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## Considering a mixed atomic basis set composed of only 1s STO and 1s GTO in molecular calculations

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**Abstract** An atomic basis set composed of only 1s orbitals is introduced, for molecular calculations in the Hartree-Fock-LCAO approximation. The 1s Slater Type Orbitals are located at the nuclei and the 1s Gaussian Type Orbitals can be used both in fixed locations and as Floating Orbitals. Surprisingly, despite the simplicity of the orbitals, this basis set provides an accurate description of molecular systems containing atoms with two shells such as oxygen and carbon, used as case studies in this work. From a numerical perspective, the basis set is first optimized for the free atoms and then they are introduced into the molecular environment. The molecular calculations for OH<sub>2</sub> and CH<sub>2</sub> show validating results for the energy and the molecular geometry. From the description of the inner atomic and the valence shells achieved with this particular basis set, we can assign a charge to the bonds and the lone pairs by using the Löwdin population analysis, with excellent result from the molecular point of view.

**Keywords** 1s Gaussian Orbital, 1s Slater Orbital, SCF-LCAO, Basis sets, Floating Gaussian Orbital, lone pair, bond, inner shell, Löwdin's population analysis

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### 1. Introduction

Recently, we have introduced a mixed atomic basis for small molecules like LiH, OH<sub>2</sub> and SH<sub>2</sub>, which has given encouraging results at the SCF-LCAO level of molecular electronic structure calculation [1-2].

The definition and construction of this particular basis set, take procedures from the previous work on the subject, i.e. of basis sets composed only of 1s orbitals [3-8]. It also introduces new topics, concerning the numerical mixed multi-centre integral evaluations and a chemically founded treatment of the floating Gaussian orbital set.

If we analyse the results corresponding to the systems we have computed up to date, we can better visualise the new ideas of the actual model of this paper.



For example, considering the calculations on LiH [1]. The full quantum mechanical variational possibilities are considered in this case. Reliable geometry and energy compared with other basis sets are obtained [1].

With the purpose of generating a more general applicability of this model, we have considered arrangements of 1s GTO at the vertices of regular solids, which, in effect, introduces higher order angular momentum functions [4]. Within this context, the mixed 1s orbitals to be used for, firstly are “calibrated” in atomic calculations, as usual in defining a basis set for molecular calculations. This was the approach used in reference [2], where a model of three and five “concentric and aligned tetrahedral structures” describe the oxygen and sulphur atoms. We predicted the geometries and energies of OH<sub>2</sub> and SH<sub>2</sub>, respectively, see the details in reference [2]. We mention that despite such a simple basis set, we have obtained three digits accuracy in molecular energies and also the very different molecular geometries for OH<sub>2</sub> and SH<sub>2</sub>.

However, unexpectedly, we observed that the bond angle corresponding to OH<sub>2</sub> was too large, i.e. the predicted value 109.7° contrasts with the experimental one 104.5°. This disagreement suggests that we must revise the fixed tetrahedral structure. This structure seems to be too rigid for describing the atomic shell structure of oxygen, i.e. the basis set must introduce differences in symmetry between the inner and the valence electronic regions.

Following these observations, an atomic model with enough flexibility for describing the closed shell and valence electrons simultaneously is possible. In this work, we propose to use two distinct sets of regular solids.

Considering atoms with only two shells, the new proposal for describing the inner shell, consists of a set of two concentric and aligned octahedra together with a 1s STO at the nucleus.

The outer part of the atom, i.e. the valence shell, is described by using a set of three concentric and aligned tetrahedra. These tetrahedra, explicitly are placed on external positions relative to the outer most octahedron.

Positions and orbital exponents of these GTO are determined variationally considering free atoms, with the corresponding orbital exponent of the STO at the nucleus.

Once that the optimized free atom structures are ready, they are used for molecular systems. For the cases considered in this work, two of the “atomic tetrahedral arms” will follow the bond segment to build up the atomic bond charge contribution and, the other two will describe the lone pairs.

The most important and distinctive feature of this approach, is the easy mobility presented by subsets of 1s GTO. These subsets represent the electron valence contributions to bonds and lone pairs. In other words, with the great variational flexibility that this basis set possesses, atomic response to the molecular environment is modelled.

In the following sections we give the details of the new methodology, then we apply it to the OH<sub>2</sub> and CH<sub>2</sub> (singlet) systems. In this paper, we also introduce the Löwdin population analysis, because with the actual basis set, there is a correspondence between each GTO spatial position and an electronic charge associated to it.

## 2. Spatial arrangements of the 1s orbitals for C and O atoms, in view of their application to the molecular systems CH<sub>2</sub> and OH<sub>2</sub>, respectively.

### 2.1. Inner shell

The main subset of 1s mixed orbitals that may represent the closed shell, are spatially distributed as follows: one 1s STO is located at the nucleus and twelve 1s GTO are at the vertices of two concentric and aligned octahedra. In the Figure 1, the inner shell real main contributors are schematized.

These 1s orbitals are optimized for the free atom, i.e. their positions and sizes are obtained according to the methodology presented in reference [2]. However, in this case the relation between position and size is different.

Because for an octahedron it must be  $\varepsilon = 2 R \alpha^{1/2}$  [4], where  $\alpha$  is the orbital exponent,  $R$  is the distance to the nucleus of the corresponding 1s GTO and  $\varepsilon$  is a dimensionless Taylor expansion coefficient which, in this work is fixed at  $\varepsilon = 0.1$ .



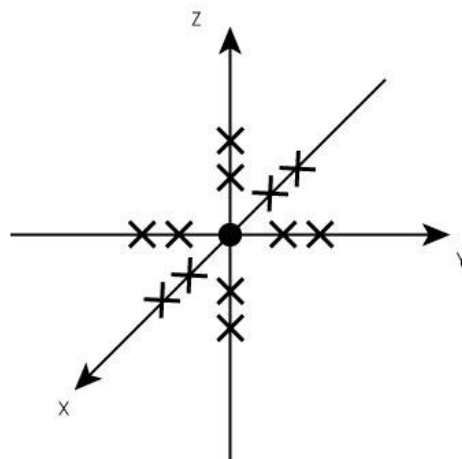


Figure 1: Caption for Figure 1: A cross “x” means a 1s GTO and a dot “•” means a 1s STO.

## 2.2. Valence shell

The 1s GTO that mainly represent the valence shell, are twelve 1s GTO spatially distributed at the vertices of three concentric and aligned tetrahedra. In the Figure 2 the valence shell construction is schematized.

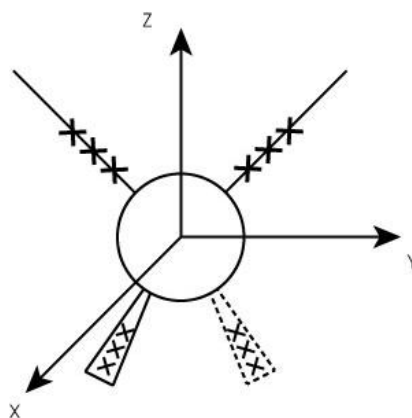


Figure 2: Caption for Figure 2: A cross “x” means a 1s GTO. The dashed sphere represents the inner shell region

This subset of 1s GTO is optimized partially, i.e. only their orbital exponents. In order to keep these “tetrahedral arms” as the directional response of the valence electrons in a given molecule, we constrain these three 1s GTO fixing their relative positions within each tetrahedral line. Let us denote this relative distance by  $d$ . We have found appropriate that  $d$  be the variational distance between the octahedra. Then, accordingly, all the regular polyhedra are equidistant, as shown in Figure 3.

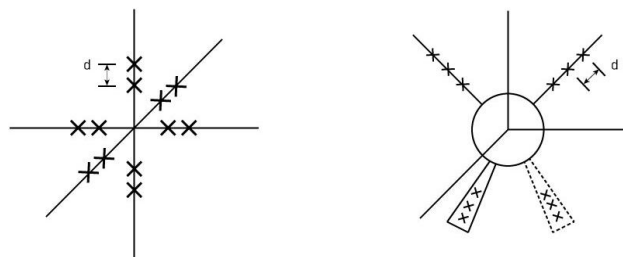


Figure 3: A cross “x” means a 1s GTO and a dot “•” means a 1s STO. The distance  $d$  is the separation between consecutive polyhedra, and corresponds to the distance between the octahedra, which is a variational quantity.



The orbital exponent optimizations of these 1s GTO proceeds as in reference [2]. Again, we consider the even tempered relation:  $\alpha_j = a b^j$  [9], where  $a$ , and  $b$  are parameters optimized and,  $\alpha_j$  is the orbital exponent corresponding to the  $j$ -th tetrahedron.

### 3. Spatial arrangements of the 1s orbitals for the XH<sub>2</sub> molecule with X=C, O.

The atomic calculations give the STO orbital exponent, the positions and orbital exponents corresponding to the GTO in octahedral arrangements and, the orbital exponents for the tetrahedral GTO, i.e. five variational parameters for each atom.

From these data, we can obtain  $d$ . This design, with the relative distance equal between every polyhedron, is a simplifying extra hypothesis for keeping shell regions well defined. For a contrasting approach, see reference [2] where we use no such restriction.

Now, the atoms can be included into the molecular structure. For systems like XH<sub>2</sub> with X = C, O, among the four “tetrahedral arms” we can align two of them in the X-H line; this structure is ready for molecular optimizations. In Figure 4, the complete molecular model to be used in this paper, is shown.

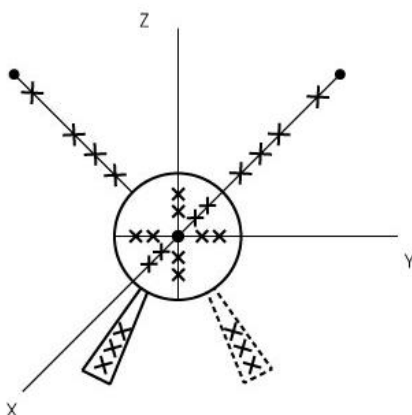


Figure 4: A cross “x” means a 1s GTO and a dot “•” means a 1s STO

The arrangement shown in Figure 4 has a great variational flexibility. Because of this, keeping the octahedral set and the 1s STO at the X nucleus fixed during a whole molecular optimization, there remain six variational parameters. They are the bond length, the position and size of the floating GTO (those nearest to the hydrogen nuclei), the size of the STO at the hydrogen nuclei, the bond angle and, the angle between the “arms” that will model the corresponding lone pairs. The Figure 5, shows some of these variational parameters.

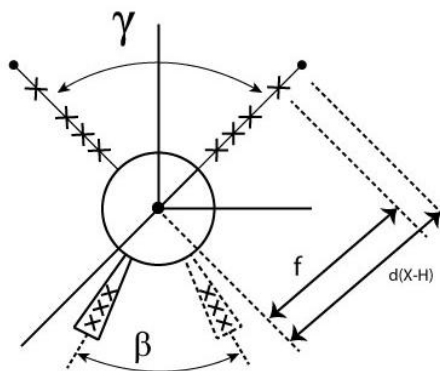


Figure 5: A cross “x” means a 1s GTO and a dot “•” means a 1s STO. Bond angle:  $\gamma$ ; angle between the tetrahedral axes that will describe the corresponding lone pair structures:  $\beta$ ; bond length:  $d(X-H)$  and “ $f$ ” is the distance from the floating GTO to nucleus “X”. The dashed sphere represents the inner shell region.

#### 4. Results

The model described in sections II and III, considering the molecules OH<sub>2</sub> and CH<sub>2</sub>, gives the results presented in subsections 4.1 and 4.2.

##### 4.1. Molecular geometry and energy for OH<sub>2</sub> and CH<sub>2</sub>

The values of the optimized parameters corresponding to the Oxygen and Carbon free atoms are in Table 1.

**Table 1:** All the values are in atomic units. The parameters a and b are related to the GTO orbital exponents  $\alpha_j$ , by the constraint that:  $\alpha_j = a b^j$ .

Atom	a (Tet.)	b (Tet.)	a (Oct.)	b (Oct.)	X's Orb. Exp. STO
O	0.02576	8.0681	0.10842	5.9776	8.0205
C	0.11780	3.4171	0.02972	6.0000	6.0985

With reference to Figure 5, the values of the optimized parameters that define the molecular geometry for OH<sub>2</sub> and CH<sub>2</sub> molecules, are shown in Table 2.

**Table 2:** All the quantities are in atomic units. Experimental references for OH<sub>2</sub>:  $\gamma = 104.5^\circ$  and d(O-H) = 1.808 [10]; near Hartree-Fock energy limit -76.068 [10]. Experimental references for CH<sub>2</sub>:  $\gamma = 102.4^\circ$  and d(C-H) = 2.092 [11]; near Hartree-Fock energy limit -38.89524 [12].

Molecule	$\gamma$ (°)	$\beta$ (°)	d(X-H)	Total energy
OH <sub>2</sub>	105	160	1.776	-76.00192
CH <sub>2</sub>	103	80	2.076	-38.86388

##### 4.2. Löwdin Population Analysis for OH<sub>2</sub> and CH<sub>2</sub>

This particular basis set, by using the Löwdin Population Analysis (LPA) [13] page 152, has the nice possibility of assigning charge to each of the 1s orbitals, i.e. we can obtain a charge distribution by particular selected spatial regions.

It is well known that, see ref. [13] page 151, the following sum can be partitioned according to,

$$N = \text{Trace}[S^{1/2} P S^{1/2}] = \sum_{\mu=1}^n [S^{1/2} P S^{1/2}]_{\mu\mu} \quad (1)$$

Where  $N$  is the total number of electrons in the molecule,  $n$  is the total number of 1s orbitals,  $S$  is the overlap matrix and  $P$  is the charge and bond order matrix [13] page 139.

In equation (1), we have the very possibility of grouping together those 1s orbitals that are considered pertinent to define bonds, lone pairs and closed shells, according to chemical intuition. This model, applied to the water and methylene molecules, gives the results shown in Table 3.

**Table 3:** The labels for the 1s orbitals are given in Figure 6. The quoted numbers are in atomic units

Molecule	1s orbitals	Their partial sum in eq. (1)	Modelling the charge of
CH <sub>2</sub>	16,20,24,28,2	2.06550	C-H bond
	28	0.44056	
	2	0.86969	
	18,22,26	0.68172	One of the lobes for the lone pair
	18,22,26 twice, plus 12,13,15	2.00540	Lone pair
OH <sub>2</sub>	1,4,5,6,7,8,9,10,11,14	1.863587	Inner shell
	16,20,24,28,2	2.06661	O-H bond
	28	0.68424	
	2	0.61842	
	18,22,26, plus 12,13 and the half of 15	1.987289	Lone pair



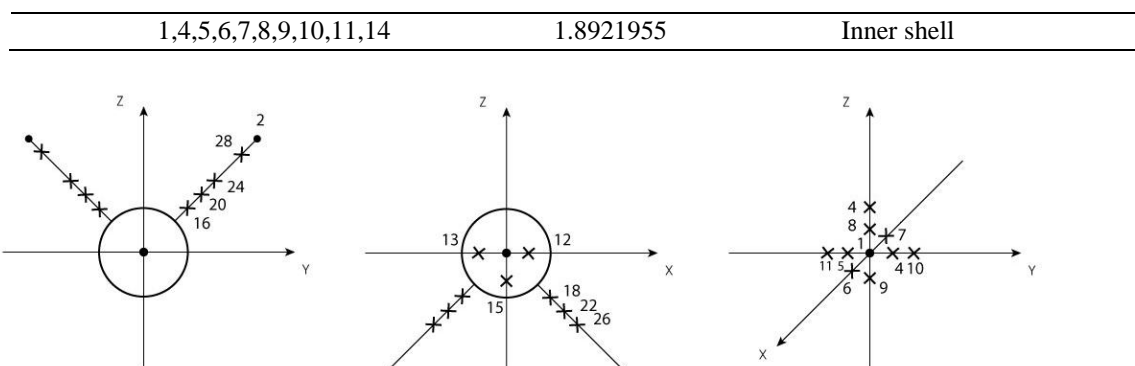


Figure 6: With reference to the Table 3, in this figure are explicitly detailed the labels for the 1s orbitals.

## 5. Concluding remarks

The results obtained for the geometry optimizations of  $\text{OH}_2$  and  $\text{CH}_2$ , confirm that the combination “fixed octahedra + mobile tetrahedra” shown in Figure 4, accounts for these molecular environments properly. Searching for results better determining the molecular geometry of water molecule is greatly satisfied. The proper molecular geometry for the first singlet methylene is also obtained.

The energy results, i.e. the three digits obtained with respect to the near Hartree-Fock limit with this very simple basis set, undoubtedly are consequence of a nice flexibility of the proposed spatial arrangements for the 1s orbitals, which also include new variational variables, (see  $\beta$  in Figure 5 and Table 2).

Considering the LPA applied to these molecules with this basis set, from the equation (1) and Table 3, we can conclude that the one to one correspondence proposed, i.e. charge per spatial place where the 1s is located, permits the chemical interpretation immediately.

In this respect, first of all, the charge associated to the bonds, i.e. at about 2.07 for both molecules with an error of 0.07 (4 %), is accurate, not only in absolute terms but also for the polarization effects that these charge distributions give inside these bonds. This can be corroborated looking at the charge assigned to the 1s orbitals with labels 28 and 2, respectively. The migration of charge to the O nucleus is notably larger than to the C nucleus, in the corresponding bonds.

The inner shells in both molecules also show modest error near 0.04 (2 %).

For the case of the lone pairs, new effects are noticeable; firstly, the assigned values are very accurate, i.e. 2.005 ( $\text{CH}_2$ ) and 1.987 ( $\text{OH}_2$ ). With the nice polarization effects evidenced from the opposed behaviour of the  $\beta$  parameter, i.e.  $160^\circ$  “opening the tetrahedral arms” for two lone pairs in water and,  $80^\circ$  “closing the tetrahedral arms” for only one lone pair in methylene.

It is a notably property of this basis set that we can assign charge by regions without performing further localization procedures, i.e. the LPA only needs to handle two matrices already used in the SCF calculation.

The nice trends obtained in the examples studied in this paper, allow us to envisage that if we can adapt appropriately, similar schemes or new ones, for more complex molecular systems, the approach presented here would have perspectives. In this respect, we could contrast calculations using pure-tetrahedra/pure-octahedra/pure-... with those like presented here, i.e. perhaps it can be revisited the descriptions using “sigma-pi” symmetry notions and those with the “banana bonds”, to extend the scope of the present work.

Studies of this kind will be carried out in a future emphasising that some particular 1s GTO spatial arrangements together with the LPA, permits us the assignation of charge by regions, according to the chemical point of view. This last point is the main contribution and perspective of the present paper.

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