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A SIMPLIFICATION IN THE THEORETICAL PRESENTATION OF CHARGE-TRANSFER INTERACTIONS

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Abstract By applying paired unitary transformations to the molecular orbitals of the electron donor and the electron acceptor, the orbitals that participate actually in charge-transfer interactions are derived. These orbitals are seen to be localized in some particular regions of the donor and acceptor, specifying the type of interaction. The charge-transfer interaction is condensed into several electron configurations.

INTRODUCTION

The charge-transfer interaction between molecules is one of the most important concepts in chemistry.[1] Not only in spectroscopic studies of molecules but also in theoretical studies of chemical reactions, the theory of charge-transfer played a key role. Coupled with the progress in molecular orbital calculations, important factors which seem to govern the selectivities in a wide variety of chemical reactions have been elucidated.[2,3] Here an important aspect of charge transfer interactions will be shown within the one-electron orbital scheme.

ORBITAL TRANSFORMATIONS

We consider here a chemical interaction between the electron donor A and the electron acceptor B. The molecular orbitals

(MOs) of A are denoted by ϕ_i ($i = 1, 2, \cdots, m$: occupied, $i = m+1, \cdots, M$: unoccupied) and the MOs of B by ψ_k ($k = 1, 2, \cdots, n$: occupied, $k = n+1, \cdots, N$: unoccupied). Provided that the fragment species A and B are frozen to the same geometries as those in the composite interacting system and provided that the basis functions are fixed, the MOs of the interacting system A–B can be expanded in the linear combinations of the MOs of the fragments.

$$\Phi_f = \sum_{i=1}^{m} c_{i,f}\phi_i + \sum_{i=1}^{M-m} c_{m+i,f}\phi_{m+i} + \sum_{k=1}^{n} c_{k,f}\psi_k + \sum_{k=1}^{N-n} c_{n+k,f}\psi_{n+k} \qquad (1)$$

The first term represents the occupied MOs of A, the second term the unoccupied MOs of A. Similarly, the third and fourth terms stand for the occupied and unoccupied MOs of B. By substituting the one-electron orbitals in the wave function of A–B with these MOs which are expanded in terms of the occupied and unoccupied MOs of the fragment species, the electronic structure of the interacting system is represented by a combination of various electron configurations.[4]

$$\Psi = \sum_{p} D_p \Psi_p \qquad (2)$$

In addition to the original configuration representing $A \cdot B$, one-electron-transferred configurations corresponding to $A^+ \cdot B^-$ (and $A^- \cdot B^+$) come to play important roles.

For instance, the coefficient for the original electron configuration without no electron shift is given by Eq. 3.

$$D_0 = N_0 \begin{vmatrix} c^{occA} \\ c^{occB} \end{vmatrix}^2 \qquad (3)$$

where:

$$\mathbf{c}^{occA} = \begin{pmatrix} c_{1,1} & c_{1,2} & \cdots\cdots & c_{1,m+n} \\ c_{2,1} & c_{2,2} & \cdots\cdots & c_{2,m+n} \\ c_{i,1} & c_{i,2} & \cdots\cdots & c_{i,m+n} \\ c_{m,1} & c_{m,2} & \cdots\cdots & c_{m,m+n} \end{pmatrix} \tag{4}$$

$\mathbf{c}^{occA}$ and $\mathbf{c}^{occB}$ are the matrices of the expansion coefficients of the occupied MOs of A and B in the occupied space of the composite interacting system and N_0 is the normalization factor. The coefficients for electron-transferred configurations are calculated in a similar manner by replacing the expansion coefficients for the occupied MOs of the donor molecule by the expansion coefficients for the unoccupied MOs of the acceptor molecule.

The following paired transformations are applied simultaneously and separately on the MOs of two fragment species A and B.[5-7] First, we find the matrices $\mathbf{V}$ by which the coefficients of the unoccupied MOs of B are rewritten in terms of the coefficients of the occupied MOs of A and B. Then, we define a couple of unitary transformations $\mathbf{U}$ given by Eqs. 6 and 7. The new expansion coefficients for the occupied MOs of A and the unoccupied MOs of B, $\mathbf{c}'^{occA}$ and $\mathbf{c}'^{unoB}$, are determined.

$$\mathbf{c}^{unoB} = (\mathbf{V}^{occA}\ \mathbf{V}^{occB}) \begin{pmatrix} \mathbf{c}^{occA} \\ \mathbf{c}^{occB} \end{pmatrix} \tag{5}$$

$$((\mathbf{V}^{occA})^{\dagger}\ \mathbf{V}^{occA})\mathbf{U}^{occA} = \mathbf{U}^{occA}\ \mathbf{\Lambda}^{occA} \tag{6}$$

$$\mathbf{U}^{unoB} = \mathbf{V}^{occA}\ \mathbf{U}^{occA}(\mathbf{\Lambda}^{occA})^{-1/2} \tag{7}$$

$$\mathbf{c}'^{occA} = (\mathbf{U}^{occA})^{\dagger}\ \mathbf{c}^{occA} \tag{8}$$

$$\mathbf{c}'^{unoB} = (\mathbf{U}^{unoB})^{\dagger}\ \mathbf{c}^{unoB} \tag{9}$$

The new orbitals are paired between A and B so that ϕ'_1 of A donates electron density only to its counterpart ψ'_{n+1} of B. The number of orbital pairs which are needed to represent the charge-transfer from A to B is determined by the smaller of m (the number of the occupied MOs of A) and N-n (that of the unoccupied MOs of B). The new orbitals are shown to be much more suited for presenting charge-transfer interactions than the usual canonical MOs are.

SIMPLE INTERACTION MODELS

Figure 1 shows the lone-pair orbitals of oxygen atom in some aldehydes, calculated within the minimal basis STO-6G level.

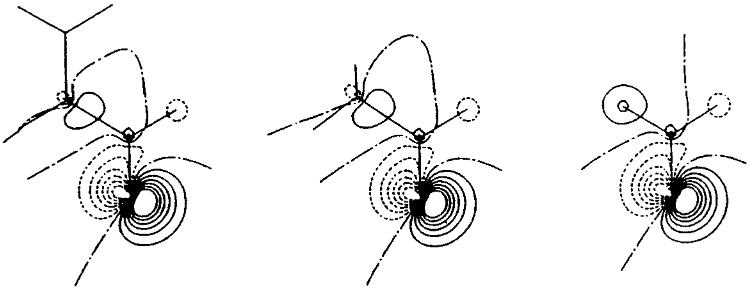
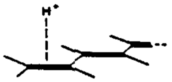


FIGURE 1 Orbitals of acrolein, acetaldehyde and formaldehyde participating in charge-transfer to the attached proton.

The canonical MOs were found to be delocalized more or less over the whole molecular region in these molecules and to be different from one molecule to another molecule. However, the orbitals which take part in charge-transfer interaction with the proton by making an orbital pair with the proton 1s orbital in each of the three molecules are seen to be localized well, having approximately the same shape. That is, the delocalized canonical MOs are recombined automatically through the delocalization interaction with the attached proton to give the most effectively localized lone-electron pair orbitals.

Figure 2 compares the orbitals of ethylene, butadiene and hexatriene which donate electron density to the incoming proton. The proton was placed tentatively 1.5Å above the midpoint of the C_1-C_2 bonds. The calculation shows clearly



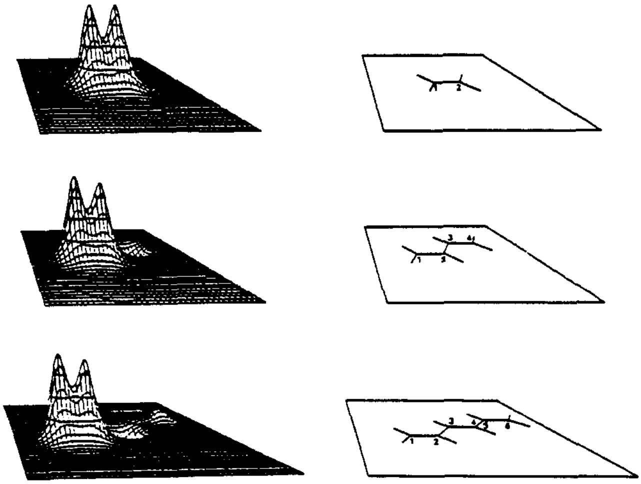


FIGURE 2 Orbitals taking part in the charge-transfer.

that the interacting orbitals are essentially the pi MOs of the terminal olefin double bonds which are slightly modified by the contribution of sigma electrons and, in case of butadiene and hexatriene, by the conjugation with the remaining part of the molecules. The highest occupied canonical MO plays the major role in each case but it has been distorted by mixing with other canonical MOs in order to yield the most effective overlap with the proton orbital. In other words, the charge-transfer interactions have an important effect of determining by themselves the reactive structural units of molecules for the given type of molecular interactions.

Figure 3 shows the interacting orbital of a graphite-like condensed aromatic molecule. A proton was attached to a carbon-carbon bond as an electron acceptor. The orbital is localized well and looks like a pi MO of an olefin bond.

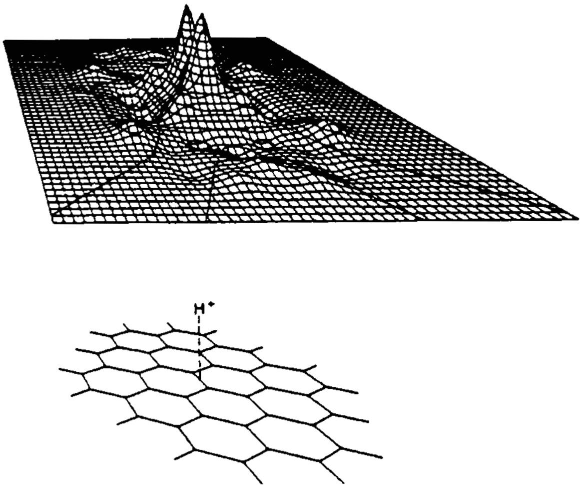


FIGURE 3 Orbital responsible for the charge-transfer. (extended Hückel canonical MOs were used)

The charge-transfer interaction between the huge aromatic molecule and the proton was described simply by the orbital shown in Figure 3 and the proton 1s orbital.

Figure 4 shows the orbital of acetylene polymer which donates electronic charge to a proton placed 1.5Å above the midpoint of a C-C bond. The orbital was calculated for the wave vector k = 0.

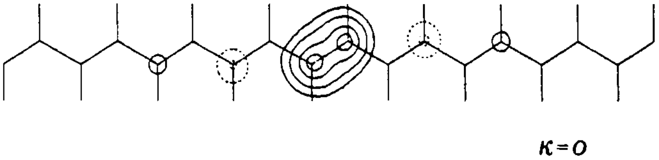


FIGURE 4 Interacting orbital of acetylene polymer.

In Figure 5 are given the orbitals of cyclopropane and bicyclobutane which donate electron density to the proton attached to an edge of the rings. They show a strong pi character rather than a sigma character, representing the liability of bent bonds to protonation.

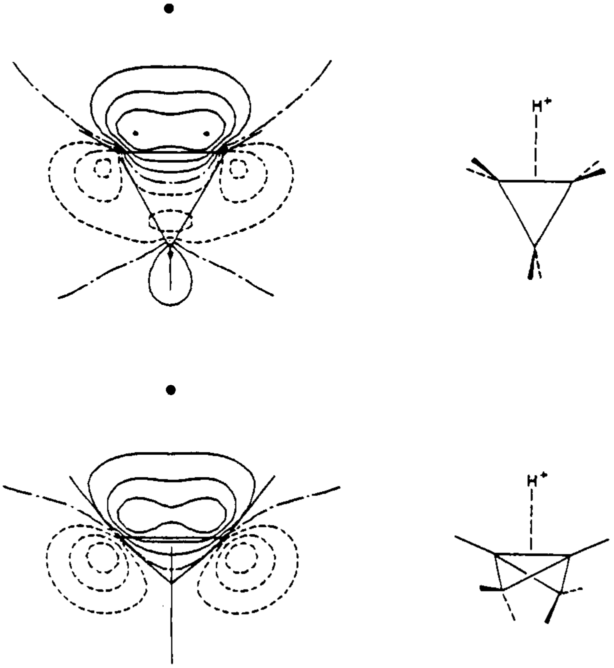


FIGURE 5 Interacting orbitals of cyclopropane and bicyclobutane.

CONCLUSION

The charge-transfer interactions possess an important effect of defining the active structural units both in the electron donor part and in the acceptor part or both in the reagent and in the reactant for each given type of chemical interaction. They are manifested in the patterns of interacting orbitals. In the models presented above, a proton was taken to be the electron acceptor in order to show the basic trends in charge-transfer interactions. Applications of the present method to sizable systems elucidate multifarious reactivities of organic and inorganic molecules.

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