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Description of interactions in molecular complexes by linear combination of educt orbitals

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The Fock-matrix of a molecular system (F) composed of several fragments is transformed into the basis of the MO's of these subsystems ($\bar{F}$). Interactions between the fragments during a chemical reaction or in molecular complexes like quinhydrone can be expressed as matrix elements of $\bar{F}$.

Key words: Transformation matrix—orbital interaction—electronic structure of transition states—charge transfer interaction

1. Introduction

Recently, Frenking and Heinrich [1] proposed a procedure to express the electronic structure of a transition state of a chemical reaction in terms of educt orbitals. The method of constructing a matrix that transforms the unperturbed molecular orbitals of the educt(s) into those of a reactive intermediate (which is not necessarily the transition state) seems to be a valuable tool to study electronic rearrangements during a chemical reaction. Although the linear combination of educt orbitals gives some insight into the transition state MO's, the *interaction energies* between the subsystems are not provided by this approach.

In the following we present an alternative approach that yields the same information on the electronic structure of the transition state as linear combination of educt orbitals but additionally leads to a quantitative description of the interactions between the basis functions.

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2. Procedure

In semiempirical or *ab initio* SCF treatments the canonical orbitals c of a system are usually obtained by diagonalization of the Fock matrix F that is conveniently built up in AO-basis:

$$Fc = c\varepsilon \tag{1}$$

$$c^{\dagger}Fc = \varepsilon. \tag{1'}$$

If we transform the matrix F by use of the unitary matrix U

$$F \rightarrow \bar{F} = UFU^{\dagger} \tag{2}$$

$$(U^{\dagger} = \text{transposed of } U)$$

the eigenvalue equation (1′) can be rewritten as

$$c^{\dagger}U^{\dagger}(UFU^{\dagger})Uc = \varepsilon$$

$$\bar{c}^{\dagger}\bar{F}\bar{c} = \varepsilon \tag{3}$$

where

$$\bar{c} = Uc$$

and

$$\bar{c}^{\dagger} = (Uc)^{\dagger} = c^{\dagger}U^{\dagger}.$$

Now we identify the matrix U with the matrix of the canonical educt orbitals. Using the transformation (2), the Fock matrix of the transition state in AO-Basis (F) is transformed into the basis of educt orbitals ($\bar{F}$). Diagonalization of $\bar{F}$ yields the canonical transition state orbitals as a linear combination of the educt-MO's.

The advantage of this approach is obvious:

1. Interactions between educt orbitals during a chemical reaction (e.g. HOMO-LUMO interactions in Diels-Alder type reactions) can be expressed in terms of matrix elements of $\bar{F}$.

2. The participation of educt orbitals in the transition state can be evaluated by defining a matrix $\bar{P}$:

$$\bar{P}_{\mu\nu} = 2 \cdot \sum_{i=1}^{\text{occ}} \bar{c}_{\mu i}\bar{c}_{\nu i}. \tag{4}$$

The elements of $\bar{P}$ can be characterized as occupation numbers ($\mu = \nu$) and bond orders ($\mu \neq \nu$) in a straightforward way.

3. Applications

We first reexamine Frenking's example (1), i.e. the conrotatory ring opening of cyclobutene to butadiene, using the same semiempirical procedure (MNDO/1)

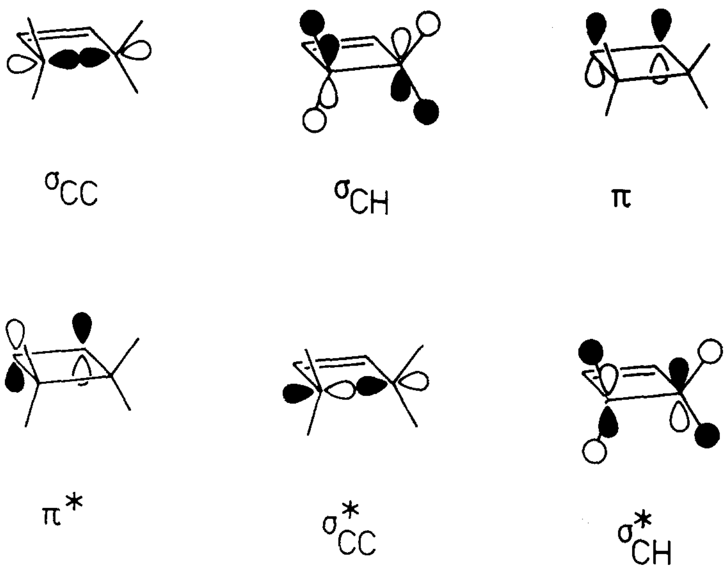

Fig. 1. Educt orbitals of cyclobutene

[2] and the geometry given in [1]. The most important educt orbitals contributing to the HOMO and the LUMO of the transition state are schematically drawn in Fig. 1.

The Fock matrix elements in educt basis as well as the matrix elements of $\bar{P}$ are collected in Table 1. It is obvious that the self energies (diagonal elements of $\bar{F}$) differ strongly from the canonical orbital energies of the educt.

As Frenking has mentioned, there exists a large coupling between π^* and σ^*_{CH}. In our approach this interaction amounts to $\langle\pi^*|\bar{F}|\sigma^*_{CH}\rangle = -1.22$ eV.

Table 1. Transition state cyclobutene to butadiene. Fragment of the Fock matrix $\bar{F}$ and the density matrix $\bar{P}$ (in parentheses) Fock matrix elements in eV

	σ_{CC}	σ_{CH}	π	π^*	σ^*_{CC}	σ^*_{CH}
σ_{CC}	−6.86 (1.42)					
σ_{CH}	2.27 (−1.33)	−12.27 (1.89)				
π	0 (0)	0 (0)	−8.05 (1.64)			
π^*	3.48 (−0.66)	1.02 (−0.25)	0 (0)	−0.68 (0.34)		
σ^*_{CC}	0 (0)	0 (0)	−2.60 (0.55)	0 (0)	−0.19 (0.32)	
σ^*_{CH}	3.11 (−0.42)	0.16 (−0.07)	0 (0)	−1.22 (0.26)	0 (0)	12.52 (0.25)

As a second example, we consider the Diels-Alder reaction of butadiene and ethylene at an early point of the reaction coordinate (*not* the transition state). The employed geometry and the most important educt orbitals involved are shown in Fig. 2.

The calculation is based on a modified INDO procedure [3]. The results are listed in Table 2.

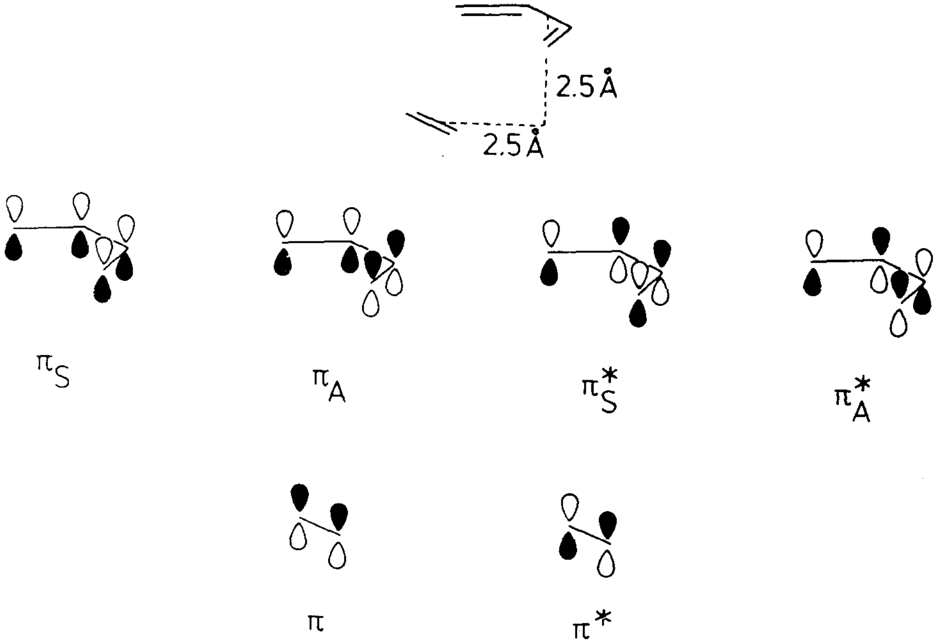

Fig. 2. Educt orbitals of the Diels-Alder reaction of butadiene + ethylene to cyclohexene.

Table 2. Diels-Alder reaction. Fragment of the Fock matrix $\bar{F}$ and the density matrix $\bar{P}$ (in parentheses) Fock matrix elements in eV

	π_S	π_A	π_S^*	π_A^*	π	π^*
π_S	−12.79 (1.99)					
π_A	0 (0)	−10.52 (1.98)				
π_S^*	0.167 (0.06)	0 (0)	−0.47 (0.03)			
π_A^*	0 (0)	−0.04 (0)	0 (0)	0.67 (0.004)		
π	−1.08 (0.1)	0 (0)	−0.99 (0.19)	0 (0)	−11.53 (1.98)	
π^*	0 (0)	0.91 (−0.17)	0 (0)	0.34 (0.003)	0 (0)	0.07 (0.03)

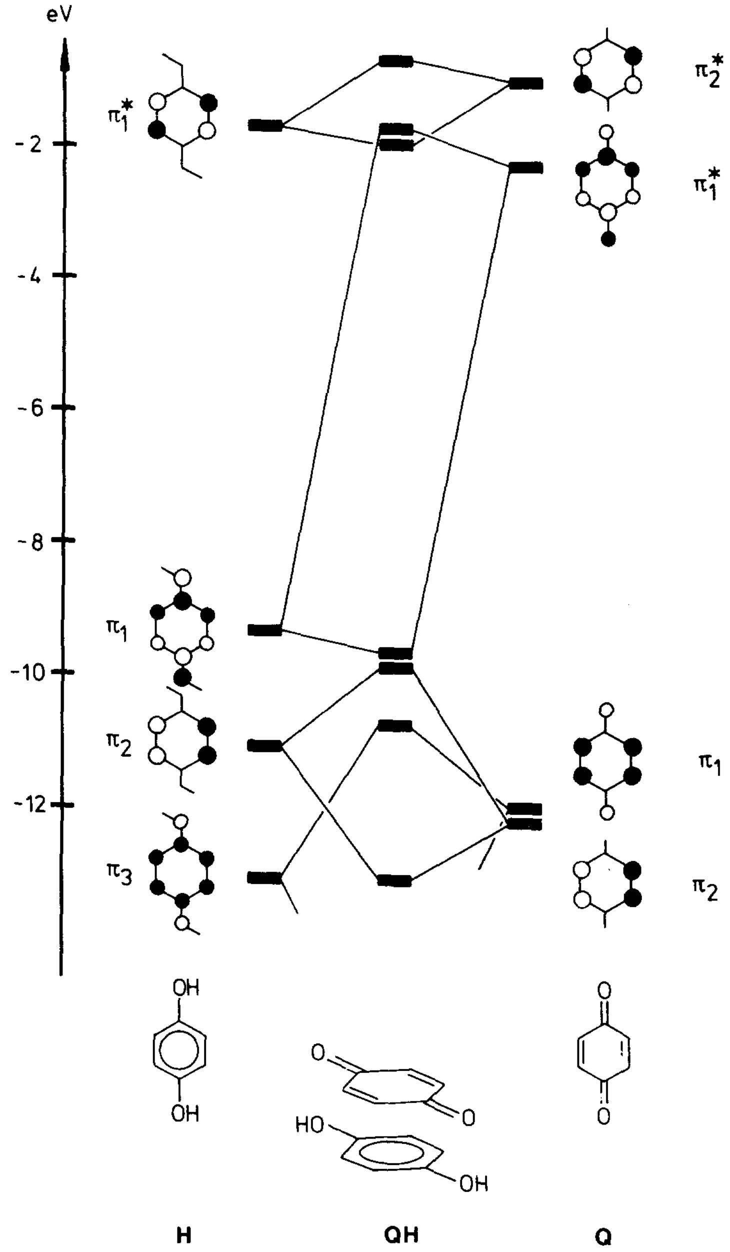

Fig. 3. Interaction diagram of hydroquinone (**left**) and *p*-benzoquinone (**right**) in quinhydrone (**middle**) according to an INDO-calculation (only π-orbitals)

Table 3. Charge-transfer interaction in Quinhydrone. Fragment of the Fock matrix $\bar{F}$ and the density matrix $\bar{P}$ (in parentheses). Only those matrix elements are listed that differ significantly from zero (in eV). Orbital labels see Fig. 3

	Quinone (Q)				Hydroquinone (H)			
	π_2^*	π_1^*	π_1	π_2	π_1^*	π_1	π_2	π_3
π_2^*	−1.0							
π_1^*	—	−2.23 (0.12)						
π_1	—	—	−12.10 (2.0)					
π_2	—	—	—	−12.16 (2.0)				
π_1^*	−0.51	—	—	—	−1.55			
π_1	—	1.72 (0.45)	—	—	—	−9.21 (1.89)		
π_2	—	—	—	−1.52	—	—	−11.04 (2.0)	
π_3	—	—	1.14	—	—	—	—	−13.04 (2.0)

It is important to mention that there are also large interaction terms between π- and σ-orbitals which have not been included in Table 2 for reasons of simplicity.

In a perturbational treatment of the Diels-Alder reaction the activation barrier is governed by the HOMO(diene)-LUMO(dienophil) and LUMO(diene)-HOMO(dienophil) interactions. In our picture, these interactions are:

$$\langle \pi_A | \bar{F} | \pi^* \rangle = 0.91 \text{ eV}$$

$$\langle \pi_S^* | \bar{F} | \pi \rangle = -0.99 \text{ eV}$$

(the sign depends on the phase definition).

Finally, we wish to outline how to expand the method described here to the analysis of other types of interactions in molecular systems. As an example, we consider the charge-transfer (CT) interaction in quinhydrone (QH). The "educts" – p-benzoquinone (Q) and hydroquinone (H) – are arranged at an arbitrary distance of 3 Å. Using the INDO version cited above [3] we obtain the molecular orbitals of quinhydrone as linear combinations of the educt orbitals. The resulting interaction pattern is shown in Fig. 3; fragments of the $\bar{F}$ and $\bar{P}$ matrices are given in Table 3. As can be seen from this Table, the interactions in the QH complex can be divided into two classes. Normal "through space" interactions occur between fully occupied ($\bar{P}_{\mu\mu} = 2.0$) fragment orbitals, e.g. between π_2 of H and π_2 of Q; the corresponding off-diagonal element of $\bar{P}$ is 0. In contrast, the CT-interaction between the occupied HOMO π_1 of H and the unoccupied LUMO π_1^* of Q leads to a Fock matrix element of 1.72 eV. The charge transfer can be obtained from the matrix elements of $\bar{P}$: the occupation number of the quinone LUMO is raised to 0.12, the corresponding matrix element of the hydroquinone

HOMO is reduced from 2 to 1.89. The bond order between these two orbitals amounts to 0.45.

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