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Orthogonalized Hybrid Orbitals in the Theoretical Study of Polyatomic Systems

I. Saturated Hydrocarbons

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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.

The first procedure is the well-known Hückel method [1] using the σ–π approximation. It was generalized by Daudel and Sandorfy [2] (approximation "*C*") and subsequently by Sandorfy [3] and Fukui [4] (approximation "*H*").

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}^{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 ($\bar{\chi}$) defined in terms of the atomic orbitals (χ) by the relation:

$$\bar{\chi} = \chi \mathfrak{S}_h \mathfrak{B} \mathfrak{T} \qquad (1)$$

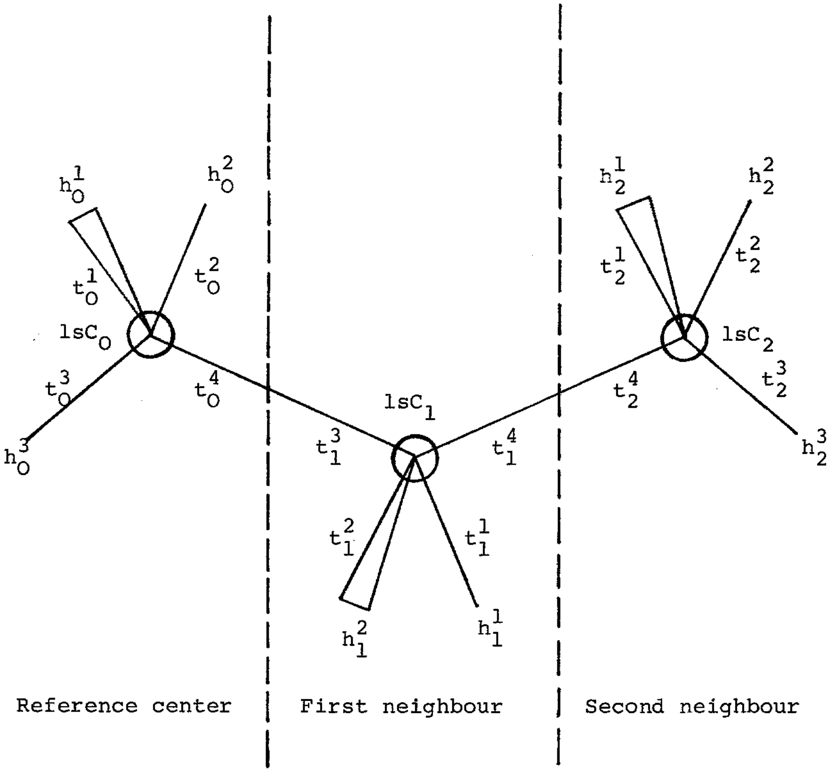

Fig. 1. Hybrid orbitals for propane

where $\mathfrak{S}_h$ orthogonalizes the 1*s* orbital of each carbon to the 2*s* orbital of the same carbon and to the 1*s* orbitals of hydrogens on this carbon; $\mathfrak{B}$ forms conventional sp^3 hybrids taking into account the experimental values of bond angles; $\mathfrak{T}$ 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:

$$\phi = \chi \mathfrak{C} . \tag{2}$$

The LCAO coefficients are obtained by solving the Roothaan equations:

$$\mathfrak{H}\mathfrak{C} = \Delta \mathfrak{C} \mathfrak{E} \tag{3}$$

with

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

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

$$\bar{\mathfrak{H}}\bar{\mathfrak{C}} = \bar{\mathfrak{C}}\mathfrak{E} \tag{4}$$

with

$$\bar{\mathfrak{C}}^{\dagger} \bar{\mathfrak{C}} = 1 .$$

In this formulation, the total energy is written as:

$$E_T = \mathrm{tr}\, \bar{\mathfrak{D}}(\bar{\mathfrak{H}}^N + \bar{\mathfrak{H}}) + \sum_{J<} \sum_{J'} \frac{Z_J Z_{J'}}{R_{JJ'}} \tag{5}$$

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

From a practical point of view, we calculate the Fock matrix elements in the basis set of orthogonalized hybrid orbitals by the relation:

$$\bar{\mathfrak{H}} = \mathfrak{T}^\dagger \mathfrak{V}^\dagger \mathfrak{S}_h^\dagger \mathfrak{H} \mathfrak{S}_h \mathfrak{V} \mathfrak{T}. \tag{6}$$

We take the matrix $\mathfrak{H}$ from an *ab initio* calculation carried out using the computer program IBMOL [12] and a $7s\,3p$ contracted basis set [13].

We have studied simple saturated hydrocarbons: methane, ethane, propane, butane, and isobutane. In the next section, we present the results obtained and discuss the transferability of matrix elements.

3. Results and Discussion

In Table 1, we given some Fock matrix elements calculated in the following basis sets.

Atomic orbitals (AO).

Orbitals orthogonalized by S_h (S_h).

Hybrid orbitals (V).

Hybrid orbitals orthogonalized by S_h ($S_h V$).

Hybrid orbitals orthogonalized by the Löwdin's procedure ($V T$).

Orbitals defined by Relation (1) ($S_h V T$).

We can see that orthogonalization systematically lowers the values of Fock matrix elements, especially when we perform a double orthogonalization ($S_h V T$).

We give in Table 2 the values calculated in the $S_h V T$ basis set for equivalent matrix elements in ethane, propane and butane. We can see a good transferability of these elements; moreover the value of a given element decreases rapidly when the distance between the corresponding centers increases.

It is interesting to notice that non diagonal matrix elements can be written as a simple function of the dihedral angle (θ) defined by the sequence of atoms HCCH. So the value of the element $t_0^i\, t_1^i$ can be obtained by the relation:

$$t_0^i\, t_0^j = 0.0011 + 0.0846 \cos\theta \tag{7}$$

with $i = 1, 2$ or 3 and $j = 1, 2$ and 4.

Table 1. HF elements of methane in different basis sets

Element	AO	S_h	V	$S_h V$	$V T$	$S_h V T$
$h^1 h^1$	− 0.6400	− 0.5717	− 0.6400	− 0.5717	− 0.0436	− 0.0362
$1sC\,1sC$	−11.3737	−11.3737	−11.3737	−11.3737	−11.0760	−11.3736
$t^1 t^1$	—	—	− 0.8353	− 0.5880	− 0.2483	− 0.1813
$2sC\,2sC$	− 1.9182	− 0.9826	—	—	—	—
$2p\,2p$	− 0.4744	− 0.4744	—	—	—	—
$h^1 h^2$	− 0.3661	− 0.2957	− 0.3661	− 0.2957	− 0.0817	− 0.0736
$1sC\,h$	− 0.9095	− 0.0218	− 0.9061	− 0.0218	− 0.1202	− 0.0083
$t^1 h^1$	—	—	− 0.8088	− 0.6865	− 0.5940	− 0.5820
$2sC\,h$	− 0.8800	− 0.6333	—	—	—	—
$2p\,h$	± 0.2459	± 0.2466	—	—	—	—
$t^1 t^2$	—	—	− 0.3610	− 0.1136	− 0.0868	− 0.0204
$1sC\,t$	—	—	− 1.7486	− 0.0221	− 0.8807	− 0.0210

Mean values of Fock matrix elements between orthogonalized hybrid orbitals can be obtained by considering the results described above. These elements may then be considered as parameters which can be used to build the matrix $\mathfrak{H}$ for any alkane and unstrained cycloalkane.

If we don't take into account interactions between one center and its third neighbours and if we put to zero values lower than $7 \cdot 10^{-3}$ a.u., we get the 32 parameters of the Table 3.

Table 2. Equivalent Fock matrix elements in alkanes (a.u.)

Element	Ethane	Propane	Butane
$h_0^1 h_0^2$	−0.0722	−0.0736	−0.0723
$h_0^1 h_1^2$	−0.0156	−0.0168	−0.0169
$h_0^1 h_2^2$	—	−0.0019	−0.0024
$h_0^1 h_3^2$	—	—	−0.0000
$1sC_0\,h_0$	+0.0112	+0.0117	+0.0110
$1sC_0\,h_1$	−0.0517	−0.0553	−0.0528
$1sC_0\,h_2$	—	−0.0070	−0.0077
$1sC_0\,h_3$	—	—	−0.0001
$t_0^1 t_0^1$	−0.1487	−0.1494	−0.1471
$t_0^1 t_0^2$	−0.0196	−0.0204	−0.0213
$t_0^1 t_1^1$	+0.0856	+0.0896	+0.0834
$t_0^1 t_2^1$	—	−0.0071	−0.0056
$t_0^1 t_3^1$	—	—	−0.0003

Table 3. Parameters for the construction of $\mathfrak{H}$ matrices (a.u.)

a) Diagonal elements		b) Elements within a center	
$h_0^1 h_0^1$	− 0.0390	$1sC_0\,h_0^i\ (i=1,2,3)$	+0.0314
$1sC\,1sC$ (CH_4)	−11.3737	$1sC_0\,t_0^4$	+0.1092
$1sC\,1sC$ (primary)	−11.3544	$h_0^l h_0^i\ (i=2,3)$	−0.0698
$1sC\,1sC$ (secondary)	−11.3457	$h_0^i t_0^i\ (i=1,2,3)$	−0.5822
$1sC\,1sC$ (tertiary)	−11.3407	$h_0^l t_0^i\ (i=2,3,4)$	−0.0587
$t_0^4 t_0^4$	− 0.1441	$t_0^1 t_0^i\ (i=2,3,4)$	−0.0204
$t_0^i t_0^i\ (i=1,2,3)$	− 0.1665		
c) Elements between a center and its first neighbours		**d) Elements between a center and its second neighbours**	
$1sC_0\,h_1^i\ (i=1,2,3)$	− 0.0486	$1sC_0\,t_2^4$	−0.0311
$1sC_0\,t_1^3$	− 0.4769	$t_0^4 t_2^4$	−0.0885
$1sC_0\,t_1^i\ (i=1,2,4)$	+ 0.0371	$t_0^4 t_2^i\ (i=1,2)$	+0.0093
$h_0^i h_1^i\ (i=1,2)$	− 0.0230	$t_0^4 h_2^3$	−0.0229
$h_0^1 h_1^2$	− 0.0153	$t_0^4 h_2^i\ (i=1,2)$	−0.0118
$h_0^i t_1^3\ (i=1,2,3)$	− 0.0693	$t_0^3 t_2^3$	−0.0368
$t_0^4 t_1^3$	− 0.6305	$t_0^3 h_2^i\ (i=1,2)$	+0.0114
$t_0^4 t_1^i\ (i=1,2,4)$	− 0.0463	$h_0^3 h_2^3$	−0.0075
$t_0^i t_1^i\ (i=1,2)$	+ 0.0891	$h_0^i h_2^i\ (i=1,2)$	−0.0256
$t_0^1 t_1^2$	− 0.0353		

In the next section, we describe the results obtained for the pattern molecules and for two new compounds, neopentane and cyclohexane for which we have complete *ab initio* results.

4. Description and Application of a Parametric LCHO-SCF-MO Procedure

4.1. Formulation

Our procedure may be considered as a Hückel method in which all electrons are included and where the numerical values of parameters α and β are known.

Table 4. Orbital energies and total energies (E_T) of alkanes (a.u.)

	$\mathfrak{H}$ diagonalization	*Ab initio* calculation		$\mathfrak{H}$ diagonalization	*Ab initio* calculation
Methane	−11.3741	−11.3738	Propane	−11.3939	−11.3917
	−0.9963	−0.9904		−11.3792	−11.3769
	−0.5886	−0.6000		−11.3693	−11.3769
	−0.5886	−0.6000		−1.1308	−1.1240
	−0.5886	−0.6000		−0.9751	−0.9844
				−0.8432	−0.8525
$E_T=$	−39.8762	−39.9633		−0.6988	−0.6857
				−0.6685	−0.6636
Ethane	−11.3853	−11.3812		−0.6195	−0.6200
	−11.3676	−11.3808		−0.5780	−0.5910
	−1.0887	−1.0767		−0.5379	−0.5491
	−0.8782	−0.8821		−0.5301	−0.5438
	−0.6618	−0.6551		−0.5050	−0.5242
	−0.6618	−0.6551			
	−0.5874	−0.5752	$E_T=$	−117.5354	−117.6692
	−0.5233	−0.5419			
	−0.5233	−0.5419			
$E_T=$	−78.7679	−78.8249			
Butane	−11.3959	−11.3860	Iso-butane	−11.4092	−11.3995
	−11.3909	−11.3855		−11.3792	−11.3728
	−11.3758	−11.3764		−11.3792	−11.3728
	−11.3693	−11.3764		−11.3680	−11.3727
	−1.1451	−1.1343		−1.1567	−1.1513
	−1.0428	−1.0385		−0.9780	−0.9803
	−0.9049	−0.9123		−0.9780	−0.9803
	−0.8365	−0.8400		−0.8219	−0.8157
	−0.7184	−0.6900		−0.7137	−0.6925
	−0.6589	−0.6506		−0.6581	−0.6522
	−0.6571	−0.6416		−0.6581	−0.6522
	−0.6245	−0.6234		−0.5808	−0.5921
	−0.5752	−0.5771		−0.5808	−0.5921
	−0.5369	−0.5491		−0.5646	−0.5656
	−0.5369	−0.5461		−0.5271	−0.5322
	−0.5144	−0.5285		−0.5271	−0.5322
	−0.4989	−0.5115		−0.5086	−0.5230
$E_T=$	−156.2719	−156.5387	$E_T=$	−157.0466	−156.5429

In order to study any saturated hydrocarbon, we have first to build the corresponding synthetic Fock matrix by using the parameters of Table 3.

This matrix satisfies the Eq. (4). So a diagonalization yields directly LCHO-SCF-MO coefficients and molecular orbital energies. Then every classical result of an *ab initio* calculation may be easily calculated. Total energy, for instance, is obtained by Eq. (5).

4.2. Test and Application of the Method

In order to test our parametric procedure, calculations have been performed on saturated hydrocarbons for which we have *ab initio* results.

In Table 4, we compare molecular orbital energies and total energies of the first terms of the alkane series obtained from an *ab initio* calculation and from our parametric procedure. This one yields satisfactory results. Orbital degeneracies are well reproduced and the order of magnitude of root mean square deviations on orbital energies is of 10^{-3} a.u.

We studied also neopentane and cyclohexane which were not used in the evaluation of parameters.

Table 5 allows us to compare their molecular orbital energies obtained from an *ab initio* calculation and from our simplified method. Once more, a good

Table 5. Orbital energies of neopentane and cyclohexane (a.u.)

Neopentane		Cyclohexane	
$\bar{\mathfrak{H}}$ diagonalization	*Ab initio* calculation	$\bar{\mathfrak{H}}$ diagonalization	*Ab initio* calculation
−11.4303	−11.4080	−11.3975	−11.3812
−11.3792	−11.3710	−11.3975	−11.3810
−11.3792	−11.3710	−11.3945	−11.3810
−11.3792	−11.3710	−11.3874	−11.3805
−11.3658	−11.3710	−11.3874	−11.3805
− 1.1791	− 1.1839	−11.3728	−11.3802
− 0.9810	− 0.9895	− 1.1818	− 1.1932
− 0.9810	− 0.9895	− 1.0678	− 1.0707
− 0.9810	− 0.9895	− 1.0678	− 1.0707
− 0.8063	− 0.7839	− 0.8819	− 0.8839
− 0.6837	− 0.6781	− 0.8819	− 0.8839
− 0.6837	− 0.6781	− 0.8132	− 0.8097
− 0.6837	− 0.6781	− 0.7317	− 0.7159
− 0.5921	− 0.6183	− 0.6731	− 0.6670
− 0.5921	− 0.6183	− 0.6731	− 0.6670
− 0.5646	− 0.5720	− 0.6585	− 0.6651
− 0.5646	− 0.5720	− 0.6068	− 0.5961
− 0.5646	− 0.5720	− 0.6068	− 0.5961
− 0.5205	− 0.5282	− 0.5898	− 0.5954
− 0.5205	− 0.5282	− 0.5362	− 0.5511
− 0.5205	− 0.5282	− 0.5362	− 0.5511
		− 0.4963	− 0.5220
		− 0.4896	− 0.4963
		− 0.4896	− 0.4963

agreement exists between the two series of values. No inversions in the ordering of the orbitals, even for closely spaced energies have been noticed, except for the 1*s* orbitals of *n*-butane which energies are less well reproduced than the others.

5. Conclusion

In a basis set of orthogonalized hybrid orbitals, the Fock matrix elements are transferable from one compound to another. Moreover, in this basis set, the values of non diagonal terms of the Fock matrix are very low.

By the comparison of results obtained for five pattern molecules, we could obtain a table of elements equivalent to the α et β Hückel's parameters. This table allows us to build the Fock matrix of any unstrained saturated hydrocarbon including all electrons.

So we proposed a very simple parametric procedure which yields LCAO coefficients (leading to a Mulliken's population analysis), orbital energies and total energy like any *ab initio* calculation. This procedure can also be used to study saturated periodic systems like polyethylene.

We intend to generalize our parametric procedure to other compounds and to perform conformational analysis by using a relation between structural parameters and Fock matrix elements. We purpose also elaborating a general computer program for systematic applications of this method.

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