_{k\nu}$, $u'_{k\nu}$ and $v'_{k\nu}$ are independent of k,ν. Therefore we remove the suffixes k,ν from these quantities.

The inverse transformation of Eq. (30) is

$$\begin{aligned} A_{k\nu} &= u\, C_{k\nu} + v\, D_{k\nu} \\ B_{k\nu} &= v\, C_{k\nu} - u\, D_{k\nu} \end{aligned} \tag{38}$$

except for the case of $k=0$, $\nu=+$. For $k=+$, $\nu=+$

$$\begin{aligned} A_{0+} &= u\, C_{0+} + v\, D_{0+} + (-uw - vw') \\ B_{0+} &= v\, C_{0+} - u\, D_{0+} + (uw' - vw) \end{aligned} \tag{39}$$

The transformation coefficients are

$$\begin{aligned} u = -v' &= -\frac{|\beta|}{\beta}\left(\frac{1}{2} + \frac{\Delta}{2\sqrt{\Delta^2 + 4\beta^2}}\right)^{\frac{1}{2}} \\ v = u' &= \left(\frac{1}{2} - \frac{\Delta}{2\sqrt{\Delta^2 + 4\beta^2}}\right)^{\frac{1}{2}} \end{aligned} \tag{40}$$

where we assume Δ to be positive as reasonably expected. By this transformation, the Hamiltonian is diagonalized as,

$$\boldsymbol{H} = \sum_{k,\nu} E\, C^+_{k\nu} C_{k\nu} + \sum_{k,\nu} E'\, D^+_{k\nu} D_{k\nu} - (Ew^2 + E'w'^2) \tag{41}$$

The zero point energy is calculated from Eqs. (36), (37) and (40),

$$Ew^2 + E'w'^2 = 2N\beta^2 \frac{\varepsilon + \Delta}{\varepsilon^2 + \varepsilon\Delta - \beta^2} \tag{42}$$

The ground wave function $|0\rangle$ can be expanded by the original representations as

$$|0\rangle = \sum_{m,n} \alpha_{mn} |m,n\rangle_0 \tag{43}$$

Here $|m,n\rangle_0$ is the state function which contains

m one-site CT excitations of $k=0$, $\nu=+$ and n two-sites CT excitations of $k=0$, $\nu=+$. The suffix o signifies the original representations. The coefficient α_{mn} is determined from the following conditions.

$$C_{0+}|0> = 0$$

$$D_{0+}|0> = 0 \tag{44}$$

$$\sum_{m,n} \alpha_{mn}^2 = 1 \quad \text{(normalization condition)}$$

The final result is

$$\alpha_{mn} = \frac{x^m y^n}{\sqrt{m!n!}} \mathrm{e}^{-\frac{1}{2}(x^2+y^2)} \quad (N \to \infty) \tag{45}$$

and

$$x = -\frac{\varepsilon + \varDelta}{E E'} \sqrt{2N}\beta \quad y = \frac{\beta}{E E'} \sqrt{2N}\beta \tag{46}$$

Discussion

First we consider the effect of the Bose approximation. The occupation number of $a_{j\sigma}^+ \ a_{j\sigma}$ is essentially 0 or 1. But the Bose approximation adopted in the present study takes off this restriction and consequently many excitations turn out to occupy the same crystals site. Therefore this approximation may be applicable only when the mean value $<a_{j\sigma}^+ \ a_{j\sigma}>_{\mathrm{av.}}$ for the concerned state is[16]

$$<a_{j\sigma}^+ a_{j\sigma}>_{\mathrm{av.}} \ll 1. \tag{47}$$

For the ground state represented by Eq. (21), the mean value is

$$<0|a_{j\sigma}^+ a_{j\sigma}|0> = \frac{\beta^2}{\varepsilon_{0+}^2} \tag{48}$$

Therefore under the restriction of $\beta^2/\varepsilon_{0+}^2 \ll 1$, the number of the virtual excitations in the ground state is small compared with N and the Bose approximation may not cause a large error. For most of the crystals which are treated here, this restriction seems to be satisfied.

The zero point energy $2N\beta^2/\varepsilon_{0+}$ in Eq. (20) represents the stabilization energy of the crystal due to the contribution of the CT configurations ($k=0$, $\nu=+$) to the ground state. This is twice as large as the simple sum of the CT stabilization energies of component pairs. The factor 2 comes from the fact that the charge transfer occurs in the two directions ($\sigma=+,-$).

From Eq. (21) the n-molecule excitation configuration is known to contribute to the ground state by α_n^2. As is seen in Eq. (25), the coefficient α_n^2 follows the Poisson distribution function. In Fig. 1 the relation between α_n^2 and n is shown for the case of $\gamma^2=10^6$. The number of virtual excitation n_{max} for the greatest α_n^2 and the average number of virtural excitations $\bar{n}$ are equal to each other, and they are evaluated form Eq. (24) as follows:

$$n_{\mathrm{max}} = \bar{n} = 2N \frac{\beta^2}{\varepsilon_{0+}^2} \tag{49}$$

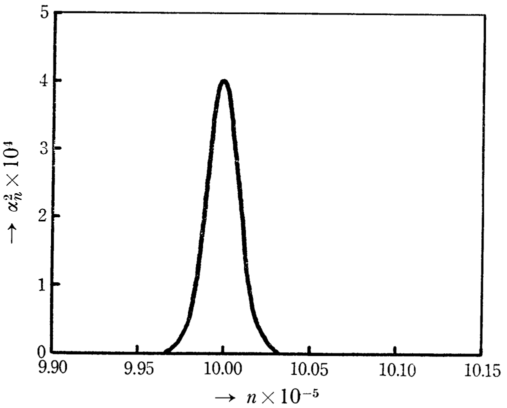

Fig. 1. The dependency of α_n^2 upon n for $\gamma^2=10^6$.

The n_{max} value is equal to N and $2N$ times the weight of the CT configuration in the corresponding component pairs for radical or molecular crystals and for CT complex crystals, respectively. The excitation density of the jth molecular site in the ground state is

$$<0|\sum_\sigma a_{j\sigma}^+ a_{j\sigma}|0> = 2\frac{\beta^2}{\varepsilon_{0+}^2} \tag{50}$$

Therefore weak CT complexes may be written schematically as $\cdots D^{+\delta}A^{-\delta}D^{+\delta}A^{-\delta}\cdots$ ($\delta=2\beta^2/\varepsilon_{0+}^2$).

According to the second quantization method combined with the Bose approximation the excitation energy between the ground and CT states is equal to $\varepsilon_{k\nu}$ in Eq. (20). In this method, the transfer energy β does not affect the excitation energy.

One may calculate the matrix of operator $\hat{\boldsymbol{\mu}}=\sum_i e\boldsymbol{r}_i$. The operator $\hat{\boldsymbol{\mu}}$ can be expanded in the second quantization form for the following two cases.

Case 1, for usual molecular crystals, radical crystals and weak CT complexes;

$$\hat{\boldsymbol{\mu}} = \sum_i e\boldsymbol{r}_i = \sum_j \{\boldsymbol{\mu}_{1+}(a_{j+}^+ + a_{j+}) + \boldsymbol{\mu}_{1-}(a_{j-}^+ + a_{j-})\}$$
$$+ \sum_j \{\boldsymbol{\mu}_d(1)\, a_{j+}^+ a_{j+} + \boldsymbol{\mu}_d(-1) a_{j-}^+ a_{j-}\} \tag{51}$$

Case 2, for strong CT complexes;

$$\hat{\boldsymbol{\mu}} = \sum_i e\boldsymbol{r}_i = \sum_j \{\boldsymbol{\mu}_{1+}(a_{j+}^+ + a_{j+}) + \boldsymbol{\mu}_{1-}(a_{j-}^+ + a_{j-})\}$$
$$- \sum_j \{\boldsymbol{\mu}_d(1)(1 - a_{j+}^+ a_{j+}) + \boldsymbol{\mu}_d(-1)(1 - a_{j-}^+ a_{j-})\} \tag{52}$$

where

$$\boldsymbol{\mu}_{1+} = <\psi(1,j)|\sum_i e\boldsymbol{r}_i|\psi(0,0)>$$

$$\boldsymbol{\mu}_{1-} = <\psi(-1,j)|\sum_i e\boldsymbol{r}_i|\psi(0,0)>$$

$$\boldsymbol{\mu}_d(m) = <(m,j,)|\sum_i e\boldsymbol{r}_i|\psi(m,j)>$$

$$- <\psi(0,0)|\sum_i e\boldsymbol{r}_i|\psi(0,0)> \; ; \; m=1,-1$$

$$\boldsymbol{\mu}_{1//} = \frac{1}{2}(\boldsymbol{\mu}_{1+}-\boldsymbol{\mu}_{1-}), \quad \boldsymbol{\mu}_{1\perp} = \frac{1}{2}(\boldsymbol{\mu}_{1+}+\boldsymbol{\mu}_{1-})$$

$$\boldsymbol{\mu}_{d//} = \frac{1}{2}(\boldsymbol{\mu}_d(1) - \boldsymbol{\mu}_d(-1)),$$

$$\boldsymbol{\mu}_{d\perp} = \frac{1}{2}(\boldsymbol{\mu}_d(1) + \boldsymbol{\mu}_d(-1)) \tag{53}$$

For case 1 every component molecule is assumed to have no dipole moment and $<\psi(0,0)|\sum_i e\boldsymbol{r}_i|\psi(0,0)>=0$. The first term in Eqs. (51) and (52) comes from the off-diagonal matrix elements between the CT and ground configurations. The second terms signify the appearance and disappearance of the dipole with a CT excitation, respectively.

Equations (51) and (52) are transformed by the use of Eqs. (16) and (19) as follows:

Case 1,

$$\hat{\boldsymbol{\mu}} = \sqrt{2N}\left(\boldsymbol{\mu}_{1\perp} - \frac{\beta}{\varepsilon_{0+}}\boldsymbol{\mu}_{d\perp}\right)(c^+_{0+}+c_{0+})$$

$$+ \sqrt{2N}\left(\boldsymbol{\mu}_{1//} - \frac{\beta}{\varepsilon_{0+}}\boldsymbol{\mu}_{d//}\right)(c^+_{0-}+c_{0-})$$

$$+ \sum_k\{\boldsymbol{\mu}_{d\perp}(c^+_{k+}c_{k+}+c^+_{k-}c_{k-}) + \boldsymbol{\mu}_{d//}(c^+_{k-}c_{k+}+c^+_{k+}c_{k-})\}$$

$$+ 2N\left(-2\boldsymbol{\mu}_{1\perp}\frac{\beta}{\varepsilon_{0+}} + \boldsymbol{\mu}_{d\perp}\left(\frac{\beta}{\varepsilon_{0+}}\right)^2\right) \tag{54}$$

Case 2,

$$\hat{\boldsymbol{\mu}} = \sqrt{2N}\left(\boldsymbol{\mu}_{1\perp} - \frac{\beta}{\varepsilon_{0+}}\boldsymbol{\mu}_{d\perp}\right)(c^+_{0+}+c_{0+})$$

$$+ \sqrt{2N}\left(\boldsymbol{\mu}_{1//} - \frac{\beta}{\varepsilon_{0+}}\boldsymbol{\mu}_{d//}\right)(c^+_{0-}+c_{0+})$$

$$+ \sum_k\{\boldsymbol{\mu}_{d\perp}(c^+_{k+}c_{k+}+c^+_{k-}c_{k-}) + \boldsymbol{\mu}_{d//}(c^+_{k-}c_{k+}+c^+_{k-}c_{k-})\}$$

$$+ 2N\left(-2\,\boldsymbol{\mu}_{1\perp}\frac{\beta}{\varepsilon_{0+}} - \boldsymbol{\mu}_{d\perp}\left(1 - \frac{\beta^2}{\varepsilon^2_{0+}}\right)\right) \tag{55}$$

As can be seen in the first and second terms of Eqs. (54) and (55), the optical transition from the ground state is allowed for the two kinds of states c_{0+} and c_{0-} within the approximation of electric dipole transition. Hereafter the corresponding state is abbreviatedly represented by the operator $c_{k\nu}$. Their transition moments are

$$<0|c_{0+}\hat{\boldsymbol{\mu}}|0> = \sqrt{2N}\left(\boldsymbol{\mu}_{1\perp} - \frac{\beta}{\varepsilon_{0+}}\boldsymbol{\mu}_{d\perp}\right)$$

$$<0|c_{0-}\hat{\boldsymbol{\mu}}|0> = \sqrt{2N}\left(\boldsymbol{\mu}_{1//} - \frac{\beta}{\varepsilon_{0+}}\boldsymbol{\mu}_{d//}\right) \tag{56}$$

for the both cases. According to Eq. (56), the absorption intensity of the transition to the c_{0-} (c_{0+}) state is $2N$ or N times larger in the component parallel (perpendicular) to the chain direction than that for a DA pair of the CT complex or that for a dimer of radicals and usual molecules, respectively.

Usually the second term on the right hand side of Eq. (56) is larger than the first term in their absolute values. Therefore the CT configurations mixing in the ground state contribute mainly to the intensity of optical absorption. In the one molecule excitation method where $\Psi(1,k,\nu)$ of Eq. (6) is taken as an excited state wave function and $\psi(0,0)$ as the ground state one, the optical transition is allowed for the two excited states of ($k=0$, $\nu=+$) and ($k=0$, $\nu=-$) and their transition moments are only the first term of Eq. (56). Therefore, the Hamiltonian $\boldsymbol{H}_3$ plays an essential role in the mechanism of optical transition.

The dipole moment of the ground state can be evaluated for cases 1 and 2.

Case 1,

$$\boldsymbol{\mu} = <0|\hat{\boldsymbol{\mu}}|0> = 2N\left(-2\boldsymbol{\mu}_{1\perp}\frac{\beta}{\varepsilon_{0+}} + \boldsymbol{\mu}_{d\perp}\frac{\beta^2}{\varepsilon^2_{0+}}\right)$$

Case 2,

$$\boldsymbol{\mu} = <0|\hat{\boldsymbol{\mu}}|0> = 2N\left(-2\boldsymbol{\mu}_{1\perp}\frac{\beta}{\varepsilon_{0+}} - \boldsymbol{\mu}_{d\perp}\left(1-\frac{\beta^2}{\varepsilon^2_{0+}}\right)\right) \tag{57}$$

Since in our model the CT complex has the translational symmetry, the CT complex of a zigzag chain has a dipole moment in the direction perpendicular to the chain. Its magnitude is $2N$ times larger than the component perpendicular to the chain direction of the dipole moment of a DA pair. Thus the zigzag chain of the CT complex is expected to have a large dipole moment, and therefore ferroelectricity is expected for crystals in which the component chain dipoles do not negate each other.

Next we discuss the results obtained in the case of complex radical crystals. The zero point energy $2N\beta^2(\varepsilon+\Delta)/(\varepsilon^2+\varepsilon\Delta-\beta^2)$ can be explained as the stabilization energy due to the mixing of the one-site and two-site CT configurations into the ground state. The main contribution to the zero point energy comes from the fourth term of Eq. (29) which is quite similar to the second terms of Eq. (18). The energy is larger than $2N\beta^2/\varepsilon$ which is the limiting value for $\beta/\varepsilon \rightarrow 0$.

The excitation energy E and E' are different from the respective diagonal matrix elements of the one-site and two-site CT states. As is seen in Eqs. (30) and (31), the excited state of the crystal can be understood as a coupled excited state of the one-site and two-site CT excitations. According to Eq. (40), the coupling strength between them becomes larger with the increase in β/Δ.

The configuration which contains m one-site and n two-site CT excitations contributes to the ground state by α^2_{mn}. The $m_{\max}$ and $\bar{m}$ values which are the m value for the greatest α^2_{mn} and the average number of m for a fixed n, respectively, are obtained from Eq. (45),

$$m_{\max} = \bar{m} = x^2 \tag{58}$$

In the similar way, for a fixed m,

$$n_{\max} = \bar{n} = y^2 \tag{59}$$

Then

$$\frac{n_{\max}}{m_{\max}} = \frac{\bar{n}}{\bar{m}} = \left(\frac{\beta}{\varepsilon+\Delta}\right)^2 \tag{60a}$$

$$\frac{m_{\max}}{N} = \frac{\bar{m}}{N} = 2\left\{\frac{(\varepsilon+\Delta)\beta}{\varepsilon^2+\varepsilon\Delta-\beta^2}\right\}^2 \tag{60b}$$

When $\beta/\varepsilon \rightarrow 0$, these quantities are

$$m_{\max} = \bar{m} \xrightarrow[\beta/\varepsilon \rightarrow 0]{} 2N\left(\frac{\beta}{\varepsilon}\right)^2 \tag{61a}$$

$$n_{\max} = \bar{n} \rightarrow 2N\left(\frac{\beta^2}{\varepsilon^2+\varepsilon\Delta}\right)^2 < 2N\left(\frac{\beta}{\varepsilon}\right)^4 \tag{61b}$$

$$\frac{m_{\max}}{N} = \frac{\bar{m}}{N} \rightarrow 2\left(\frac{\beta}{\varepsilon}\right)^2 \tag{61c}$$

Eq. (61a) corresponds to Eq. (49). The results shown by Eqs. (61a), (61b) and (61c) are reasonable.

The transition moment and the dipole moment of the system are obtained by using the equation similar to Eq. (51) except for the contribution from the two-sites CT excitation. The matrix element of transition moment is not zero only for C_{0+}, D_{0+}, C_{0-} and D_{0-}. The transition moments finally obtained are as follows:

$$\begin{aligned}
<0|C_{0+}\hat{\boldsymbol{\mu}}|0> &= \boldsymbol{\mu}_{d\perp}(-uw-vw')u \\
&= -\sqrt{2N}\,\beta\,\frac{\varepsilon+\Delta}{E\,E'}\,u\,\boldsymbol{\mu}_{d\perp}
\end{aligned}$$

$$\begin{aligned}
<0|D_{0+}\hat{\boldsymbol{\mu}}|0> &= \boldsymbol{\mu}_{d\perp}(-uw-vw')v \\
&= -\sqrt{2N}\,\beta\,\frac{\varepsilon+\Delta}{E\,E'}\,v\,\boldsymbol{\mu}_{d\perp}
\end{aligned}$$

$$\begin{aligned}
<0|C_{0-}\hat{\boldsymbol{\mu}}|0> &= \boldsymbol{\mu}_{d//}(-u^2w+uvw'-2v^2w) \\
&= -\sqrt{2N}\,\beta\,\frac{\varepsilon+\sqrt{\Delta^2+4\beta^2}}{E\,E'}\,u\,\boldsymbol{\mu}_{d//} \\
<0|D_{0-}\hat{\boldsymbol{\mu}}|0> &= \boldsymbol{\mu}_{d//}(-v^2w'+uvw-2u^2w') \\
&= -\sqrt{2N}\,\beta\,\frac{\varepsilon-\sqrt{\Delta^2+4\beta^2}}{E\,E'}\,v\,\boldsymbol{\mu}_{d//}
\end{aligned} \tag{62}$$

The dipole moment of the ground state is

$$\begin{aligned}
<0|\hat{\boldsymbol{\mu}}|0> &= \boldsymbol{\mu}_{d\perp}(-uw-vw')^2 = 2N\,\boldsymbol{\mu}_{d\perp} \\
&\quad \times\left(\beta\,\frac{\varepsilon+\beta}{\varepsilon^2+\varepsilon\Delta-\beta^2}\right)^2
\end{aligned} \tag{63}$$

where

$$\boldsymbol{\mu}_d(n) = <\phi^{\circ}(n,2j-1)|\textstyle\sum e\boldsymbol{r}_i|\phi^{\circ}(n,2j-1)> \;;$$

$$n = \pm 1, \pm 2.$$

$$\boldsymbol{\mu}_{d\perp} = \frac{1}{2}(\boldsymbol{\mu}_d(1)+\boldsymbol{\mu}_d(-1)), \quad \boldsymbol{\mu}_{d//} = \frac{1}{2}(\boldsymbol{\mu}_d(1)-\boldsymbol{\mu}_d(-1))$$

$$<\phi^{\circ}(\mathrm{n},2j-1)|\sum_i e\boldsymbol{r}_i|\phi^{\circ}(0,0)> = 0 \quad \text{(assumed)};$$

$$n = \pm 1, \pm 2$$

As is seen in Eqs. (62) and (63), the regular chain has no transition dipole for C_{0+} and D_{0+} states and no dipole moment, because of $\mu_{d\perp}=0$ for the regular chain.

For $\beta/\varepsilon \rightarrow 0$, C_{0+} and C_{0-} states are mainly composed of the one-site CT state in which an electron transfers from an anion radical A^- to the nearest neighboring neutral molecule A, whereas D_{0+} and D_{0-} states are of the two-site CT state corresponding to an electron transfer between the two neighboring A^- ions. In this case the transition probability to D_{0+} and D_{0-} states become negligibly small, since $|u| \rightarrow 1$ and $v \rightarrow 0$. On the other hand, for the case where $|\beta|/\Delta$ is large, the transitions to D_{0+} and D_{0-} states turn out to have significant intensity and their excitation energies become lower, as is seen in Eqs. (37) and (40). These CT states become the strongly coupled ones of the one-site and two-sites CT configurations.