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# THE SIGNIFICANCE OF CHARGE-TRANSFER IN THE BOND INTERCHANGE

H. Fujimoto, S. Yamabe and K. Fukui
Faculty of Engineering, Kyoto University
Sakyo-ku, Kyoto, Japan

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The energy of interaction between two molecules has been calculated in one of our previous papers[1] to obtain some information on the nature of chemical reaction. Another interesting approach is to investigate the change in the distribution of electron populations, according to the proceeding of reaction, to disclose the mechanism of the formation of new bonds between the reactant and the reagent and of the weakening of old bonds in each of the two.

We represent the ground-state wave function of the system composed of the reactant, $A$, and the reagent, $B$, which are interacting each other as:

$$\Psi = C_0\,\Psi_0 + \sum_i^{occ}\sum_l^{unoc} C_{i\to l}\,\Psi_{i\to l} + \sum_k^{occ}\sum_j^{unoc} C_{k\to j}\,\Psi_{k\to j} + \sum_i^{occ}\sum_j^{unoc} C_{i\to j}\,\Psi_{i\to j} + \sum_k^{occ}\sum_l^{unoc} C_{k\to l}\,\Psi_{k\to l} + \cdots \qquad (1)$$

The notation is the same as used in the previous paper.[1] The wave functions, $\Psi_0$, $\Psi_{i\to l}$, ··· are constructed by the molecular orbitals (MO)

$$a(1) = \sum_t c_t t(1) \qquad \text{for the molecule } A$$
$$b(1) = \sum_u c_u u(1) \qquad \text{for the molecule } B \qquad (2)$$

which are made SCF with respect to each of the two isolated molecules, $A$ and $B$.

Here we set limits to the case in which two closed-shell systems interact each other. The MO's used have been obtained from an all-valence-shell-electrons SCF MO method.[2] We have normalized the wave functions, $\Psi_0$, $\Psi_{i\to l}$, $\cdot\cdot\cdot$ to the second order of the overlap integrals of $a_i$'s and $b_k$'s. The coefficients, $C_0$, $C_{i\to l}$, $\cdot\cdot\cdot$ in equation 1 can be obtained by the usual CI procedure. The matrix elements which are necessary to solve the secular equations have already been calculated in getting the energy terms $D$ and $\Pi$ in our previous paper.[1]

First, we concentrate our attention on the electrons influent into the intermolecular region from $A$ and $B$ through the exchange. For example, the atomic orbital (AO) bond populations between the AO's $t$ belonging to the molecule $A$ and the AO's $u$ belonging to the molecule $B$ in the $\Psi_0$ will be;

$$(\phi_{tu}^{(E)})_0 \cong -4(M!)(C_0/\mathcal{N}_0)^2 \sum_{i}^{occ} \sum_{k}^{occ} c_t^{(i)} c_u^{(k)} s_{tu} S_{ik} \tag{3}$$

where $\mathcal{N}$ signifies the normalization constant, $M$ the total number of electrons, and:

$$S_{ik} = \int a_i(1) b_k(1) dv(1)$$

$$s_{tu} = \int t(1) u(1) dv(1)$$

Therefore, when both of $A$ and $B$ are closed-shell systems, the sum of the intermolecular bond populations due to the exchange interaction is negative and, as is self-evident, can never be the origin of the chemical binding between $A$ and $B$ in the case of chemical interaction.

The chemical binding between $A$ and $B$ comes from the mixing of the charge-transfer states $\Psi_{i\to l}$ into $\Psi_0$ state. This is because

$$\int \Psi_0 \Psi_{i\to l} d\tau \cong \sqrt{2}\, S_{il} = \sqrt{2} \sum_{t}^{A} \sum_{u}^{B} c_t^{(i)} c_u^{(l)} s_{tu}$$

and the quantity $C_0 C_{i\to l} \int \Psi_0 \Psi_{i\to l}\, d\tau$ can be positive in the ground-state. In this connection, we should like to refer to the following important novel quantity as "intermolecular AO bond population due to charge-transfer":

$$\phi_{tu}^{(D)} \cong 2\sqrt{2}C_0\left(\sum_{i}^{occ}\sum_{l}^{uno} C_{i\to l}c_t^{(i)}c_u^{(l)}s_{tu} + \sum_{k}^{occ}\sum_{j}^{uno} C_{k\to j}c_t^{(j)}c_u^{(k)}s_{tu}\right) \qquad (4)$$

When negative AO bond population of the intermolecular AO pair $t$ and $u$ due to the electron exchange is overcome by the positive AO bond population arising from the mixing of the electron delocalization between the reactant and the reagent, the interaction between the AO's $t$ and $u$ comes to be bonding. Further, by the mixing of the charge-transfer states, atomic and bond populations in both of the two reacting molecules will change. The change in the AO bond population between the AO's $t$ and $t'$ of the molecule $A$ due to the charge-transfer interaction will be:

$$\varphi_{tt'} \cong 2\left\{-\sum_{i}^{occ}\sum_{l}^{uno}(C_{i\to l})^2c_t^{(i)}c_{t'}^{(i)}s_{tt'} + \sum_{k}^{occ}\sum_{j}^{uno}(C_{k\to j})^2c_t^{(j)}c_{t'}^{(j)}s_{tt'} - 2\sqrt{2}C_0\sum_{i}^{occ}\sum_{l}^{uno}C_{i\to l}S_{il}c_t^{(i)}c_{t'}^{(i)}s_{tt'}\right\} \qquad (5)$$

The fraction of electrons influent into the intermolecular region may be partitioned into two, one of which reverts to the AO $t$ and the other to the AO $u$, extending the concept of the population analysis of Mulliken[3] to an AO pair between two interacting molecules.

The example taken as typical in this calculation is the bimolecular substitution reaction of methyl chloride where the attacking base is simply represented by chloride ion. The calculated changes in atomic and atomic bond populations in regard to the two assumed models are given in Figure 1. It can be seen that the formation of the new bond and the weakening of the old bond are not effective in Model II in comparison with Model I. Thus, the course which leads to the inversion is clearly favourable for the occurrence of the reaction.

The polarization terms have been tentatively neglected in this calculation, since they are expected to have no significant contribution to the change in the electron populations. It seems probable that in the interaction of the two molecules both having closed-shells, in general, the charge-transfer interaction would be dominantly responsible for the occurrence of the intermolecular chemical bonding.

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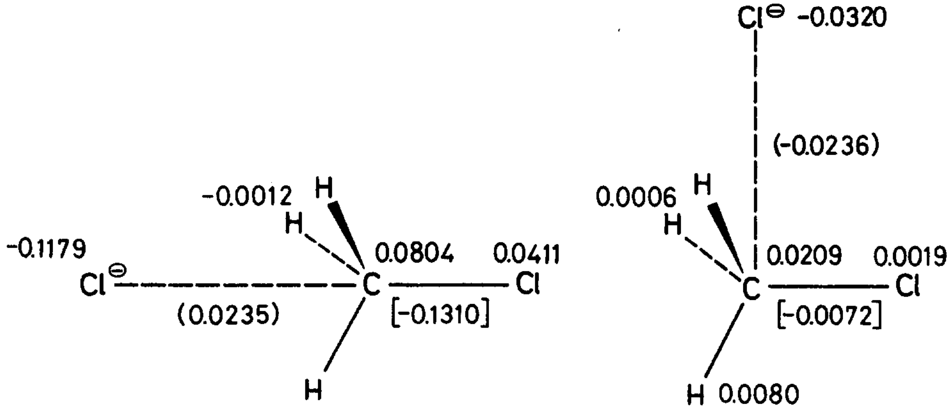

Model I    Model II

( $C-Cl^{\ominus}$ ; 3.0Å, C-Cl ; 1.78Å, C-H ; 1.09Å, ∠HCCl ; 109.5° )

Figure 1. The changes in the atomic populations calculated with respect to assumed models. The values in ( ) represent $\sum_{t}^{C}\sum_{u}^{Cl^{\ominus}}(\phi_{tu}^{(D)} + \phi_{tu}^{(E)})$ and the values in [ ] indicate $\sum_{t}^{C}\sum_{t'}^{Cl}\varphi_{tt'}$.

## REFERENCES and NOTES

1. K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Japan*, 41, 1989 (1968).
2. Our method of SCF calculation, employed to obtain the MO's of each of the two reacting molecules in isolated state, is almost the same as the one developed by Yonezawa et al. ( See, for instance, T. Yonezawa, K. Yamaguchi and H. Kato, *Bull. Chem. Soc. Japan*, 40, 536 (1967).)
3. R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841, 2338, 2343 (1955).