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Ring Functions, as Polarization Functions, for *ab initio* Calculations on Small Rings: Dioxirane

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The exponents and relative positions have been optimized for bond functions to be used as polarization functions in the theoretical treatment of small cycles. The transferability of the conventional bond functions to this type of "compact" systems is analyzed for the particular case of dioxirane and it is shown that they can be replaced by a single function located inside the ring (ring function) which describes equally well the polarization effects on the equilibrium geometry, charge distribution and dipole moment. These conclusions are corroborated by the characteristics exhibited by the corresponding localized molecular orbitals.

Key Words: Polarization functions—ring function—dioxirane.

1. Introduction

It is a well-known fact that, to adequately describe the distortion undergone by the atomic charge distribution when an atom forms part of a molecule, it is necessary to use a flexible enough basis set. Actually, in the frame of the monodeterminantal molecular orbital theory, only if the basis set is very large, one can guarantee that the molecular properties obtained would be basis independent. However, economical reasons prevent the generalized use of near-limit basis sets in molecular calculations. A quite good compromise is achieved by including polarization functions (*p* functions on hydrogen and *d* functions on non-hydrogen atoms) in a basis set of a double-zeta quality [1–6]. This polarization of the basis makes possible to describe [5] the electronic charge located far from the nuclei and, as a consequence, this kind of basis set leads to equilibrium geometries [7, 8] and other molecular properties [3, 9] close to the single determinant limit. Nevertheless, the inclusion of this type of polarization functions can be practically prohibitive for molecular systems of medium size.

A rather good and cheaper alternative is to use basis functions, of *s*- and *p*-type, centered in the bond region (bond functions) [10–15]. It has been shown [16, 17] that these BF's can be transferred from molecule to molecule, at least in those molecular systems which are not very "compact" [16b], since their exponents and relative positions are quite insensitive to the molecular environment.

However, the possible interaction between BF's in "compact" systems is an aspect of the problem which has not received much attention. The aim of this paper is to analyze the drawbacks of using BF's in this kind of system and the possible alternatives.

We have selected for our study the molecule of dioxirane, because it is an adequate model for "compact" systems and the presence of a peroxidic bond assures the existence of important polarization effects. We shall study whether the usual bond functions can be transferred to these systems and the possibility of replacing the BF's by "ring functions" (RF), as suggested by Neisius and Verhaegen [16b], by means of a comparative analysis of their influence on the equilibrium geometries and other molecular properties.

2. Basis sets and computational details

Since one of the aims of this paper is to compare our BF's with those obtained by Neisius and Verhaegen for non-compact systems [16], we shall use, as bond functions, one *s*-type and three *p*-type (x, y, z) GTO's centered at the same point in space and with identical exponents. These BF's will be added to the 6-31G split-valence basis set [18]. In this way we shall define four levels of polarized bases:

Basis A: 6-31G
Basis B: $6\text{-}31G+BF_{O\text{–}O}+BF_{C\text{–}O}$
Basis C: $6\text{-}31G+BF_{O\text{–}O}+BF_{C\text{–}O}+BF_{C\text{–}H}$
Basis D: $6\text{-}31G+RF+BF_{C\text{–}H}$
Basis E: $6\text{-}31G+RF+BF_{O\text{–}O}+BF_{C\text{–}O}+BF_{C\text{–}H}$.

In each case, with the only exception of the BF's centered on the CH bonds, we have carried out a simultaneous optimization of the exponent and position of each BF and the equilibrium geometry of the molecule. For the BF's centered on the CH bonds we have adopted the mean values of exponent and position, reported by Neisius and Verhaegen [16b]., which have been kept constant throughout the optimization of the remaining parameters.

We have used, as a starting point for these calculations, the optimized geometry of dioxirane at the 6-31G level which has been reported elsewhere [19]. The optimization has been considered to be complete when variations of ±0.005 in the exponents, ±0.03 Å in the bond lengths and positions of the BF's and ±0.1

degrees in the bond angles, caused variations in the total energy, smaller than 10^{-5} a.u.

We have also slightly modified the Gaussian-70 series of programs to evaluate the charge densities located not only on the atomic centers but also on the BF's.

Finally we have carried out a localization of the MO's by the Foster–Boys method [20], in order to complete our analysis of the polarization effects on small cycles.

3. Results and discussion

3.1. Optimized Bond functions

We present, in Table 1, the optimized values of exponents and relative positions of the bond functions included in each basis set. It is obvious that, for symmetry reasons, the BF_{O-O} is always located at the central point of the peroxidic bond.

Several facts should be singled out for comment:

a) The optimized exponents of BF_{C-O} and BF_{O-O} are not very different from those obtained for non-compact systems [16b].
b) The variations observed in the exponents, in going from one basis set to another, indicate that, in the present case, the interaction between these functions is not negligible.
c) The relative position of each BF is substantially affected by the close vicinity of the remaining ones, due to the peculiarities of the system. For instance, the strong interaction between the BF(O–O) and those centered on the C–O bonds, explains why the latter are always quite close to the carbon atom, in contrast with the standard position ($\gamma = 0.5$) proposed [16b] for this kind of BF. Moreover, when one includes BF's on the CH bonds (in going from basis B to C) the BF_{C-O} moves only slightly away from the carbon atom.
d) It should be emphasized that, with the only exception of set *E*, as we shall discuss later, no redundancy problems have been detected in the basis sets

Table 1. Optimized exponents (α) and relative positions (γ)[a] of the bond functions included in this study

	Basis set							
	B		C		D		E	
Function	α	γ	α	γ	α	γ	α	γ
BF_{O-O}	0.81	0.5	0.91	0.5			0.81	0.5
BF_{C-O}	0.75	0.32	0.74	0.41			0.72	0.38
BF^{b}_{C-H}			0.9	0.3	0.9	0.3	0.9	0.3
RF					0.58	0.63[c]	0.76	0.77[c]

[a] Relative position of the BF defined as the fractional distance from the heavy atom in the bond

[b] Mean values taken from Ref. [16b]

[c] Fractional distance from the carbon atom measured on the straight line which joins this atom with the central point of the O–O bond

under consideration. In fact, the energy obtained using basis *C*, is a little lower than the one reported by Cremer [21], when *d* functions centered on the heavy atoms are added to the 6-31G basis.

3.2. Equilibrium geometries

The corresponding equilibrium geometries have been summarized in Table 2.

In all cases, the inclusion of polarization functions in the basis set, causes a shortening of all bonds involving non-hydrogen atoms and a slight lengthening of the CH bonds. This is a well-known effect of large bases, since in the single-determinant molecular orbital theory the left–right correlation of electrons in the bond is not taken into account [7, 2]. This correlation arises from the contribution of configurations which include antibonding molecular orbitals, leading to longer bonds. This implies that the agreement between the optimized values, at the SCF level, and the experimental ones (See Table 2) is worse when including polarization functions in the basis.

Table 2. Optimized equilibrium geometries for dioxirane

Basis set	A	B	C	D	E
Bond lengths (Å)					
O–O	1.533[a] (1.156)[b]	1.450	1.448	1.461	1.446
C–O	1.411 (1.388)	1.371	1.366	1.372	1.365
C–H	1.068 (1.090)	1.07	1.078	1.077	1.078
Bond angles (degrees)					
O–C–O	65.8 (66.2)	63.8	64.0	64.3	63.9
H–C–H	117.9 (117.3)	116.0	116.4	117.0	116.3
β	121.05 (121.35)	122.0	121.8	121.5	121.9
Total energy (a.u.)	−188.50302	−188.59004	−188.60311	−188.58481	−188.6056
Computation time (min)[d]	—	16	20	12	27

[a] Values taken from ref. [19]

[b] Experimental values taken from Ref. [23]

[c] see Fig. 1 for definition of β

[d] Average computation time for a single SCF calculation involving the same number (8) of SCF cycles

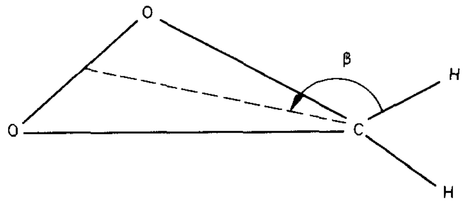

Fig. 1. Definition of parameter β

A very important point is that basis D, in which the three BF's ($BF_{O-O}+2BF_{C-O}$) basis of C, have been replaced by a single ring function (RF) centered inside the ring, yields an equilibrium geometry quite similar to the one obtained when basis C is used. Moreover, the energy obtained (see Table 2) is only 0.018 a.u. (0.01%) worse than that calculated using the larger basis (C). This seems to indicate that, to a good extent, the polarization effects described by the three BF's (BF_{O-O} and BF_{C-O}) are well matched by the RF. Furthermore, in going from basis set C to basis set D the corresponding computation time (See Table 2) is significantly reduced.

On the other hand, the geometry obtained using basis E is practically identical to the one obtained using basis C and although the former basis is larger (55 AO's vs. 51 AO's) the improvement in the total energy is only of the order of 0.0014 a.u. (0.0007%). This shows that no additional flexibility is reached in the basis set when one includes both kinds of functions (BF's and RF's), since, as indicated above, they present practically the same ability to reproduce polarization effects in small cycles. Therefore, one can conclude that either basis set C or D are practically saturated from the polarization point of view and, in this sense, basis set E can be considered redundant. This redundancy is also responsible for the great variation observed in the exponent of the RF in set E relative to set D.

3.3. Charge distributions

All these geometrical changes can be rationalized in terms of variations in the charge distribution of the molecule. These charge distributions, obtained by Mulliken population analysis, are presented in Table 3, for each basis set.

With respect to the 6-31G basis, it is clear that the inclusion of polarization functions favors a noticeable migration of charge into the bonding regions, except for CH bonds where this effect is very small. This charge accumulated in the bonding region reduces the repulsion between the two nuclei involved in the bond which in consequence, becomes shorter. On the contrary, the polarization

Table 3. Electronic distribution of dioxirane, obtained by Mulliken population analysis and calculated dipole moment

Basis set	A	B	C	D	E
Center					
C	5.678[a]	5.673	5.547	5.591	5.591
O	8.369	7.996	8.008	7.988	8.006
H	0.791	0.812	0.811	0.805	0.807
$BF_{(O-O)}$	—	0.277	0.236	—	0.531
$BF_{(C-O)}$	—	0.217	0.257	—	0.216
$BF_{(CH)}$	—	—	0.032	0.019	0.043
RF	—	—	—	0.786	−0.268
μ(Debyes)	3.72 (2.49)[b]	3.05	3.00	3.16	2.97

[a] Values taken from Ref. [17]

[b] Experimental value taken from Ref. [21]

of the electronic cloud in the CH bond regions induces an increase of the charge density located on the hydrogen atoms (see Table 3) and a parallel increase of the corresponding bond length.

The mechanism which explains the sortening of the C–O and O–O bonds when the BF's are replaced by a RF, is similar: when using basis *D* a strong migration of charge toward the interior of the ring takes place. Such an electronic charge exerts an attraction on the three nuclei of the cycle, which results in a shortening of the bonds. Moreover, the net charge associated to the RF (basis D) is practically equal to that retired by the three BF's ($BF_{O-O}+2BF_{C-O}$) included in set C. This indicates that the RF produces analogous effects on the charge distribution of the molecule as the three BF's replaced by it, through a mechanism which, in both cases, involves a migration of charge away from the nuclei. Therefore one can conclude that both sets of polarization functions are practically equivalent. Actually, when both are included simultaneously in the basis set (basis E) a negative charge on the RF is found, indicating that such a basis has, somehow a redundant character regarding the description of polarization effects.

It should also be pointed out that the inclusion of polarization functions yields a considerable decrease of the calculated dipole moment (see Table 3), in better agreement with the experimental value [23]. This is an indication that the electronic distribution obtained using a polarized basis set is more realistic than the one described by a basis which does not include polarization effects.

3.4. Localized molecular orbitals description

It would be useful to analyze the influence of polarization functions on the description of "compact" systems by means of the set of localized molecular orbitals (exclusive orbitals), obtained from the corresponding canonical set, using the Foster–Boys method [20]. This type of analysis has been carried out previously on similar systems, but using minimal basis sets [24] or FSGO's [15]; therefore little is known on the effect of polarization functions on the characteristics of the corresponding localized molecular orbitals.

As it could be expected the LMO corresponding to the threee bonds of the ring are considerably bent. We present, in Table 4, the distance from the centroid of the LMO to the axis of the corresponding bond. It is clear that, using a non-polarized basis set (A), the C–O bonds are considerably more bent than the

Table 4. Perpendicular distance (a.u.) from the centroid of each localized molecular orbital to the axis of the corresponding bond

Basis set	A	B	C	D	E
Bond					
C–O	0.286	0.289	0.291	0.285	0.295
O–O	0.130	0.095	0.092	0.074	0.080

peroxidic one, in agreement with the criterium of Talaty and Simons [15] that the degree of bending of a given bond increases as the bond length decreases. However, when one includes polarization functions in the basis set, only the C–O bond (now shorter) becomes slightly more bent, while the O–O bond (also shorter) becomes less bent. This agrees with the fact that only in the O–O localized molecular orbital, the participation of the corresponding bond function is clearly significative. Finding this is not surprising since, it is reasonable to assume that within the dioxirane-ring the polarization of the electronic cloud must be more intense in the neighborhood of the peroxidic bond, that becomes stabilized by the contribution of the BF and less bent. The same behavior is observed when a single RF replaces the conventional BF's in the sense that this RF contributes substantially to the O–O localized molecular orbital but its participation in the C–O bonds is negligible.

Finally, it should be indicated that the LMO's obtained using basis *E* are quite similar to those calculated using basis *C*, being the participation of the RF in all the bonds of the ring negligible. This confirms that the basis becomes practically saturated (from the polarization point of view) provided only one type of polarization functions (BF's or RF's) is included in it.

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