Chem 612 - Fall, 2008
Assignment 8 - Solutions

4.1 The reducible representation, symmetry-allowed AOs, and possible combinations are listed for each part.

(a) trigonal planar

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	3	0	1	3	0	1

$$\Gamma = A_1' + E'$$

$$A_1': s, d_{z^2} \qquad E': (p_x, p_y), (d_{xy}, d_{x^2-y^2})$$

A_1'	E'	Notation
s	(p_x, p_y)	sp^2
s	$(d_{xy}, d_{x^2-y^2})$	sd^2
d_{z^2}	(p_x, p_y)	$p^2d \equiv dp^2$
d_{z^2}	$(d_{xy}, d_{x^2-y^2})$	d^3

(b) square planar

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	2	0	0	0	4	2	0

$$\Gamma = A_{1g} + B_{1g} + E_u$$

$$A_{1g}: s, d_{z^2} \qquad B_{1g}: d_{x^2-y^2} \qquad E_u: (p_x, p_y)$$

A_{1g}	B_{1g}	E_u	Notation
s	$d_{x^2-y^2}$	(p_x, p_y)	dsp^2
d_{z^2}	$d_{x^2-y^2}$	(p_x, p_y)	d^2p^2

(c) trigonal bipyramid

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	5	2	1	3	0	3

$$\Gamma = 2A_1' + A_2'' + E'$$

$$A_1': s, d_{z^2} \quad A_2'': p_z \quad E': (p_x, p_y), (d_{xy}, d_{x^2-y^2})$$

$2A_1'$	A_2''	E'	Notation
s, d_{z^2}	p_z	(p_x, p_y),	dsp^3
s, d_{z^2}	p_z	$(d_{xy}, d_{x^2-y^2})$	d^3sp

(d) octahedral

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

$$\Gamma = A_{1g} + E_g + T_{1u}$$

$$A_{1g}: s \quad E_g: (d_{z^2}, d_{x^2-y^2}) \quad T_{1u}: (p_x, p_y, p_z)$$

Only possibility is d^2sp^3.

4.2 The indicated distortion takes the symmetry down to D_{2d}.

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ	4	0	0	0	2

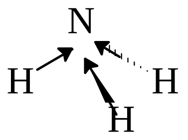
$$\Gamma = A_1 + B_2 + E$$

$$A_1: s, d_{z^2} \quad B_2: p_z, d_{xy} \quad E: (p_x, p_y), (d_{xz}, d_{yz})$$

A_1	B_2	E	Notation
s	p_z	(p_x, p_y)	sp^3
s	p_z	(d_{xz}, d_{yz})	$spd^2 \equiv d^2sp$
s	d_{xy}	(p_x, p_y)	$sp^2d \equiv dsp^2$
s	d_{xy}	(d_{xz}, d_{yz})	sd^3
d_{z^2}	p_z	(p_x, p_y)	$dp^3 \equiv p^3d$
d_{z^2}	p_z	(d_{xz}, d_{yz})	$pd^3 \equiv d^3p$
d_{z^2}	d_{xy}	(p_x, p_y)	$p^2d^2 \equiv d^2p^2$
d_{z^2}	d_{xy}	(d_{xz}, d_{yz})	d^4

As with the perfect tetrahedron (T_d), the sp^3 and sd^3 are still possible hybrids, although the actual wave functions would differ, because the contributions of individual *p* or *d* orbitals would depend upon the angles in the distorted tetrahedron. The lowered symmetry admits the possibility of the other six combinations, but in most cases these would be less likely contributors to bonding than the modified sp^3 and sd^3 hybrids.

4.5 The approach to NH_3 is similar to that for H_2O (see 4.4).



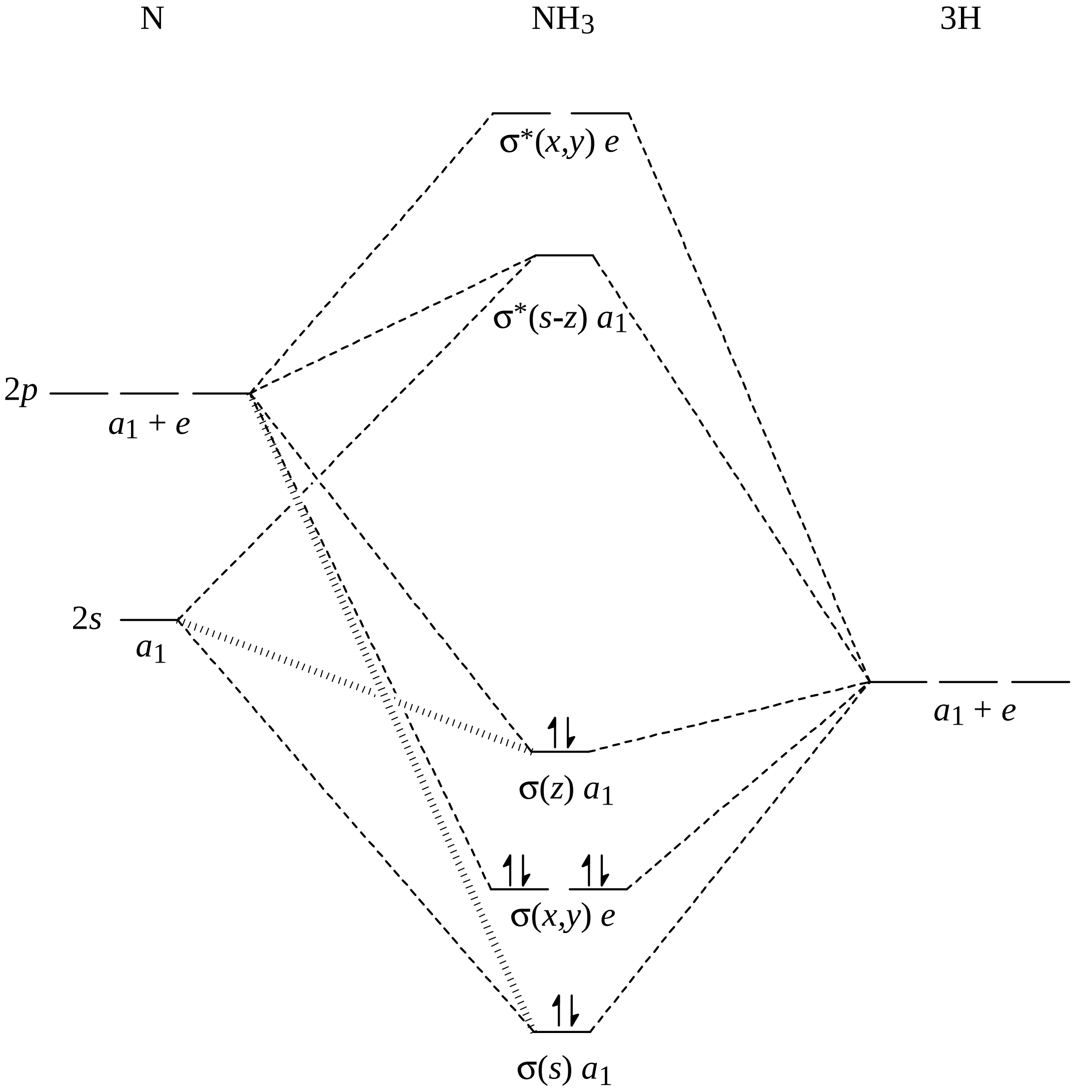
C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{SALC}	3	0	1

$$\Gamma_{\text{SALC}} = A_1 + E$$

Nitrogen AO symmetries are

$$s = A_1 \quad p_z = A_1 \quad (p_x, p_y) = E$$

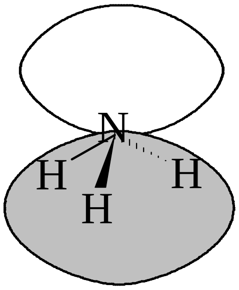
All AOs match with SALCs, so there are no nonbonding levels. Both *s* and p_z AOs match the A_1 SALC, so *s*-*p* mixing is likely. If bonding and antibonding combinations were formed for both *s* and p_z AOs, we would end up with eight MOs, but only seven AOs on N and H are available (disregarding the 1*s* AO on N). We must make only three MOs from the *s* and p_z AOs and the A_1 SALC. For simplicity, we will assume that the *s* and p_z AOs each form essentially separate bonding MOs, but that together they form a single mixed antibonding MO. The resulting MO scheme is shown below, where hashed lines indicate lesser contributions from *s*-*p* mixing.



(b) The P.E.S. has three bands with vibrational fine structure, indicative of ionizations from bonding MOs. This is consistent with the MO scheme above.

(c) The VB model assumes one nonbonding lone pair in an sp^3 hybrid. As the scheme above indicates, this pair is weakly bonding. This is not inconsistent with the well-known

Lewis base character of NH_3, because the $\sigma(z)$ MO has considerable electron density above the nitrogen, not unlike the customary picture of the VB model's lone-pair sp^3 hybrid. A rough sketch of the MO is shown below:



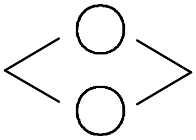
(d) In a planar MH_3 molecule, such as BH_3, the p_z AO on the central atom is a nonbonding π^n (a_2'') MO in D_{3h}. If the three hydrogen atoms move downward to form a pyramidal structure (C_{3v}), they can form the $\sigma(z)$ bonding MO. There is no advantage in doing this unless there exists an electron pair to form the bonding and thereby lower the overall energy of the molecule. Consequently, the addition of another electron pair to an otherwise planar MH_3 molecule becomes the driving force to assume a pyramidal geometry.

4.11 Boron sp^3 SALCs.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_B	4	0	0	0	0	0	4	0

$$\Gamma_B = A_g + B_{2g} + B_{1u} + B_{3u}$$

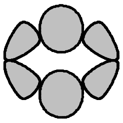
H SALCs



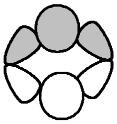
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_H	2	0	0	2	0	2	2	0

$$\Gamma_H = A_g + B_{3u}$$

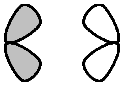
The H SALCs have matching B SALCs and will form bonding and antibonding combinations. The B_{1u} and B_{2g} B SALCs remain nonbonding. The LCAOs are shown below for the bonding and nonbonding MOs.



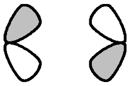
a_g



b_{3u}

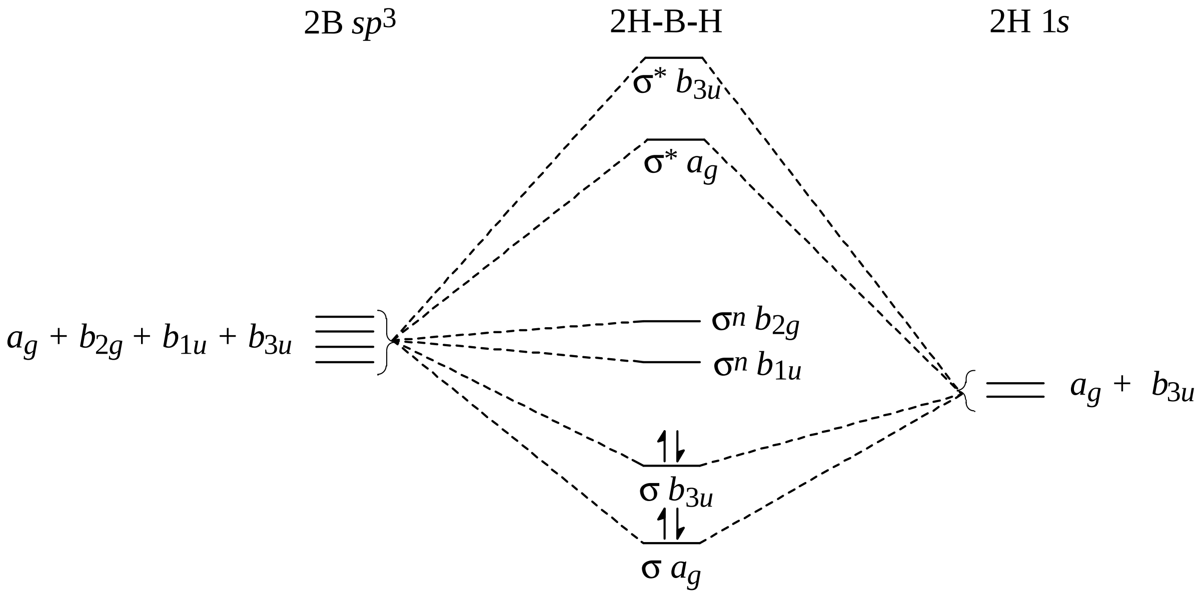


b_{1u}



b_{2g}

These give the following MO scheme for the two bridges:



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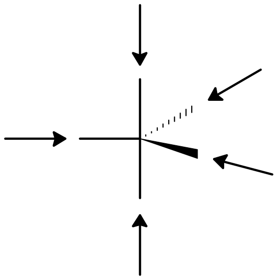
4.13 Fluorine σ-SALCs:



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	5	2	1	3	0	3

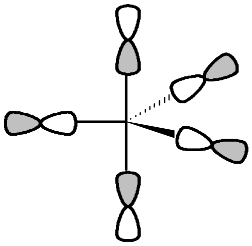
$$\Gamma = 2A_1' + E' + A_2''$$

Symmetry of phosphorus AOs:

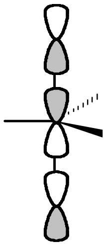
$$s = A_1' \quad (p_x, p_y) = E' \quad p_z = A_2'' \quad [d_{z^2} = A_1']$$

If we assume virtually no d_{z^2} participation, then one of the two A_1' fluorine SALCs will be nonbonding. As the LCAOs shown below indicate, this A_1' fluorine SALC has appropriate form for bonding and antibonding combinations with d_{z^2} on phosphorus.

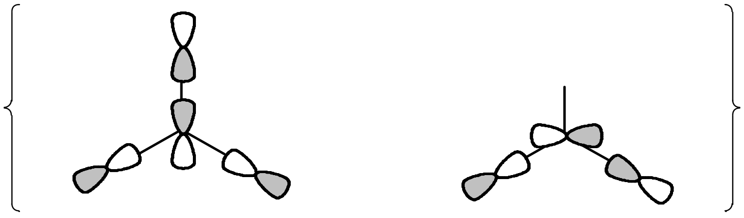
a_1'



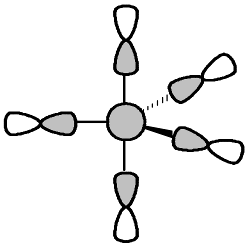
a_2''



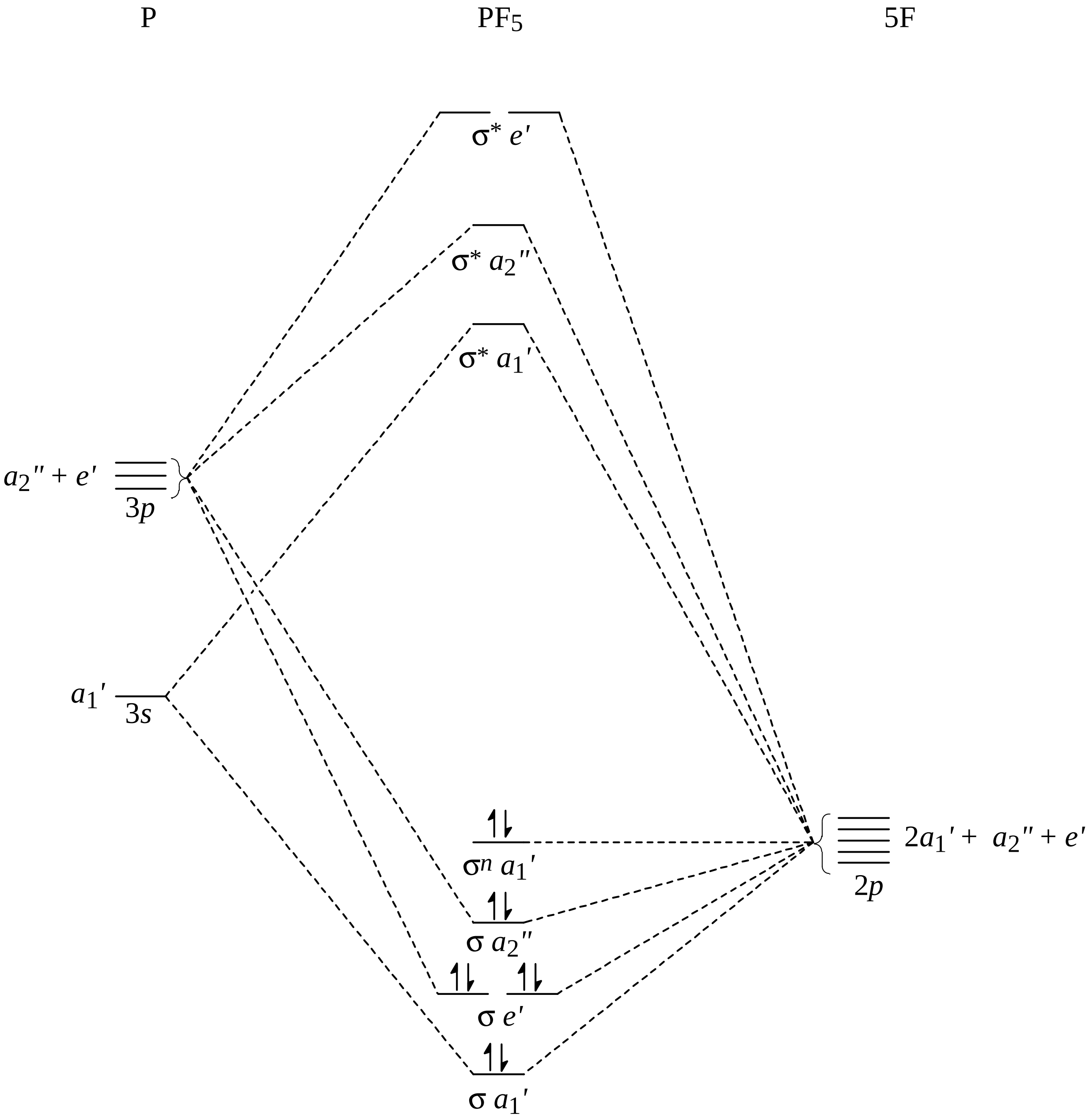
e'



a_1'



The complete sigma-only MO scheme for PF_5 is shown below.



With phosphorus d_{z^2} participation, the σ a_1' HOMO would be stabilized (lowered in energy) to become a bonding MO.