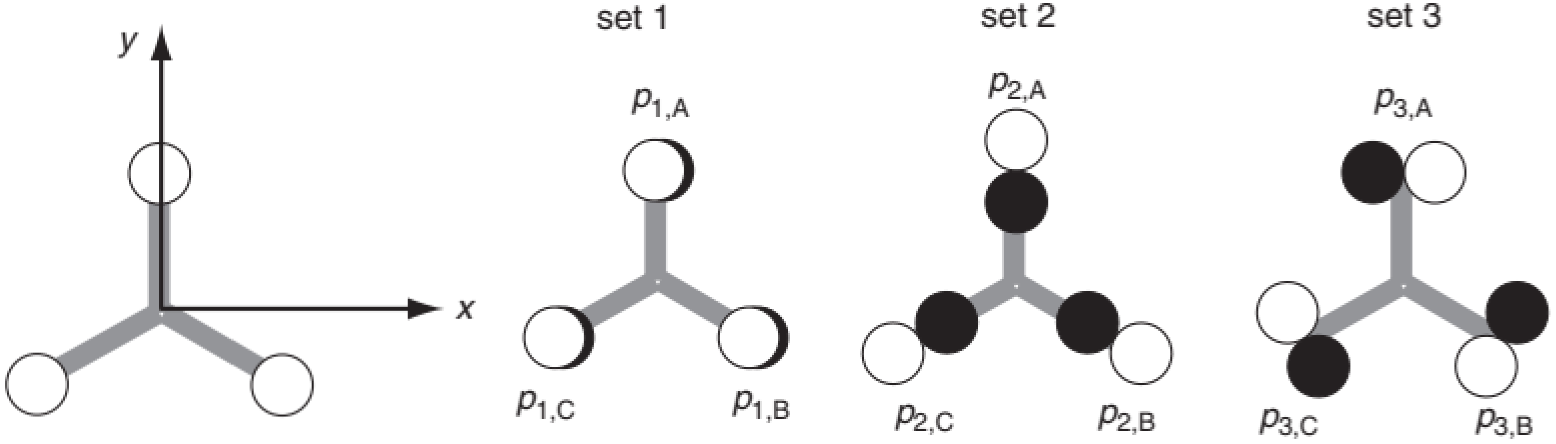
Ex. 17-18

This exercise is concerned with constructing the symmetry orbitals arising from each of the sets of 2*p* orbitals in BF_3 (point group D_{3h}) shown below. *Do not use the projection formula*



(a) For each set find the characters of the representation and then reduce the representation.

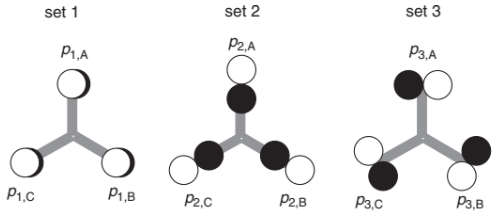
(b) By drawing an analogy between the orbital coefficients and relevant cartesian functions, sketch the form of the SOs clearly labelling each with the appropriate IR.

(c) Give the normalization form of each SO.

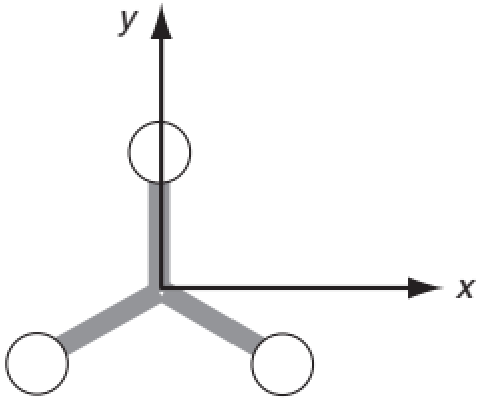
(d) Construct an MO diagram for BF_3 which has a trigonal planar geometry. Consider the boron 2*s* and 2*p* AOs, and *only* the fluorine 2*p* AOs (you will need the results of the previous exercise). Determine which MOs are occupied and comment on the result. (You are *not* asked to sketch the MOs.)

Ex. 17-18

(a)



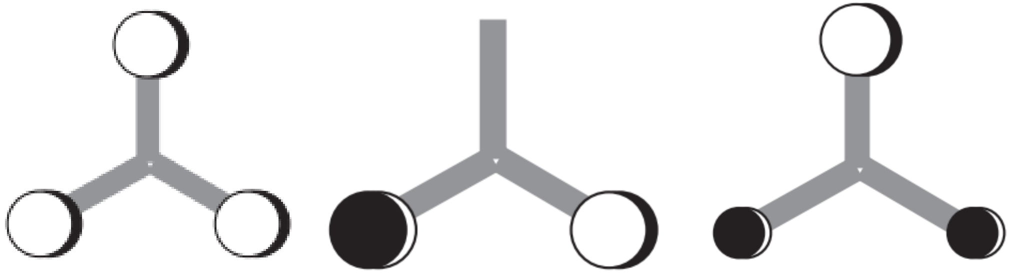
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A'_1	1	1	1	1	1	1			$x^2+y^2; z^2$
A'_2	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A''_1	1	1	1	−1	−1	−1			
A''_2	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)



Γ(set1)	3	0	-1	-3	0	1	$A_2'' \oplus E''$
Γ(set2)	3	0	1	3	0	1	$A_1' \oplus E'$
Γ(set3)	3	0	-1	3	0	-1	$A_2' \oplus E'$

(b,c) Set1 SOs

- $\theta_{A_2''} = (p_{1,A}+p_{1,B}+p_{1,C})/\sqrt{3}$
- $\theta_{E''xz} = (p_{1,B}-p_{1,C})/\sqrt{2}$
- $\theta_{E''yz} = (2p_{1,A}-p_{1,B}-p_{1,C})/\sqrt{6}$

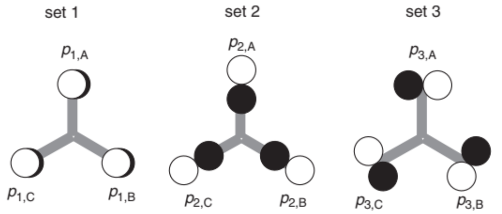


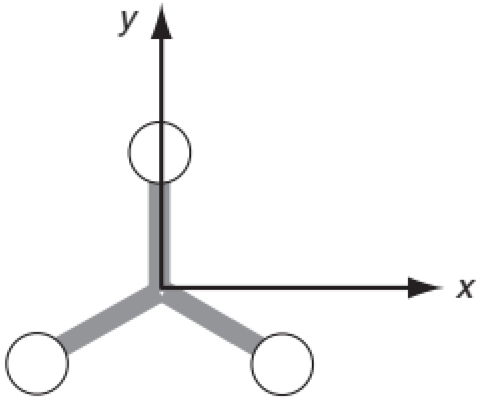
Ex. 17-18

(a)

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)		$(x^2-y^2, 2xy)$
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)

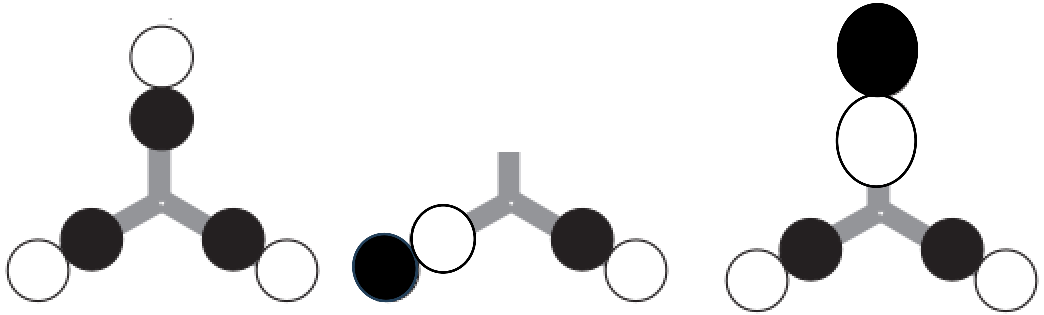
Γ(set1)	3	0	-1	-3	0	1	$A_2'' \oplus E''$
Γ(set2)	3	0	1	3	0	1	$A_1' \oplus E'$
Γ(set3)	3	0	-1	3	0	-1	$A_2' \oplus E'$





(b) Set2 SOs

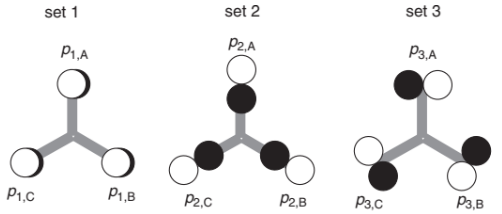
- $\theta_{A_1'} = (p_{2,A}+p_{2,B}+p_{2,C})/\sqrt{3}$
- $\theta_{E'x} = (p_{2,B}-p_{2,C})/\sqrt{2}$
- $\theta_{E'y} = (2p_{2,A}-p_{2,B}-p_{2,C})/\sqrt{6}$

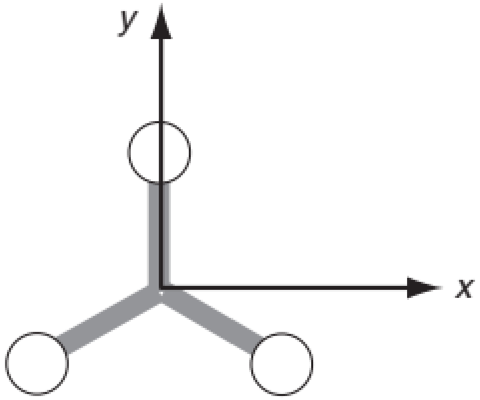


Ex. 17-18

(a)

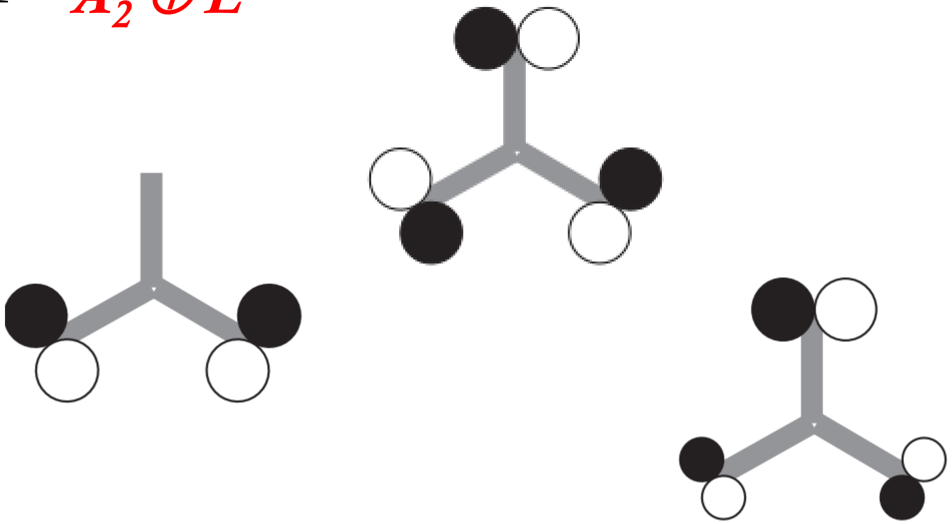
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)
Γ(set1)	3	0	-1	-3	0	1	$A_2'' \oplus E''$		
Γ(set2)	3	0	1	3	0	1	$A_1' \oplus E'$		
Γ(set3)	3	0	-1	3	0	-1	$A_2' \oplus E'$		





(b) Set3 SOs

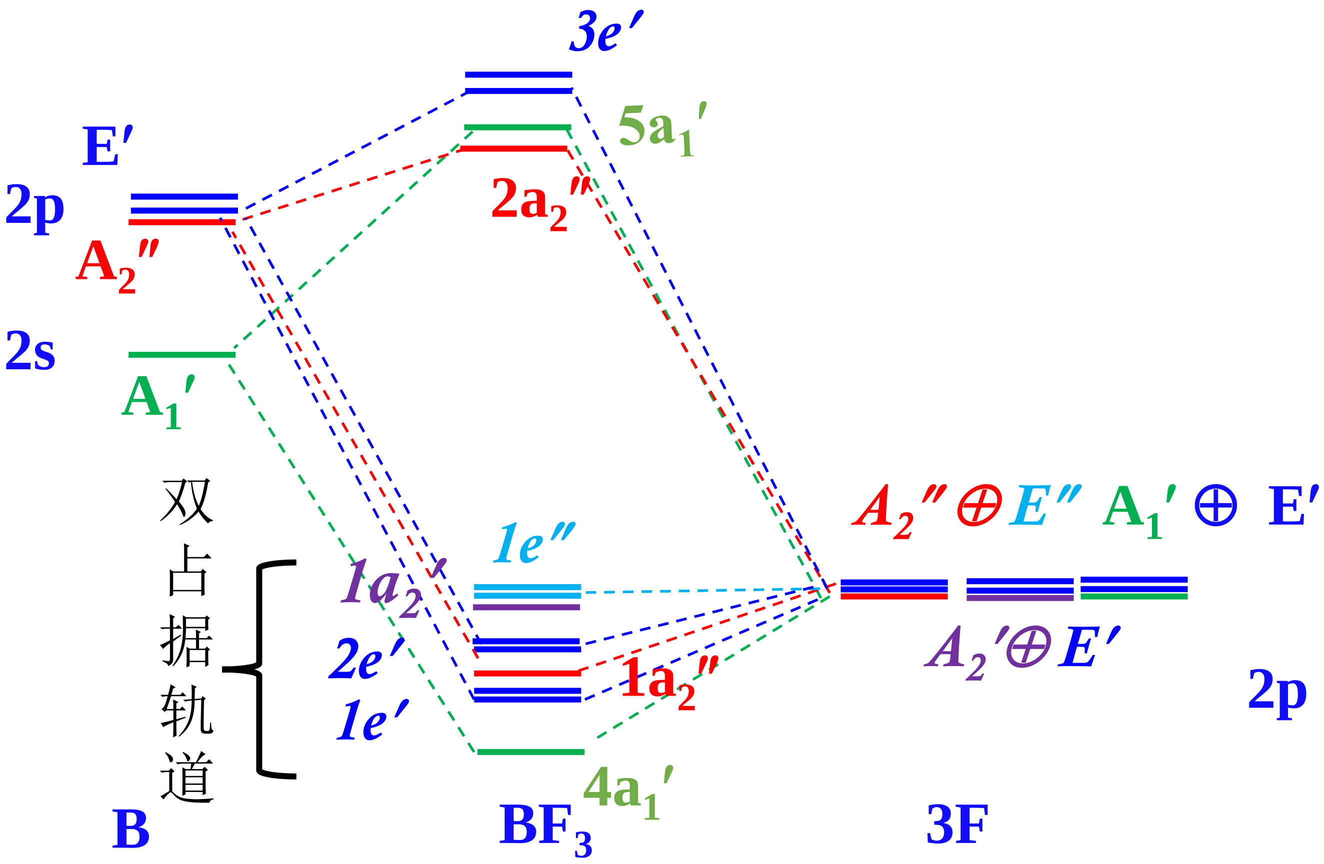
- $\theta_{A_2'} = (p_{3,A} + p_{3,B} + p_{3,C})/\sqrt{3}$
- $\theta_{E'x} = (p_{3,B} - p_{3,C})/\sqrt{2}$
- $\theta_{E'y} = (2p_{3,A} - p_{3,B} - p_{3,C})/\sqrt{6}$



Ex. 17-18

(d)

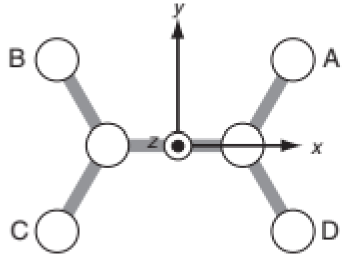
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)



ex19

This exercise refers to ***tetrafluoroethene***; use the axis system and labelling indicated below.

(a) State the point group. ***D_{2h}***



(b) Determine the characters of the representation generated by the four fluorine $2p_z$ AOs; reduce the representation.

(c) *Using the projection formula* find the SO corresponding to each irreducible representation found in (b) (apply the projection operator to the orbital at position A).

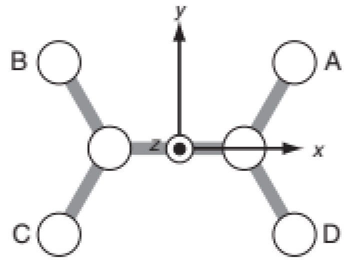
(d) Sketch the SOs you have found in (c) and check that they match up with the form you would expect simply by drawing an analogy between the orbital coefficients are relevant cartesian functions.

(e) Repeat the process for: (i) the four fluorine $2p_y$ AOs; (ii) the four fluorine $2p_x$ AOs. In each case apply the projection operator to the orbital at position A.

(f) Returning to the four fluorine $2p_z$ AOs repeat the process, but this time apply the projection operator to the orbital at position B.

ex19

tetrafluoroethene; use the axis system and labelling indicated below.

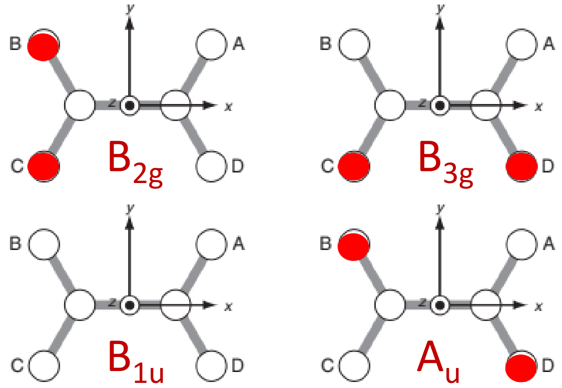


(b,d) Determine the characters of the representation generated by the four fluorine $2p_z$ AOs; reduce the representation.

D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		xyz
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	
(4 F p_z)	4	0	0	0	0	−4	0	0	$B_{2g} \oplus B_{3g} \oplus A_u \oplus B_{1u}$	

$(B_{1g} \otimes B_{1u} = A_u)$

运用相应坐标的简单函数值为组合系数!



xz-like $\theta(B_{2g}) = (p_{z,A} - p_{z,B} - p_{z,C} + p_{z,D})/2$

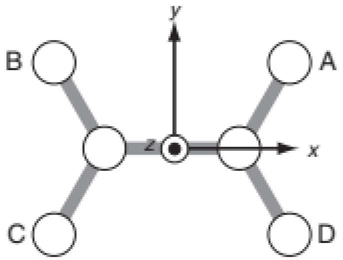
yz-like $\theta(B_{3g}) = (p_{z,A} + p_{z,B} - p_{z,C} - p_{z,D})/2$

z-like $\theta(B_{1u}) = (p_{z,A} + p_{z,B} + p_{z,C} + p_{z,D})/2$

xyz-like $\theta(A_u) = (p_{z,A} - p_{z,B} + p_{z,C} - p_{z,D})/2$

ex19

tetrafluoroethene; use the axis system and labelling indicated below.



(c) *Using the projection formula* find the SO corresponding to each irreducible representation found in (b) (apply the projection operator to the orbital at position A).

D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

$B_{2g} \oplus B_{3g} \oplus A_u \oplus B_{1u}$

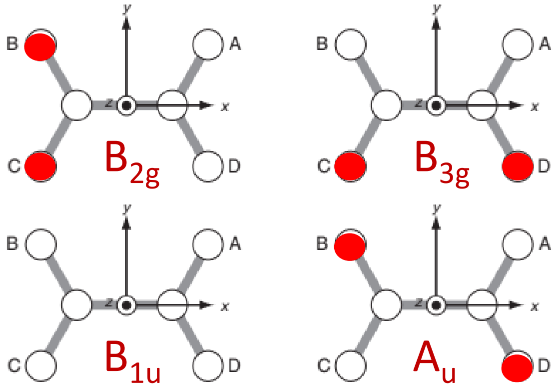
$\boldsymbol{R}p_{z,A}$ $\quad p_{z,A}$ $p_{z,C}$ $-p_{z,B}$ $-p_{z,D}$ $-p_{z,C}$ $-p_{z,A}$ $p_{z,D}$ $p_{z,B}$

$\theta(B_{2g}) = (p_{z,A} - p_{z,B} - p_{z,C} + p_{z,D})/2$ (normalized, *xz*-like)

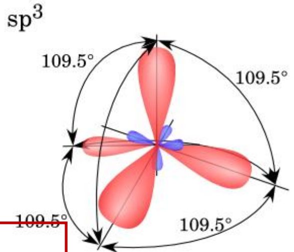
$\theta(B_{3g}) = (p_{z,A} + p_{z,B} - p_{z,C} - p_{z,D})/2$ (normalized, *yz*-like)

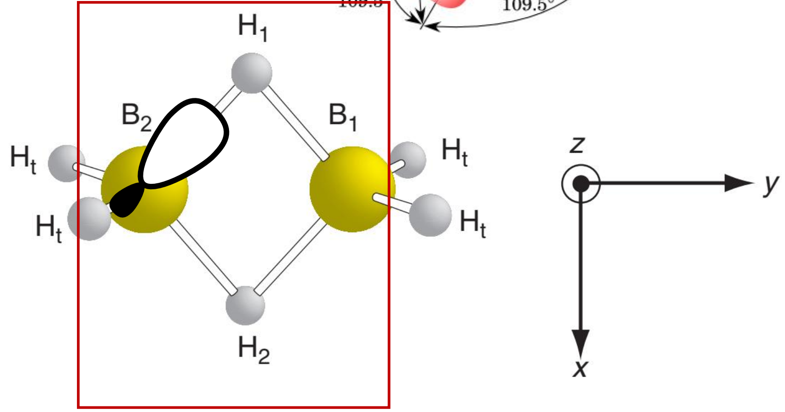
$\theta(B_{1u}) = (p_{z,A} + p_{z,B} + p_{z,C} + p_{z,D})/2$ (normalized, *y*-like)

$\theta(A_u) = (p_{z,A} - p_{z,B} + p_{z,C} - p_{z,D})/2$ (normalized, *xyz*-like)



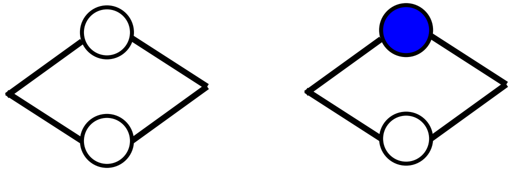
20. B_2H_6中假定B sp^3杂化, 4个2c-2e B-H_t 键已用去8个价电子, 要构筑B_2H_2四面环中的化学键? **(S&B Ex.20)**





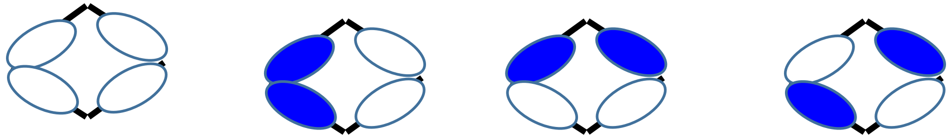
- To solve this problem, each sp^3 HAO can be simply regarded as an orbital directing to the bridging H atom!
- Classify the AO/HAOs first:

H_1,H_2: $A_g \oplus B_{3u}$



$\theta_{Ag} = (H_1 + H_2)/\sqrt{2}$ $\theta_{B3u} = (-H_1 + H_2)/\sqrt{2}$

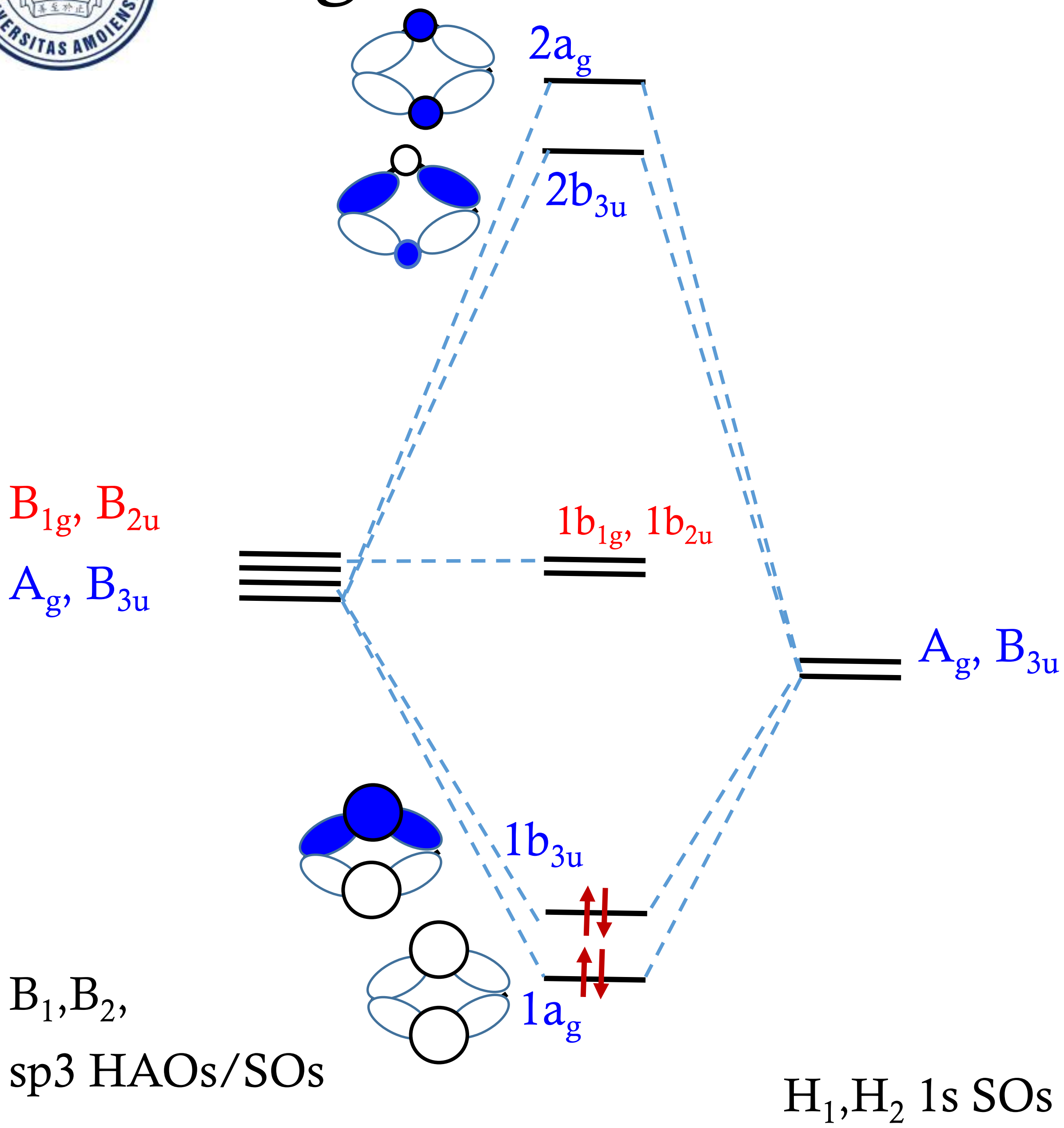
2xB, 4 HAOs: $A_g \oplus B_{1g} \oplus B_{2u} \oplus B_{3u}$



A_g | B_{2u} (y-like) | B_{3u} (x-like) | B_{1g} (xy-like)

D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	$\boxed{1}$	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	$\boxed{1}$	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	$\boxed{1}$	−1	1	y	
B_{3u}	1	−1	−1	1	−1	$\boxed{1}$	1	−1	x	
(H_1,H_2)	2	0	0	2	0	2	2	0	$A_g \oplus B_{3u}$	
B_1,B_2(4HAO)	4	0	0	0	0	4	0	0		

Diagram of MOs in the xy plane



Total valence electrons of B_2H_6:
3x2 + 1x6 = 12

VEs used for terminal B-H bonds:
2x4 = 8

VEs for the B-H-B bondings: 4

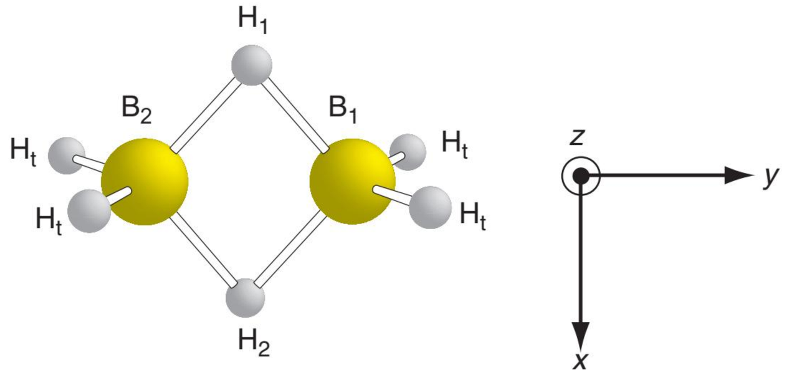
- The ***two bonding*** MOs involve a total of ***6*** AO/HAOs that otherwise could form *three bonding* orbitals to contain *6 bonding electrons*, but actually only ***4 bonding electrons***. ~***electron deficiency***!
- VB or LMO: Two **3c-2e** B-H-B bonds.

Normal bonding analysis for B_2H_6

- Classify of AOs: $(B_1,2s,\ B_2,2s)$

$(B_1,2p_z,\ B_2,2p_z)$ $(B_1,2p_x,\ B_2,2p_x)$ $(B_1,2p_y,\ B_2,2p_y)$

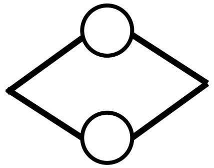
(H_1,H_2) $(H_{t1},H_{t2},H_{t3},H_{t4})$



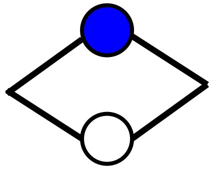
- Determine the IRs and SOs by inspection:

(H_1,H_2): (2,0,0,2,0,2,2,0) $\boldsymbol{A_g \oplus B_{3u}}$

D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	



$(H_1 + H_2)/\sqrt{2}$ A_g

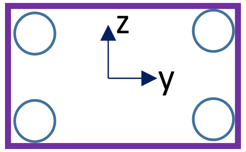


$(-H_1 + H_2)/\sqrt{2}$ B_{3u} x-like

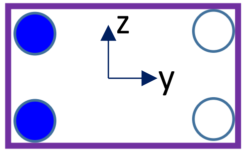
Normal bonding analysis for B_2H_6

- Determine the IRs and SOs by inspection:

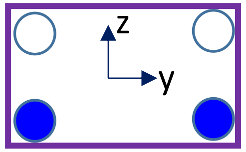
$(H_{t1},H_{t2},H_{t3},H_{t4})$: $(4,0,0,0,0,0,0,4)$ $A_g \oplus B_{3g} \oplus B_{1u} \oplus B_{2u}$



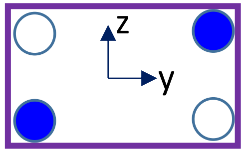
A_g



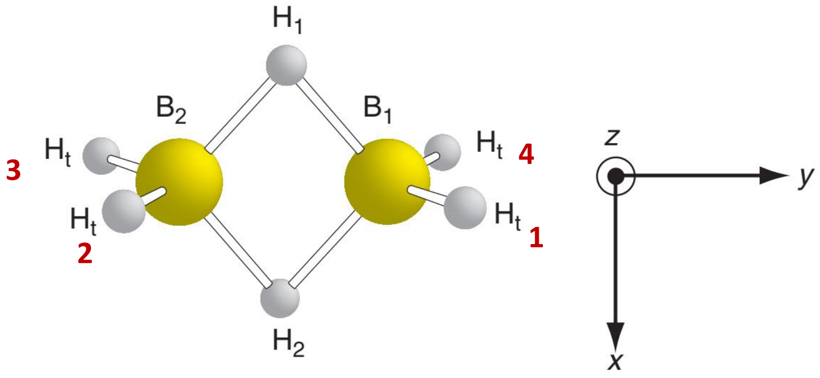
B_{2u}
y-like



B_{1u}
z-like



B_{3g}
yz-like



$$\theta(H_t)_{A_g} = (H_{t1} + H_{t2} + H_{t3} + H_{t4})/2$$

$$\theta(H_t)_{B_{2u}} = (H_{t1} - H_{t2} - H_{t3} + H_{t4})/2$$

$$\theta(H_t)_{B_{1u}} = (H_{t1} + H_{t2} - H_{t3} - H_{t4})/2$$

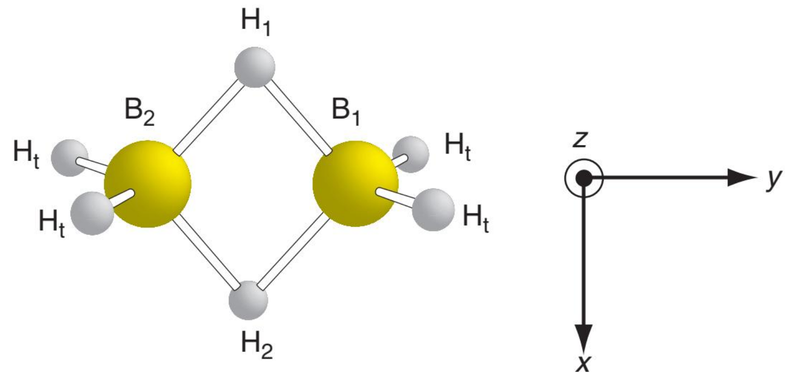
$$\theta(H_t)_{B_{3g}} = (H_{t1} - H_{t2} + H_{t3} - H_{t4})/2$$

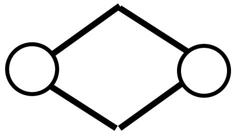
D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

Normal bonding analysis for B_2H_6

- Determine the IRs and SOs by inspection:

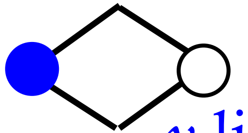
$(B_1,2s,\ B_2,2s)$ $(2,0,2,0,0,2,0,2)$ $A_g \oplus B_{2u}$





A_g

$$\theta(B2s)_{A_g} = (s_1 + s_2)/\sqrt{2}$$



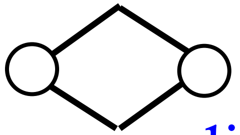
B_{2u}

y-like

$$\theta(B2s)_{B_{2u}} = (s_1 - s_2)/\sqrt{2}$$

$(B_1,2p_z,\ B_2,2p_z)$ $(2,0,-2,0,0,-2,0,2)$ $B_{3g} \oplus B_{1u}$

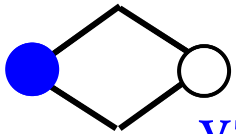
D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2; y^2; z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	



B_{1u}

z-like

$$\theta(B2pz)_{B_{1u}} = (p_{z1} + p_{z2})/\sqrt{2}$$



B_{3g}

yz-like

$$\theta(B2pz)_{B_{3g}} = (p_{z1} - p_{z2})/\sqrt{2}$$

Normal bonding analysis for B_2H_6

- Determine the IRs and SOs by inspection:

$(B_1,2p_x, B_2,2p_x)$ $(2,0,-2,0,0,2,0,-2)$ $B_{1g} \oplus B_{3u}$

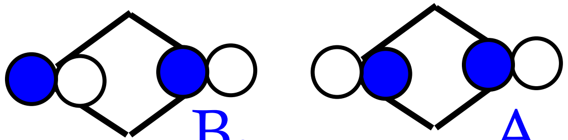
B_{3u} *x*-like *xy*-like B_{1g}

$$\theta(B2px)_{B_{3u}} = (p_{x1} + p_{x2})/\sqrt{2}$$

$$\theta(B2px)_{B_{1g}} = (p_{x1} - p_{x2})/\sqrt{2}$$

$(B_1,2p_y, B_2,2p_y)$: $(2,0,2,0,0,2,0,2)$ $A_g \oplus B_{2u}$

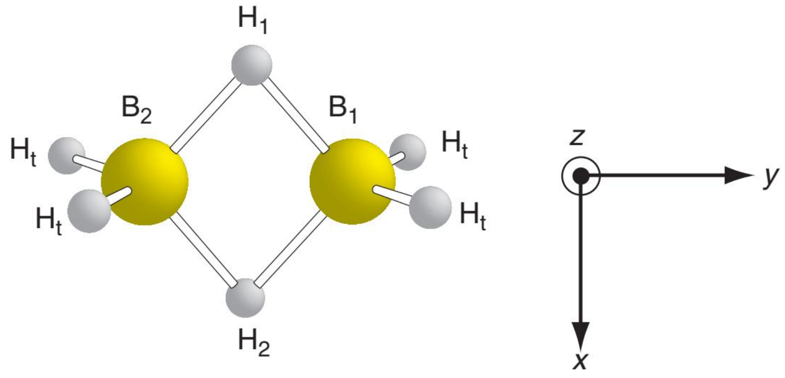
y-like



B_{2u} A_g

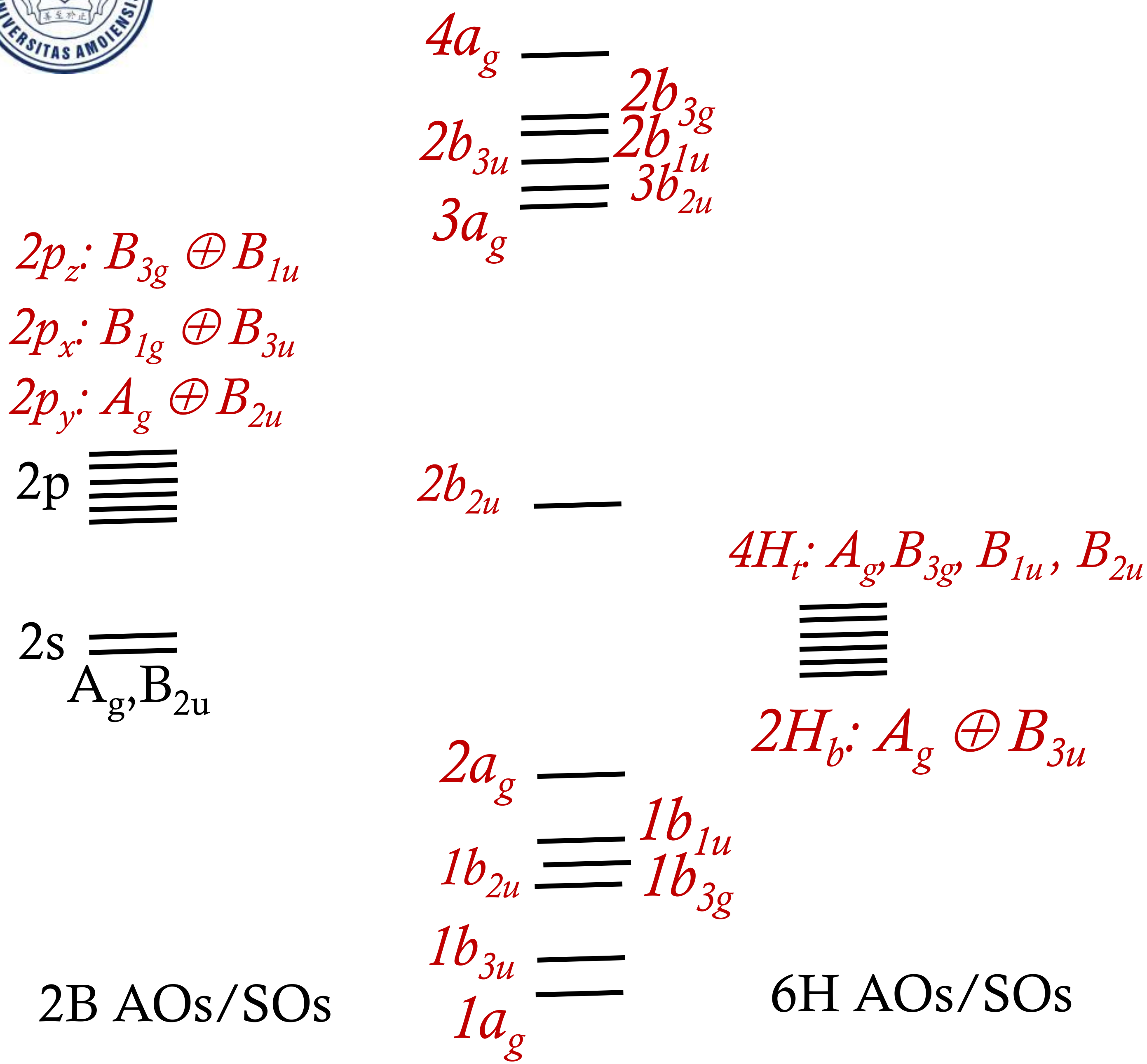
$$\theta(B2py)_{B_{2u}} = (p_{y1} + p_{y2})/\sqrt{2}$$

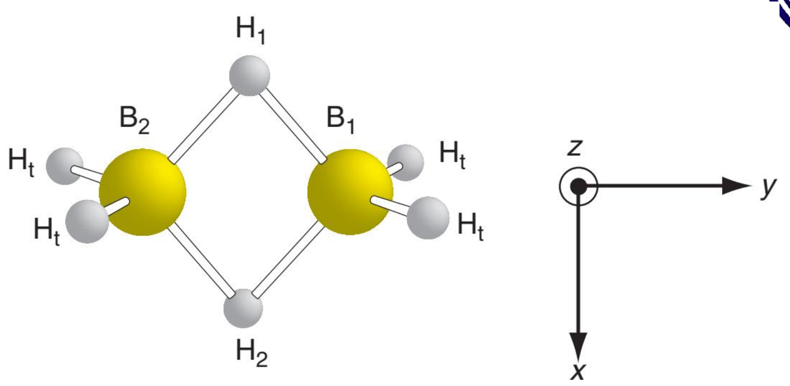
$$\theta(B2py)_{A_g} = (p_{y1} - p_{y2})/\sqrt{2}$$



D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2;y^2;z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

MO diagram of B_2H_6





- Without QM computations, we have problem to determine exactly the relatively energies for most of the bonding MOs.