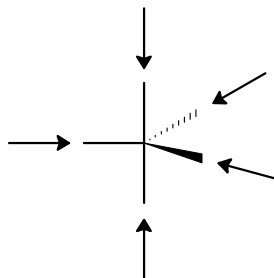


**Chem 370 - Spring, 2019**  
**Assignment 6 - Solutions**

1. Fluorine  $\sigma$ -SALCs:



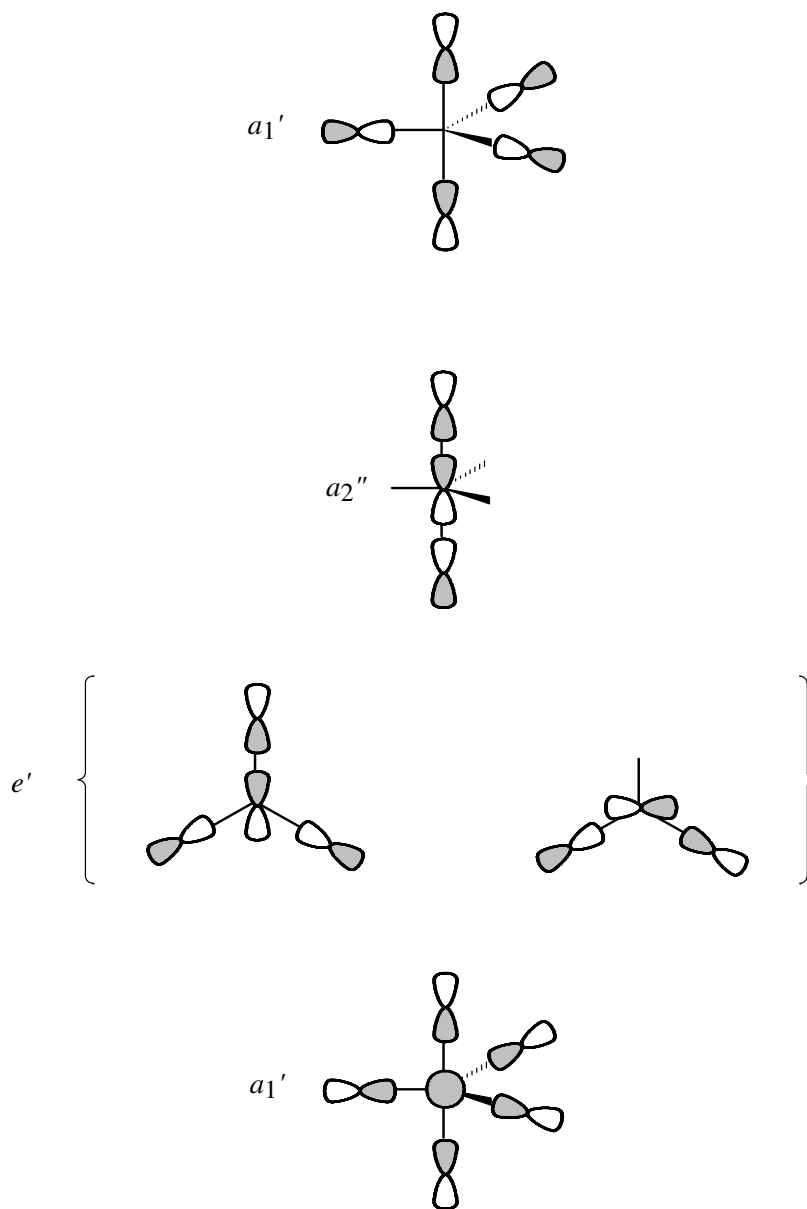
$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$
$\Gamma$	5	2	1	3	0	3

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

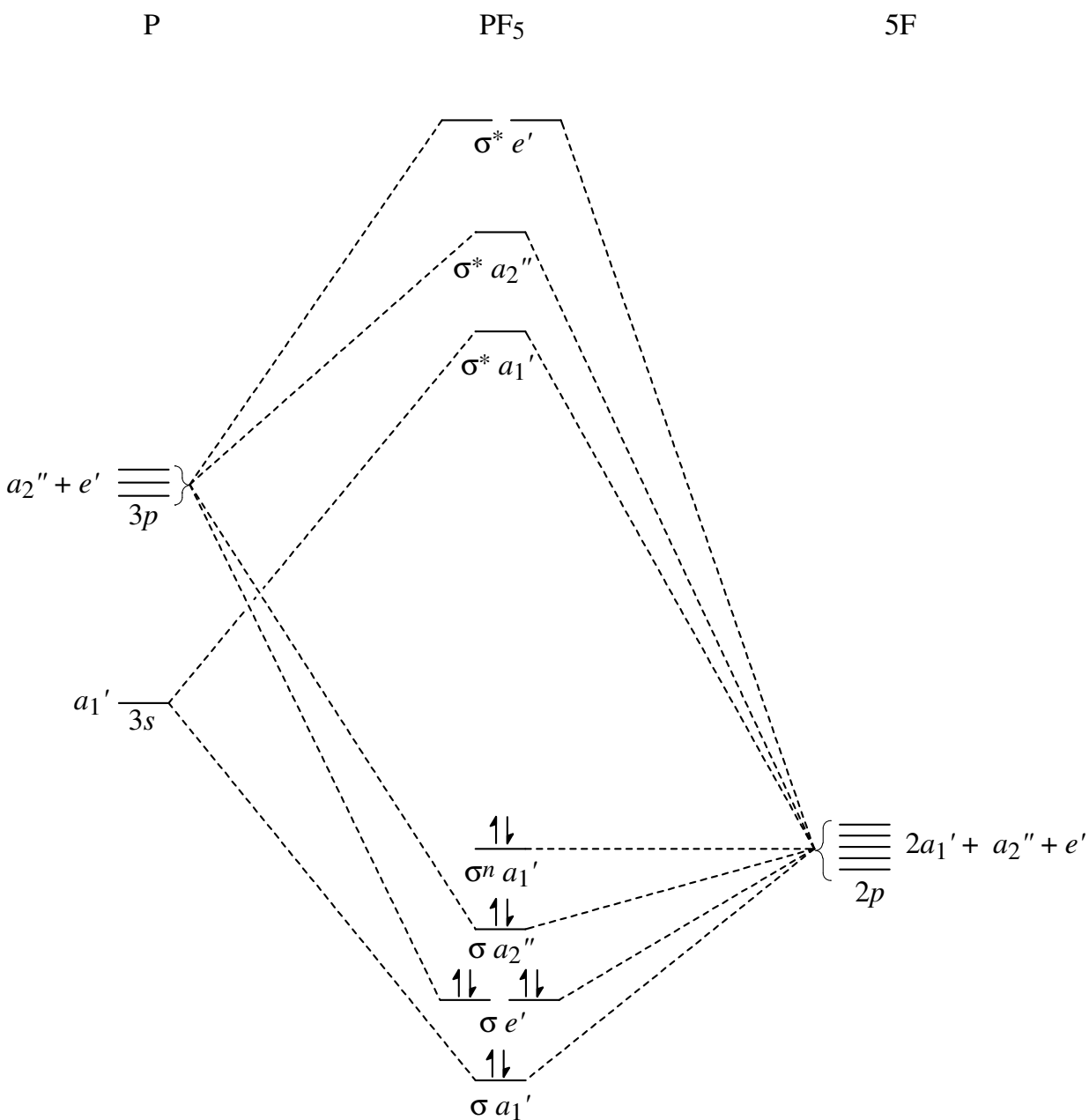
Symmetry of phosphorus AOs:

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

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.



The complete sigma-only MO scheme for PF<sub>5</sub> is shown below.



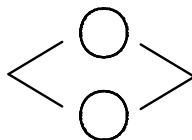
With phosphorus  $d_{z^2}$  participation, the  $\sigma a_1'$  HOMO would be stabilized (lowered in energy) to become a bonding MO.

2. Boron  $sp^3$  SALCs.

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

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

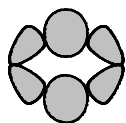
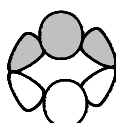
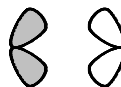
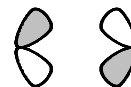
## H SALCs



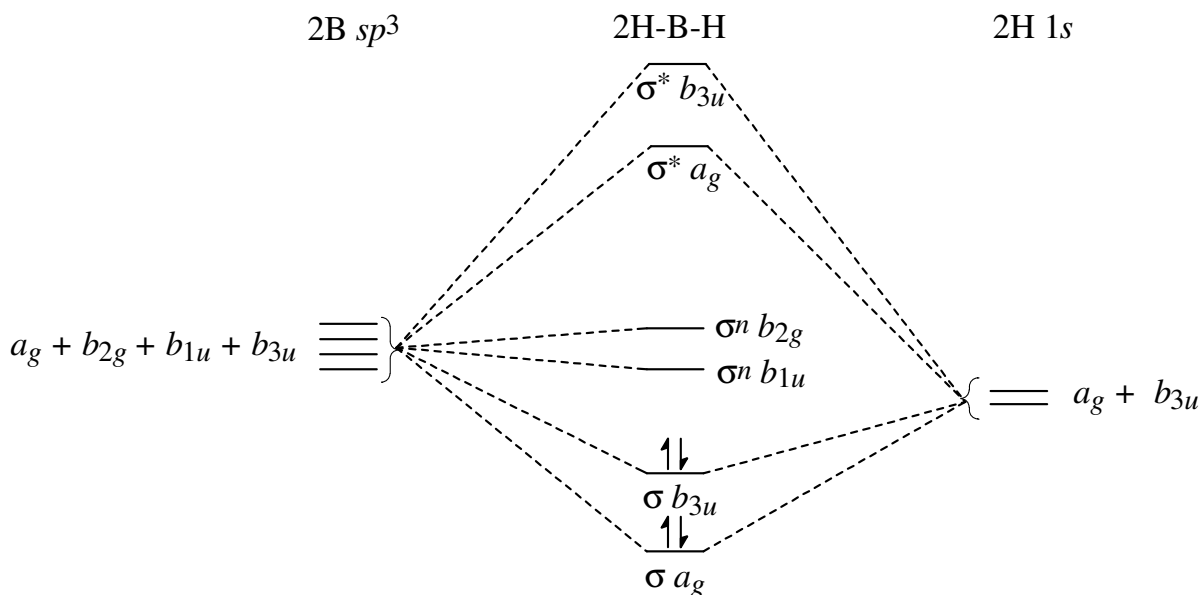
$D_{2h}$	$E$	$C_2(z)$	$C_2(y)$	$C_2(x)$	$i$	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_H$	2	0	0	2	0	2	2	0

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

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:



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

(a) trigonal planar

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$
$\Gamma$	3	0	1	3	0	1

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

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

$A_1'$	$E'$	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

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

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

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

$A_{1g}$	$B_{1g}$	$E_u$	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

$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$
$\Gamma$	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

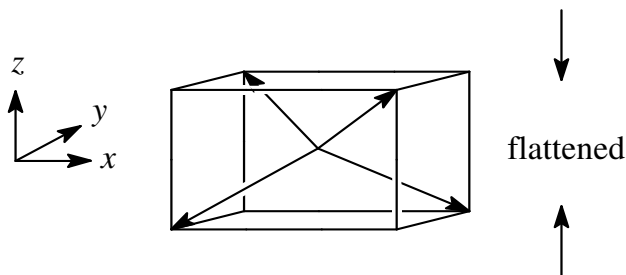
$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma$	6	0	0	2	2	0	0	0	4	2

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

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

Only possibility is  $d^2sp^3$ .

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



$D_{2d}$	$E$	$2S_4$	$C_2$	$2C_2'$	$2\sigma_d$
$\Gamma$	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.