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Orbitals and Structures of Pentafluorides

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The electronic and geometric structures of PF_5, AsF_5, and BrF_5 are studied by computing orbital energies for the three molecules in trigonal bipyramidal and square pyramidal structures. The computations are done with a modified Wolfsberg-Helmholz approximation, based on all fluorine 2*s* and *p* orbitals, and the valence shell *s*, *p* and *d* orbitals of the central atoms. Atomic basis functions approaching Hartree-Fock accuracy are used. The trigonal bipyramid structure is by far the more stable for PF_5 and AsF_5, and the square pyramid is the more stable for BrF_5, in terms of orbital energies. Moreover the trigonal bipyramid would give an orbital degeneracy and therefore a Jahn-Teller distortion for BrF_5. Both PF_5 and AsF_5 have very large energy gaps between highest filled and lowest empty orbitals. The highest occupied orbital of BrF_5 has nodal properties that account qualitatively for the effective short-range repulsive force between the so-called lone pair and the adjacent bonds. The origin of the effective repulsive force between "lone pairs" and adjacent bonds is shown to be due to an orthogonality — Exclusion Principle effect.

I. SCOPE OF PROBLEM AND METHOD

Potential energy surface of pentafluorides have considerable interest now, particularly in view of the attention given to these molecules as examples of nonrigid structures. It is now reasonably well known that molecules like PF_5 are capable of undergoing large-amplitude vibrational motions, passing from one energy minimum on the molecular hypersurface to another equivalent one.[1–7] Each passage is a pseudorotation, equivalent to a spatial rotation of the molecule and a permutation of equivalent nuclei which could not be achieved by any rotation of the rigid molecule.[5] Determining the electronic potential surfaces of the molecules would permit theoretical calculation of the pseudorotation rates, from which one could determine the mechanism of

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pseudorotation (tunnelling, thermal excitation over the barrier, or an intermediate situation) and hopefully begin to understand the origin of the flexibility of these molecules, and perhaps of the stiffness of most others.

Another less ambitious but just as tantalizing objective also tempts us to study pentafluorides; this is the simple question of the stability of the static equilibrium structure. The Group V pentafluorides, surely PF_5,[8] probably AsF_5,[9] and presumably the others are trigonal bipyramids. However, BrF_5, exemplifying the Group VII pentafluorides, is a distorted structure more like a square pyramid than a trigonal bipyramid.[10]

The trigonal bipyramid and square pyramid, with symmetries D_{3h} and C_{4v}, respectively, are closely related by moderately small distortions. Both structures must be stationary points — local maxima, local minima or saddle points — on the energy surface of an MX_5 molecule, simply because of their symmetry. In the simplest trajectory between two equivalent trigonal bipyramids, the square pyramid stands at the midpoint, and conversely, a trigonal bipyramid lies midway between two equivalent square pyramids. The pseudorotation of PF_5 presumably carries the molecule through a square pyramid structure or something close to it, and pseudorotation of BrF_5 passes through or near a trigonal bipyramidal structure.

If we are to understand the potential surfaces and dynamics of these and still more complex nonrigid molecules, we ought first to understand the reasons for the particular maxima and minima chosen by a given molecule. Why do group V compounds choose one structure and group VII compounds, the other? Some qualitative arguments have been given which may serve to rationalize and order our interpretations.[11–16] However, it seemed appropriate to us to carry the problem one step closer to a quantitative analysis, by computing approximate molecular orbital energies for the valence shell electrons of PF_5, AsF_5, and BrF_5. We have proceeded in a spirit somewhat akin to that of a recent investigation by van der Voorn and Drago.[17] These authors also investigated 5-coordinated phosphorus halides, but with a goal quite different from ours, namely of trying to explain the bond lengths and choices of sites in the mixed phosphorus chlorofluorides. The aims of our calculations were limited to these:

1) to see what the general pattern of orbital levels is for MF_5 molecules, and what the orbitals are like;

2) to see whether the orbital energies alone are responsible for the observed structures,

and

3) to see whether the orbital pattern gives any dynamic basis, particularly through the Jahn-Teller effect, for the observed structures.

In addition it was hoped that such an investigation might offer some rough guide for future spectroscopy, and for an interpretation of relative bond lengths and strengths. We shall see in the following discussion that the results also give us some insight into the behaviour of so-called lone-pair repulsions.

The calculation was carried out by estimating the orbital energies for PF_5, AsF_5, and BrF_5, and doing this for both the trigonal bipyramid and square pyramid structure for each molecule. Note that any confidence in the results must rest on the gross orbital pattern, not on details, and on the

Table 1. Basic atomic orbitals: principal quantum numbers, coefficients, exponents and energies.

	n	Exponent	Coefficient	Orbital energy $(10^3 cm^{-1})$
a) Fluorine [a]				
2*s*	1	8.5126	−0.22924	
	1	14.4130	−0.00534	
	2	1.8599	0.27178	
	2	2.7056	0.65367	
	2	4.9019	0.33031	
	2	6.4440	−0.23130	
				−374
2*p*	2	1.2655	0.17003	
	2	2.0301	0.55982	
	2	3.9106	0.34875	
	2	8.6363	0.01691	
				−151
b) Phosphorus [b]				
3*s*	1	17.4370	0.060406	
	2	15.2390	0.045089	
	3	8.7990	0.000405	
	2	4.8330	−0.396780	
	3	2.3330	0.723752	
	3	1.4700	0.397737	
				−193.1
3*p*	2	12.5050	−0.008374	
	2	7.1370	−0.086949	
	2	4.3250	−0.183247	
	3	2.0130	0.645961	
	3	1.1900	0.446393	
				−113.5
3*d*	3	6.4000	0.003312	
	3	2.2500	0.052187	
	3	1.0303	0.243268	
	3	0.3928	0.851656	
				−14.4
c) Arsenic [b]				
4*s*	1	31.0400	−0.037784	
	1	38.2327	−0.000013	
	2	26.0107	−0.025440	
	2	15.0969	0.124890	
	3	13.3253	0.092195	
	3	8.0600	−0.182023	
	3	5.4776	−0.246073	
	4	3.1181	0.497991	
	4	1.9958	0.580944	
	4	1.4085	0.044161	
				−189.6

Table 1. Continued.

4*p*	2	14.1928	0.080804	
	2	22.3500	0.008531	
	3	13.4000	0.024048	
	3	8.2953	−0.092939	
	3	5.5239	−0.206608	
	4	4.3000	0.031379	
	4	2.4020	0.586862	
	4	1.4376	0.486239	
	4	0.9100	0.007768	
				−106.6
4*d*	3	4.1981	−0.062561	
	3	2.5395	0.061468	
	3	6.4900	0.007050	
	3	9.0029	−0.019897	
	3	15.2500	−0.000603	
	4	2.2500	−0.025778	
	4	1.2500	0.269440	
	4	0.4819	0.867552	
				−13.52
d) Bromine[c]				
4*s*	1	33.7893	−0.045480	
	1	40.8722	0.003353	
	2	26.2276	−0.039214	
	2	16.0679	0.161334	
	3	13.6300	0.098002	
	3	8.6851	−0.199844	
	3	5.9500	−0.298290	
	4	3.6079	0.503785	
	4	2.3638	0.587821	
	4	1.6195	0.052952	
				−265.4
4*p*	2	15.6239	0.090318	
	2	23.8437	0.009231	
	3	15.0953	0.029334	
	3	8.5420	−0.112188	
	3	5.8330	−0.259436	
	4	5.1219	0.063105	
	4	2.7939	0.637011	
	4	1.6818	0.451797	
	4	1.2010	−0.009473	
				−147.4
4*d*	3	4.7584	−0.032692	
	3	2.9823	0.015594	
	3	7.2761	−0.003650	
	3	10.0792	−0.012095	
	3	16.2500	−0.000679	
	4	2.7500	0.031149	
	4	1.3000	0.205324	
	4	0.4827	0.903933	
				−13.6

[a] See Ref. 20. [b] Supplied by Paul Cade. [c] Supplied by John C. Tully.

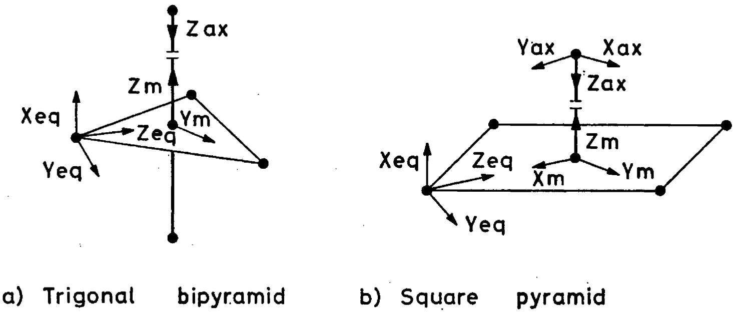
fact that the trigonal bipyramid and the square pyramid represent two not-too-distant points on the *same potential surface*. This means that, provided the orbital energies differ sufficiently from structure to structure, the variations can be neglected in core energies, two-electron Coloumb energies and exchange energies from one structure to the other. If a crude calculation does elucidate the orbital and structural questions, well and good; if not, one ought not to stop short of anything but a full Hartree-Fock calculation, and preferably something at least comparable in sophistication to the calculations of the internal rotation barrier in ethane.[18] This was the philosophy of the calculation; the conclusions of the work are that the calculation does yield considerable understanding of the orbitals and their energies, and more important, of the bases for the two structures. The results should at least be of use until one can determine the potential surface for an 80-electron molecule like BrF_5 or a 78-electron AsF_5. Then, but presumably not much earlier, one could hope to calculate actual pseudorotation rates.

II. CALCULATIONS

The molecular orbital energies were calculated according to the modified Wolfsberg-Helmholz approximation,[19] with the off-diagonal matrix elements of the orbital Hamiltonian

$$h_{ij} = -KS_{ij}(h_{ii}h_{jj})^{1/2}$$

with $K = 2$. The overlap integrals were calculated with functions approaching as closely as practical to the actual atomic Hartree-Fock functions. The basis set included all the $2s$ and $2p$ orbitals of the fluorines, and the ns, np and nd orbitals of the central atom, with $n = 3$ for P, and 4 for As and Br. The d functions were computed for the ns^2np^2nd configuration of P and As and for the ns^2np^4nd configuration of Br, ^2G term, by Paul E. Cade and John C. Tully. The phosphorus function had all d exponents optimized; the As and Br orbitals had only the most important exponent optimized. The atomic basis functions were expressed as a sum of Slater orbitals with principal quantum numbers, coefficients, exponents and eigenvalues shown in Table 1. The



a) Trigonal bipyramid b) Square pyramid

Fig. 1. Coordinate systems for trigonal bipyramid and square pyramid structures.

fluorine orbitals are those given by Clementi, Roothaan and Yoshimine[20] and are included here only for convenience. The *s* and *p* orbitals of P, As, and Br are almost the same as those reported by Clementi;[21,22] the *d* orbitals of P, As, and Br have not been previously computed (except as single Slater functions[17]). The atomic orbital overlaps are given in Table 2. The coordinates are designated in Fig. 1.

We arbitrarily set all bond lengths equal, with values of 1.57 Å for PF_5,[8] 1.74 Å for AsF_5[9] and 1.76 for BrF_5[10] (the average length), and used the same length for both structures. The central atom was located in the plane of the four fluorines, in the square planar structure.

Table 2. Atomic orbital overlaps.

a) Fluorine-fluorine

R (compound)	$2s-2s$	$2s-2p\sigma$	$2p\sigma-2p\sigma$	$2p\pi-2p\pi$
2.22(PF_5)	0.019004	0.050499	0.076851	0.020872
2.461(AsF_5)	0.010052	0.031089	0.052617	0.012573
2.49(BrF_5)	0.009295	0.029288	0.050185	0.011821
2.719(PF_5)	0.005007	0.018295	0.034399	0.007296
3.014(AsF_5)	0.002237	0.009940	0.020887	0.003934
3.05(BrF_5)	0.002024	0.009218	0.019627	0.003647
3.14(PF_5)	0.001578	0.007643	0.016805	0.003021
3.48(AsF_5)	0.000612	0.003757	0.009283	0.001487
3.52(BrF_5)	0.000547	0.003455	0.008651	0.001368

b) Central atom-fluorine

R:	PF 1.570 Å	AsF 1.740 Å	BrF 1.76 Å
$(ns\|2s)$	0.230088	0.185948	0.141621
$(ns\|2p\sigma)$	0.243685	0.213009	0.197226
$(np\sigma\|2s)$	0.386466	0.346776	0.275500
$(np\sigma\|2p\sigma)$	0.234223	0.227506	0.240476
$(np\pi\|2p\pi)$	0.179821	0.149651	0.118217
$(nd\sigma\|2s)$	0.226107	0.202827	0.187570
$(nd\sigma\|2p\sigma)$	−0.054083	−0.051051	−0.045142
$(nd\pi\|2p\pi)$	0.178978	0.149432	0.137677

As a matter of interest, the central atom *s* and *p* radial functions have their maximum amplitudes at distances *r* corresponding closely about 1/2 to the equilibrium central atom-fluorine separations, whereas the *d* orbitals are spread out to much larger radii. This can be recognized immediately from the values of exponents and coefficients in Table 1.

The Hamiltonian matrix was written with group symmetry orbitals as the basis functions. Thus the diagonal elements h_{ii} were simply the atomic orbital energies given in Table 1, multiplied by appropriate renormalizing factors (all near unity) in the case of fluorine group orbitals. Diagonalization was carried out on a GIER computer and a program written previously by one

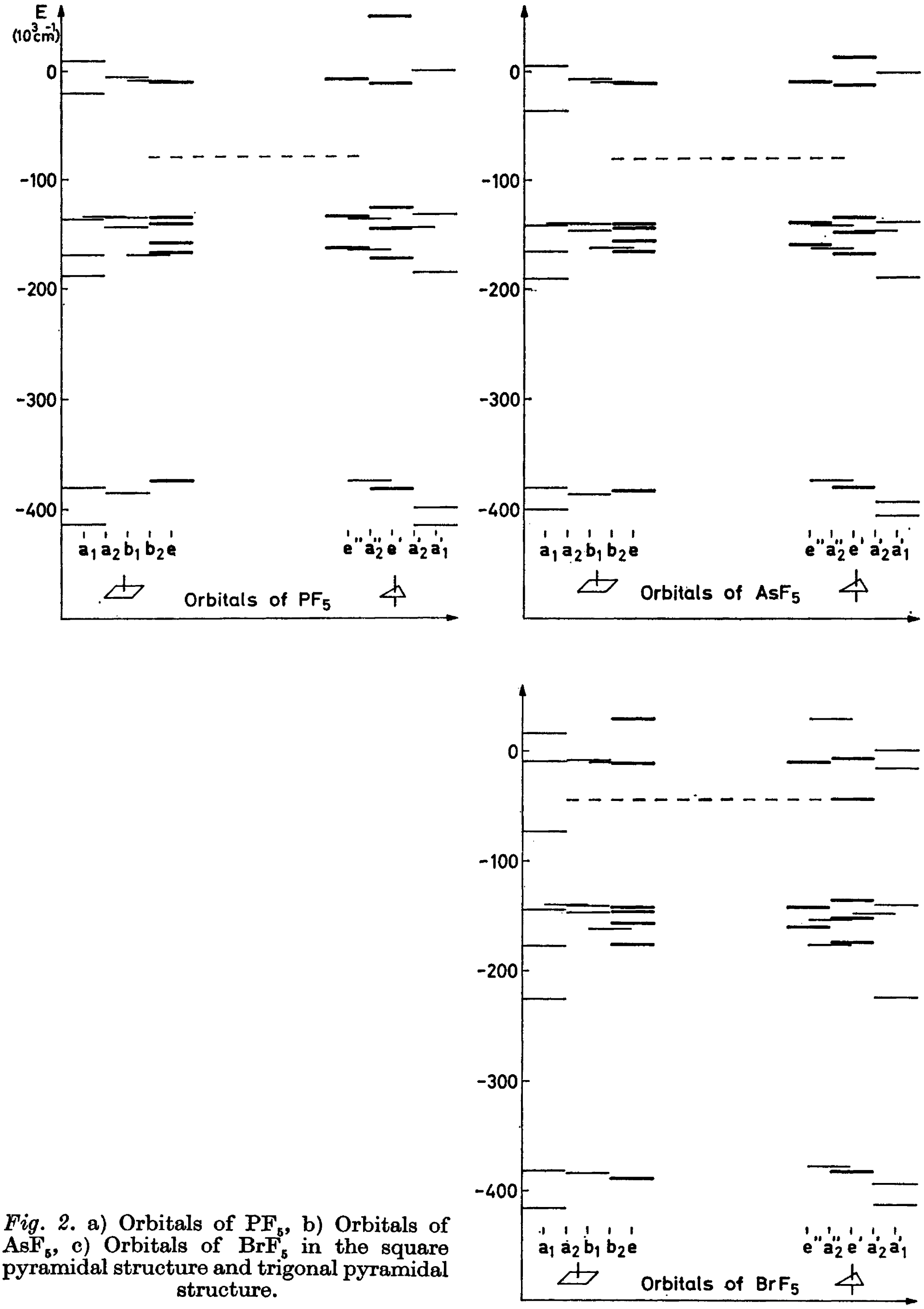


Fig. 2. a) Orbitals of PF_5, b) Orbitals of AsF_5, c) Orbitals of BrF_5 in the square pyramidal structure and trigonal pyramidal structure.

Table 3. Orbitals of the pentafluorides. Orbitals are listed conventionally, in order according to energy, and are denoted by symmetry type. Atomic orbitals are listed if their Mulliken populations ($c_i^2 + \sum_{j\neq i} c_i c_j S_{ij}$) are greater than 0.1, and in order of decreasing population. The numbers in parentheses are the coefficients c_i of these orbitals, not the Mulliken populations. (Full tables of eigenvectors, eigenvalues and populations are available from any of the authors). The dotted lines divide the normally filled and normally empty orbitals. The following abbreviations are used: $3s$, $3p$, $3d$ = Phosphorus orbitals, and similarly with $4s$, $4p$ and $4d$ for arsenic and bromine; eq = equatorial, ax = axial, for fluorines; s = fluorine $2s$; π_x = $2p\pi$ perpendicular to equatorial plane, π_y = $2p\pi$ in equatorial plane, as shown in Fig. 1; σ = fluorine $2p\sigma$, directed toward central atom.

PF_5 Square pyramid

Orbital	Principle AO contributions (coefficients)	Energy (10^3 cm^{-1})
$8a_1$	$3s(1.24)$, $3p(0.63)$, σ eq(-0.63)	227.0
$7e$	$3p(1.35)$	159.2
$7a_1$	$3d(0.75)$, $3p(0.77)$	9.3
$4b_1$	$3d(1.05)$	−5.2
$2b_2$	$3d(-1.05)$	−8.9
$6e$	$3d(1.03)$	−10.1
$6a_1$	$3d(-0.72)$, $3p(0.64)$	−21.0
$1a_2$	π_y eq(1)	−134.0
$3b_1$	σ eq(1.00)	−135.5
$5e$	π ax(-0.73), π_x eq(0.60), σ eq(0.40)	−136.7
$5a_1$	σ ax(-0.76), π_x eq(0.61), σ eq(0.40)	−137.6
$4e$	π_y eq(0.84), σ eq(0.46)	−141.7
$2b_1$	π_x eq(1.00)	−144.9
$3e$	π_x eq(0.70), σ eq(-0.41), π ax(0.42), π_y eq(0.35)	−159.3
$1b_2$	π_y eq(-1.04)	−168.4
$2e$	σ eq(-0.55), π ax(-0.50), π_y eq(0.36), π_x eq(-0.34)	−168.7
$4a_1$	π_x eq(-0.69), σ ax(-0.49), $3p(-0.28)$	−170.0
$3a_1$	σ eq(-0.74), $3s(-0.32)$	−188.4
$1e$	s eq(-0.96)	−375.2
$2a_1$	s ax(-0.94), s eq(0.44)	−380.4
$1b_1$	s eq(1.07)	−385.3
$1a_1$	s eq(-0.80), $3s(-0.24)$, s ax(-0.30)	−414.9

Total orbital energy $E_0 = \sum n_i \varepsilon_i = -8445.8 \times 10^3$cm^{-1}

PF_5 Trigonal bipyramid

Orbital	Principal AO contributions (coefficients)	Energy (10^3 cm^{-1})
$6a_1'$	$3s(1.31)\sigma$ eq(-0.63)	183.4
$4a_2''$	$3p(1.35)$	159.1
$6e'$	$3p(1.17)$	49.2
$5a_1'$	$3d(-1.09)$	0.76
$3e''$	$3d(1.04)$	−9.3
$5e'$	$3d(-0.98)$	−12.5
$4e'$	π ax(-0.81), π_y eq(-0.67)	−128.0
$4a_1'$	σ ax(-0.82), σ eq(0.68)	−134.3
$2e''$	π_x eq(-0.75), π ax(0.73)	−136.1

Table 3 cont.

$3a_2''$	π_x eq(0.83), σ ax(−0.62)	−138.9
$1a_2'$	π_y eq(1)	−146.6
$3e'$	σ eq(−0.86), π_y eq(−0.46)	−147.8
$1e''$	π ax(0.72), π_x eq(0.69)	−165.8
$2a_2''$	σ ax(−0.68), π_x eq(−0.54), 3p(−0.21)	−166.3
$2e'$	π_y eq(−0.61), π ax(0.56), σ eq(0.32)	−174.7
$3a_1'$	σ eq(−0.61), σ ax(−0.49) 3s(−0.31)	−187.6
$1a_2''$	s ax(0.95)	−375.2
$1e'$	s eq(−0.99)	−382.2
$2a'$	s ax(−1.01)	−399.3
$1a_1'$	s eq(0.94), 3s(0.21)	−416.2
	Total orbital energy $E_0 = \sum n_i \varepsilon_i =$	-8469.0×10^3 cm^{-1}

E_0 (trigonal bipyramid) − E_0 (square pyramid) = -23.2×10^3cm^{-1} or −2.88 eV

AsF$_5$ Square pyramid

Orbital	Principal AO contributions (coefficients)	Energy
$8a_1$	4s(1.04), 4p(0.66), σ eq(−0.59)	101.9
$7e$	4p(1.26)	85.7
$7a_1$	4d(−0.99)	−5.4
$4b_1$	4d(1.04)	−6.9
$2b_2$	4d(−1.03)	−9.9
$6e$	4d(1.02)	−10.7
$6a_1$	4p(−0.85), σ eq(−0.48), 4s(0.46)	−37.2
$1a_2$	π_y eq(1)	−140.2
$3b_1$	σ eq(−1.00)	−141.3
$5e$	π ax(−0.71), π_x eq(0.58), σ eq(0.41)	−141.8
$5a_1$	σ ax(−0.75), π_x eq(0.60), σ eq(0.38)	−142.5
$4e$	π_y eq(0.82), σ eq(0.45)	−145.1
$2b_1$	π_x eq(1)	−147.3
$3e$	π_x eq(0.74), π ax(0.49), σ eq(−0.33)	−157.2
$1b_2$	π_y eq(−1.03)	−163.0
$2e$	σ eq(−0.60), π ax(−0.44), π_y eq(0.41)	−166.1
$4a_1$	π_x eq(0.71), σ ax(0.47), 4p(0.28)	−166.2
$3a_1$	σ eq(−0.68), 4s(−0.41), σ ax(−0.29)	−191.9
$1e$	s eq(−0.98)	−374.4
$2a_1$	s ax(0.96), s eq(−0.38)	−381.2
$1b_1$	s eq (1.06)	−387.2
$1a_1$	s eq(−0.85), 4s(−0.23)	−401.3
	Total orbital energy $E_0 = -8463.4 \times 10^3$cm^{-1}	

AsF$_5$ Trigonal bipyramid

$4a_2''$	4p(1.26)	85.8
$6a_1'$	4s(1.15), σ eq(−0.63), σ ax(−0.50)	66.6
$6e'$	4p(1.03), 4d(−0.52)	12.0
$5a_1'$	4d(1.05)	−3.3
$3e''$	4d(1.03)	−10.3
$5e'$	4d(0.89), 4p(0.51)	−14.8

Table 3 cont.

$4e'$	π ax(−0.78), π_y eq(−0.66)	−136.0
$4a_1'$	σ ax(−0.81), σ eq(0.66)	−140.6
$2e''$	π_x eq(−0.74), π ax(0.72)	−141.5
$3a_2''$	π_x eq(−0.81), σ ax(0.62)	−143.2
$1a_2'$	π_y eq(1)	−148.5
$3e'$	σ eq(−0.86), π_y eq(−0.47)	−149.5
$1e''$	π ax(0.72), π_x eq(0.69)	−161.2
$2a_2''$	σ ax(−0.68), π_x eq(−0.55), $4p$(−0.23)	−164.9
$2e'$	π ax(−0.58), π_y eq(0.60), σ eq(−0.35)	−169.3
$3a_1'$	σ eq(−0.57), σ ax(−0.46), $4s$(−0.40)	−191.6
$1a_2''$	s ax(−0.97)	−374.4
$1e'$	s eq(1.01)	−380.9
$2a_1'$	s ax(−0.96)	−394.6
$1a_1'$	s eq(−1.00)	−406.4

Total orbital energy $= -8482.5 \times 10^3$ cm^{-1}

E_0 (trigonal bipyramid) − E_0 (square pyramid) $= -19.1 \times 10^3$ cm^{-1} or -2.37 eV.

BrF_5 Square pyramid

Orbital	Principal AO contributions (coefficients)	Energy
$7e$	$4p$(1.12), σ eq(−0.68)	28.3
$8a_1$	$4s$(−0.80), $4p$(−0.66), σ eq(0.59), σ ax(0.58)	16.1
$4b_1$	$4d$(1.04)	− 8.0
$7a_1$	$4d$(1.02)	− 9.2
$2b_2$	$4d$(−1.03)	− 10.5
$6e$	$4d$(1.02)	− 11.3
$6a_1$	$4p$(−0.74), σ eq(−0.67), π_x eq(0.42)	− 73.7
$1a_2$	π_y eq(1)	−140.8
$3b_1$	σ eq(−1.00)	−141.8
$5e$	π ax(−0.75), π_x eq(0.64)	−142.7
$5a_1$	π_x eq(−0.73), σ ax(0.64)	−144.2
$4e$	π_y eq(0.92), σ eq(0.38)	−146.2
$2b_1$	π_x eq(1.00)	−147.6
$3e$	π_x eq(0.77), π ax(0.59)	−157.5
$1b_2$	π_y eq(−1.03)	−162.1
$2e$	σ eq(0.67), $4p$(0.37), π_y eq(−0.32)	−176.6
$4a_1$	π_x eq(−0.55), σ ax(−0.51), $4p$(−0.45)	−177.9
$3a_1$	$4s$(0.59), σ eq(0.51), s eq(−0.47)	−226.8
$1e$	s eq(−0.93)	−379.2
$2a_1$	s ax(−0.91), s eq(0.44)	−382.0
$1b_1$	s eq(1.05)	−384.4
$1a_1$	s eq(−0.76), $4s$(−0.36), s ax(−0.31)	−416.1
	Total orbital energy	-8803×10^3 cm^{-1}

Table 3 cont.

	BrF_5 Trigonal pyramid	
Orbital	Principal AO contributions (coefficients)	Energy
$4a_2''$	$4p(1.12)$	28.4
$6a_1'$	$4d(0.98)$	− 0.99
$6e'$	$4d(1.01)$	− 8.3
$3e''$	$4d(1.02)$	− 10.8
$5a_1'$	$4s(-0.84)$, σ eq(0.66), σ ax(0.50)	− 17.5
$5e'$— — —	$4p(1.01)$, σ eq(−0.51) — — — — — — — — — — — — — —	− 45.2
$4e'$	π ax(0.79), π_y eq(0.66)	−136.8
$4a_1'$	σ ax(0.81), σ eq(−0.65)	−141.1
$2e''$	π_x eq(−0.74), ax(0.72)	−142.0
$3a_2''$	π_x eq(−0.90), σ ax(0.48)	−144.8
$1a_2'$	π_y eq(1)	−148.7
$3e'$	σ eq(−0.73), π_y eq(−0.59)	−152.5
$1e''$	π ax(0.72), π_x eq(0.69)	−160.4
$2e'$	π ax(−0.50), π_y eq(0.48), σ eq(−0.46), $4p(-0.33)$	−174.9
$2a_2''$	σ ax(−0.68), $4p(-0.37)$, π_x eq(−0.40)	−176.2
$3a_1'$	$4s(0.58)$, σ eq(0.43), σ ax(0.35)	−225.5
$1a_2''$	s ax(0.93)	−379.2
$1e'$	s eq(0.97)	−383.4
$2a_1'$	s ax(0.92), s eq(−0.55)	−394.7
$1a_1'$	s eq(−0.78), $4s(-0.36)$, s ax(−0.30)	−415.9
	Total orbital energy	-8743×10^3 cm^{-1}

E_0 (trigonal bipyramid) − E_0 (square pyramid) = 60×10^3 cm^{-1} or 7.4 eV.

of us (HJ).[23] In this work, no attempt was made to readjust the matrix elements for charge transfer.

The results of the diagonalization are summarized in Fig. 2, a-c, and in Table 3. These give the orbital symmetry, energy and basic character in terms of principal atomic orbital contribution.

III. DISCUSSION OF RESULTS

A. Structures and configurations

Note first that for both PF_5 and AsF_5, the trigonal bipyramid is the more stable structure according to the simple sum of one-electron energies $\sum n_i \varepsilon_i$, by amounts large enough that we can expect the pure one-electron terms to dominate any differences in the omitted two-electron Coulomb and exchange terms and core terms. The calculated difference in energies is, not surprisingly, much higher than the barrier height for pseudorotation, as derived from

NMR line shape studies on related compounds [2–4] and infrared spectra,[9] 1000—3500 cm^{-1} for PF_5 and 250—2100 cm^{-1} for AsF_5.

By contrast, the lowest-energy form of BrF_5 is the square pyramid. Again, the stable structure based on orbital energies lies far enough below the other that we can expect the neglected terms to change the results only qualitatively.

Note that the Group V compounds have essentially closed-shell structures. The calculated energy gaps between the group of normally-filled orbitals and normally-empty orbitals is of order 10^5 cm^{-1}. Then, the two extra electrons of BrF_5 must go into the "new shell", the highest group of levels shown in Fig. 2. Two points about the BrF_5 orbitals are particularly interesting. First, the highest occupied orbital is lower for BrF_5 than the corresponding empty orbital in PF_5 or AsF_5, particularly in the square pyramid form. This is the most important single factor in accounting for the stabilization of BrF_5's square orbital stability. Second, and particularly interesting, is the fact that the trigonal bipyramid for BrF_5 is *orbitally degenerate.* Therefore the trigonal bipyramid must undergo a first-order displacement according to the Jahn-Teller Theorem, and cannot be the ground state structure for BrF_5 or, presumably, for any 5-coordinated molecule isoelectronic with a Group VII pentahalide. The possibility that such a situation might account for the stability of the observed structures was one of the foremost ideas in our minds at the outset. That the orbital energies alone would be in accord with the actual structures was considered possible, but was not particularly expected. This view was particularly tempting in light of the way the simple orbital repulsion model is in accord with observation.[11,12] One might expect the orbital energies of BrF_5 to put the square pyramid higher, so that only inclusion of the repulsions and Jahn-Teller coupling would predict any structure but the trigonal bipyramid for BrF_5, but this just doesn't turn out to be the case.

B. Orbitals and bonding

The only previous calculations reporting the level pattern for orbital energies was that of Rundle,[14] based on a Hückel-type calculation, for IF_5, and including only iodine $5s$ and $5p$ and fluorine $2p\sigma$ orbitals. One other Hückel calculation was done for BrF_5,[13] aimed at relating bond lengths and bond orders, and the recent Wolfsberg-Helmholz calculation of van der Voorn and Drago [17] was carried out for phosphorus chlorofluorides to interpret the bonding, and particularly of the positions chosen by chlorine and fluorine atoms in the trigonal bipyramid. Neither of the sets of authors discuss the orbital levels; van der Voorn and Drago did compute energies for square pyramidal PF_4Cl and $PFCl_4$, and found the former to be more stable in a square pyramid. We did not perform any computations with chlorine, so cannot make any direct comparison. Issleib and Gründler [26] has further during the printing of this paper looked at PH_5.

The basic orbital pattern is as follows: at the bottom are the fluorine $2s$ orbitals, with only a slight mixing, in most cases, with the valence s orbital of the central atom. Next comes a totally-symmetric orbital, the $3a_1$, combining a $2p\sigma$ equatorial fluorine orbital with the valence s-orbital of the central atom. This is parallel to the finding of van der Voorn and Drago; they associate this with the "greater electronegativity" of equatorial phosphorus orbitals, *i.e.* with the preference of chlorines to move to equatorial and fluorines to move to axial positions. In any event, this mixing is surely consistent with the equatorial bonds being shorter and stronger than axial bonds.

The next group of orbitals, from about $-170\,000$ cm^{-1} to $-130\,000$ cm^{-1}, contains all the fluorine $2p\pi$ orbitals, the rest of the $2p\sigma$'s and the contribution from the pz orbital of the central atom to the axial bond. This bonding contribution comes from the $4a_1$ of the square pyramid and the $2a_2''$ of the trigonal bipyramid. The axial fluorine $p\sigma$-central atom p_z mixing is greatest by far in BrF_5. In BrF_5 only, there is also considerable F—Br $p\sigma$—$p\sigma$ mixing in the equatorial plane, in the $2e$ ($2e'$ in trigonal bipyramid) orbital. The higher orbitals in this set are composed principally of fluorine $2p$ orbitals. There is a great deal of mixing among the equatorial π_x and axial σ orbitals, and some among equatorial π_y and axial π orbitals.

The third major group of orbitals follows only after a large gap in energy. The lowest show an interesting trend toward more central atom-fluorine mixing, as one goes from PF_5 to AsF_5 to BrF_5. In PF_5, all the normally empty orbitals are essentially phosphorus orbitals, while in BrF_5, the $6a_1$ (square pyramid) and both $5e'$ and $5a_1'$ (trigonal bipyramid) contain large $2p\sigma$ contributions from fluorine. Within the normally-empty or partly-filled orbitals, the central atom d orbitals strongly dominate the lower group, while the p's and whatever is left of the s appear on top. Incidentally, Hansen and Bartell's inference, and Rundle's assumption, that the d orbitals play a small part in the ground states, is entirely justified by our results. They are absolutely dominant in the lowest excited states, but hardly enter in the normally occupied orbitals.

In all cases the equatorial orbitals lie deeper than the axial orbital containing the same sort of atomic orbital composition. Thus, for example, $1a_1'$ of the trigonal structure is essentially equatorial and $2a_1'$ is axial; $2e'$ of the trigonal structure contains more equatorial contribution than axial, while $4e'$, the axial-equatorial antibonding complement of $2e'$, is dominated by its axial contribution. This is all consistent with the greater strength of the equatorial bonds and suggestive of it, but does not necessarily prove that the equatorial bonds are shorter and stronger.

The character of the highest occupied orbital of BrF_5 deserves comment. In the trigonal bipyramid, this orbital is the $5e'$, a mixture of $Br4p_{x,y}$ and F $2p\sigma$ equatorial orbitals, *antibonding* between Br and F.

In the square pyramid, the highest occupied orbital is the $6a_1$, slightly hybridized on Br to be depressed a bit below the equatorial plane and, most important, it is strongly mixed with equatorial fluorine orbitals, especially $2p\sigma$ fluorine orbitals. There is some contribution from the $2p\pi_x$ orbitals (perpendicular to equatorial plane) which tilts the maxima of the inner lobe of the fluorine-orbitals below the F_4 plane. The phase of Br and F orbitals are such that the $6a_1$ orbital is *F—Br bonding above the F_4 plane* and *antibonding below it*. The "lone pair" orbital does concentrate on the open base of the pyramid, but it is by no means a noninteracting orbital, as can be seen from the coefficients and Mulliken population in Table 4. The nodal character of the

Table 4. Coefficients and Mulliken populations of the $6a_1$ orbital for square planar BrF_5 and AsF_5.

BrF_5	$4s$	$4p$	$4d$	$2s$ eq	$2s$ ax	$2p\sigma$ eq	$2p\sigma$ ax	$2p\pi_x$ eq
Coefficient	0.4501	−0.7428	0.0693	−0.2088	0.1705	−0.6742	0.2617	0.4188
Population	0.0946	0.3975	0.0069	0.0231	0.0049	0.3277	0.0355	0.1098
AsF_5(normally empty)								
Coefficient	0.4630	−0.8576	0.2866	−0.2175	0.1873	−0.4853	0.1860	0.4193
Population	0.1194	0.5373	0.0960	0.0250	0.0051	0.1316	0.0096	0.0761

$6a_1$ orbital gives it precisely the character to make this orbital accountable for the observed distortion of the F_{axial}—Br—$F_{\text{equatorial}}$ angle to slightly less than 90°. Because of the relatively small amount of *s*-character and hybridization, we should properly say that *this orbital produces both Br—F repulsions below the equatorial plane and Br—F attractions above this plane.* The effective repulsions, it is important to note, come from the existence of a node between Br and F, with considerable electron density on both the bromine and fluorine sides of the node. The result is an electron density distribution that produces a torque and an angle distortion, due to the electron charge distribution's net force on the bromine and fluorine nuclei.

The effective force that distorts the square pyramid seems at first sight to be due to delocalization and not to electron-electron repulsion, implying that the qualitative arguments based on lone pair repulsions give a misleading picture. However, one cannot use quite such a simplistic line; rather we should note that the concept of lone pair repulsion is implicitly based on a calculation of forces with a localized orbital basis, a basis obtained by a unitary transformation of the symmetry orbitals. The two approaches choose different ways of allotting total electron density to individual electrons. The symmetry orbital argument we have followed says, in effect, that the distortion of BrF_5 can be associated with forces arising primarily from one orbital, the highest occupied orbital. Were we to use localized orbitals for our representation, the individual orbital energies would be of little meaning to us, and we couldn't be sure that the highest occupied orbital would be that of the "lone pair". Nevertheless we could surely identify the "lone pair" orbital, and it would be essentially nonbonding in the traditional sense,[24] it would contribute very little electron density to the regions between Br and F nuclei. Nevertheless, the energy of the total system would be (we can now say, reasoning after the fact) lower if the lone pair were allowed to spread out, by having the fluorines' equatorial plane move slightly up toward the axial fluorine. The net result is again an effective repulsion, but due to the orthogonality conditions on the lone pair and adjacent localized bond orbitals. There is one very important point then, about the origin of this effective repulsion of the lone pair for other bonds, whether it is described in terms of nodes of delocalized symmetry orbitals or of repulsions of localized orbitals. It is a result of the properties of the one-electron waves in their effective potential, or, from another viewpoint, of the

Exclusion Principle. It occurs even if electron-electron electrostatic repulsion is neglected. In other words the shortrange effective repulsive forces invoked in the Gillespie model do seem real and justified, they simply do not necessarily involve electrostatic repulsions between electrons. This description of the forces called upon by Gillespie clarifies why these forces should be short-ranged, and primarily between orbitals around a single center, and how they differ from the longer-ranged nonbonded repulsions discussed by Bartell.[25] It also answers, at least in part, the dilemma posed so clearly by Bartell,[16] of why both the orbital model, without any explicit electron-electron interactions, and the Gillespie model, based on local repulsions, could both give such consistently useful predictions.

In conclusion we should point out that the calculations imply that BrF_5 should exhibit reasonably low-lying optical transitions between the $6a_1$ and $6e$ orbitals, with equatorial polarization. Both are transitions to $4d$ orbitals of bromine, and get their intensity from charge transfer, with electrons moving from F to Br. The other two compounds, PF_5 and AsF_5, will only absorb in the vacuum ultraviolet region. They may exhibit bound excited states if the phosphorus and arsenic d orbitals are sufficiently nonbonding. These spectra are currently under investigation.

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