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Contribution of Charge Transfer Structure to Exchange Interaction in the Crystal of Organic Free Radical

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It has been well known that the relatively high negative Curie temperature θ is often obtained from the susceptibility *vs.* temperature data for the crystalline-stable free radicals. For instance, $\theta=-17°\mathrm{K}$[1] and $-45°\mathrm{K}$[2] for DPPH and violanthrone-B, respectively. Furthermore, for a number of solid ionic aromatic free radicals such as TCNQ ionic radical[3] the large singlet-triplet splitting Δ has been observed in the ESR measurement. Both θ and Δ can be related to the exchange interaction J in the crystal. If we assume that every molecule in solid has interaction with one nearest neighbor, the relation can be derived by the Weiss field theory as

$$\Delta=2J=4k|\theta| \tag{1}$$

It seems improbable for the molecular crystals that such values of the Curie temperature or the S-T splitting are attributable to the simple exchange interaction. The large S-T splitting has been discussed by Hausser and Murrell[4] and McConnell[5] introducing the charge transfer structure of Mulliken type.

In the present paper we discuss the problem by the LCMO approach, which will give a simpler physical image.

The orbitals of the unpaired electrons of two interacting radicals A and B may be written in the form of LCMO as

$$\left.\begin{aligned}\varphi_A&=a\varphi_A{}^\circ+b\varphi_B{}^\circ\\ \varphi_B&=a\varphi_B{}^\circ+b\varphi_A{}^\circ\end{aligned}\right\} \tag{2}$$

in which $\varphi^\circ{}_{A,B}$ is the orbital for the isolated molecule. Then we have the wave function for a pair of radicals

$$\Psi_{AB}(1,2)=C[\varphi_A(1)\varphi_B(2)\pm\varphi_A(2)\varphi_B(1)] \tag{3}$$

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[1] J. Turkevich and P. Selwood, *J. Am. Chem. Soc.*, **63**, 1077 (1941).

[2] H. Akamatu, T. Maekawa, Y. Iida and M. Kinoshita, This Bulletin, **37**, 849 (1964).

[3] D. B. Chesnut and P. Arthur, Jr., *J. Chem. Phys.*, **36**, 2969 (1962).

[4] K. H. Hausser and J. N. Murrell, *ibid.*, **27**, 500 (1957).

[5] H. M. McConnell, "Molecular Biophysics," ed. by B. Pullman and M. Weissbluth, Academic Press, New York and London (1965), p. 317.

or

$$\Psi_{AB}(1,2) = c_1\Psi_1(1,2) + c_2\Psi_2(1,2) + c_3\Psi_3(1,2) \quad (4)$$

where

$$\left.\begin{aligned} \Psi_1(1,2) &= \varphi_A{}^\circ(1)\varphi_B{}^\circ(2) \\ \Psi_2(1,2) &= \varphi_A{}^\circ(2)\varphi_B{}^\circ(1) \\ \Psi_3(1,2) &= C'[\varphi_A{}^\circ(1)\varphi_A{}^\circ(2) + \varphi_B{}^\circ(1)\varphi_B{}^\circ(2)] \end{aligned}\right\} \quad (5)$$

C and C' are the normalization constants.

The secular equation derived from (4) is

$$\begin{vmatrix} H_{11}-W & H_{12}-S_{12}W & H_{13}-S_{13}W \\ H_{12}-S_{12}W & H_{11}-W & H_{13}-S_{13}W \\ H_{13}-S_{13}W & H_{13}-S_{13}W & H_{33}-W \end{vmatrix} = 0 \quad (6)$$

where the relations $H_{22}=H_{11}$, $H_{23}=H_{13}$ and $S_{23}=S_{13}$ are used. Readily factorized, Eq. (6) can be reduced to

$$\begin{vmatrix} \dfrac{H_{11}+H_{12}}{1+S_{12}} - W & \dfrac{H_{13}-S_{13}W}{1+S_{12}} \\ 2(H_{13}-S_{13}W) & H_{33}-W \end{vmatrix} = 0 \quad (7)$$

and

$$(H_{11}-H_{12}) - (1-S_{12})W = 0 \quad (8)$$

Equation (7) can be solved by the ordinary method of approximation and gives the energy of the lowest singlet state

$$W_s = W_s{}^\circ - \frac{2(H_{13}-S_{13}W_s{}^\circ)^2}{(1+S_{12})(H_{33}-W_s{}^\circ)} \quad (9)$$

corresponding to

$$c_1 = c_2, \quad c_3 \neq 0$$

where

$$W_s{}^\circ = \frac{H_{11}+H_{12}}{1+S_{12}} \quad (10)$$

On the other hand, from Eq. (8) we can obtain the solution for the triplet state

$$W_T = W_T{}^\circ = \frac{H_{11}-H_{12}}{1-S_{12}} \quad (11)$$

corresponding to

$$c_1 = -c_2, \quad c_3 = 0$$

$W_s{}^\circ$ and $W_T{}^\circ$ are the eigenvalues corresponding to the wave functions

$$\Psi_0{}^s(1,2) = \frac{1}{\sqrt{2+2S_{12}}}[\varphi_A{}^\circ(1)\varphi_B{}^\circ(2) + \varphi_A{}^\circ(2)\varphi_B{}^\circ(1)] \quad (12)$$

and

$$\Psi_0{}^T(1,2) = \frac{1}{\sqrt{2-2S_{12}}}[\varphi_A{}^\circ(1)\varphi_B{}^\circ(2) - \varphi_A{}^\circ(2)\varphi_B{}^\circ(1)] \quad (13)$$

respectively. Furthermore, it can be readily verified that Eq. (9) is equivalent to the equation obtained by Mulliken's method, that is, the eigenvalue for $\Psi = a\Psi_0{}^s + b\Psi_3$, while the triplet state is unaffected by the introduction of the charge transfer structure. This is the natural consequence resulting from Pauli's principle.

Finally, we can obtain the energy of the S-T splitting

$$\Delta = W_s - W_T = W_s{}^\circ - W_T{}^\circ - \frac{(H_{03}^s - {S^s}_{03}W_s{}^\circ)^2}{H_{33} - W_s{}^\circ} \quad (14)$$

where

$${H^s}_{03} = \int \Psi_0{}^s H \Psi_3 \mathrm{d}\tau, \quad {S^s}_{03} = \int \Psi_0{}^s \Psi_3 \mathrm{d}\tau \quad (15)$$

If the higher orbitals $\varphi_A{}^1$ and $\varphi_B{}^1$ are taken into consideration, starting from

$$\left.\begin{aligned} \varphi_A &= a\varphi_A{}^\circ + b\varphi_B{}^\circ + c\varphi_B{}^1 \\ \varphi_B &= a\varphi_B{}^\circ + b\varphi_A{}^\circ + c\varphi_A{}^1 \end{aligned}\right\} \quad (16)$$

we can finally obtain

$$\begin{aligned} W_s - W_T = W_s{}^\circ - W_T{}^\circ &- \frac{({H^s}_{03} - {S^s}_{03}W_s{}^\circ)^2}{H_{33} - W_s{}^\circ} \\ &- \frac{({H^s}_{01} - {S^s}_{01}W_s{}^\circ)^2}{{H^s}_{11} - W_s{}^\circ} + \frac{({H^T}_{01} - {S^T}_{01}W_T{}^\circ)^2}{{H^T}_{11} - W_T{}^\circ} \quad (17) \end{aligned}$$

where ${H^s}_{01}$, ${S^s}_{01}$, ${H^T}_{01}$, ${S^T}_{01}$, ${H^s}_{11}$ and ${H^T}_{11}$ are the quantities related to

$$\begin{aligned} \Psi_1{}^s = C''[&\varphi_A{}^\circ(1)\varphi_A{}^1(2) + \varphi_A{}^\circ(2)\varphi_A{}^1(1) \\ &+ \varphi_B{}^\circ(1)\varphi_B{}^1(2) + \varphi_B{}^\circ(2)\varphi_B{}^1(1)] \quad (18) \end{aligned}$$

$$\begin{aligned} \Psi_1{}^T = C'''[&\varphi_A{}^\circ(1)\varphi_A{}^1(2) - \varphi_A{}^\circ(2)\varphi_A{}^1(1) \\ &- \varphi_B{}^\circ(1)\varphi_B{}^1(2) + \varphi_B{}^\circ(2)\varphi_B{}^1(1)] \quad (19) \end{aligned}$$

in which C'' and C''' are the normalization constants.

In Eq. (17) the fourth and the fifth terms on the right-hand side are the correcting terms of small value and tend to cancel each other. Thus, it seems to be probable that Eq. (14) is a good approximation for the S-T splitting. In Eq. (14) the last term on the right-hand side is the contribution of the intermolecular charge transfer structure. It should be noted that in this approximation the intermolecular charge transfer in the triplet state is absent owing to Pauli's principle.