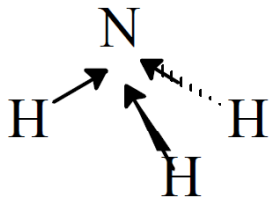
Constructing a MO of NH_3



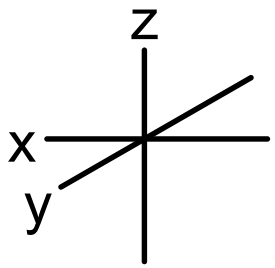
C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{SALC}	3	0	1

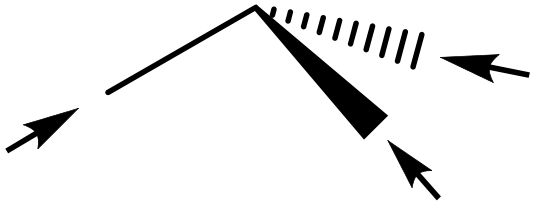
$$\Gamma_{SALC} = A_1 + E$$

Nitrogen AO symmetries are

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

- To develop a MO scheme for NH_3 assume that only the 2*s* and2*p* orbitals of nitrogen interact with the hydrogen 1*s* orbitals (i.e., the nitrogen 1*s* orbital is nonbonding).
- 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.
- Two AOs of nitrogen match symmetry with one of the SALCs, thereby forming three MOs. Of these, the lowest energy MO is essentially a bonding combination formed between the hydrogen SALC and the 2*s* AO on nitrogen, and the highest MO is an antibonding combination formed from a mixture of the two AOs from nitrogen and the same symmetry SALC.





$\Gamma_{SALC} = A_1 + E$

Symmetry

SALCs

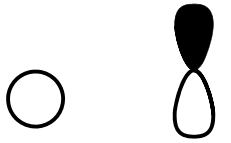
AOs

E'
(1 node)

Energy

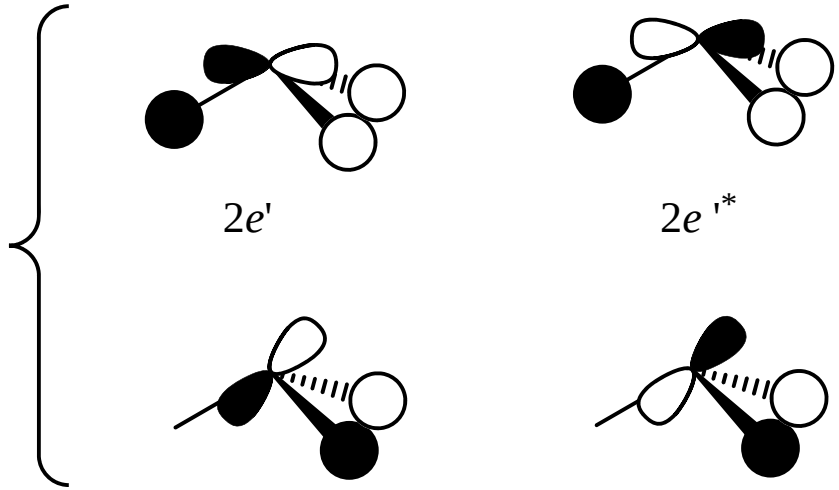
p_x p_y

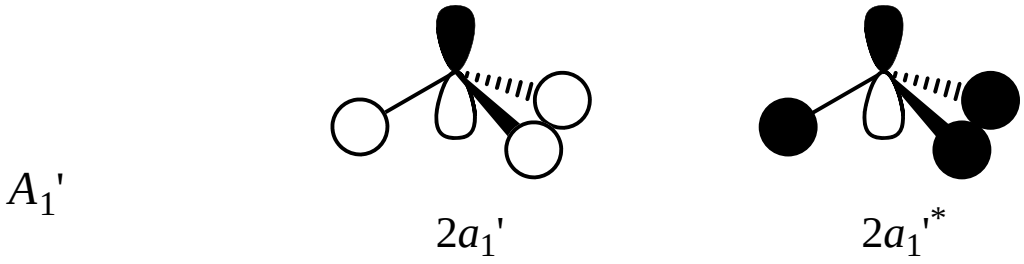
A_1'
(0 nodes)

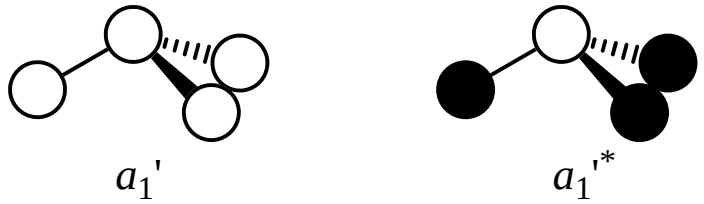


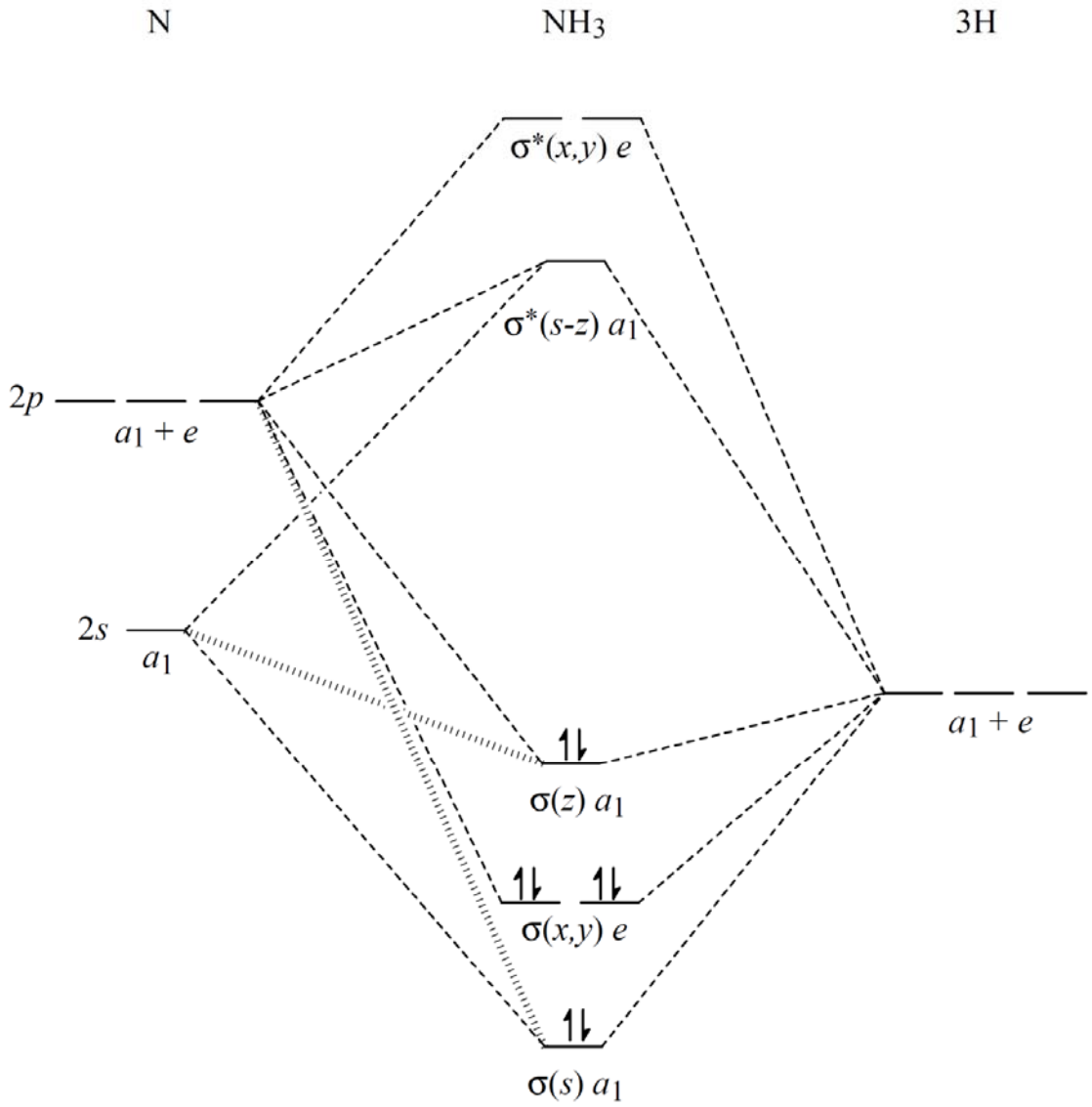
s p_z

Symmetry MOs





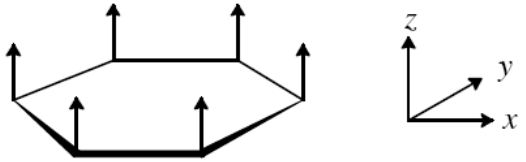




Lewis base character of NH_3, because the σ(z) MO has considerable electron density above the nitrogen, not unlike the customary picture of the VB model's lone-pair sp^3 hybrid.

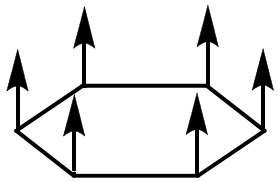
π MOs of Benzene, C_6H_6

- C_6H_6, has three pairs of electrons delocalized in a π system extending around the hexagonal ring.
- The six 2*p* orbitals perpendicular to the ring on the six carbon atoms combine to form three bonding (π^1, π^2, π^3) and three antibonding (π^{4*}, π^{5*}, π^{6*}) MOs.
- The symmetries and forms of these MOs can be deduced by applying the operations of the point group D_{6h} to a set of six vectors perpendicular to the ring, one at each carbon, to generate a reducible representation Γ_π.



D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2

$$\Gamma_\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u}$$



π MOs of Benzene, C_6H_6

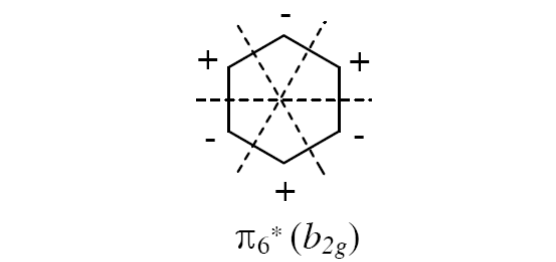
$h = 24$

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Σ	Σ/h
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2		
A_{1g}	6	0	0	0	-6	0	0	0	0	-6	0	6	0	0
A_{2g}	6	0	0	0	6	0	0	0	0	-6	0	-6	0	0
B_{1g}	6	0	0	0	-6	0	0	0	0	6	0	-6	0	0
B_{2g}	6	0	0	0	6	0	0	0	0	6	0	6	24	1
E_{1g}	12	0	0	0	0	0	0	0	0	12	0	0	24	1
E_{2g}	12	0	0	0	0	0	0	0	0	-12	0	0	0	0
A_{1u}	6	0	0	0	-6	0	0	0	0	6	0	-6	0	0
A_{2u}	6	0	0	0	6	0	0	0	0	6	0	6	24	1
B_{1u}	6	0	0	0	-6	0	0	0	0	-6	0	6	0	0
B_{2u}	6	0	0	0	6	0	0	0	0	-6	0	-6	0	0
E_{1u}	12	0	0	0	0	0	0	0	0	-12	0	0	0	0
E_{2u}	12	0	0	0	0	0	0	0	0	12	0	0	24	1

$$\Gamma_\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u} \qquad d_\Gamma = 1 + 2 + 1 + 2 = 6$$

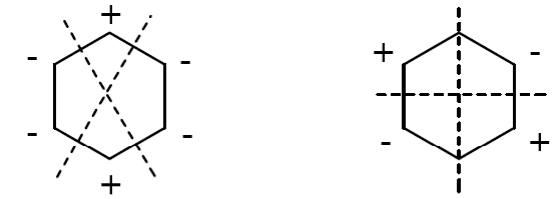
$\Gamma_\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u}$

π MOs of Benzene, C_6H_6



$\pi_6^*(b_{2g})$

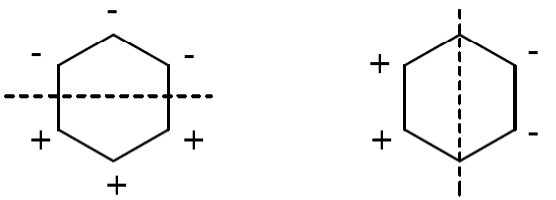
$\pi_6(B_{2g}) = (1/\sqrt{6})\ (\phi_a - \phi_b + \phi_c - \phi_d + \phi_e - \phi_f)$



π_4^* (e_{2u}) π_5^*

$\pi_4^*(E_{2u}) = (1/2\sqrt{3})\ (2\phi_a - \phi_b - \phi_c + 2\phi_d - \phi_e - \phi_f)$

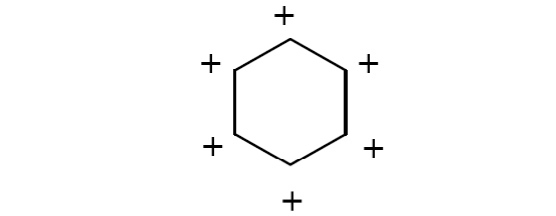
$\pi_5^*(E_{2u}) = (1/2)\ (-\phi_b + \phi_c - \phi_e + \phi_f)$



π_2 (e_{1g}) π_3

$\pi_2(E_{1g}) = (1/2\sqrt{3})\ (2\phi_a + \phi_b - \phi_c - 2\phi_d - \phi_e - \phi_f)$

$\pi_2(E_{1g}) = (1/2)\ (\phi_b + \phi_c - \phi_e - \phi_f)$



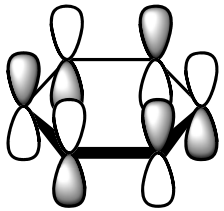
$\pi_1\ (a_{2u})$

$\pi_1(A_{2u}) = (1/\sqrt{6})\ (\phi_a + \phi_b + \phi_c + \phi_d + \phi_e + \phi_f)$

$\Gamma_\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u}$

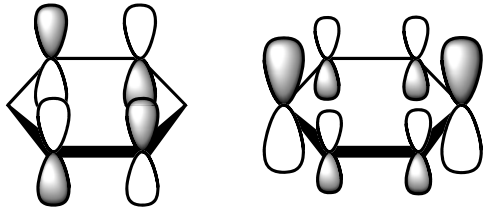
π MOs of Benzene, C_6H_6

B_{2g}
(6 nodes)
anti-bonding



$\pi_6(B_{2g}) = (1/\sqrt{6})\ (\phi_a - \phi_b + \phi_c - \phi_d + \phi_e - \phi_f)$

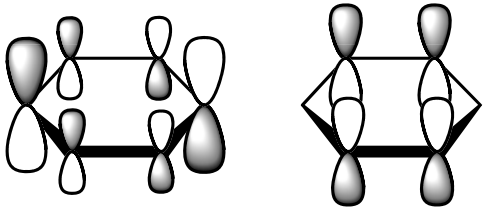
E_{2u}
(4 nodes)
anti-bonding



$\pi_4^*(E_{2u}) = (1/2\sqrt{3})\ (2\phi_a - \phi_b - \phi_c + 2\phi_d - \phi_e - \phi_f)$

$\pi_5^*(E_{2u}) = (1/2)\ (-\phi_b + \phi_c - \phi_e + \phi_f)$

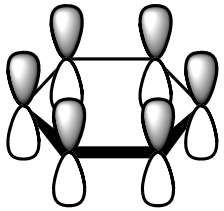
E_{1g}
(2 nodes)
bonding



$\pi_2(E_{1g}) = (1/2\sqrt{3})\ (2\phi_a + \phi_b - \phi_c - 2\phi_d - \phi_e + \phi_f)$

$\pi_2(E_{1g}) = (1/2)\ (\phi_b + \phi_c - \phi_e - \phi_f)$

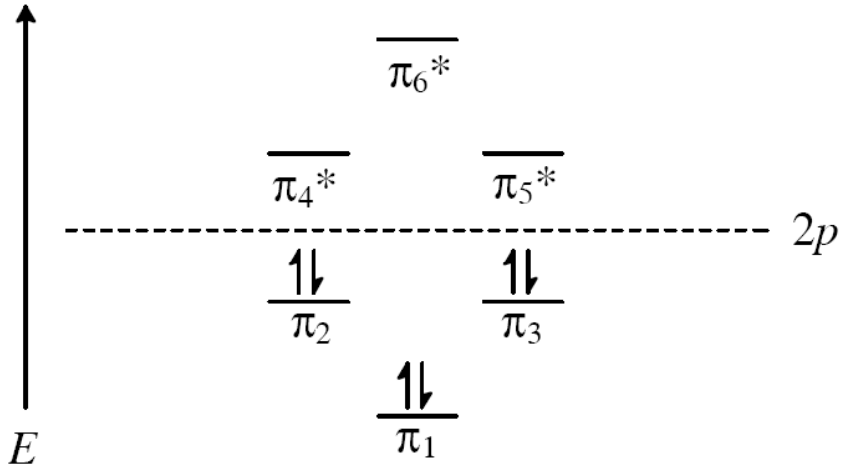
A_{2u}
(0 nodes)
bonding



$\pi_1(A_{2u}) = (1/\sqrt{6})\ (\phi_a + \phi_b + \phi_c + \phi_d + \phi_e + \phi_f)$

π MO Energy Level Scheme for Benzene, C_6H_6

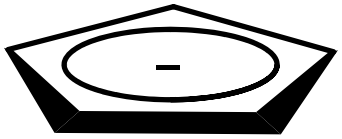
- By the "shadow method" we can anticipate that the π-MO scheme will look like the following:

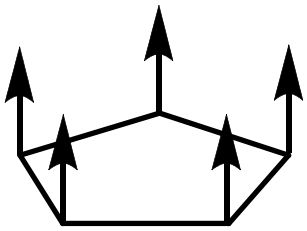


- Three pairs in bonding MOs add a total of three bond orders over six C–C linkages, or 0.5 for each.
- When this is added to the sigma bond between each carbon pair, the C–C bond order becomes 1.5.

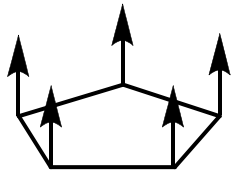
π MOs of Cyclopentadienyl, $C_5H_5^-$

- $C_5H_5^-$, has three pairs of electrons delocalized in a π system extending around the pentagonal ring.
- The five 2*p* orbitals perpendicular to the ring on the five carbon atoms combine to form three bonding (π^1, π^2, π^3) and three antibonding (π^4*, π^5*, π^6*) MOs.
- The symmetries and forms of these MOs can be deduced by applying the operations of the point group D_{5h} to a set of five vectors perpendicular to the ring, one at each carbon, to generate a reducible representation Γ_π.





π MOs of Cyclopentadienyl, $C_5H_5^-$



D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_3^5$	$5\sigma_v$	Σ	Σ/h
Γ_π	5	0	0	-1	-5	0	0	1		
A_1'	5	0	0	-5	-5	0	0	5	0	0
A_2'	5	0	0	5	-5	0	0	-5	0	0
E_1'	10	0	0	0	-10	0	0	0	0	0
E_2'	10	0	0	0	-10	0	0	0	0	0
A_1''	5	0	0	-5	5	0	0	-5	0	0
A_2''	5	0	0	5	5	0	0	5	20	1
E_1''	10	0	0	0	10	0	0	0	20	1
E_2''	10	0	0	0	10	0	0	0	20	1

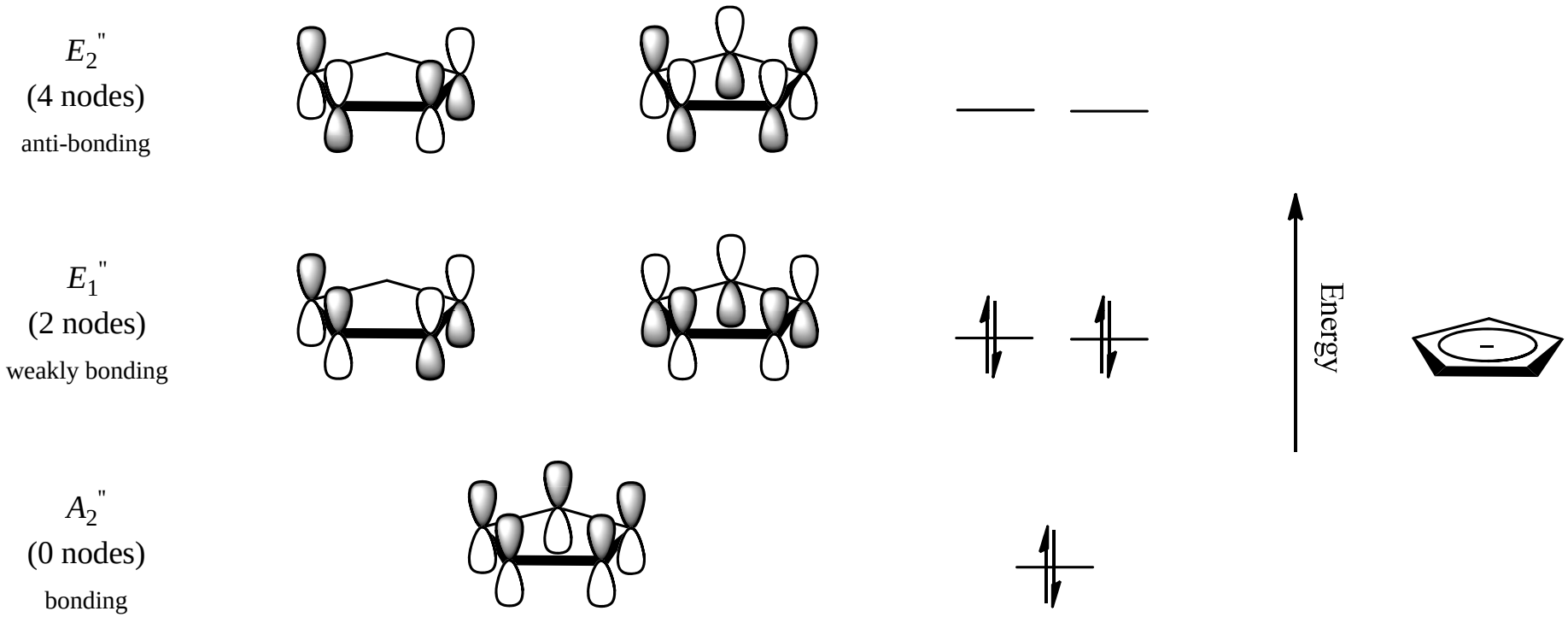
$h = 20$

$$\Gamma_\pi = A_2'' + E_1'' + E_2'' \qquad d_\Gamma = 1 + 2 + 2 = 5$$

- The five p-orbitals on the planar Cp ring (D_{5h} symmetry) can be combined to produce five molecular orbitals according to the reducible representation:

$$\Gamma_{\pi} = A_2'' + E_1'' + E_2''$$

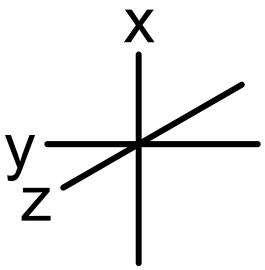
- One combination has the full symmetry of the ring (a_2'')
- There are two doubly degenerate combinations (e_1'' and e_2'') having one and two planar nodes at right angles to the plane of the ring.
- The relative energies of these orbitals increase as the number of nodes increases.
- The a_2'' and e_1'' orbitals are both fully occupied in the electronic configuration of the Cp^- anion whereas the e_2'' orbitals are net anti-bonding and are unfilled.

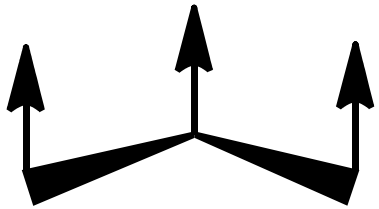


The π-molecular orbitals of the cyclopentadienyl ring *(D_{5h})*

π MOs of the Allyl anion, $C_3H_5^-$

- The alkyl anion has a delocalized, open, three-center π system.
- Although it is customary to assume that p_z orbitals are involved in forming π orbitals, in this case for constructing the MO diagram we will assume that p_x orbitals are used, in keeping with the standard character table and conventions of defining z as the principal axis and the yz plane as the plane of the C-C-C chain.





C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v}'_{(yz)}$	Σ	Σ/h
Γ_π	3	-1	1	-3		
A_1	3	-1	1	-3	0	0
A_2	3	-1	-1	3	4	1
B_1	3	1	1	3	8	2
B_2	3	1	-1	-3	0	0

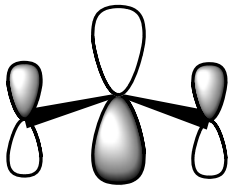
$h = 4$

$$\Gamma_\pi = A_2 + 2B_1$$

$$d_\Gamma = 1 + 2 = 3$$

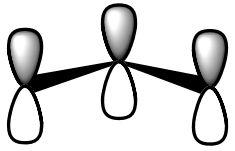
$$\Gamma_\pi = A_2 + B_1$$

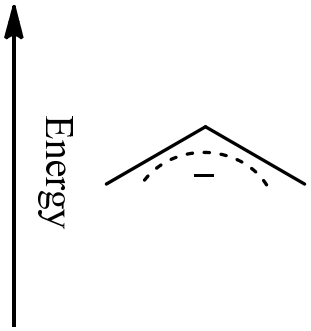
B_1
(2 nodes)
anti-bonding



A_2
(1 node)
weakly bonding

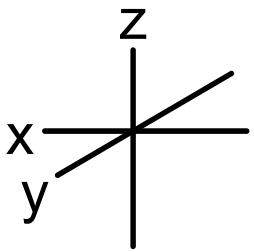
B_1
(0 nodes)
bonding

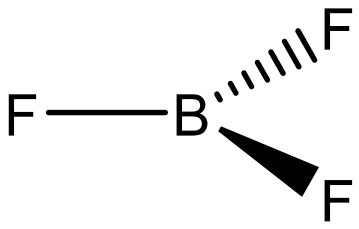


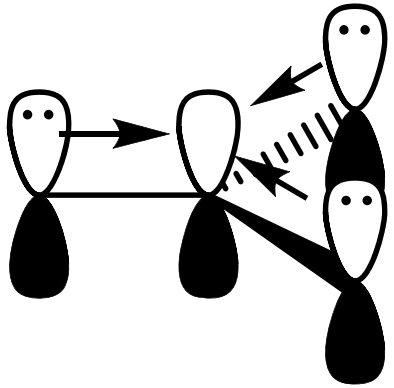


σ and π MOs of Boron Trifluoride, BF_3

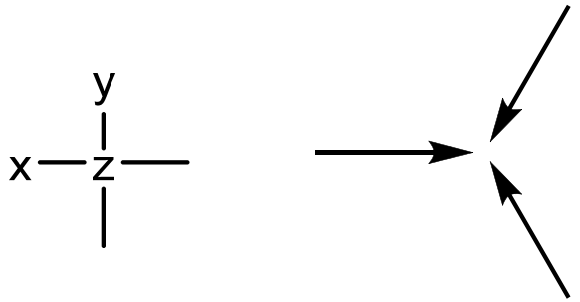
- Although BH_3 is unstable, the BX_3 trihalides (X = F, Cl, Br) are stable but reactive compounds that have been well characterized.
- A significant advantage of the BX_3 compounds is the potential for π bonding between the $2p_z$ orbital of boron and the np_z orbitals of the halogens (n = 2, 3, 4).
- Although fluorine is the most electronegative of the halides this bonding is most significant for BF_3 due to closely matched energies with the central boron atom.







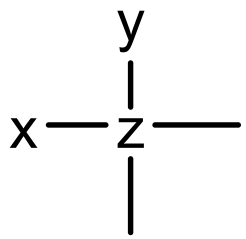
σ MOs of BF_3

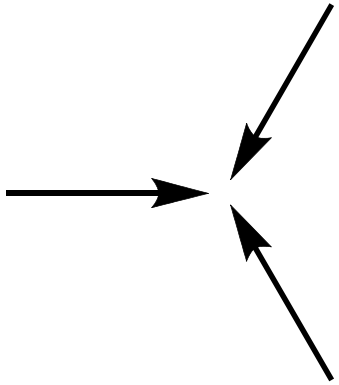


$h = 12$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Σ	Σ/h
Γ_σ	3	0	1	3	0	1		
A_1'	3	0	3	3	0	3	12	1
A_2'	3	0	-3	3	0	-3	0	0
E'	6	0	0	6	0	0	12	1
A_1''	3	0	3	-3	0	-3	0	0
A_2''	3	0	-3	-3	0	3	0	0
E''	6	0	0	-6	0	0	0	0

$$\Gamma_\sigma = A_1' + E' \qquad d_\Gamma = 1 + 2 = 3$$

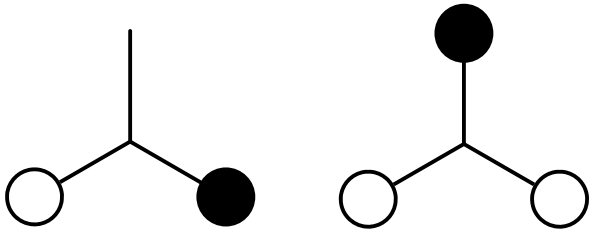


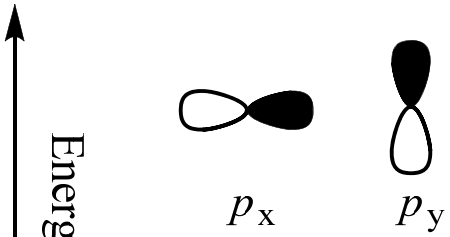


$\Gamma_\sigma = A_1' + E'$

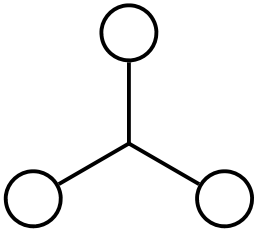
Symmetry SALCs AOs

E'
(1 node)



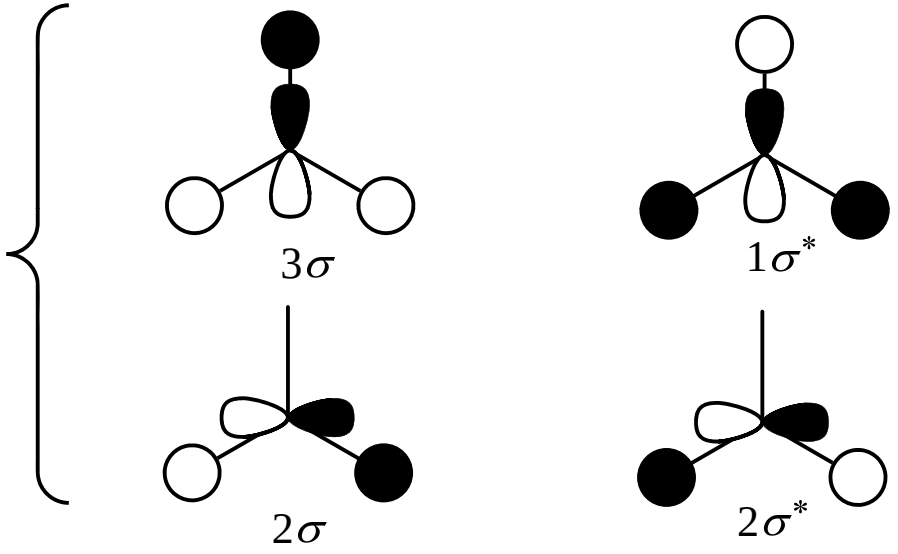


A_1'
(0 nodes)



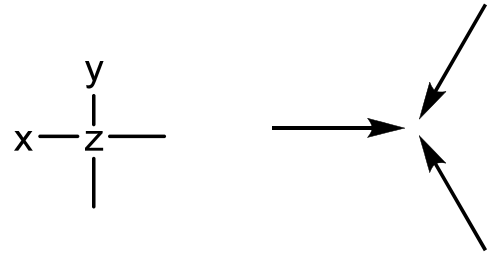
- Based upon the symmetry of the 3F SALCs derived from the F 1*s* orbitals symmetry allowed overlap with the B 2*s* 2p_x and 2p_y orbitals is predicted.
- Due to energy considerations however this interaction is very weak and generally ignored.

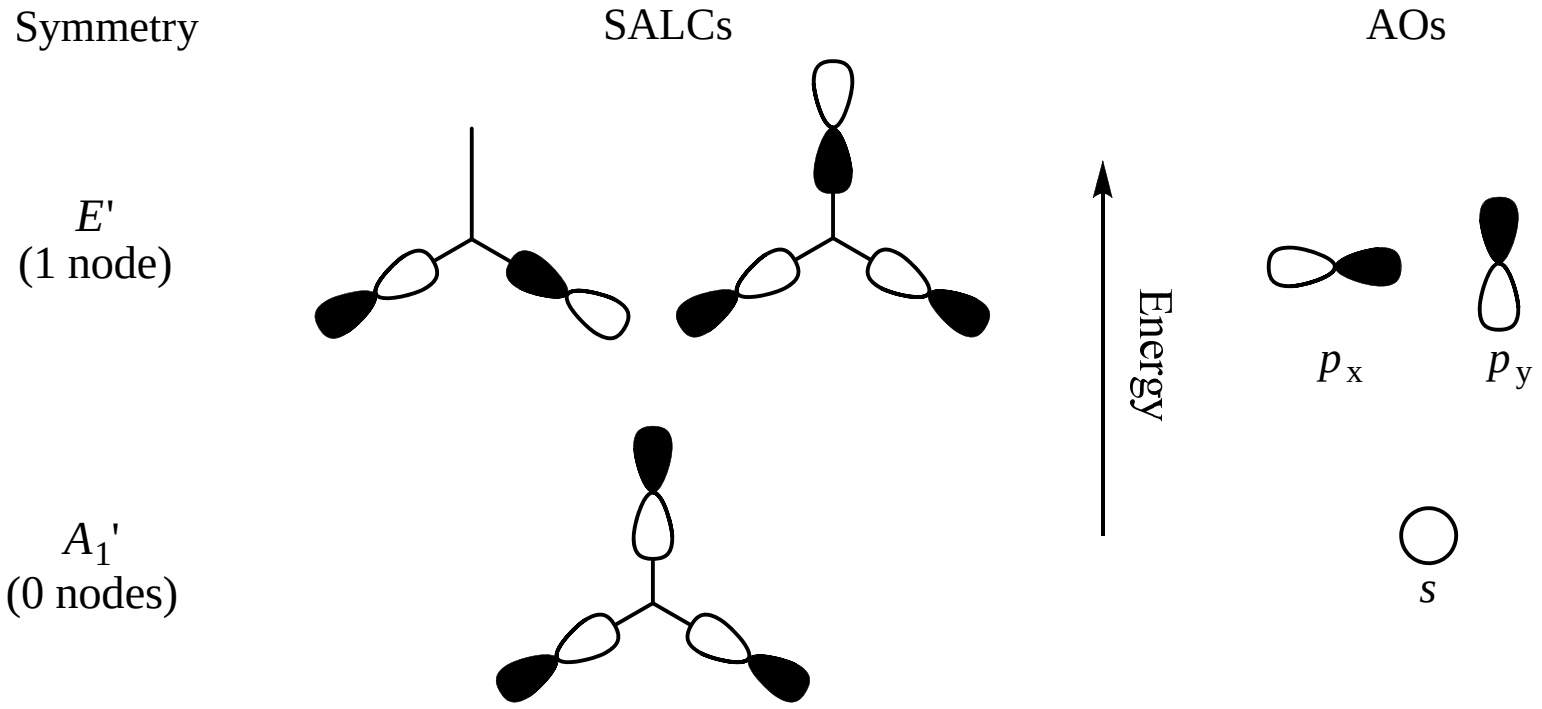
$\Gamma_\sigma = A_1' + E'$



- Overlap of the B 2*s* 2p_x and 2p_y orbitals with the 3F SALCs derived from the F 2p_x orbitals is more prominent.
- The 2p_y orbitals of the 3F atoms are considered non-bonding and are not considered here.

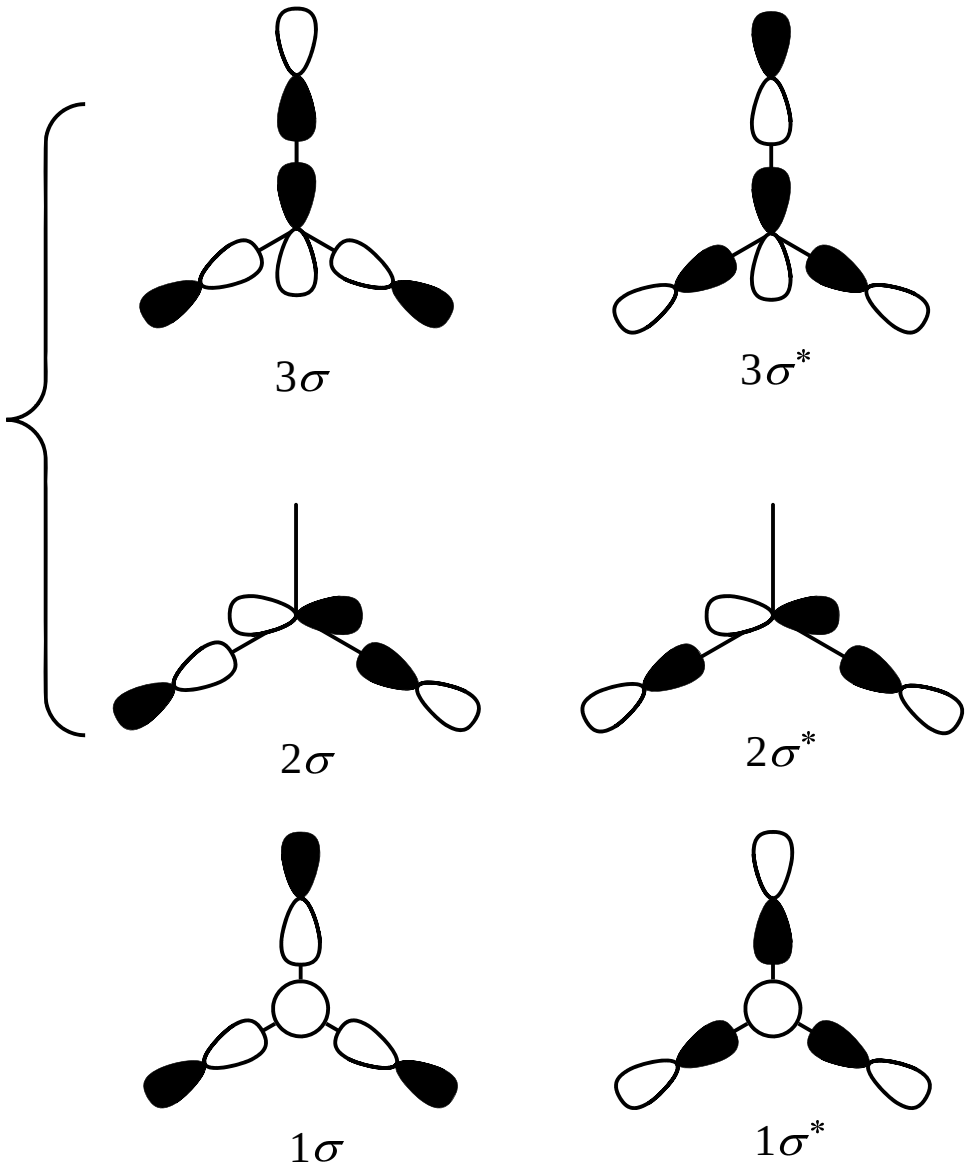
$$\Gamma_\sigma = A_1' + E'$$





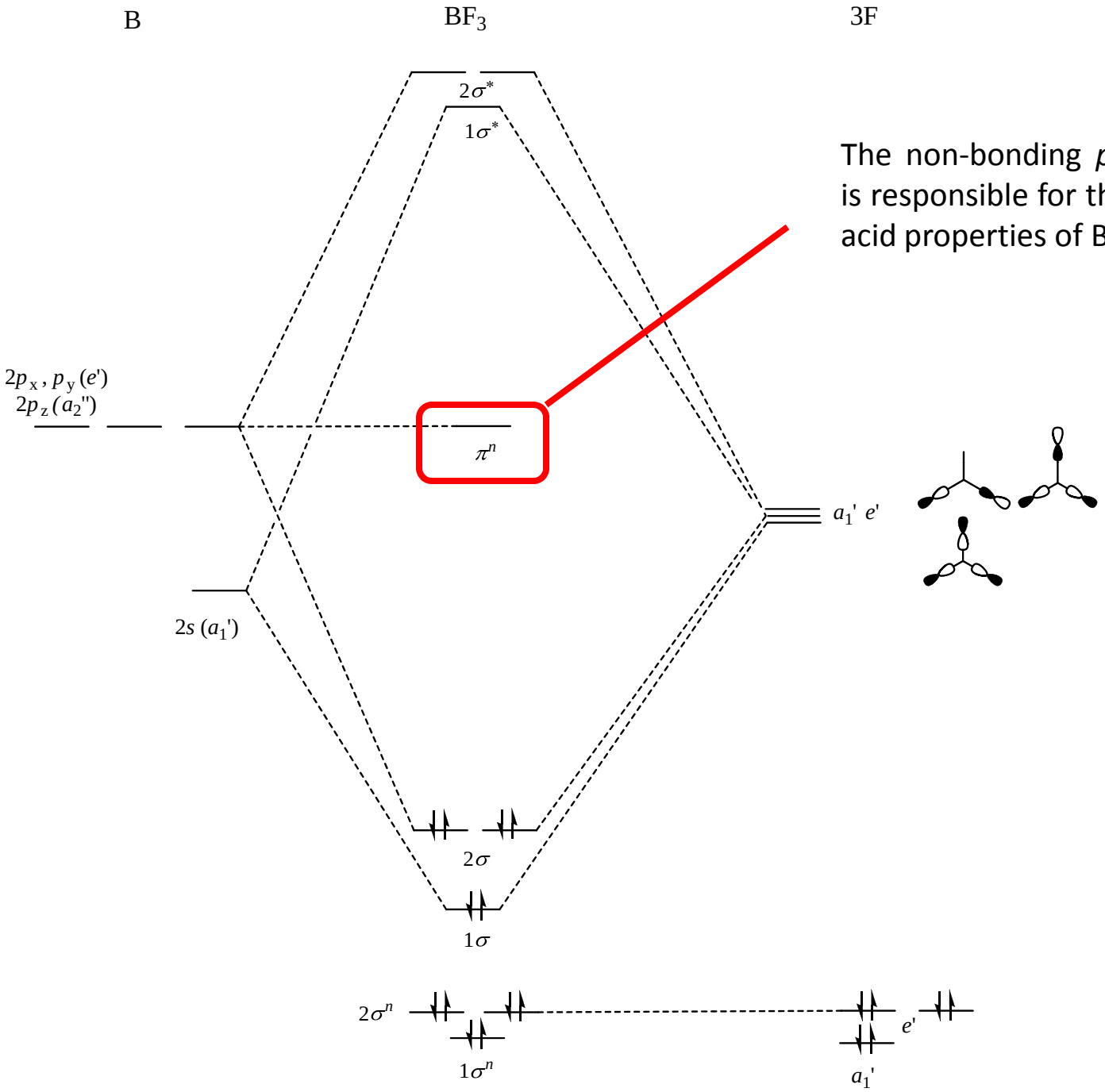
- Symmetry allowed sigma MOs derived from the 3F ($2p_x$) SALCs and the B $2s$ $2p_x$ and $2p_y$ orbitals.

$\Gamma_\sigma = A_1' + E'$



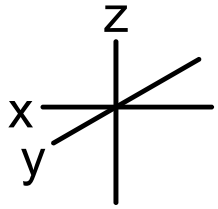
E'
(1 node)

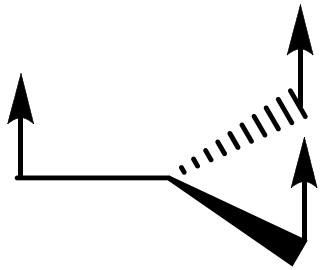
A_1'
(0 nodes)



The non-bonding *p* orbital is responsible for the Lewis acid properties of BF_3

π MOs of BF_3



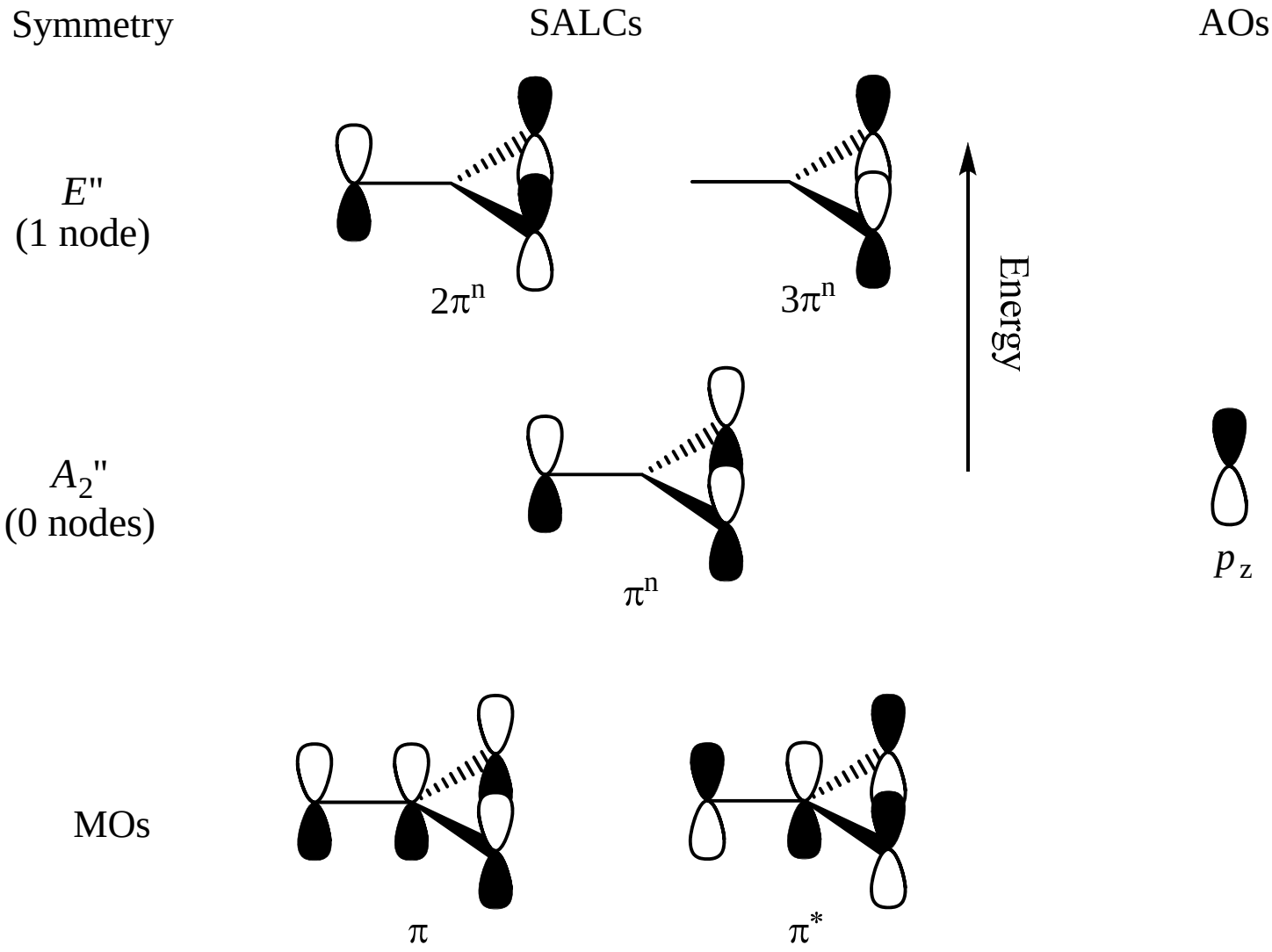


$h = 12$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Σ	Σ/h
Γ_π	3	0	-1	-3	0	1		
A_1'	3	0	-3	-3	0	3	0	0
A_2'	3	0	3	-3	0	-3	0	0
E'	6	0	0	-6	0	0	0	0
A_1''	3	0	-3	3	0	-3	0	0
A_2''	3	0	3	3	0	3	12	1
E''	6	0	0	6	0	0	12	1

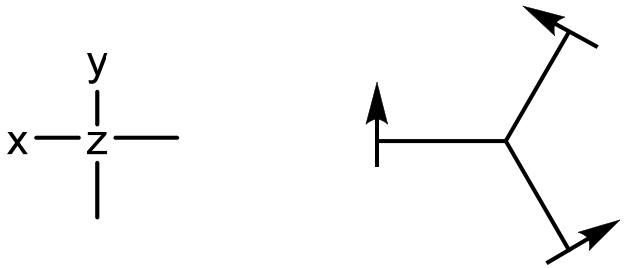
$\Gamma_\pi = A_2'' + E''$ $\qquad$ $d_\Gamma = 1 + 2 = 3$

$$\Gamma_{\pi} = A_2'' + E''$$


Symmetry
SALCs
AOs
E"
(1 node)
2πn
3πn
Energy
A2"
(0 nodes)
πn
pz
MOs
π
π*

Non-bonding SALCs of BF_3

- The $2p_y$ orbitals of the 3F atoms are considered non-bonding and are considered separately when deriving their irreducible representation.



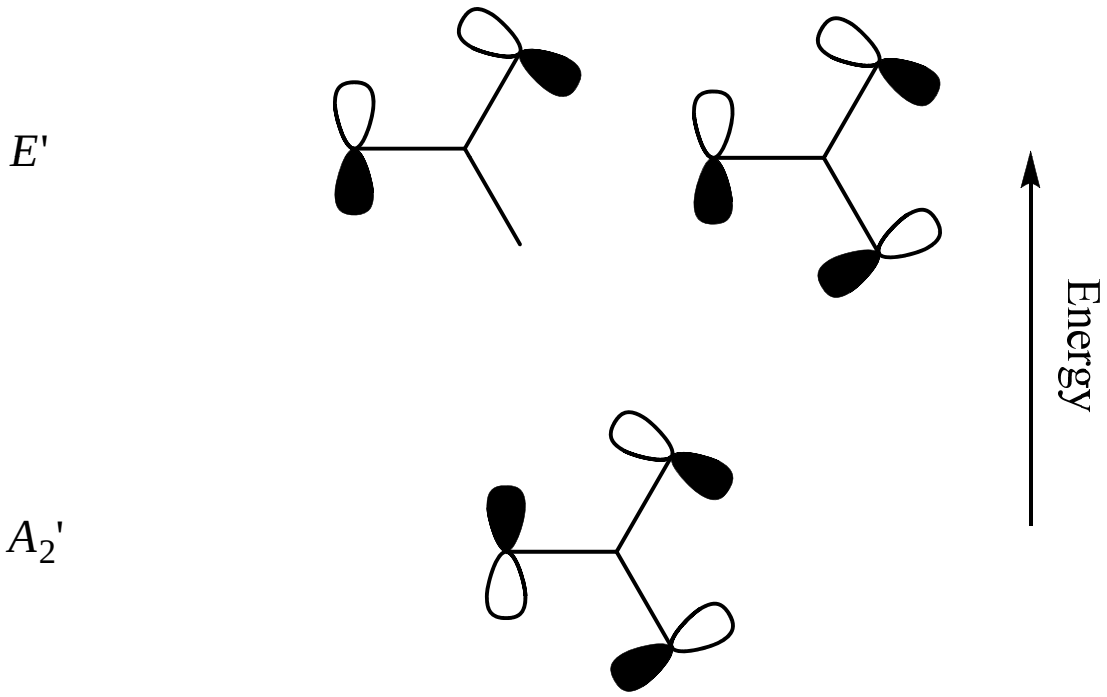
$h = 12$

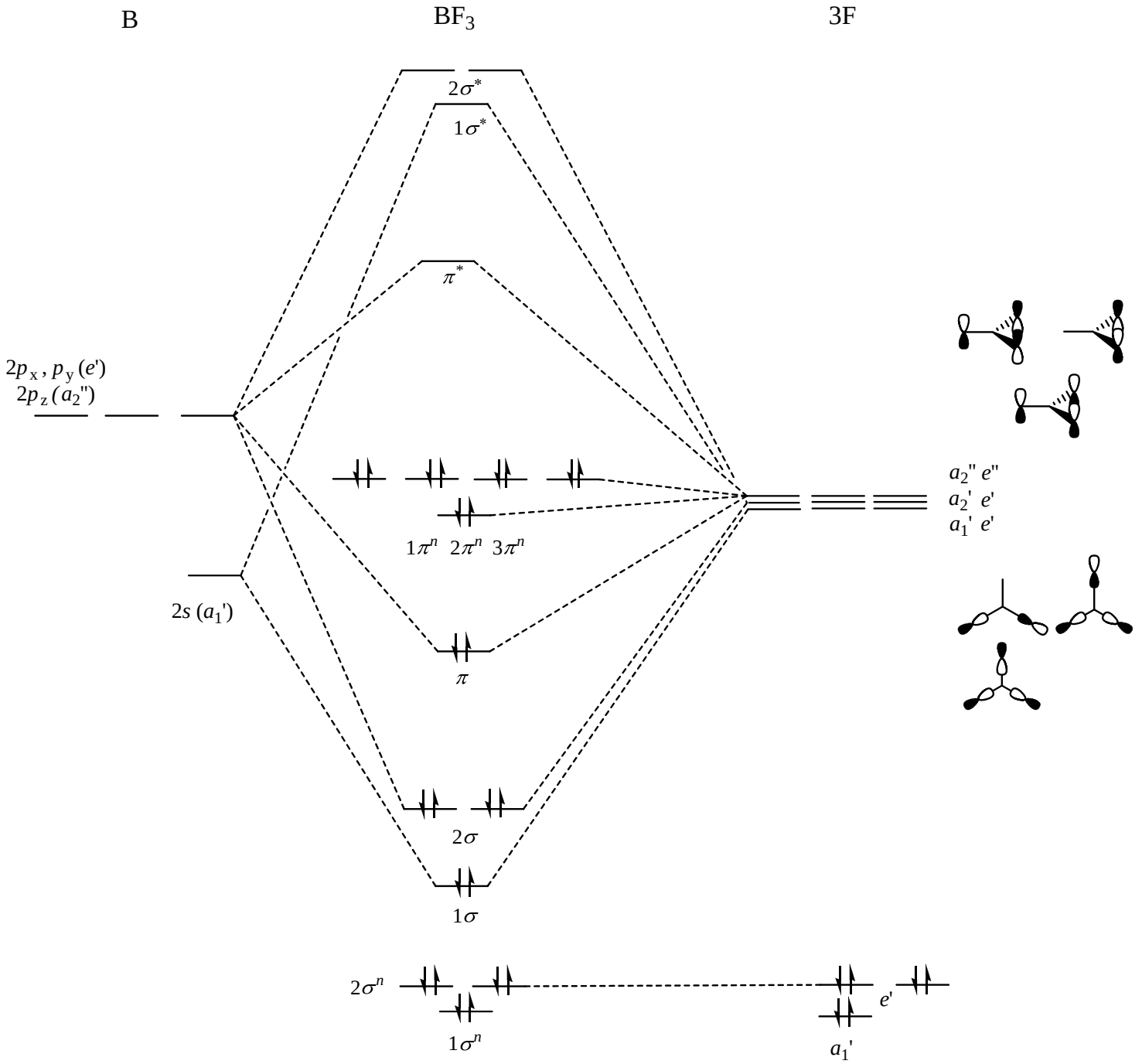
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Σ	Σ/h
Γ_n	3	0	-1	3	0	-1		
A_1'	3	0	-3	3	0	-3	0	0
A_2'	3	0	3	3	0	3	12	1
E'	6	0	0	6	0	0	12	1
A_1''	3	0	-3	-3	0	3	0	0
A_2''	3	0	3	-3	0	-3	0	0
E''	6	0	0	-6	0	0	0	0

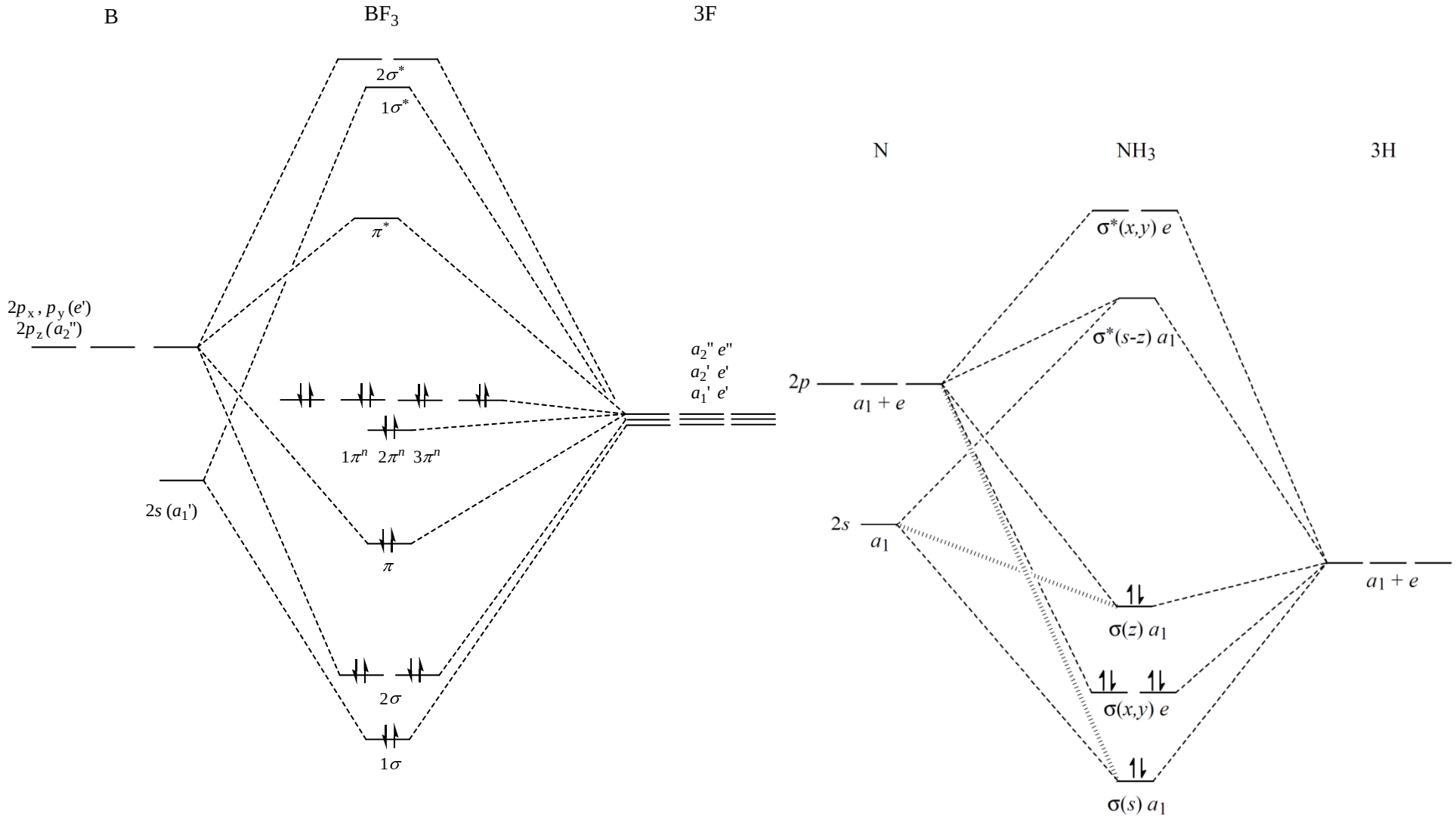
$\Gamma_\pi = A_2' + E'$ $\qquad$ $d_\Gamma = 1 + 2 = 3$

$$\Gamma_n = A_2' + E'$$

Symmetry SALCs




B
BF3
3F
2σ*
1σ*
π*
2px , py (e')
2pz (a2")
a2" e"
a2' e'
a1' e'
1πn 2πn 3πn
2s (a1')
π
2σ
1σ
2σn
1σn
e'
a1'



- Consider the MO diagrams for both NH_3 and BF_3 and how the mechanism for the Lewis acid-base reaction may proceed.