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A Self-Consistent Molecular Field Theory for Aggregates of Neutral Molecules. I

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A self-consistent theory is presented for aggregates of neutral molecules. According to the LCAO Hartree-Fock formalism a set of effective Hartree-Fock equations for molecules in the aggregate is derived. The molecular orbitals of each molecule are to be determined from the effective H–F equation for the molecule in which the interactions between the molecule and the surrounding ones are included as an intermolecular interaction field (molecular field). A self-consistent treatment leads to the molecular orbitals which are self-consistent with the molecular field. By this method, the *n*-molecule problem becomes *n* times of one-molecule problem.

Eine selbstkonsistente Theorie für Aggregate neutraler Moleküle wird entwickelt. Entsprechend der LCAO-Hartree-Fock-Theorie wird eine Reihe effektiver Hartree-Fock-Gleichungen für die Moleküle des Aggregats abgeleitet. Die Molekülorbitale sind aus den effektiven H–F-Gleichungen eines Moleküls zu bestimmen, wobei die Wechselwirkungen mit den Nachbarmolekülen als intermolekulares Wechselwirkungsfeld (Molekülfeld) berücksichtigt werden. Die Molekülorbitale werden selbstkonsistent bezüglich des Molekülfeldes berechnet. Nach dieser Methode wird das *n*-Molekülproblem zum *n*-fachen Einmolekül-Problem.

Introduction

Since the LCAO Hartree-Fock equation for a molecule were derived [1, 2], the molecular orbital theory including electron-electron interactions, which had not been considered explicitly in the Hückel theory, has been developed; in the theory, both *ab initio* and semi-empirical calculations have often succeeded to estimate the transition energies or many other electronic properties of molecules.

On the other hand, a considerable progress has been made in the theoretical treatments for the electronic structures of molecular crystals [3–8] based on the Heitler-London method. In the H–L method, the zeroth-order wave-function for a crystal is expressed as an antisymmetrized or a simple product of the wave-functions of isolated molecules. Moreover, in this method the intermolecular interactions are introduced as perturbation to the Hamiltonian for the oriented gas model in which the molecules do not interact one another. In most of the previous articles [3–16], the following approximate treatments have been often taken:

(1) The wave-functions for the constituent molecules are assumed to be orthogonal one another, or all the overlaps between the wave-functions of the molecules are neglected.

(2) The exchange interactions between the molecules are often neglected in the numerical calculation or even in the formulation.

(3) In calculating the transition energies and the intensities of real optical transitions or other physical properties of molecular crystals, the intermolecular

interaction terms are usually approximated as the dipole-dipole interaction terms, or at best the quadrupole-quadrupole terms are also considered. The higher order terms are neglected.

(4) As the transition dipoles the values determined from the experimental oscillator strengths for the molecules are often used in the dipole-dipole approximation method. Even if the transition dipoles are calculated by the conventional MO methods, the directions of the dipoles in the crystal are always assumed for the molecules with a high symmetry such as benzene and coronene.

(5) Although the Davydov splittings of typical aromatic hydrocarbon crystals have been calculated and compared with the experimental findings [5–16], the spectral displacement[1], called D in Frenkel's and Craig's notation, is often neglected or at least not calculated directly from the theoretical method.

(6) The configuration interactions to be considered between the configurations, which do not belong to the same irreducible representation in the free-molecule, are often restricted a few.

In these respects more general and appropriate theoretical treatments should be required[2].

It has been considered as a good approximation method to introduce the perturbation theory in the frame of the Heitler-London model as far as the intermolecular overlap is small. However, in the case of large molecules, the dimension of molecule itself is often much larger than the nearest intermolecular distance[3], then this perturbation approximation method may not be appropriate one even if the intermolecular overlap is small. Therefore, it may be advisable that the electronic wave-function of the aggregate of large molecules should be described as a more appropriate antisymmetrized whole electron wave-function instead of the product of the wave-functions of the isolated molecules used in the previous articles [3–16].

In this paper a self-consistent theory for molecular aggregates is developed in which all the molecular orbitals can be determined self-consistently based on the many electron Hamiltonian including the intermolecular interactions explicitly. Once the SCF molecular orbitals for a molecular aggregate are given, we can start from more appropriate zeroth-order wave functions expressed as antisymmetrized products of these orbitals.

In Section I a self-consistent method is presented for aggregates of neutral molecules. In this method, each one-electron orbital for a molecular aggregate can be described as a linear combination of atomic orbitals of a constituent molecule like a usual MO, since each electron in the molecular aggregate may be tightly bound around one of the molecules. Moreover, an antisymmetrized product of the one-electron orbitals of all the molecules in the aggregate is taken as an electronic configuration of the system. Then, according to the LCAO Hartree-Fock formalism [1, 2] a set of effective Hartree-Fock equations for the

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[1] This term is a measure of the change in potential energy of interaction between a molecule and the surrounding molecules if this molecule is raised to an excited electronic state.

[2] In the recent work by Tanaka and Tanaka [8], most of these approximate treatments are not needed, and now their theoretical treatment seems to be one of the most acceptable ones.

[3] In benzene crystal, the diameter of molecule is about 5 Å, while the nearest intermolecular distance is 2.75 Å [17].

molecules in the aggregate is derived, where the intermolecular overlap between atomic orbitals is completely neglected. The one-electron orbitals of every molecule are to be determined from the effective H–F equation for the molecule in which the interactions between the molecule and the surrounding ones are included as an intermolecular interaction field (molecular field). A self-consistent treatment leads to the one-electron orbitals which are self-consistent with the molecular field (self-consistent molecular field). By this method the n-molecule problem becomes n times of one-molecule problem under the molecular field. Particularly for molecular crystals the n-molecule problem is reduced to just one-molecule problem under an equivalent molecular field.

Starting from these SCF one-electron orbitals (not from the SCF orbitals of isolated molecules) the excited electronic states of molecular crystals are described in Section II according to the Frenkel-Pierles method [18–21]. One of the important results in this section, which seems to be rather obvious, is that the configuration interaction matrix elements between the ground electronic configuration and the one-electron excitation ones are vanishing. Therefore, the ground state can be expressed by the ground electronic configuration alone. Furthermore, it will be shown that the calculations and the estimations of many physical properties, which are peculiar to molecular crystals and not found in an isolated molecule, become facile using this method.

For the numerical calculations of real systems semi-empirical methods are presented in Section III. At first, the π-electron approximation method is taken for the studies of the electronic transitions. Next, the all valence electron treatment is used to analyze the intermolecular interactions.

In Section IV two main problems of this theory are discussed; (1) to what system the self-consistent molecular field method is applicable and (2) whether the calculation in the real SCF procedure can converge or not.

I. Self-Consistent Molecular Field Method

1. Hartree-Fock Equation and the Molecular Field

According to the Born-Oppenheimer approximation [22], the total electron Hamiltonian operator for the N-molecule system is expressed in the form;

$$\boldsymbol{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{n_e} \nabla_i^2 + \frac{1}{2}\sum_{\substack{i,j\\(i\neq j)}} \frac{e^2}{r_{ij}} - \sum_{n=1}^{N}\sum_{q=1}^{q_n}\sum_{i=1}^{n_e} \frac{Z_{nq}e^2}{R_{nqi}}, \tag{1}$$

where e^2/r_{ij} is the electrostatic repulsion between electrons i and j, Z_{nq} is the nucleus charge on the q-th atom in the n-th molecule, and R_{nqi} is the distance between atom nq and electron i. Electronic wave-functions for the n_e-electron system will be constructed from normalized antisymmetrized product functions of the type[4];

$$\psi = \frac{1}{\sqrt{n_e!}} \det|(\phi_1\alpha)(\phi_1\beta)(\phi_2\alpha)\ldots|, \tag{2}$$

where ϕ_i is the one-electron orbital and α or β is the spin function. Since each electron in the molecular aggregate may be tightly bound around one molecule,

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[4] Although the extension to an open-shell case is not so difficult, a closed-shell case in each molecule is only considered in this paper.

the appropriate one-electron orbitals ϕ_i may be taken to be orthonormal linear combinations of atomic orbitals $\chi_{nq\mu}$ on one molecule;

$$\phi_{ni} = \sum_{q\mu} C_{inq\mu} \chi_{nq\mu} , \tag{3}$$

where ϕ_{ni} is the localized one-electron orbital on the n-th molecule corresponding to the i-th MO of a molecule in the familiar LCAO–MO approximation and $\chi_{nq\mu}$ is the μ-th AO on the q-th atom in the n-th molecule. Because of the small overlap between the molecules in molecular aggregates, a following approximation (complete neglect of intermolecular overlap) may be taken[5];

$$\int \chi^*_{nq\mu} \chi_{mp\nu} d\tau = \delta_{n,m} \int \chi^*_{nq\mu} \chi_{np\nu} d\tau . \tag{4}$$

Then, the partial orthogonality between the one-electron orbitals is obtained;

$$\int \phi^*_{ni} \phi_{mj} d\tau = a_{ij} \delta_{n,m} , \tag{5}$$

where $a_{ij} = \delta_{i,j}$ when the set of ϕ_{ni} is properly determined. Using ϕ_{ni}, the ground electronic configuration will be expressed in the scheme of Eq. (2) as follows;

$$\psi^0 = A \prod_{ni\sigma}^{\text{occ}} \phi_{ni\sigma} , \tag{6}$$

where A is an antisymmetrization operator permuting electrons and $\phi_{ni\sigma}$ is a spin-orbital which is the product of ϕ_{ni} and the spin function α or β. The electrons are accommodated in turn into the lower orbitals as in the case of the usual MO theory.

Under the condition, $a_{ij} = \delta_{i,j}$, the energy expectation value of the ground electronic configurations is given by the formula;

$$E^0 = 2 \sum_{ni}^{\text{occ}} H_{ni} + \sum_{nimj}^{\text{occ}} (2J_{nimj} - K_{nimj}) , \tag{7}$$

where

$$H_{ni} = \int \phi^*_{ni}(1) \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \sum_{mq} \frac{Z_{mq} e^2}{R_{mq1}} \right) \phi_{ni}(1)\, d\tau_1 , \tag{8}$$

$$J_{nimj} = \int\int \phi^*_{ni}(1)\, \phi_{ni}(1) \frac{e^2}{r_{12}} \phi^*_{mj}(2)\, \phi_{mj}(2)\, d\tau_1\, d\tau_2 , \tag{9}$$

and

$$K_{nimj} = \int\int \phi^*_{ni}(1)\, \phi_{mj}(1) \frac{e^2}{r_{12}} \phi^*_{mj}(2)\, \phi_{ni}(2)\, d\tau_1\, d\tau_2 . \tag{10}$$

The condition, $a_{ij} = \delta_{i,j}$, leads to

$$\sum_{p\mu q\nu} C^*_{inp\mu} C_{inq\nu} S^n_{p\mu q\nu} = 1 \quad (i = 1, n'_e \quad \text{and} \quad n = 1, N)^6 , \tag{11}$$

where $S^n_{p\mu q\nu}$ is the overlap integral;

$$S^n_{p\mu q\nu} = \int \chi^*_{np\mu} \chi_{nq\nu} d\tau . \tag{12}$$

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[5] This approximation is, on the other hand, based on the interpretation [23] that the atomic orbitals used in the semi-empirical molecular orbital theory should be considered as the orthogonalized atomic orbitals determined by the Löwdin's method [24]. Therefore, as far as the intermolecular overlap is not so large as an intermolecular bonding is made, this approximation may be valid, if the atomic integrals, such as two-electron repulsion integrals, are evaluated semi-empirically using the zero-differential overlap approximation.

[6] The symbol, $n = 1, N$, means that the n varies from unity to N. n'_e denotes the number of electrons in the n-th molecule.

To determine the coefficients, $C_{inp\mu}$, the variation principle is used to lead a following equations; for the variation of $C^*_{inp\mu}$ (cf. Appendix),

$$\sum_q C_{inq\nu}(F^n_{p\mu q\nu} - \varepsilon_{ni} S^n_{p\mu q\nu})\,\delta C^*_{inp\mu} = 0\,, \tag{13}$$

where $F^n_{p\mu q\nu}$ is an element of the n-th Fock matrix;

$$\begin{aligned} F^n_{p\mu q\nu} = I^n_{p\mu q\nu} + \sum_m \sum_{p'\mu' q'\nu'} P^m_{p'\mu' q'\nu'} \, [& (np\mu nq\nu \,|\, mp'\mu' mq'\nu') \\ & - \tfrac{1}{2}(np\mu mq'\nu' \,|\, mp'\mu' nq\nu)] \,. \end{aligned} \tag{14}$$

$P^n_{p\mu q\nu}$ is a bond-order;

$$P^n_{p\mu q\nu} = 2 \sum_i^{\mathrm{occ}} C^*_{inp\mu} C_{inq\nu}\,, \tag{15}$$

$$I^n_{p\mu q\nu} = \int \chi^*_{np\mu}(1) \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \sum_{mq'} \frac{Z_{mq'} e^2}{R_{mq'1}} \right) \chi_{nq\nu}(1)\, d\tau_1 \tag{16}$$

and

$$\begin{aligned} (np\mu mq\nu \,|\, n'p'\mu' m'q'\nu') = \iint & \chi^*_{np\mu}(1)\, \chi_{mq\nu}(1) \frac{e^2}{r_{12}} \\ & \chi^*_{n'p'\mu'}(2)\, \chi_{m'q'\nu'}(2)\, d\tau_1\, d\tau_2 \,. \end{aligned} \tag{17}$$

$I^n_{p\mu q\nu}$ is the Coulomb integral when $p\mu = q\nu$, otherwise a resonance integral. $(np\mu mq\nu \,|\, n'p'\mu' m'q'\nu')$ is the electron repulsion integral. Because of the arbitrary character of the variation set, a set of simultanious equations (Hertree-Fock equations for a molecular aggregate) is obtained,

$$\sum_{q\nu} C_{inq\nu}(F^n_{p\mu q\nu} - \varepsilon_{ni} S^n_{p\mu q\nu}) = 0 \quad (n = 1, N). \tag{18}$$

One of these equations (the effective Hartree-Fock equation for a constituent molecule) is very similar to that of a molecule, but $F^n_{p\mu q\nu}$ depends upon the coefficients of other molecules, $C_{imp\mu}(m \neq n)$, so that the equations $(n = 1, N)$ are not independent of each other.

Although to solve the equations there arises a difficulty due to the non-linearity of $C_{inq\nu}$, if the Fock matrix elements are estimated by a set of $C_{inq\nu}$ assumed, the simultaneous equation becomes linear and feasible and then the equations are decoupled into seqular equations of the next form (the effective seqular equations for constitutent molecules);

$$\det |F^n_{p\mu q\nu} - \varepsilon_n S^n_{p\mu q\nu}| = 0 \quad (n = 1, N)\,. \tag{19}$$

Eq. (19) for the m-th molecule, which can be solved independently of other equations $(n \neq m)$, determines the one-electron orbitals belonging to the m-th molecule. However, this equation differs from the similar equation for an isolated molecule, since Eq. (19) includes the intermolecular interactions as a field (molecular field). Thus, the concept of the molecular field is introduced.

The general procedure to obtain the SCF solution or self-consistent molecular field is diagrammatized in Fig. 1. For the first step a set of $C_{inq\mu}$ should be assumed. For the n-th molecule the coefficients can be given from the Hückel orbitals or the SCF molecular orbitals of the free molecule. If all the coefficients for the molecules in the aggregate are given, then all the Fock matrix elements (Eq. (14)) can be

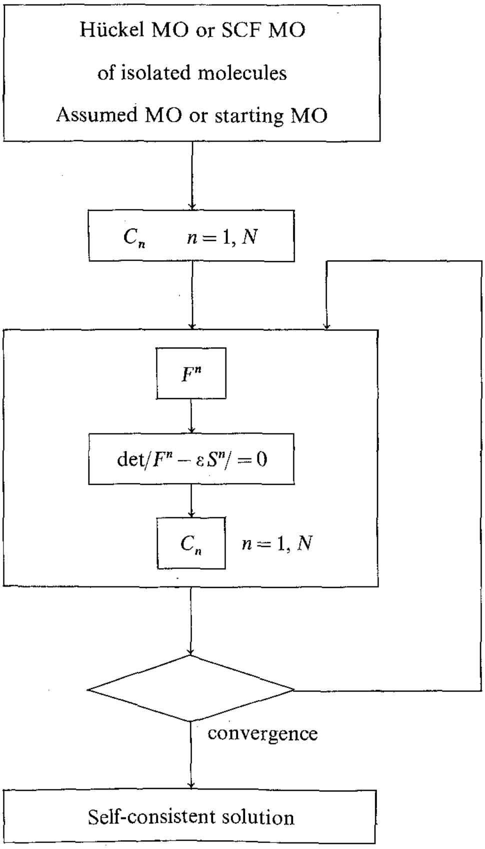

Fig. 1. Computational procedure to obtain a self-consistent solution

determined. Next, the seqular equation (Eq. (19)) for the n-th molecule (one-molecule problem) can be solved separately to give the new coefficients for the molecule. When all the equations are solved and a new set of the coefficients are obtained, the new Fock matrix elements will be determined to solve the new seqular equations. This procedure should be repeated until the cycle becomes self-consistent.

As shown above, N-molecule problem is decoupled into N times of one-molecule problem[7]. However, the one-molecule problems should be solved simultaneously, so that if N becomes large the process will be infeasible.

In the case of the molecular crystals where all the molecules are equivalent under the crystal symmetry operations in the ground state, the Fock matrices $(n=1, N)$ must be mathematically equivalent. Then, the N-molecule problem

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[7] Such decoupling is also derived when the one-electron orbitals in a crystal or a regular high polymer are expressed as linear combinations of basis sets constructed from the Bloch type sum of translationally equivalent atomic orbitals. In this case the problem is reduced to a set of one-unit-cell problems [25–27]. In molecular crystals, however, electrons are considered to be tightly bound to or localized on one molecule so that one-electron orbitals may be localized within a molecule rather than delocalized over the whole crystal.

reduces to just one-molecule problem under an equivalent molecular field. In this case it is possible to omit the suffix n if the numbering of equivalent atoms under the crystal symmetry operations are chosen to be the same[8].

Furthermore, if the molecules in a crystal are located on the crystal lattice points, the effective Fock operator should be invariant under the symmetry operations of the crystal point group. Then the one-electron orbitals of the molecule on the invarient lattice point must be the representations of the crystal point group.

2. *A Simple Numerical Application*

To examine whether the one-electron orbitals in a crystal are really deformed from those of a free molecule, this self-consistent equivalent molecular field method is applied to the typical aromatic hydrocarbon crystals. In the calculation, the usual π-electron approximation is employed (Section III.1). For the intramolecular electron repulsion integrals the π-electron correlation effect is considered along with Little and Gutefreund's method [28], and for the intermolecular electron repulsion integrals the bare Coulomb potential is used.

In Table 1, the orbital energies of coronene which has D_{6h} geometry are shown. For the free molecule there are several exactly degenerated orbitals. While, for

Table 1. Orbital energies of coronene

Free molecule (eV)		Crystal (eV)	Crystal field splitting (eV)
−16.0372	a_{2u}	−16.0799	
−14.9829	e_{1g}	−15.0298	
−14.9829	e_{1g}	−15.0186	0.0112
−13.6586	e_{2u}	−13.6994	
−13.6586	e_{2u}	−13.6983	0.0011
−13.3524	a_{2u}	−13.3937	
−12.2191	b_{2g}	−12.2576	
−12.1925	b_{1g}	−12.2343	
−11.9004	e_{1g}	−11.9467	
−11.9004	e_{1g}	−11.9391	0.0076
−10.7182	e_{2u}	−10.7600	
−10.7182	e_{2u}	−10.7574	0.0026
− 4.6726	e^*_{1g}	− 4.7146	
− 4.6725	e^*_{1g}	− 4.7113	0.0033
− 3.4525	e^*_{2u}	− 3.4988	
− 3.4525	e^*_{2u}	− 3.4912	0.0076
− 3.3241	a^*_{1u}	− 3.3622	
− 3.2010	a^*_{2u}	− 3.2429	
− 2.1383	b^*_{2g}	− 2.1798	
− 1.9099	e^*_{1g}	− 1.9508	
− 1.9099	e^*_{1g}	− 1.9495	0.0013
− 0.6868	e^*_{2u}	− 0.7338	
− 0.6868	e^*_{2u}	− 0.7227	0.0111
0.2895	b^*_{2g}	0.2465	

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[8] There is an exception in Eq. (14). In electron repulsion integrals the suffix n cannot be omitted. The possible cases are F, P, S, C, I, and ε. Other impossible cases are ϕ_{ni} and $\chi_{np\mu}$, etc.

the crystal the orbitals degenerated in the free molcule reveal the crystal field splitting. The π-electron densities on the carbon network also show the difference between the free molecule and the crystal. As shown in Table 2, the π-electron distribution of the free molecule satisfies the D_{6h} symmetry, while that of the

Table 2. Electron densities and orbital coefficients of coronene

a	b	c	d	e	f	g	h
1	A′	0.9946	0.9960	0.0000	−0.0037	−0.3148	−0.3144
2	I	1.0058	1.0073	−0.3109	−0.3109	−0.0028	0.0074
3	H	1.0058	1.0048	−0.1580	−0.1537	0.2679	0.2698
4	G	0.9946	0.9943	0.2727	0.2750	0.1575	0.1530
5	F	1.0058	1.0046	0.1531	0.1493	−0.2708	−0.2734
6	E	1.0058	1.0048	−0.1531	−0.1560	−0.2708	−0.2696
7	D	0.9946	0.9940	−0.2727	−0.2711	0.1575	0.1599
8	C	1.0058	1.0047	0.1580	0.1604	0.2679	0.2660
9	B	1.0058	1.0070	0.3109	0.3111	−0.0028	−0.0001
10	J′	0.9936	0.9942	0.0000	−0.0025	−0.2020	−0.2013
11	L	0.9936	0.9939	0.1749	0.1763	0.1010	0.0992
12	K	0.9936	0.9939	−0.1749	−0.1741	0.1010	0.1036
13	A	0.9946	0.9960	0.0000	−0.0037	−0.3148	−0.3144
14	I′	1.0058	1.0073	−0.3109	−0.3109	0.0028	0.0074
15	H′	1.0058	1.0048	−0.1580	−0.1537	0.2679	0.2698
16	G′	0.9946	0.9943	0.2727	0.2750	0.1575	0.1530
17	F′	1.0058	1.0046	0.1531	0.1493	−0.2708	−0.2734
18	E′	1.0058	1.0048	−0.1531	−0.1561	−0.2708	−0.2696
19	D′	0.9946	0.9940	−0.2727	−0.2711	0.1575	0.1599
20	C′	1.0058	1.0048	0.1580	0.1604	0.2679	0.2660
21	B′	1.0058	1.0070	0.3109	0.3111	−0.0028	−0.0001
22	J	0.9936	0.9942	0.0000	−0.0025	−0.2020	−0.2013
23	L′	0.9936	0.9939	0.1749	0.1763	0.1010	0.0992
24	K′	0.9936	0.9939	−0.1749	−0.1741	0.1010	0.1036

[a] Atomic position illustrated in Fig. 2.
[b] Atomic position in the crystal [29].
[c] π-electron densities of a free coronene molecule.
[d] π-electron densities of coronene in the crystal.
[e] One of the highest occupied orbitals of a free coronene molecule.
[f] The next highest occupied orbital of coronene in the crystal.
[g] The other highest occupied orbitals of a free coronene molecule.
[h] The highest occupied orbital of coronene in the crystal.

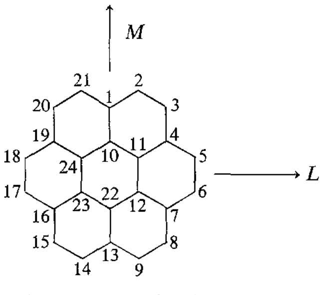

Fig. 2. Carbon skeleton of a coronene molecule: the molecular axes *M* and *L* indicate the orientation of the molecule in the crystal lattice [29]

molecule in the crystal is deformed into D_{2h} or even into C_i, which is seen easily to pick up the equivalent atoms. In the free molecule there are three groups of equivalent atoms, (1, 4, 7, 13, 16, 19), (2, 3, 5, 6, 8, 9, 14, 15, 17, 18, 20, 21), and (10, 11, 12, 22, 23, 24). Whereas in the crystals a crude grouping is as follows, (1, 13), (2, 9, 14, 21), (3, 5, 6, 8, 15, 16, 18, 20), (4, 7, 16, 19), (11, 12, 23, 24), and (10, 22), which may correspond to the D_{2h} symmetry. If the minor differences are noted, only the C_i symmetry can be seen.

Another demonstration is the difference of the orbital coefficients. The highest occupied orbitals of a free coronene molecule (e_{2u} degenerated orbitals) are compared with the highest and the next highest occupied orbitals of a molecule in the coronene crystal (Table 2, where the degenerated orbitals of a free molecule are symmetry-adapted to be the correct representations of D_{6h}). As can be seen from Table 2, the orbital coefficients for the isolated molecule and those for the crystal only differ by 10^{-1}–10^{-3}. However, the inclusion of these differences yields remarkable contributions to the values of the CI matrix elements and the transition moments. This, of course, affects the values of the excitation energies and oscillator strengths.

In this example, coronene is a nonpolar molecule which is expected to produce "fairly weak molecular field". Therefore, if polar molecules such as heterocyclic compounds are concerned, much more serious effects is expected on the molecular orbitals in the crystal.

II. The Excited States of Molecular Crystals

In this section, the excited states of molecular crystals are described. The excited states are at first approximated by a single electronic configuration and then configuration interactions are considered.

1. Ionized Configuration

When an electron is removed from the occupied orbital $\phi_{mk\alpha}$, the electronic configuration is expressed as

$$\psi_{mk\alpha} = A\left[\prod_{ni\sigma} \phi_{ni\sigma} \cdot \phi_{mk\alpha}^{-1}\right]. \tag{20}$$

Considering the translational symmetry, the corresponding ionized state should be expressed as

$$^2\psi_k(\boldsymbol{k}) = \begin{cases} \sum\limits_m \frac{1}{\sqrt{N}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_m} \psi_{mk\alpha} \\ \sum\limits_m \frac{1}{\sqrt{N}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_m} \psi_{mk\beta} \end{cases}, \tag{21}$$

where $\boldsymbol{k}$ is the crystal momentum, $\boldsymbol{r}_m$ is the position vector of the m-th molecule, and N is the total number of lattice points. The expectation value of the energy for $\psi_k(\boldsymbol{k})$, $E_k(\boldsymbol{k})$, is written as

$$E_k(\boldsymbol{k}) = E^0 - \varepsilon_k . \tag{22}$$

This equation shows that the Koopmans' thorem [30] holds as in the case of the usual SCF MO theory.

2. *Frenkel Exciton (One Molecule in Each Unit Cell)*

The electronic configuration of one-electron excitation within a molecule is given by

$$\psi_{mk\alpha,\, ml\alpha'} = A\left[\prod_{ni\sigma} \phi_{ni\sigma}\cdot \phi_{mk\alpha}^{-1}\cdot \phi_{ml\alpha'}\right]. \tag{23}$$

Then, the localized excitation configurations for singlet and triplet are expressed as

$$^{1}\psi_{mk,\, ml} = \frac{1}{\sqrt{2}}\left(\psi_{mk\alpha,\, ml\alpha} - \psi_{mk\beta,\, ml\beta}\right) \quad \text{(singlet)} \tag{24-1}$$

and

$$\begin{aligned} ^{3}\psi_{mk,\, ml} &= \frac{1}{\sqrt{2}}\left(\psi_{mk\alpha,\, ml\alpha} + \psi_{mk\beta,\, ml\beta}\right) \\ ^{3}\psi_{mk,\, ml} &= \psi_{mk\alpha,\, ml\beta} \qquad\qquad \text{(triplet)} \\ ^{3}\psi_{mk,\, ml} &= \psi_{mk\beta,\, ml\alpha}\,. \end{aligned} \tag{24-2}$$

According to the Frenkel-Pierles method [18–21], singlet and triplet Frenkel excitons should be written as

$$^{1,3}\psi_{k,l}(\boldsymbol{k}) = \sum_{m} \frac{1}{\sqrt{N}}\, e^{i\boldsymbol{k}\cdot \boldsymbol{r}_m}\, {}^{1,3}\psi_{mk,\, ml} \tag{25}$$

and the energies are

$$\begin{aligned} ^{1,3}E_{k,l}(\boldsymbol{k}) = E^{0} + \varepsilon_l - \varepsilon_k - \sum_{m'} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_{m'} - \boldsymbol{r}_m)} \\ \left[\int\!\!\int \phi_{ml}^{*}(1)\, \phi_{m'l}(1)\, \frac{e^2}{r_{12}}\, \phi_{m'k}^{*}(2)\, \phi_{mk}(2)\, d\tau_1\, d\tau_2 \right. \\ \left. - \binom{2}{0} \int\!\!\int \phi_{ml}^{*}(1)\, \phi_{mk}(1)\, \frac{e^2}{r_{12}}\, \phi_{m'k}^{*}(2)\, \phi_{m'l}(2)\, d\tau_1\, d\tau_2 \right], \end{aligned} \tag{26}$$

where

$$\binom{a}{b} = \begin{cases} a\text{: singlet} \\ b\text{: triplet}. \end{cases} \tag{27}$$

3. *Charge-Transfer Exciton (One Molecule in Each Unit Cell)*

Charge-transfer exciton should be expressed as the lattice sum of translationally equivalent electronic configurations of electron transfer between two molecules. When the electron transfer vector is $\boldsymbol{x} = \boldsymbol{r}_n - \boldsymbol{r}_m$, the corresponding charge-transfer exciton may be written as

$$^{1,3}\psi_{k,l}(\boldsymbol{k}, \boldsymbol{x}) = \sum_{nm}{}' \frac{1}{\sqrt{N}}\, e^{i\boldsymbol{k}\cdot \boldsymbol{r}_m}\, {}^{1,3}\psi_{mk,\, nl}\ , \tag{28}$$

where the lattice sum runs keeping $\boldsymbol{r}_n - \boldsymbol{r}_m = \boldsymbol{x}$ and

$$\begin{aligned} ^{1}\psi_{mk,\, nl} &= A\left[\prod_{ni\sigma} \phi_{ni\sigma}\cdot \left(\phi_{mk\alpha}^{-1}\phi_{nl\alpha} - \phi_{mk\beta}^{-1}\phi_{nl\beta}\right)/\sqrt{2}\right] \\ ^{3}\psi_{mk,\, nl} &= A\left[\prod_{ni\sigma} \phi_{ni\sigma}\cdot \left(\phi_{mk\alpha}^{-1}\phi_{nl\alpha} + \phi_{mk\beta}^{-1}\phi_{nl\beta}\right)/\sqrt{2}\right] \\ ^{3}\psi_{mk,\, nl} &= A\left[\prod_{ni\sigma} \phi_{ni\sigma}\cdot \phi_{mk\alpha}^{-1}\phi_{nl\beta}\right] \\ ^{3}\psi_{mk,\, nl} &= A\left[\prod_{ni\sigma} \phi_{ni\sigma}\cdot \phi_{mk\beta}^{-1}\phi_{nl\alpha}\right]. \end{aligned} \tag{29}$$

The energies are given by

$$
\begin{aligned}
{}^{1,3}E_{k,l}(\boldsymbol{k},\boldsymbol{x}) = E^0 + \varepsilon_l - \varepsilon_k - \sum_{m'} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_{m'} - \boldsymbol{r}_{m\ldots}} \\
\Bigg[\int\int \phi^*_{m'k}(1)\,\phi_{mk}(1)\,\frac{e^2}{r_{12}}\,\phi^*_{m+xl}(2)\,\phi_{m'+xl}(2)\,d\tau_1\,d\tau_2 \\
-\binom{2}{0}\int\int \phi^*_{m'k}(1)\,\phi_{m'+xl}(1)\,\frac{e^2}{r_{12}}\,\phi^*_{m+xl}(2)\,\phi_{mk}(2)\,d\tau_1\,d\tau_2\Bigg].
\end{aligned}
\tag{30}
$$

4. Davydov Splitting [3, 4] *of Frenkel Exciton*

In the real light absorption process, the momentum conservation law leads to the selection rule;

$$\boldsymbol{k} \cong \boldsymbol{0}\,.$$

If $\boldsymbol{k}$ equals just to zero, the excited states of the crystal having more than one molecule in each unit cell must be representations of the factor group. When the number of molecules in each unit cell is t, the excited states corresponding to the Frenkel exciton (${}^{1,3}\psi_{k,l}(\boldsymbol{0})$) are expressed as

$$ {}^{1,3}\psi_j(k,l) = \sum_{ms} \frac{1}{\sqrt{t}}\,{}^{1,3}\psi_{msk,\,msl}\,\delta_j(s)\;, \tag{31}$$

where s denotes a site in a unit cell and $\delta_j(s)$ is a coefficient of j-th branch. The $\delta_j(s)$ should be determined by solving the following secular equation and obtaining the eigen-vectors.

$$\det|A(k,l)_{s_1,s_2} - E\delta_{s_1,s_2}| = 0\;, \tag{32}$$

where

$$A(k,l)_{s_1 s_2} = \int \psi^*(k,l)_{s_1}\,\boldsymbol{H}\psi(k,l)_{s_2}\,dv \tag{33}$$

and

$$\psi(k,l)_{s_1} = \sum_m \frac{1}{\sqrt{t}}\,\psi_{ms_1k,\,ms_1l}\;. \tag{34}$$

The energy eigenvalue of a Davydov branch, ${}^{1,3}E_j(k,l)$, is also obtained from the solution of the Eq. (32) as following,

$$ {}^{1,3}E_j(k,l) = E^0 + \varepsilon_l - \varepsilon_k + \sum_{m's'} \frac{1}{t}\,\delta_j(s')\,{}^{1,3}M_{m1m's'}(k,l) \tag{35}$$

and

$$
\begin{aligned}
{}^{1,3}M_{msm's'}(k,l) = -\int\int \phi^*_{msl}(1)\,\phi_{m's'l}(1)\frac{e^2}{r_{12}}\,\phi^*_{m's'k}(2)\,\phi_{msk}(2)\,d\tau_1\,d\tau_2 \\
+\binom{2}{0}\int\int \phi^*_{msl}(1)\,\phi_{msk}(1)\frac{e^2}{r_{12}}\,\phi^*_{m's'k}(2)\,\phi_{m's'l}(2)\,d\tau_1\,d\tau_2\,.
\end{aligned}
\tag{36}
$$

Then, Eq. (19) leads to the Davydov splitting between the j-th branch and the j'-th;

$$ {}^{1,3}\Delta(k,l)_{jj'} = \sum_s \left[(\delta_j(s) - \delta_{j'}(s)) \sum_m {}^{1,3}M_{11ms}(k,l)\right]. \tag{37}$$

5. *Configuration Interaction between Excitons*

Although the excited states has been described as $\psi_k(\boldsymbol{k})$, $\psi_{k,l}(\boldsymbol{k})$, and $\psi_{k,l}(\boldsymbol{k}, \boldsymbol{x})$, this approximation may or may not be good to the total wave-function $\psi_i(\boldsymbol{k})$ for an actual electronic state i of the crystal. In case for which a combination of several single exciton configurations is needed, a configuration interaction calculation should be performed by carrying out a linear variational calculation with $\psi_{k,l}(\boldsymbol{k}, \boldsymbol{x})$ (including $\psi_k(\boldsymbol{k})$ and $\psi_{k,l}(\boldsymbol{k})$ in the symbol) as starting functions:

$$\psi_i(\boldsymbol{k}) = \Sigma a_{k,l}(\boldsymbol{k}, \boldsymbol{x})_i \, \psi_{k,l}(\boldsymbol{k}, \boldsymbol{x}) \,, \tag{38}$$

determining the energy and the coefficients $a_{k,l}(\boldsymbol{k}, \boldsymbol{x})_i$ by solving a seqular equation

$$\det |\Lambda(\boldsymbol{k})_{kl\boldsymbol{x}, k'l'\boldsymbol{x}'} - \delta_{kl\boldsymbol{x}, k'l'\boldsymbol{x}'} E| = 0 \,, \tag{39}$$

where

$$\Lambda(\boldsymbol{k})_{kl\boldsymbol{x}, k'l'\boldsymbol{x}'} = \int \psi^*_{k,l}(\boldsymbol{k}, \boldsymbol{x}) \, \boldsymbol{H} \, \psi_{k',l'}(\boldsymbol{k}, \boldsymbol{x}') \, dv \,. \tag{40}$$

In this configuration interaction scheme, the interactions between different $\boldsymbol{k}$ and also between different terms are neglected.

6. *Configuration Interaction Between Ionized Configurations*

As in the SCF theory of one molecule, the CI matrix elements between the ionized configurations also vanish;

$$\int {}^2\psi^*_k(\boldsymbol{k}) \, \boldsymbol{H} \, {}^2\psi_{k'}(\boldsymbol{k}) \, dv = 0 \quad (k \neq k') \,. \tag{41}$$

7. *Configuration Interaction Between the Ground Electronic Configuration and One-Electron Excitation Configurations*

The CI matrix elements between the ground electronic configuration and one-electron excitation configurations are also vanishing;

$$\int \psi^{0*} \boldsymbol{H} \psi_{mk, m+xl}(\boldsymbol{k}) \, dv = 0 \,. \tag{42}$$

Therefore, Brillouin's theorem [31] holds in this theory. In other words, exciton states do not mix with the ground one. This is one of the most important points of this theory, since the ground state can be expressed purely as the ground electronic configuration.

8. *Davydov Splitting and Configuration Interaction*

If more than one molecule are there in a unit cell, it is easy to consider the configuration interactions. The Davydov splitting is obtainable by solving

$$\det |{}^{1,3}_{j}\Lambda_{kl\boldsymbol{x}, k'l'\boldsymbol{x}'} - \delta_{kl\boldsymbol{x}, k'l'\boldsymbol{x}'} E| = 0 \,, \tag{43}$$

where

$${}^{1,3}_{j}\Lambda_{kl\boldsymbol{x}, k'l'\boldsymbol{x}'} = \int {}^{1,3}\psi_j(k, l, \boldsymbol{x}) \, \boldsymbol{H} \, {}^{1,3}\psi_j(k', l', \boldsymbol{x}) \, dv \,, \tag{44}$$

$${}^{1,3}\psi_{ji} = \Sigma^{1,3} a_{ji}(k, l, \boldsymbol{x}) \, {}^{1,3}\psi_j(k, l, \boldsymbol{x}) \,, \tag{45}$$

and ${}^{1,3}\psi_j(k, l, \boldsymbol{x})$ are the solution of Eq. (32) or its simple version with $\boldsymbol{x} \neq \boldsymbol{0}$. It should be noted that the configuration interactions between different Davydov branches are vanishing and then the excited states are labeled by branch number j and another quantum-number i.

9. Characteristics of This Theory

When the descriptions of the electronic states given above are appropriate for the actual molecular crystals, the calculations and estimations of following physical properties of molecular crystals become facile. (a) Stabilization energy of a molecule in crystallization; according to the vanishing character of the CI matrix elements between the ground electronic configuration and one electron excitation configurations, if the configuration interactions with two-electron excitation configuration and others are neglected, the stabilization energy of a molecule when it is brought into the crystal from vacuum (crystal lattice energy) can be calculated from the total energy of an isolated molecule and the total energy of the ground electronic configuration of the crystal. The former is easily obtainable by solving the conventional one-molecule Hartree-Fock equation and the latter also by solving the effective one-molecule problem. (b) Spectral shifts. (c) Removal of electronic degeneracy (crystal field splitting of the degenerated states). (d) Violation of selection rules (allowance of the forbidden transition of the isolated molecule in the crystal). (e) Crystal field mixing (configuration interaction between the configurations which do not belong to the same irreducible representation in an isolated molecule). (f) Removal of the arbitrary character of the direction of the transition moment of a high symmetry molecule such as benzene and coronene; once the SCF orbitals for the ground electronic configuration are obtained, these properties from (b) to (f) are determined from the eigen-values and eigen-vectors of Eq. (39). Although in the usual calculation of Davydov splitting the direction of the transition moment of a high symmetry molecule in a crystal is assumed and the number of configurations for CI calculation are usually limited a few [32], by this method the assumption is not needed and CI calculation can be carried out as in the case of a molecule, because the CI matrix elements are considerably simplified. Therefore, from the solution of the simple secular Eq. (32) or (43) it is hopeful to get more reliable results in the calculation of the Davydov splitting and the polarization of each Davydov branch.

III. Semi-Empirical Methods

In this section semi-empirical treatments are presented, because the *ab initio* calculation may not be feasible in a large system. At first π-electron approximation is taken to calculate the electronic transition energies and their oscillator strengths. Next, all valence electron treatment is used to study the intermolecular interactions.

1. π-Electron Approximation

If attention is paid to the properties of mobile electrons of the system (for example, electronic spectra of aromatic hydrocarbons), the usual π-electron approximation may be taken. Within this limitation an extension of the conventional Pariser-Parr method may be an appropriate method to test this theory. Now, the following approximations are taken.

(a) Zero-Differential Overlap Approximation

Using zero-differential overlap (ZDO) approximation, the electron repulsion integrals of Eq. (17) vanish unless they are one center or two center Coulomb repulsion integrals;

$$(npn'p'|mqm'q') = \delta_{n,n'}\,\delta_{p,p'}\,\delta_{m,m'}\,\delta_{q,q'}\,\gamma_{npmq} \tag{46}$$

and

$$\gamma_{npmq} = \int\int \chi^*_{np}(1)\,\chi_{np}(1)\,\frac{e^2}{r_{12}}\,\chi^*_{mq}(2)\,\chi_{mq}(2)\,d\tau_1\,d\tau_2\,. \tag{47}$$

(b) Pariser Approximation [33]

According to Pariser approximation one center Coulomb repulsion integrals become,

$$\gamma_{npnp} = I_{np} - A_{np}\,, \tag{48}$$

where I_{np} and A_{np} are the ionization potential and the electron affinity of p-th atom in the n-th molecule, respectively.

(c) Two Center Coulomb Repulsion Integrals

Two center Coulomb repulsion integrals, γ_{npmq}, are evaluated by Pariser-Parr [34] or Nishimoto-Mataga [35] approximation.

(d) Coulomb Integrals

Starting from Goeppert-Mayer-Sklar approximation [36] and neglecting all the penetration integrals, Coulomb integrals, I^n_{pp}, are expressed as

$$I^n_{pp} = W_{np} - \sum_{mq}{}' \gamma_{npmq}\,, \tag{49}$$

where $-W_{np}$ is the ionization potential of the valence state of np-th atom and the summation is taken over the whole system except $mq = np$.

(e) Resonance Integrals

As in the case of usual methods, resonance integrals, I^n_{pq} $(p \neq q)$, are considered to be empirical parameters. They should be determined to reproduce one-molecule properties.

From the approximations, (a) and (d), the Fock matrix elements are written as

(diagonal)
$$F^n_{pp} = W_{np} + \sum_{mq} (P^m_{qq} - 1)\,\gamma_{npmq} - \tfrac{1}{2}(P^n_{pp} - 2)\,\gamma_{npnp} \tag{50-1}$$

and

(off-diagonal)
$$F^n_{pq} = I^n_{pq} - \tfrac{1}{2} P^n_{pq}\,\gamma_{npnq}\,, \tag{50-2}$$

where P^m_{qq} is the π-electron density on q-th atom in the m-th molecule;

$$P^n_{pq} = 2 \sum_{i}^{\text{occ}} C^*_{inp}\,C_{inq}\,. \tag{51}$$

It should be noted that from the ZDO approximation the excitation energy of a single Frenkel exciton or charge transfer exciton is expressed as

$$
\begin{aligned}
&{}^{1,3}E_{k,l}(\boldsymbol{k},\boldsymbol{x}) - E^0 = \varepsilon_l - \varepsilon_k - \sum_{pq} C^*_{lm+xp} C_{lm+xp} \\
&C^*_{kmq} C_{kmq} \gamma_{m+xpmq} + \binom{2}{0} \sum_{pqm'} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_{m'}-\boldsymbol{r}_m)} \\
&C^*_{lmp} C_{kmp} C^*_{km'q} C_{lm'q} \gamma_{mpm'q} \delta_{\boldsymbol{x},\boldsymbol{0}} \,.
\end{aligned}
\tag{52}
$$

This equation shows that only the singlet Frenkel exciton has non-zero bandwidth as far as the ZDO approximation is valid. This feature agrees well with the experimental results [37] from which the bandwidth of triplet exciton is expected to be much smaller than that of singlet exciton, however, in order to calculate the bandwidth of triplet exciton the ZDO approximation should not be used.

In the frame of the ZDO approximation, the configuration interaction matrix elements are written as

$$
\begin{aligned}
A(\boldsymbol{k})_{kl\boldsymbol{x},k'l'\boldsymbol{x}'} = &- \sum_{pq} C^*_{lm+xp} C_{l'm+xp} C^*_{k'mq} C_{kmq} \gamma_{m+xpmq} \delta_{\boldsymbol{x},\boldsymbol{x}'} \\
&+ \binom{2}{0} \sum_{pqm'} e^{i\boldsymbol{k}\cdot(\boldsymbol{r}_{m'}-\boldsymbol{r}_m)} C^*_{lmp} C_{kmp} C^*_{k'm'q} C_{l'm'q} \gamma_{mpm'q} \delta_{\boldsymbol{x},\boldsymbol{x}'} \delta_{\boldsymbol{x},\boldsymbol{0}} \,.
\end{aligned}
\tag{53}
$$

Eq. (53) reveals that the non-zero interactions only occur between Frenkel excitons and also between charge-transfer excitons, and the **k**-dependence appears only in the case of singlet Frenkel excitons. It should be noted that this vanishing character of the configuration interaction matrix elements extremely reduces the effort to calculate the electronic states; it is not needed to consider charge-transfer excitons when calculating Frenkel exciton states, though the mixing of C–T excitons with Frenkel exciton states has been previously considered [6, 38–40].

2. All Valence Electron Treatment

In order to discuss the total energy of the system, it may be appropriate to use all valence electron treatment following the CNDO (complete neglect of differential overlap) method proposed by Pople, Santry, and Segal [41, 42]. The expressions for the Fock matrix elements and for the total energy of the system are obtained as in Eqs. (57) and (59), respectively, according to the following approximations;

$$I^n_{p\mu p\nu} = W_{np\mu} \delta_{\mu,\nu} - \sum_{n'p'} U_{np,n'p'} \delta_{\mu,\nu} \quad (p=q)\,, \tag{54}$$

$$I^n_{p\mu q\nu} = \beta^n_{pq} S^n_{p\mu q\nu} \quad (p \neq q)\,, \tag{55}$$

$$(np\mu n'p'\mu' \,|\, mq\nu m'q'\nu') = \gamma_{npmq} \delta_{np\mu,n'p'\mu'} \delta_{mq\nu,m'q'\nu'} \,, \tag{56}$$

where W, β, and γ are the empirical parameters and $-U_{np,n'p'}$ is a parameter representing the potential energy of an electron on the np-th atom under the potential of the core of the $n'p'$-th atom.

Fock matrix elements; for $p=q$ and $\mu=\nu$

$$F^n_{p\mu p\mu} = W_{np\mu} + (P^n_p - \tfrac{1}{2} P^n_{p\mu p\mu}) \gamma_{npnp} + \sum_{n'p'} (P^n_{p'} \gamma_{npn'p'} - U_{npn'p'})\,, \tag{57-1}$$

for $p=q$ and $\mu \neq v$

$$F^n_{p\mu q v} = -\tfrac{1}{2} P^n_{p\mu q v} \gamma_{npnp} , \tag{57-2}$$

and for $p \neq q$

$$F^n_{p\mu q v} = \beta^n_{pq} S^n_{p\mu q v} - \tfrac{1}{2} P^n_{p\mu q v} \gamma_{npnq} , \tag{57-3}$$

where P^n_p is the electron density on the p-th atom in the n-th molecule,

$$P^n_p = \sum_{\mu} P^n_{p\mu p\mu} . \tag{58}$$

The total energy of the system is written as

$$\begin{aligned} E_{\text{tot}} = & \sum_{np} \left[\sum_{\mu} P^n_{p\mu p\mu} W_{np\mu} + \tfrac{1}{2} \sum_{\mu} \left(P^n_{p\mu p\mu} P^n_{pvpv} - \tfrac{1}{2} {P^n_{p\mu pv}}^2 \right) \gamma_{npnp} \right] \\ & + \sum_{n} \sum_{\substack{pq \\ (p \neq q)}} \sum_{\mu v} \left(\beta^n_{pq} S^n_{p\mu q v} P^n_{p\mu q v} - \tfrac{1}{4} {P^n_{p\mu q v}}^2 \gamma_{npnq} \right) \\ & + \tfrac{1}{2} \sum_{\substack{npn'p' \\ (np \neq n'p')}} \left(Z_{np} Z_{n'p'} e^2 / R_{npn'p'} - P^n_p U_{np,n'p'} - P^{n'}_{p'} U_{n'p',np} + P^n_p P^{n'}_{p'} \gamma_{npn'p'} \right) , \end{aligned} \tag{59}$$

where $R_{npn'p'}$ is the distance between atoms, np and $n'p'$. The first term of Eq. (59) represents the atomic energies and the second term the binding energies of the bond formation. To clarify the physical meaning of the third term of Eq. (59) it is rewritten as

$$\tfrac{1}{2} \sum_{\substack{npn'p' \\ (np \neq n'p')}} \left(E(1)_{npn'p'} + E(2)_{npn'p'} + E(2)_{n'p'np} + E(3)_{npn'p'} \right) ,$$

where

$$E(1)_{npn'p'} = (P^n_p - Z_{np})(P^{n'}_{p'} - Z_{n'p'}) \gamma_{npn'p'} , \tag{60-1}$$

$$E(2)_{npn'p'} = (P^n_p - Z_{np})(Z_{n'p'} \gamma_{npn'p'} - U_{np,n'p'}) , \tag{60-2}$$

$$E(3)_{npn'p'} = Z_{np} Z_{n'p'} \gamma_{npn'p'} + Z_{np} Z_{n'p'} e^2 / R_{npn'p'} - Z_{np} U_{np,n'p'} - Z_{n'p'} U_{n'p',np} . \tag{60-3}$$

$E(1)$ is the static Coulomb interaction between the net charges on the atoms, which involves not only the usual electrostatic interaction between the unperturbed net charges as they exist in the isolated molecules but also the usual polarization effect and even higher-order effects.

$E(2)_{npn'p'}$ is interpreted as the interaction between the net charge on the np-th atom and the neutral $n'p'$-th atom.

$E(3)_{npn'p'}$ represents the interaction between the neutral atoms, np and $n'p'$.

In the CNDO/2 parametrization for $U_{np,n'p'} (U_{np,n'p'} = Z_{np} \gamma_{npn'p'})$, $E(2)$ is vanishing and $E(3)$ becomes $Z_{np} Z_{n'p'} (e^2/R_{npn'p'} - \gamma_{npn'p'})$ which is repulsive in the usual parametrization of γ. While, $E(2)$ and $E(3)$ can be attractive from the point of view of their physical meaning: $E(2)$ should be replaced by the interaction between the net charge and the induced dipole on the neutral atom (which is of the form $-\varrho_1^2 e^2 \alpha_2 / 2R_{12}^4$)[9] and $E(3)$ should be replaced by "van der Waals interaction" between the neutral atoms (which is of the form $-\frac{3}{2} \frac{I_1 I_2}{I_2 + I_2} \alpha_1 \alpha_2 / R_{12}^6$)[9] except for very small distance.

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[9] ϱ is the net charge, I is the ionization potential, and α is the polarizability.

So long as the heat of formation of an isolated molecule is concerned, these attractive terms may be negligible. When the intermolecular interaction is taken up, however, these terms should not be neglected, which may be seen very clearly when interacting energies between two rare gas atoms are approximated in this way: the lack of the dispersion energy results in the absence of an attractive minimum. Therefore, we propose one of the most simple treatments as follows;

(A) For the Fock matrix elements and $E(2)$, CNDO/2 approximation ($U_{np,n'p'} = Z_{np}\gamma_{npn'p'}$) is used[10].

(B) For the intramolecular interaction terms of $E(3)$, CNDO/2 approximation or MINDO/1 expression (the latter is of the form $Z_A Z_B(e^2/R_{AB} - \gamma_{AB})\exp(-\alpha_{AB}R_{AB})$) [43] is used.

(C) For the intermolecular interaction terms of $E(3)$, the pair-wise potential [44, 45], $A/R^{12} - B/R^6$ or $A\exp(-\alpha R) - B/R^6$ is used.

Among the above parameters for the all valence electron treatment, the same parameters used for the isolated molecules may be available except for the intermolecular electron repulsion integrals $\gamma_{npn'p'}$ $(n \neq n')$ and the parameters of the pair-wise potential.

According to this approximate treatment, the intermolecular interaction is decomposed into three parts; (1), molecular energy shifts by electron redistribution (positive)[11], (2) static Coulomb interactions between the net charges modified through an SCF procedure, which involves not only usual electrostatic energy but also the polarization energy (negative), (3), dispersion (or London) energy and intercore repulsion energy (negative under the appropriate location of the molecules). Among these parts the first two ones can be estimated directly from the electron distribution determined by this SCF method, and the calculations based only on the pair-wise potential can be corrected easily from the two parts, (1) and (2).

IV. Discussion

1. *Applicability of the Self-Consistent Molecular Field Theory*

As indicated in Section III, Brillouin's theorem holds in this theory. Therefore, it is clear that the ground electronic configuration does not mix with one-electron charge-transfer configurations, and then the charge-transfer resonance [46, 47] does not contribute to lowering the ground state energy. This is due to the following two assumptions; one-electron orbitals are expressed as the linear combination of atomic orbitals on one molecule and the intermolecular overlaps are neglected. As far as these two assumptions are used and more than one-electron excitation configurations are not considered, this theory should be only applicable to the

---

[10] In the calculation of hydrogen bond, the induction term $E(2)$ may play an important role.

[11] In Eq. (59) the first and second terms, and the third term for $n = n'$ represent the molecular energies. Although these terms are the same expression of the molecular energies as that of the system of isolated molecules, the electron distribution of the molecules in the aggregate will be different from that of isolated molecules. Furthermore, the equilibrium positions of nuclei in the former may be distorted from those in the latter. Therefore, the molecular energies in the aggregate should be shifted from those in the isolated system. This molecular energy shifts may be positive, since the molecular energies are minimal in the isolated system.

systems in which each molecule is almost purely neutral or almost purely ionic[12], and not applicable to the systems of intermediate charge-transfer[13].

Furthermore, if an intermolecular overlap is too large to neglect, there should be an intermolecular bonding, and then it is not appropriate to use the localized one-electron orbitals on a molecule. Therefore, this theory is only applicable to the system in which there is no large overlap or no chemical bonding between the molecules.

2. *Problems Arising from Convergence*

On the numerical application, there are two convergence problems peculiar to the SCF calculation on infinite systems[14]. The first is associated with the divergence of the integral sums over an infinite lattice. When the attractive terms and repulsive terms are summed separately in the Fock matrix elements, both of the partial sums are divergent. If these two sums are combined, the resulting elements are at best conditionally convergent. More pricisely, the divergence arises from the infinite sums of the integrals which diminish not more rapidly than $1/r^2$, therefore, the condition of convergence is due to the process of the next sum in the Fock matrix elements (Eq. (50));

$$\sum_{\substack{n'p' \\ (n'p' \neq np)}} (P_{p'}^{n'} - Z_{n'p'})\, \gamma_{npn'p'} \,.$$

If this sum is taken over the charges on a molecule and then over those on another molecule, this procedure may lead to convergence.

Although there is no clear proof of this prediction, it is very hopeful, since the electric field induced by a neutral molecule in the distance is in the first approximation to be that by the permanent dipole of the molecule. Furthermore, if many electron correlations are included in γ, γ may be a dielectrically screened Coulomb potential and the value of γ may reduce much more rapidly with r than that of bare Coulomb potential.

The second problem is associated with the infinite number of SCF equations, Eq. (18). Although the SCF procedure cannot be done in real computation, it is important to know what number of equations to be solved in order to obtain

---

[12] To apply this theory to almost purely ionic radical salt crystals an open-shell treatment is needed.

[13] Even if the intermolecular charge transfer is not neglected, this theory is applicable to the special systems in which the intermolecular charge transfer chains do not extend over the fairly large region of a hundred molecules, a thousand molecules, or all over the crystal. For a simple example, two interacting molecules such as an electron donor-acceptor pair or a hydrogen-bonded dimer in the aggregate are considered to be "one molecule" so that the one-electron orbitals may be expanded in the atomic orbital bases of these two molecules. In such a case, this SCF theory is applicable to it with no modification.

[14] Another infinite sum is needed on calculating excitation energies [15]. In Eq. (52) the lattice sum for a Frenkel exciton with $\boldsymbol{k} = \boldsymbol{0}$ becomes

$$\sum_{m'} \sum_{pq} C_{lmp}^{*} C_{kmp} C_{km'q}^{*} C_{lm'q} \gamma_{mpm'q} \,.$$

The convergence character of this sum may be seen as the same way as the first problem because $C_{lmp}^{*} C_{kmp}$ and $C_{km'q}^{*} C_{lm'q}$ can be interpreted as the charge on the mp-th atom and that on the $m'q$-th atom, respectively.

sufficient convergence. This question is closely correlated with another one, what number of terms are to be summed in the Fock matrix elements. If the long-range intermolecular interactions can be neglected, the SCF orbitals may be determined by the short-range terms. Thus, it can be concluded that as far as the convergence of the sum of Fock matrix elements are fulfilled in fairly short-range, the number of secular equations to be solved becomes finite and sufficiently small for real computation.

In molecular crystals, the second difficulty disappears automatically because of the effective one-molecule problem under the equivalent molecular field. Moreover, the first one is also removed: the well-known methods for the evaluation of Madelung sums [48, 49] are available, since the translational symmetry makes it possible to replace the lattice sum by the Fourier-integral or the reciprocal lattice sum.

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Appendix

The energy of the ground electronic configuration is expressed as follows in terms of the orbital coefficients and atomic integrals defined in Section I.

$$\begin{aligned} E^0 = {} & 2 \sum_{ni}^{\text{occ}} \sum_{p\mu q\nu} C^*_{inp\mu} C_{inq\nu} I^n_{p\mu q\nu} \\ & + \sum_{nimj}^{\text{occ}} \sum_{p\mu q\nu p'\mu' q'\nu'} (2C^*_{inp\mu} C_{inq\nu} C^*_{jmp'\mu'} C_{jmq'\nu'}) \\ & \cdot [(np\mu nq\nu | mp'\mu' mq'\nu') - \tfrac{1}{2}(np\mu mq'\nu' | mp'\mu' nq\nu)] \,. \end{aligned}$$

According to the variation principle, the following equation should be fulfilled for an arbitrary variation set of the orbital coefficients;

$$\delta\left(E^0 - \sum_{ni} 2\varepsilon_{ni}\right) = 0 \,,$$

where the variation parameters ε_{ni} are introduced based on the orthogonality conditions (Eq. (11)). For the variation of $C^*_{inp\mu}$, Eq. (13) can be easily derived.

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