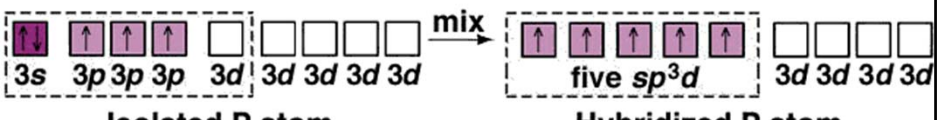
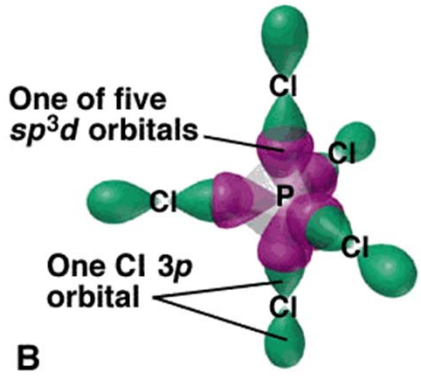
The sp^3d Hybrid Orbitals in PCl_5

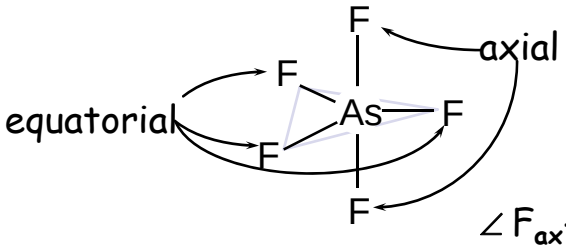


A



Trigonal bipyramidal

Pentafluoroarsenic(V)
Trigonal Bipyramidal Geometry



$\angle F_{ax}\text{-}As\text{-}F_{ax} = 180°$

$\angle F_{ax}\text{-}As\text{-}F_{eq} = 90°$

$\angle F_{eq}\text{-}As\text{-}F_{eq} = 120°$

Axial and equatorial positions are non-equivalent.

$r_{axial} > r_{equatorial}$

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

$$\Gamma_{5H} = 2A' + A_2'' + E'$$

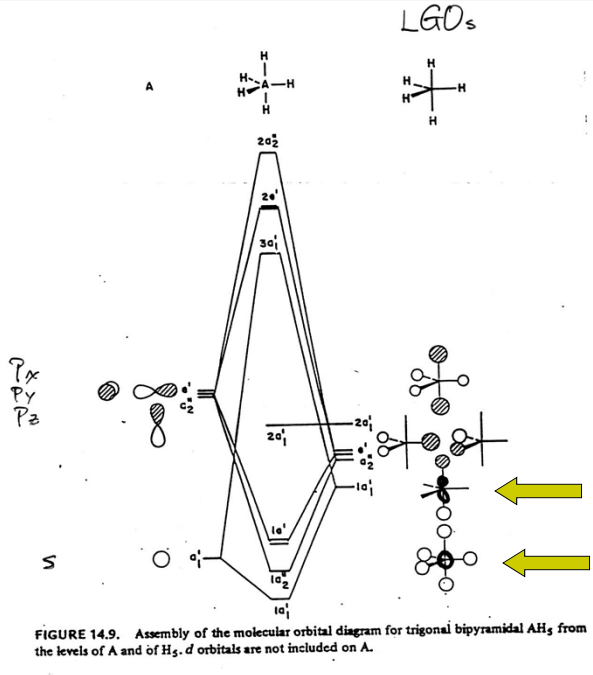


FIGURE 14.9. Assembly of the molecular orbital diagram for trigonal bipyramidal AH_5 from the levels of A and of H_5. *d* orbitals are not included on A.

Average Bond Order: 4/5

Axial P-F bond order:

$$\frac{1}{5}[\frac{1}{2}(2)] + \frac{1}{2}[\frac{1}{2}(2)] = 0.7$$

Equatorial P-F bond order

$$\frac{1}{5}[\frac{1}{2}(2)] + \frac{1}{3}[\frac{1}{2}(4)] = 0.87$$

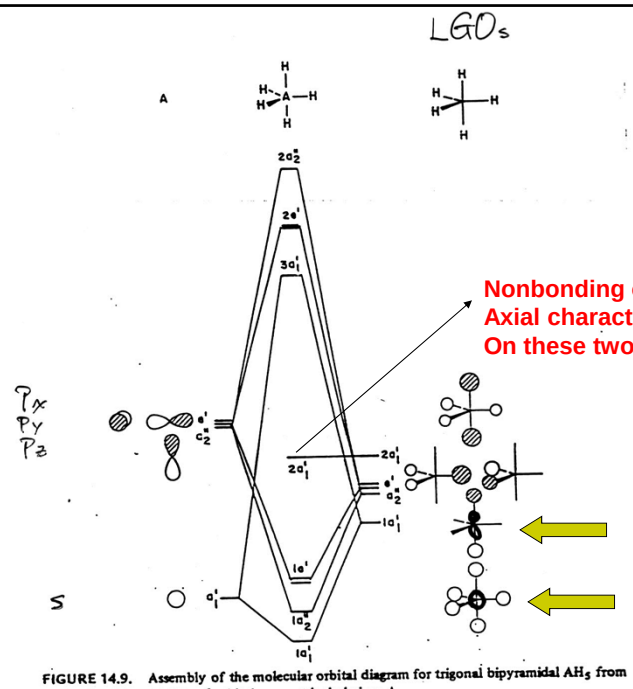
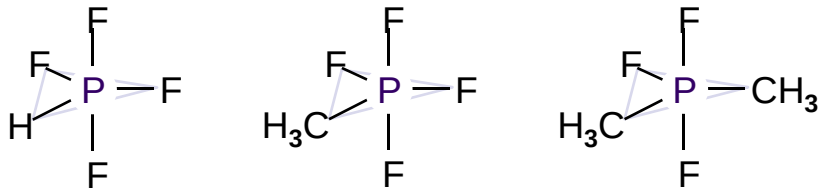


FIGURE 14.9. Assembly of the molecular orbital diagram for trigonal bipyramidal AH_5 from the levels of A and of H_5. *d* orbitals are not included on A.

Trigonal Bipyramidal
Electronegative Element Position

Electronegative elements favor the axial positions.



The orbitals of the central atom used for bonding are different for axial and equatorial.

ClF_5

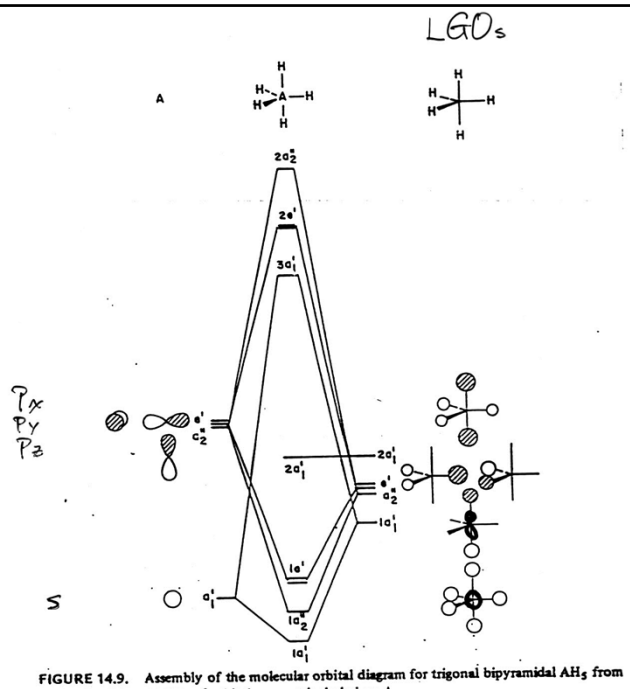


FIGURE 14.9. Assembly of the molecular orbital diagram for trigonal bipyramidal AH_5 from the levels of A and of H_5. *d* orbitals are not included on A.

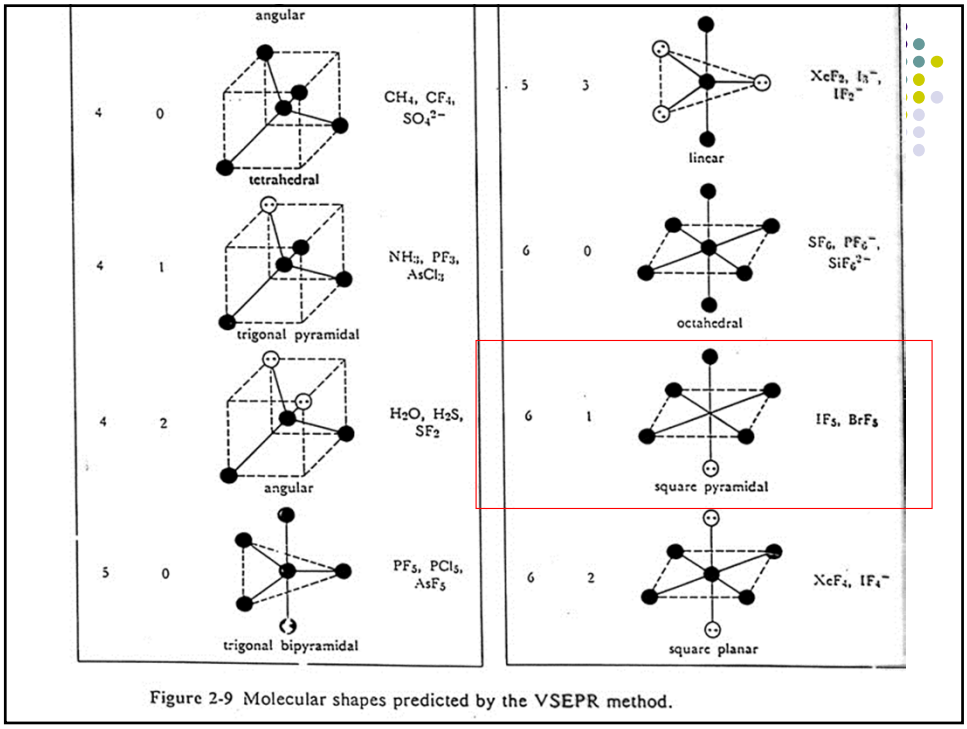
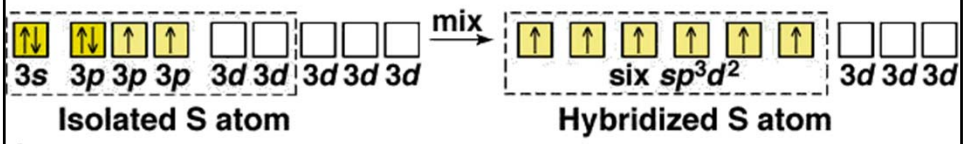


Figure 2-9 Molecular shapes predicted by the VSEPR method.

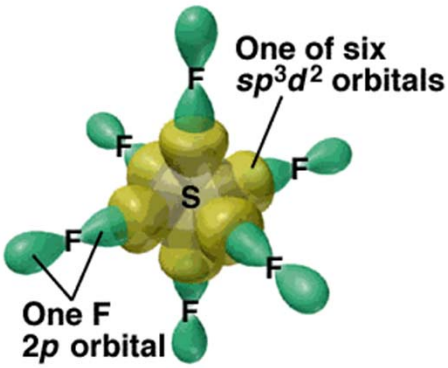
Character table for C_{4v} point group

	E	$2C_4$ (z)	C_2	$2\sigma_v$	$2\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)

The sp^3d^2 Hybrid Orbitals in SF_6



A



B

octahedral

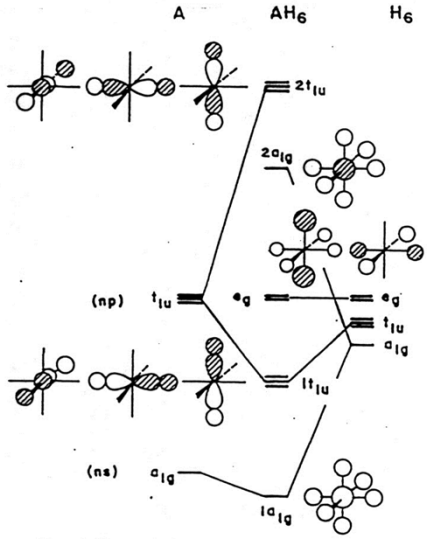
AH_6

VBT?

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	1	2	0		$2z^2-x^2-y^2, x^2-y^2$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	R_x,R_y,R_z	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		xz,yz,xy
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	x,y,z	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

$$\Gamma_{6H} = A_{1g} + T_{1u} + E_g$$

LGO



Bond order??

FIGURE 14.1. Assembly of the molecular orbital diagram of an octahedral AH_6 molecule from the orbitals of A and of H_6. *d* orbitals are not included on A.

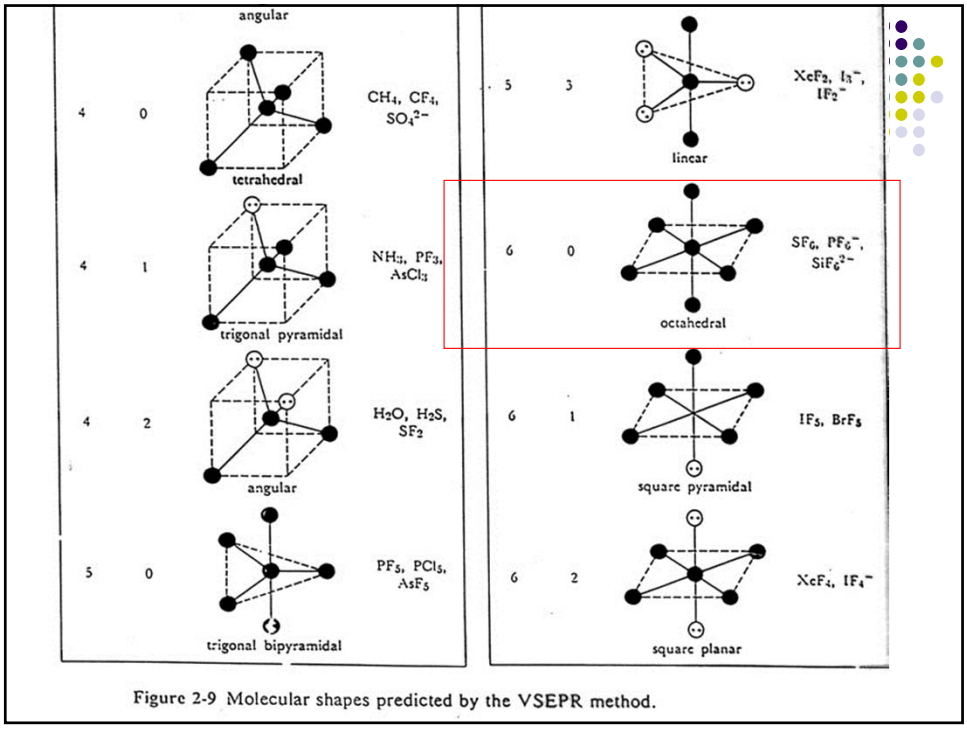


Figure 2-9 Molecular shapes predicted by the VSEPR method.

XeF_6 14 e SN=7

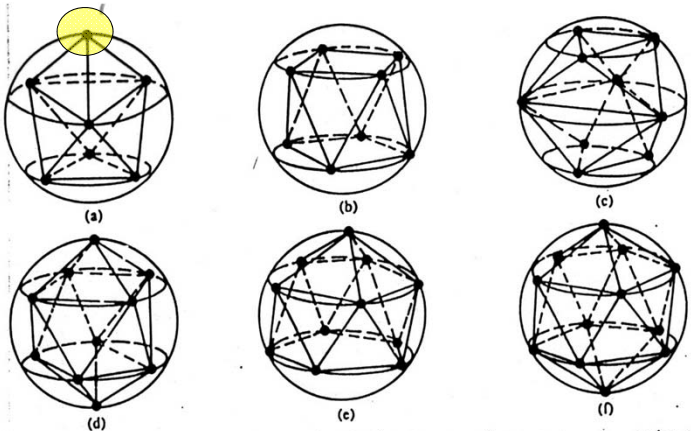
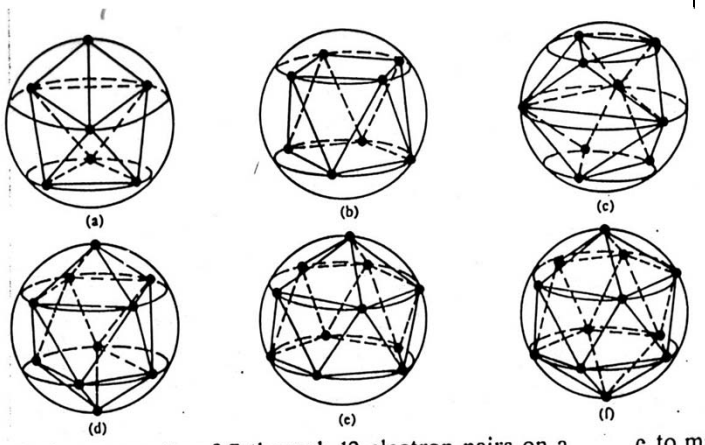


Figure 2-10 Arrangements of 7 through 12 electron pairs on a sphere to maximize distance between pairs. (a) 7 pairs: monocapped octahedron; (b) 8 pairs: square antiprism; (c) 9 pairs: tricapped trigonal prism; (d) 10 pairs: bicapped square antiprism; (e) 11 pairs: monocapped pentagonal antiprism; (f) 12 pairs: icosahedron.

IF_7 14 e SN=7 Pentagonal bipyramidal



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Some failure of VSEPR:

Does not predict geometries of molecules with unpaired electron (USE MO instead)

$$\cdot CH_3, NH_3^+$$

Trigonal planar

Does not predict geometries of transition metal complexes

$$[CoF_6]^{3-}$$

18 e, SN=9???

VBT

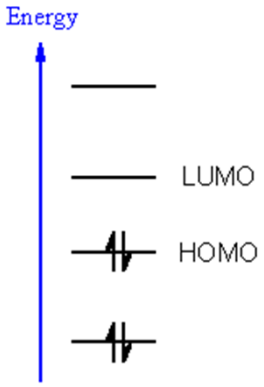
Localized picture
Orbital hybridization, electron promotion, using d orbital
Ground state, molecular geometry
No excited state information
Can not explain oxygen paramagnetism

MOT

Delocalized picture
Without using high energy d orbitals
Both occupied and empty orbital
Excited state information, allow spectroscopic study:
example: PES
Explain unpaired electron in oxygen and others.
Molecular geometry
Orbital character: CH_4
Exact bond order: PF_5
Chemical reaction: LUMO, HOMO, frontier orbital

Chem 104A, UC, Berkeley

Case Study: Reaction



LUMO receives electrons
lowest energy orbital available
characteristic for **electrophilic** component

electrons from the **HOMO** are donated
most available for bonding
most weakly held electrons
characteristic for **nucleophilic** component