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Tetrahedral Lobe Functions

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The representation of atomic *p* orbitals in terms of tetrahedral Gaussian lobe functions is shown to be a viable alternative to more conventional representations in terms of cartesian Gaussians or octahedral lobe functions. Fairly accurate SCF calculations for the methane and ethane molecules show that the flexibility of the tetrahedral representation can be used to introduce a degree of polarization into the atomic basis in a molecular environment. Combined with the use of molecular bond functions, this flexibility provides an economical description of polarization effects in molecules.

Key words: Tetrahedral lobes – Methane – Ethane – Cusped-Gaussian basis – Polarization functions.

1. Introduction

The use of tetrahedral Gaussian lobe functions [1] for the representation of atomic *p* orbitals has recently been discussed by Poshusta [2] and by Spangler and Christoffersen (SC) [3]. The use of just four lobe functions to represent the three *p* orbitals requires less computational effort than the more conventional use of six octahedral lobe functions [4], but SC have pointed out that care must be taken in choosing the distances of the lobes from the nucleus in order to ensure both the maintenance of numerical precision and a high degree of invariance of molecular properties to the orientation of the tetrahedron in a molecular environment.

The minimal representation of a set of $2p$ atomic orbitals makes use of four identical spherical Gaussians

$$\phi_i(\boldsymbol{r}, \boldsymbol{R}) = [8\gamma(2\gamma/\pi)^{1/2}]^{1/2} \exp(-\gamma|\boldsymbol{r}-\boldsymbol{R}_i|^2)$$

where $\boldsymbol{R}_i$ are the vertices of a regular tetrahedron. The (unnormalized) atomic orbitals can then be chosen as

$$p_x^T = \phi_1 + \phi_2 - \phi_3 - \phi_4$$
$$p_y^T = \phi_1 - \phi_2 + \phi_3 - \phi_4$$
$$p_z^T = \phi_1 - \phi_2 - \phi_3 + \phi_4.$$

SC have proposed that satisfactory values of the distance R of the lobes from the centre of the tetrahedron are given by the rule $\gamma^{1/2}R = \delta$, where δ is a constant dependent on the word length of the computer used to perform the calculations:

$0.002 \le \delta \le 0.005$ for a 72-bit word

$0.005 \le \delta \le 0.01$ for a 64-bit word.

The lower limit is required to ensure the numerical precision of the molecular integrals, whilst the upper limit ensures a degree of rotational invariance. The precise value of δ is not critical however, and the work of SC and Poshusta suggests that at least total energies are rather insensitive to variations of δ within the given range.

The work of Poshusta was concerned with hydrogenic functions only, whilst SC considered only the simplest representations of p orbitals. In this paper the investigation is taken a little further by a consideration of the use of tetrahedral lobe functions for the construction and use of accurate atomic basis sets.

2. The Carbon Atom

In Table 1 are shown the results of SCF calculations for the ground state of the carbon atom. The basis sets are of the cusped-Gaussian type $(c + ns, mp)$, consisting of a $1s$ cusp function c and n $1s$ Gaussians to describe the s orbitals, and m sets of p Gaussians [5]. The s basis sets $(c + ns)$ have been taken from previous work [5], whilst the exponents of the p Gaussians are those calculated by Huzinaga [6] for the all-Gaussian sets $(9s, 5p)$, $(10s, 6p)$, $(11s, 7p)$. The reoptimization of these functions has been found to have no significant effect on properties, with changes in the total energy in the seventh significant figure only.

In calculations 1 to 4 the p orbitals are of tetrahedral type with distances R given by the rule $\gamma^{1/2}R = \delta$. The total energy decreases with decreasing value of δ, as expected, but it is clear that no significant changes in properties can be expected for values of δ smaller than 0.01, the upper limit proposed by SC. Although double-length arithmetic (64-bit words) has been used for all the work described in this paper, the calculations 3 and 4 were checked using quadruple arithmetic. The only changes observed were in the eighth significant figure in calculation 4.

Calculation 5 differs from the first four only in that the distances of the tetrahedral lobes from the nucleus have all been set equal to the same value of $R = 0.015$. This corresponds to exponent $\gamma = 0.36$ and $\delta = 0.009$. The value $\gamma = 0.36$ is that appropriate for a minimal representation of the $2p$ orbital in carbon, whilst

Table 1.[a] The ground state of carbon

Basis	δ	$-E$	$-\varepsilon_{1s}$	$-\varepsilon_{2s}$	$-\varepsilon_{2p}$
By rule $\gamma^{1/2}R = \delta$					
1. $(c+4s, 5p)$	0.05	37.68481	11.32676	0.70534	0.43182
2.	0.01	37.68632	11.32568	0.70496	0.43237
3.	0.005	37.68636	11.32565	0.70494	0.43239
4.	0.002	37.68638	11.32564	0.70494	0.43239
With $R = 0.015$					
5. $(c+4s, 5p)$		37.68618	11.32586	0.70501	0.43232
6. $(c+4s, 5p) \to [c+4s, 1p]$		37.68618	11.32563	0.70493	0.43229
7. $(c+5s, 6p) \to [c+5s, 1p]$		37.68758			
8. $(c+6s, 7p) \to [c+6s, 1p]$		37.68821			
With octahedral lobes, $R = 0.045$[b]					
9. $(c+4s, 5p) \to [c+4s, 1p]$		37.68637	11.32582	0.70497	0.43239
10. $(c+5s, 6p) \to [c+5s, 1p]$		37.68776			
11. $(c+6s, 7p) \to [c+6s, 1p]$		37.68840			

[a] Unless otherwise stated, all quantities in the tables are given in atomic units: energies in units of E_H, distances in units of a_0.

[b] From Ref. [5].

$\delta = 0.009$ for the tetrahedral representation is equivalent to the commonly used $\delta = 0.03$ for the octahedral representation [3]. This calculation demonstrates the insensitivity of the energies to the precise formula used to determine the distances R, the change in total energy on going from calculation 4 to 5 being only $0.0002\ E_H$ ($0.5\ \mathrm{kJ\ mol^{-1}}$).

In calculations 6 to 11 the *m* sets of *p* functions have been contracted into a single set using the coefficients of Huzinaga's all Gaussian sets [6]. The tetrahedral representation with $R = 0.015$ has been used in 6 to 8, the octahedral representation with $R = 0.045$ in 9 to 11. It has been shown [5] that the use of the fixed value of R for all exponents in the octahedral representation has not significant effect on the results, so that calculations 9 to 11 can be regarded as reference calculations for 1 to 8. A comparation of 2, 4 and 9 shows that values of $\delta \leq 0.01$ for the tetrahedral representation give energies close to those expected in the limit $\delta \to 0$. In addition, a comparison of 6 to 8 and 9 to 11 shows that replacing the rule $\gamma^{1/2}R = constant \leq 0.01$ by $R = 0.015$ gives an almost constant increase of only $0.5\ \mathrm{kJ\ mol^{-1}}$ in the total energy, despite the wide range of γ values (0.07 to 40.8 for $7p$).

3. The Methane Molecule

In Table 2 are shown the results of a number of SCF calculations for the ground state of methane (bond length 2.05 a_0) with basis sets derived from the uncontracted basis $(c+4s, 5p/4s)$. In calculations 7 to 10 the contraction $5p \to (4p)+p$ makes use of the Huzinaga coefficients [6] for the inner function. The Gaussian

Table 2. The ground state of methane

Basis[a]		Lobes on bonds $-E$	Lobes opposite bonds $-E$	ΔE/kJ mol^{-1}
Tetrahedral lobes				
By rule $\gamma^{1/2}R=\delta$				
1. $[c+4s, 5p/2s]$	$\delta=0.005$	40.18907	40.18724	4.8
2.	$\delta=0.01$	40.18997	40.18624	9.8
3.	$\delta=0.14$	40.20121		
4. $[c+4s, 5p/2s]+b$	$\delta=0.01$	40.20645		
5.	$\delta=0.1$	40.20862		
6.	$\delta=0.14$	40.20809		
With $R=0.015$				
7. $[c+4s, 2p/2s]$		40.19065	40.18499	14.9
8. $[c+4s, 2p/2s]+b$		40.20462		
Octahedral lobes with $R=0.045$				
9. $[c+4s, 2p/2s]$		40.18803		
10. $[c+4s, 2p/2s]+b$		40.20393		

[a] All basis sets are derived from the uncontracted basis $(c+4s, 5p/4s)$. b represents a set of four Gaussian lobes located on the bonds.

set for hydrogen, and its contraction, is taken from the work of Dunning [7] with scale factor 1.2.

Calculations 1, 2 and 7 show the effect of changing the orientation of the tetrahedron of p-orbital lobe functions, the lobes lying either on the CH bonds or opposite the bonds. As SC have pointed out, the former should be the more favourable, and they have shown that the energy difference increases approximately linearly with (small) δ, with a value of about 10 kJ mol^{-1} for $\delta=0.01$. This is confirmed by the present (more accurate) calculations 1 and 2. The somewhat larger difference in 7 is a consequence of using a fixed value of $R=0.015$. As a result of this dependence of calculated properties on the orientation of the tetrahedron, some care must be taken when considering properties arising in particular from changes in conformation. An obvious example is the barrier to internal rotation in ethane, whose magnitude of 12 kJ mol^{-1} is comparable with the values of ΔE in Table 2 but, as shown in the following Section, this problem is readily overcome in practice.

Calculations 1 to 3 show that, in contrast to the atomic case, the lowest energy of a molecule is not obtained in general in the limit $\delta \rightarrow 0$. Allowing the lobes to move away from the central nucleus towards neighbouring atoms introduces a degree of polarization into the atomic basis. In the present case the lowest energy is obtained with $\delta=0.14$ and, comparing calculations 3 and 9, a polarization energy of about 0.013 E_{H}. This is similar to the lowering in energy obtained from the addition of a set of d-type polarization functions on the central atom in a

Table 3. Parameters of the polarization functions in CH_4

Calculation	γ	x
4	1.108	0.583
5	1.539	0.746
6	1.785	0.793
10	1.225	0.625

conventional treatment [8, 9], but with no extra labour once a suitable value of δ has been chosen for each atom.

A more accurate description of polarization is obtained in a simple way by the addition of a set of four equivalent Gaussian lobes centred on the bonds. Calculations 9 and 10 show that the direct effect of these polarization functions is to lower the energy by about 0.016 E_H. Calculations 4 to 6 demonstrate a competition between the polarization functions and the tetrahedral *p*-orbital lobes. Even with the small value of $\delta = 0.01$ the polarization energy has been increased to 0.018 E_H, and the maximum value of 0.021 E_H is obtained with $\delta = 0.1$. Table 3 shows the (optimized) parameters of the polarization functions; the exponent γ and the fractional distance x of the lobes along the bonds from carbon. The parameters in calculation 4 are similar to those in 10, with the polarization functions lying close to the centres of the bonds, and readily classified as "bond functions". For $\delta = 0.1$ and greater however the role of the polarization functions is probably similar to that of conventional *p*-type functions on the hydrogens. Indeed, the polarization energy of about 0.02 E_H obtained in calculations 5 and 6 is close to that obtained with a set of *d*-type functions on the central atom and a set of *p*-type functions on each hydrogen in a conventional approach.

4. The Ethane Molecule

The calculations summarized in Table 4 of the barrier to internal rotation in ethane show that the "orientation problem" associated with the use of tetrahedral lobes can be avoided if the tetrahedron is allowed to follow the change of conformation. The basis set used in calculation 1 is essentially the same as that used in calculation 7 of Table 2. The only difference is that, because the lobes are constrained to lie on the bonds, the disposition of a set of four lobes about a carbon is no longer an exact tetrahedron (the assumed geometry for both conformations is $R_{CC} = 2.90\ a_0$, $R_{CH} = 2.07\ a_0$, $\angle HCH = 108°$). The small difference in angles was ignored when constructing the atomic *p*-functions.

Table 4. The ground state of ethane

Basis	$-E$ (staggered)	$-E$ (eclipsed)	$\Delta E/\mathrm{kJ\ mol^{-1}}$
1. $[c+4s, 2p/2s]$	79.21600	79.21120	12.6
2. $+b_{CH}$	79.23852	79.23343	13.4
3. $+b_{CC}+b_{CH}$	79.24203	79.23698	13.3

Calculations 2 and 3 in Table 4 illustrate the efficacy of lobe functions as polarization functions in ethane. b_{CH} represents a set of six identical lobes centred on the CH bonds, with exponent and distance from carbon taken from the methane calculation 4 (the corresponding methane calculation with this basis is 8 in Table 2). b_{CC} is a single lobe function at the centre of the CC bond, again with the same exponent. Both the reoptimization of the polarization functions and the use of two functions on the CC bond were found to have only very small effects on the energy.

The energies obtained with calculations 2 and 3 are comparable with those obtained from more sophisticated (conventional) calculations. The polarization recovered with a set of d functions on the carbons and a set of p functions on the hydrogens is about 0.028 E_H [10], the bulk coming from the hydrogen functions. These values are almost exactly paralleled by the results in Table 4. All three calculations give values of the rotational barrier close to the experimental value (12.3 kJ mol^{-1}), and similar to the values obtained from nearly all (published) SCF calculations.

The usefulness of tetrahedral functions for the representation of p orbitals in molecules therefore appears to be established, at least for the simple structures considered in this paper. The calculations suggest that the tetrahedral representation gives rise to no significant loss of accuracy, and may in some cases even be superior to the more conventional representations in terms of cartesian Gaussians or octahedral lobe functions. In addition, the computational effort should be smaller. For example, a typical atomic Gaussian basis like ($9s$, $5p$) is made up of 39 primitive spherical Gaussians in the octahedral representation but only 29 in the tetrahedral representation. In general therefore the number of such primitive functions in a molecular basis is reduced by 20–25%, giving a reduction of 60–70% in the number of primitive integrals. Any additional labour generated by the tetrahedral basis should be small compared with this saving.

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