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HYBRID MOLECULAR ORBITALS FOR REACTING SYSTEMS

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Abstract: A method of describing the interactions between two systems in terms of coupled hybrid molecular orbitals of fragments is discussed and is applied to simple interacting systems to provide information on the processes of bond formation.

Chemical interactions are local by nature. The electron reorganization takes place in most cases in the limited regions of the reagent and reactant and the remaining parts are left almost unaffected throughout the course of reaction. Despite of this fact, we have been accustomed to interpret the selectivities of reactions in terms of the molecular orbitals (MO's) which are delocalized over the constituent atoms.[1-4] Some sorts of localized orbitals seem to be desirable for representing interactions between sizable molecules. We report in this letter a new scheme of orbital interactions which will offer hopefully a useful tactics to clarify reaction mechanisms. An insight into the evolution of reactive domains will be obtained.

The electron density of the interacting system A-B calculated by the use of some appropriate MO method can be divided into the intramolecular part of the fragment A, that of the fragment B and the intermolecular part between A and B:

$$\rho(1) = \rho_A(1) + \rho_B(1) + \rho_{A-B}(1) \tag{1}$$

The last term which stands for the interaction between A and B is defined by;

$$\rho_{A-B}(1) = \sum_r^A \sum_s^B \{ q_{rs}\chi_r(1)\chi_s(1) + q_{sr}\chi_s(1)\chi_r(1) \} \tag{2}$$

where χ_r and χ_s denote the rth atomic orbital (AO) of the fragment A and the sth AO of the fragment B and q_{rs} signifies the well-known quantity called the bond-order between χ_r and χ_s.[5] The integration of the density terms in the braces over the space gives rise to the (r,s) element of the overlap population between A and B,[6] from which we can construct an intermolecular overlap population matrix P ($r = 1, 2, \cdots, t$; $s = 1, 2, \cdots, u$). We assume here without loss of generality that $t \leqq u$.

Starting from the matrix P given above, we try to find out a new set of orbitals of A and a new set of orbitals of B for which all the off-diagonal elements of the matrix product $P^{\dagger}P$ will vanish. A procedure to answer our present purpose is an iterative application of the corresponding orbital formalism.[7,8] Upon convergence, the interaction between A and B should be represented in terms of t pairs of coupled orbitals of the fragments irrespective of the size of B, since an orbital of the fragment A thus obtained is allowed to interact only with its counterpart of B and *vice versa*. These orbitals determined to represent most directly the interaction between A and B are delocalized to some extent over the constituent atoms in each of the fragments and are rewritten as the hybrids of the canonical MO's of the fragments. We present in the following the results of calculation on some simplest cases with $t = 1$. *Ab initio* STO-6G MO method is used to build up the initial matrix P.[9]

The first example is protonation to ethylene. The geometries were taken after Hariharan *et al.*[10] The orbitals of the ethylene fragment which take part exclusively in the interaction with the incoming proton, being called here the "interactive hybrid MO's", are shown in Fig. 1 in regard to the nonclassical and classical structures. They are found to be very different from each other, depending explicitly on the relative locations of the fragments.

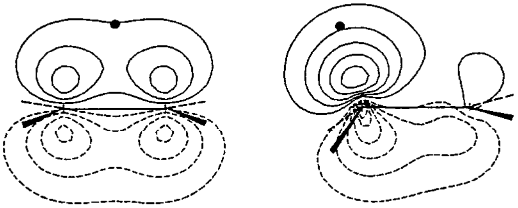

Fig. 1 Interactive hybrid MO's of the ethylene fragment to interact with the proton 1s orbital in nonclassical and classical structures of $C_2H_5^+$. Locations of the cation are marked by dots.

In Fig. 1 full lines indicate the region of bonding interaction and broken lines show the region of antibonding interaction with the proton 1s orbital. The interactive hybrid MO of the ethylene fragment in the bridged cation looks somewhat similar to the π MO of ethylene, possessing the greatest amplitude not in the bonding region but in the antibonding region. This is obviously due to the very strong electron affinity of proton. That is, in the canonical MO description, the effective charge transfer from the ethylene π MO to the proton 1s AO causes the latter to be partially filled and, consequently, the exchange repulsion arises between the proton and the ethylene σ part.[11] Anyway, the repulsion is weak and depends more or less on the method of MO calculation. The interactive hybrid MO in the calssical structure is seen, on the other hand, to be condensed in the region where a new carbon-hydrogen bond should appear. The localization of the orbital is obviously a clear indication for the significant participation of the polarization interaction in the formation of a tight sigma bond in ethyl cation.[12]

In Fig. 2 is presented the interactive hybrid MO of the ethylene fragment in ethyl anion. The geometry of the anion was taken after Hopkinson *et al.*[13] The bonding region is shown to be compressed in comparison with that in ethyl cation, being surrounded by the antibonding region. The exchange repulsion is the primary source to make the difference in the bonding trends.[11]

Figure 3 illustrates the interactive hybrid MO's of bicyclo [2.2.1] hept-2-ene to interact with an attacking proton. The cation was placed 1.5Å above (*exo* addition) and below (*endo* addition) the midpoint of the C_2-C_3 bond perpendicular to the $C_1C_2C_3C_4$ plane, respectively. It is seen that the antibonding region is slightly more contracted in the *exo* approach than in the *endo* approach, indicating probably that the *exo* addition of electrophiles should be more favourable. This result seems to be somewhat

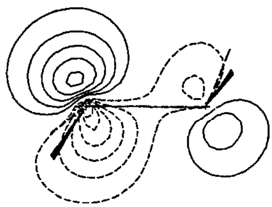

Fig. 2 Interactive hybrid MO of the ethylene fragment in ethyl anion.

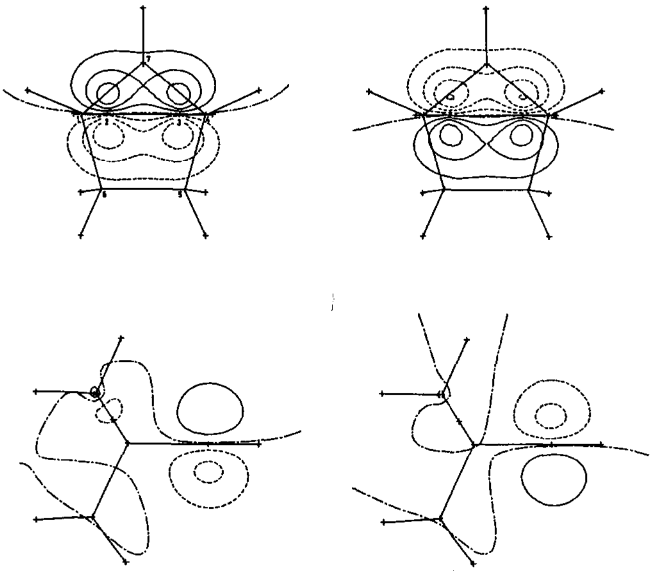

Fig. 3 Interactive hybrid MO's of bicyclo [2.2.1] hept-2-ene for *exo* addition (left) and for *endo* addition (right) of proton.

different from our previous proposition based on the perturbation approximation,[14] though they are not necessarily incompatible with each other. The side view of the hybrid MO's shows that the region of the molecule participating in the bonding interaction with the attacking cation is confined to a specific area of the molecular framework.

Applications to more complicated systems have shown that interactions are described generally in terms of one or a few principal pairs and several subsidiary pairs of interactive hybrid MO's, covering all the orbital interactions and orbital mixings in a usual sense. The hybrid MO's of fragments obtained are nicely adapted in pairs for the symmetry of the composite interacting system.[15] Incidentally, the overlap populations in the matrix *P* can be replaced by any other integrals representing adequately the interaction between two systems.[16]

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