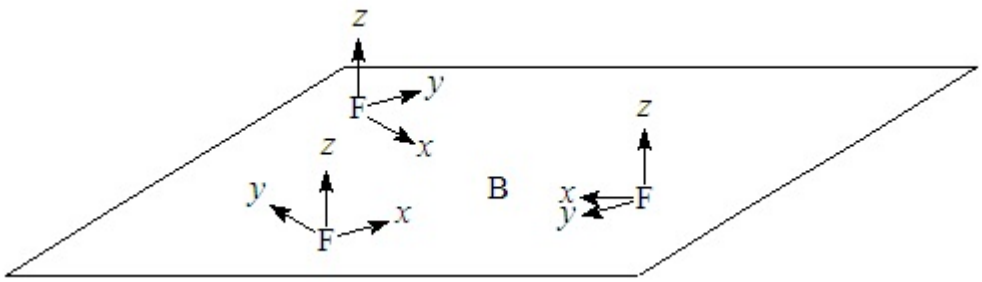
MO Scheme of BF_3
Fluorine SALCs and Boron AOs

- Assume that fluorine 2*s* orbitals are not involved in the bonding and only consider the 2*p* orbitals.



- The $2p_z$ orbital on each fluorine is perpendicular to the BF_3 plane and capable of forming out-of-plane pi interactions ($\pi_{\perp}$).

- The $2p_x$ orbital points toward the B atom and forms sigma interactions (σ)

- The $2p_y$ orbital is parallel to the BF_3 plane and has the potential to form in-plane pi interactions ($\pi_{\parallel}$).

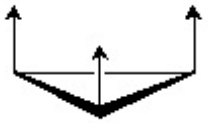
The symmetries of the central boron AOs are as follows:

$$s = A_1' \quad (p_x, p_y) = E' \quad p_z = A_2''$$

Out-of-Plane Pi Interactions

- The effective $p\pi$ interactions are the out-of-plane type formed from combinations of $2p_z$ AOs on both B and F atoms.

- The formation of the SALCs is based on the following vector set.



- The reducible representation and its decomposition are

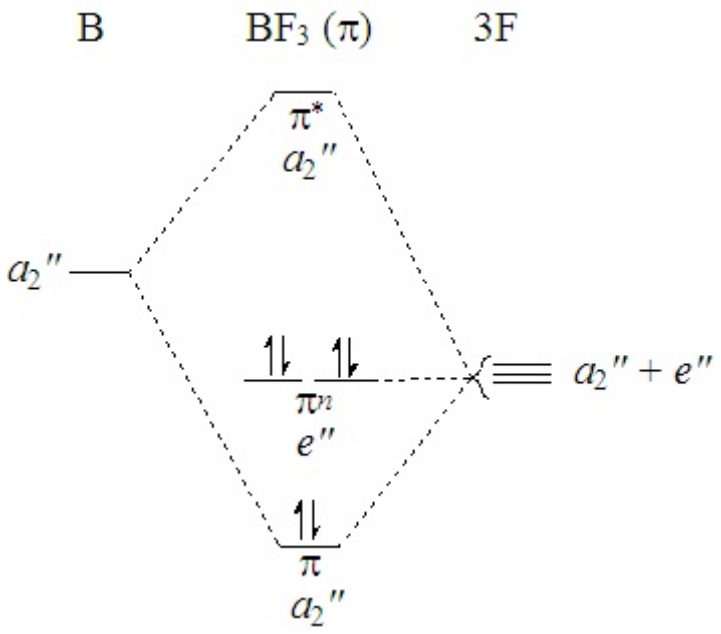
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_π	3	0	-1	-3	0	1

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

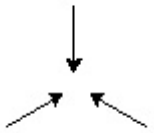
- The A_2'' SALC matches with the "empty" $2p_z$ AO on B.

- The E'' SALCs have no match on B and remain nonbonding.

Pi-Only MO Scheme for BF_3



SALCs for Core (Nonbonding) F 2*s*



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

$$\Gamma_{2s} = A_1' + E'$$

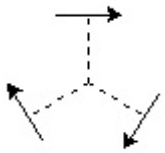
Sigma SALCs for F $2p_x$

- The vector set of $2p_x$ sigma bonding is identical to the set shown for $2s$.
    - Therefore, $\Gamma_\sigma = A_1' + E'$.

- The A_1' SALC matches with the boron $2s$ AO.

- The E' SALCs match with the degenerate boron $2p_x$ and $2p_y$ AOs.

In-Plane Pi-SALCs



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

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

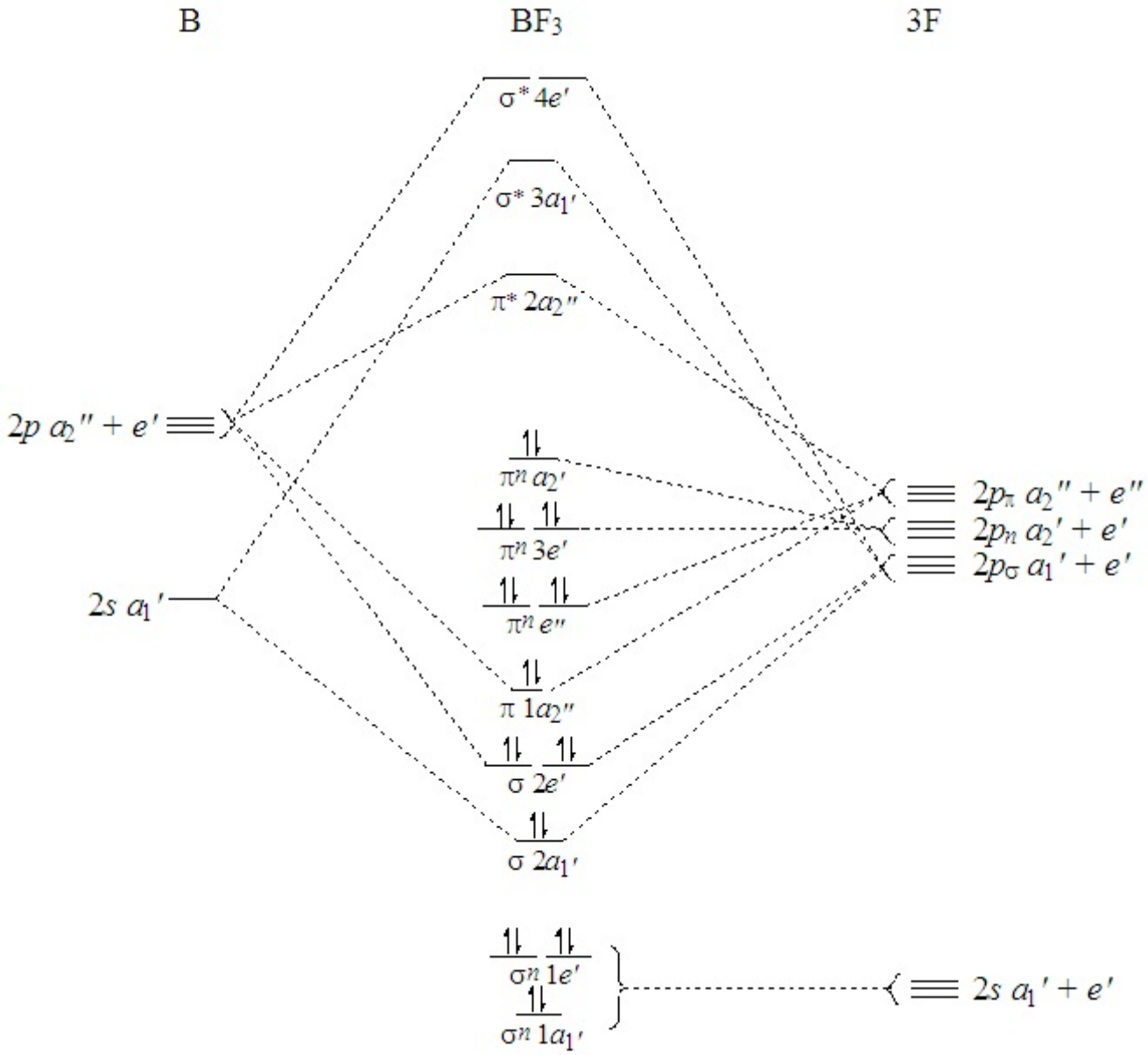
- The A_2' SALC has no match in B AOs and must be strictly nonbonding.

- The E' SALCs do match with boron $2p_x$ and $2p_y$, which are involved in sigma bonding.

- Assuming that the sigma interactions are more effective, the in-plane pi interactions of the E' SALCs can be taken to be essentially nonbonding.

Complete MO Scheme of BF_3

The ordering of levels in the following complete MO scheme is based on the P.E.S. data of G. H. King, et al.[1]



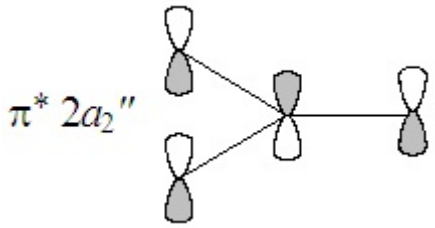
[1]G. J. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Faraday Disc. Chem. Soc.*, **1972**, *54*, 70.

Lewis Acid Behavior of BF_3
$BF_3 + NH_3 \rightarrow F_3B{:}NH_3$

- In terms of frontier orbital theory, the LUMO in BF_3 is the $\pi^* 2a_2''$ MO, which can receive an electron pair from a Lewis base.
    - This MO, formed from $2p_z$ orbitals, is

$$\Phi = c_1\varphi(B) - c_2[\varphi(F_a) + \varphi(F_b) + \varphi(F_c)]$$

    - The LCAO for this is



- For the base NH_3, the HOMO is the weakly bonding $\sigma\ a_1$ MO (cf. MO scheme), which can provide electrons to the boron $\pi^* 2a_2''$ MO in the following manner: