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In Situ Atomic Orbitals and Extended Basis Molecular Calculations

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Little use has been made so far of large-basis calculations of SCF molecular orbitals to bring up to date old questions like the nature of the atomic orbitals referred to in the standard theory of directed valency. In this paper, along with some novelties concerning the inclusion of *d* orbitals in hybrids, we indicate some of the points waiting to be discussed, give the whole scheme needed to express canonical orbitals as combinations of one *in situ* orbital per atom, and present a sample application of that scheme to a double-zeta study of the halogeno-methanes, as studied by Berthier and coll. Interesting indications regarding radial distortion and hybridization have been obtained.

INTRODUCTION

The widespread availability of sophisticated *ab-initio* programs for the SCF orbitals of molecules has made analysis of results an urgent problem. In the literature, attempts to tackle it are numerous, but, as far as we know, they either work on energy partitions[1] or on linear transformations of canonical orbitals, especially with a view to localizing them[2]. In this paper we wish to consider the more modest, but perhaps equally essential problem, of direct analysis of the canonical orbitals issued from a standard extended-basis *ab-initio* computation.

Our point of view, already briefly tested in an application to model dipeptides[3], is that it should be possible to recast a canonical orbital in a form that can be interpreted in terms of one possibly hybrid atomic orbital per atom, so as to divide the interpretational problem into the tradional two: weights of atoms in an MO and characteristics of AO's representing them.

The analysis suggested in this paper is a return to the old and still unsolved question of the MAO's (Modified Atom Orbitals)[4,5]. This is based on the philosophy which has guided the quantum chemistry of great pioneers like Mulliken, Pauling, Coulson, and still guides most applications of theory to organic chemistry — as is proven by the work of R. Hoffmann[6]: namely, that there

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exist minimal-basis atomic orbitals, which are entitled to represent each specific atom in the electronic wave function of a molecule.

In attempts to put this point of view on firmer formal grounds Mulliken referred to the united-atom and separated-atoms limit, and was led to emphasize that an atomic orbital *in situ* may be a MAO not only because of hybridization, but because of radial distortions due to promotion and to the environment[4b]. As concerns hybridization, questions like the consequences of differences in the radial parts of the *s*, *p*, and *d* components, as well as the very characterization of *d*-including hybrids remain largely unexplored.

Therefore, before giving some indications concerning the formal analysis of canonical MO's — quite a straightforward business — we shall present a few remarks on the much more intricate problem of the interpretation of results.

RADIAL DISTORTION

Overlap can be used as a compact and quite sensitive measure of differences in the radial behavior of atomic orbitals. Therefore, it is used in Tables I and II to illustrate two different effects: the artificial radial distortion introduced by the choice of the basis, and the physically significant distortion due to promotion.

Table I provides a comparison between different LCSTO forms of the 4*s* AO of nickel: the quadruple-ζ (practically HF) forms for the $3d^94s$ (^{3}D) and for the $3d^84s^2$ (^{3}F) configurations, and the approximate double-zeta and single-zeta forms for the latter configuration[7a]. The overlap values at the standard Ni—Ni distance in the crystal and at the distances of successive neighbors are given.

Inspection of Table I shows that double-zeta orbitals give quite reasonable overlap values, indeed values larger than those of the HF AO's for distances up to twice the equilibrium distance. Therefore, they are only dangerous in *s*-band calculations in solids, where larger order neighbors are very important to ensure the convergency of computations. The values shown also remind us of the fact that, although the statement that limited-basis calculations tend to underestimate tails holds true in general, the inference that the corresponding overlap integrals are smaller than in the »best-atom« case is not generally valid even at distances of the order of the bond length.

TABLE I

(4s,4s) Overlap Values for ^3D ($3d^94s$) and ^3F ($3d^84s^2$) of Nickel at the Distances R_n of Neighbours of Various Orders in the Hartree-Fock Limit (HF1 and HF2 Respectively). For the d^8s^2 Configurations also Overlaps According to Double-zeta (DZ), Single-zeta (SZ) Approximations[a]

R_n	HF1	HF2	DZ	SZ
2.492	.5176	.4491	.4613	.4320
3.524	.2935	.2265	.2346	.1973
4.316	.1709	.1197	.1226	.0864
4.984	.1028	.0665	.0659	.0379
6.593	.0263	.0144	.0117	.0036

[a] Linear combination of STO's according to Clementi and Roetti (Ref. 7a). In all cases the linear combination orthogonalized to inner shells has been taken.

A comparison of HF 4s orbitals for the states ^3F and ^3D indicates that radial distortion by *promotion* is very important: the overlap values associated with the d^9s^1 configuration are between 15% and 82% higher that those of the d^8s^2 configuration. Now, it may be expected that other two-center matrix elements behave like overlap: then, one may suspect that many cases where 'correlation' has been invoked as a source of error are in fact related to lack of adaptability of the basis to promotion — *i. e.* failure to use a suitable prepared and sufficiently flexible basis. This is all the more important since the molecular environment can also be a cause of radial distortion.

We do not know of any published study explicitly devoted to this question: it is currently tackled only indirectly when some flexibility is allowed in Gaussian-type bases. The latter can be excellent approximation of HF atomic orbitals even at comparatively large distances at least as overlap values go; this is illustrated in Table II, with the confidence suggested by Table II, radial distortion can be discussed in terms of current GO basis sets; in the subsequent section we shall propose a pattern for such a discussion of the example of carbon in the methylhalogenides as computed by Berthier and coll.[8]

TABLE II

Overlap Integrals: Gaussian vs. STO Bases (Carbon-Carbon Bond)

R		$ss^{1,2}$			$pp\sigma^{1,2}$			$pp\pi^{1,2}$	
Å	1	2	3	1	2	3	1	2	3
1.54	.3572	.3566	.3570	.2645	.2648	.2650	.2678	.2677	.2222
1.64	.3164	.3158	.3157	.2719	.2723	.2653	.2350	.2350	.1924
1.74	.2788	.2781	.2779	.2731	.2736	.2612	.2058	.2058	.1662
2.00	.1966	.1955	.1959	.2557	.2564	.2370	.1445	.1443	.1121
2.50	.0939	.0918	.0946	.1863	.1873	.1655	.0711	.0708	.0491

[1] column (1) contains HF overlaps according to Clementi and Roetti (Ref. 7a)
column (2) contains overlaps for 10*s*6*p* GO proposed by Huzinaga (Ref. 7b)

[2] column (3) contains overlap integrals obtained when the double zeta basis of the following tables (Ref. 8) is assigned coefficients *a* and *b*.

a) atomic orbital: $\Sigma\,(a \cdot 1s_C\,(\zeta_j) + b \cdot 1s_C\,(\zeta_j'))c_j$

ζ	ζ'	c	
12.6727	5.02536	—.054620	
.479273	.190056	.655905	$a = .745895$
.186530	.073969	.390346	$b = .279695$

b) atomic orbital: $\Sigma\,(a \cdot 2p_C\,(\zeta_j) + b \cdot 2p_C\,(\zeta_j'))c_j$

ζ	ζ'	c	
9.92496	2.101970	.093444	
2.36586	.051057	.475417	$a = .375187$
.73330	.155303	.575982	$b = .706207$

HYBRIDIZATION

A mathematical formulation of the qualitative theory of directed valency was given long ago by one of us[9]. For each atom, hybrid orbitals were determined so as to maximize separately the overlaps of the bonds in which the given atom participated; and then they were made orthogonal to one another by a least-square procedure, suitable weights ensuring certain physically important conditions (lower flexibility for hybrids corresponding to higher overlap and lone-pair hybrids). The resulting hybrid atomic orbitals could even be used to predict the geometries of molecules[10]. They were used to construct zero-order bond-orbitals in the PCILO method[11].

The resulting »maximum-localization hybrid orbitals« (MLHO) provide a description of binding which, in the case of familiar molecules, clearly appears to be in agreement with the simple idea of directed valency[12].

Two difficulties appear, one technical, the other conceptual: the inclusion of d orbitals, and the significance of hybrids when the radial parts of the 'pure' orbitals are different.

Inclusion of d Orbitals

So far, no computing program has been made available to extend the MLHO procedure to d-orbitals. We have therefore tackled the problem, and a program determining general s, p, d hybrid types has been prepared. The results are best illustrated by diagrams of the types shown in Figures 1 and 2. In Figure 1 we present the hybrid orbitals of the central iron atom in two planar clusters of five iron atoms, in a square and rectangular arrangement, respectively.

The distortions due to the presence of d orbitals are evident in the smaller lobes, even though the hybrids have a familiar shape.

The role of d-hybrids in determining the direction of a general hybrid

$$| h_j \rangle = a_{1j} | s \rangle + b_{1j} | p\,\sigma \rangle + b_{2j} | p\,\pi \rangle + b_{3j} | p\,\pi' \rangle + c_{1j} | d\,\sigma \rangle + c_{2j} | d\,\pi \rangle + \\ + c_{3j} | d\,\pi' \rangle + c_{4j} | d\,\delta \rangle + c_{5j} | d\,\delta' \rangle \qquad (1)$$

(where we shall normally assume that the σ axis is the z axis) is not intuitively clear. We have adopted the following definitions: The *direction* of an s, p, d hybrid orbital (taken as the direction of the p component in the case of $s, p,$ hybrids) as well as its polarization are obtained from the radius vector of the centroid of the hybrid, *i. e.* from the expectation-value vector $\langle x \rangle\, \underline{i} + \langle y \rangle\, \underline{j} + \langle z \rangle\, \underline{k}$. It is easy to show that:

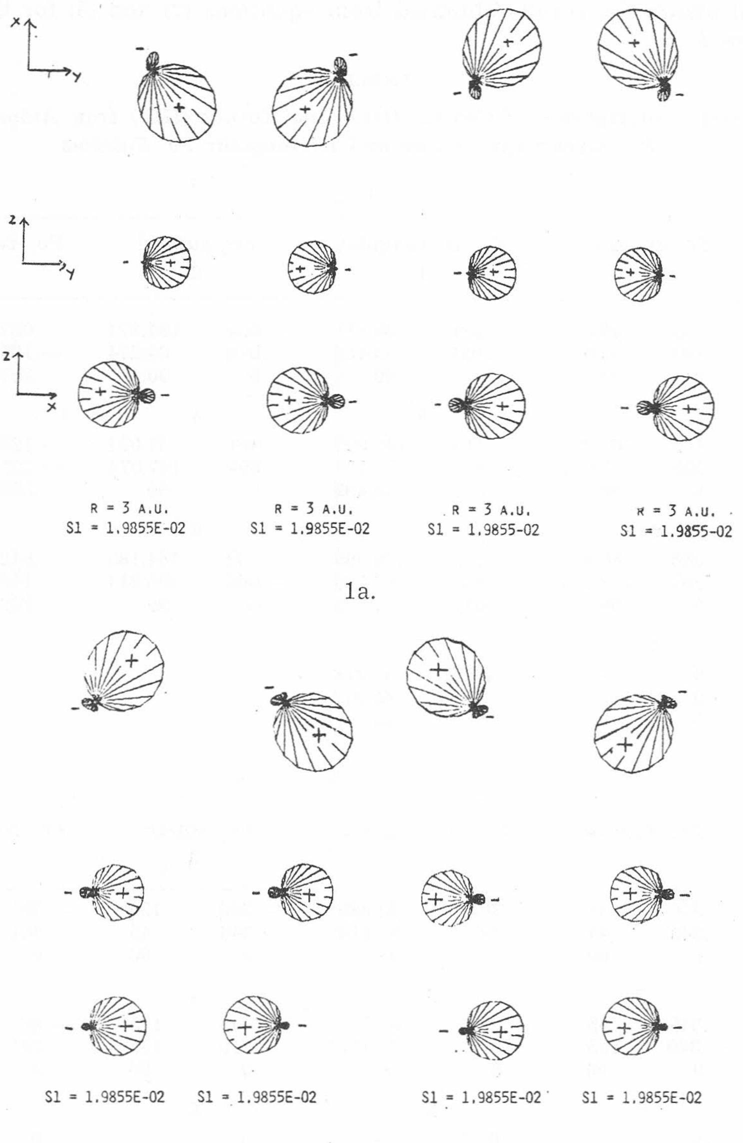
$$\begin{aligned} \langle x \rangle &= a_1 b_2 W_1 + \sqrt{3}\,(b_2 c_5 + b_3 c_4 + b_1 c_2 - b_2 c_1/\sqrt{3})\, W_2 \\ \langle y \rangle &= a_1 b_3 W_1 + \sqrt{3}\,(b_2 c_4 + b_3 c_5 + b_1 c_3 - b_3 c_1/\sqrt{3})\, W_2 \qquad (2) \\ \langle z \rangle &= a_1 b_1 W_1 + (2\, b_1 c_1 + \sqrt{3}\, b_2 c_2 + \sqrt{3}\, b_3 c_3)\, W_2 \end{aligned}$$

with

$$W_1 = \langle s\, | \, z \, | \, p\,\sigma \rangle \quad \text{and} \quad W_2 = - \langle p\,\pi \, | \, x \, | \, d\,\sigma \rangle \qquad (3)$$

In the case of $4s$, $4p$, $3d$ STO's with orbital exponents ζ_s, ζ_p, ζ_d the two parameters of Eq. (3) are

$$W_1 = \left(\frac{2\sqrt{\zeta_s \zeta_p}}{\zeta_s + \zeta_p} \right)^9 \frac{1}{\zeta_s + \zeta_p} \frac{9}{\sqrt{3}} \quad ; \quad W_2 = \left(\frac{2\sqrt{\zeta_p \zeta_d}}{\zeta_p + \zeta_d} \right)^9 \frac{1}{\zeta_d} \sqrt{\frac{14}{15}}$$



1a.

1b.

Figure 1. (a) Angular dependence of the four hybrids of the central iron atom for the square five atoms arrangement I (side : 4.05 Å based on the crystal structure). The overlap integrals have been calculated with the following basis : single zeta STO's for 4*s* and 4*p* ($\zeta_s = \zeta_p = 1.379$) and double zeta STO's for 3*d* ($\zeta_{d1} = 5.35$, $\zeta_{d2} = 1.80$, $c_1 = .5366$ and $c_2 = .6678$); only the four bonds of the central atom were taken into account in the process of determining hybrids. The values of S_1 give the scaling factors used for each series of drawings. The centroid components and angle are given in Table III.

(b) Same as (a) for the rectangular arrangement II (sides 2.86 and 4.05 Å).

Table III shows the results obtained from equations (2) and (3) for the system of Figure 1.

TABLE III

Characteristics of Hybrids of Central (IIIa) and Corner (IIIb) Iron Atoms (Fe_c and Fe_v respect.) in Square and Rectangular Fe_5 Systems

III a

Hybrid	Fe_v square 1		Fe_v rectangular 1		Fe_v square 2		Fe_v rectangular 2	
	.363	45.0	.409	36.531	—.054	154.274	.087	75.659
	.363	45.0	.303	53.468	.026	64.274	—.165	118.043
	0	90	0	90	0	90	.297	32.091
	3		3		4		4	
	—.145	167.297	—.215	140.907	.061	57.074	—.198	131.327
	.033	77.297	.170	52.192	—.094	147.074	—.225	138.616
	0	90	—.041	98.499	0	90	.009	88.211
	5		5		6		6	
	.008	88.174	—.108	138.995	—.232	164.185	.042	83.603
	—.263	178.174	.054	67.723	—.066	105.814	—.146	112.976
	0	90	.077	57.575	0	90	—.342	156.049
	7		7					
	0	—	—.016	152.318				
	0	—	.009	62.318				
	0	—	0	90				

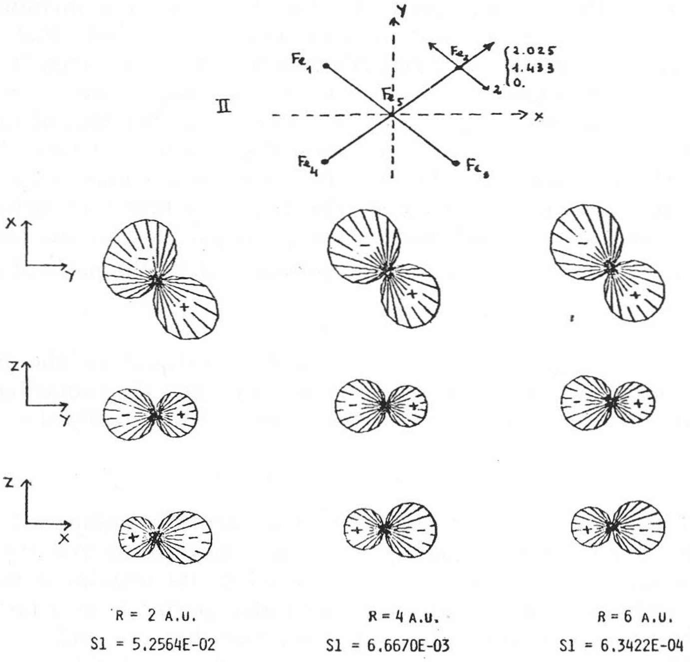
III b

Hybrid	Fe_c square 1		Fe_c rectangular 1		Fe_c square 2		Fe_c rectangular 2	
	.340	45	.361	38.889	—.340	135	—.291	128.889
	.340	45	.291	51.110	.340	45	.361	38.889
	0	90	0	90	0	90	0	90
	3		3		4		4	
	.340	45	.291	51.110	—.340	135	—.361	141.110
	—.340	135	—.361	141.110	—.340	135	—.291	128.889
	0	90	0	90	0	90	0	90
	5		5		6		6	
	0	—	0	—	0	—	0	—
	0	—	0	—	0	—	0	—
	0	—	0	—	0	—	0	—

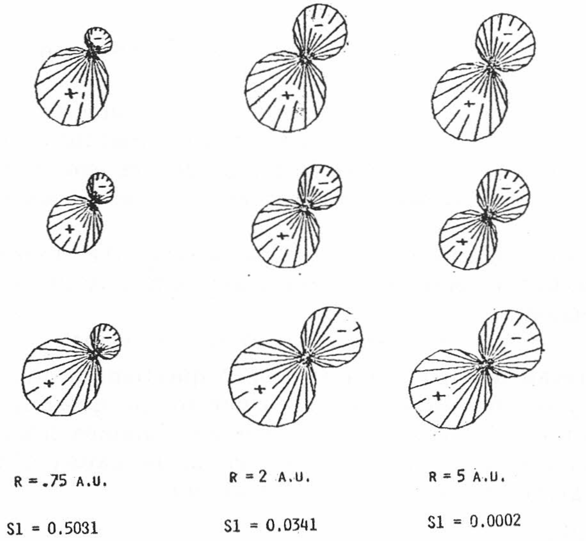
For each hybrid, the components (a. u.) of the radius vector of the centroid as well as its angles with the reference axes x, y, z are given.

The expected square arrangement of the binding hybrids of central iron atom in the square system is correctly produced.

Note that the »lone pair« hybrids of Fe_v are pushed out of the x, y plane because of the weight $\lambda \neq 0$ (.15) assigned to them (λ is a measure of the tendency for the lone pair hybrid to retain an s character in spite of the orthogonalization to other hybrids (Ref. 15).



2a. Fe_5



2b. AsF_3

Figure 2. (a) Rectangular Fe_5 (*cf.* Figure 1b): angular dependence of the »lone-pair« hybrid 2 of the corner atom Fe_2. This hybrid has been obtained in the same way as those of Figure 1. The curves are given for different distances R from the center Fe_2 with suitable scaling factors S_1. (b) Same as (a) for As in AsF_3.

Eq. (2) solve the problem posed by the direction of d including hybrids when these contain a p-contribution; and they clearly show that, if ζ_d is of the order 7/11 ζ_p, even a small d-contribution may seriously modify the direction of the hybrid as defined by the p orbitals. This may create very interesting situations as regards the »shapes« of the hybrids. Another special limiting case is found when the p contribution vanishes. Clearly, in that case the centroid of the orbital coincides with the center of the pure components. Yet, as is well-known s, d hybrids are oriented. The reason is that they behave like an ellipsoid; the axes can be obtained as the principal axes of the tensor $\langle \underline{r}\,\underline{r} \rangle$ consisting of the expection values of the products of all the pairs of coordinates $\langle z^2 \rangle$, $\langle x\,z \rangle$, *etc*...

RADIAL DEPENDENCE

Even when d hybridization is not a source of difficulties, the definition of the p-character of a hybrid is a delicate question when the radial factors of the p orbitals are different from those of the s ones. In the standard expression

$$| sp^n \rangle = \cos \alpha \,| s \rangle + \sin \alpha \,| p \vec{\zeta} \rangle \tag{4}$$

$\vec{\zeta}$ denotes the axis of the hybrid and $\sin^2 \alpha$ is currently assumed to denote its p weight (n being given by $\mathrm{tg}^2\, \alpha$) : $\sin^2 \alpha$ somehow measures the degree to which the given hybrid resembles a p orbital in its angular behavior. This, however, is only rigorously true when the radial parts of the s and p orbitals are the same up to a constant factor. For suppose that $| s \rangle$ and $| p \rangle$ are represented by STO's with orbital exponents 2 and .02 respectively, then a ($2s$, $2p$) digonal hybrid ($\alpha = 45°$) directed along the z-axis will have the form

$$\langle r \,|\, sp \rangle = \frac{N}{\sqrt{2}}\, r \cdot (\frac{1}{3}\, e^{-2r} + e^{-0{\cdot}02} \cos \Theta);$$

which means that, whereas for $r \to 0$ this is a standard sp hybrid, when r is very large the p part dominates to such an extent that the hybrid is practically p. A more realistic case is illustrated in Figure 2b: the evolution with the distance of an (s, p, d) hybrid orbital of an iron atom at the corner of the rectangle of Figure 1.

Much work remains to be done to develop the interpretation based on hybridization, but we believe that the question briefly illustrated here deserves further reflection.

ANALYSIS OF CANONICAL ORBITALS

Having recalled some of the still open questions in the elementary atomic orbital theory of chemistry, we now come to the question mentioned above: extract from the canonical molecular orbitals, obtained from an extended basis *ab-initio* computation, information concerning the nature of the atomic orbitals used by the given atoms in the given molecule.

General Analysis

Let $| Anlm \rangle$ be a pure AO centered on atom A and let $| Anlm\mu \rangle$ be an LGCO—AO, (*i. e.* a given contracted GO, which will be normally associated with a specific principal quantum number even if it consists of 1s Gaussians):

$$| Anlm \rangle = \sum_{\mu} D^{nlm}_{A\mu} \,| Anlm\, \mu \rangle \tag{5}$$

In terms of LCGO -AO's and pure -AO's, the j-th molecular orbital is written:

$$|\, j \,\rangle = \sum_{A,n,l,m,\mu} \mathrm{d}^{nlm}_{Aj\mu} \,|\, Anlm\mu \,\rangle = \sum_{A,n,l,m} C^{nlm}_{Aj} \,|\, Anlm \,\rangle \tag{6}$$

When an extended basis is used the coefficients D^{nlm}_{A} of Eq. (5) vary according to the MO under consideration, and therefore Eq. (5) must be replaced by

$$|\, Anlmj \,\rangle = \sum_{\mu} D^{nlm}_{Aj\mu} \,|\, Anlm\mu \,\rangle \tag{7}$$

Consider in the j-th MO the LCGO-AO's associated to A and to the same quantum number set nlm, with their coefficients in $|\, j \,\rangle$. Their contributions can be reduced to that of a single pure AO carrying a coefficient C^{nlm}_{Aj} when in $|\, j \,\rangle$. Therefore, the coefficients D of Eq. 7 must be obtained from the relationship

$$D^{nlm}_{Aj\mu} = d^{nlm}_{Aj\mu} \,/\, C^{nlm}_{Aj} \tag{8}$$

and

$$c^{nlm}_{Aj} = U \left\{ \sum_{\mu,\nu} d^{nlm}_{Aj\mu} \, d^{nlm}_{Aj\nu} \,\langle\, Anlm\mu \,|\, Anlm\nu \,\rangle \right\}^{1/2} \tag{9}$$

(U being the sign of the major contribution).

The linear combination $|\, Anlmj \,\rangle$ thus obtained is not necessarily the correct representation of the atomic orbital representing A in $|\, j \,\rangle$ with quantum numbers nlm, because it is not in general orthogonal to other LCGO orbitals with the same l, m pair. This results in the appearance in $|\, j \,\rangle$ of contributions of lower-n orbitals of A wich may be just due to the intra-atomic orthogonality requirement. We take care of this by Schmidt orthogonalization so as never to admix outer shells to inner shells.

With the simplified notation:

$$M \text{ stands for } Almj \tag{10}$$

we obtain for the orthogonalized AO:

$$|\, \overline{Mn} \,\rangle = \frac{|\, Mn \,\rangle - \Sigma \,|\, Mn' \,\rangle \langle\, Mn' \,|\, Mn \,\rangle}{(1 - \Sigma \,|\, \langle\, Mn' \,|\, Mn \,\rangle \,|^{2})^{1/2}} \tag{11a}$$

where the summations are taken over $n' = 1, \ldots, n-1$. Eq. (11a) defines a triangular linear transformation $\mathbf{T}$ taking the nonorthogonal AO set $|\, \mathbf{M} \,\rangle$ into the orthogonalized one $|\, \overline{\mathbf{M}} \,\rangle$:

$$|\, \overline{\mathbf{M}} \,\rangle = |\, \mathbf{M} \,\rangle \,\mathbf{T} \tag{11b}$$

In the same matrix notation Eq. (6) can be written

$$|\, j \,\rangle = \sum_{M} |\, \mathbf{M} \,\rangle \, C_{\cdot j}^{M}$$

($\cdot j$ denoting the j-th column of the given matrix); and therefore

$$|\, j \,\rangle = C \sum_{M} |\, \overline{\mathbf{M}} \,\rangle \,\mathbf{T}^{-1} \,\mathbf{C}_{j}^{M} \tag{12}$$

Using the notation

$$\bar{C}^{nlm}_{Aj} \quad (\mathbf{T}^{-1} \cdot \mathbf{C}_j^{M})_n \tag{13}$$

Eqs. (6) and (7) may be rewritten in the form

$$|\, j \rangle = \sum_{A,n,l,m} \bar{C}^{nlm}_{Aj} \,|\, \overline{Anlmj} \rangle \tag{14a}$$

$$|\, \overline{Anlmj} \rangle = \sum_{\mu} \bar{D}^{nlm}_{Aj\mu} \,|\, \overline{Anlm\mu} \rangle \tag{14b}$$

where the bars denote that the orthogonalization procedure has been applied: the bar on the LCGO-AO $|\, Anlm\mu \rangle$ reminds us that now also GO combination originally associated with principal quantum numbers lower than n are included in the set for n.

In the following, we *shall drop the bars* and assume that the orthogonalization procedure has been performed, or, — as is the case with pseudopotential calculations — has not been necessary.

The last step in the general analysis is construction of hybrid orbitals $|\, Aj \rangle$. As the $|\, Anlmj \rangle$ orbitals form an orthonormal set, we write

$$C_{Aj} = U \sqrt{\sum_{nlm} |\, C^{n,l,m}_{Aj} \,|^2} \qquad (U = \text{sign of } s \text{ component}) \tag{15a}$$

$$c^{nlm}_{Aj} = C^{nlm}_{Aj} \,/C_{Aj} \tag{15b}$$

$$|\, Aj \rangle = \sum_{n,l,m} c^{nlm}_{Aj} \,|\, Anlmj \rangle \tag{15c}$$

so that the given MO is finally cast into the form

$$|\, j \rangle = \Sigma\, C_{Aj} \,|\, Aj \rangle \tag{15d}$$

which corresponds to the chemical idea of an LCAO molecular orbital.

We can now proceed to interpret and further elaborate the coefficients and orbitals defined above. Instead of discussing all the general possibilities we shall refer to a specific example which provides an interesting case study and, together with the examples of Ref. 3, covers the most important transformations of the preceding general analysis. The case chosen is a pseudopotential double-zeta calculation of methylhalogenides carried out by Berthier and coll[8]. These calculations do not include inner shells but are most instructive as concerns other important problems like radial distortion.

RADIAL DISTORTION

Table IV presents the double-zeta *in situ* s orbitals of carbon in the four halogenides. The coefficients a and b are nothing but the coefficients $D^{200}_{Aj_1}$ and $D^{200}_{Aj_2}$ of Eq. 7. They may be compared with the free-atom values, evaluated by us by imposing a CC ($2s$, $2s$) overlap value of .357 at an internuclear distance of 1.54 Å. Cases like the fifth MO of CH_3F suggest that in some cases the radial distortion may be very important. The overlap values shown for comparison are consistent with this impression, even though the picture they provide is not dramatic at all. Should we conclude that the current assumption that a reasonable description of a molecule can be provided by standard atomic

TABLE IV

Radial Distortion of Carbon 2s AO's in Halogeno-Methanes CH_3X. Pseudopotential Double-Zeta Calculation with the Basis of Table II[8]. *CC Overlap Obtained from* in situ *2s Orbitals at Various Distances R*

MO	X	a	b	R/Å 1.54	 2.0	 2.5	C_s
1	F	.8655	.1506	.3139	.1592	.0697	—.1310
	Cl	.6074	.4242	.4048	.2379	.1241	.4414
	Br	.6318	.3990	.3965	.2305	.1189	.5695
	I	.6362	.3945	.3959	.2299	.1184	.7454
2	F	.7033	.3247	.3719	.2089	.1036	.7161
	Cl	.6949	.3335	.3749	.2114	.1054	.6328
	Br	.6935	.3350	.3754	.2119	.1057	.5269
	I	.7761	.2475	.3463	.1866	.0883	—.2273
5	F	—.1181	1.1018	.5991	.4271	.2719	—.0922
	Cl	1.2224	—.2632	.1799	.0514	.0020	.0192
	Br	.6848	.3441	.3784	.2145	.1076	.0411
	I	.5186	.5139	.4339	.2641	.1431	—.0721
free at.		.7459	.2797	.3570	.1959	.0946	1

The inclusion of polarization orbitals (*d* on C and F, *p* on H) gives the following results in CH_3F:

MO	X	a	b	1.54	2.0	2.5	C_s
1	F	.9230	.0533	.2817	.1323	.0520	—.1256
2	F	.7893	.2333	.3415	.1827	.0855	.6073
5	F	—.0083	1.0072	.5770	.4032	.2515	.1658

Note: For the meaning of the coefficients *a* and *b* *cf.* note 2a to Table II.

orbitals is not correct? This conclusion would be somewhat surprising in view of the comparative success of minimal basis calculations. The origin of this apparent contradiction lies in the non-orthogonality of the two LCGO-AO's used to represent the two STO's entering the 2*s* orbital. Call $|2s_0\rangle$ the free-atom 2*s* orbital of carbon as defined in Table II. It is easy to construct another orbital $|2s_0'\rangle$ which is orthogonal to $|2s_0\rangle$, and thus represent a standard linear combination of upper shell *s* orbitals. Then, an *in situ* 2*s* orbital can be recast in the form:

$$|2s\rangle = \cos\beta\,|2s_0\rangle + \sin\beta\,|2s_0'\rangle \tag{16}$$

and its percentage of free-atom character can be written

$$u_s = 100\cos^2\beta.$$

This orthogonal decomposition, which assigns radial distortion to some general promotion, leads to a surprising conclusion: even in the seemingly dramatic case of the fifth occupied MO of CH_3F the 2*s* orbital contains 83% of the free-atom one! On the other hand, overlap values show that very small amounts of radial distortion (as measured by weights of $|2s_0\rangle$) may involve serious changes in overlap values: an extreme example is the carbon 2*s* AO in the second MO of CH_3F without and with polarization function: the free-atom orbital weights are 99.952 and 99.949% respectively, but the overlap values at 1.54 Å differ by 10%.

The results for *p* orbitals are similar, except for the fact that only the lowest-lying molecular orbital involves an important distortion.

The morality to be drawn from the above results in not only that, even though free-atom AO's are resonable first order choices for *in situ* AO's — thus confirming a conclusion often drawn from energies, distortions can appear that do not correspond to an obvious trend; but also that slight changes in the basis set or further flexibility might seriously affect conclusions regarding orbital distortion in molecules. A proof of this is given by the analysis of carbon-2*s* distortion when polarization functions are included: the percentage of $|2s_0\rangle$ in the fifth occupied MO of CH_3F goes up by almost four points (cf. Table V).

TABLE V

Radial Distortion and Hybridization of Carbon in the Symmetric Canonical Orbitals of CH_3X. (Pseudopotential Double-Zeta Calculation with the Basis of Table II (Ref. 8))

MO	X	u_s	u_p	c_s	c_p	C
1	F	99.61	91.31	.8719	.4896	.1503
	Cl	99.50	99.65	.9878	.1554	.4468
	Br	99.66	98.12	.9981	.0627	.5706
	I	99.68	86.60	.9996	.0289	.7457
2	F	99.95	99.39	.9885	—.1513	.7253
	Cl	99.93	99.98	.9763	—.2161	.6481
	Br	99.93	99.99	.9628	.2701	.5472
	I	99.98	99.76	.7745	—.6325	.2935
5	F	82.97	99.99	—.2028	.9792	.4545
	Cl	93.25	99.48	.0379	.9992	.5064
	Br	99.90	99.21	.0774	.9970	.5312
	I	98.68	98.85	.1295	.9915	.5409

Explanation:

u_s: percent of free-atom 2*s* orbital (as defined in Table II) resulting from orthogonal decomposition (see text) of the 2*s* orbital;

u_p: *idem* for the *p* orbital;

c_s, c_p: coefficients of the normalized carbon (*s*, *p*) hybrid in the given MO;

C: coefficient of the whole atomic orbital in the given MO.

Hybridization

Combination of *in situ* (radially distorted) pure orbitals gives hybrids, whose *s* and *p* coefficients are presented in Table V. Here again the main question is: are these hybrids transferable, at least between molecular orbitals of the same molecule?

The same answer as for radial distortion holds: they are transferable when the overall weight of the hybrid in the MO is comparatively high. On the contrary, they vary a lot when they obviously correspond to fine details of the molecular electronic structure (weight .3).

A special feature of the hybrids of carbon in the halogenomethanes is that they are practically *s* and *p* when they carry on important weight. This result is quite surprising in view of the fact that we are dealing with an almost tetrahedral carbon, and that it applies in particular to the lowest lying MO, which is clearly the CX bond-orbital. In the case of chlorine it takes the form:

$$.7555\ (.9921\,|s_{\mathrm{Cl}}\rangle - .1255\,|pz_{\mathrm{Cl}}\rangle) + .4469\ (.9879\,|s_{\mathrm{C}}\rangle + .1554\,|pz_{\mathrm{C}}\rangle) \qquad (17)$$

The analysis of hybridization in the case of our test molecules is made particularly difficult by symmetry. Taking into account that, if there were no coupling between bonds, the second symmetric MO should be degenerate with the two immediately higher degenerate antisymmetric orbitals, one may proceed to recombine them in the case of CH_3F so as to have only one hydrogen with a non-vanishing coefficient (neglecting differences in radial distortion of hydrogen 1*s* orbitals). This results in molecular orbitals like the following:

$$|\,2'\,\rangle = -\,.56862\,|\,h_{F2'}\,\rangle = .74575\,|\,h_{C2'}\,\rangle + .27769\,|\,1s_{H3\,2'}\,\rangle \qquad (18a)$$

where

$$|\,h_{F2'}\,\rangle = .31654\,|\,s_{F2}\,\rangle + .23309\,|\,pz_{F2}\,\rangle - .42251\,|\,px_{F2}\,\rangle + .81668\,|\,py_{F2}\,\rangle \qquad (18b)$$

$$|\,h_{C2'}\,\rangle = .84650\,|\,s_{C2}\,\rangle - .12960\,|\,pz_{C2}\,\rangle + .25817\,|\,px_{C3}\,\rangle - .44719\,|\,py_{C3}\,\rangle \qquad (18c)$$

This is clearly an antibonding combination between a lone-pair hybrid of fluorine (at 76° from the *z*-axis oriented along CF) and a CH bond, the two hybrids being parallel. Work along the same lines on the molecular orbitals 5, 6, 7 would finally produce almost complete separation of the lone pairs and the CH bonds. However, the result obtained allows already a clear physical interpretation, for it represents one of the 'hyperconjugation' orbitals, the »π« components of the carbon and fluorine orbitals lying in the same plane.

It may be claimed that the MO mixing advocated here is nothing but an artificial localization procedure such as those discussed in Ref. 2. We suggest that it is only required because of the high symmetry of the molecules studied: when no bonds equivalent by symmetry are present (as in the case with the CF bond) no difficulty in direct interpretation arises.

Coming back to hybridization, note that the hybrids (18) have much higher *p*-character than those resulting from Table V. This is an indication that symmetry, by separating *x*, *y* and *z* components out, may give misleading indications regarding what is strictly related to bonds[13] and this explains the somewhat surprising hybrids obtained for, say, water, when a procedure like Ruedenberg's[14] is applied.

CONCLUSION

The above sample discussion is by no means an exhaustive illustration of the posibilities open for theoretical reflection by the straightforward analysis presented here as interpreted in terms of the *physically significant* atomic orbitals defined in Eq. 15. As has been mentioned, the whole elementary orbital theory of chemistry — an invaluable tool for experimentalists regardless of its status in the value-scale of computational chemistry — can be put on firmer grounds by elaboration of good *ab initio* SCF results: which need not be used only to discuss energies and populations.

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REFERENCES

1. K. Morokuma, *J. Chem. Phys.* **55** (1971) 1236.
2. Ph. Millie, B. Levy, and G. Berthier, in *Localisation and Delocalisation in Quantum Chemistry,* O. Chalvet, R. Daudel, S. Diner, and J. P. Malrieu (Eds.), Vol. 1, Reidel Dortrecht-Holland.
3. P. Mezey, G. Del Re, P. Otto, S. Suhai, and J. Ladik, *Int. J. Quantum Chem.* **21** (1982) 677.
4. R. Mulliken, (a) *J. Chem. Phys.* **36** (1962) 3428; (b) *J. Amer. Chem. Soc.* **72** (1950) 4493; (c) *J. Chem. Phys.* **19** (1951) 900; (d) *J. Phys. Chem.* **56** (1952) 295.
5. A. Rastelli and G. Del Re, *Int. J. Quantum Chem.* **3** (1969) 543.
6. R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.* **87** (1965) 395.
7. (a) *Atomic Data and Nuclear Data Tables,* E. Clementi and C. Roetti Vol. 14, no. 3—4, (1974) 181, (b) S. Huzinaga, *J. Chem. Phys.* **42** (1965) 1293.
8. T. Ben Laktar, M. Suard, E. Taillandier, and G. Berthier, *Mol. Phys.* **36** (1978) 509; T. Ben Laktar, E. Taillandier, and G. Berthier, *Mol. Phys.* **39** (1980) 881.
9. G. Del Re, *Theor. Chim. Acta* **1** (1963) 188.
10. S. A. Pozzoli, A. Rastelli, and M. Tedeschi, *J. Chem. Soc. Faraday Trans. 2* **69** (1973) 256.
11. S. Diner, J. P. Malrieu, J. P. Claverie, and F. Jordan, *Chem. Phys. Lett.* **2** (1969) 319; S. Diner, J. P. Malrieu, and P. Claverie, *Theor. Chim. Acta* **13** (1969) 1; J. P. Malrieu, P. Claverie, and S. Diner, *Theor. Chim. Acta* **13** (1969) 18; S. Diner, J. P. Malrieu, F. Jordan, and M. Gilbert, *Theor. Chim. Acta* **15** (1969) 100; F. Jordan, M. Gilbert, J. P. Malrieu, and U. Pincelli, *Theor. Chim. Acta* **15** (1969) 211.
12. A. Veillard and G. Del Re, *J. Chem. Soc.* (1969) 3129.
13. R. Mc Weeny and G. Del Re, *Theor. Chim. Acta* **10** (1968) 13.
14. C. Edmiston and R. Ruedenberg, *Rev. Mod. Phys.* **35** (1963) 457.
15. G. Del Re, U. Esposito, and M. Carpentieri, *Theor. Chim. Acta* **6** (1966) 36.

SAŽETAK

In situ atomske orbitale i molekulski računi s proširenim skupovima osnovnih funkcija

Giuseppe Del Re i Claudette Barbier

Razmotren je problem određivanja modificiranih atomskih orbitala (MAO) u molekularnim MO računima. Posebna pažnja posvećena je nalaženju minimalnog skupa atomskih orbitala, koji bi dobro opisivao kemijska svojstva vezanih atoma, a bio bi primjenljiv na vrlo velike molekule kao što su to npr. dipeptidi. Vrlo interesantni rezultati dobiveni su s tzv. atomskim orbitalama. Svaka od njih karakterizira jedan atom u kanonskim MO orbitalama. S pomoću tih orbitala analizirani su *ab initio* DZ rezultati za halometane koji su uzeti iz literature. Izvedeni su zanimljivi zaključci o radijalnoj distorziji AO kao i o *d*-hibridizaciji.