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Resonance Energy Stabilization in Crystalline Ion Radical Salts

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Synopsis. In solid ion radical salts, the ion radical molecules form a segregated stacking into columns, and the charge-transfer interaction occurs between ion radicals. The resonance energy stabilization due to the charge-transfer interaction was estimated for non-alternant one-dimensional system of solid ion radical salts.

The prominent magnetic, electrical, and optical properties of solid ion (cation or anion) radical salts have been the subject of many theoretical and experimental investigations over the past seventeen years.[1–5] In such solid ion radical salts, the planar ion radical molecules are known to form, in themselves, a segregated stacking into columns so as to make a large overlap between their half-occupied molecular orbitals.[2,3] In this case, any individual radical molecule interacts through charge transfer most strongly with other neighboring radicals, and the electronic and magnetic properties of the solid salts differ distinctly from those of ion radical monomer. In previous papers,[4,5] we applied half-filled Hubbard Hamiltonian to one-dimensional system of ion radical molecules, and explained the optical and magnetic properties of solid ion radical salts in terms of such a model. In the present paper, by using the same model, we examine the magnitude of the resonance energy stabilization due to the charge-transfer interaction in one-dimensional system of solid ion radical salts and apply this approach to certain crystalline ion radical salt such as Würster's Blue perchlorate cation radical salt.

Since every ion radical salt belongs to a kind of ionic crystals, Madelung energy is the most important factor for the cohesive energy. However, in contrast to typical ionic crystals such as alkali halides, resonance energy stabilization due to intermolecular charge-transfer interaction between ion radical molecules is the next important factor for the total cohesive energy in solid ion radical salts. In other words, because of half-occupied molecular orbital of the ion radical, there acts intermolecular covalent bonding between the ion radicals along infinite one-dimensional column. Calculation of the Madelung energy of solid ion radical salt is rather difficult, but we have found a way to estimate the magnitude of the resonance energy stabilization on the basis of a many-body problem. For this purpose, we consider only one-dimensional column of ion radicals in simple ion radical salt, where each ion radical carries one unpaired electron. The half-occupied molecular orbital of unpaired electron is taken for one site of ion radical molecule. We assume a model of non-alternant one-dimensional system composed of infinite number of such sites and neglect the effect of intramolecular electronic transitions of ion radical. In this model, each ion radical site has one identical molecular orbital with equal energy level, and there is one electron per each site. Along such one-dimensional column, an unpaired electron transfers from one site to another site, but a strong repulsive potential will take place when an electron happens to come onto a site which is already occupied by another electron with opposite spin. Let us denote the intrasite Coulomb repulsive energy as I, and consider a system of electrons described by the following Hamiltonian, which is often called the Hubbard Hamiltonian,[6)]

$$\mathscr{H} = \sum_{i,j,\sigma} T_{ij} C_{i\sigma}{}^{+} C_{j\sigma} + I \sum_{i} n_{i\downarrow} n_{i\uparrow}, \tag{1}$$

where $n_{i\sigma} = C_{i\sigma}{}^{+} C_{i\sigma}$, and $C_{i\sigma}{}^{+}$ and $C_{i\sigma}$ are the creation and annihilation operators of an electron with σ-spin at the i-th site, respectively, and where T_{ij} is the transfer matrix element between the i-th and j-th sites, and the repulsive potential, I, appears only when two electrons with up and down spins are at the same site. Since each ion radical has identical molecular orbital with equal energy level, we put $T_{ii}=0$ without loss of generality. In the case of non-alternant one-dimensional model, we further assume that the transfer matrix elements exist only between nearest neighbor sites, and the value of this transfer matrix element is denoted by T (<0).

It is rather difficult to obtain the ground state energy of Eq. 1 in general case. However, Takahashi showed that, in the case of half-filled Hubbard model with $I \gg |T|$, the Hamiltonian of Eq. 1 becomes equivalent to the following effective Hamiltonian,[7)]

$$\mathscr{H}_{\mathrm{eff}} = \frac{4T^2}{I} \sum_{i} \left(\boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} - \frac{1}{4} \right) + 0\left(\frac{T^3}{I^2} \right), \tag{2}$$

where $\boldsymbol{S}_i$, $(S=1/2)$, is the spin operator of an electron at the i-th site. In other words, in the limit of $I/|T| = \infty$, we can neglect such higher terms as $0(T^3/I^2)$, and the one-dimensional half-filled Hubbard model is reduced to one-dimensional Heisenberg antiferromagnetic model with exchange interaction, $J=2T^2/I$. Hereafter, we denote the number of sites in one-dimensional system as N. If we know the ground-state energy of the following non-alternant one-dimensional Heisenberg antiferromagnet,

$$\mathscr{H}' = 2J \sum_{i} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1}, \qquad (J=2T^2/I>0), \tag{3}$$

we can obtain the value of the ground-state energy of Eq. 2 in the limit of $I/|T| = \infty$. It is well known that the exact ground-state energy of Eq. 3, as indicated by E', was obtained by Bethe and Hulthén.[8)] For infinite number of sites, the value of E' is given by

$$E' = -2NJ \ln 2 + \frac{1}{2} NJ. \tag{4}$$

Therefore, if in the limit of $I/|T| = \infty$ we denote the exact ground-state energy of Eq. 2 as E, we can obtain

$$E = E' - \frac{1}{2}J\sum_{i}1 = E' - \frac{1}{2}NJ$$
$$= -2NJ\ln 2 = -4N\frac{T^2}{I}\ln 2. \qquad (5)$$

When we go back to our original system of ion radicals, we can see that the magnitude of E in Eq. 5 corresponds to the resonance energy stabilization due to charge-transfer interaction between ion radicals in one-dimensional system of solid ion radical salts and that the value of $E/N=-4(T^2/I)\ln 2$ is the resonance energy per one site of ion radical molecule. Obviously, if $T=0$, that is, if no electron transfer occurs between ion radical molecules, we have $E=0$ in Eq. 5, and no resonance energy stabilization takes place in such a system.

In the following, we shall estimate the magnitudes of E and E/N for certain system of solid ion radical salt. For example, we apply the present method to the high-temperature phase of Würster's Blue perchlorate crystal, which is one of stable cation radical salts derived from *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine. Although a solid-state phase transition occurs at 186 K,[3,9] the crystal structure of the high-temperature (room-temperature) phase of Würster's Blue perchlorate is known to be orthorhombic and to be built up from non-alternant one-dimensional columns composed of segregated stacking of equivalent Würster's Blue cation radicals along the a-axis, the intermolecular spacing between nearest neighbor cation radicals being 3.550 Å.[3] In a previous paper,[5] we examined the electronic state of the system of the cation radicals on the basis of the above-mentioned non-alternant one-dimensional Hubbard model. We could well understand the optical and magnetic properties of this Würster's Blue perchlorate salt in terms of the parameter values of $I=11900\ \mathrm{cm}^{-1}$ and $T=-650\ \mathrm{cm}^{-1}$. In this case, since the magnitude of $I/|T|=18.3$ is much larger than unity, we can apply, in place of Eq. 1, the effective Hamiltonian of Eq. 2 to the one-dimensional system of Würster's Blue cation radicals. Then, in the approximation of $I/|T|=\infty$ limit, the magnitude of E in Eq. 5 was estimated by using the $I=11900\ \mathrm{cm}^{-1}$ and $T=-650\ \mathrm{cm}^{-1}$ values. The calculated resonance energy of the high-temperature phase of Würster's Blue perchlorate was $E=-277$ cal/mol or $E/N=-97\ \mathrm{cm}^{-1}$ per one site of the cation radical. On the other hand, for this salt, Metzger performed calculation of Madelung energy by using Ewald's method in order to clarify the mechanism of the phase transition at 186 K.[10] Although the Madelung energy is rather sensitive to details in the atomic charge distribution, he estimated the Madelung energy for the 300 K (high-temperature phase) Würster's Blue perchlorate crystal to be −94550±690 cal/mol. Therefore, the total cohesive energy is found to be −94827±690 cal/mol by summing the Madelung energy and the resonance energy. Although the resonance energy is very small compared to the Madelung energy and is only 0.29% of the total cohesive energy in Würster's Blue perchlorate, it is important to note that the resonance energy stabilization does not take place in usual ionic crystals but only takes place in solid ion radical salts.

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