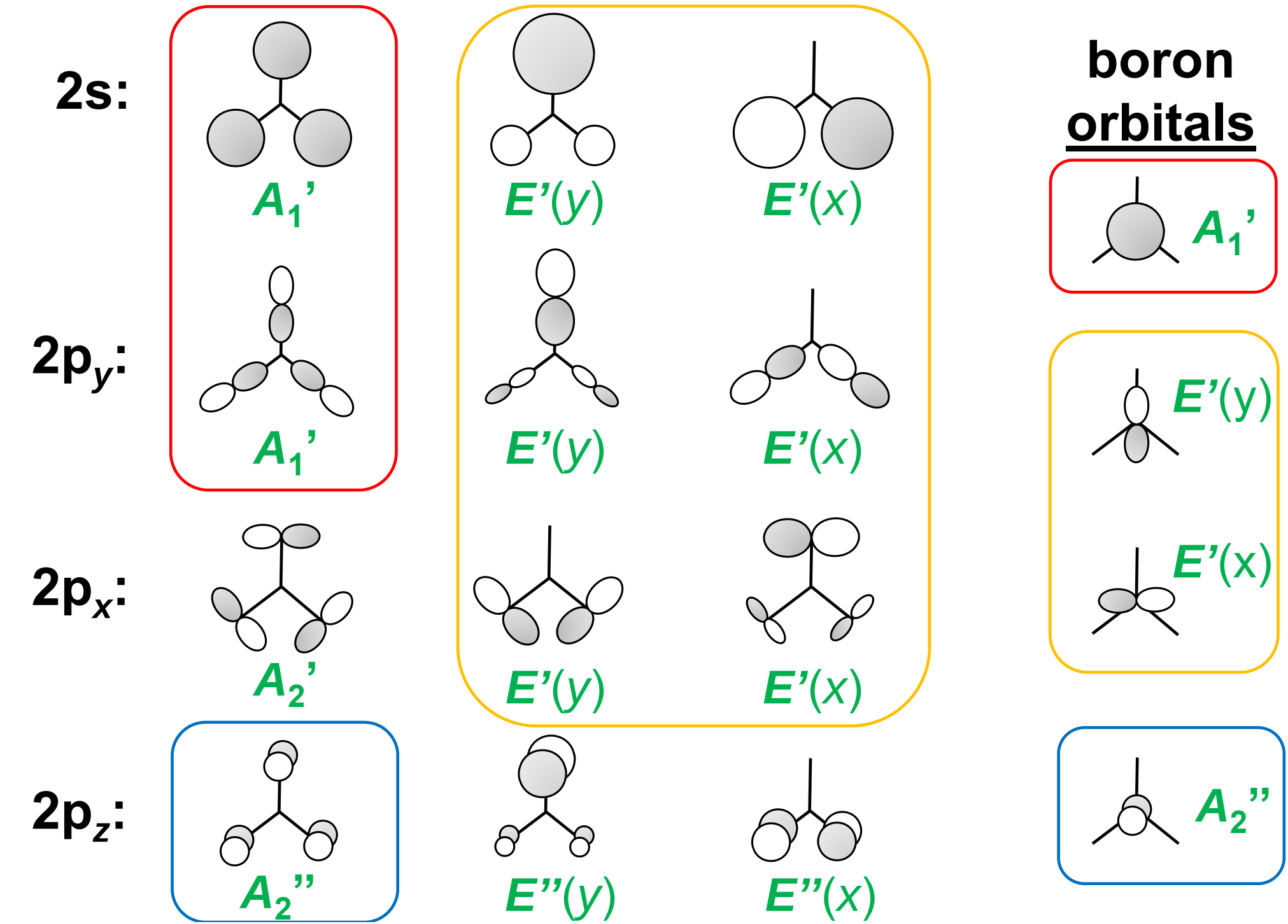
MO Diagrams for More Complex Molecules

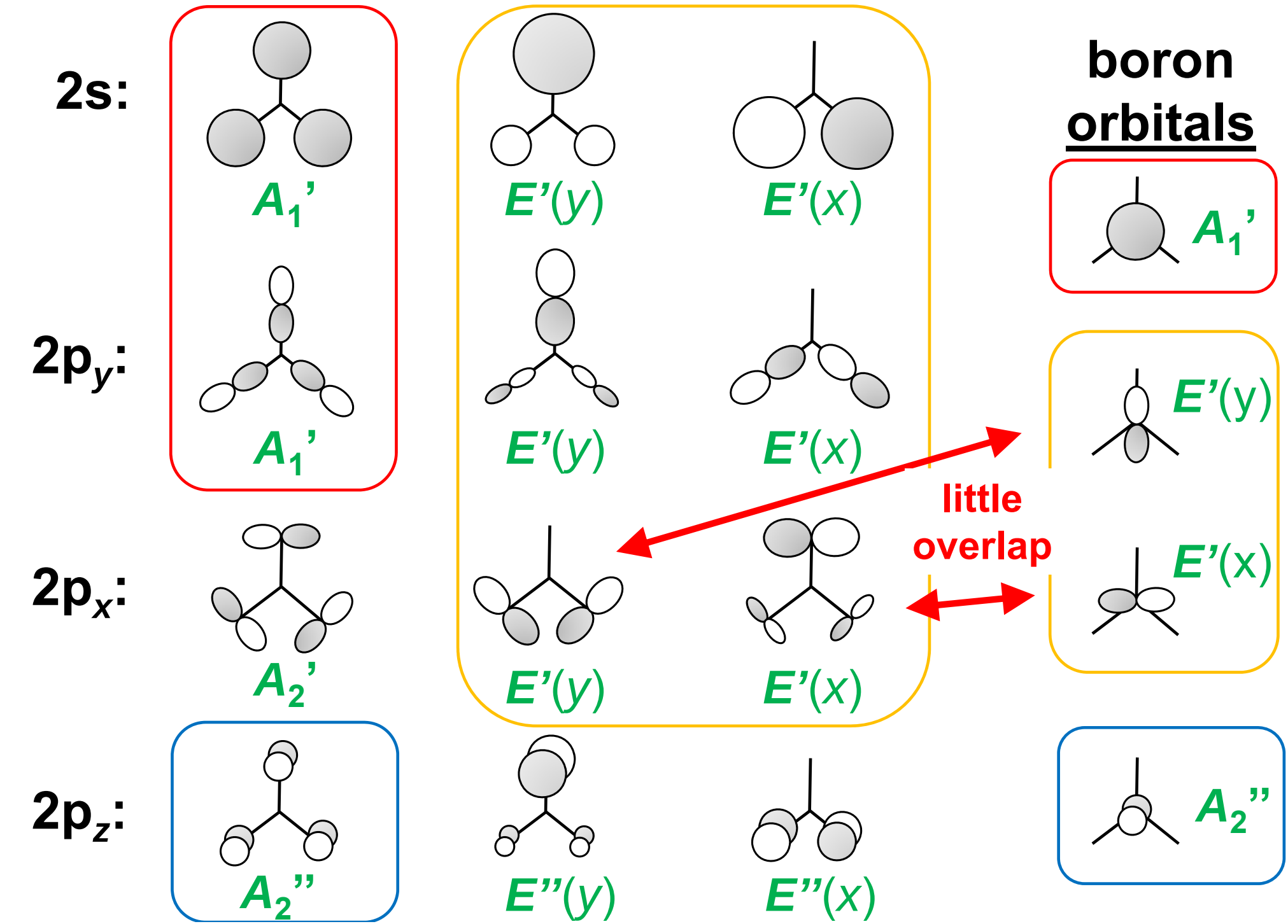
Chapter 5

Friday, October 16, 2015

BF_3 - Projection Operator Method

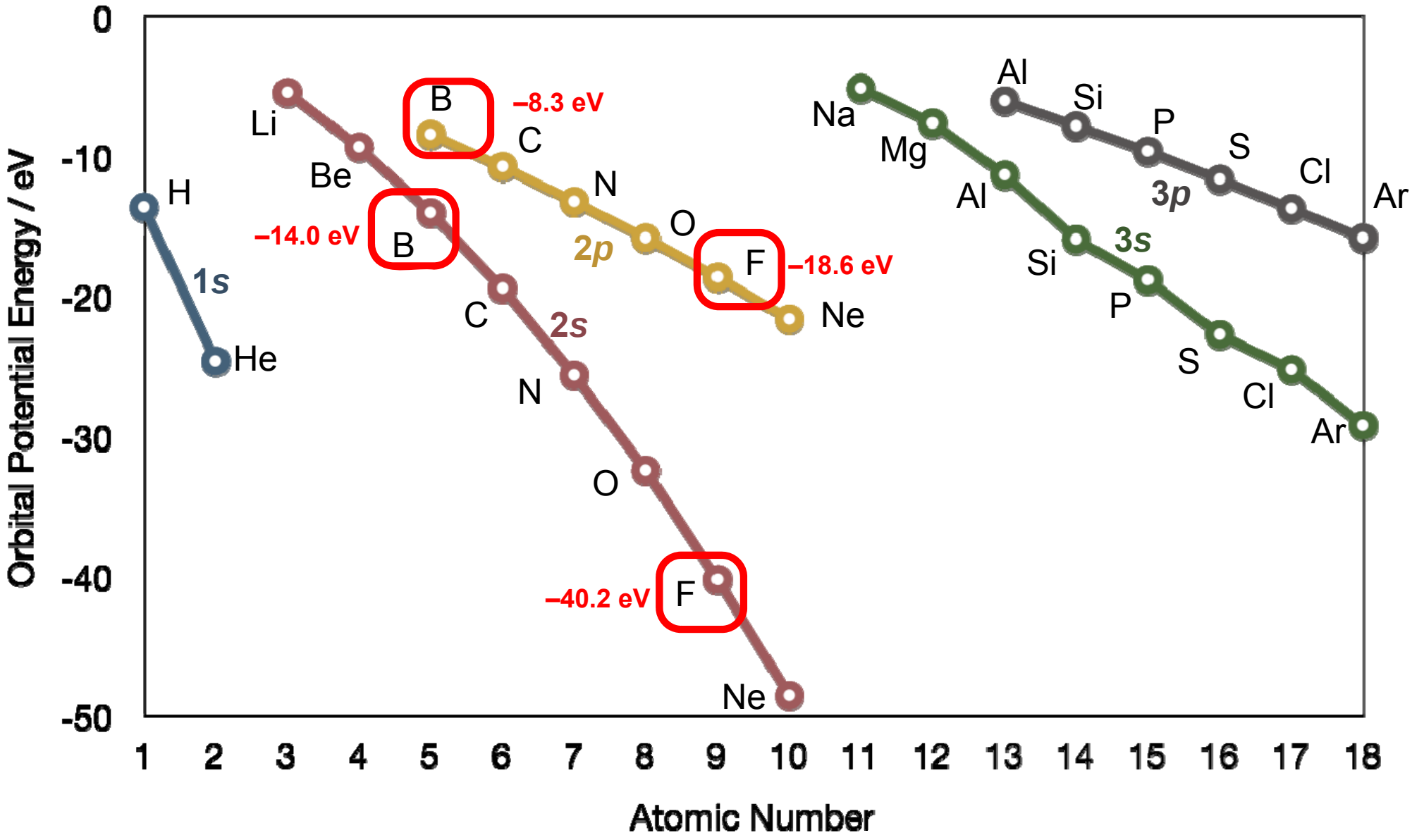


BF_3 - Projection Operator Method

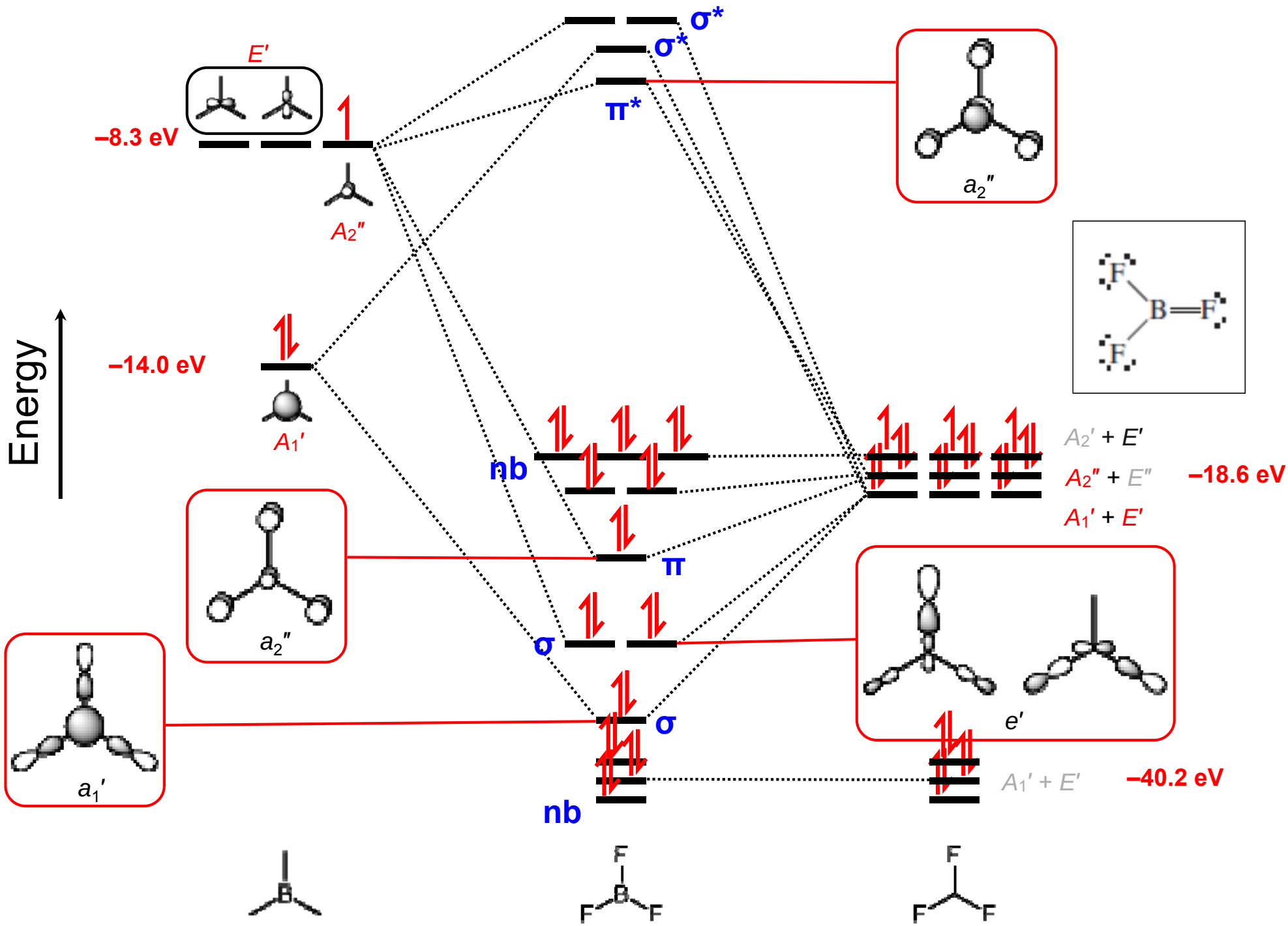


Boron trifluoride

F 2*s* is very deep in energy and won't interact with boron.

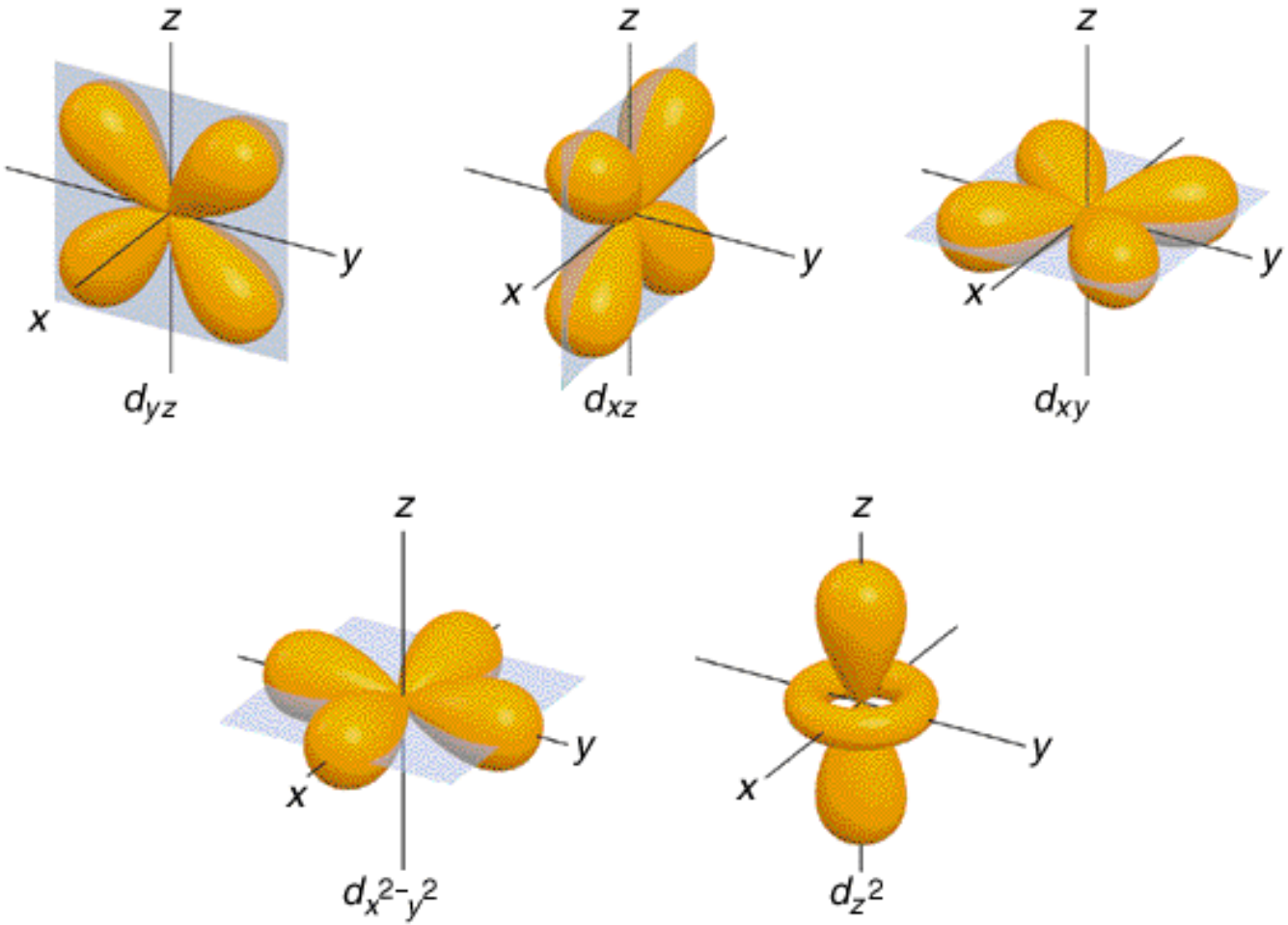


Boron Trifluoride



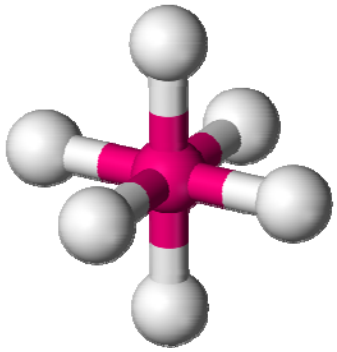
d orbitals

- $\ell = 2$, so there are $2\ell + 1 = 5$ *d*-orbitals per shell, enough room for 10 electrons.
- This is why there are 10 elements in each row of the *d*-block.



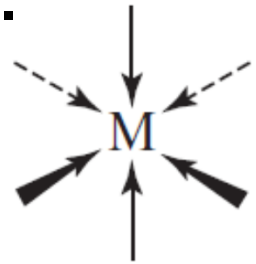
σ-MOs for Octahedral Complexes

1. Point group O_h



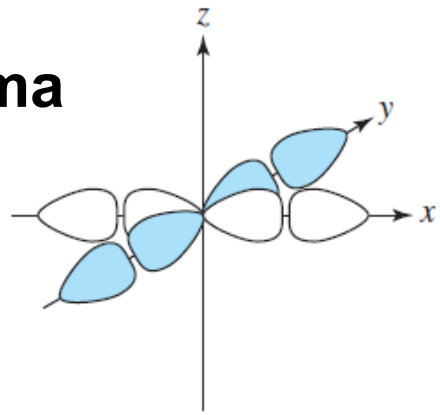
The six ligands can interact with the metal in a sigma or pi fashion. Let's consider only sigma interactions for now.

2.



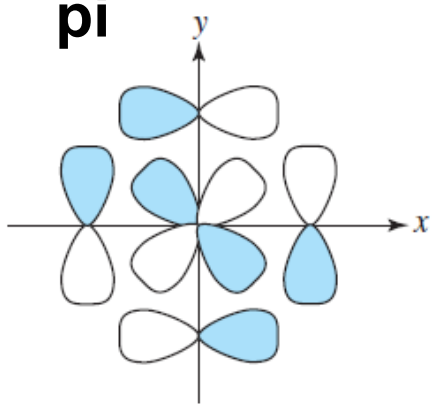
sigma

Sigma bonding interaction between two ligand orbitals and metal d_{z^2} orbital



Sigma bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital

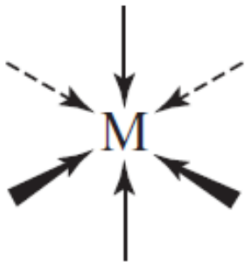
pi



Pi bonding interaction between four ligand orbitals and metal d_{xy} orbital

σ-MOs for Octahedral Complexes

2.



3. Make reducible reps for sigma bond vectors

TABLE 10.4 Character Table for O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
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		(xy, xz, yz)
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		

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_σ	6	0	0	2	2	0	0	0	4	2

4. This reduces to: $\Gamma_\sigma = A_{1g} + E_g + T_{1u}$ **six GOs in total**

σ-MOs for Octahedral Complexes

5. Find symmetry matches with central atom. $\Gamma_\sigma = A_{1g} + E_g + T_{1u}$

TABLE 10.4 Character Table for O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
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		(xy, xz, yz)
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		

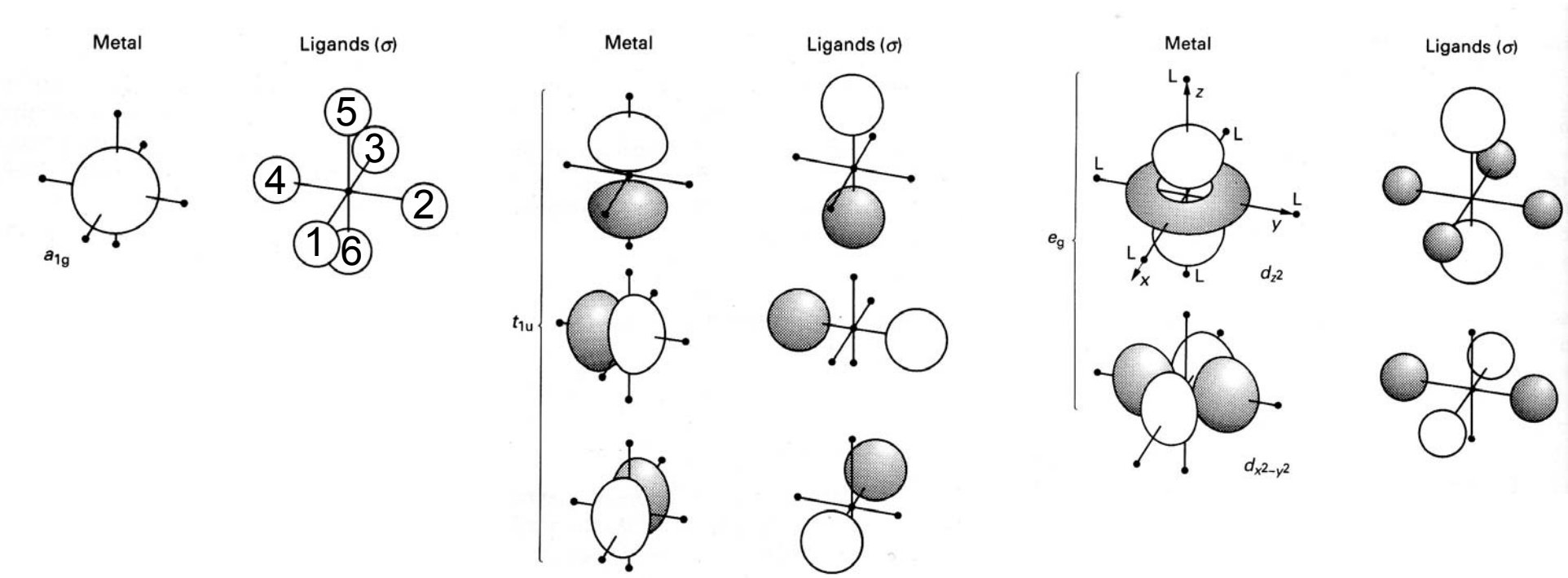
Reading off the character table, we see that the group orbitals match the metal *s* orbital (A_{1g}), the metal *p* orbitals (T_{1u}), and the d_{z2} and d_{x2-y2} metal *d* orbitals (E_g). We expect bonding/antibonding combinations.

The remaining three metal *d* orbitals are T_{2g} and σ-nonbonding.

σ-MOs for Octahedral Complexes

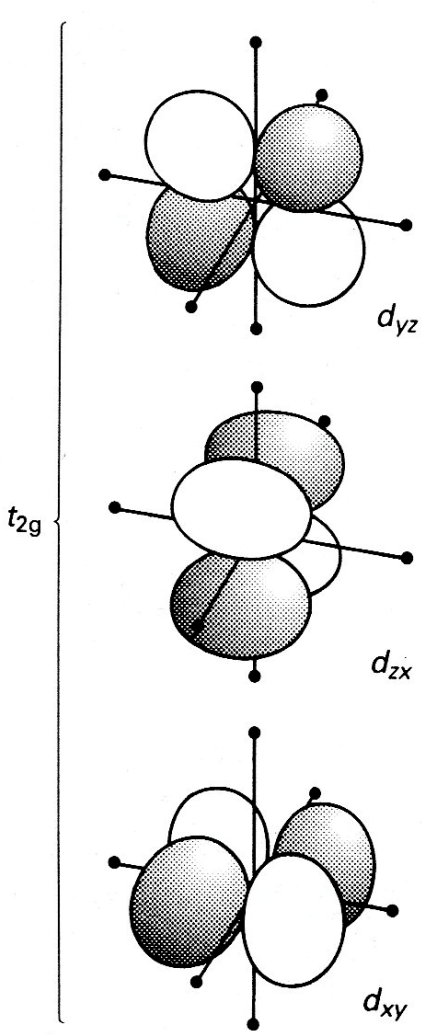
We *can* use the projection operator method to deduce the shape of the ligand group orbitals, but let's skip to the results:

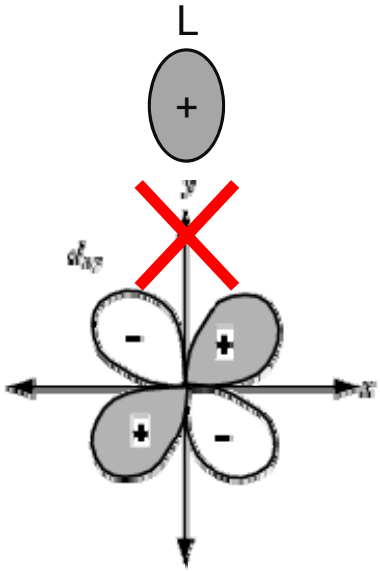
L_6 SALC	symmetry label
$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$	A_{1g} (non-degenerate)
$\sigma_1 - \sigma_3$, $\sigma_2 - \sigma_4$, $\sigma_5 - \sigma_6$	T_{1u} (triply degenerate)
$\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$, $2\sigma_6 + 2\sigma_5 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4$	E_g (doubly degenerate)



σ-MOs for Octahedral Complexes

There is no combination of ligand σ orbitals with the symmetry of the metal T_{2g} orbitals, so these do not participate in σ bonding.





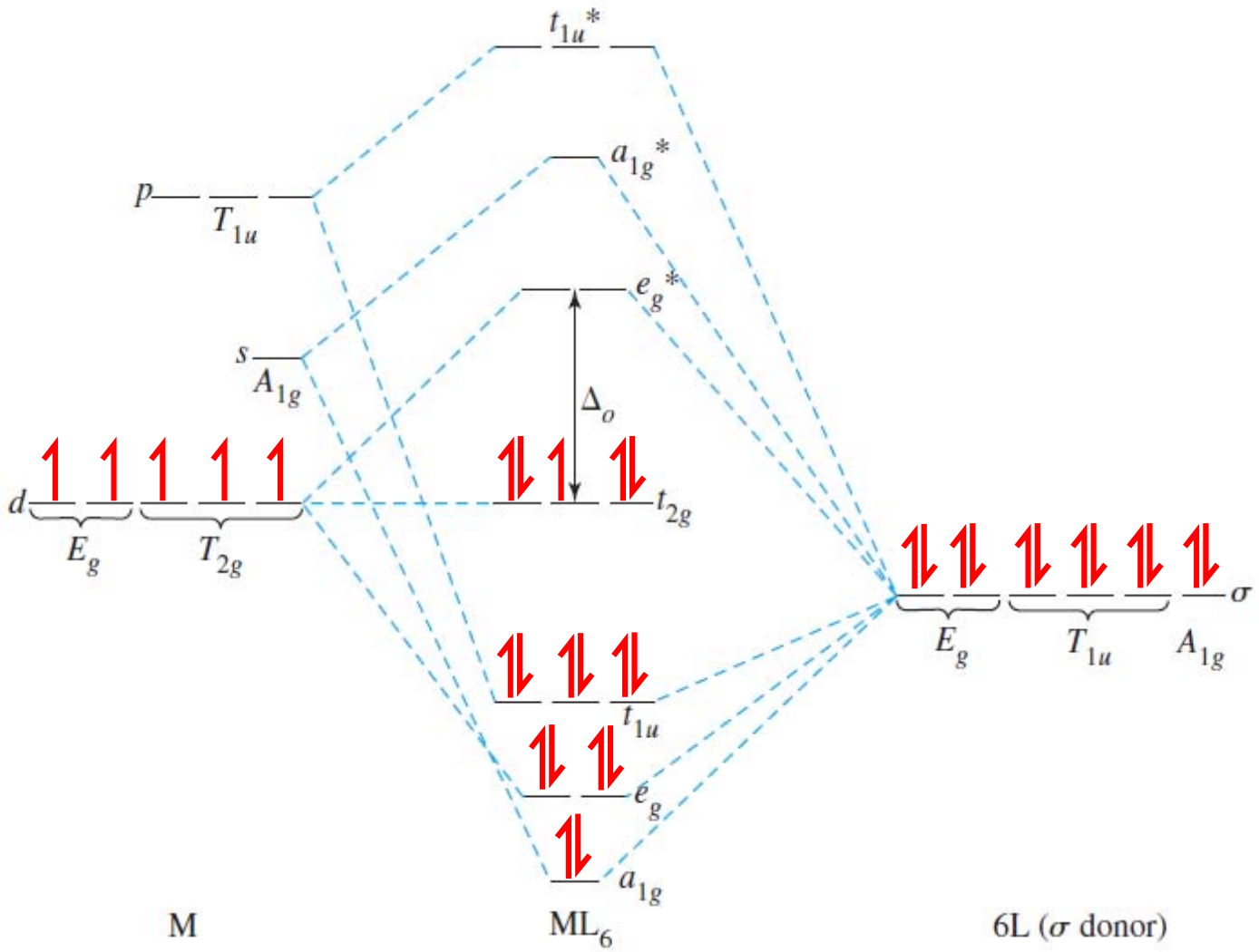
T_{2g} orbitals cannot form sigma bonds with the L_6 set.

$S = 0$.

T_{2g} are non-bonding

σ-MOs for Octahedral Complexes

6. Here is the general MO diagram for σ bonding in O_h complexes:



Summary

MO Theory

- MO diagrams can be built from group orbitals and central atom orbitals by considering orbital symmetries and energies.
- The symmetry of group orbitals is determined by reducing a reducible representation of the orbitals in question. This approach is used only when the group orbitals are not obvious by inspection.
- The wavefunctions of properly-formed group orbitals can be deduced using the projection operator method.
- We showed the following examples: homonuclear diatomics, HF, CO, H_3^+, FHF^-, CO_2, H_2O, BF_3, and σ-ML_6