

On the Use of Localized Orbitals and Restricted Alternant Orbitals in Chemical Systems

Daniel Peeters and Georges Leroy

Laboratoire de Chimie Quantique, Bâtiment Lavoisier, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

An analysis of the transformation of localized orbitals into restricted alternant orbitals is proposed. This approach has the advantage of expressing the wavefunction in an orbital product while some electron correlation is introduced permitting the study of dissociation reactions. All applications of the orbital technique may be made as easily as with RHF, but with the additional possibility of studying chemical radicals. Some illustrations of this fact are shown for the molecules HF, H₂O, NH₃, CH₄, C₂H₆ and for the dissociation reactions of CH₄ and C₂H₆ generating CH₃ radicals.

Key words: Localized orbitals – Alternant orbitals – Radical dissociation, MO description of

1. Introduction

The description of the electronic structure of molecules in terms of bonds, or better of localized orbitals, has enlarged our understanding of their behavior.

The orbital representation has the great advantage of describing the system in a simple way from a formal point of view as well as in the interpretation of the results.

Recently this method was applied to, among others, chemical reactivity [1] and amply demonstrates the interest of this approach. In the same way, the description of open shell systems [2] might be quite attractive. A well-known failure of this model is the bad molecular dissociation curves obtained within the Restricted Hartree–Fock method (RHF) due to the neglect of electron correlation.

The use of Localized Orbitals in configuration interaction was suggested many years ago [3] and more recently some multiconfiguration calculations have been

performed by K. Ishida *et al.* [4]. These two methods introduce some amount of correlation energy, but on the other hand there will be many determinants in the wavefunction so that all the simplicity of the orbital representation is lost. Of course, natural orbitals [5] may be used but unfortunately these are not localized, and are localizable only through the relaxation of the orthogonality constraint [6]. We thought it would be advisable, in this paper, to go beyond the RHF level but also to keep the simple LMO model. In this way one should improve the wavefunction and allow a study of radical formation in terms of localized orbitals. The orbital model constraint leads us immediately to an unrestricted Hartree–Fock method [7], suitably projected in order to obtain eigenfunctions of the spin operators. Indeed these wavefunctions have the advantage of being reducible to a Hartree product for the spatial functions, thus keeping the desired simplicity.

This paper comprises three parts. In the first part, we shall present the methodological approach which we used, as well as the technique by which we obtained our results.

In the second part, we shall illustrate the method by some applications on small molecules, namely HF, H₂O, NH₃, CH₄ and C₂H₆ and on the dissociation of CH₄ and C₂H₆ into methyl radicals.

In the third part, we shall discuss the results obtained and emphasized on the applications of the method in the field of chemical reactivity.

2. Theoretical Approach

In the RHF method, the wavefunction of a system containing $2n$ electrons may be written

$$\psi = |\phi_1(1)\bar{\phi}_1(2)\phi_2(3)\cdots\bar{\phi}_n(2n)| \quad (1)$$

If we relax the double occupation of the molecular orbitals, the wavefunction will be expressed by Different Orbitals for Different Spin functions (DODS) which in its monodeterminantal version is associated with the Unrestricted Hartree–Fock (UHF) method. One drawback of this function is that it is not an eigenfunction of the S^2 spin operator, and one must have recourse to the projection operators technique described by Löwdin [8] in order to obtain an eigenfunction. In this case, the function is projected after variation of the trial function. The total wavefunction has not been fully optimized. Only the Extended Hartree–Fock (EHF) [9] fully optimizes the trial function. If we consider a RHF wavefunction, the alternant orbital method (AMO) [10] allows us to generate an UHF wavefunction, projected or not and even an EHF wavefunction.

In the all-electron case, the projected UHF and EHF methods lead to increasingly complicated spin functions, in spite of the simple form of the spatial function. To overcome this difficulty, we decided to limit the development of the wavefunction in AMO only to those orbitals which are directly involved in the chemical process under study.

Let ϕ_i be a spatial localized orbital involved in any chemical process. We may generate restricted alternant orbitals by considering a corresponding orbital [11], which will be the virtual orbital localized in the same region of space as ϕ_i . We shall represent that orbital by ϕ_i^* .

These alternant orbitals restricted to the one parameter case may be obtained by the equations:

$$\begin{aligned}\chi_i &= \cos \theta_i \phi_i + \sin \theta_i \phi_i^* \\ \chi_i' &= \cos \theta_i \phi_i - \sin \theta_i \phi_i^*\end{aligned}\quad (2)$$

The wavefunction becomes:

$$\psi_1 = |\phi_1(1)\bar{\phi}_1(2)\cdots\chi_i(\mu)\bar{\chi}_i'(v)\cdots\bar{\phi}_n(2n)|\quad (3)$$

in its unprojected form, or:

$$\begin{aligned}\psi_2 = \frac{1}{\sqrt{2}} \{ & |\phi_1(1)\bar{\phi}_1(2)\cdots\chi_i(\mu)\bar{\chi}_i'(v)\cdots\bar{\phi}_n(2n)| \\ & - |\phi_1\bar{\phi}_1\cdots\bar{\chi}_i(\mu)\chi_i'(v)\cdots\bar{\phi}_n(2n)| \}\end{aligned}\quad (4)$$

in its projected form for the singlet state.

This function corresponds to a sum of two determinants and may be brought to an antisymmetrized product of an Hartree function and a spin function [10].

If one looks at the transformation giving AMO's, one finds that these orbitals are obtained by mixing an occupied orbital with a virtual orbital. This corresponds of course to a CI 2×2 .

The identity between such a CI function and our projected function is well known [12, 13]. The relation between the rotation angle θ_i and the coefficients a of the RHF configuration and b of the other configuration is given by the formula:

$$\cos 2\theta = \frac{a+b}{a-b}\quad (5)$$

We now are able to express the possibility of transforming a 2×2 CI computation in a classical orbital form for the spatial orbitals besides the three following advantages.

- 1) Introduction of some intrapair electron correlation.
 - 2) As we shall see later on, a reasonable dissociation curve and the possibility of investigating the reactivity of free radicals.
 - 3) An expression of molecular properties in a form similar to RHF calculations.
- Nevertheless, it should be borne in mind that these orbitals are non-orthogonal.

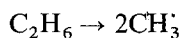
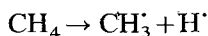
This approach looks interesting as, in most chemical reactions, especially in dissociations, only one bond is affected by an electron reorganization. Therefore the LMO describing that bond may be transformed in two AMO's while all the other mono-electronic functions will remain unchanged. As there is only one doubly occupied LMO concerned, the spin function will be quite simple.

If more than one bond is affected by the reaction, we may follow the same approach as described above, but now, instead of working with the RHF wavefunction (1), we shall have to transform the already projected wavefunction (4) and generate two new AMO's χ_j and χ'_j by rotation of the orbitals ϕ_j and ϕ_j^* describing one of the other bonds affected by the reaction.

The spin function will, of course, be less simple and for a computation involving n bonds, the spin function will be equivalent to a function of 2^n determinants. The main advantage of this approach lies in the fact that we preserve the simplicity of an orbital representation and that it does not use sophisticated techniques. Nevertheless, no interpair correlation is introduced, and our projected function, equivalent to a function containing 2^n determinants ($n > 1$), is, in that sense, not as good as a CI calculation using the same number of determinants.

3. Applications of the Method

We have applied the procedure described above on a few molecules, namely HF, H₂O, NH₃, CH₄ and C₂H₆, and on the two dissociation reactions:



The experimental equilibrium geometries were used [14]. All the calculations were performed with the STO-3G basis set of Pople *et al.* [15]. The HF molecule has also been studied with the 4-31G basis set of the same author [16]. The GAUSSIAN 70 programs [17] generated the canonical molecular orbitals, which were localized by the Boys procedure [18] using the BOYLOC program [19]. Occupied and virtual orbitals were localized separately and the AMO's were obtained through relation (2) using the θ angle of relation (5).

Table 1 gives for all the molecules the following information obtained using the STO-3G basis set: the concerned bond, the gain of energy, the rotation angle θ , the distance between the heavy atom and the centroid of the AMO, and the expansion coefficients for these orbitals.

Table 2 gives, for comparison, the results obtained by the RHF method namely total energy, nature of the localized orbital, bond length, distance between the heavy atom and the centroid of the orbital, contribution of the orbital to the total energy [20] and the coefficients of the development for this orbital.

Table 3 compares the results for HF obtained in the two basis sets.

Table 4 gives for the dissociation reactions, the evolution of the AMO centroids during the dissociation, total RHF energy, and the total energy obtained by our procedure.

Fig. 1 gives the evolution of the contribution of each localized orbital to the total energy during the dissociation process. Nevertheless, the localized orbital under

Table 1. Properties of the AMO

Molecule	Bond	ΔE		δ centroid-X a.u.	LCAO-AO
		a.u.	θ_i		
HF	HF	-0.0172	16.77°	0.586	-0.176(H)+0.074(1S)-0.325(2S)+0.830(p_x) +0.000(p_y)+0.000(p_z)
				1.435	-0.811(H)+0.038(1S)-0.050(2S)+0.361(p_x) +0.000(p_y)+0.000(p_z)
H ₂ O	HO	-0.0175	17.10°	0.646	-0.150(H)+0.095(1S)-0.433(2S)-0.045(p_x) +0.000(p_y)+0.809(p_z)+0.096(H')
				1.579	-0.835(H)+0.040(1S)-0.068(2S)-0.052(p_x) +0.000(p_y)-0.298(p_z)+0.113(H')
NH ₃	NH	-0.0155	16.73°	0.756	-0.140(H)+0.108(1S)-0.519(2S)-0.711(p_x) +0.320(p_y)+0.000(p_z)+0.091(H') 2 *
				1.176	-0.846(H)+0.046(1S)-0.100(2S)-0.215(p_x) +0.131(p_y)+0.000(p_z)+0.087(H') 2 *
CH ₄	HC	-0.0150	16.86°	0.899	-0.157(H)+0.115(1S)-0.536(2S)+0.356(p_x) +0.612(p_y)+0.250(p_z)+0.066(H') 3 *
				1.916	-0.881(H)+0.042(1S)-0.067(2S)+0.093(p_x) +0.161(p_y)+0.065(p_z)+0.050(H') 3 *
C ₂ H ₆	HC	-0.0149	16.82°	0.906	-0.162(H)+0.115(1S)-0.535(2S)-0.708(p_x) -0.000(p_y)+0.249(p_z)+0.068(H') 2 * + ...
				1.916	-0.882(H)+0.043(1S)-0.067(2S)-0.181(p_x) +0.000(p_y)+0.065(p_z)+0.052(H') 2 * + ...
	CC	-0.0135	16.44°	0.939	+0.115(1S)-0.526(2S)+0.000(p_x)+0.000(p_y) +0.728(p_z)+0.044(1S')-0.100(2S')+0.000(p_x) +0.000(p_y)-0.201(p_z)+0.065(H) 3 * +0.044(H') 3 *
				1.971	+0.115(1S)-0.526(2S)+0.000(p_x)+0.000(p_x') +0.000(p_y)-0.201(p_z)+0.065(H) 3 * +0.044(H') 3 *

Table 2. Properties of the LMO

Molecule	E_T	Bond	r_e a.u.	δ centroid-X a.u.	E_i	LCAO-LO
HF	-98.5708	HF	1.733	0.984	-5.672	-0.515(H)+0.059(1S)-0.196(2S) +0.622(p_x)+0.000(p_y)+0.000(p_z)
		lp		0.503	-9.124	-0.102(H)+0.090(1S)-0.583(2S) -0.195(p_x)+0.789(p_y)+0.209(p_z)
H ₂ O	-74.9632	OH	1.814	1.091	-4.579	-0.520(H)+0.070(1S)-0.262(2S) -0.579(p_x)-0.051(p_y)+0.000(p_z) +0.109(H')
		lp		0.578	-7.111	-0.096(H)+0.094(1S)-0.649(2S) +0.240(p_x)+0.313(p_y)+0.707(p_z) +0.096(H')

Table 2. Continued.

Molecule	E_T	Bond	r_e a.u.	δ centroid-X a.u.	E_i	LCAO-LO
NH ₃	-55.4543	NH	1.918	1.223	-3.609	-0.515(H)+0.081(1S)-0.323(2S) -0.484(p_x)+0.235(p_y)+0.000(p_z) +0.093(H') 2 *
		<i>lp</i>		0.673	-5.282	-0.068(H)+0.086(1S)-0.655(2S) +0.000(p_x)-0.803(p_y)+0.000(p_z) +0.068(H') 2 *
CH ₄	-39.7267	CH	2.060	1.409	-2.747	-0.542(H)+0.082(1S)-0.315(2S) +0.000(p_x)+0.000(p_y)-0.405(p_z) +0.061(H') 3 *
C ₂ H ₆	-78.3055	CH	2.060	1.414	-2.636	-0.546(H)+0.086(1S)-0.314(2S) -0.465(p_x)+0.000(p_y)+0.164(p_z) +0.063(H') 2 * + ...
		CC	2.910	1.455	-5.002	-0.033(1S)-0.327(2S)+0.000(p_x) +0.000(p_y)-0.484(p_z)+0.083(1S') -0.327(2S')+0.000(p_x)+0.000(p_y) +0.484(p_z)+0.057(H) 6 *

Table 3. Comparison between STO-3G and STO-4-31G results

Basis	E_T RHF	Bond	ΔE	θ_i	E_i	LMO δ c-X	AMO δ c-X	
STO-3G	-98.5708	HF	-0.0172	16.77°	-5.672	0.984	0.586	1.435
		<i>lp</i>	—	—	-9.124	0.503	—	—
4-31G	-99.8873	HF	-0.0132	14.30°	-6.386	0.853	0.518	1.185
		<i>lp</i>	-0.0059	11.09°	-9.072	0.518	0.428	0.617

Table 4. Evolution of AMO's during a dissociation process

	δ c-C	CH ₄ → CH ₃		E_T AMO
		δ c-H	E_T	
r_e	0.8987	0.1443	-39.7267	-39.7417
$r_e+0.5$	0.9225	0.1938	-39.6833	-39.7098
1.0	0.8905	0.1873	-39.6049	-39.6500
1.5	0.8200	0.1463	-39.5233	-39.5956
2.0	0.7391	0.1004	-39.4508	-39.5583
2.5	0.6702	0.0699	-39.3913	-39.5374
3.0	0.6200	0.0542	-39.3453	-39.5279
4.0	0.5466	0.0479	-39.2671	-39.5235
5.0	0.5263	0.0479	-39.2446	-39.5249

Table 4. *Continued.*

	δ c-C	$C_2H_6 \rightarrow 2CH_3$ E_T	E_T AMO
r_e	0.9393	-78.3055	-78.3190
$r_e + 0.5$	0.9613	-78.2695	-78.2936
1.0	0.9260	-78.1967	-78.2376
1.5	0.8523	-78.1187	-78.1844
2.0	0.7699	-78.0493	-78.1472
2.5	0.7016	-77.9926	-78.1263
3.0	0.6542	-77.9490	-78.1170

dissociation is corrected by the energy gain due to the 2×2 CI. This point will be justified in the discussion.

Fig. 2 gives the evolution of the centroids of the AMO describing the formation of the CH_3 radical in these two dissociations. The distance carbon atom, carbon centroid is given in ordinate.

4. Discussion of the Results

4.1. Concerning the Molecules

We may note that the energy gain obtained is quite important. This is well known and due to the fact that the localized orbitals ϕ_i and ϕ_i^* have their spatial distributions confined in the same domain of space R^3 . The relative constance of the gain may be expected if one considers that in each molecule the correlation is introduced for a pair of electrons which is almost the same in all cases.

The AMO's are systematically generated by very similar θ rotation angles. This means, looking at relation (2), that in all cases, even if the spatial distribution of ϕ_i^* is different, the mixing of ϕ_i and ϕ_i^* is similar. This conclusion is of course consistent with the first one.

One may say that the two AMO's, one associated to the H atom, the other one to the heavy atom, describe the chemical bond between these two atoms. Owing to the introduction of some correlation, this description is even better than in a LMO description. Furthermore, the energy gain is exclusively yielded to the affected bond, which means that the LMO energy given in Table 2, may be corrected by the corresponding energy increment of Table 1.

The use of symmetry in molecules such as H_2O , NH_3 , CH_4 and C_2H_6 allows us to transfer on equivalent bonds the energy gain and the AMO. The total energy corrected for intra-pair correlation may be estimated. Moreover, we obtain a wavefunction built on a Hartree product of AMO's which for methane is equivalent to a function of 16 determinants, and that only by one 2×2 CI computation. For the ethane molecule two 2×2 CI computations generate a wavefunction containing 128 determinants. The use of localized orbitals entails a notable gain of

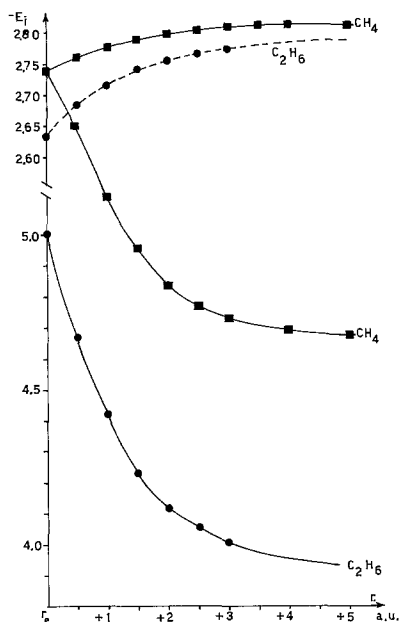


Fig. 1. Evolution of the bond energy increments

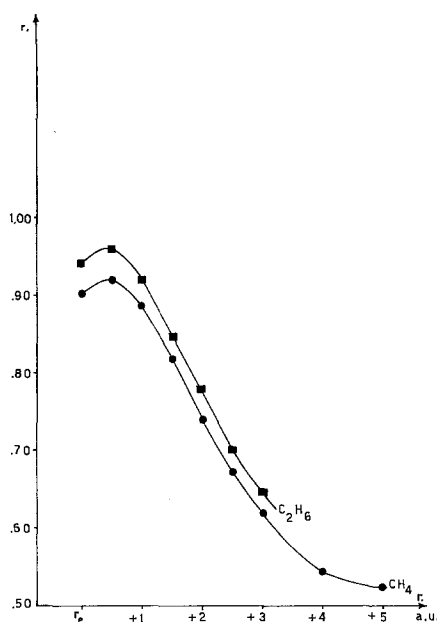


Fig. 2. Evolution of AMO centroids

energy and by computing the energy associated to the function of 2^n determinants the interpair correlation might be found.

The use of AMO's allows us to compute easily the molecular properties owing to the separability of space and spin functions. The centroid of charge position reported in Table 1 could lead to the dipole moment for example. Nevertheless, comparing the mean position of Table 1, with the centroids of the RHF-LMO's, one will find a very good correlation, showing the relatively small effect of intra-pair electron correlation on this first-order property.

If we examine Table 3, and compare for HF, the results using minimal and valence split basis sets, we may find that the introduction of more than one virtual orbital leads to an AMO description of the lone pairs. The LMO virtual orbitals contain indeed one LMO describing the HF bond, three LMO's describing the lone pairs plus 2 diffuse orbitals. The mixing of a lp LMO with a lp^* LMO, although a θ angle of 11° is found, does not introduce much correlation energy (0.007 a.u.). This surely is due to the fact that lone pair orbitals are quite more diffused. The centroids of these AMO's are placed symmetrically around the centroid of the localized orbital, in the plane H-F- lp . Concerning the H-F bond description, the two AMO's found are quite similar to those obtained in the minimal basis set, even though the rotation angle is a little bit smaller and the energy decrease slightly less important. This is due to the greater completeness of a valence split basis set.

4.2. Concerning the Dissociation

We have tried to illustrate our procedure on two very simple examples. The dissociation was studied by looking only after the LMO which is affected by the reaction. All the other LMO's remain unchanged. By generating the AMO's the two radicals do appear dynamically. Once again all the energy gain obtained during the dissociation may be transferred on the LMO involved in the process. Fig. 1 shows that the most impressive effect appears in the first a.u. displacement. The C-H bonds stabilize their energies while the dissociating orbital energy CH of CC increases quickly and finally stabilizes for the radicalar entities. This point is confirmed by Fig. 2 which shows the evolution of the AMO's centroids during the dissociation.

At first the AMO centroid moves off the heavy atom, as if the bond would resist to dissociation. Afterwards the centroid moves back to the atom until it stabilizes in the radical position.

The closeness of the two curves for CH_4 and C_2H_6 shows the similarity of the dissociation. At large distance the two curves go asymptotically to the same limit. Nevertheless, the Coulomb interactions, being quite different for CH_3 and H , justify the slow convergence of the curves. The position of the centroid describing the hydrogen AMO in the CH_4 dissociation suggests that at 3 a.u. (cf. Table 4) the free atom already appears and that the dissociation is completed. For C_2H_6 , this distance seems to be a bit larger, and once again the Coulomb interactions may justify this behavior.

In these dissociations, the procedure may also be improved by transforming all LMO's into AMO's. The wavefunction and the energy recalculated for 16 and 128 determinants, must be better, but it is our feeling that this improvement, which will sophisticate the procedure, is not necessary as it will bring information from spatial domains which are not involved in the chemical reaction. One should maintain the golden mean between sophistication and easy application.

5. Conclusions

In this paper, we have shown how the use of localized orbitals may introduce an improvement in the energy, and in the wavefunction by the transformation of these orbitals into restricted alternant orbitals. This transformation preserves a simple expression of the wavefunction and allows in this sense a better description of any chemical system. The use of an orbital model leads to an easy computation of the properties of the system. Orbital contributions to the total energy and orbital centroids of charge gave a good insight into the dissociation process, and may be applied to any reaction, involving radical formation or rearrangement.

The introduction of electron correlation, limited to the spatial domains where the electron reorganization really takes place, as well as the use of a simple orbital description will induce many new applications.

References

1. Leroy, G., Sana, M., Burke, L. A., Nguyen, M. T.: The theoretical study of chemical reactivity. Reidel 1978 (to appear) Dordrecht-Holland
2. Peeters, D., Leroy, G.: *Bull. Soc. Chim. Belg.* **86**, 833 (1977)
3. Foster, J. M., Boys, S. F.: *Rev. Mod. Phys.* **32**, 300 (1960)
4. Ishida, K., Konde, K., Yonesawa, T.: *J. Chem. Phys.* **66**, 2883 (1977)
5. Löwdin, P. O.: *Phys. Rev.* 1474 (1955); 1490 (1955); 1509 (1955)
6. Certain, P. R., Hirschfelder, J. O.: *Chem. Phys. Letters* **2**, 274 (1968)
7. Pratt Jr., G. W.: *Phys. Rev.* **102**, 1303 (1956)
8. Löwdin, P. O.: *Rev. Mod. Phys.* **36**, 966 (1964); Löwdin, P. O.: *Calcul des fonctions d'onde moléculaire*, p. 23. Paris: CNRS 1958
9. Löwdin, P. O.: *Rev. Mod. Phys.* **32**, 328 (1960)
10. Pauncz, R.: *Alternant orbital method*. Saunders 1967, Philadelphia
11. Löwdin, P. O.: *Symposium of molecular physics*, p. 13. Tokio: Maruzen Co. 1953; Löwdin, P. O.: *Phys. Rev.* **97**, 1509 (1955)
12. Goscinski, O. Calais, J. L.: *Arkiv for Fysik* **29**, 135 (1965)
13. Coulson, C. A., Fischer, I.: *Phil. Mag.* **40**, 386 (1949)
14. *Tables of interatomic distances*. London: Chemical Society 1958
15. Hehre, W. J., Stewart, R. F., Pople, J. A.: *J. Chem. Phys.* **51**, 2657 (1969); *J. Chem. Phys.* **52**, 2969 (1970)
16. Ditchfield, R., Hehre, W. J., Pople, J. A.: *J. Chem. Phys.* **54**, 724 (1970)
17. Hehre, W. J., Lathan, W. A., Ditchfield, R., Pople, J. A.: GAUSSIAN-70: Q.C.P.E. n° 236
18. Boys, S. F.: *Rev. Mod. Phys.* **32**, 296 (1960)
19. Peeters, D.: BOYLOC: Q.C.P.E. n° 330
20. Leroy, G., Peeters, D.: *Localization and delocalization in quantum chemistry*, Vol. 1, pp. 207–221. Dordrecht-Holland: D. Reidel Publishing Company 1975

Received March 31, 1978/June 19, 1978