MO Diagrams for More Complex Molecules

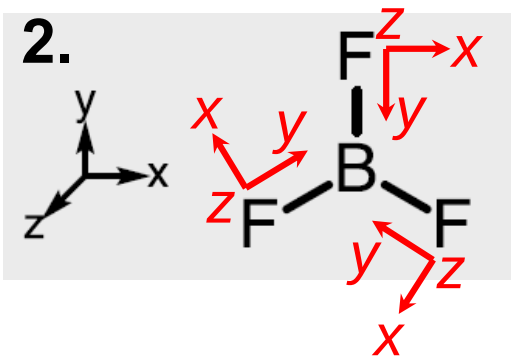
Chapter 5

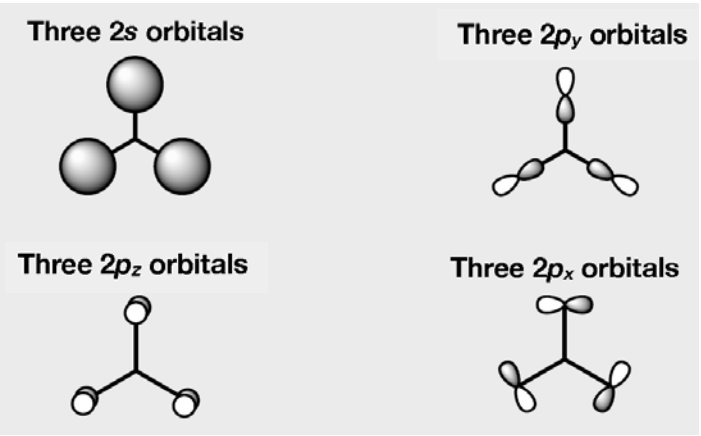
Wednesday, October 14, 2015

Boron trifluoride

1. Point group D_{3h}

2.





3. Make reducible reps for outer atoms

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

Γ_{2s}	3	0	1	3	0	1
Γ_{2pz}	3	0	-1	-3	0	1
Γ_{2px}	3	0	-1	3	0	-1
Γ_{2py}	3	0	1	3	0	1

4. Get group orbital symmetries by reducing each Γ

$$\text{\# of irreducible representations of a given type} = \frac{1}{\text{order}} \sum_R \left(\text{\# of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation} \right)$$

$\Gamma_{2s} = A_1' + E'$ $\quad\quad$ $\Gamma_{2px} = A_2' + E'$

$\Gamma_{2pz} = A_2'' + E''$ $\quad\quad$ $\Gamma_{2py} = A_1' + E'$

Boron trifluoride

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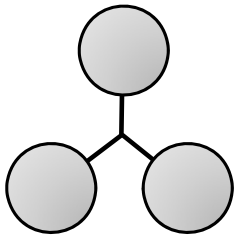
What is the shape of the group orbitals?

2s:



A_1' $\quad$? $\quad$?

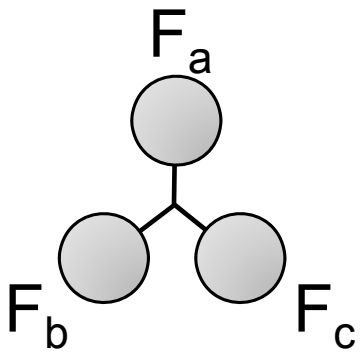
$E'(y)$ $\quad$ $E'(x)$

Which combinations of the three AOs are correct?

The *projection operator method* provides a systematic way to find how the AOs should be combined to give the right group orbitals (SALCs).

BF_3 - Projection Operator Method

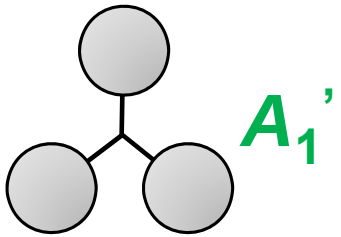
In the *projection operator method*, we pick one AO in each set of identical AOs and determine how it transforms under each symmetry operation of the point group.



AO	E	C_3	C_3^2	$C_{2(a)}$	$C_{2(b)}$	$C_{2(c)}$	σ_h	S_3	S_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
F_a	F_a	F_b	F_c	F_a	F_c	F_b	F_a	F_b	F_c	F_a	F_c	F_b
A_1'	1	1	1	1	1	1	1	1	1	1	1	1

$$A_1' = F_a + F_b + F_c + F_a + F_c + F_b + F_a + F_b + F_c + F_a + F_c + F_b$$

$$A_1' = 4F_a + 4F_b + 4F_c$$



The group orbital wavefunctions are determined by multiplying the projection table values by the characters of each irreducible representation and summing the results.

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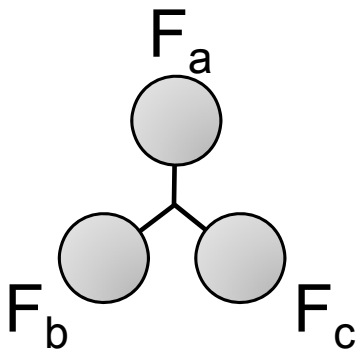

AO	E	C_3	C_3^2	$C_{2(a)}$	$C_{2(b)}$	$C_{2(c)}$	σ_h	S_3	S_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
F_a	F_a	F_b	F_c	F_a	F_c	F_b	F_a	F_b	F_c	F_a	F_c	F_b
A_2'	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1

$$A_2' = F_a + F_b + F_c - F_a - F_c - F_b + F_a + F_b + F_c - F_a - F_c - F_b$$

$$A_2' = 0$$

There is no A_2' group orbital!

The group orbital wavefunctions are determined by multiplying the projection table values by the characters of each irreducible representation and summing the results.

BF_3 - Projection Operator Method

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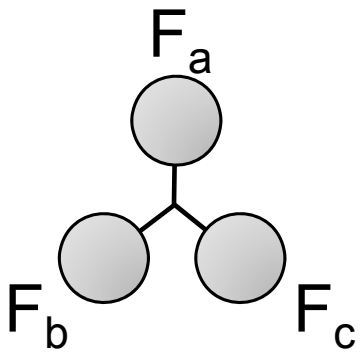
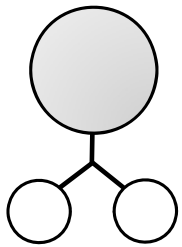


AO	E	C_3	C_3^2	$C_{2(a)}$	$C_{2(b)}$	$C_{2(c)}$	σ_h	S_3	S_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
F_a	F_a	F_b	F_c	F_a	F_c	F_b	F_a	F_b	F_c	F_a	F_c	F_b
E'	2	-1	-1	0	0	0	2	-1	-1	0	0	0

$$E' = 2F_a - F_b - F_c + 0 + 0 + 0 + 2F_a - F_b - F_c + 0 + 0 + 0$$

$$E' = 4F_a - 2F_b - 2F_c$$



$E'(y)$

The group orbital wavefunctions are determined by multiplying the projection table values by the characters of each irreducible representation and summing the results.

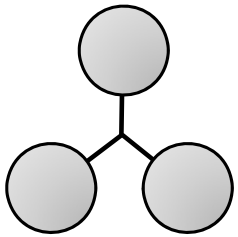
BF_3 - Projection Operator Method

$\Gamma_{2s} = A_1' + E'$ $\quad\quad$ $\Gamma_{2px} = A_2' + E'$

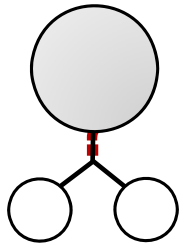
$\Gamma_{2pz} = A_2'' + E''$ $\quad\quad$ $\Gamma_{2py} = A_1' + E'$

What is the shape of the group orbitals?

2s:



A_1'



$E'(y)$

?

$E'(x)$

We can get the third group orbital, *E*'(*x*), by using normalization.

$$\int \psi^2 d\tau = 1$$

Normalization condition

BF_3 - Projection Operator Method

Let's normalize the A_1' group orbital:

$$\psi_{A_1'} = c_a[\phi(2s_{F_a}) + \phi(2s_{F_b}) + \phi(2s_{F_c})]$$ A_1' wavefunction

$$\int \psi^2 d\tau = 1$$ Normalization condition for group orbitals

$$c_a^2 \int [\phi(2s_{F_a}) + \phi(2s_{F_b}) + \phi(2s_{F_c})]^2 d\tau = 1$$ nine terms, but the six overlap (*S*) terms are zero.

$$c_a^2 \left[\int \phi^2(2s_{F_a}) d\tau + \int \phi^2(2s_{F_b}) d\tau + \int \phi^2(2s_{F_c}) d\tau \right] = 1$$

$$c_a^2[1 + 1 + 1] = 1 \Rightarrow \boxed{c_a = \frac{1}{\sqrt{3}}}$$

So the normalized A_1' GO is: $$\boxed{\psi_{A_1'} = \frac{1}{\sqrt{3}}[\phi(2s_{F_a}) + \phi(2s_{F_b}) + \phi(2s_{F_c})]}$$

BF_3 - Projection Operator Method

Now let's normalize the *E'*(*y*) group orbital:

$$\psi_{E'(y)} = c_{\mathrm{a}}[2\phi(2s_{\mathrm{F_a}}) - \phi(2s_{\mathrm{F_b}}) - \phi(2s_{\mathrm{F_c}})]$$

E'(*y*) wavefunction

$$c_{\mathrm{a}}^2 \int [2\phi(2s_{\mathrm{F_a}}) - \phi(2s_{\mathrm{F_b}}) - \phi(2s_{\mathrm{F_c}})]^2 d\tau = 1$$

nine terms, but the six overlap (*S*) terms are zero.

$$c_{\mathrm{a}}^2 \left[4 \int \phi^2(2s_{\mathrm{F_a}}) d\tau + \int \phi^2(2s_{\mathrm{F_b}}) d\tau + \int \phi^2(2s_{\mathrm{F_c}}) d\tau \right] = 1$$

$$c_{\mathrm{a}}^2[4 + 1 + 1] = 1 \quad \Rightarrow \quad \boxed{c_{\mathrm{a}} = \frac{1}{\sqrt{6}}}$$

So the normalized *E'*(*y*) GO is:

$$\boxed{\psi_{E'(y)} = \frac{1}{\sqrt{6}}[2\phi(2s_{\mathrm{F_a}}) - \phi(2s_{\mathrm{F_b}}) - \phi(2s_{\mathrm{F_c}})]}$$

BF_3 - Projection Operator Method

$$\psi_{A_1'} = \frac{1}{\sqrt{3}}[\phi(2s_{F_a}) + \phi(2s_{F_b}) + \phi(2s_{F_c})]$$

$$\psi_{E'(y)} = \frac{1}{\sqrt{6}}[2\phi(2s_{F_a}) - \phi(2s_{F_b}) - \phi(2s_{F_c})]$$

c_i^2 is the probability of finding an electron in ϕ_i in a group orbital, so $\sum c_i^2 = 1$ for a normalized group orbital.

TABLE 5.6 SALC Coefficients and Evidence of Normalization

	Coefficients in Normalized SALCs			Squares of SALC Coefficients			Sum of the Squares = 1 for Normalization Requirement
	c_a	c_b	c_c	c_a^2	c_b^2	c_c^2	
A_1	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1
$E(y)$	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	1
$E(x)$	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1
Sum of the squares for each 1*s* wave function must total 1 for an identical contribution of each atomic orbital to the group orbitals				1	1	1	

So the normalized *E*'(*x*) GO is:

$$\psi_{E'(x)} = \frac{1}{\sqrt{2}}[\phi(2s_{F_b}) - \phi(2s_{F_c})]$$

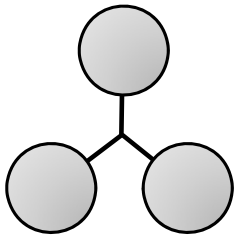
BF_3 - Projection Operator Method

$$\Gamma_{2s} = A_1' + E' \qquad \Gamma_{2px} = A_2' + E'$$
$$\Gamma_{2pz} = A_2'' + E'' \qquad \Gamma_{2py} = A_1' + E'$$

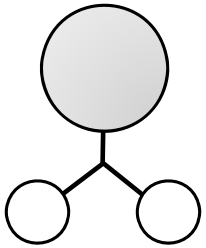
What is the shape of the group orbitals?

notice the GOs are orthogonal ($S = 0$).

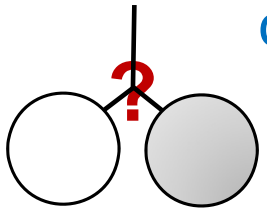
2s:



A_1'



$E'(y)$

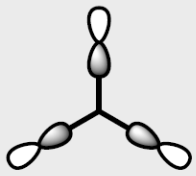


$E'(x)$

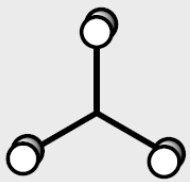
Now we have the symmetries and wavefunctions of the 2*s* GOs.

We *could* do the same analysis to get the GOs for the p_x, p_y, and p_z orbitals (see next slide).

Three $2p_y$ orbitals



Three $2p_z$ orbitals



Three $2p_x$ orbitals