Localized Bond Orbitals and the Correlation Problem

IV. Stability of the Perturbation Energies with Respect to Bond Hybridization and Polarity

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The stability of the results of the Perturbative Configuration Interaction using Localized Orbitals (PCI LO) with respects to the choice of the hybrids and to the bond polarities is studied for several small strained molecules. The stability of 2nd and 3rd orders is quite satisfactory. The pertinence of the maximum overlap criterion to build hybrids is discussed.

An verschiedenen kleinen Ringen wird die Stabilität der Ergebnisse einer Störungs-CI-Rechnung studiert, wobei bezüglich der Wahl der Hybride und der Bindungspolaritäten lokalisierte Orbitale benutzt werden. Die Stabilität der Ergebnisse für Störungen 2. und 3. Ordnung ist zufriedenstellend. Das Kriterium der maximalen Überlappung zum Aufbau von Hybriden wird diskutiert.

On étudie la stabilité des résultats de la méthode: Développement Perturbatif de la matrice d'Interaction de Configuration en base d'Orbitales de Liaison (PICOL) par rapport aux paramètres qui déterminent les orbitales de liaison hybridation et polarité pour plusieurs petites molécules contraintes. La stabilité aux 2è et 3è ordres est assez bonne. On discute les rapports du critère de Recouvrement Maximum avec les problèmes énergétiques.

1. Introduction

In part I of this series [1] we proposed to build a fully localized determinant using bond orbitals, to build "excited" determinants with the corresponding antibonding orbitals and to express the energy of the ground state by a perturbation expansion of the Configuration Interaction matrix built in this basis set (Perturbationnal Configuration Interaction using localized orbitals: PCI-LO). The ZDO formulas have been given in part III [2] and a certain number of examples concerning small molecules with the CNDO hypothesis [3] about the atomic integrals.

In the previous paper the bond orbitals were built in the simpliest way: we used two atomic hybrid orbitals, and the assumed state of hybridization was in general determined by the classical chemical picture. We only used sp^3, sp^2 or sp canonical hybrids. The only degree of freedom concerned the oxygen lone pairs in the carbonyl group and the choice of sp^2 or sp hybridization did not influence

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significantly the results. But in certain cases, and especially for small strained molecules, no canonical hybridization appears as natural, and the choice of some "best hybrids" could appear necessary. The first purpose of this paper is to analyse the influence of the assumed hybridization state on the zeroth, second and third order results of the ground state energy. By this analysis we try to verify the stability of the perturbation expansion with respect to the choice of the bond orbitals. The final result of the Configuration Interaction, and of the perturbation expansion if it converges, are of course insensitive to the choice of the hybrids, but the sum over the first terms of the series only are not. The differences should be more important at the zeroth than after third order. This study should give an indication about the rate of convergence of the series. The same type of investigation has been performed about the other parameter of the bond orbital, namely the bond polarity which fixes the coefficients of the two hybrids in the bond orbital.

The PCI-LO Method is very attractive for treating large systems, because of its high speed. But it needs a systematic method to choose the atomic hybrids. One could think of a systematic attribution of a canonical hybridization according to the number and the position of the neighbouring atoms. Another possibility is to determine the hybrids which give the maximum overlap in the chemical bonds. We decided to use this technique in our current programs. It is important then to see whether the maximum overlap criterion, which is a spatial criterion, and not an energetic one, is not too far from the hybridization which gives the lowest energy for the fully localized determinant. A special attention is thus devoted to the calculation using the maximum-overlap hybrids.

2. Method and Results

A. Method

We used the formulas given in Paper III for the zeroth, second and third order energy. Only the zeroth order energy, which is the mean value of the Hamiltonian for the fully localiced determinant is an upper bound to the energy. The second and third order corrected energies may be below the exact energy. It is tempting then to calculate an upper bond for the corresponding wave function. If Ψ_0 is the zeroth order determinant and Ψ_1 the first order correction to the wave function, the first order wave function is

$$\Phi_1 = \Psi_0 + \Psi_1 \quad \text{with} \quad \langle \Psi_0 | \Psi_1 \rangle = 0 \quad \text{(intermediate normalization)}$$

and its energy is given by

$$\varepsilon_1 = \frac{\langle \Phi_1 | H | \Phi_1 \rangle}{\langle \Phi_1 | \Phi_1 \rangle} = E_0 + \frac{E_2 + E_3}{1 + N} \tag{1}$$

where E_2 and E_3 are the second and third order corrections to the energy and $N = \langle \Psi_1 | \Psi_1 \rangle$ is the norm of the first order correction to the energy. One may improve slightly the result with little supplementary work by putting as Hylleraas proposed [4]

$$\Phi_1' = \Psi_0 + \alpha \Psi_1 , \tag{2}$$

where α is a parameter which is determined variationaly. Then

$$\varepsilon_1' = E_0 + \frac{(2\alpha - \alpha^2)\,E_2 + \alpha^2 E_3}{1 + \alpha^2 N} \tag{3}$$

and α is determined by a minimization of ε_1'. This leads to a second degree equation in α.

In the text ε_1 will be referred to as the energy of the first order wave function and ε_1' as the energy of variated first order wave function. Brueckner [5] has criticized the use of these bounds for the correlation problem. When the number n of particles increases, E_2, E_3 and N increase as n. Thus the ratio $\dfrac{E_2 + E_3}{1 + N}$ does not increase as n, as it should do, and one only gets a decreasing part of the correlation energy. This is due to the fact that the normalization introduces some higher order terms which are in fact cancelled by properly fourth-order terms. The use of ε_1 and ε_1' is not recommended for large systems but was interesting in our case to compare the conditions (hybridization and polarity) which minimize the energies of the fully localized determinant and of the first order perturbed wave function. We used the classical CNDO hypothesis [3] with hydrogen Slater exponent Z_μ equal to 1.2. The values of $(I_\mu + A_\mu)/2$ and of β for carbon and hydrogen differ somewhat from those proposed by Pople and Segal [3] by a reduction factor, choosen to fit energies on *ab initio* calculations in ethane, ethylene and acetylene [6].

The problem has been extensively examined in the case of cyclopropane and cyclobutane, and some comparisons are given between two types of hybridization (canonical and maximum overlap) for a series of small strained molecules.

B. Cyclopropane and Cyclobutane

If we assume a planar and regular geometry these molecules have a threefold and fourfold symmetry and all the CH (CC) bonds are equivalent. Then the orthogonality requirements only let two parameters in our zeroth-order wave function if we want it to keep the molecular symmetry. We may fix for instance the C hybrid directed toward the neighbouring carbon atom by fixing for instance its s character. This is the first parameter. Then the other hybrids are fixed either by symmetry or by orthogonality. There is no polarity in the C–C bonds. But one may choose arbitrarily the polarity of the CH bonds. This gives a second parameter. If we call d the polarity of the bond, the coefficients of the bonding CH orbital are

$$x_H = \sqrt{\frac{1-d}{2}}$$

$$x_C = \sqrt{\frac{1+d}{2}} \tag{4}$$

respectively the H $1s$ atomic orbital, and C hybrid.

The *fully localized determinant* presents a minimum in energy which corresponds to the polarity 0.03 and an s character of 0.47. The energy is quite sensitive

to the hybridization state: the minimum for the 0.4 s character is 0.8 eV above the absolute minimum. The Del Re's [7] procedure to obtain the maximum overlap gives an s character of 0.43. It appears that this criterion, which is purely spatial, only gives a minimum 0.3 eV above the absolute minimum for a fully localized determinant. On the contrary the pure sp^3 hybridization, which seems to be wrong for such bond angles, gives an energy closer to the absolute minimum.

The energy is of course also dependent of the CH bond polarity. But the value 0.03 is very close the polarity that one gets from the SCF calculation or from a typical saturated CH bond dipole moment. One may remark however that the best polarity is not the same for the various states of hybridization.

The *second order correction* is negative and large (about 8.9 eV) and comes mainly from delocalization monoexcited states ($\simeq 3$ eV), the intra-bond correlation ($\simeq 3.2$ eV) and the inter-bond correlation energies ($\simeq 1.6$ eV). The second order corrected energy (Fig. 2) presents now a reversed picture of Fig. 1: there is a *maximum* for $s = 0.48$ and $d = 0.03$. One may notice that the amplitude of the
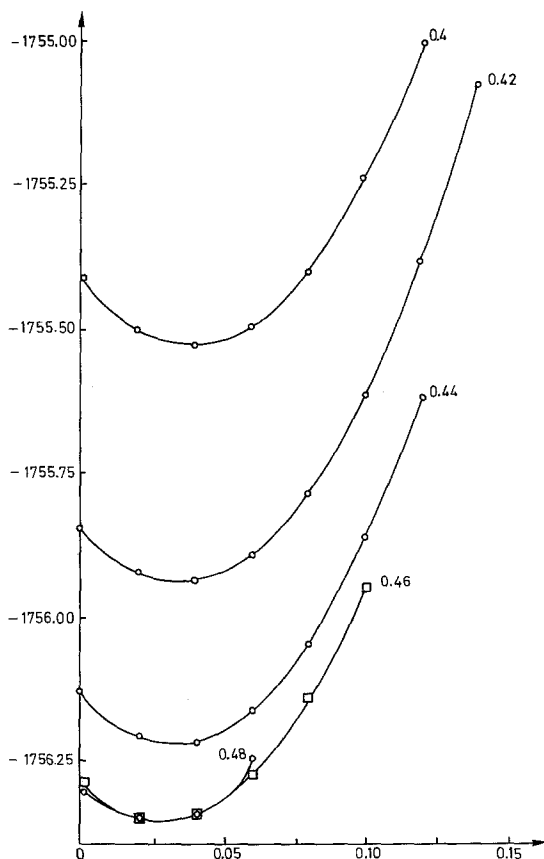
Figs. 1–5 give the various energies for the cyclopropane molecule (calculated with the following geometry: $l_{CH} = 1.08$ Å; $l_{CC} = 1.53$ Å, $\widehat{HCH} = 118°$)

Fig. 1. Cyclopropane zeroth order energy, E_0: energy of the fully localized determinant as a function of the polarity (in abscissa) of CH bonds and of the s character of the CC bonds
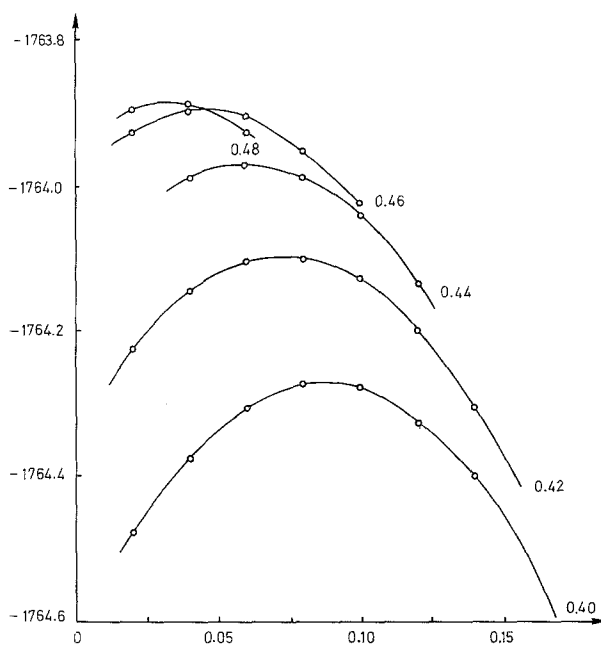
Fig. 2. Cyclopropane second order corrected energy, $E_0 + E_2$. (same variables)
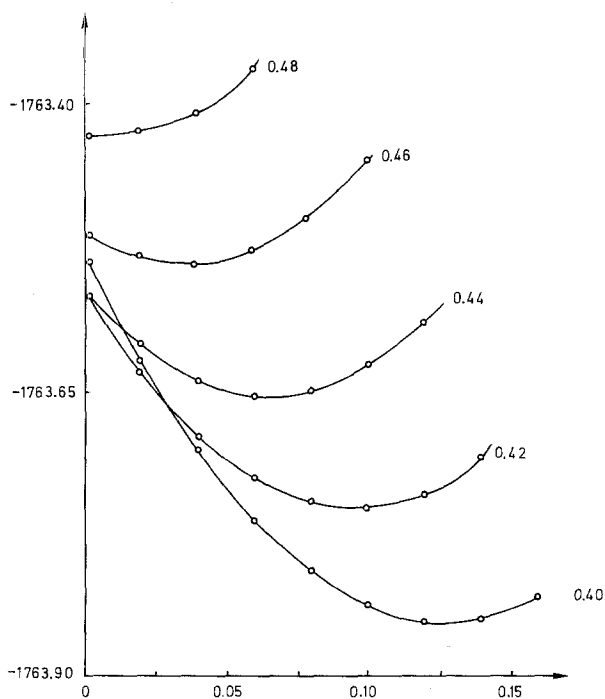

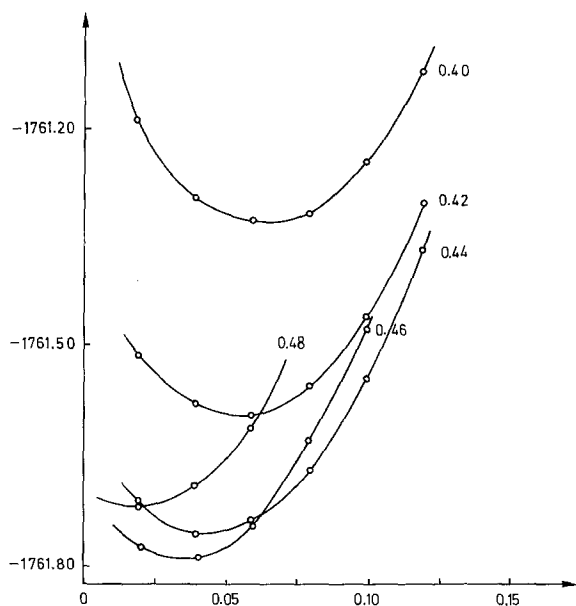Fig. 3. Cyclopropane third order corrected energy, $E_0 + E_2 + E_3$. (idem)

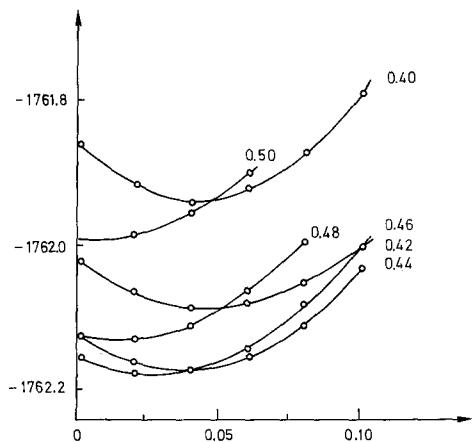Fig. 4. Cyclopropane energy of the first order corrected wave function Ψ_1, ε_1. (idem)

Fig. 5. Cyclopropane energy of the best wave function of the form $\Psi_0 + \alpha \Psi_1, \varepsilon_1'$. (idem)

variations are diminished; the maximum for $s = 0.40$ is only 0.4 eV below the maximum for $s = 0.48$. The best polarity depends more strongly of the s character. These results seem to indicate that the worse the zeroth order wave function is, the stronger is the second order correction; when the starting point is too bad, the second order corrected energy becomes too low, far below the reasonable value.

The *third order energy* is positive, but depends strongly ($-0.2 < E_3 < 1.0$ eV) of the values of the parameters. The third order energy curves (Fig. 3) are more complex. For each value of s, the curve presents a minimum as a function of the polarity. But for small unrealistic values of s, the best polarity seems meaningless,

Table 1. *Cyclobutane 0 polarity structures as a function of the 2s character in CC bonds*

s	0.40	0.42	0.44	0.46	0.48	0.50	0.52	0.54
E_0	−2736.931	−2737.715	−2738.363	−2738.843	−2739.123	−2739.187	−2739.035	−2739.545
m_1	− 0.247	− 0.205	− 0.166	− 0.129	− 0.095	− 0.065	− 0.040	− 0.020
m_2	− 5.404	− 4.373	− 3.564	− 2.988	− 2.675	− 2.649	− 2.944	− 3.596
d_1	− 4.474	− 4.458	− 4.446	− 4.439	− 4.437	− 4.442	− 4.452	− 4.470
d_2	− 1.890	− 1.871	− 1.853	− 1.838	− 1.826	− 1.816	− 1.808	− 1.804
$E_0 + E_2$	−2748.947	−2748.623	−2748.393	−2748.238	−2748.158	−2748.160	−2748.280	−2748.487
$m_1 - d_1$	0.057	0.047	0.038	0.030	0.022	0.015	0.009	0.004
$m_1 - m_1$	0.052	0.043	0.035	0.027	0.020	0.014	0.008	0.004
$m_1 - m_2$	0.437	0.338	0.249	0.170	0.103	0.049	0.009	− 0.013
$m_1 - d_2$	0.064	0.053	0.043	0.034	0.025	0.017	0.010	0.005
$m_2 - d_2$	− 0.020	− 0.041	− 0.056	− 0.065	− 0.069	− 0.066	− 0.056	− 0.038
$d_1 - d_2$	0.827	0.811	0.797	0.785	0.775	0.768	0.763	0.761
$m_2 - m_2$	0.714	0.402	0.192	0.093	0.112	0.256	0.526	0.921
$d_2 - d_2$	0.254	0.254	0.254	0.254	0.255	0.257	0.260	0.263
E_3	2.386	1.909	1.553	1.329	1.244	1.212	1.532	1.908
$E_0 + E_2 + E_3$	−2946.561	−2746.713	−2746.839	−2746.909	−2746.912	−2746.848	−2746.748	−2746.578

Same notations than in Ref. [2].

and there is no appearent absolute minimum. For bad values of s and d the series seem to diverge. The result is not very stable but for a reasonable range of values of s and d the deviation is not larger than 0.3 eV.

The stability is significantly improved when one takes an upper bound ε_1 or ε_1' (Figs. 4–5). The normalisation costs about 2 eV when compared with the third order result. The scalar variation leading to ε_1' only gives an improvement of 0.3 eV for the absolute minimum, but it stabilizes strongly the results for less realistic values of s and d. The absolute minimum is obtained for $s \simeq 0.46$ and $d \simeq 0.035$, which are not far from the best values for the zeroth order determinant. But now the curves are much closer. For ε_1' for instance the minimum curve $s = 0.43$ lies only about 0.05 eV higher than the absolute minimum. This means that the first order corrections compensate nicely the defects of the zeroth order wave function.

We only give the values of the energies for a zero polarity (Table 1) for the cyclobutane molecule [1]. The differences of the zeroth order energies are much more pronounced but the second and third order corrections give a good stability for reasonable values of hybridization and polarity ($|\Delta E| < 0.2$ eV). The third order corrected energies seem anyway less sensitive to the choice of the parameters than in the case of cyclopropane. The best zeroth order value of the s character is 0.50 (i.e. the sp^3 hybridization state) while Del Re's best overlap gives 0.47 and Randic's criterion [8] gives 0.435.

C. Influence of the Choice of the Hybrids in a Series of Small Strained Molecules

In order to see whether the method could be applied with enough accuracy to some chemical problems we decided to compare the results obtained by three different ways for a series of small molecules

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[1] Calculated with the following geometry: $l_{CH} = 1.09$ Å, $l_{CC} = 1.548$ Å, $\widehat{HCH} = 114°$.

Table 2. *Comparison of the results of canonical and maximum overlap hybridization on small strained molecules. For a detailed description of hybridization see appendix*

	Bicyclobutane		Methylene cyclopropane		Methylene cyclopropene		Cyclobutadiene	
	can. hybrid.	Del Re's hybrid.	can. hybrid.	Del Re's hybrid.	can. hybrid.	Del Re's hybrid.	can. hybrid.	Del Re's hybrid.
E^0	−2422.042	−2426.286	−2333.893	−2334.229	−2026.315	−2026.926	−2109.855	−2110.093
m_1	− 0.111	− 0.203	− 0.100	− 0.141	− 0.114	− 0.181	− 0.155	− 0.189
m_2	− 9.086	− 5.502	− 4.041	− 3.997	− 4.990	− 4.273	− 2.646	− 2.395
$E^0 + m_1 + m_2$	−2431.239	−2431.991	−2338.034	−2338.367	−2031.419	−2031.419	−2112.556	−2112.677
d_1	− 4.471	− 4.059	− 4.037	− 4.036	− 3.678	3.681	− 3.679	− 3.670
d_2	− 3.653	− 3.321	− 3.141	− 3.132	− 4.741	4.698	− 4.788	− 4.787
$E^0 + E^2$	−2439.365	−2439.373	−2345.213	−2345.537	−2039.839	−2039.761	−2121.085	−2121.136
$m_1 - d_1$	0.024	0.045	0.022	0.030	0.025	0.038	0.026	0.041
$m_1 - m_1$	0.021	0.036	0.010	0.016	0.006	0.016	0.018	0.029
$m_1 - m_2$	0.255	0.211	0.024	0.131	0.050	0.108	0.045	0.147
$m_1 - d_2$	0.026	0.045	0.012	0.019	0.007	0.020	0.022	0.035
$m_2 - d_2$	0.105	− 0.353	− 0.079	− 0.204	− 0.078	− 0.143	− 0.031	− 0.041
$d_1 - d_2$	2.124	1.481	1.501	1.498	2.412	2.386	2.512	2.513
$m_2 - m_2$	− 1.130	− 0.445	0.570	− 0.304	− 0.164	− 0.536	0.003	− 0.184
$d_2 - d_2$	0.847	0.521	0.791	0.772	1.647	1.620	1.993	1.972
$E^0 + E^2 + E^3$	−2437.080	−2437.830	−2342.360	−2343.575	−2035.933	−2036.249	−2116.495	−2116.631
E_{SCF}	−2432.866		−2338.900		−2032.167		−2112.966	
E_v [a]	1676.616		1585.042		1313.847		1396.026	
$E_{SCF} + E_v$	− 756.250		− 753.858		− 718.320		− 716.940	
$E^0 + E_v$	− 745.426	− 749.670	− 748.851	− 749.187	− 712.468	− 713.829	− 713.829	− 714.067
$E^0 + m_1 + m_2 + E_v$	− 754.623	− 755.375	− 752.992	− 753.325	− 717.572	− 717.533	− 716.630	− 716.651
$E^0 + E^2 + E_v$	− 762.749	− 762.749	− 760.171	− 760.495	− 725.992	− 725.914	− 725.059	− 725.110
$E^0 + E^2 + E^3 + E_v$	− 760.464	− 761.214	− 757.318	− 758.538	− 722.086	− 722.402	− 720.469	− 720.605

[a] E_v = nuclear repulsion energy − other notations as in Ref. [2].

1. The simple SCF procedure,
2. Our perturbative method with two different starting points,
   - the canonical hybridization,
   - the Del Re's best overlap choice of the hybrids.

We give in Table 2 the detailed results for a series of four molecules. This small list involves two pairs of isomers the bicyclobutane and methylene cyclopropane on one hand, and the methylene cyclopropene and the cyclobutadiene on the other hand.

These calculations are interesting from two points of view.

As concerns the stability of the method, and the choice of the atomic hybrids, it appears that the results of the two perturbation expansions are very close. The maximum overlap criterion gives a better zeroth order determinant in four cases, sometimes by a very important amount, and it seems a convenient procedure.

Concerning the comparison of the energies of the isomers, it should be mentioned that Thornton and Jordan noticed that the CNDO-SCF results [6] often predict incorrect relative energies (stabilities) of isomers, especially when they have a different number of double bonds. We reproduce in Table 3 the differences between the energies of respectively bicyclobutane (I) (methylene cyclopropene (III))

Table 3. *Energy differences between isomers (in eV) (including nuclear repulsions)*

mole-cules \ method	0th order	SCF	2nd order monoexc. only	2nd order total	3rd order monoexc. only	3rd order total
$E_I - E_{II}$	− 0.483	− 2.392	− 2.050	− 2.272	− 2.091	− 2.681
$E_{III} - E_{IV}$	+ 0.988	− 1.380	− 0.882	− 0.804	− 1.286	− 1.797

and methylene cyclopropane (II) (cyclobutadiene (IV)). The relative stabilities of these isomers are not known experimentally, but it is interesting to analyse the behaviour of the difference in the perturbation series.

The fully localized energies are completely off. The main difference comes from the delocalization monoexcitations (m_2) which are taken into account in the SCF process: the diexcitations which lead to the so called correlation energy do not introduce significant modifications in the 2nd order energy (compare columns 3 and 4 of Table 3). This result is actually surprising for these isomers are very different, with very different bond lengths and one could have imagined that the correlation energy would be very different and contribute much to the isomerization energy. Appearingly approximate cancellations occur and the differences between the 2nd order energies, much below the SCF levels, are not far from the differences between the SCF energies. However the diexcited configurations give an important contribution at the third order.

3. Discussion: The Maximum Overlap Hybridization and Energetic Properties

The main conclusion of this analysis is that:

1. The zeroth order, fully localized determinant energy is quite sensitive to the choice of the bond orbitals and, when they are constructed of two hybrids, to the choice of the hybrids. This confirms the "ab initio" analysis on NH_3 [9], H_2O [10], and other small polyatomics molecules [11], mainly by Del Re, Mc Weeny and Ohno.

At this step the investigation has only a conceptual interest, to demonstrate that a "chemical-formula" wave function in which each pair of electron is in a chemical bond or lone pair, could have a large overlap with the SCF wave function and an energy not far above the SCF energy. But one cannot remain at this step. It is of poor interest to improve this zeroth order wave function, which needs a certain work to be built, in the direction of the SCF determinant, as Hamano did [12].

An approximation as the fully localized determinant is only interesting as the zeroth order step of a process which enables to go beyond the classical SCF scheme, or which presents a greater simplicity and intelligibility.

2. The perturbative development of the correspondant configuration interaction matrix leads to both advantages (inclusion of a part of the correlation energy and clear physical significance of the various terms). Using this technique, the final result becomes less sensitive to the choice of the basic parameters (bond hybridation and polarity of the bonds). The perturbation expansion compensates

most of the defects of the zeroth order determinant: the classical hybridization or the maximum overlap hybridization lead to energies which are very close to the minimal energy.

An other amazing phenomenon is that the maximum overlap criterion does not give the best energy for the fully localized determinant. In other words the best bond orbitals to construct the fully localized determinant are not built with the hybrids optimizing the overlap in the bonds. This fact is not surprising, since the maximum overlap criterion is a spatial criterion, while we look for an energy. One could imagine that the disagreement would disappear when the non diagonal monoelectronic matrix elements are supposed to be proportional to the overlap:

$$\beta_{XY} = K S_{XY}. \tag{5}$$

This is not a sufficient condition. It is also necessary that

1. K is independant of the bond.
2. There is no polarity in the bond Molecular Orbitals.
3. The approximations over the nuclear and coulombic atomic orbitals are those of the CNDO II scheme (all tri- and quadriorbital bielectronic integrals neglected, all bielectronic bi-orbital integrals equal between all the charge distributions pp of atom A and qq of atom B, nuclear integrals equal to bielectronic integrals).

With the two last assumptions the bielectronic repulsion and nuclear attraction are constant when one changes the hybridization and are not concerned in the variation of the hybridization.

The diagonal monoelectronic elements α_i may depend of the hybridization state (and for instance their value may be different for s and p). But the ortho-normality conditions of the hybridization transformation and the second condition insures that the sum of the diagonal monoelectronic matrix elements

$$\sum \alpha_i = c \tag{6}$$

is constant, although the α_i depend of the hybridization.

Then the energy may be written as

$$\sum_i C_i + \sum_i (\alpha_i + \alpha'_i) + \sum_i 2\beta_i \tag{7}$$

where the α summations over i indicate summations over all bonds (and lone pairs), α_i and α'_i concern the two hybrids of the bond i, and c_i is characteristic of the electrostatic energy of bond i. The conditions 0 and 1 insure that the energy will be minimum if $\sum_i S_i$ (i.e. the sum of bond overlaps) is maximum.

When one forgives one of these conditions, for instance if one introduces polarities in the bond, or if one uses the Wolfsberg-Helmholtz approximation [13] as in the CNDO scheme:

$$\beta_{XY} = K S_{XY} \frac{(\alpha_X + \alpha_Y)}{2}. \tag{8}$$

The maximum overlap does not give the best energy. In the last case for instance, one still has $\sum \alpha_i = c$, but the condition: $\sum_i 2\beta_i$ maximum leads to

$$\sum_i \left[\frac{dS_i}{ds}(\alpha_i + \alpha'_i) + S_i\left(\frac{d\alpha_i}{ds} + \frac{d\alpha'_i}{ds}\right)\right] = 0 . \tag{9}$$

For instance in the case of cyclopropane, one must minimise $\beta_{CC} + 2\beta_{CH}$ with respect to the s character, and one obtains:

$$\frac{dS_{CC}}{ds}\alpha_C + \frac{d\alpha_C}{ds}S_{CC} + (\alpha'_C + \alpha_H)\frac{dS_{CH}}{ds} + \frac{d\alpha'_C}{ds}S_{CH} = 0 \tag{10}$$

where α_C is the monoelectronic diagonal element of the C–C carbon hybrid, and α'_C corresponds to the C hybrids directed towards the proton. Then, due to the Eq. (6)

$$\frac{d\alpha_C}{ds} = -\frac{d\alpha'_C}{ds} \tag{11}$$

and the condition may be rewritten:

$$\frac{dS_{CC}}{ds}\alpha_C + \frac{dS'_{CH}}{ds}(\alpha'_C + \alpha_H) + \frac{d\alpha_C}{ds}(S_{CC} - S_{CH}) = 0 \tag{12}$$

which is different from $\dfrac{dS_{CC}}{ds} + \dfrac{2dS_{CH}}{ds} = 0$ (Randic's maximum overlap criterion) except if $\alpha'_C = \alpha_H = \alpha_C$ $\qquad S_{CH} = S_{CC}$.

With the Wolfsberg-Helmholtz approximation, the maximum overlap criterion cannot give the minimal energy for the fully localized determinant except if the system is homogeneous (same α and S), which is a rather uninteresting case.

What we called the maximum overlap criterion herebefore was the maximum of the sum of bond overlaps. This is a special case of Randic *et al.* procedure [8]. The Del Re's process [7] that we used actually maximizes the overlap in each bond with hybrids exactly pointing along the bonds, then orthogonalize these by a local transformation allowing variations in the directional properties of the hybrids according to the relative values of initial bond overlaps. Randic *et al.* [8] introduced a different ponderation of the bond overlaps; they maximize actually the function

$$\sum_i a_i S_i$$

where the a values are characteristics of the bonds. It is clear however that this improvement cannot reproduce the optimal behaviour required by the Wolfsberg-Helmholtz approximation (Cf. Eq. [9]). The fact that the Randic *et al.* criterion [8] has given poorer results in our case than the Del Re's procedure may come either from a bad choice of the constants a_i (related to the overlaps) or to the fact that their calculations were derived with $Z_H = 1.00$ while ours are done with $Z_H = 1.2$.

Anyway the results after the third order are not very different and for unstrained molecules the deviation from one of the canonical hybridizations of the best fully localized MOs is sufficiently small to be neglected or accounted for by one of the classical Maximum Overlap criterions.

Appendix

Properties of typical hybridization schemes

Cyclopropane

	Canonical	Del Re's criterion
C–C overlap		0.5878
C–H overlap		0.7003
Hybrid character		
C–C	sp^3	sp^5
C–H	sp^3	sp^2
Angle between orbital		
C–C	24°44′	23°32′
C–H	4°16′	0°37′

Cyclobutane

	Canonical	Del Re's criterion
C–C overlap		0.6213
C–H overlap		0.6897
Hybrid character		
C–C	sp^3	$sp^{3.72}$
C–H	$sp^{3'}$	$sp^{2.47}$
Angle between orbital and bond.		
C–C	9°44′	7°48′
C–H	2°16′	0°3′

Bicyclobutane
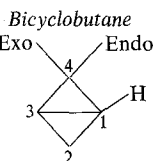
C_3–C_1–H *angle 133°*

	Canonical	Del Re's criterion
Overlaps		
C_1–C_2		0.5916
C_1–C_3		0.4981
C_2–H_{exo}		0.7030
C_2–H_{endo}		0.7002
C_1–H		0.7119
Hybrid character		
1–3	p	sp^9
1–2	sp^2	sp^3
1–H	sp^2	$sp^{1.54}$
2–1	sp^3	$sp^{4.3}$
2–H	sp^3	$sp^{2.2}$

Methylene cyclopropane
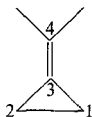
	Canonical	Del Re's criterion
Overlaps		
C_1–C_2		0.5878
C_1–C_3		0.5968
C_3–C_4		0.8029
		$(0.2699\,\pi)$
C_1–H		0.7003
CH–H		0.7050
Hybrid character		
C_1–C_2	sp^3	$sp^{4.26}$
C_1–C_3	sp^3	$sp^{4.26}$
C_3–C_1	sp^2	$sp^{3.13}$
C_3–C_4	$sp^2(+p\pi)$	$sp^{0.94}$
C_4–C_3	$sp^2(+p\pi)$	$sp^{1.58}$
C_1–H	sp^3	$sp^{2.23}$
C_4–H	sp^2	$sp^{2.27}$

Methylene Cyclopropene
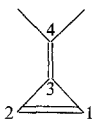
	Canonical	Del Re's criterion
Overlaps		
C_1–C_2		0.7375 $(0.2699\,\pi)$
C_1–C_3		0.6084 $(0.2098\,\pi)$
C_3–C_4		0.8026 $(0.2699\,\pi)$
C_1–H		0.7202
C_4–H		0.7050
Hybrid character		
C_1–C_2	$sp^2(\sigma)$	$sp^{1.86}$
C_1–C_3	$sp^2(\sigma)$	$sp^{3.48}$
C_1–H	sp^2	$sp^{1.35}$
C_3–C_1	sp^2	$sp^{3.08}$
C_3–C_4	$sp^2(\sigma)$	$sp^{0.96}$
C_4–C_3	$sp^2(\sigma)$	$sp^{1.58}$
C_4–H	sp^2	$sp^{2.27}$

Cyclobutadiene

	Canonical	Del Re's criterion
Overlaps		
C_1–C_2		0.6495 (0.2009 π)
C_1–C_4		0.7619 (0.2699 π)
C_1–H		0.7098
Hybrid character		
C_1–C_2	$sp^2(\sigma)$	$sp^{2.44}$
C_1–C_4	$sp^2(\sigma)$	$sp^{2.09}$
C_1–H	sp^2	$sp^{1.60}$

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