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An MS Xα Study of the Potential Energy Surface and Electronic Structure of the PF_4 Radical

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The problem of determining the most adequate calculation parameters in the multiple scattering Xα method is investigated in the PF_4 radical case. A full geometry optimization of the radical is made using overlapping and non-overlapping atomic spheres and the corresponding spin density distribution in the various regions is calculated. Comparisons with both SCF LCAO results and experiment show that a very reasonable description of the structure and electronic properties of the radical can be derived from the calculations using overlapping atomic spheres.

Key words: PF_4 radical - Multiple scattering Xα method (MS Xα)

1. Introduction

Phosphoranyl radicals have recently been the subject of several experimental [1, 2] and theoretical [3–6] investigations. An analysis of the ESR spectra of PF_4 radicals trapped in a crystalline matrix [2] leads to a structure considerably distorted from tetrahedral symmetry for this radical, in agreement with the calculations which predict a trigonal bipyramidal structure of C_{2v} symmetry [3–6]. However, there is a quantitative disagreement among the theoretical predictions concerning bond lengths and bond angles.

As for hyperfine coupling constants, the agreement between theory and experiment is generally rather poor, even when including *d* orbitals of phosphorus in basis set, which emphasizes the difficulty of describing adequately the unpaired electronic orbital of radicals.

Recently the multiple scattering Xα (MS Xα) method [7] has been shown to give a reasonably accurate description of the electronic structure of compounds containing fluorine ligands [8–12]. Furthermore, even though it is not its main virtue, this model, in some cases [13, 14], seems able to provide potential energy surfaces showing satisfactory agreement with experiment.

In this work the MS Xα method is used, in both "touching" and overlapping atomic spheres approximations, to determine the lowest minimum on the potential energy surface and the corresponding electronic structure of the PF_4 radical. An evaluation is

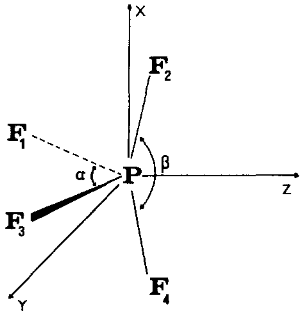

Fig. 1. Structure of the PF_4 radical (C_{2v} symmetry)

then made of the spin densities in the various regions of the radical. Whenever possible, the present results are compared with both experiment and previous theoretical estimates in order to thoroughly evaluate the ability of the MS Xα method of predicting the properties of radicals.

2. Calculation Parameters

The molecular structure of PF_4 (Fig. 1) belongs to the C_{2v} symmetry with two pairs of respectively equatorial (F_1, F_3) and axial (F_2, F_4) equivalent fluorine atoms. In this work the search for the equilibrium geometry is made by varying in turn bond distances R_{PF_1} and R_{PF_2} and bond angles α and β (see Fig. 1).

The values of the MS Xα parameters are presented in Table 1. The atomic α values are taken from the calculations of Schwarz [15]. A weighted average of the atomic values (four parts of fluorine to one part of phosphorus) is chosen for the α value in both the interatomic and extramolecular regions.

As an important feature of this work is to compare in detail the results obtained using "touching" and overlapping atomic spheres, two different sets of sphere radii are used. Set *A* is our "touching spheres" parameter set and it is found using the procedure described by Norman [16]: from the initial molecular charge distribution, constructed by superposing atomic charge densities, the radii of atomic spheres containing the

Table 1. MS Xα parameters

Region	Xα Exchange Parameter	Sphere Radii (a.u.)[a] Set *A*	Set *B*
P atom	0.72620	1.71057	2.13821
F (equatorial) atom	0.73732	1.61161	1.73578
F (axial) atom	0.73732	1.52091	1.77121
Outer sphere	0.73510	4.93380	4.89875
Intersphere	0.73510	–	–

[a] For both parameter sets *A* and *B*, the values reported correspond to the equilibrium geometry of the radical.

atomic number of electrons are determined; then the ratio of these values is kept constant and absolute values of the atomic sphere radii are found by requiring "touching spheres", using an R_{PF} distance of 1.70 Å for both equatorial and axial ligands. Although somewhat arbitrary, this value represents a compromise of the different equilibrium geometries predicted for the PF_4 radical in previous publications [4–6]. This procedure of determining the radii of non-overlapping atomic spheres has recently been shown to give slightly better results for the electronic structure of similar compounds [17, 18]. Then, in the search of optimum geometry, the radius of the phosphorus sphere is kept constant in any case, the radii of equatorial and axial fluorine spheres being determined for each geometry by the "touching spheres" requirement. This procedure has the advantage of simplicity while allowing full relaxation (of both their sizes and center positions) of the fluorine spheres around the phosphorus sphere.

Parameter set B corresponds to the use of overlapping atomic spheres, whose radii are found by multiplying by a factor 1.25. The radii determined according to the aforementioned procedure. This factor is of course arbitrary, but such a choice can be roughly justified by both the virial ratio criterion and an examination of results obtained with this procedure for other compounds [19, 20]. As in the case of parameter set A, the size of the phosphorus sphere is kept constant during geometry optimization, the radii of equatorial and axial fluorine spheres being determined by the geometry and the 25% overlap requirement. The amount of overlap has of course to be kept constant during the whole procedure of geometry optimization because the only variational parameters of the problem are the structural ones.

An externally tangent outer sphere is used in each calculation with both parameter sets A and B. Partial waves up to $l = 3$ are included in the multiple scattering expansions in the phosphorus sphere and extramolecular region, and up to $l = 2$ in fluorine spheres. As it is preferable to allow core orbitals to relax when using overlapping atomic spheres [13], the "thawed" core approximation [17], instead of the "frozen" core, is used for inner shell electrons.

Due to the large energy gap (~5 eV) between the highest doubly occupied orbital and the singly occupied one, spin-polarization effects are expected to be small. Therefore all the calculations are made using the non-spin-polarized version of the MS Xα computer programs and the distribution of spin densities is simply given by a population analysis of the unpaired orbital made according to the angular momentum contributions within each atomic sphere.

3. Results and Discussion

Table 2 presents the MS Xα optimized geometry of the PF_4 radical, together with predictions made by different methods. No accurate data are available concerning the structure of this radical, but Hasegawa *et al.* [2b] conclude that angle β should be nearly equal to 180° on the basis of an analysis of the principal axes of the hyperfine tensor of the axial fluorine atoms.

Keeping apart the Extended Hückel calculations, for which no bond length optimization has been performed, the results of Table 2 show that none of the methods predicts

Table 2. Comparison of the equilibrium geometry of the PF_4 radical as predicted by different methods. Distances are in Angströms and angles in degrees

Method	R_{PF_1}	R_{PF_2}	α	β
Extended Hückel[a]	-	-	109 ± 9	174 ± 5
CNDO[b]	1.722	1.727	105.6	140.6
INDO[c]	1.82	1.92	96	156
Ab initio[d]	1.620	1.669	104.7	166.4
This work, set *A*	1.758	1.710	108.1	122.4
This work, set *B*	1.640	1.655	99.6	159.0

[a] Ref. [3]. [b] Ref. [4b]. [c] Ref. [5]. [d] Ref. [6].

an angle β close to 180°. Furthermore, important discrepancies are to be noticed among the different estimates for both bond distances and bond angles, which is not very surprising. It is well known that the standard CNDO and INDO methods generally overestimate bond lengths, while leading to more satisfactory values for bond angles. Hence the most reliable SCF LCAO results quoted in Table 2 are the *ab initio* ones, even though they have been obtained with a minimal basis set (augmented by *d* polarization functions for phosphorus). The MS Xα equilibrium geometry is strongly dependent on the parameter set used: whereas the non-overlapping spheres procedure leads to an unreasonable geometry with a larger bond distance for equatorial than for axial fluorine atoms and a surprisingly small value of β (122.4°), the potential energy surface obtained using overlapping spheres has a minimum very close to the *ab initio* result. The equilibrium geometries predicted by *ab initio* and MS Xα (set *B*) differ by not more than 0.02 Å in bond length and 5.4° in bond angle. Such agreement between two very different methods suggests that the structure of the free radical PF_4 should be close to their prediction, and the value 180° for the bond angle β deduced experimentally [2b] for PF_4 radicals trapped in a solid matrix might be due to intermolecular interactions.

The ground-state orbital energies of the PF_4 radical calculated at equilibrium geometry for both parameter sets are presented in Table 3. It is seen that with each parameter set the unpaired electron occupies a molecular orbital of a_1 symmetry, in agreement with previous predictions [1a]. Due to the large energy gap between the $2a_2$ and $12a_1$ orbitals (about 5 eV in both calculations), the unpaired electron orbital is significantly antibonding, which indicates that the first ionization energy of the radical should be rather small.

Examination of Table 3 shows that the use of overlapping spheres leads to electronic levels strongly shifted upwards. This is not a surprising result since, by allowing atomic spheres to overlap, a large amount of charge is transferred from the interatomic region into the atomic spheres (see Table 4). However there is no important change in both level ordering and energy separations when going from one parameter set to the other. Unfortunately no photoelectron data are available for the PF_4 radical, which makes it impossible to compare with experiment the MS Xα ionization energies we could easily derive using the transition state concept [21]; thus we cannot use the results of Table 3

Table 3. MS Xα electronic energy levels[a] of the PF_4 radical. Energies are in Rydberg units

Orbital[b]	Set *A*	Set *B*
$12a_1$	−0.602	−0.365
$2a_2$	−0.985	−0.765
$6b_1$	−0.990	−0.773
$6b_2$	−0.983	−0.782
$11a_1$	−1.012	−0.813
$5b_2$	−1.013	−0.822
$5b_1$	−1.025	−0.858
$10a_1$	−1.026	−0.861
$1a_2$	−1.033	−0.863
$9a_1$	−1.107	−1.000
$4b_2$	−1.107	−1.043
$4b_1$	−1.135	−1.054
$8a_1$	−1.420	−1.283
$7a_1$	−2.374	−2.209
$3b_1$	−2.400	−2.226
$3b_2$	−2.366	−2.241
$6a_1$	−2.422	−2.311
P 2*p*	−10.122	−9.403
P 2*s*	−13.630	−12.906
F 1*s* (axial)	−48.675	−48.556
F 1*s* (equatorial)	−48.677	−48.569
P 1*s*	−153.573	−152.912

[a] Calculated at equilibrium geometry for each parameter set.

[b] All the orbitals listed are fully occupied except the $12a_1$ which contains the unpaired electron.

for determining which parameter set gives the better description of the electronic structure of PF_4.

Table 4 contains the distribution of the total electronic charge among the various regions of the radical. It is seen that a drastic decrease of interatomic charge results from the use of overlapping spheres, whereas the extramolecular charge remains essen-

Table 4. Total electronic charges[a] (in electronic charge units) in the various regions and total energies (in Rydberg units) of the PF_4 radical

	Set *A*	Set *B*
Electronic charges in		
phosphorus sphere	11.822	13.685
equatorial fluorine sphere	8.383	8.727
axial fluorine sphere	8.214	8.767
interatomic region	5.542	1.947
extramolecular region	0.380	0.385
Total energies	−1475.4051	−1478.9023
Virial ratio[b]	1.00705	0.99936

[a] Calculated at equilibrium for each parameter set.

[b] Defined as $-T/E_{tot}$, where T is the kinetic energy and E_{tot} the total energy.

tially the same because the radii of outer sphere are practically unchanged when going from parameter set *A* to *B*. Furthermore the small differences of charge between equatorial and axial fluorine spheres in each calculation are due to the different distances R_{PF_1} and R_{PF_2}: a larger bond distance leads to a larger radius of the corresponding atomic sphere which includes, finally, a greater electronic charge.

Total energies and virial ratios are also presented in Table 4. It is seen that the use of overlapping spheres leads simultaneously to a substantial lowering of the total energy and to a significant improvement of the virial ratio.

A comparison of the predicted and observed distributions of spin densities in the various regions of the PF_4 radical is shown in Table 5. INDO and *ab initio* predictions cannot be included in this table because corresponding publications [5, 6] do not explicitly report the detailed distribution of spin densities. In the MS Xα results displayed in Table 5, we did not attempt to distribute the interatomic and extramolecular spin densities among the atomic spheres. Such a procedure is rather arbitrary and it seems to us that it could possibly introduce erroneous trends in the analysis of the electronic population of the $12a_1$ orbital.

Examination of Table 5 shows that the MS Xα results obtained using non-overlapping spheres again lead to poor argument with experiment: the spin densities on equatorial and axial fluorine atoms are predicted to be roughly the same, which is in strong contradiction with the analysis of ESR spectra [2b]. Furthermore the spin density in the $3p$ orbital of phosphorus is much too small and the importance of the spin density in

Table 5. Comparison of the distribution of spin densities in the various regions of the PF_4 radical

	MS Xα[a]			
Region	Set *A*	Set *B*	CNDO[b]	Experiment[c]
Phosphorus sphere				
total	0.256	0.380	0.395	0.581
$3s$	0.242	0.046	0.369	0.282
$3p_z$	0.014	0.334	0.026	0.299
Axial fluorine sphere				
total	0.154	0.140	0.221	0.215
$2s$	0.004	0.004	0.010	0.016
$2p_z$	0.026	0.011	-	0.046
$2p_x$	0.124	0.125	0.211	0.153
Equatorial fluorine sphere				
total	0.135	0.035	-	0.036
$2s$	0.003	0.001	0.008	0.003
$2p_z$	0.049	0.030	-	0.033
$2p_y$	0.083	0.004	-	-
Intersphere	0.140	0.233	-	-
Extramolecular	0.026	0.037	-	-

[a] Estimation made at equilibrium geometry for each parameter set by means of an analysis of the electronic population of the singly occupied orbital $12a_1$.

[b] Ref. [4b]. [c] Ref. [2b].

the $2p_y$ orbital of equatorial fluorine is overestimated. The MS Xα results of parameter set B, on the other hand, are in much better agreement with experiment: the ratio of total spin densities on phosphorus and axial fluorine is practically identical to the observed one, and the spin density on equatorial fluorine is much smaller than that on axial fluorine. The only disagreement with experiment is related to the relative importance of $3s$ and $3p_z$ spin densities on phosphorus, but the relative populations of $3s$ and $3p_z$ orbitals of phosphorus arising from the $12a_1$ molecular orbital depend critically on the geometry of the radical, and a change in β angle of a few degrees strongly modifies their relative importance. On the whole it is seen that the MS Xα results obtained with overlapping spheres are superior to CNDO predictions.

Of course, total spin densities in atomic spheres depend on the radii of these spheres and the MS Xα model can only provide estimates of these quantities. But the analysis of the spin density within an atomic sphere according to angular momentum contributions is fairly independent of the size of that sphere. Thus the results of Table 5 show that a reasonable description of the electronic structure of the PF_4 radical can be given by the MS Xα model using again overlapping atomic spheres.

4. Conclusions

Through careful comparison of the results obtained using two different sets of parameters in MS Xα calculations, this work emphasizes a major difficulty encountered when making calculations with this model: the results may be somewhat dependent on the radii of atomic spheres and it is really useful to perform test calculations with different sets of parameters. This problem is in fact analogous to the one-particle basis set choice in *ab initio* calculations or to the empirical parameter determination in semiempirical methods, and the answer can only be found by performing extensive comparative calculations. The present work and the MS Xα results of Cotton *et al.* [22] for di- and trisulfide radicals seem to indicate that the use of overlapping spheres is suitable for a reasonably accurate description of the properties of radicals.

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