Orthogonalized Hybrid Orbitals in the Theoretical Study of Polyatomic Systems

I. Saturated Hydrocarbons

André Deplus, George Leroy, and Daniel Peeters
Laboratoire de Chimie Quantique, Université Catholique de Louvain, Belgium

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Ab initio calculations on simple saturated hydrocarbons have been carried out using a basis set of orthogonalized hybrid orbitals. We propose a simple parametric procedure based on the observed transferability of Fock matrix elements calculated in this basis set. Some applications are performed in order to test this simplified non empirical method.

Key words: Orthogonalized hybrid orbitals – Saturated hydrocarbons

1. Introduction

Ab initio calculations are still impractical for large and very large molecules. Many approximations have been suggested to simplify the LCAO-SCF-MO method, especially to avoid the evaluation of electron repulsion integrals. We shall only consider here techniques based on the transferability of Fock matrix elements calculated in different kinds of basis sets.


Later on, Newton, Boer, and Lipscomb [5] used the transferability of diagonal Fock matrix elements in a basis set of atomic orbitals; and recently, Eilers and Whitman [6] showed the excellent transferability of $h_{pq}^{\text{SCF}}$ elements in a basis set of hybrid orbitals and developped a simplified method (SAMO) for applications to large molecules. Their results were generalized by Duke, Eilers, and O'Leary [7].

We have to notice the parametric procedure of Degand, Leory, and Peeters [8] based on the use of localized orbitals.

Our work is the generalization of a method suggested simultaneously by Adams and Miller [9] and by Leroy and Jaspers [10] to study conjugated systems.

In the procedure described here, we use a basis set of orthogonalized hybrid orbitals similar to that proposed by McWeeny in order to justify methods based on zero differential overlap approximation [11].

2. Method

We use a basis set of orthogonalized hybrids ($\chi$) defined in terms of the atomic orbitals ($\chi$) by the relation:

$$\chi = \chi \sum_{k} \Psi_k$$

(1)
where $\mathcal{E}_h$ orthogonalizes the 1s orbital of each carbon to the 2s orbital of the same carbon and to the 1s orbitals of hydrogens on this carbon; $\mathcal{B}$ forms conventional $sp^3$ hybrids taking into account the experimental values of bond angles; $\mathcal{I}$ is a matrix which orthogonalizes all orbitals by the symmetric procedure of Löwdin. We shall discuss later this particular choice of basis set. Figure 1 shows a typical representation of orbitals used for propane.

In the LCAO-SCF-MO method, molecular orbitals are written in matrix form as:

$$\phi = \gamma \mathbf{C}.$$  \hspace{1cm} (2)

The LCAO coefficients are obtained by solving the Roothaan equations:

$$\mathbf{H} \mathbf{C} = \Delta \mathbf{C} \mathbf{C}$$  \hspace{1cm} (3)

with

$$\mathbf{C}^\dagger \Delta \mathbf{C} = 1.$$

In the basis set of orthogonalized hybrid orbitals, Eq. (3) becomes:

$$\mathbf{H} \mathbf{C} = \mathbf{C} \mathbf{C}$$  \hspace{1cm} (4)

with

$$\mathbf{C}^\dagger \mathbf{C} = 1.$$

In this formulation, the total energy is written as:

$$E_T = \text{tr} \mathcal{D} (\mathcal{H}^N + \mathcal{H}) + \sum \sum \frac{Z_j Z_{j'}}{R_{jj'}}$$  \hspace{1cm} (5)

where $\mathcal{D}$ is the density matrix defined in terms of the orthogonalized hybrid orbitals.