Reviewing—direct products

- 如果两个函数分别按不可约表示 $\Gamma^{(i)}$ 和 $\Gamma^{(j)}$变换, 那么他们的积当按这两个不可约表示的直积$\Gamma^{(i)}\otimes \Gamma^{(j)}$变换.
- 两个不可约表示直积中各对称操作的特征标就是两个不可约表示相应特征标的乘积每个对称操作的特征标的乘积: $(a, b, c, \ldots) \otimes (p, q, r, \ldots) = (a\times p, b\times q, c\times r, \ldots)$
- 全对称不可约表示$\Gamma^{tot.\, sym.}$中所有操作的特征标均为 +1。
- 任一不可约表示$\Gamma^{(i)}$与全对称不可约表示的直积就是该表示本身: $\Gamma^{(i)}\otimes \Gamma^{tot.\, sym.} = \Gamma^{(i)}$.
- 任意一维不可约表示和它自身的直积就是全对称不可约表示: $\Gamma^{(i)}\otimes \Gamma^{(i)} = \Gamma^{tot.\, sym.}$
- 任意高维不可约表示和它自身的直积$\Gamma^{(i)}\otimes\Gamma^{(i)}$必然包含全对称不可约表示$\Gamma^{tot.\, sym.}$.
- *标量(数字)* (*numbers*) 按全对称不可约表示变换.

Reviewing—vanishing integrals

1. 若函数ψ不按全对称不可约表示变换，则其积分$I = \int \psi d\tau$ 必为**零**。

2. 若两个原子的AO波函数ψ_i和 ψ_j不依同一不可约表示变换，则其重叠积分$S_{ij} = \int \psi_i^* \psi_j d\tau$ 必为零。换句话说，对称性相同(匹配)的原子轨道间才可以重叠。

3. 矩阵元$Q_{ij} = \int \psi_i^* \hat{Q} \psi_j d\tau$ 的值必为零若对应的直积 $\Gamma^{(i)} \otimes \Gamma^{(Q)} \otimes \Gamma^{(j)}$不含全对称不可约表示。

4. 对称性相同的轨道才可以形成分子轨道。

Part III Symmetry and Bonding

Chapter 5 Molecular Orbitals（分子轨道）

Prof. Dr. Xin Lu（吕鑫）
Email: xinlu@xmu.edu.cn
http://pcossgroup.xmu.edu.cn/old/users/xlu/group/courses/theochem/

5. Molecular orbitals

- Now that we have developed the necessary ***Group Theory*** tools, we can use them to draw up (qualitative) **MO diagrams**. （注：这是正则分子轨道（canonical molecular orbital）图像，而非大一时学过的定域分子轨道图像！）

- ***Symmetry arguments*** greatly simplify this process and help us not only to ***work out which interactions are important*** but also make it possible to ***sketch the form*** of the MOs in a straightforward way.

- In addition, we will be able to say something about the ***resulting electronic properties*** of the molecule and discuss why molecules have a preference for one shape over another.

5. Molecular orbitals

The procedure we will adopt for drawing up MO diagrams：

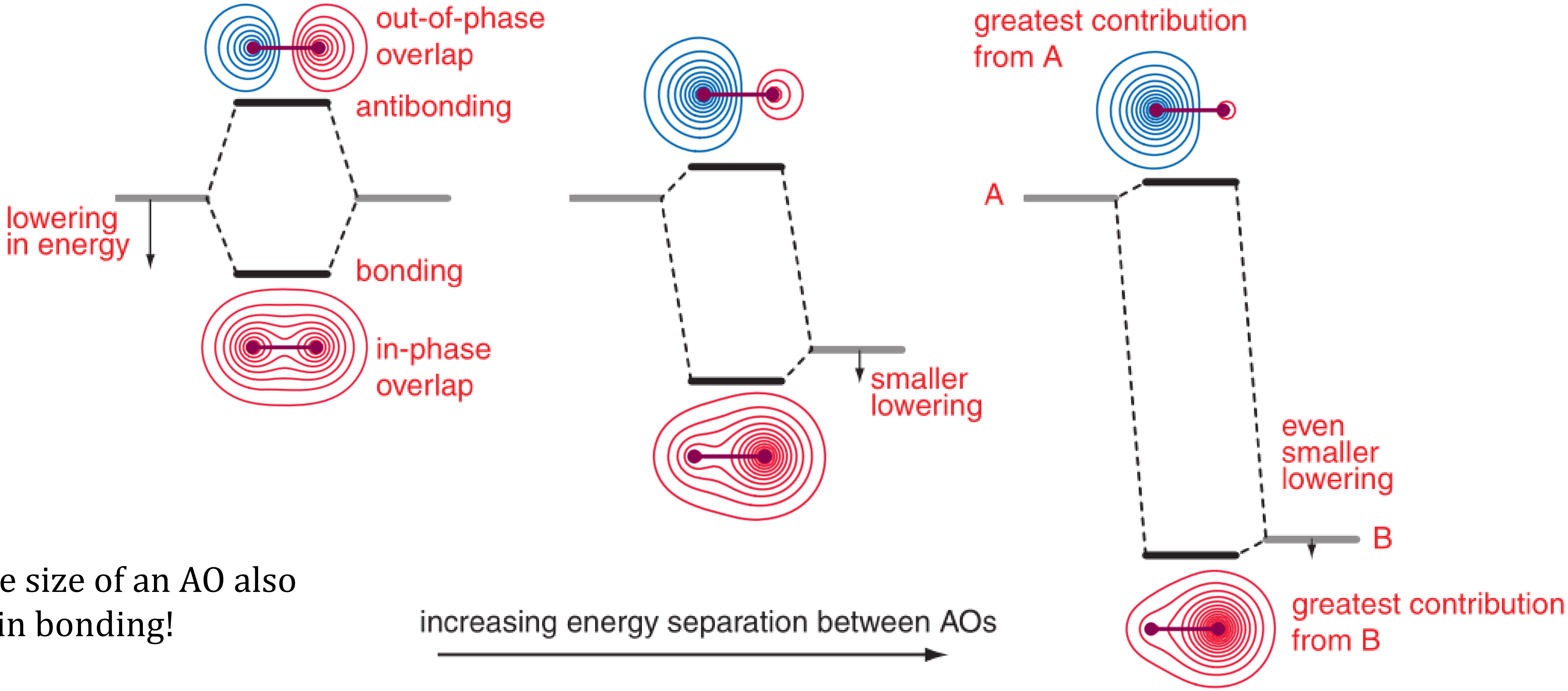
1. **Identifying the point group** of the molecule to be concerned.
2. **Identifying the AOs** (valence orbitals) to be involved in bonding.
3. **Classifying the AOs according to symmetry** and, if necessary, combining those symmetrically equivalent AOs to form **symmetry orbitals**, ***SO***s.
4. Allowing **orbitals** of the same symmetry to overlap (*both in phase and out of phase*), and hence constructing **the MO diagram**.

(In the Chapter of "***Representations***", we have learnt some concepts needed in step 3.)

Before we embark on the details of this process we will quickly review the key points about how the energies and form of the MOs are related to the constituent AOs.

5.1 Basic observations about MOs

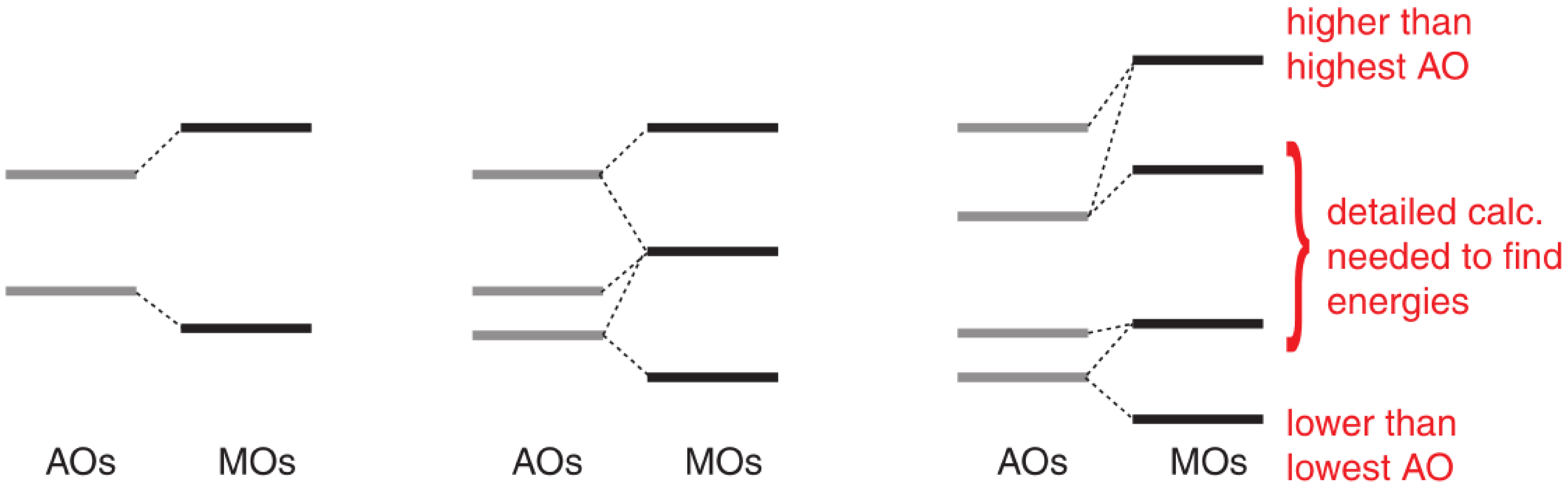
- When two AOs ***of the same symmetry*** interact, a ***bonding*** MO is formed which is ***lower*** in energy than the lowest energy AO and an ***antibonding*** MO is formed which is ***higher*** in energy than the highest energy AO.



Note: the size of an AO also matters in bonding!

5.1 Basic observations about MOs

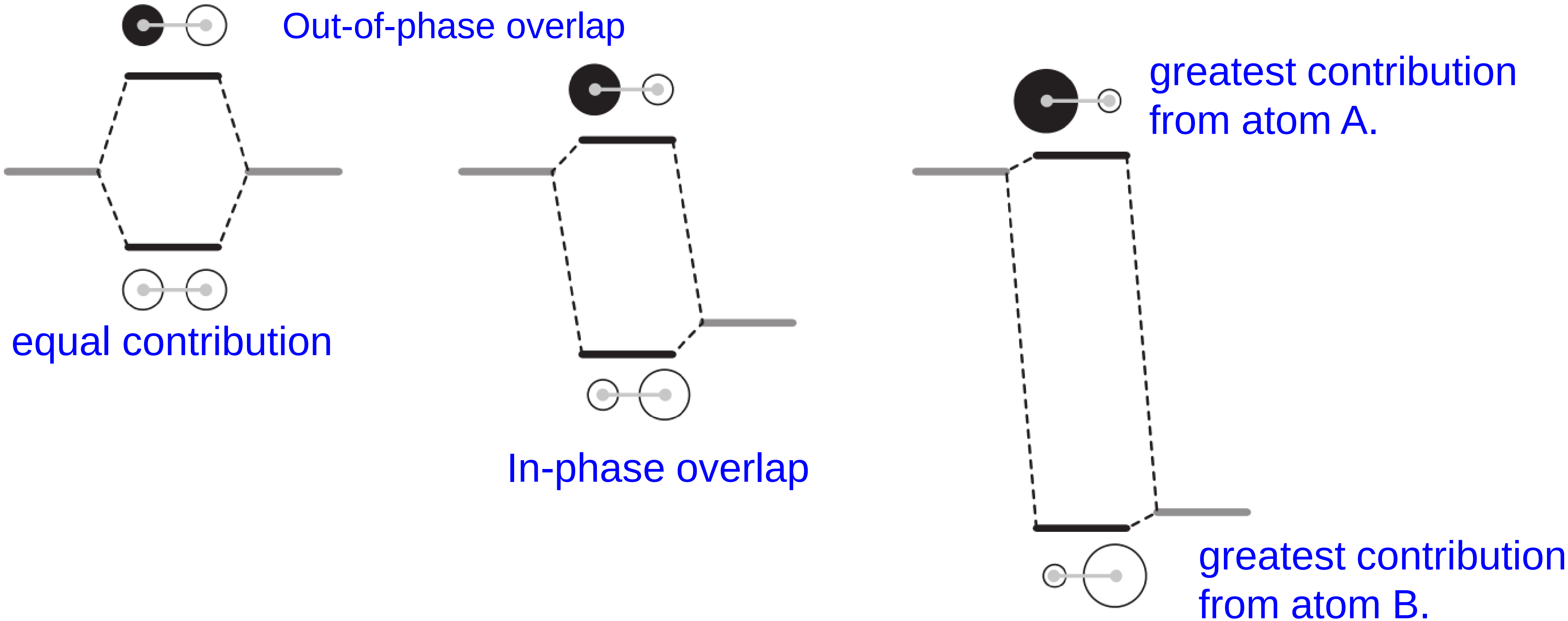
- When several AOs interact to form MOs, the number of the MOs is the same as the number of the AOs.



- In this more complex case it remains true that a particular MO will have the greatest contribution from the AOs which are ***closest to it in energy***.

Representing MOs

- To draw MOs, we need to show the result of the *in-phase* or *out-of-phase* **overlap**, as well as the *relative contributions* made by the different AOs.



(white ~ positive, black ~ negative)

5.2 MO diagram for water

- Example: H_2O (point group C_{2v})
- The O *1s* AO is too contracted and too low in energy, transforming as A_1.

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz
(s_a, s_b)	2	0	2	0	$\Gamma = A_1 \oplus B_1$		

- **O:** $2s$ (spherical) as A_1;

  $2p_z$ (z-like) as A_1.

  $2p_x$ (x-like) as B_1

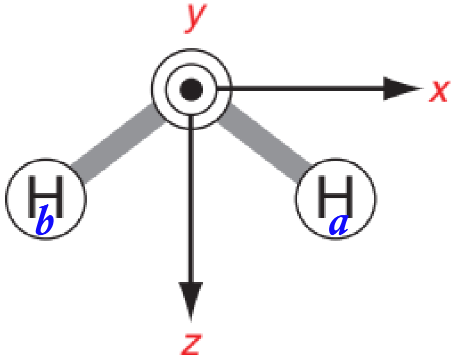
  $2p_y$ (y-like) as B_2

By inspection! (For a AO without equivalent AOs)

- 2H: (s_a, s_b) $A_1 \oplus B_1$ *(Already considered in chapter 2)*

  $\theta_1 = (s_a + s_b)$ as A_1

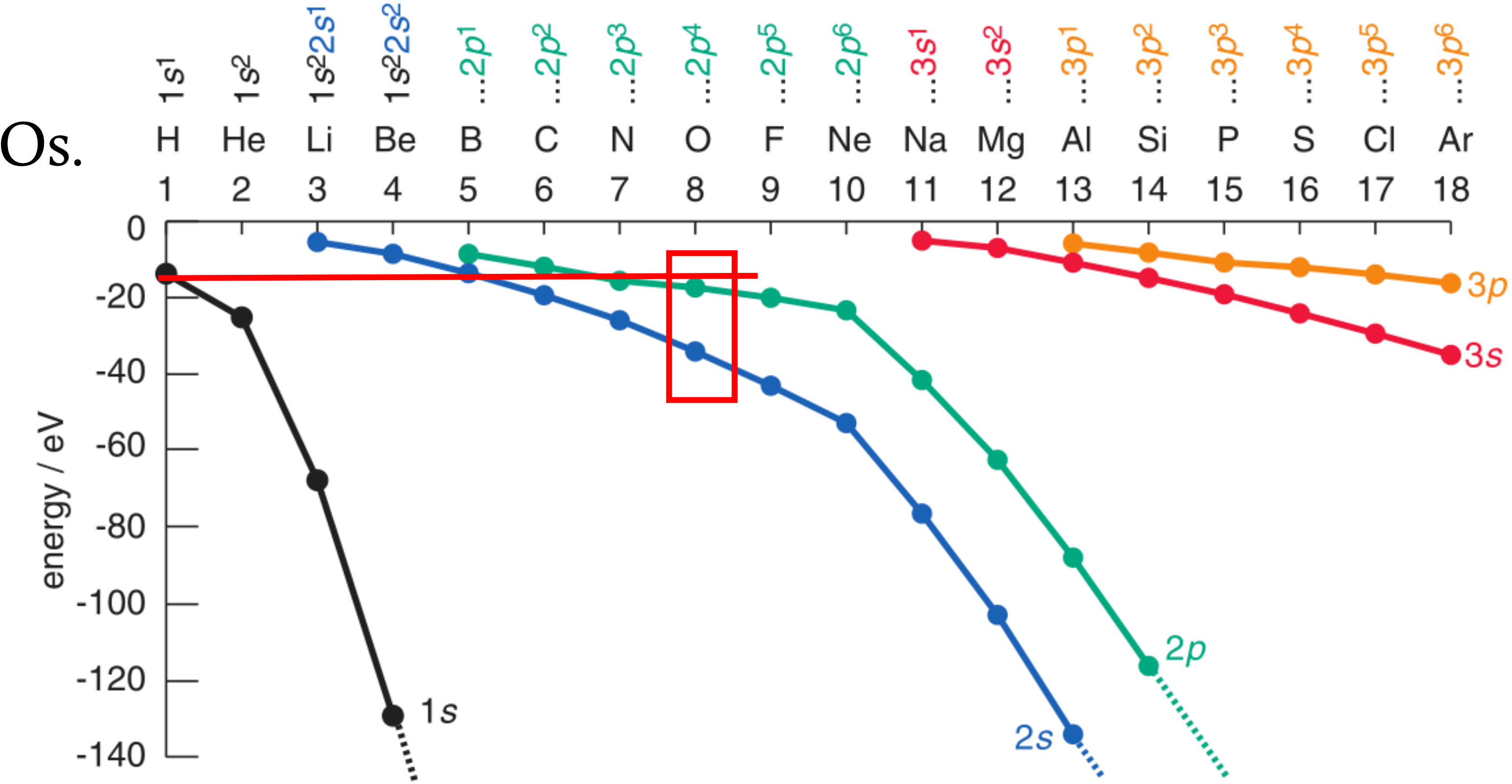
  $\theta_2 = (s_a - s_b)$ (x-like) as B_1



5.2 MO diagram for water

- A rough sense of the relative energies of the AOs involved is needed *to draw up the MO diagram*.

- O ***2s*** AO < ***2p*** AO,
- H 1s AOs ~ the oxygen ***2p*** AOs.



5.2 MO diagram for water

- Now put the AOs(SOs) ***in the order of energy***.
- ***Now use the key principle***: only AOs(SO)s with the *same symmetry* will interact to form MOs.

1) O2p$_x$ (B_1) + the B_1 SO(θ_2) of H1s.

$\psi(B_1) = c_1 2p_x + c_2\,\theta_2$ (c_1, c_2 ~coefficients)

→ **Two** MOs of B_1 IR! (in-phase & out-of-phase)

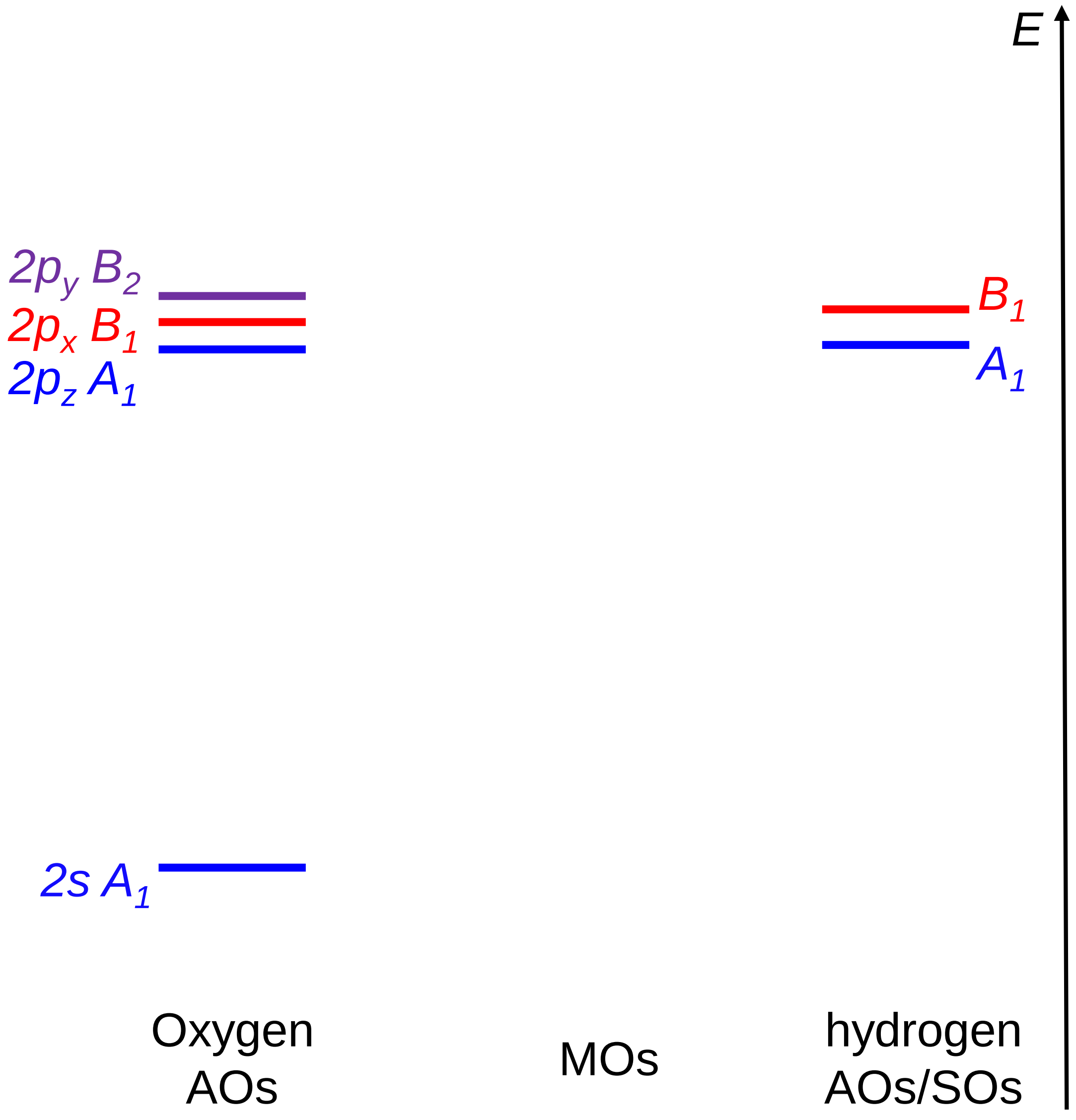
2) O2s, 2p$_z$ (A_1) + the A_1 SO.

$\psi(A_1) = d_1 2s + d_2 p_z + d_3\theta_1$ (d_1~d_3 ~coefficients)

→ **Three** MOs of A_1 IR!

3) O2p$_y$ (B_2) non-bonding

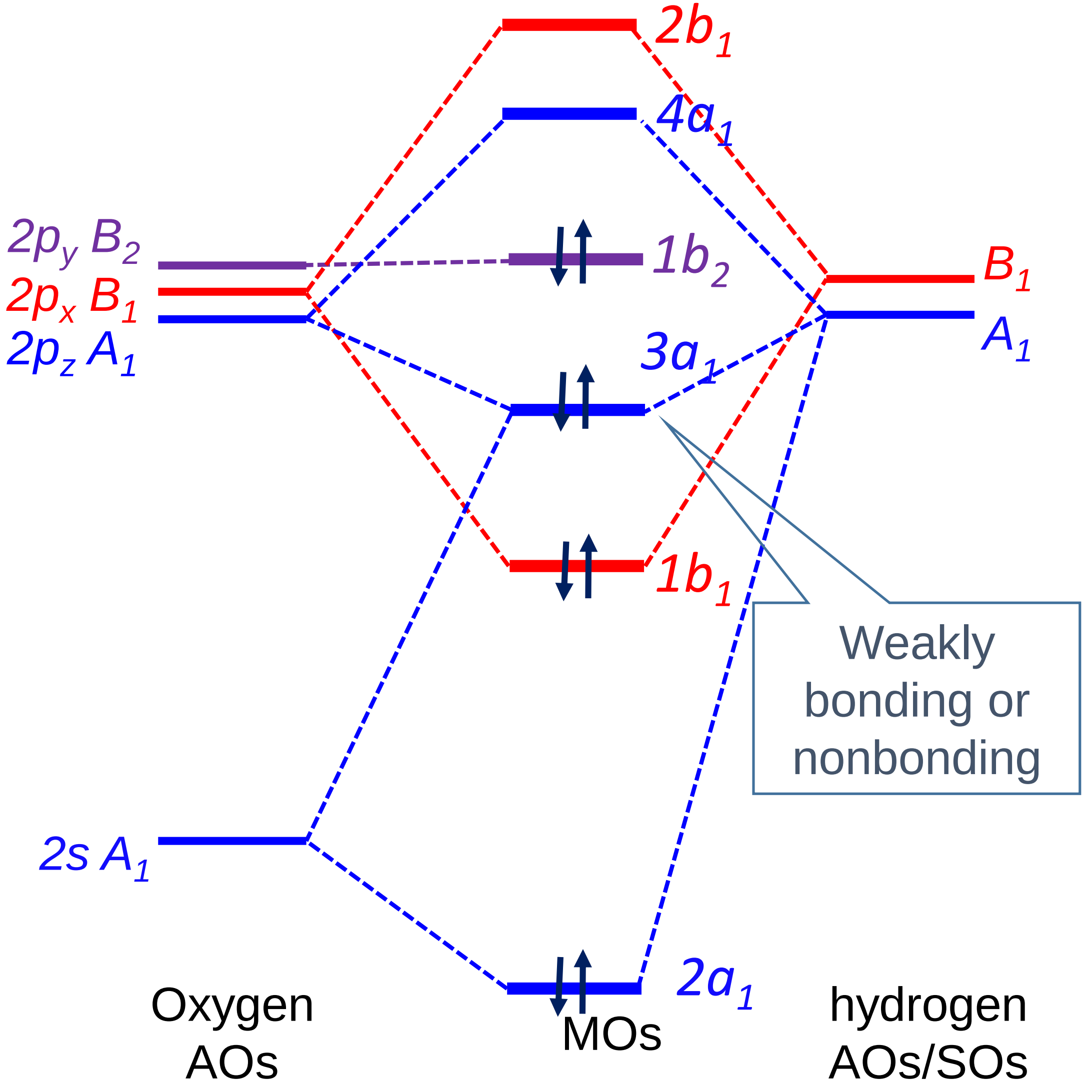
→ A total of **six** VMOs (valence molecular orbitals)



5.2 MO diagram for water

- The inner **O1s** gives the lowest-energy, non-bonding ***MO*** of A_1 *IR*, therefore labelled $1a_1$.
- The **O2**p_y gives a non-bonding ***MO*** of B_2 *IR*, labelled $1b_2$.
- The **O2**p_x interacts with the B_1 ***SO*** to form a bonding ***MO*** $1b_1$ and an anti-bonding MO $2b_1$.
- The **O2**p_z and $2s$ interact with the A_1 ***SO*** to give *three* ***MO***s, labelled $2a_1$, $3a_1$ and $4a_1$.
- Computer calculation is needed to determine the position of $3a_1$ in relation to $1b_1$ and $1b_2$.
- *8 VEs* → *The lowest four VMOs are occupied.*
- *Electronic configuration:* $2a_1^2 1b_1^2 3a_1^2 1b_2^2$

Valence molecular-orbital (VMO) diagram of H_2O (C_{2v})



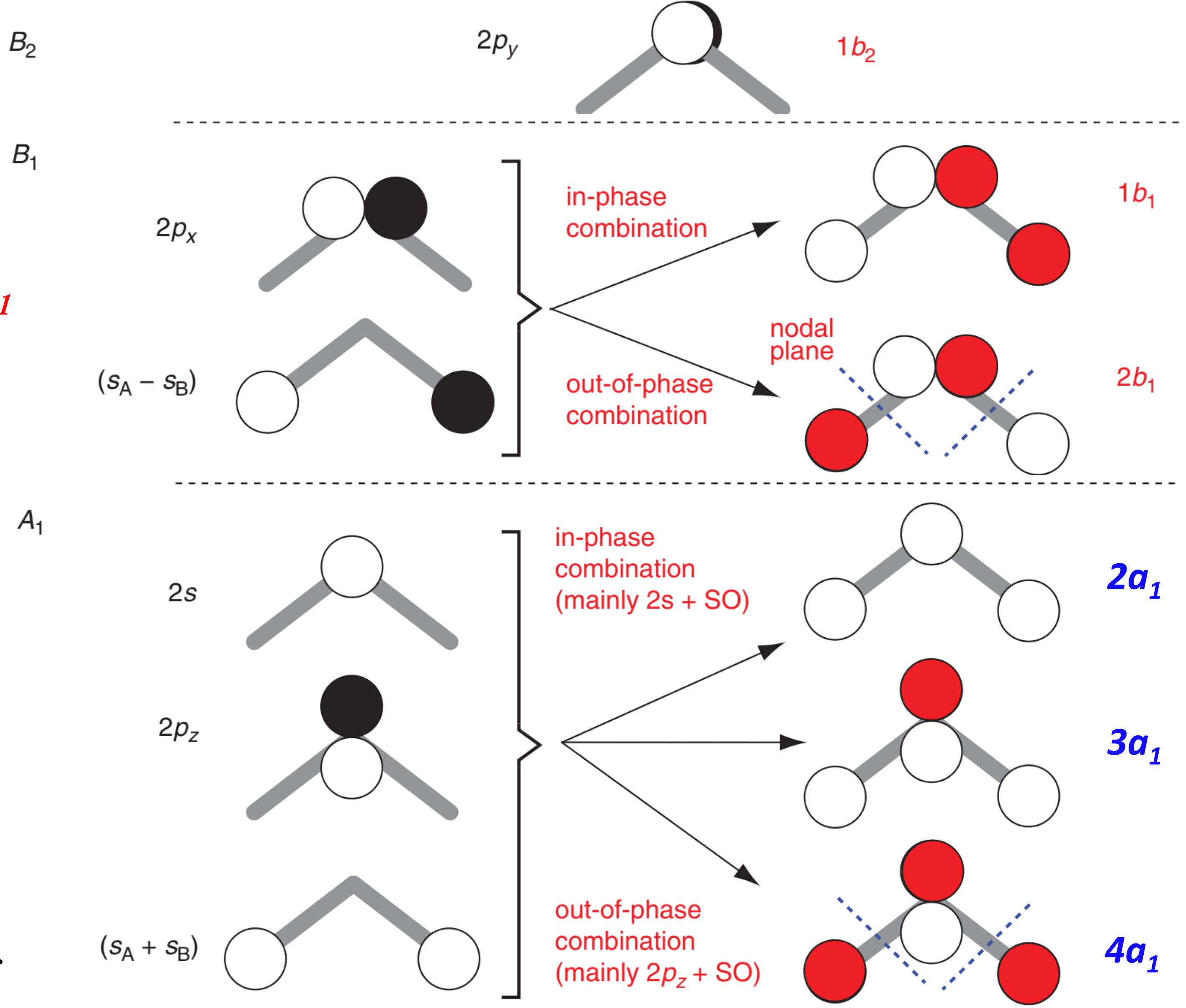
Form of the MOs

Construction of the MOs for H_2O.

- We can also make some educated guesses about *the form of the MOs*.
- The $1b_2$ MO is solely the O$2p_y$ AO.
- The interaction of the O $2p_x$ and θ_2 SO of B_1 *IR* leads to the formation of a bonding MO, $1b_1$, and an anti-bonding MO, $2b_1$.
- The interaction of the AOs and SO with symmetry A_1 gives *three* MOs:

➢ The A_1 MO, $2a_1$, arises from in-phase combination of the O2s, O$2p_z$ (minor) and the θ_1 SO.

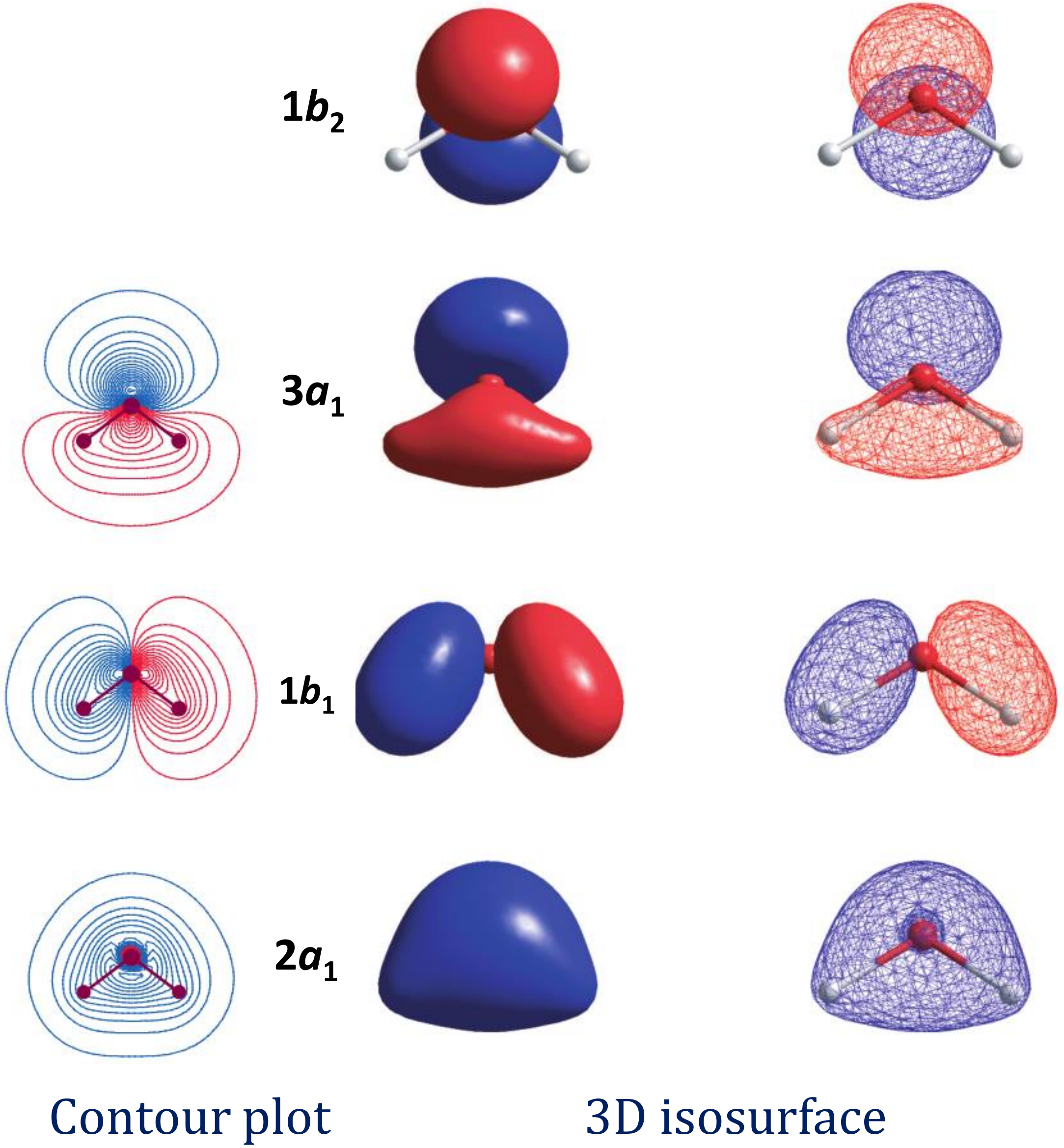
➢ The $3a_1$ MO arises from *out-of-phase* combination of O2s (minor) and *in-phase* combination of O$2p_z$ (major) with the θ_1 SO.



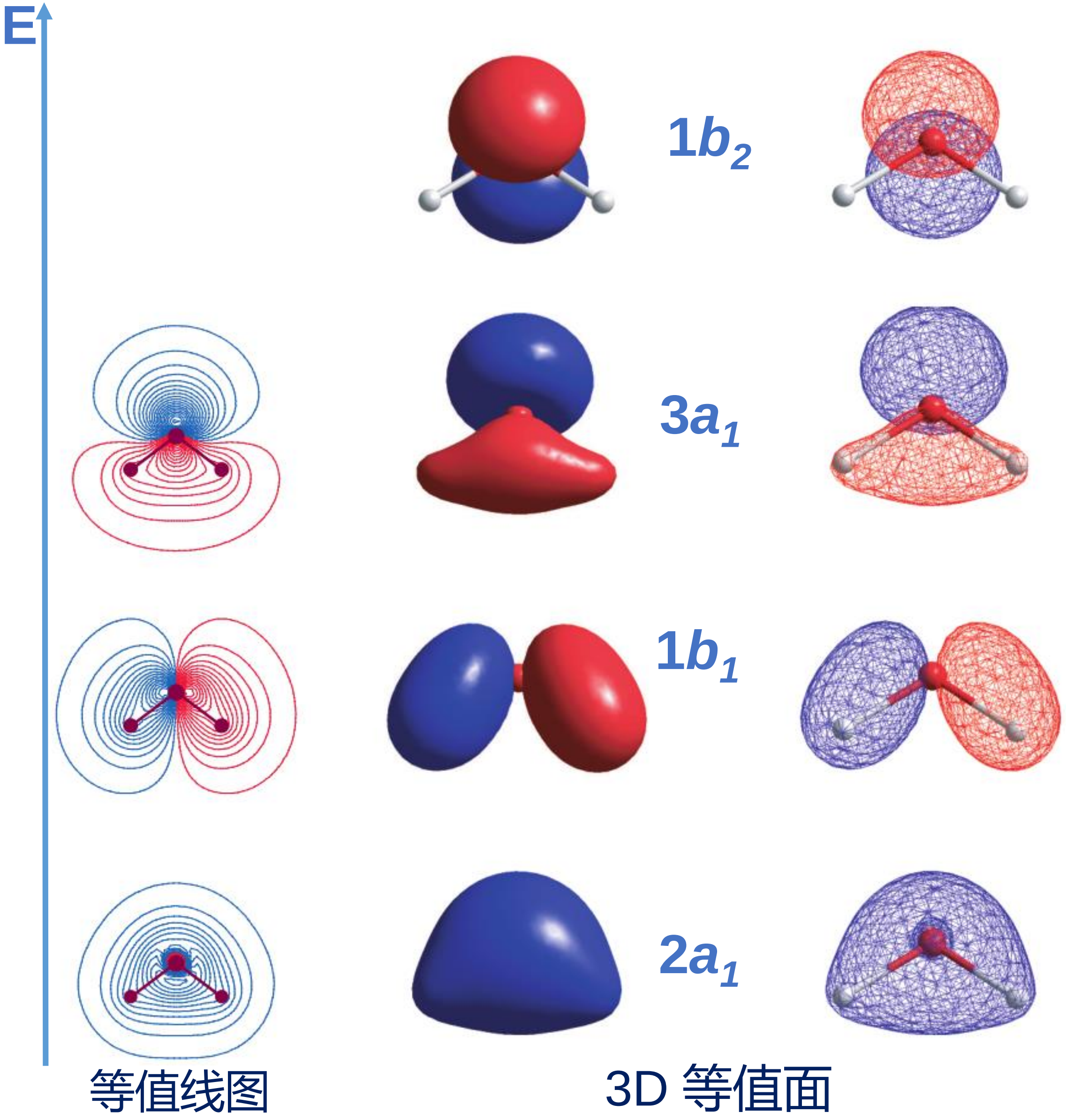
Form of the MOs

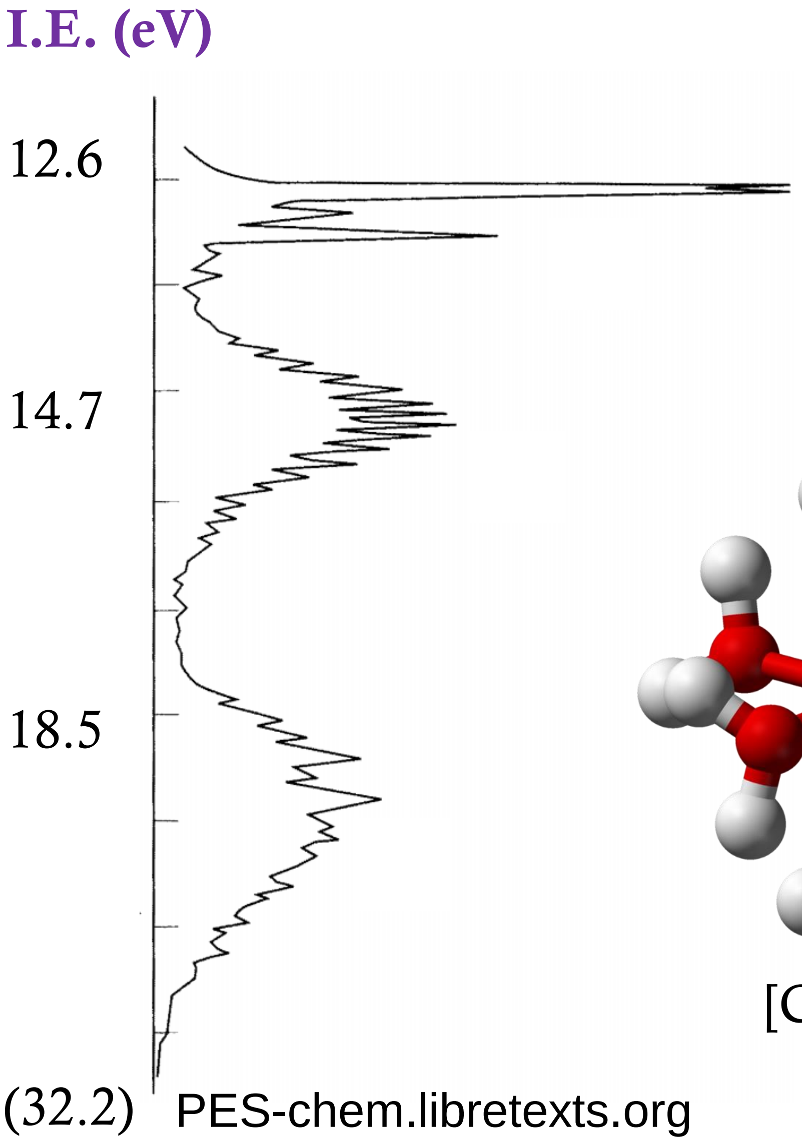
- This picture shows plots of the occupied MOs of water based on a computer calculation using the ***Hyperchem program***.
- The ***$2a_1$***, ***$1b_1$*** and ***$1b_2$*** MOs do indeed match up with our expectations based on the qualitative arguments given above.
- The ***$3a_1$*** MO is weakly bonding, as evidenced by the small amount of electron density between the O and H atoms.

Q: Which MO of H_2O will be used when coordinating to a metal center?

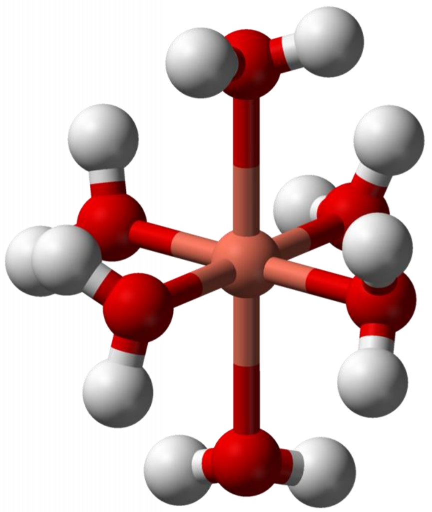


H_2O的占据分子轨道 & PES





PES-chem.libretexts.org



$[Cu(H_2O)_6]^{2+}$

5.3 Symmetry orbitals

- A ***symmetry orbital*** is a linear combination of other orbitals (usually AOs) which are chosen in such a way that ***the symmetry orbital transforms as a single irreducible representation***.

In some texts these linear combinations are called ***symmetry adapted linear combinations, SALCs***.

- We will describe two approaches to the construction of **SO**s:

(1) by making use of the additional information presented in character tables;

(2) by use of the ***projection formula***.

In practice, the first one is by far the easiest.

5.3.1 SOs in BH_3

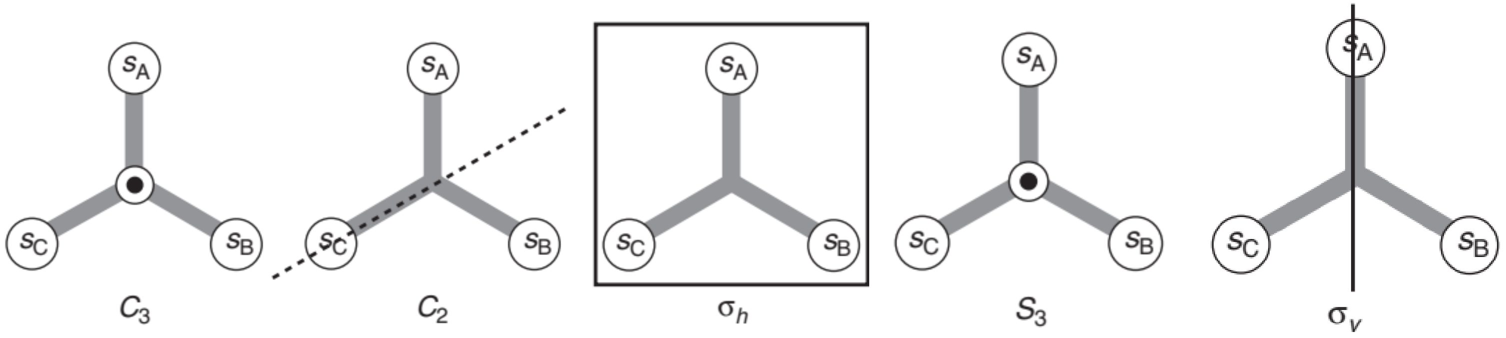
- Point group: D_{3h}

- First consider a basis consisting of ***three H 1s*** AOs and '***count***' the characters.

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	$\boxed{(x, y)}$		$(x^2-y^2, 2xy)$
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	**3**	**0**	**1**	**3**	**0**	**1**	**$= A_1' \oplus E'$**		

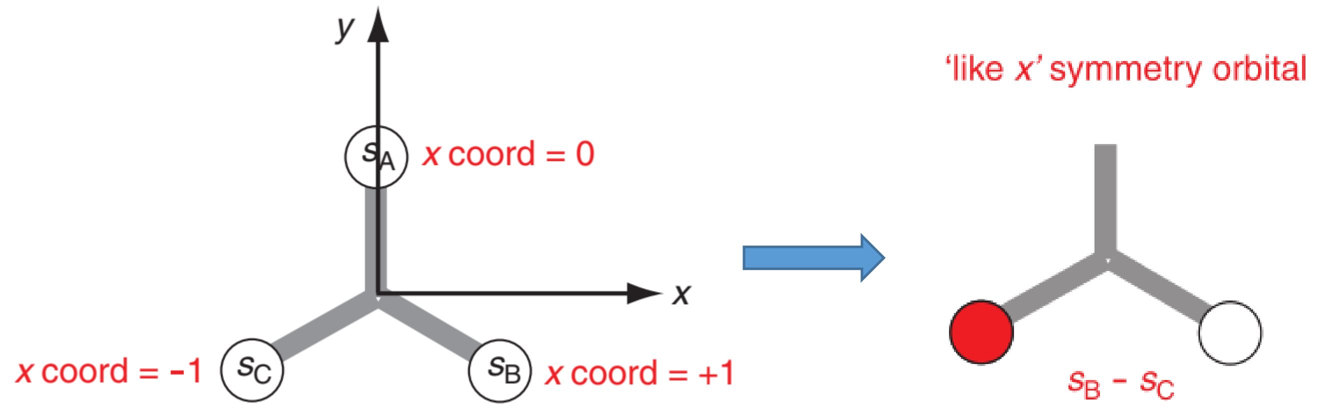
- Obviously, the combination of the hydrogen ***1s*** AOs which transforms as the totally symmetric ***IR*** A_1' is $(s_A + s_B + s_C)$.

- The remaining two SOs transform as E', similar to the basis (x,y).



5.3.1 SOs in BH$_3$

- For the SO that transforms like the function ‘***x***’,



$SO_1 = 0 \times s_A + 1 \times s_B + (-1) \times s_C$

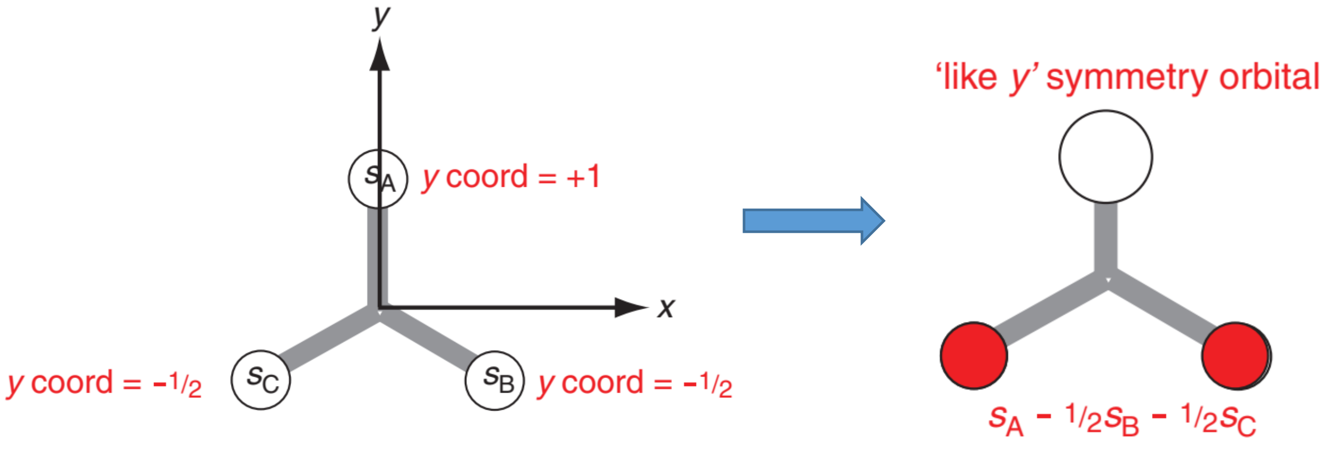
$= s_B - s_C$

$\uparrow$

Not normalized yet!

$\downarrow$

- For the SO that transforms like the function ‘***y***’,



$SO_2 = 1 \times s_A + (-1/2) \times s_B + (-1/2) \times s_C$

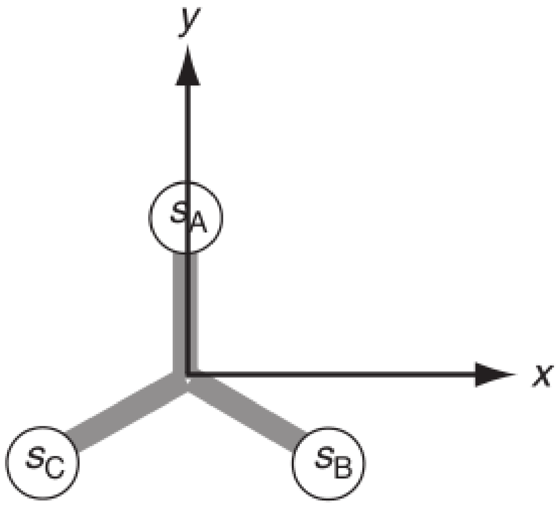
$= s_A - (s_B + s_C)/2$

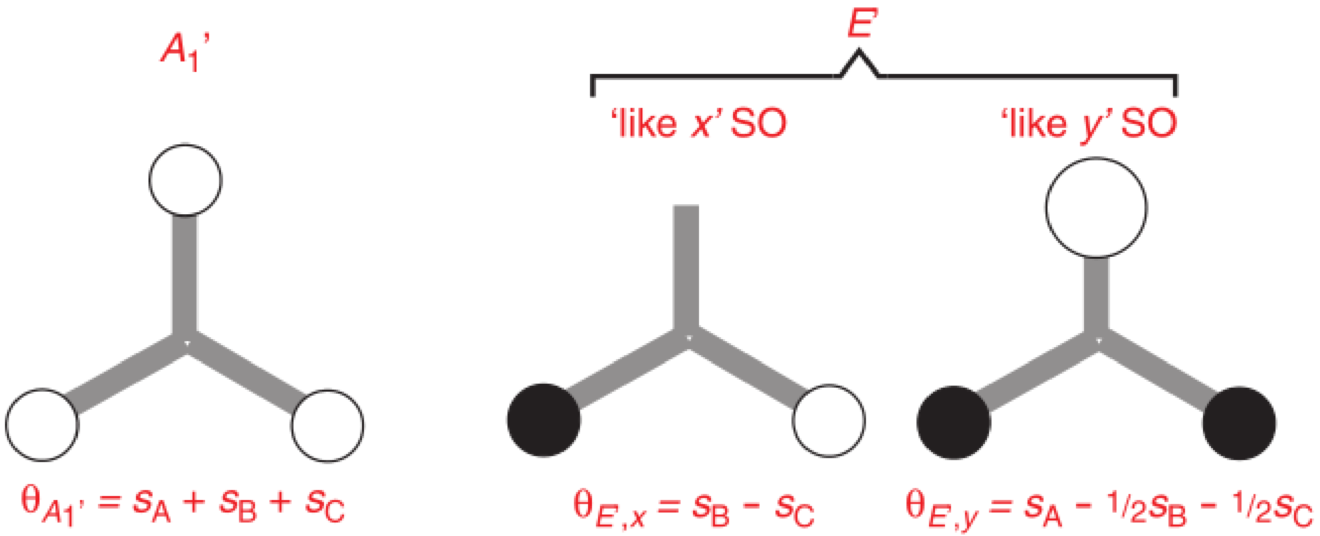
5.3.1 SOs in BH_3

- Hence the three H 1s AOs in BH_3 give the following three **SOs**,

$$\boldsymbol{\theta_{A_1'} = s_A + s_B + s_C\,; \qquad \theta_{E',x} = s_B - s_C\,, \quad \theta_{E',y} = s_A - (s_B + s_C)/2}$$

- It is important to realise that $\boldsymbol{\theta_{E',x}}$ and $\boldsymbol{\theta_{E',y}}$ together transform as the two-dimensional IR $\boldsymbol{E'}$: it is not that each alone transforms as $\boldsymbol{E'}$.





5.3.2 Normalization of symmetry orbitals

- In quantum mechanics a wavefunction ψ is normalized if $\int \psi^* \psi d\tau = 1$
- If a wavefunction ψ is not normalized, then define

$N = \sqrt{\frac{1}{\int \psi * \psi d\tau}}$ (normalization factor), and $(N\psi)$ is normalized.

- A ***symmetry orbital*** is written ***as a linear combination*** of atomic orbitals Φ_i:

$$\theta = c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3 + \cdots$$

- If the AO wavefunctions are themselves normalized, and if we assume that the AOs on different atoms ***do not overlap***, i.e., $\int\Phi_i\Phi_j d\tau = \delta_{ij}$,

then the SO can be normalized as $\theta = \frac{c_1\Phi_1 + c_2\Phi_2 + c_3\Phi_3 + \ldots}{\sqrt{c_1^2 + c_2^2 + c_3^2 + \cdots}}$

or if the SO is normalized then $c_1^2 + c_2^2 + c_3^2 + \ldots = 1.$

5.3.2 Normalization of symmetry orbitals

- For the A_1' **SO**, the coefficients give $\sqrt{1^2+1^2+1^2}=\sqrt{3}$.

  Then the normalized SO is $\theta_{A_1'}=\frac{1}{\sqrt{3}}(s_A+s_B+s_C)$

- For $\theta_{E',x}$ the coefficients give $\sqrt{0^2+(+1)^2+(-1)^2}=\sqrt{2}$

  Then the normalized SO is $\theta_{E',x}=\frac{1}{\sqrt{2}}(s_B-s_C)$

- For $\theta_{E',y}$, the normalized SO is $\theta_{E',y}=\frac{1}{\sqrt{6}}(2s_A-s_B-s_C)$

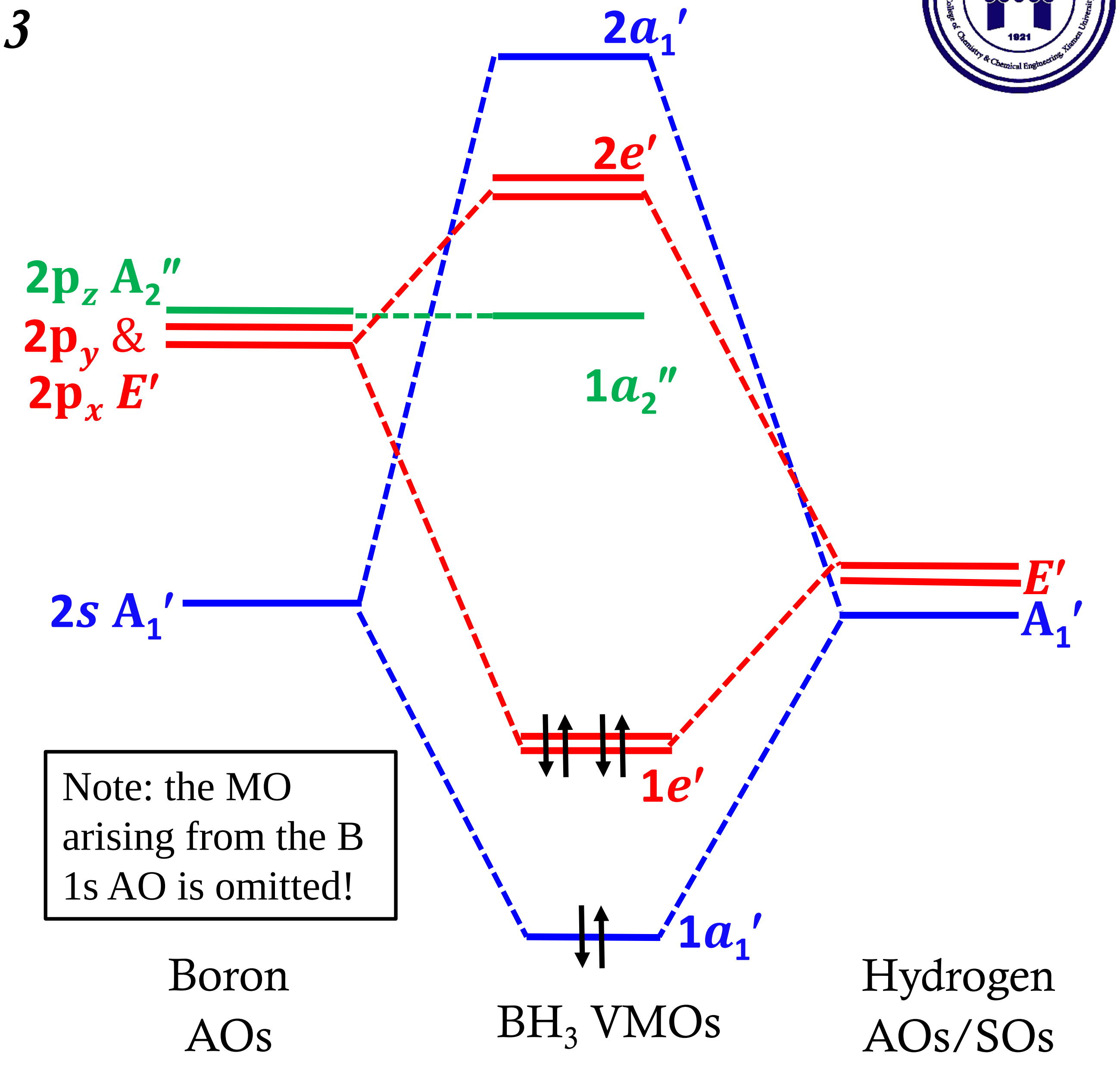
- Using a similar procedure, the two SOs (of H 1s) in H_2O can be normalized as

$$\theta_{A_1}=\frac{1}{\sqrt{2}}(s_A+s_B) \qquad \theta_{B_1}=\frac{1}{\sqrt{2}}(s_A-s_B)$$

5.3.3 MO diagram for BH_3

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	−1	1	1	−1	
E'	2	−1	0	2	−1	0	(x, y)
A_1''	1	1	1	−1	−1	−1	
A_2''	1	1	−1	−1	−1	1	z
E''	2	−1	0	−2	1	0	

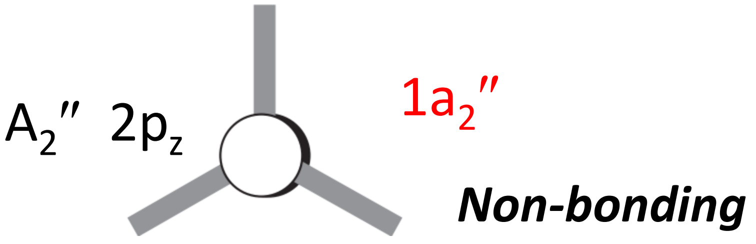
- H: (s_A,s_B,s_C) → **SOs**: A_1', E'
- B: $2s \sim A_1'$, $(2p_x,2p_y) \sim E'$ $2p_z \sim A_2''$
- The $2p_z$ gives the non-bonding MO, $1a_2''$.
- The 2s interacts with the A_1' SO, giving the MOs, $1a_1'$ (in-phase) and $2a_1'$ (out of phase).
- The $2p_x$ and $2p_y$ interact with the E' SO_x and SO_y, respectively.
- 6 VEs

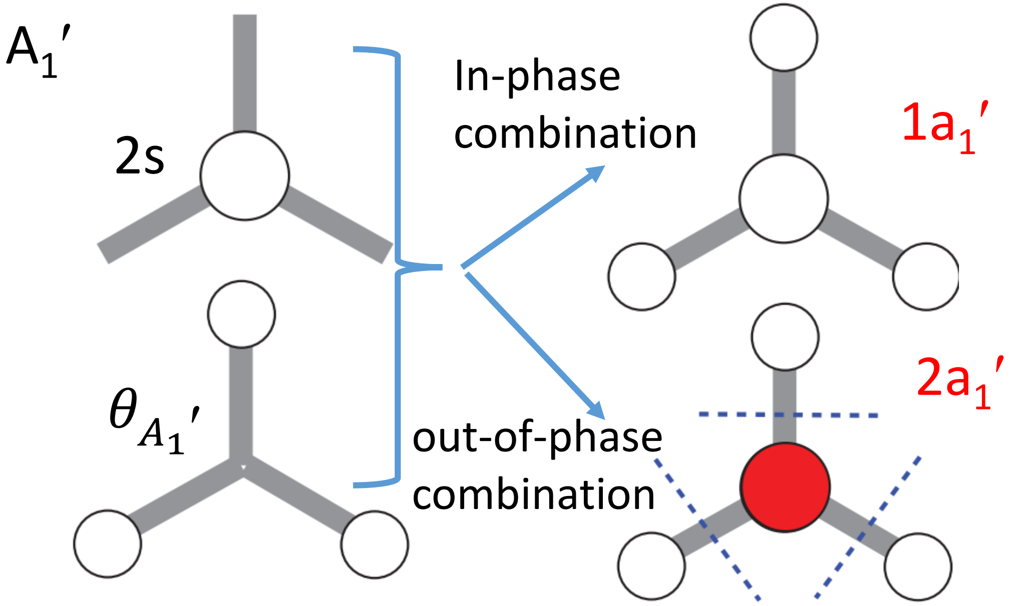


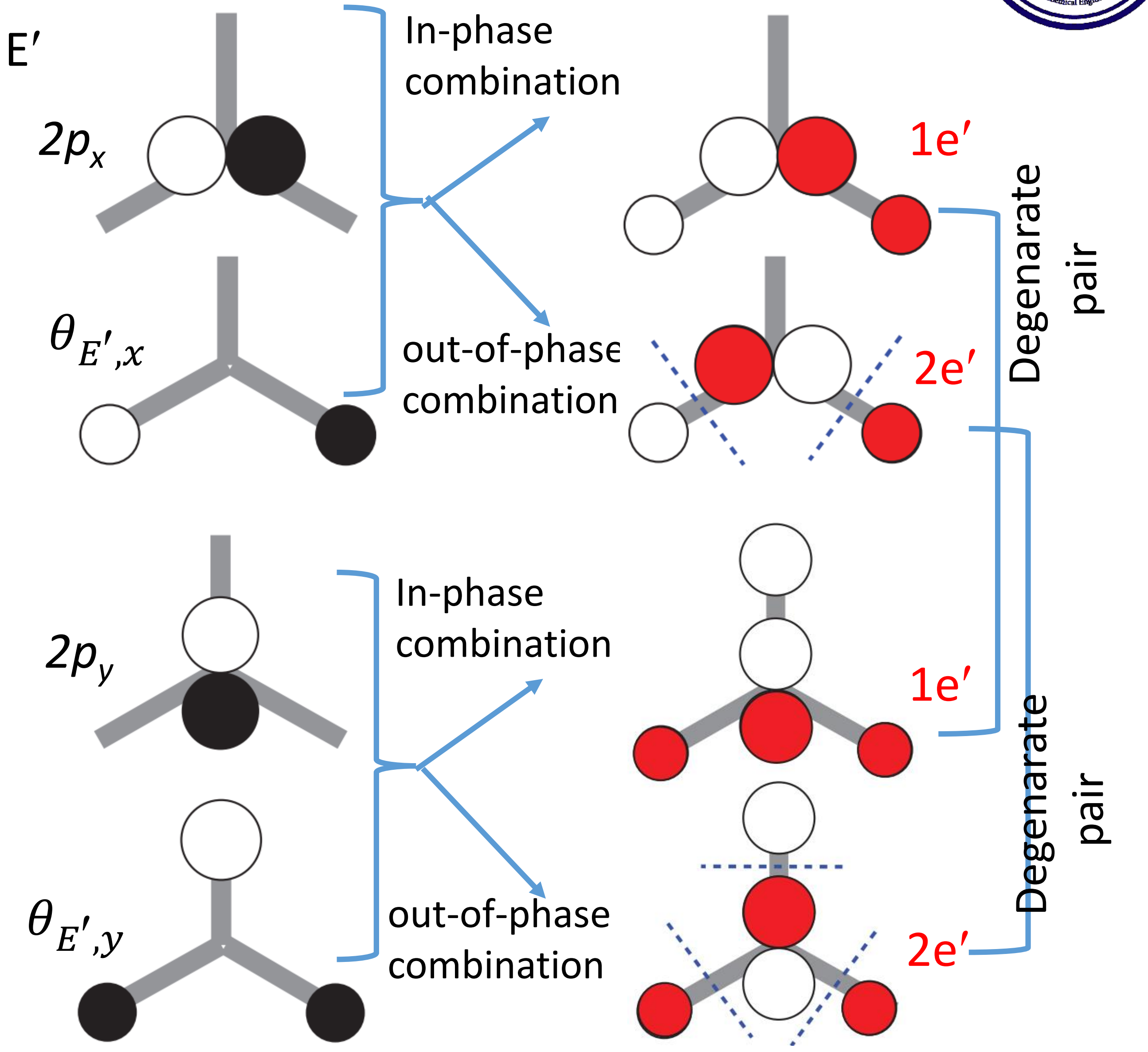
Note: the MO arising from the B 1s AO is omitted!

The form of the MOs of BH_3

Ex.15&16



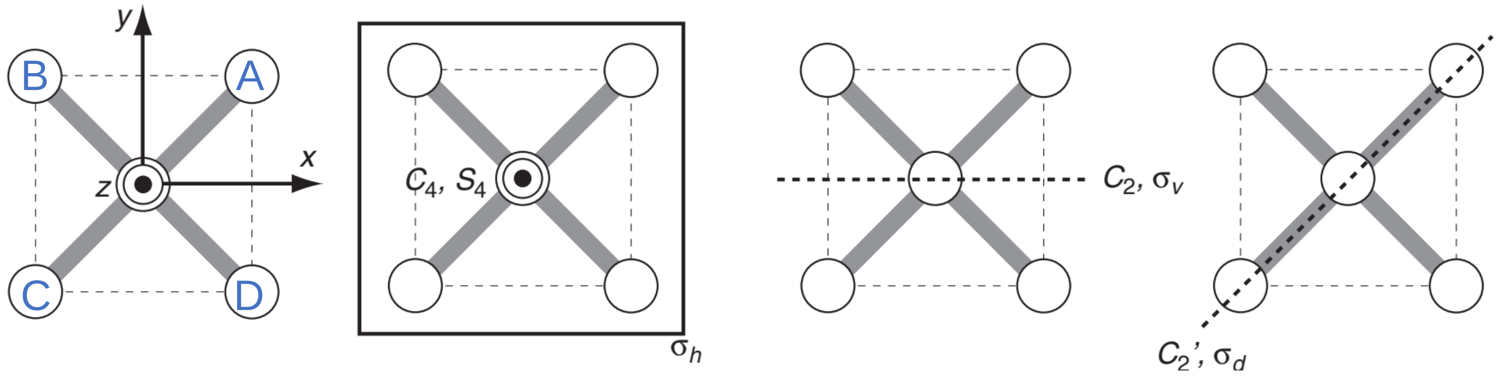




5.3.4 SOs in ‘OH_4’

- Example: a hypothetic molecule ***OH_4*** in ***a square planar geometry*** (***D_{4h}***). 4xH1s → 4 SOs

D_{4h}	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		$\boxed{xy}$
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(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	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	$\boxed{(x, y)}$	
$\Gamma^{(4H1s)}$	4	0	0	0	2	0	0	4	0	2	$A_{1g} \oplus B_{2g} \oplus E_u$	



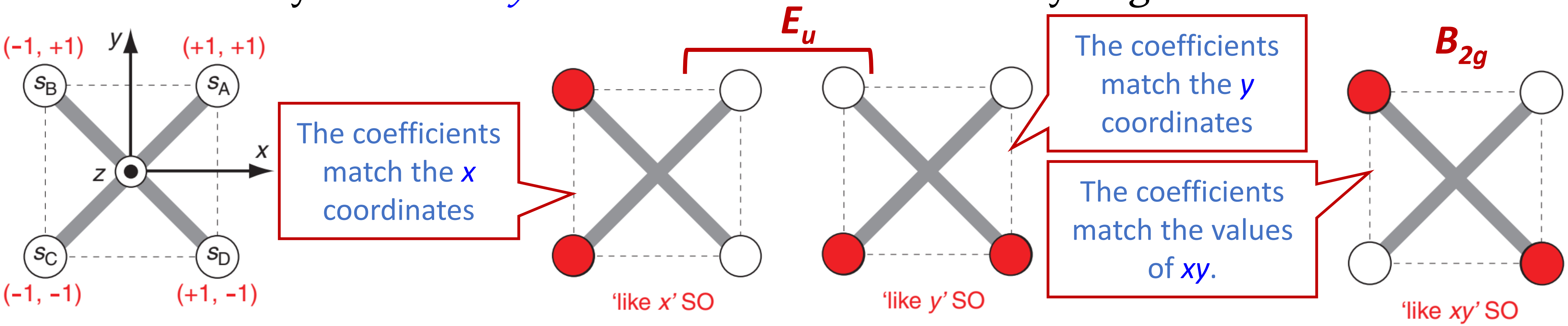
- We encounter 2-dimensional ***IR*** again.
- ***A_{1g}*** ~ totally symmetric IR.

$$\theta_{A_{1g}} = s_A + s_B + s_C + s_D$$

- ***(x,y)*** transforms like ***E_u*** and ***xy*** transforms like ***B_{2g}***.
- Now make the coefficients match the corresponding functions.

5.3.4 SOs in ‘OH$_4$’

- We first identify the *x*- and *y*-coordinates of each of the hydrogen atoms.



The coefficients match the *x* coordinates

The coefficients match the *y* coordinates

The coefficients match the values of *xy*.

- One of E_u SO ‘*like x*’ is $\theta_{E_{u.x}} = (+1)\times s_A + (-1)\times s_B + (-1)\times s_C + (+1)\times s_D$
- One of E_u SO ‘*like y*’ is $\theta_{E_{u.y}} = (+1)\times s_A + (+1)\times s_B + (-1)\times s_C + (-1)\times s_D$
- The B_{2g} SO ‘*like xy*’ is $\theta_{B_{2g}} = (+1)\times s_A + (-1)\times s_B + (+1)\times s_C + (-1)\times s_D$
- The ***normalized*** SOs are $\theta_{A_{1g}} = (s_A + s_B + s_C + s_D)/2$ $\theta_{B_{2g}} = (s_A - s_B + s_C - s_D)/2$

$\theta_{E_{u.x}} = (s_A - s_B - s_C + s_D)/2$ $\theta_{E_{u.y}} = (s_A + s_B - s_C - s_D)/2$

5.3.4 SOs in ‘OH_4’ -- MO diagram

- 4H 1s SOs： A_{1g}, B_{2g}, E_u;
- O: $2p_z$ A_{2u}

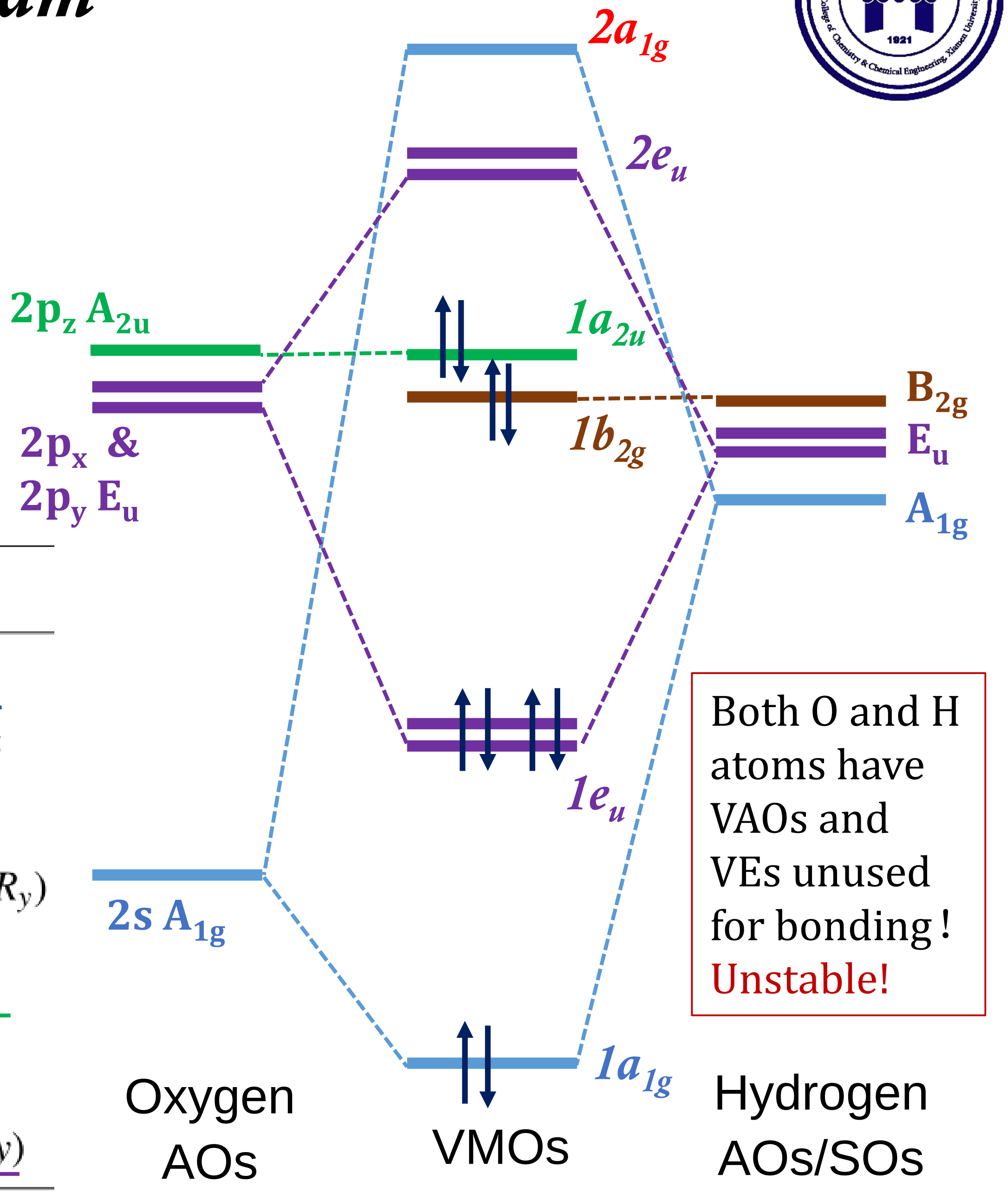
$(2p_x,2p_y)$ E_u

$2s$ A_{1g}

→ 8 VMOs
10 VEs

Q: 请画出各分子轨道组成的简图。

D_{4h}	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1	
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1	
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1	
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1	
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)



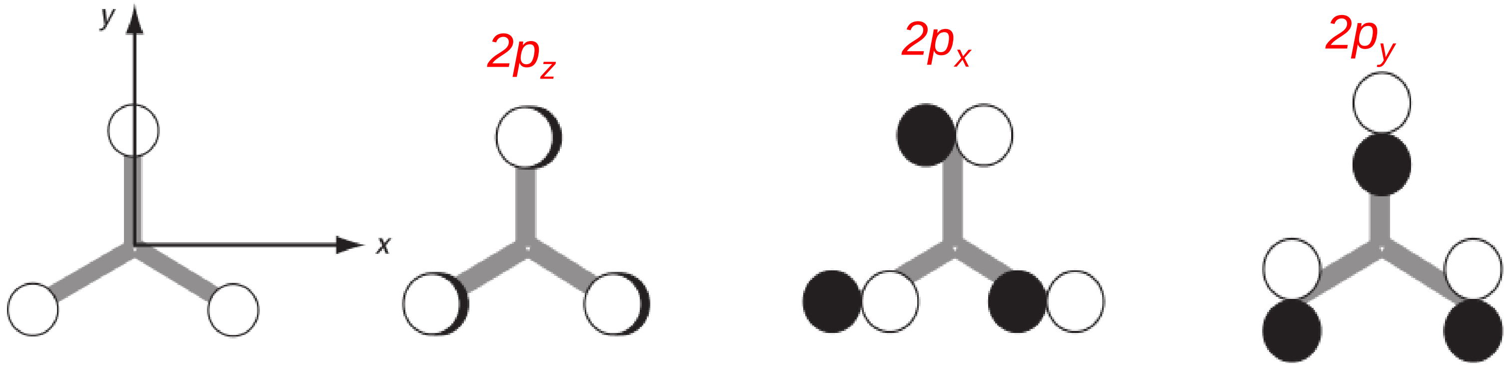
Both O and H atoms have VAOs and VEs unused for bonding !
Unstable!

5.3.5 Constructing SOs in an intelligent way

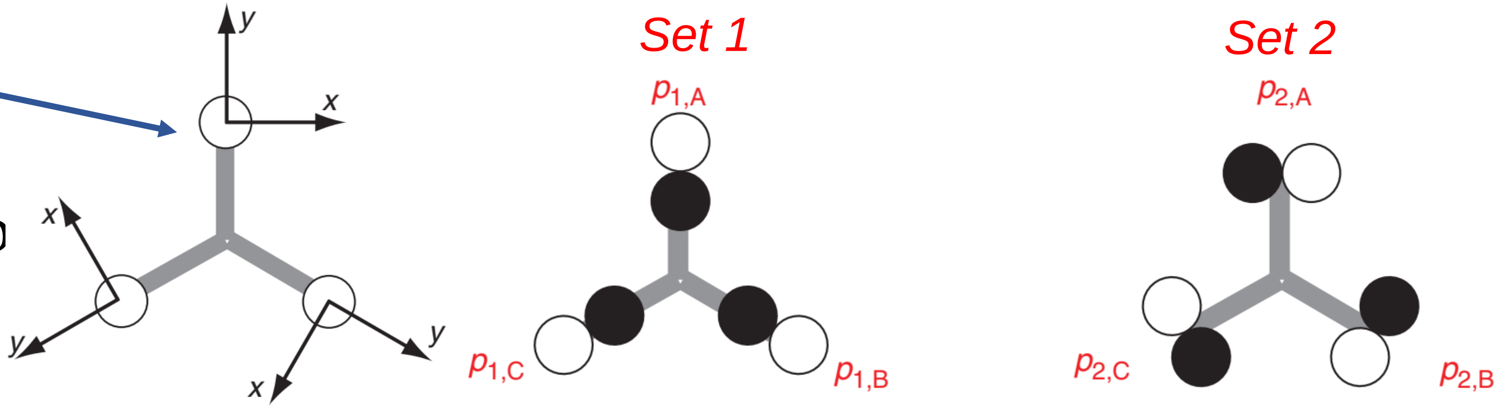
- Example: BF_3 (point group D_{3h}). F: $2s$, $2p_x$, $2p_y$, $2p_z$
- Three F $2s$ AOs → three **SO**s ($A_1' \oplus E'$); three F $2p_z$ AOs → three **SO**s. (recall Q11!)
- However, the $2p_x$ and $2p_y$ AOs are all mixed together in a rather complicated way by the operations of the group.

→Producing an annoying ?-D rep.!

How to simplify the situation?



- The situation can be simplified by using a different *local axis system*.
- Now the **SO**s for **set 1** is similar to those for the 2s AOs.

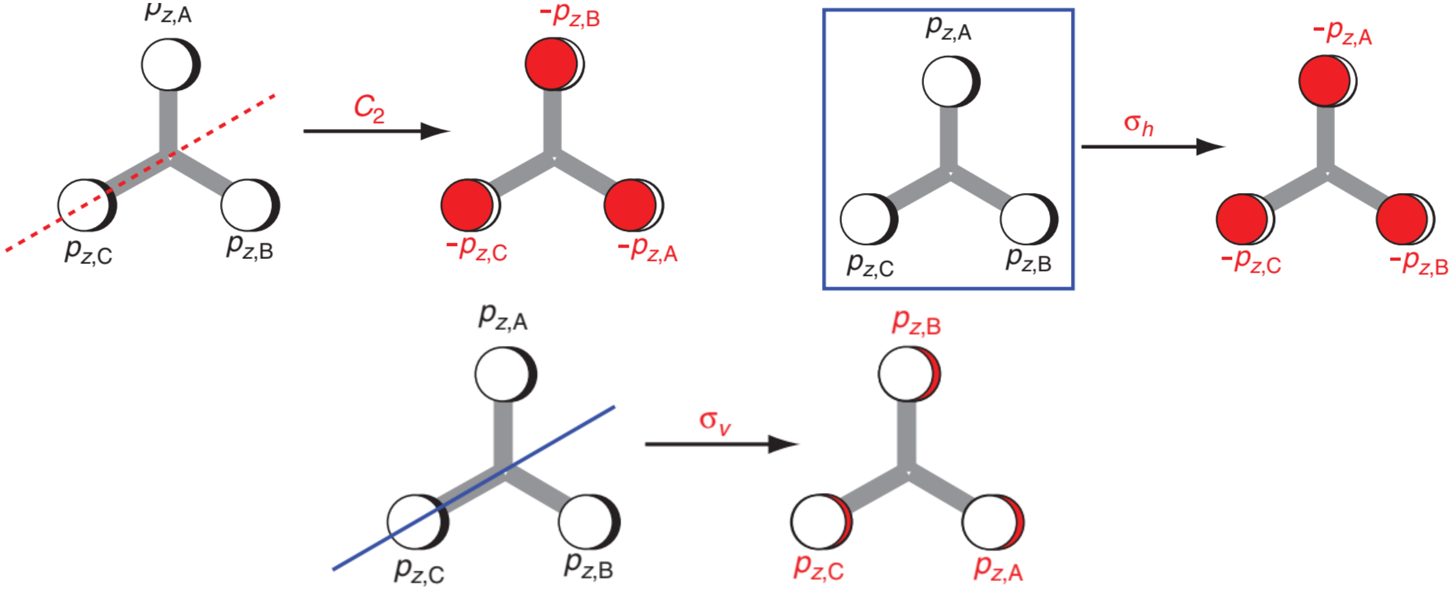


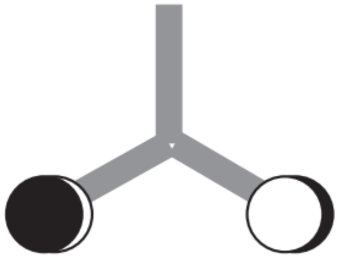
Finding the SOs

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	***3***	***0***	***-1***	***-3***	***0***	***1***		$= A_2'' \oplus E''$	

- Now find the characters of the representation in the basis of the three ***2p$_z$*** AOs. (recall Q11)

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




$\theta_{E'',xz} = p_{z,B} - p_{z,C}$


$\theta_{E'',yz} = p_{z,A} - 1/2\ p_{z,B} - 1/2\ p_{z,C}$

Finding the SOs

Ex. 17 & 18

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	3	0	-1	3	0	-1	$= A_2' \oplus E'$		

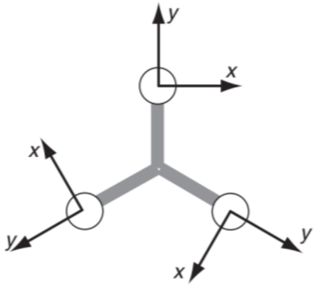
- Now find the characters for **set 2**. (three p_x AOs)
- The E' SOs:

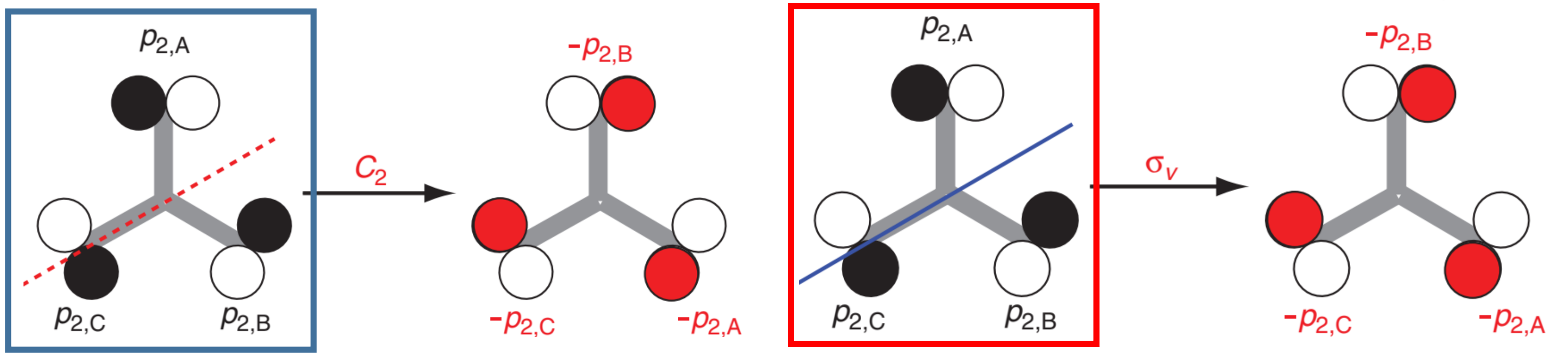
$$\theta_{E',x} = p_{2,B} - p_{2,C}$$

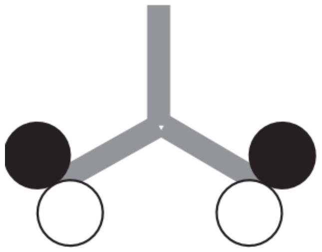
$$\theta_{E',y} = p_{2,A} - (p_{2,B} + p_{2,C})/2$$

- A good guess for the A_2' SO,

$$\theta_{A_2'} = p_{2,A} + p_{2,B} + p_{2,C}$$







$\theta_{E',x} = p_{2,B} - p_{2,C}$

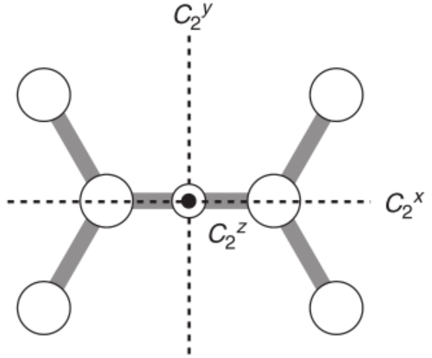
$\theta_{E',y} = p_{2,A} - 1/2\, p_{2,B} - 1/2\, p_{2,C}$

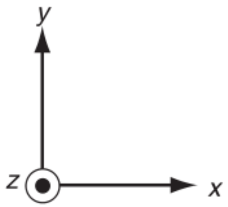
5.3.6 One last example

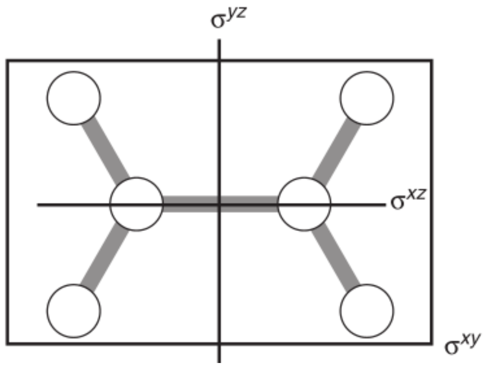
- C_2H_4, point group D_{2h}

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	
Γ	4	0	0	0	0	4	0	0		

$= A_g \oplus B_{1g} \oplus B_{2u} \oplus B_{3u}$

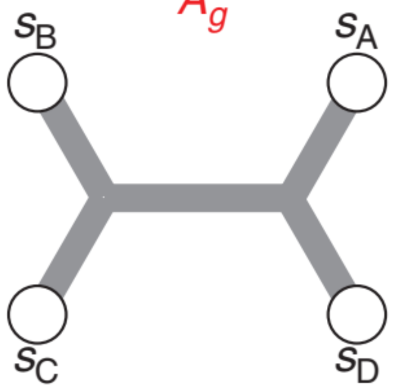






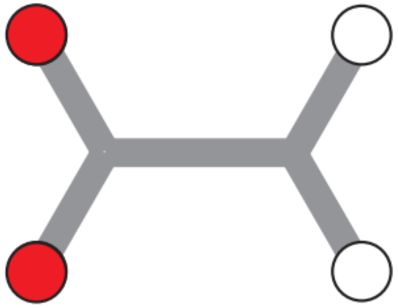
- Constructing the SOs arising from the four hydrogen *1s* AOs in C_2H_4.

A_g



$\theta_{A_g} = s_A + s_B + s_C + s_D$

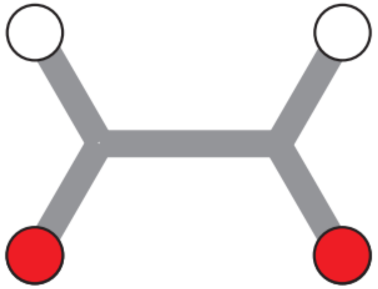
B_{3u}



'like *x*' SO

$\theta_{B_{3u}} = s_A - s_B - s_C + s_D$

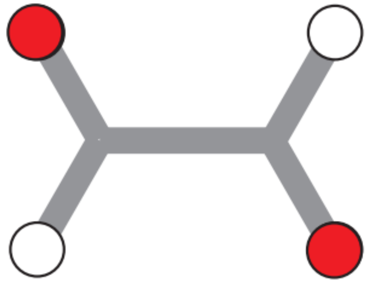
B_{2u}



'like *y*' SO

$\theta_{B_{2u}} = s_A + s_B - s_C - s_D$

B_{1g}



'like *xy*' SO

$\theta_{B_{1g}} = s_A - s_B + s_C - s_D$

5.4 Projection operator

- A more formal way of finding the ***symmetry orbitals*** is using the ***projection operator***.
- However, using projection operator is ***laborious*** and in addition it is not straightforwardly two- and higher-dimensional ***IR***s.

e.g., symmetrically equivalent AOs

- Suppose that we have a set of basis orbitals $\{\phi_i\}$ which are being used to construct **SO**s. The **SO** transforming as the irreducible representation k, $\theta^{(k)}$, can be found by applying the projection operator $\hat{P}^{(k)}$ to one of the basis functions,

$$\boxed{\theta^{(k)} = \hat{P}^{(k)} \phi_i}$$

~ Projection formula

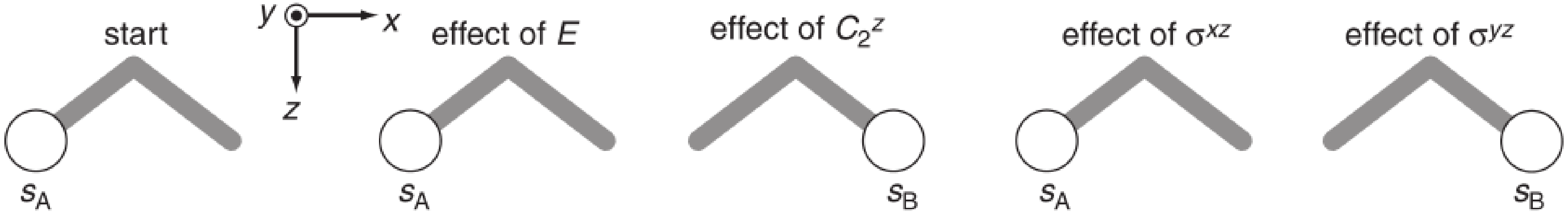
in which ***the projection operator*** is

$$\hat{P}^{(k)} = \frac{1}{h} \sum_{R} [\chi^{(k)}(R)]^{*} \hat{R}$$

Sum over all symmetry operations

5.4.1 SOs in H_2O

- The two hydrogen 1s AOs together transform as $A_1 \oplus B_1$.
- Now work out the effects of all operations on s_A.



$$\hat{E}s_A = s_A \qquad \hat{C}_2{}^z s_A = s_B \qquad \hat{\sigma}^{xz} s_A = s_A \qquad \hat{\sigma}^{yz} s_A = s_B$$

$$\hat{P}^{(k)} s_A = \frac{1}{h}\sum_R [\chi^{(k)}(R)]^* \hat{R} s_A$$

$$= \frac{1}{4}[\chi^{(k)}(E)\hat{E} + \chi^{(k)}(C_2)\hat{C}_2 + \chi^{(k)}(\sigma^{xz})\hat{\sigma}^{xz} + \chi^{(k)}(\sigma^{yz})\hat{\sigma}^{yz}] s_A$$

$$= \frac{1}{4}[\chi^{(k)}(E)s_A + \chi^{(k)}(C_2)s_B + \chi^{(k)}(\sigma^{xz})s_A + \chi^{(k)}(\sigma^{yz})s_B]$$

5.4.1 SOs in H_2O

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

$$\hat{P}^{(k)} s_A = \frac{1}{h}\sum_R [\chi^{(k)}(R)]^* \hat{R} s_A$$

$$= \frac{1}{4}[\chi^{(k)}(E)s_A + \chi^{(k)}(C_2)s_B + \chi^{(k)}(\sigma^{xz})s_A + \chi^{(k)}(\sigma^{yz})s_B]$$

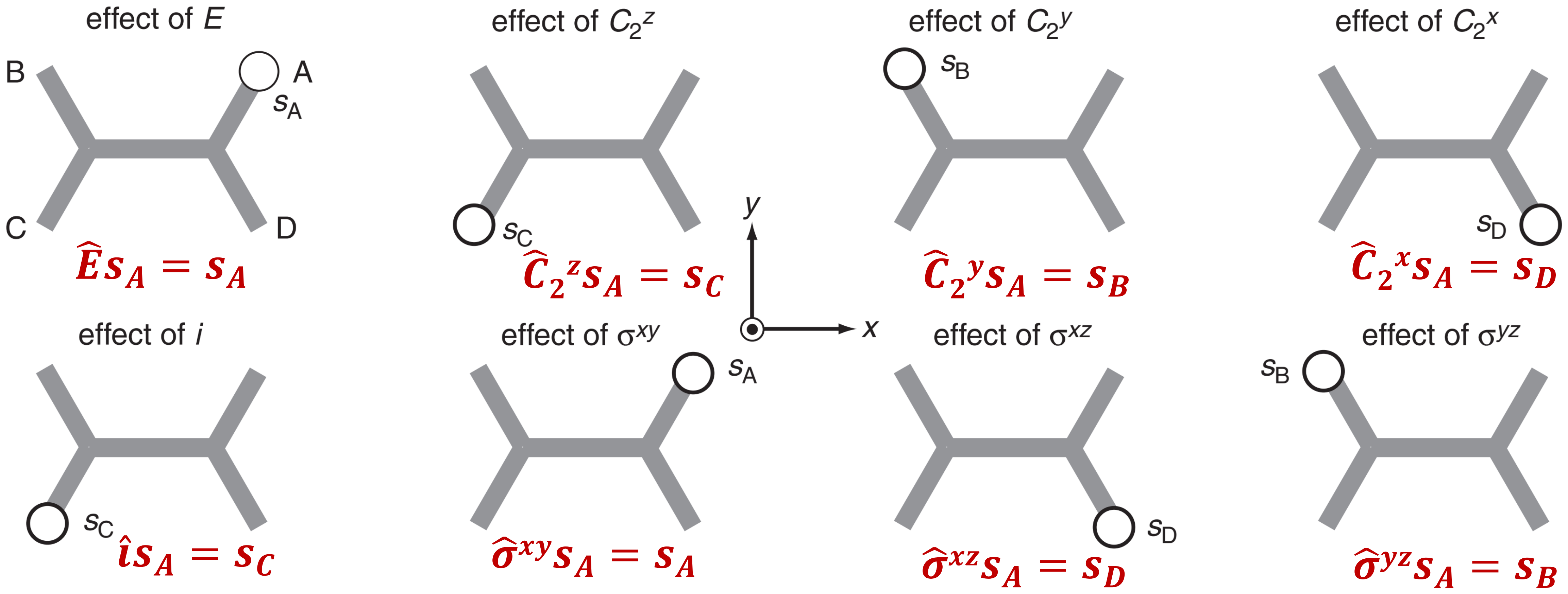
- For the SO that transforms as A_1, $\hat{P}^{(A_1)} s_A = (s_A + s_B)/2$
- For the SO that transforms as B_1, $\hat{P}^{(B_1)} s_A = (s_A - s_B)/2$
- Using the projection operator for the IR A_2 gives

$$\hat{P}^{(A_2)} s_A = \frac{(s_A + s_B - s_A - s_B)}{4} = 0$$

5.4.2 SOs in ethene

- The four hydrogen 1s AOs in ethene transform as $A_g \oplus B_{1g} \oplus B_{2u} \oplus B_{3u}$.
- The effects of operations on s_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
B_{1g}	1	1	−1	−1	1	1	−1	−1
B_{2u}	1	−1	1	−1	−1	1	−1	1
B_{3u}	1	−1	−1	1	−1	1	1	−1



$\hat{E}s_A = s_A$

$\hat{C}_2{}^z s_A = s_C$

$\hat{C}_2{}^y s_A = s_B$

$\hat{C}_2{}^x s_A = s_D$

$\hat{\imath} s_A = s_C$

$\hat{\sigma}^{xy} s_A = s_A$

$\hat{\sigma}^{xz} s_A = s_D$

$\hat{\sigma}^{yz} s_A = s_B$

5.4.2 SOs in ethene

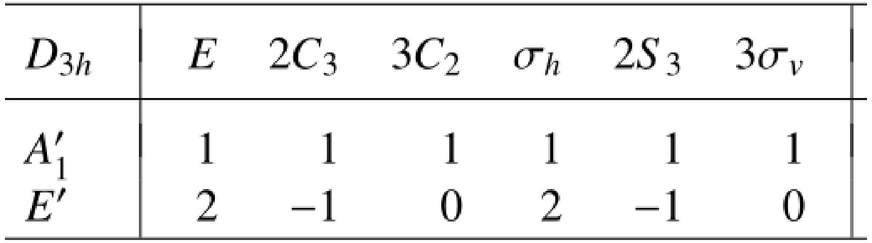
Ex.19&20

D_2 ~ a subgroup of D_{2h}

Operation	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}	
Effect on s_A	s_A	s_C	s_B	s_D	s_C	s_A	s_D	s_B	
Characters for A_g	1	1	1	1	1	1	1	1	
Result	s_A	s_C	s_B	s_D	s_C	s_A	s_D	s_B	$=(2s_A + 2s_B + 2s_C + 2s_D)/8$
Characters for B_{1g}	1	1	-1	-1	1	1	-1	-1	
Result	s_A	s_C	$-s_B$	$-s_D$	s_C	s_A	$-s_D$	$-s_B$	$=(2s_A - 2s_B + 2s_C - 2s_D)/8$
Characters for B_{2u}	1	-1	1	-1	-1	1	-1	1	
Result	s_A	$-s_C$	s_B	$-s_D$	$-s_C$	s_A	$-s_D$	s_B	$=(2s_A + 2s_B - 2s_C - 2s_D)/8$
Characters for B_{3u}	1	-1	-1	1	-1	1	1	-1	
Result	s_A	$-s_C$	$-s_B$	s_D	$-s_C$	s_A	s_D	$-s_B$	$=(2s_A - 2s_B - 2s_C + 2s_D)/8$

Q: How can we make the process less tedious? Use a subgroup that keeps the equivalence of atoms!

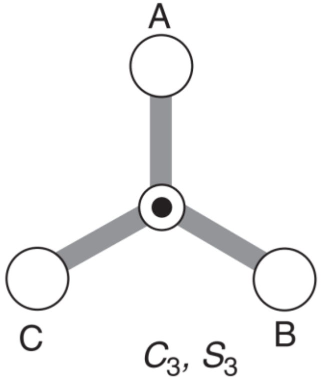
5.4.3 SOs in BH$_3$

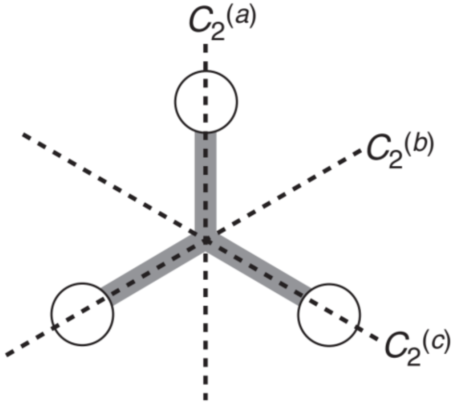


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A'_1	1	1	1	1	1	1
E'	2	−1	0	2	−1	0

- The three hydrogen 1s AOs in BH$_3$ (point group D_{3h}) transform as $A'_1 \oplus E'$.

Operation	E	C_3	C_3^2	$C_2^{(a)}$	$C_2^{(b)}$	$C_2^{(c)}$	σ_h	S_3	S_3^5	$\sigma^{(a)}$	$\sigma^{(b)}$	$\sigma^{(c)}$
Effect on s_A	s_A	s_C	s_B	s_A	s_B	s_C	s_A	s_C	s_B	s_A	s_B	s_C
Characters for A_1'	1	1	1	1	1	1	1	1	1	1	1	1
Result	s_A	s_C	s_B	s_A	s_B	s_C	s_A	s_C	s_B	s_A	s_B	s_C
Characters for E'	2	-1	-1	0	0	0	2	-1	-1	0	0	0
Result	$2s_A$	$-s_C$	$-s_B$	0	0	0	$2s_A$	$-s_C$	$-s_B$	0	0	0



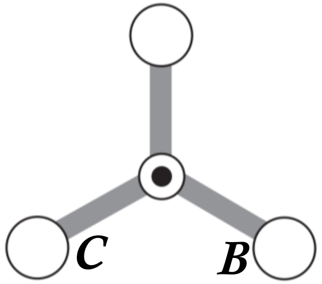


- $\theta_{A_1'} = (4s_A + 4s_B + 4s_C)/12$
- $\theta_{E'} = (4s_A - 2s_B - 2s_C)/12$ (like 'y')
- Another SO of E' can not be found by using the PO!
- Similar problem will be encountered for 3-D IRs.

PO problem with a degenerate IR: the way-out

C_3	E	C_3	C_3^2	$\omega = \exp(2\pi i/3)$		
A	1	1	1	z	R_z	$x^2+y^2;\ z^2$
E	1	ω	ω^2	$x-iy$	R_x-iR_y	$xz-iyz;\ x^2+2ixy-y^2$
	1	ω^2	ω	$x+iy$	R_x+iR_y	$xz+iyz;\ x^2-2ixy-y^2$
Γ	3	0	0	**(note: $\omega^* = \omega^2$)**		

- Alternatively, lower the symmetry of the molecule from D_{3h} to its pure rotation subgroup, C_n, for which the degenerate *E* IR becomes ***two associate 1-D representations***.
  - Again for BH_3, 3H 1s SOs $\Gamma = A \otimes E$



Operation	E	C_3	C_3^2
Effect on s_A	s_A	s_C	s_B
Characters for $E^{(1)}$	1	ω	ω^*
Result	s_A	$\omega^* s_C$	ωs_B
Characters for $E^{(2)}$	1	ω^*	ω
Result	s_A	ωs_C	$\omega^* s_B$

$$\hat{P}^{(k)} s_A = \frac{1}{h}\left\{\sum_R [\chi^{(k)}(R)]^* \hat{R}\right\} s_A$$

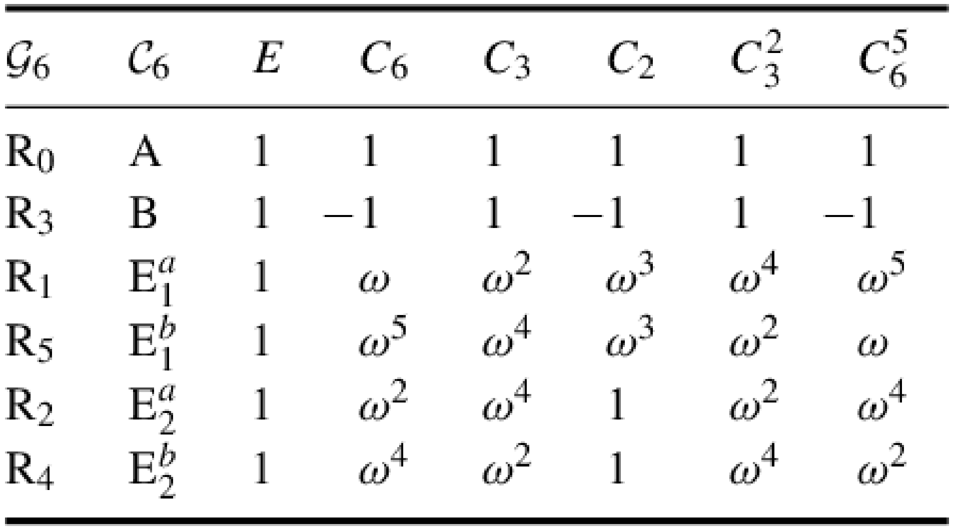
$$\theta_{E,1} = (s_A + \omega^* s_C + \omega s_B)/3$$

$$\theta_{E,2} = (s_A + \omega s_C + \omega^* s_B)/3$$

$$\rightarrow\ \theta_{E,a} = N(\theta_{E,1} + \theta_{E,2}) = N(2s_A - s_B - s_C) \qquad \theta_{E,b} = N(\theta_{E,1} - \theta_{E,2}) = N(s_B - s_C)$$

PO problem with a degenerate IR: the way-out

Q: Benzene belongs to point group $\mathbf{D_{6h}}$. Please construct the π-MOs of benzene by using the p_z AOs of the six carbon atoms. 1) first use the projection operator by lowering the symmetry of the molecule to pure rotation group C_6; 2) use the additional information in the character table of $\mathbf{D_{6h}}$ group.



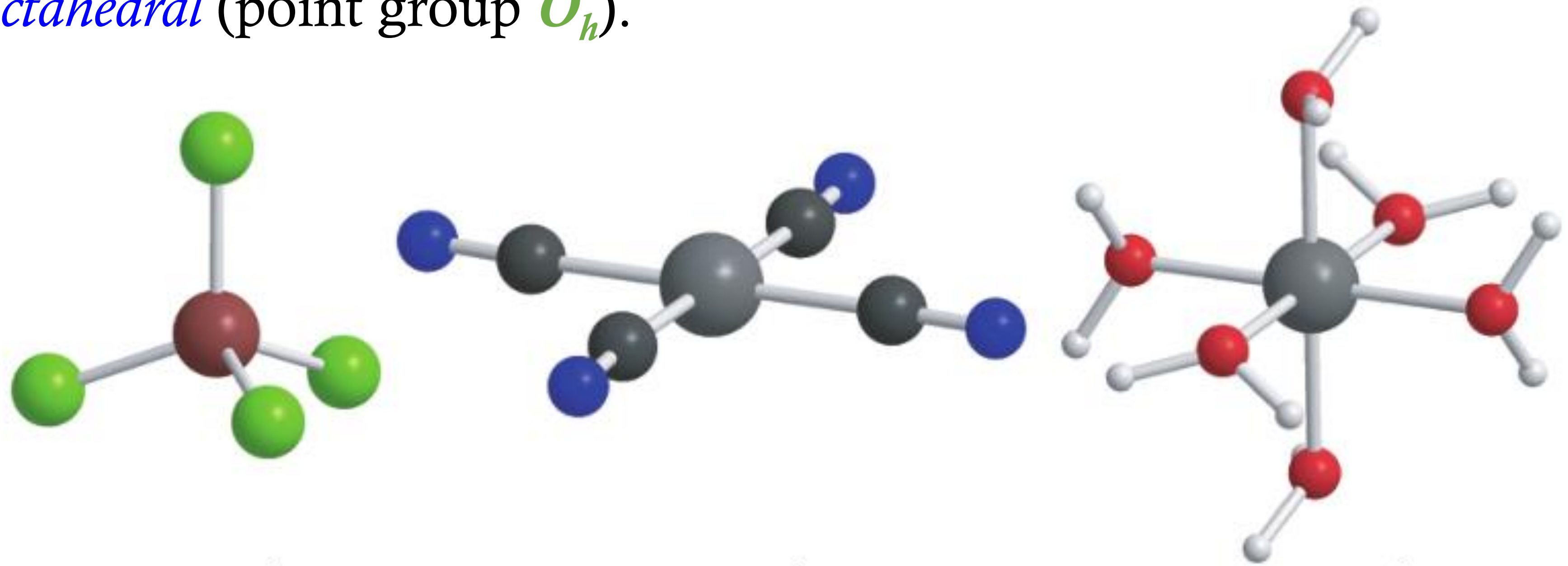
$\mathcal{G}_6$	$\mathcal{C}_6$	E	C_6	C_3	C_2	C_3^2	C_6^5
R_0	A	1	1	1	1	1	1
R_3	B	1	-1	1	-1	1	-1
R_1	E_1^a	1	ω	ω^2	ω^3	ω^4	ω^5
R_5	E_1^b	1	ω^5	ω^4	ω^3	ω^2	ω
R_2	E_2^a	1	ω^2	ω^4	1	ω^2	ω^4
R_4	E_2^b	1	ω^4	ω^2	1	ω^4	ω^2

$\omega = exp(2\pi i/6)$

$\mathcal{D}_{6h}$	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2$	$3C_2'$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		$(x^2-y^2, 2xy)$
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

5.5 Transition metal complexes

- *Transition metals* form an astounding number of *coordination compounds*, or *complexes*, in which a *central metal* atom is surrounded by a number of *ligands*.
- The *ligands* are anions, such as Cl^-, or small molecules.
- Some frequently encountered coordination geometries: (a) is *tetrahedral* (point group ***T_d***), (b) is *square planar* (point group ***D_{4h}***) and if we concentrate on just the ligating atoms, (c) is *octahedral* (point group ***O_h***).

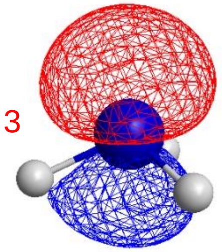

(a) $[FeCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$ (c) $[Cr(H_2O)_6]^{2+}$

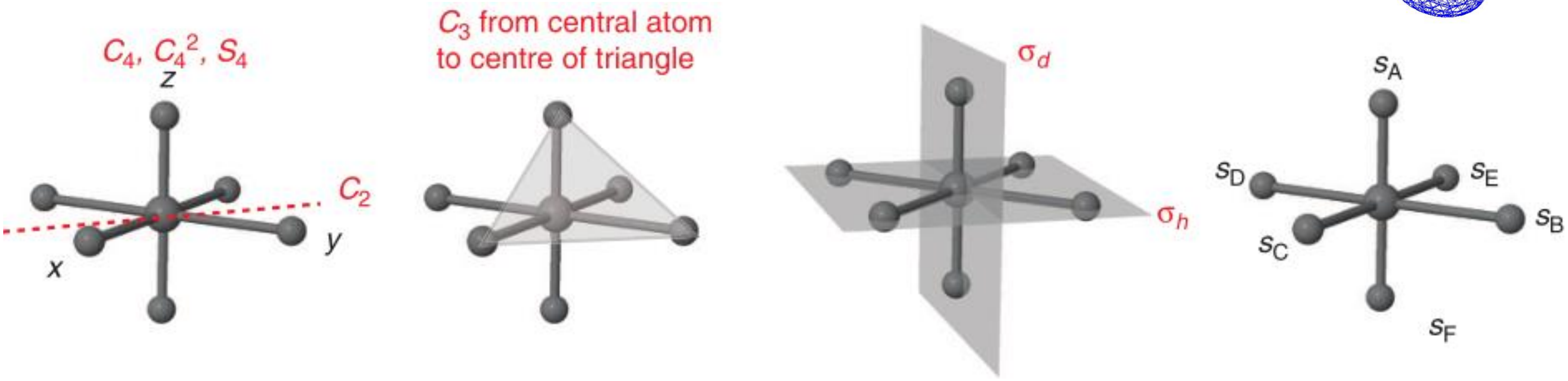
5.5.1 MO diagram of an octahedral complex with σ-only ligands

- Suppose an ***octahedral*** complex in which the central metal ion is surrounded by six ***structureless ligands***, each directing a ***σ-type orbital*** towards the metal atom.
- Typically these ligand orbitals will be those occupied by lone pairs, such as in NH_3.

Key symmetry operations of the ***O_h*** group:

HOMO of NH_3





5.5.1 MO diagram of an octahedral complex with σ-only ligands

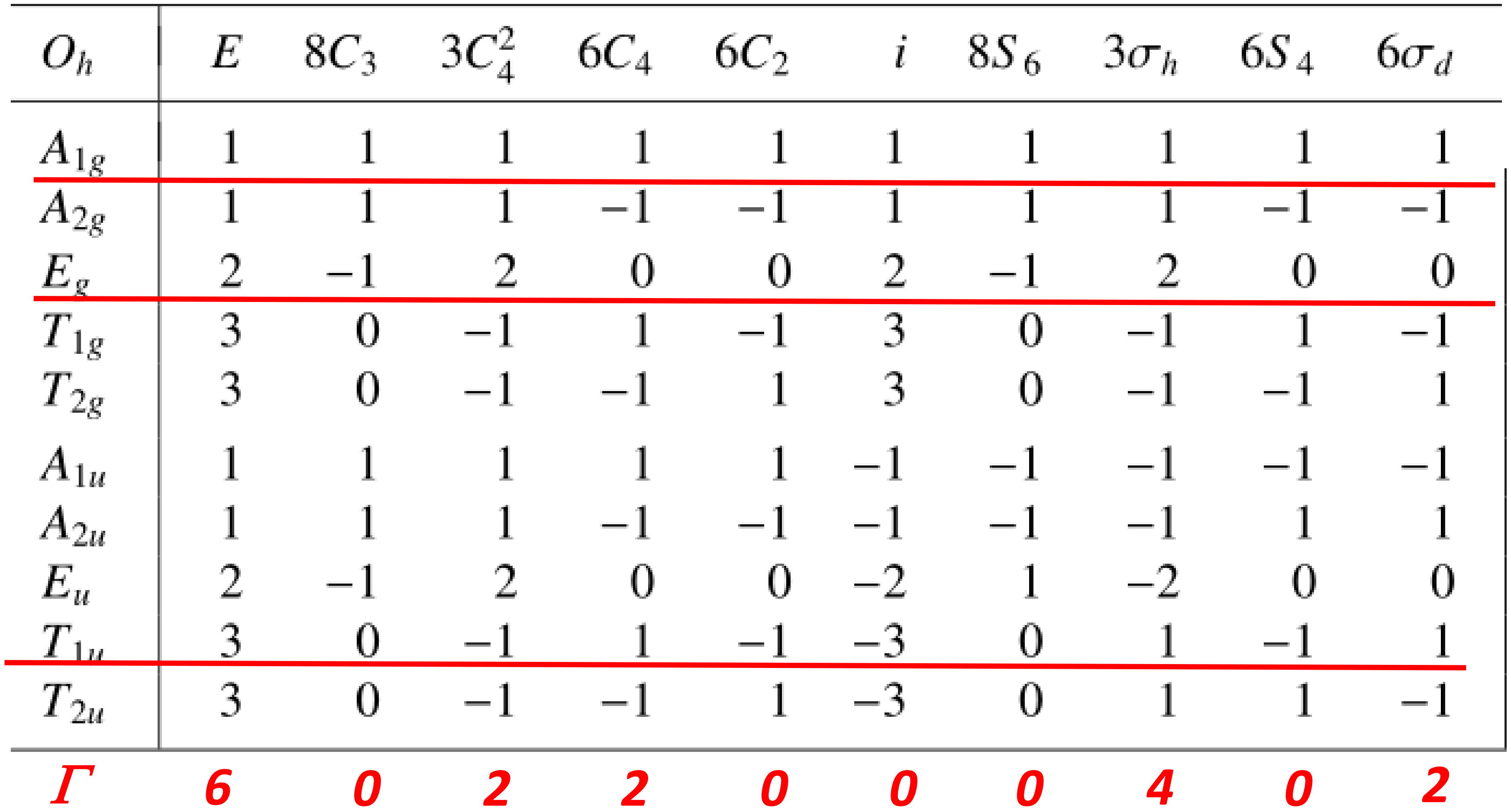
VAOs of the central metal

Cartesian function	orbital	*IR*
	$4s$	A_{1g}
(x,y,z)	$4p_x$, $4p_y$, $4p_z$	T_{1u}
(xz,xy,yz)	$3d_{xz}$, $3d_{xy}$, $3d_{yz}$	T_{2g}
$(2z^2\text{-}x^2\text{-}y^2,\sqrt{3}(x^2\text{-}y^2))$	$3d_{z^2}$, $3d_{x^2-y^2}$	E_g

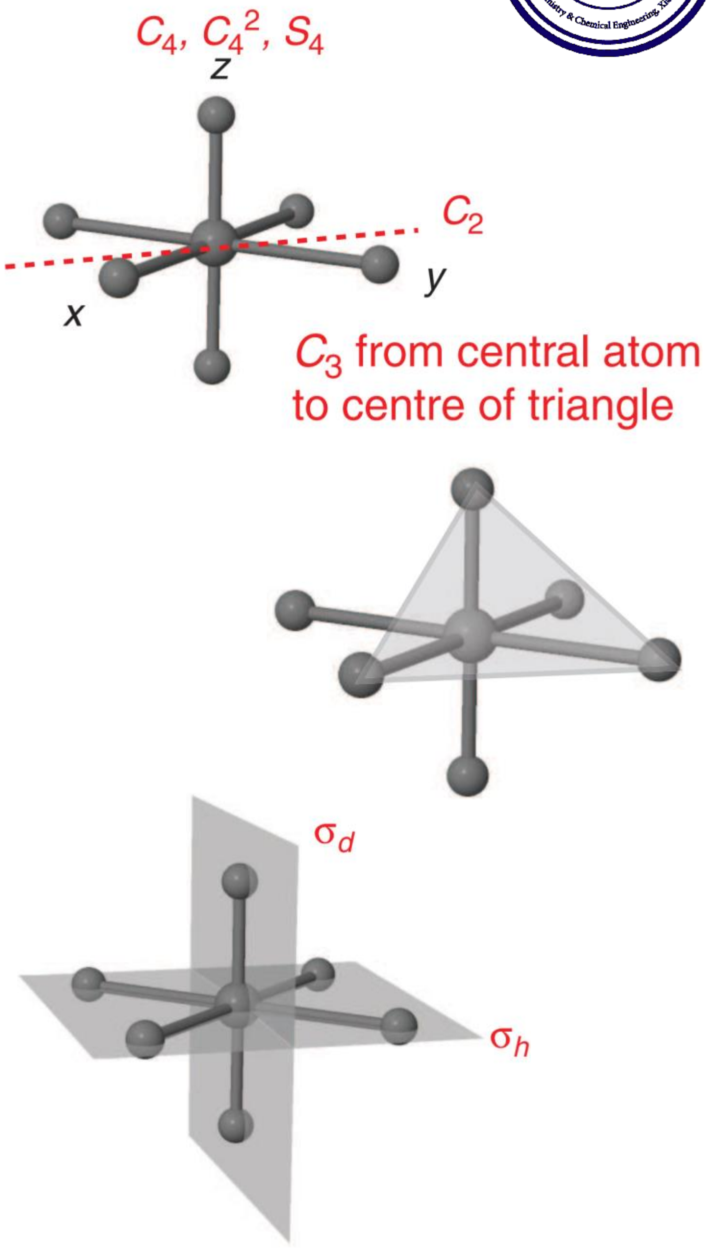
O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$\boxed{x^2+y^2+z^2}$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		
E_g	2	−1	2	0	0	2	−1	2	0	0		$\boxed{((2z^2-x^2-y^2),\ \sqrt{3}(x^2-y^2))}$
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1		$\boxed{(xz, xy, yz)}$
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	2	0	0	−2	1	−2	0	0		
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1	$\boxed{(x, y, z)}$	
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1		

5.5.1 MO diagram of an octahedral complex with σ-only ligands

- The six ***σ***-type ligand MOs transform as ***$A_{1g} \oplus E_g \oplus T_{1u}$.***

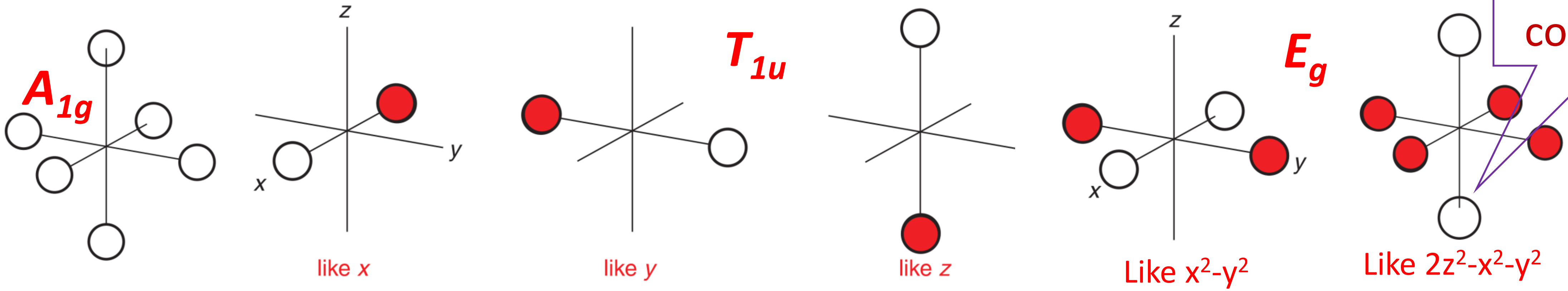


O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1
E_g	2	−1	2	0	0	2	−1	2	0	0
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
E_u	2	−1	2	0	0	−2	1	−2	0	0
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1
Γ	***6***	***0***	***2***	***2***	***0***	***0***	***0***	***4***	***0***	***2***



5.5.1 MO diagram of an octahedral complex with σ-only ligands

- The six σ-type ligand MOs transform as $A_{1g} \oplus E_g \oplus T_{1u}$.



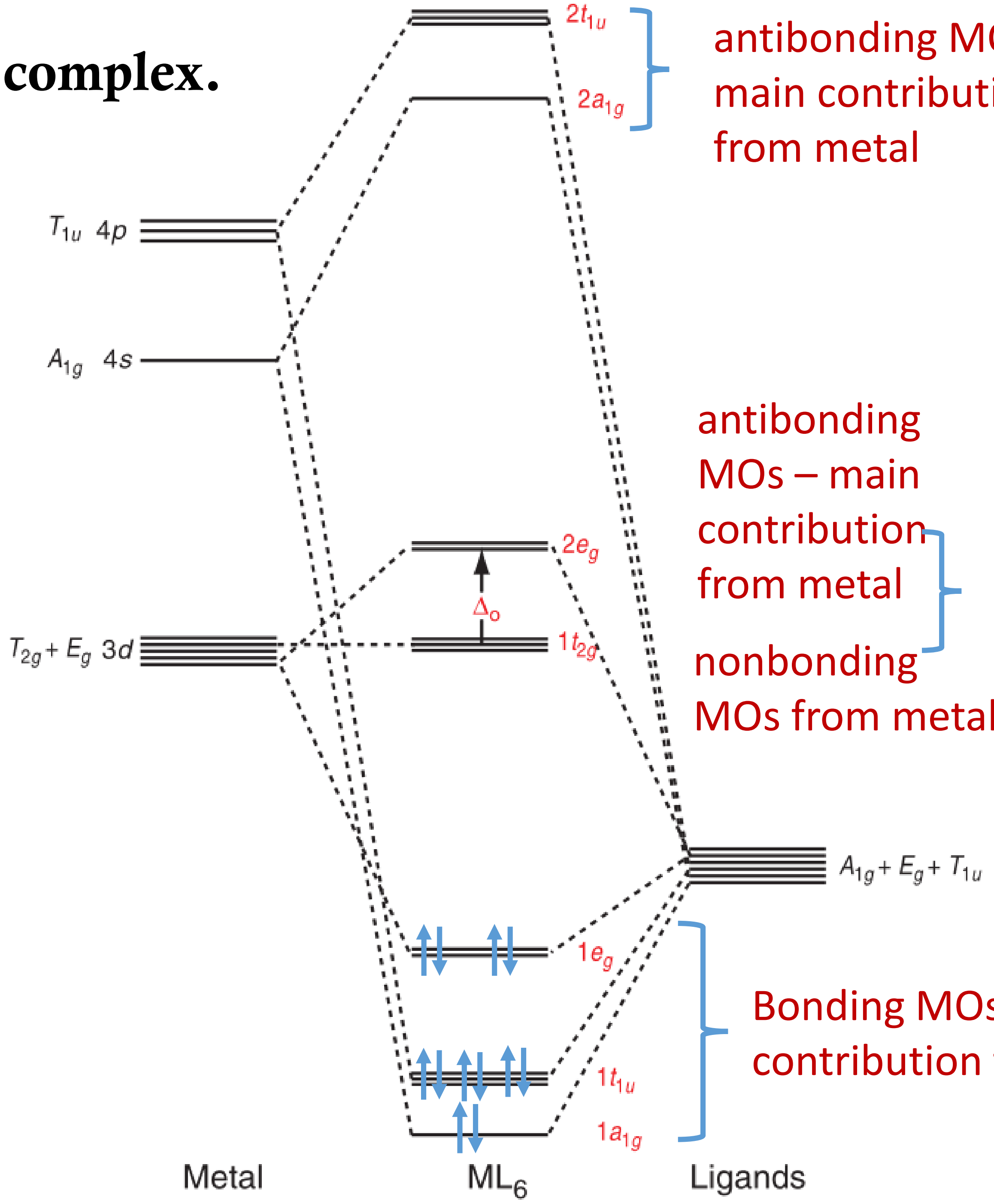
Larger coefficient

O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$\boxed{x^2 + y^2 + z^2}$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		
E_g	2	−1	2	0	0	2	−1	2	0	0		$\boxed{((2z^2 - x^2 - y^2), \sqrt{3}(x^2 - y^2))}$
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1		(xz, xy, 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	2	0	0	−2	1	−2	0	0		
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1	$\boxed{(x, y, z)}$	
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1		

Ex. 21

MO diagram for an ML_6 complex.

- Now work out the MOs using the symmetry principle.
- Then the occupations of MOs.
- The metal ***3d*** electrons should go to ***$1t_{2g}$*** and ***$2e_g$*** MOs; the energy gap between them is called ***the ligand-field splitting***, Δ_o.
- The size of Δ_o depends on the strength of the M-L bonding interaction. ***why?***



antibonding MOs – main contribution from metal

antibonding MOs – main contribution from metal

nonbonding MOs from metal

Metal 3d-based MOs

Bonding MOs – main contribution from ligands

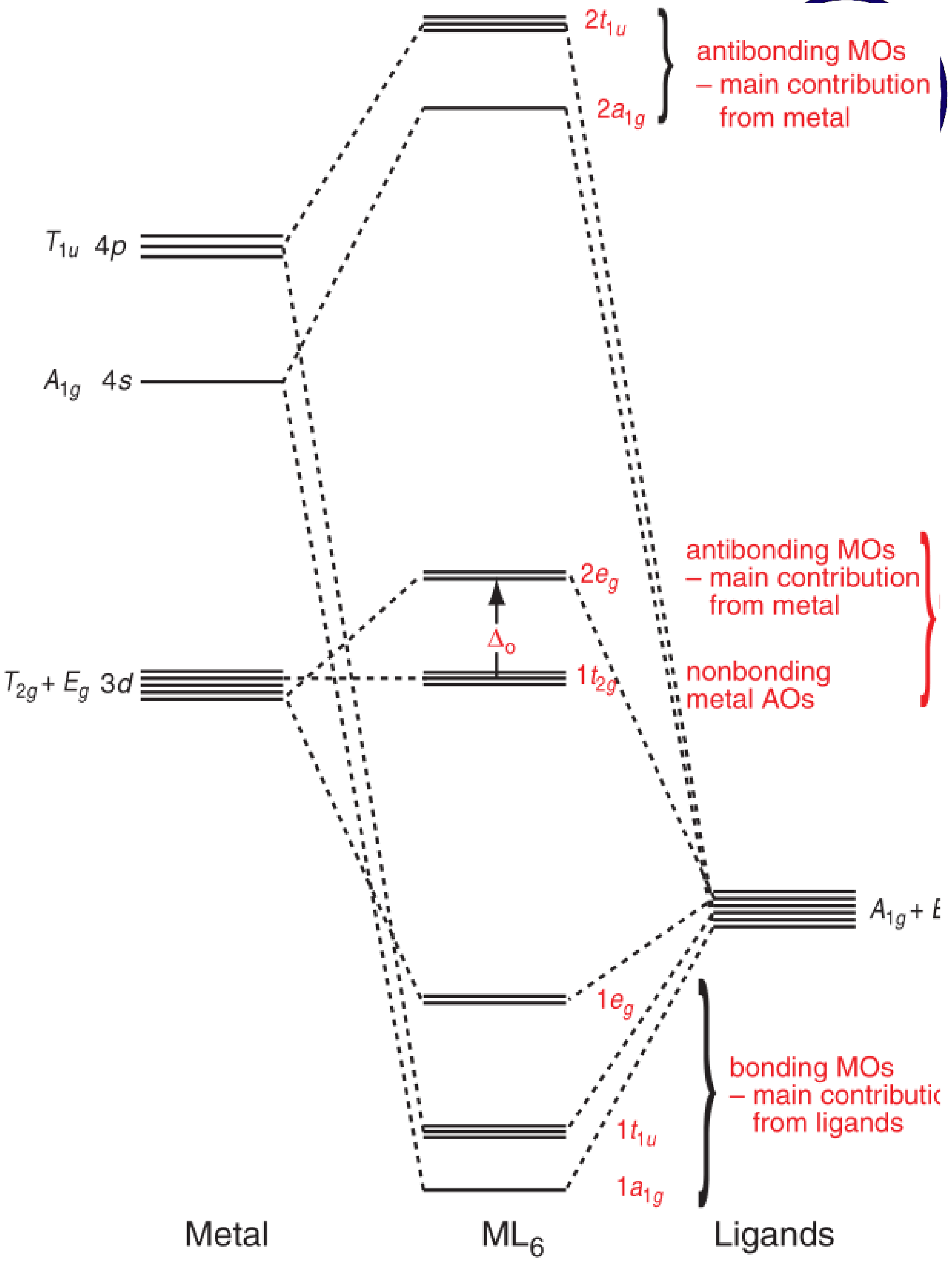
Ligand-field splitting

- For a fixed set of ligands, Δ_o increases as the oxidation state of the metal increases and also as we move across the first transition series. Why?

i) Both increasing the oxidation state and increasing the atomic number will result in the ***3d*** AOs falling in energy and so becoming more closely matched in energy to the ligand orbitals.

ii) The result is a stronger M-L σ-interaction, and hence a greater shift of the antibonding MOs ($2e_g$).

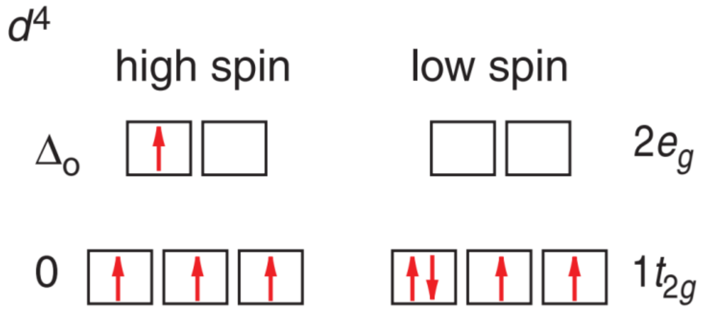
- The way in which Δ_o varies with ligand is rather more complex, and is a point deserves further discussion.



5.5.2 High- and low-spin complexes

- Now let us focus on how the electrons which derive from metal ***3d*** orbitals are accommodated in the non-bonding ***$1t_{2g}$*** and antibonding ***$2e_g$*** MOs –*Ligand field theory.*
- Assume that the energy of the ***$1t_{2g}$*** MOs is ***0***, the energy of the ***$2e_g$*** MOs is Δ_0, and each pair of electrons of parallel spins lowers the energy by an amount of ***K*** (***exchange energy***).

(Note: for d^1-d^3 or d^8-d^{10}, there is only one electronic configuration!)

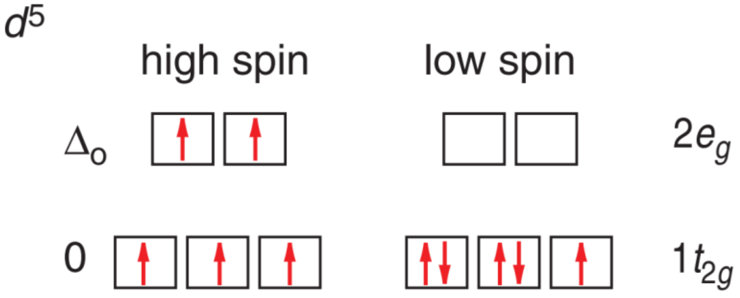


$$E_{high\text{-}spin} = (3x0 + \Delta_o) - 6K = \Delta_o - 6K$$

C_4^2

$$E_{low\text{-}spin} = (4x0) - 3K = -3K$$

If $\Delta_o < 3K$, high spin is favored!

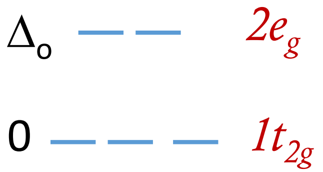


$$E_{high\text{-}spin} = (3x0 + 2\Delta_o) - 10K = 2\Delta_o - 10K$$

$$E_{low\text{-}spin} = (5x0) - 4K = -4K$$

If $\Delta_o < 3K$, high spin is favored!

5.5.2 High- and low-spin complexes



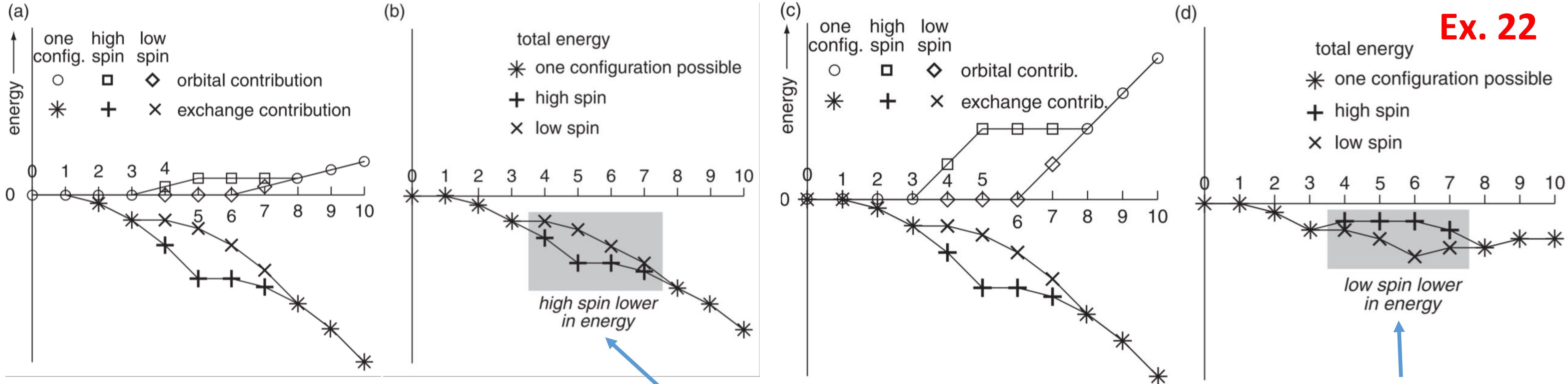
Similarly, we can tabulate the exchange energy and orbital energy for each state:

		d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
High-spin	Orbital (Δ_0)											
	Exchange(K)											
Low-spin	Orbital(Δ_0)											
	exchange(K)											

i) For small Δ_o, exchange contribution dominates.

ii) For large Δ_o, orbital contribution dominates.

Ex. 22



- For small Δ_o, the d^4-d^7 may favor *high spin state*.
- For large Δ_o, the d^4-d^7 may favor *low spin state*.

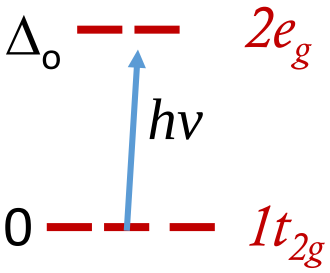
5.5.3 Spectroscopic and magnetic properties

- ***Electronic spectroscopy***, in which the transitions can be thought of as involving electrons moving from one orbital to another, is an excellent way of studying the electronic structure of transition metal complexes and the energies of the orbitals involved.

- Naively, we might think that a transition in which an electron is promoted from the $1t_{2g}$ to the $2e_g$ would give us a direct measure of Δ_o.

- Unfortunately this is not the case since *the act of promoting an electron from one orbital to another alters the energy of all of the orbitals* due to changes in the electron–electron repulsion.

- Yet, it is possible to infer ***the value of the ligand-field splitting*** from the electronic spectra of these complexes, but the details of how this can be done are beyond the scope of this course.



5.5.3 Spectroscopic and magnetic properties

Ex. 23

- The presence of ***unpaired electrons*** in a complex leads to ***paramagnetism***.
- For first-row transition metal complexes it turns out that the effective magnetic moment, μ_{eff}, which is a measure of the degree of paramagnetism, is given by

$$\boldsymbol{\mu_{eff} = 2\sqrt{S(S+1)}}$$ in Bohr magnetons, B.M. (μ_B).

S is the quantum number for the *total spin angular momentum*. **--总自旋(角动量)量子数**

- As ***S =n/2***, where ***n*** is the number of unpaired spins. The expression can therefore be re-written as

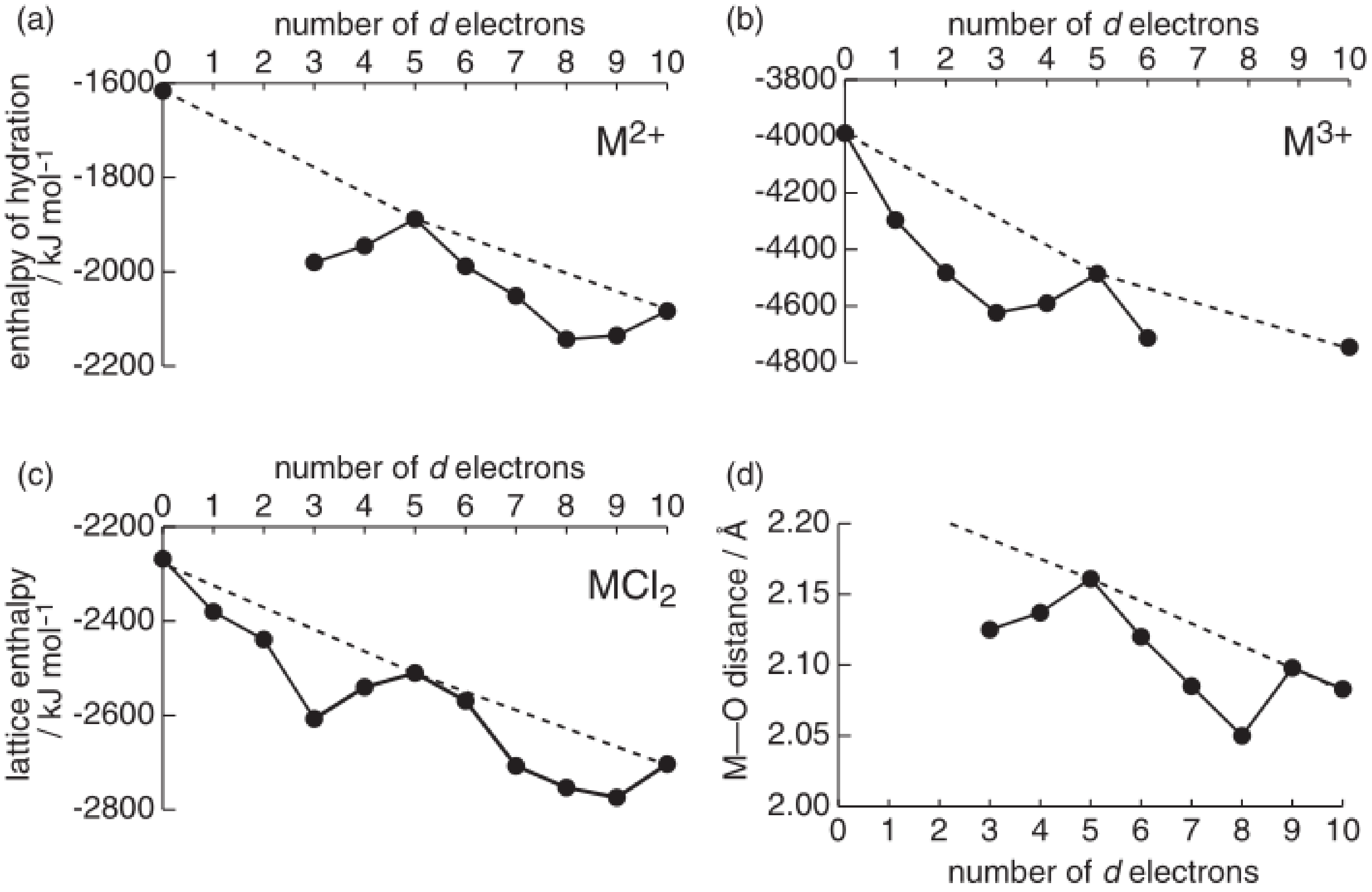
$$\boldsymbol{\mu_{eff} = \sqrt{n(n+2)}} \text{ B.M.}$$

- A complex containing ***Mn^{2+}*** in high-spin state, $n = 5$ and $\boldsymbol{\mu_{eff} = \sqrt{5(5+2)} = 5.9}$ B.M..
  Its low-spin state has only one unpaired electron, $\boldsymbol{\mu_{eff} = \sqrt{1(1+2)} = 1.7}$ B.M..

5.5.4 Thermodynamics properties

- This figure shows how the **hydration enthalpies** (水合热) of M^{2+} and M^{3+} ions and **the lattice energies** (晶格能) of divalent chlorides vary along the first transition series.

- If on the plot we connect the values for **d^0**, **d^5** and **d^{10}** configurations we see that all the other data fall beneath these lines in ***two dips***, one between **d^0** and **d^5**, and the second between **d^5** and **d^{10}**.



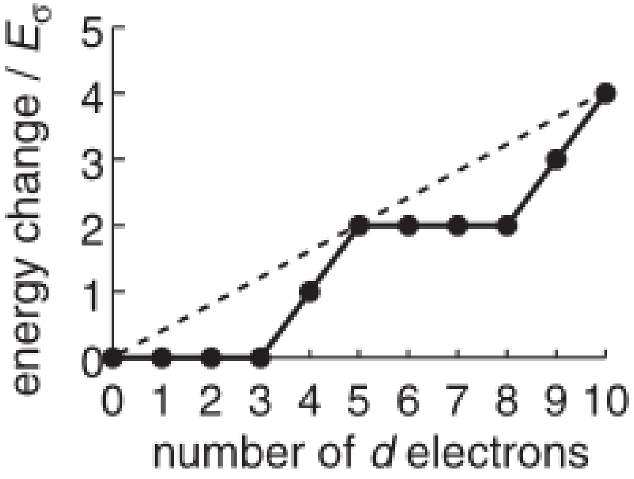
5.5.4 Thermodynamics properties

- The predominately ligand-based $1a_{1g}$, $1t_{1u}$ and $1e_g$ bonding MOs are fully occupied regardless of the number of *d* electrons.

Assume that the reduction in energy due to the occupation of these MOs as $-E_L$ and that each electron in the $2e_g$ MOs increases the energy by an amount E_σ.

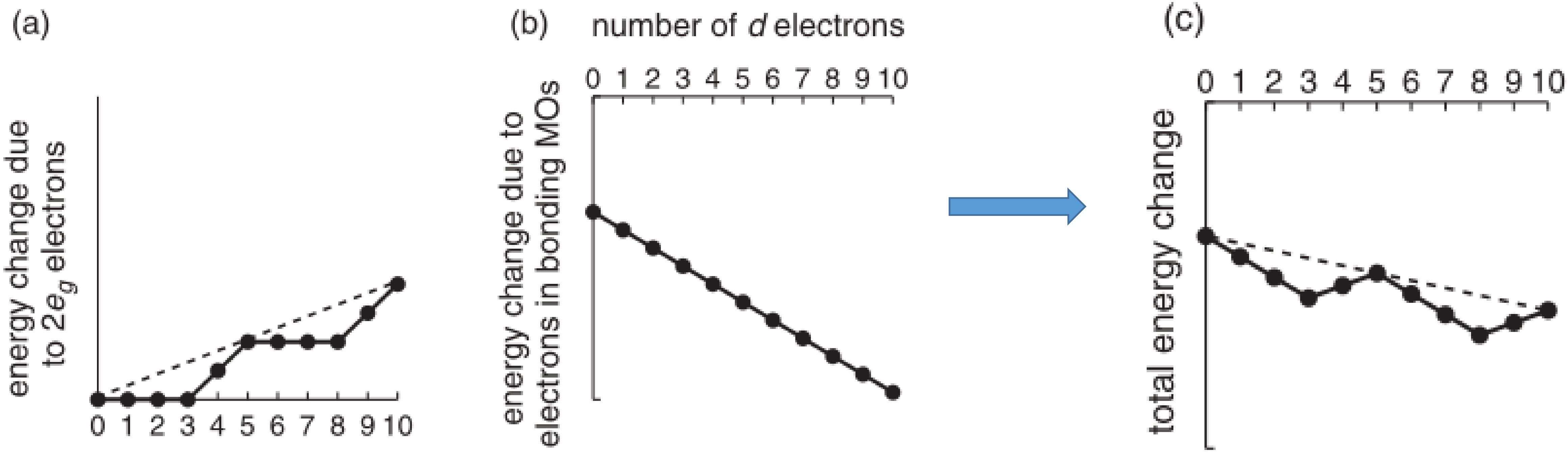
- Then overall the energy change upon forming the complex is $-E_L + n_{E_\sigma} \times E_\sigma$ (n_{E_σ} ~ the number of electrons in the *2eg* MOs).

- For high-spin complex, the energy change solely depending on the occupation in the $2e_g$ MOs is given here.



5.5.4 Thermodynamics properties

- As the interaction between the metal and ligand MOs becomes stronger as we go across the first row, i.e., E_L is expected to increase across the row.
- ***The overall energy change on forming the complex*** is the combination of two effects: the increase in energy due to the occupation of the ***$2e_g$*** MOs, shown in (a) below; and the general decrease in energy due to the increase in E_L, shown in (b).



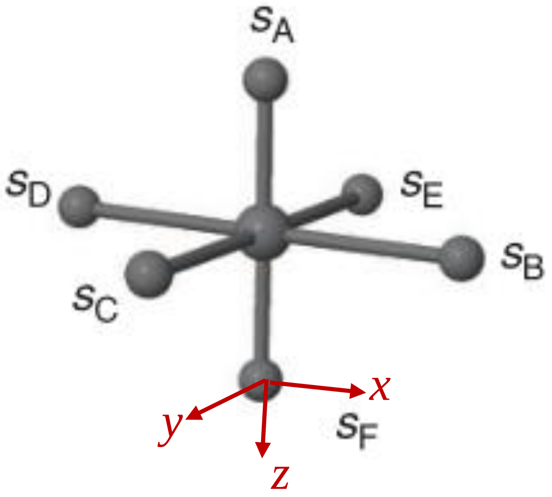
5.5.4 Thermodynamics properties

- We have assumed that E_σ is constant across the row, whereas in reality it should increase for the same reasons that E_L increases. However, this extra subtlety does not alter the basic picture.
- Historically, the lowering in energy of the complex beneath the d^0–d^5–d^{10} line has been called the ***crystal-field or ligand-field stabilization energy (CFSE or LFSE)***. Our analysis here shows that this characteristic behavior is entirely understandable from the form of the MO diagram for these complexes.

5.5.5 *Effect of π interactions with the ligands*

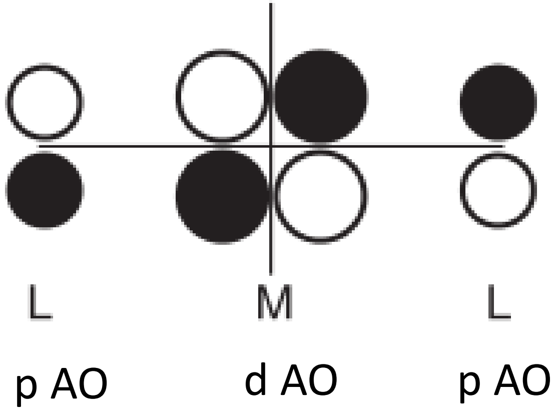
- In general we should expect ligands to have other orbitals of suitable symmetry to interact with the metal.

- For example, in the case where the ligand is a simple anion (e.g. *Cl^-*) the ***p*** orbitals which are perpendicular to the **M–L** axis can interact with some of the metal orbitals as shown below. In general, this type of interaction is described as ***π interaction***.



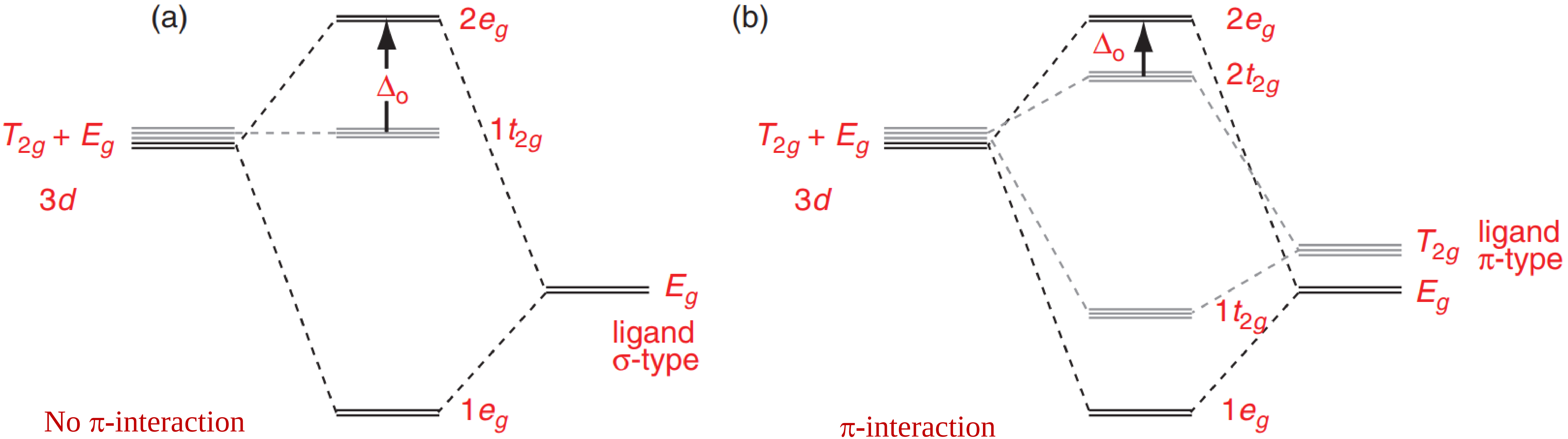
- If each ligand ***L*** has a pair of ***p*** (or π) orbitals pointing perpendicular to the **M–L** bond, then the resulting set of **12** orbitals can be shown to transform as $T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$.

(***after-class Ex.: prove this!***)



5.5.5 Effect of π interactions with the ligands

- Now there are ligand SOs with T_{2g} symmetry which can interact with the T_{2g} metal orbitals: the latter will therefore no longer be non-bonding.
- The diagram below shows the effect of introducing these T_{2g} SOs. For simplicity, only the MOs involving the metal ***3d*** AOs are shown.

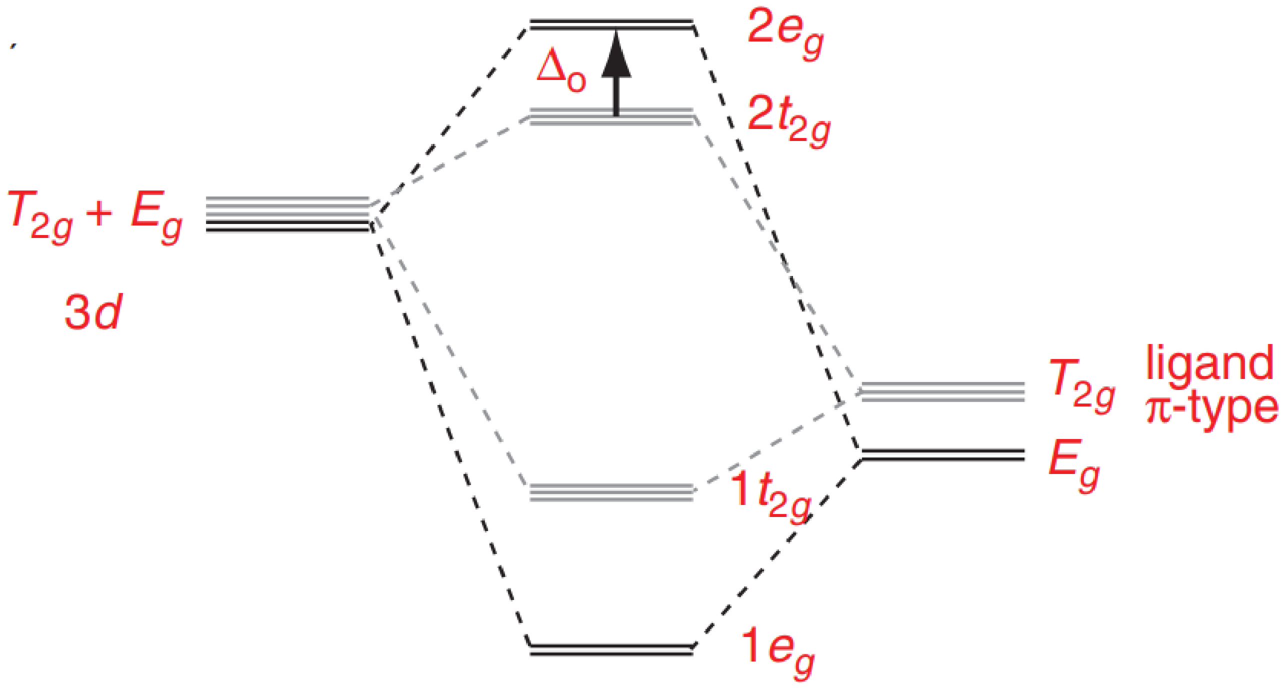


No π-interaction

π-interaction

5.5.5 *Effect of π-interactions with the ligands*

- Such π-interaction gives bonding ***$1t_{2g}$*** and antibonding ***$2t_{2g}$*** MOs.
- As a result the separation between the two predominantly metal-based sets of orbitals (here the ***$2t_{2g}$*** and the ***$2e_g$***) has been decreased, i.e. Δ_o ***is decreased***.
- The ligand ***T_{2g}*** SOs are filled, so in the complex the ***$1t_{2g}$*** bonding MOs are filled as well.
- The extent to which the antibonding ***$2t_{2g}$*** are occupied depends on the number of ***3d*** electrons present.
- Ligands which interact in this way so as to decrease Δ_o are called ***π donors***.

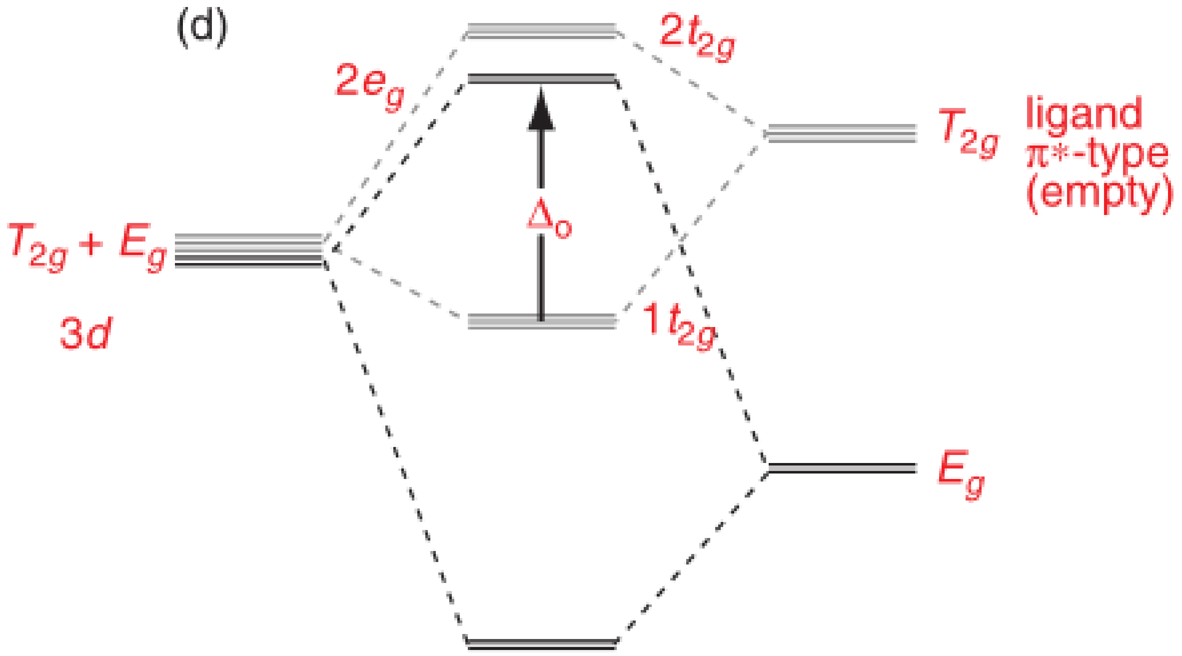


π-acceptor ligands

Ex. 24

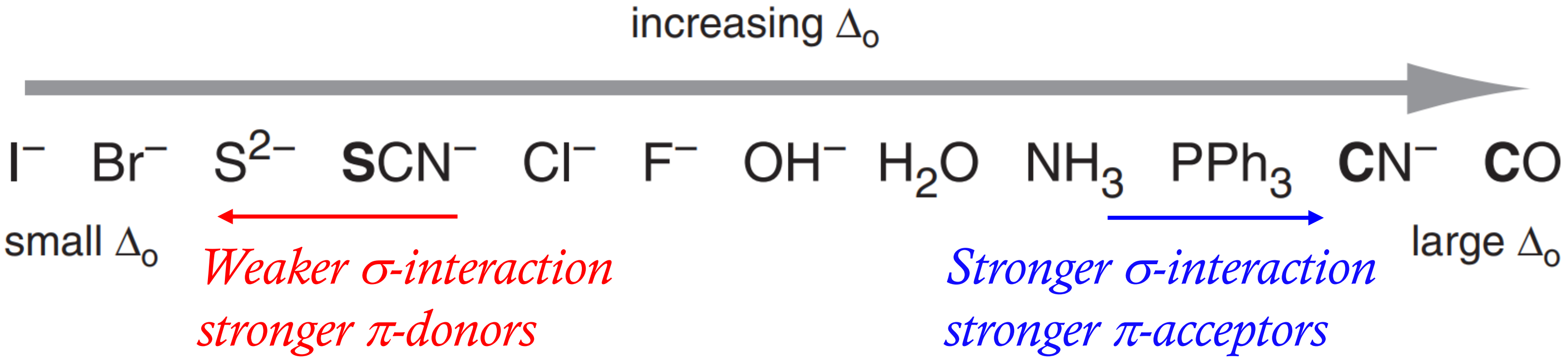
- Ligands such as CO and CN⁻ also have ***empty*** π-type orbitals, generally the π^* MOs, available for interacting with the metal.
- Such type of π-interactions results in an ***increase in Δ_o***, and ***transfer of electron density*** from the metal to the π-acceptor ligands.

- The aforementioned σ- and π-bonding between transition metal and π-acceptor ligands (e.g., CO, CN⁻, *alkene*, and *alkyne*) thus result in ***σ-donation*** of electron density from the ligands to mental and ***π-backdonation*** of electron density from metal to the ligands! (a widely used model in organometallics and catalysis!)



5.5.6 *Spectrochemical series*

For a given metal and oxidation state, altering the ligand changes the value of Δ_o. Δ_o increases from left to right in the following sequence of ligands, called the ***spectrochemical series***.



increasing Δ_o

I^- Br^- S^{2-} SCN^- Cl^- F^- OH^- H_2O NH_3 PPh_3 CN^- CO

small Δ_o

Weaker σ-interaction
stronger π-donors

Stronger σ-interaction
stronger π-acceptors

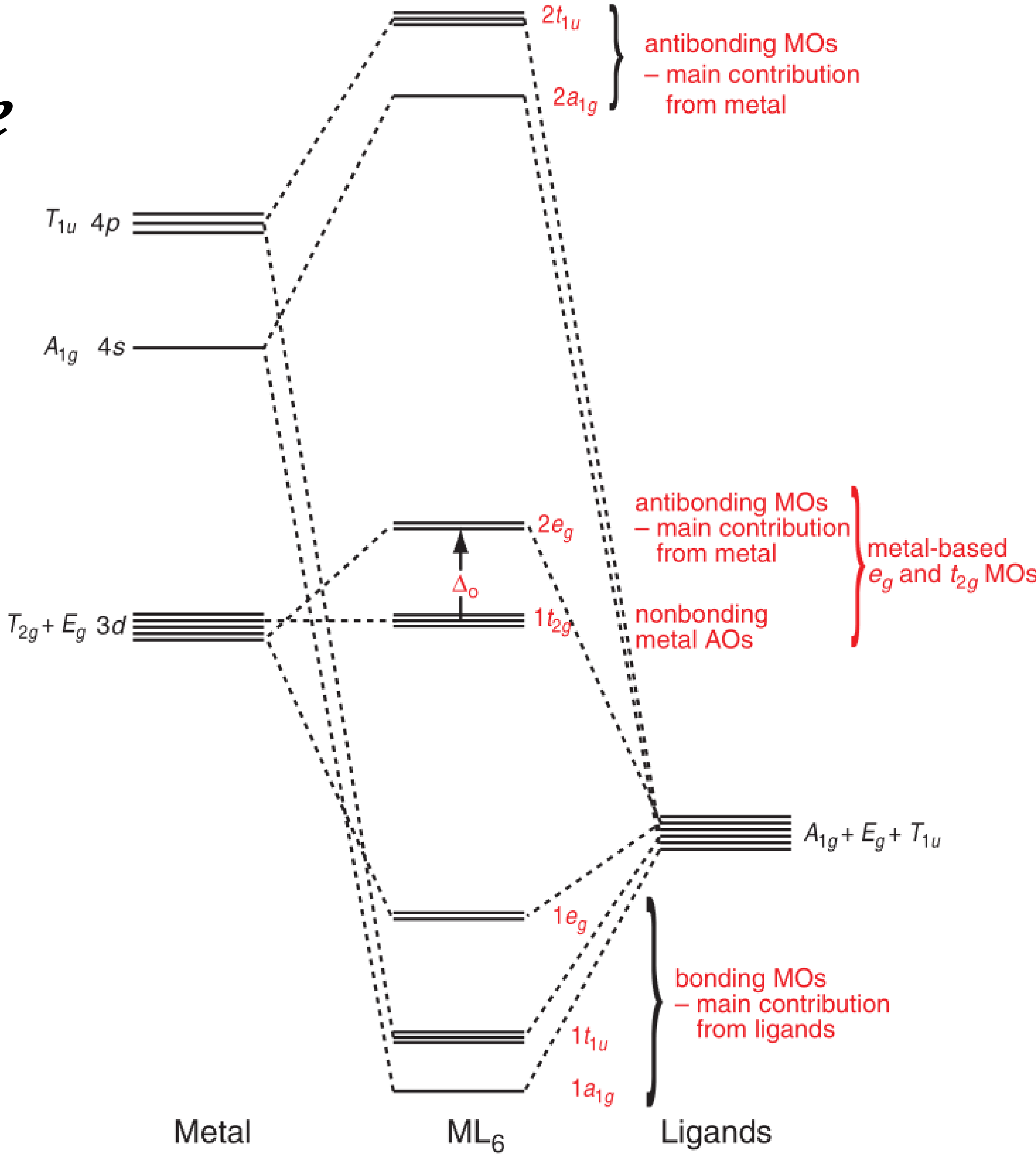
large Δ_o

Resulting from a subtle balance between **σ-** and **π-**type interactions:

- ***The stronger*** σ-type interaction → ***the greater*** the value of Δ_o.
- The ligating atom going from ***O*** → ***N*** → ***C*** → increasing energy of ligand σ orbital → better matching the energy of metal 3d AOs → stronger σ-type interaction.
- ***Enhanced σ-type interaction leads to shorter M-L bond length*** and thus facilitates a ***stronger π-backbonding interaction***, further increasing Δ_o.
- CN^- and CO lead to particularly large values of Δ_o: strong **σ** donor & **π** acceptor.

5.5.7 Eighteen-electron rule

- In an octahedral complex with ***π-acceptor*** ligands, there are a total of ***nine*** bonding MOs: **$1a_{1g}$**, **$1t_{1u}$**(triply degenerate), **$1e_g$**(doubly degenerate) and **$1t_{2g}$**(triply degenerate).
- It takes ***eighteen electrons*** to fill completely all of these bonding MOs, so we can say the maximum amount of bonding is achieved when there are ***eighteen valence electrons*** present.
- Alternatively, this is to say that the metal atom has ***nine valence orbitals***: the five ***3d***, the ***4s*** and the three ***4p***. If suitable ligand orbitals are available, all these metal orbitals will be involved in the formation of the ***nine bonding MOs***, which can be occupied by up to ***eighteen electrons***.



5.5.7 Eighteen-electron rule

- It has been observed that many transition metal complexes which involve ***π-acceptor ligands*** do indeed have ***eighteen valence electrons***, whereas complexes with fewer or more valence electrons are much less common.

- This has lead to the formulation of the ***eighteen-electron rule*** which says that ***the most stable complexes are likely to be those with this full compliment of bonding electrons***.

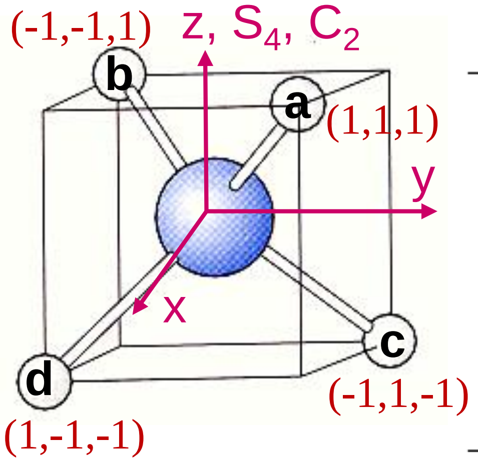
- ***Classical complexes involving ligands which are not π acceptors*** are not likely to obey the eighteen electron rule since the metal-based **t_{2g}** MOs are either non-bonding or antibonding.

5.5.8 Other coordination geometries

Ex. 25

i) Tetrahedral coordination

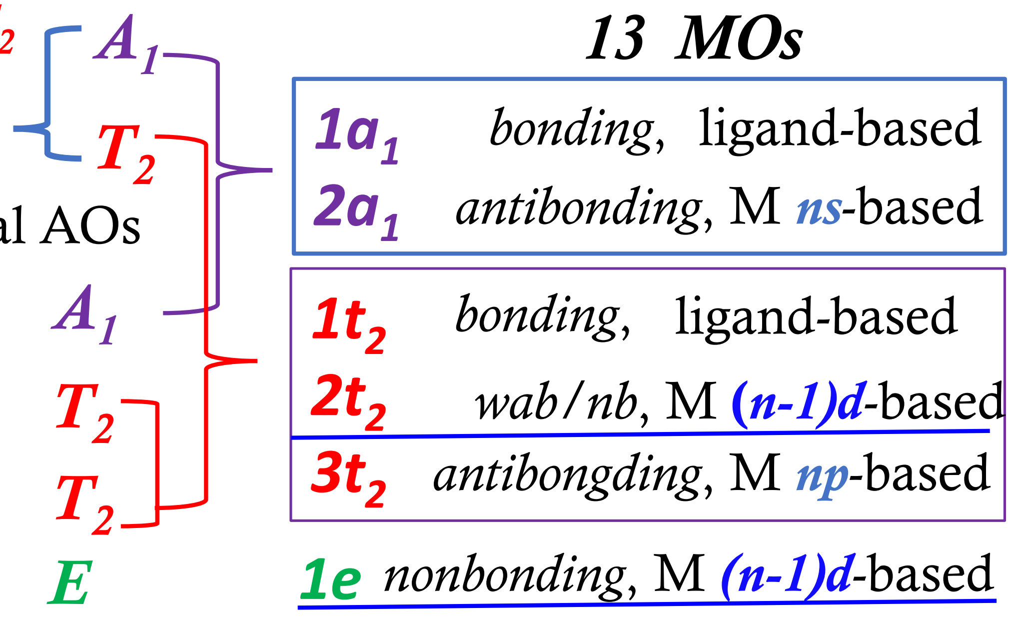
- *4 σ-type* ligand orbitals (each like a s-type AO)



T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$((2z^2-x^2-y^2), \sqrt{3}(x^2-y^2))$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)	(yz, xz, xy)

basis {4σ} → Γ **4 1 0 0 2** $= A_1 \oplus T_2$

(Q: plz write out their forms after class!) IR of ligand SOs



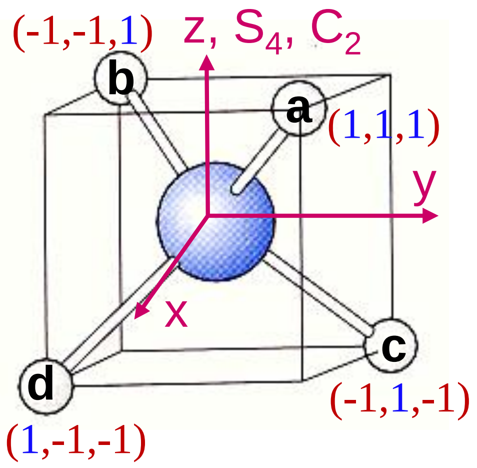
13 MOs

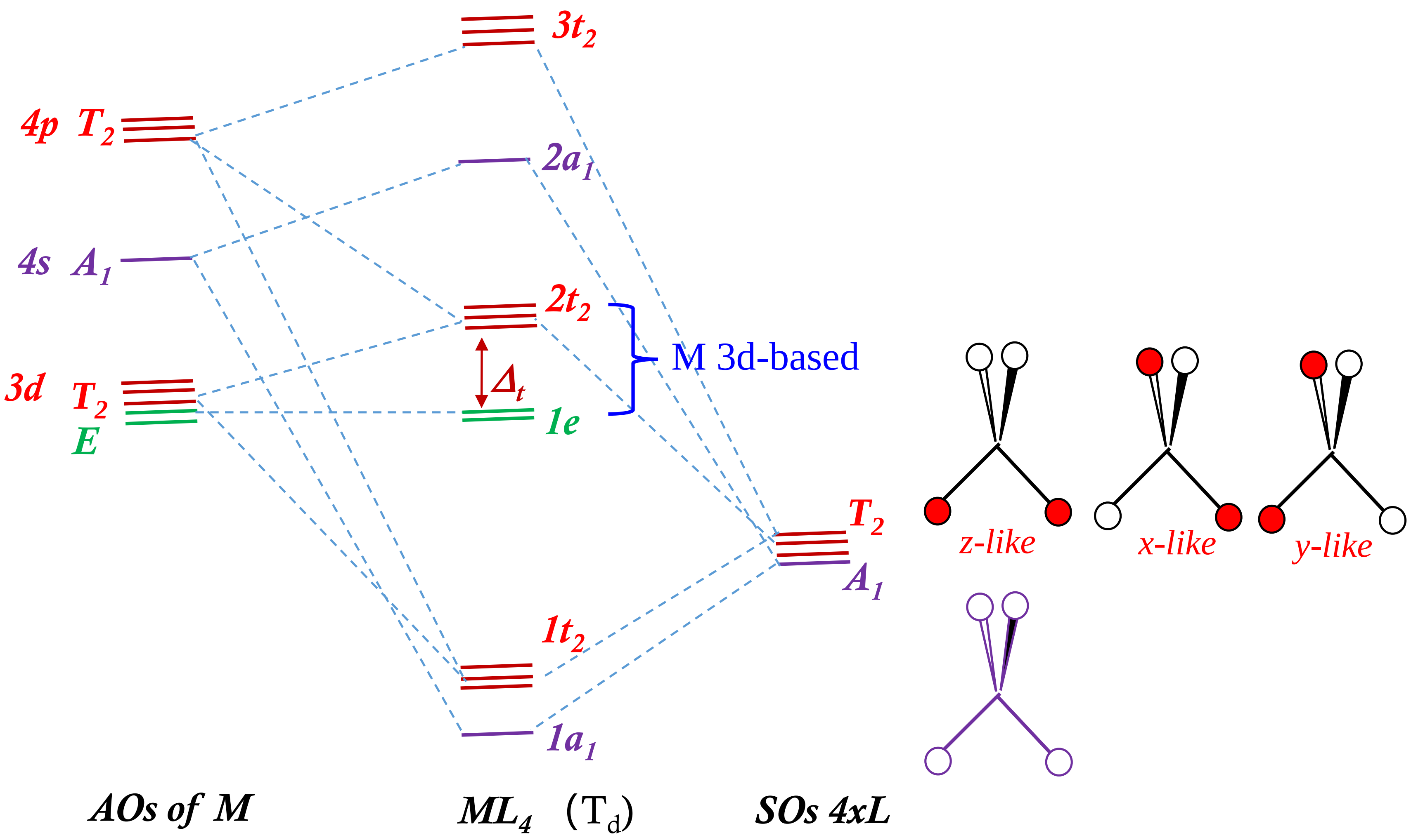
$1a_1$	*bonding*, ligand-based
$2a_1$	*antibonding*, M ***ns***-based
$1t_2$	*bonding*, ligand-based
$2t_2$	*wab/nb*, M ***(n-1)d***-based
$3t_2$	*antibongding*, M ***np***-based
$1e$	*nonbonding*, M ***(n-1)d***-based

cartesian function	corresponding orbital(s)
	$4s$
(x, y, z)	$4p_x, 4p_y, 4p_z$
(xz, xy, yz)	$3d_{xz}, 3d_{xy}, 3d_{yz}$
$(2z^2-x^2-y^2), (x^2-y^2)$	$3d_{z^2}, 3d_{x^2-y^2},$

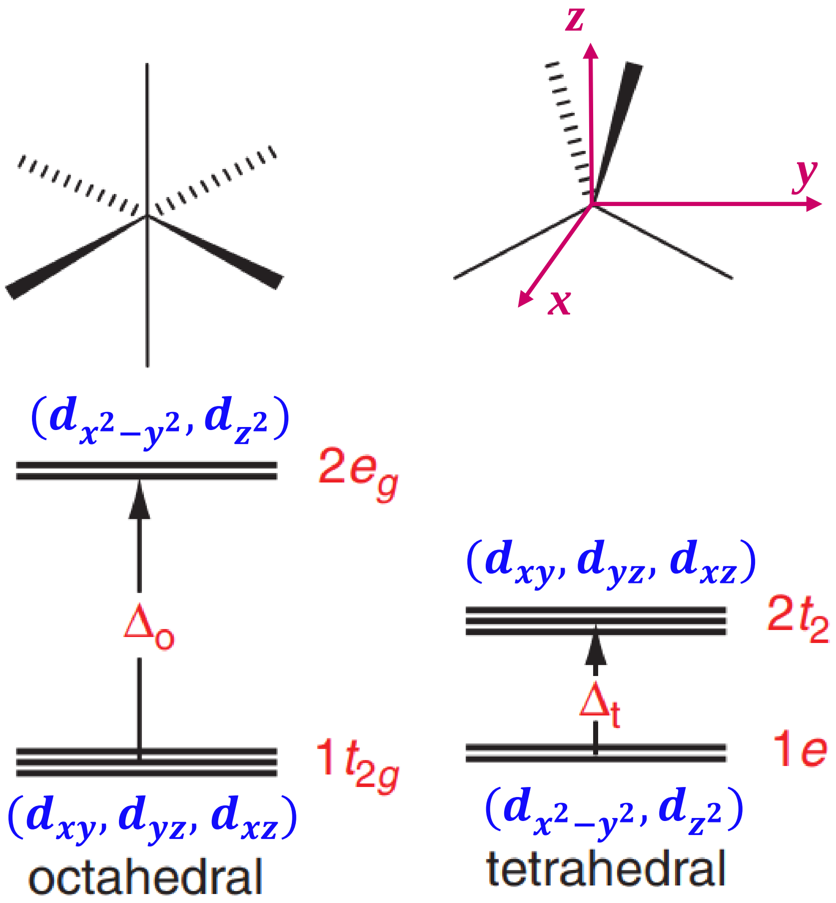
IR of metal AOs

MO diagram of tetrahedral metal complex, ML_4



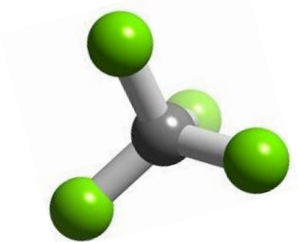


5.5.8 Other coordination geometries



metal-based MOs of the octahedral and tetrahedral complexes.

- In the ***octahedral complex*** the ***lobes*** of the ***3d*** AOs ($2e_g$) point directly at the ligands, whereas this is not for the *tetrahedral* complex. ***The former therefore has a stronger bonding interaction*** and, hence, *an elevated energy of* $2e_g$.
- In the ***tetrahedral*** case, the separation between the metal-based orbitals is denoted Δ_t. $\Delta_t \approx 0.44\Delta_o$
- This smaller value for Δ_t means that the exchange term dominates and high-spin complexes are invariably found, e.g., **$[FeCl_4]^{2-}$**.

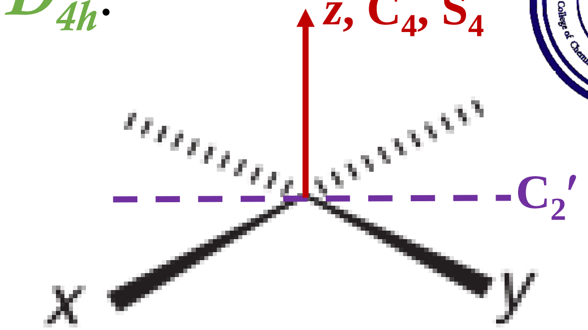


Q: 1) estimate the ***effective magnetic moment*** of $[FeCl_4]^{2-}$;

2) Most tetrahedral transition mental complex prefer a **d^{10}** electronic configuration on its central metal atom. Why?

Square-planar coordination

- The point group D_{4h}:

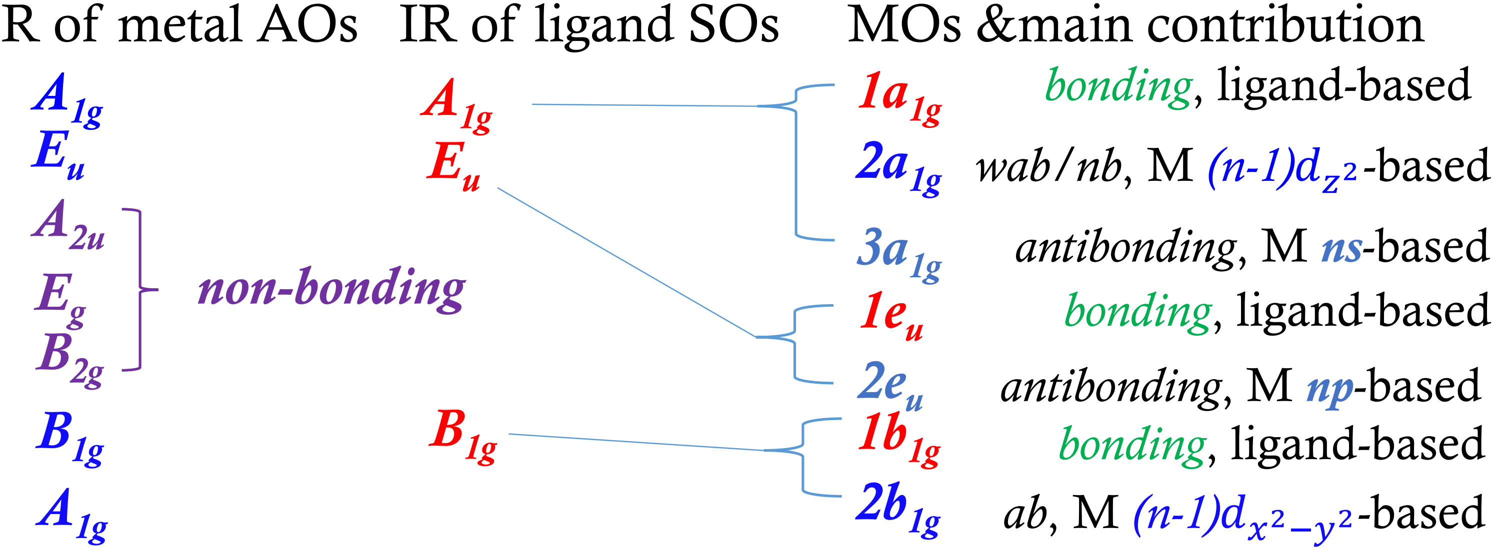


D_{4h}	E	$2C_4$	C_4^2	$2C_2$	$2C_2'$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2; z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

Γ 4 0 0 2 0 0 0 4 2 0 $= A_{1g} \oplus B_{1g} \oplus E_u$

- The four σ-type ligand orbitals.

cartesian function	corresponding orbital(s)
	$4s$
(x, y)	$4p_x, 4p_y$
z	$4p_z$
(xz, yz)	$3d_{xz}, 3d_{yz}$
xy	$3d_{xy}$
x^2-y^2	$3d_{x^2-y^2}$
z^2	$3d_{z^2}$



IR of metal AOs | IR of ligand SOs | MOs &main contribution

A_{1g} | A_{1g}

E_u | E_u

A_{2u}, E_g, B_{2g} *non-bonding*

B_{1g} | B_{1g}

A_{1g}

$1a_{1g}$ *bonding*, ligand-based

$2a_{1g}$ *wab/nb*, M *$(n-1)d_{z^2}$*-based

$3a_{1g}$ *antibonding*, M *ns*-based

$1e_u$ *bonding*, ligand-based

$2e_u$ *antibonding*, M *np*-based

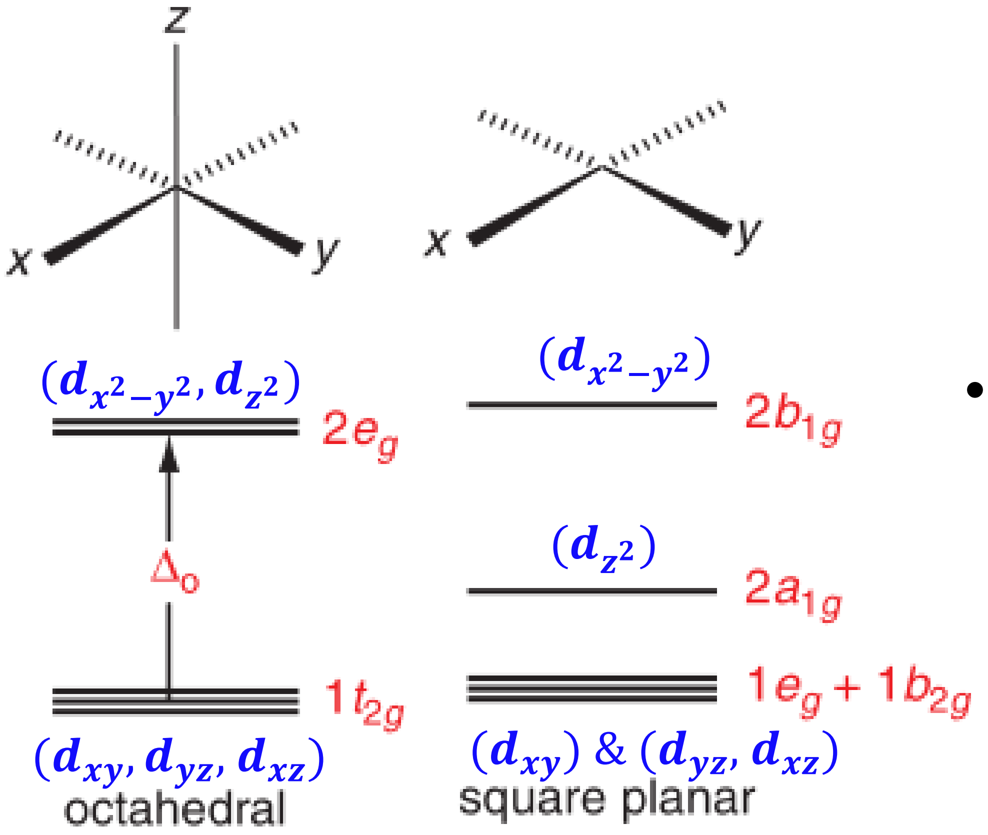
$1b_{1g}$ *bonding*, ligand-based

$2b_{1g}$ *ab*, M *$(n-1)d_{x^2-y^2}$*-based

Square-planar coordination

Ex. 26

- The $d_{x^2-y^2}$ (B_{1g}) AO has a stronger interaction with the ligands than the $3d_{z^2}$ (A_{1g}).



- As a result, among all the metal *(n-1)d*-based MOs, the antibonding ***2b***$_{1g}$ MO is the highest in energy, followed by the antibonding ***2a***$_{1g}$ MO, and the non-bonding ***1e***$_g$ and ***1b***$_{2g}$ MOs.

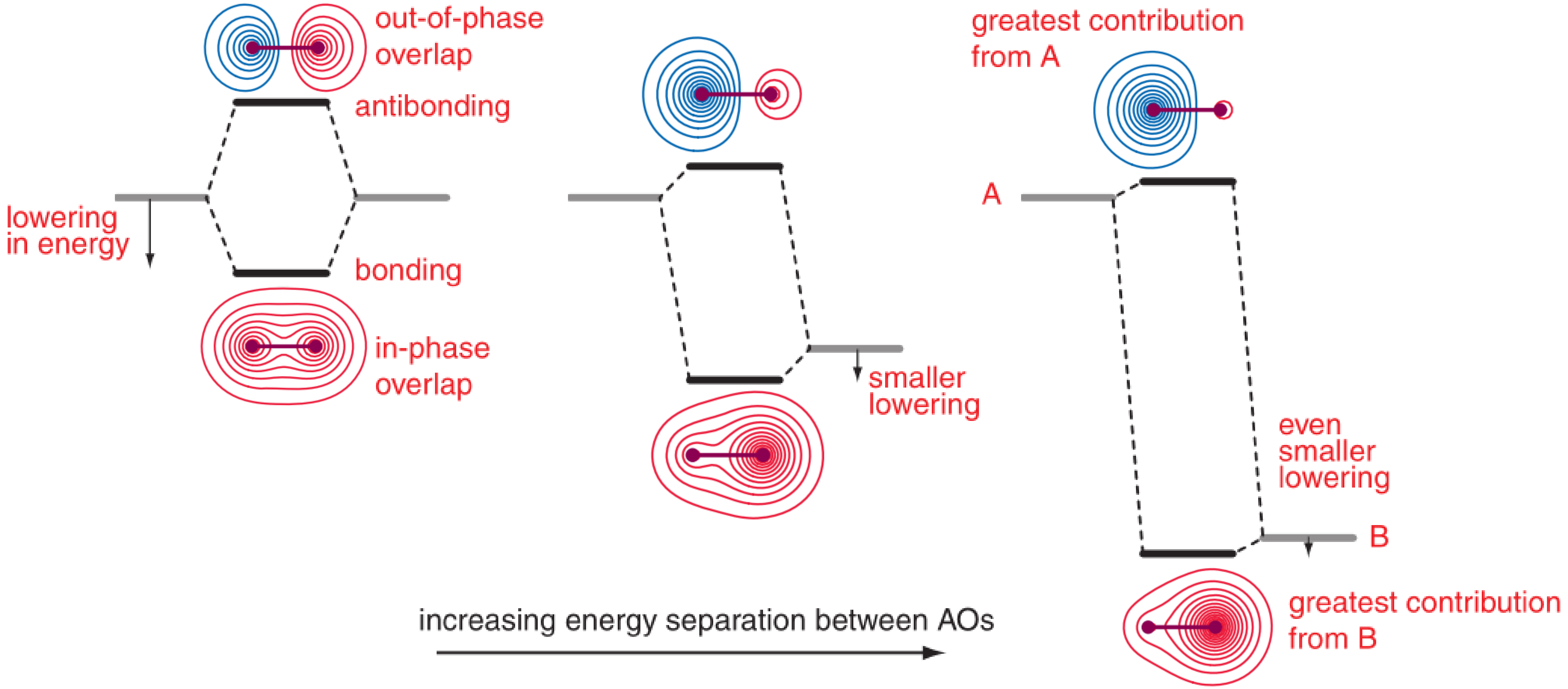
- If ***π*** interactions with the ligands are also present, the ***1e***$_g$ and ***1b***$_{2g}$ orbitals separate, with the ***1b***$_{2g}$ moving higher in energy, possibly above the ***2a***$_{1g}$.

(Is the ligand π-donor or π-acceptor?)

Q: Why does the central metal cation in a stable square-planar coordination complex prefer a ***(n-1)d***^{8} configuration?

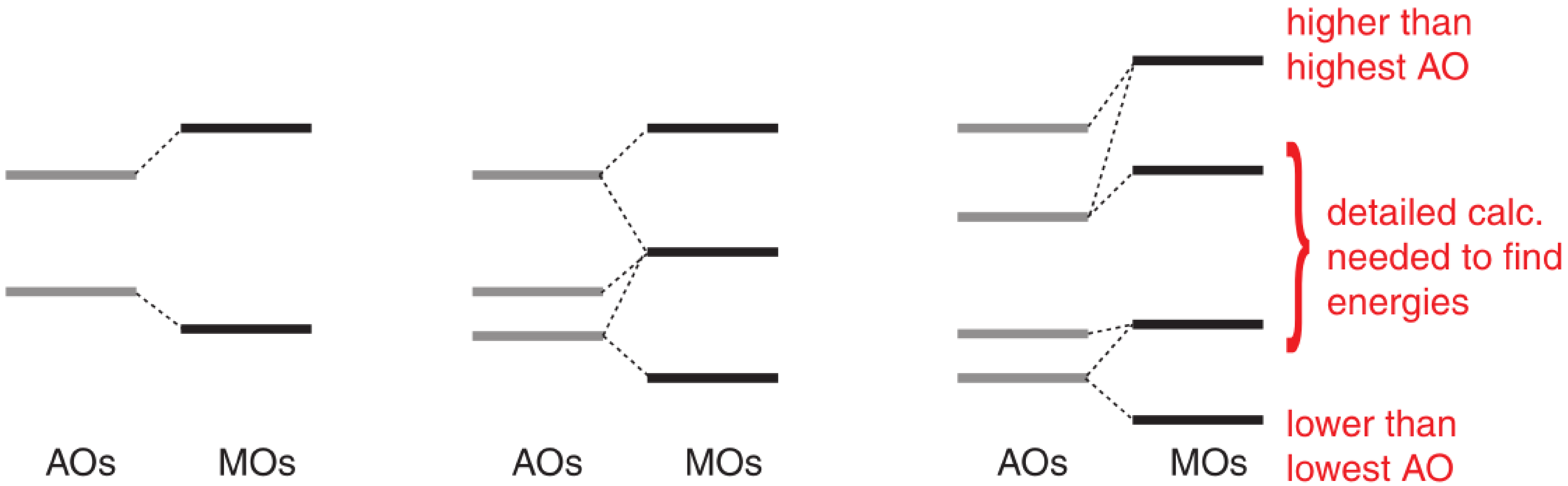
Summary

1. When two AOs interact, a bonding MO is formed which is lower in energy than the lowest energy AO and an antibonding MO is formed which is higher in energy than the highest energy AO.



Summary

2. When several AOs interact to form MOs, the number of the MOs is the same as the number of the AOs.



- In this more complex case it remains true that a particular MO will have the greatest contribution from the AOs which are ***closest to it in energy***.

Summary

3. A ***symmetry orbital*** (SO) is a combination of (usually) atomic orbitals designed so that the combination ***transforms as a single irreducible representation***.

- The form of a particular SO can usually be found by drawing an analogy between its orbital coefficients and a cartesian function which transforms in the same way as the SO.

- In constructing SOs, it is important to spot which groups of AOs are mapped onto one another by the operations of the group, as well as any ***further simplification*** which can arise ***as a result of a judicious choice of a local axis system***.

- SOs can be generated using the ***projection formula***, but this is rarely a convenient process and it fails for degenerate representations.

Summary

4. In transition metal complexes there exist ***high-*** and ***low-spin*** configurations depending on how the electrons are arranged in the predominately metal-based MOs; which is the lower in energy depends on the comparison between the ***ligand field splitting*** and the ***exchange interaction***.

- The characteristic '***double dip***' behaviour of various properties of transition metal complexes can be understood by thinking about how the metal-based MOs are filled.
- ***π donor ligands*** generally ***reduce*** Δ_o, whereas ***π acceptor ligands*** generally ***increase*** Δ_o.
- Ligands can be arranged into a spectrochemical series according to the Δ_o values of the complex.

More considerations

1. How to understand the so-called ***octet rule***, ***eighteen-electron rule*** or even ***the generalized octet rule*** in terms of MO theory?

Rules	**O_i**	**i**	**VO′s**	**Examples**
2e	1	2	s	LiH, LiR, Li2
4e	2	4	sp	BeR_2, R-Mg-Cl
6e	3	6	sp^2	BEt_3, $La(Ph)_3$
8e	4	8	sp^3	CH_4, NF_3, H_2O
10e	5	10	sp^3d	PF_5, SF_4, XeF_2
12e	6	12	sp^3d^2	SF_6, MoF_6, PF_6^-, SiF_6^{2-}
14e	7	14	sp^3d^3/d^5sp	IF_7/ AgI_2^-, $Au(CN)_2^-$
16e	8	16	d^5sp^2	Cp_2Cr, $Au(CN)_4^-$
18e	9	18	d^5sp^3	$Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$

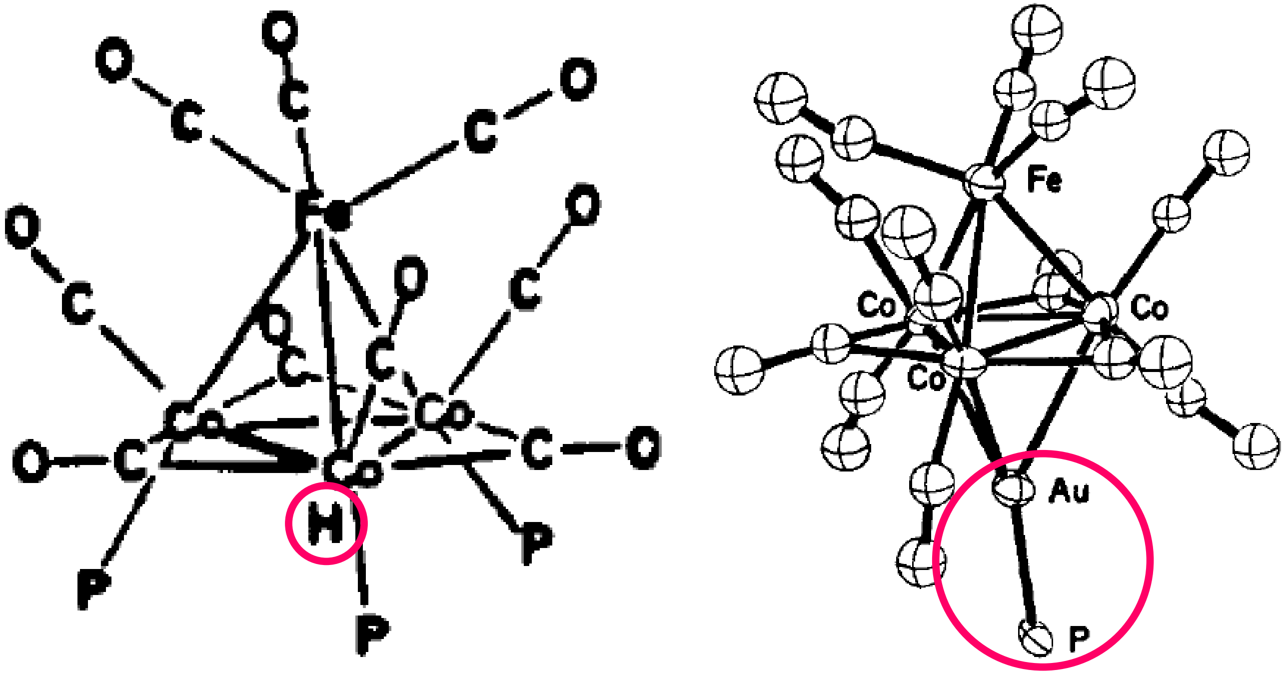
More considerations

2. How to understand the concept of ***Molecular fragment*** and ***isolobal analogy*** (等瓣相似，proposed by Roald Hoffmann) in terms of Molecular orbital theory?

- A molecule can be regarded as a combination of molecular fragments chemically bonded with each other, e.g, ***C_2H_2 as two CH fragments***.
- Molecular fragments having ***same number of VEs*** (or ***$VE_a = VE_b$-10***) and ***similar frontier orbitals*** are ***isolobal***.
- A fragment in a molecule can be substituted with an isolobal fragment. e.g., **CR_2 vs $Fe(CO)_4$**, → Metal-carbene complexes: **$(L)_nM{=}CR_2$**
- ***Isolobal analogy*** has been widely exploited in synthetic chemistry and led to the production of numerous cluster compounds.

Early experimental evidences of isolobal $AuPR_3$ ~H analogy.

- isostructural $[Co(CO)_4$**X**$]$ (**X=H, $AuPR_3$**)
- isostructural $[FeCo_3(CO)_{12}(\mu_3$-**X**$)]$ (**X=H, $AuPR_3$**) compounds



- Blundell and Powell, *J. Chem. Soc. A*, **1971**, 1685;
- McNeil and Scholer, *J. Am. Chem. Soc.* **1977**, *99*, 6243.
- Lauher and Wald, *J. Am. Chem. Soc.* **1981**, *103*, 7649.

3. Polyhedral Skeletal Electron Pair Theory (PSEPT)

--also known as ***Wade's rules*** or ***Wade-Mingos rules***

- PSEPT provides electron counting rules useful for predicting the structures of clusters such as borane and carborane clusters.
- The rules were originally formulated by Kenneth Wade and were further developed by Michael Mingos and others;
- The rules are based on a molecular orbital treatment of the bonding.
- These rules have been extended and unified in the form of the ***Jemmis mno rules.***

Wade, K. J. Chem. Soc. D. ***1971****: 792–793.*
Mingos, D. M. P. *Nature Physical Science*. 1972, **236**: 99–102.
Jemmis, E. D. et al. *J. Am. Chem. Soc.2001*, **123** (18): 4313–4323

MOs of linear AH$_2$ ($D_{\infty h}$)

- A: 1s ~Σ_g^+ (core AO)

  2s~Σ_g^+

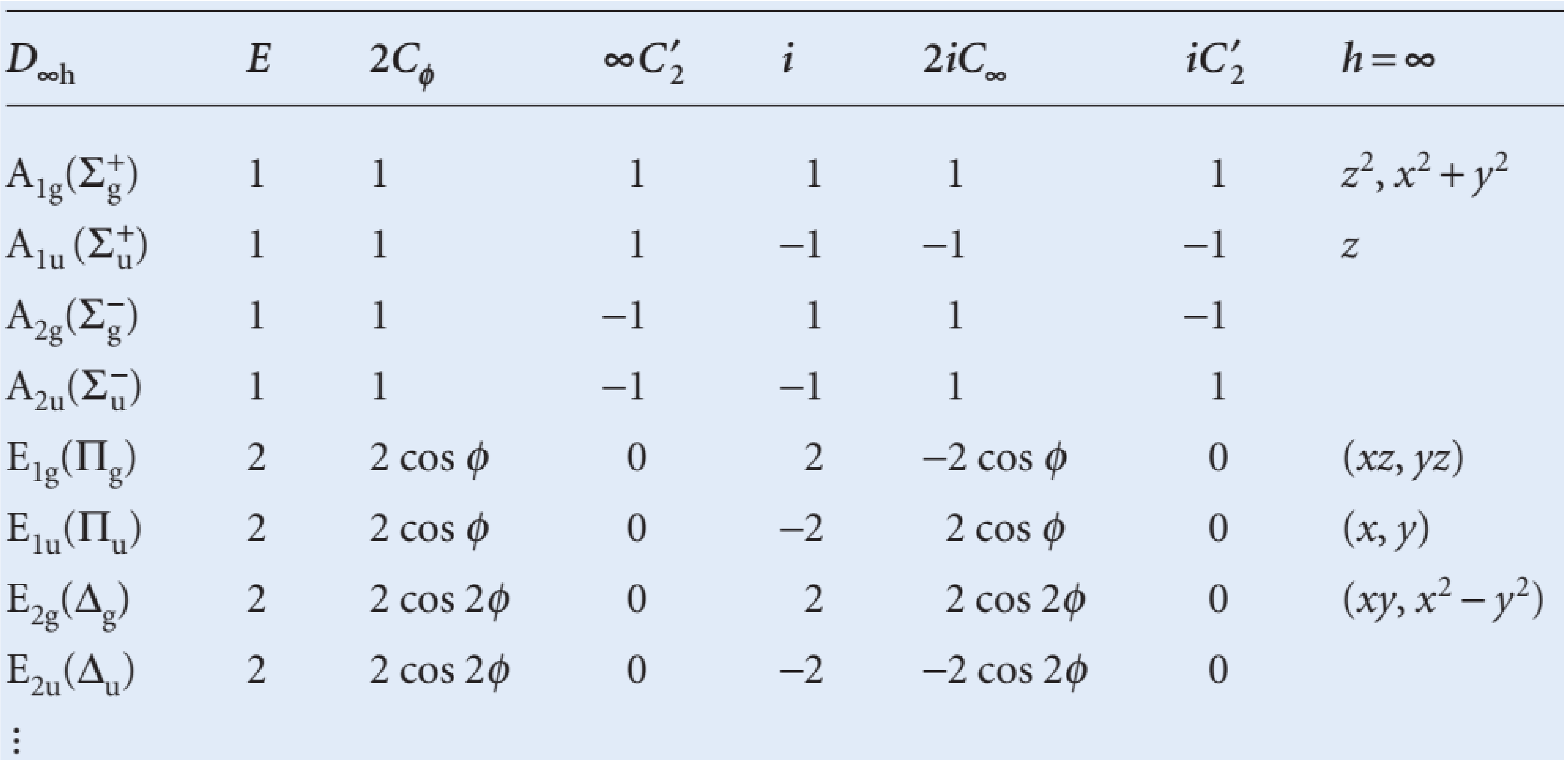
  2p$_z$ ~Σ_u^+

  (2p$_x$,2p$_y$)~ Π_u

2H 1s:

(s$_A$ +s$_B$) ~Σ_g^+

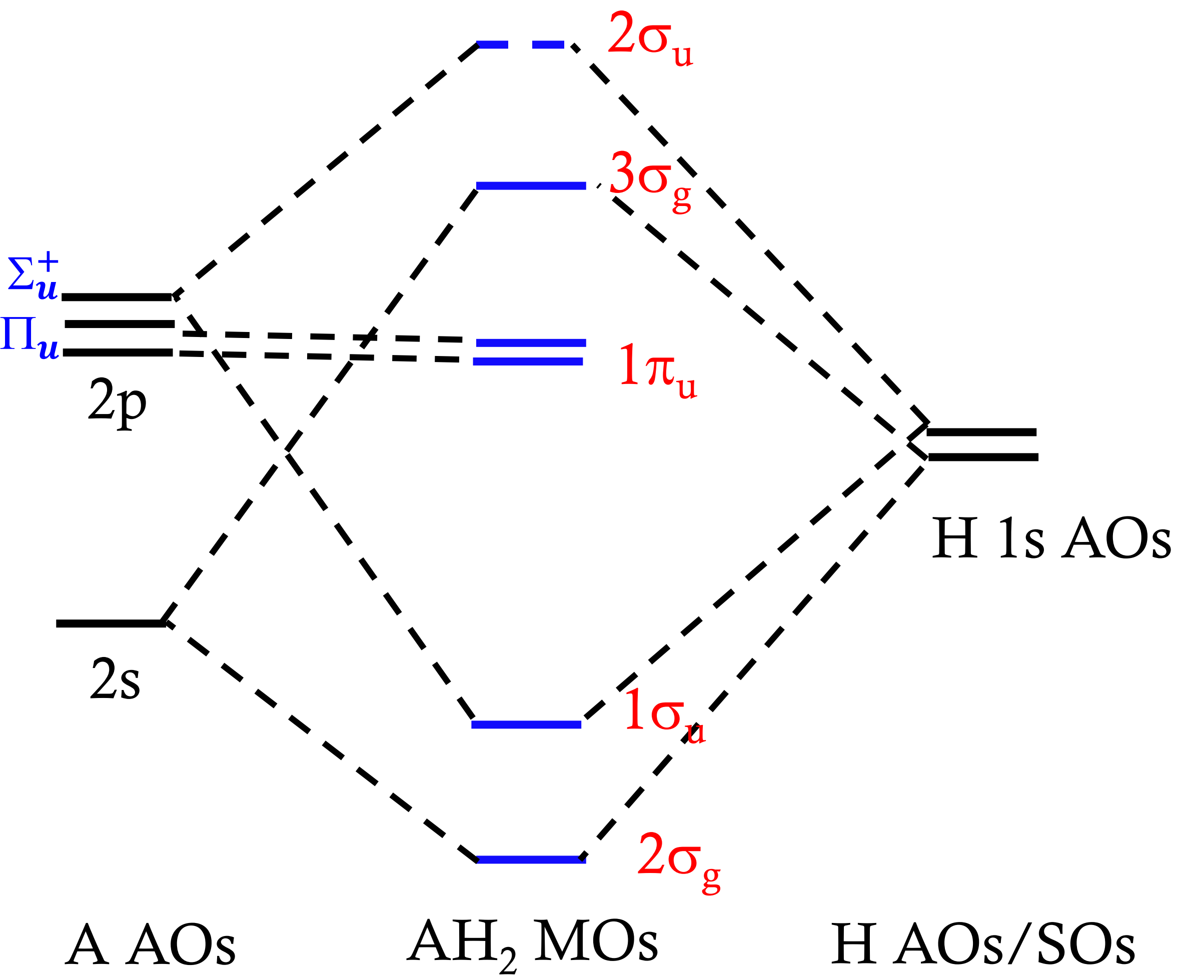
(s$_A$ - s$_B$) ~Σ_u^+

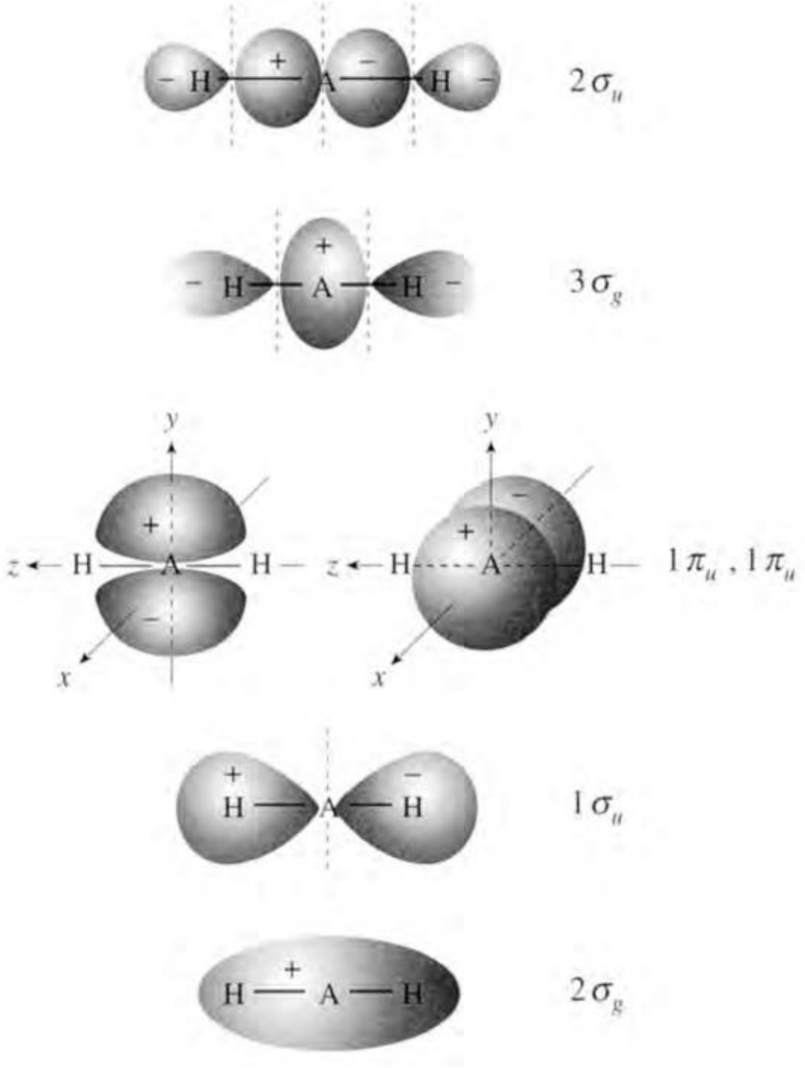


$D_{\infty h}$	E	$2C_\phi$	$\infty C_2'$	i	$2iC_\infty$	iC_2'	$h=\infty$
$A_{1g}(\Sigma_g^+)$	1	1	1	1	1	1	z^2, x^2+y^2
$A_{1u}(\Sigma_u^+)$	1	1	1	−1	−1	−1	z
$A_{2g}(\Sigma_g^-)$	1	1	−1	1	1	−1	
$A_{2u}(\Sigma_u^-)$	1	1	−1	−1	1	1	
$E_{1g}(\Pi_g)$	2	$2\cos\phi$	0	2	$-2\cos\phi$	0	(xz, yz)
$E_{1u}(\Pi_u)$	2	$2\cos\phi$	0	−2	$2\cos\phi$	0	(x, y)
$E_{2g}(\Delta_g)$	2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0	(xy, x^2-y^2)
$E_{2u}(\Delta_u)$	2	$2\cos 2\phi$	0	−2	$-2\cos 2\phi$	0	
⋮							

MOs of linear AH$_2$ ($D_{\infty h}$)

linear





AH_2 : linear ($D_{\infty h}$) vs. bent(C_{2v})

- BH_2: 4 VEs

L: $2\sigma_g^2 1\sigma_u^2$

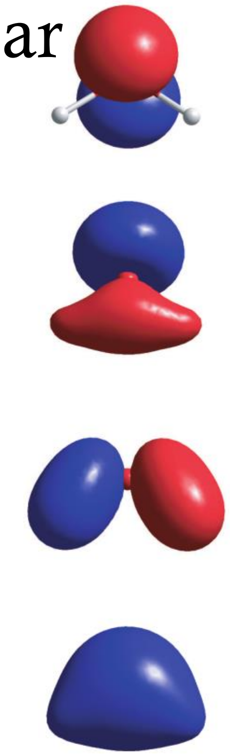
B: $2a_1^2 3a_1^2$

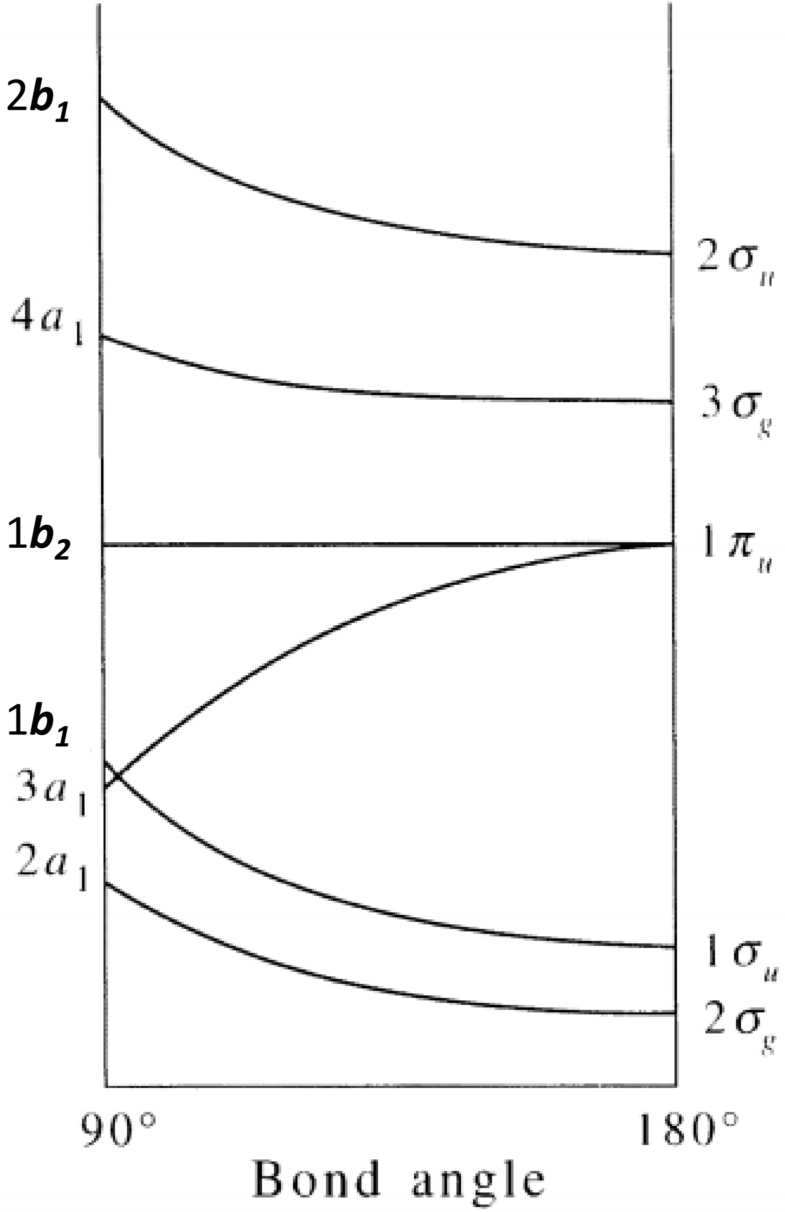
BH_2 prefers the linear structure.

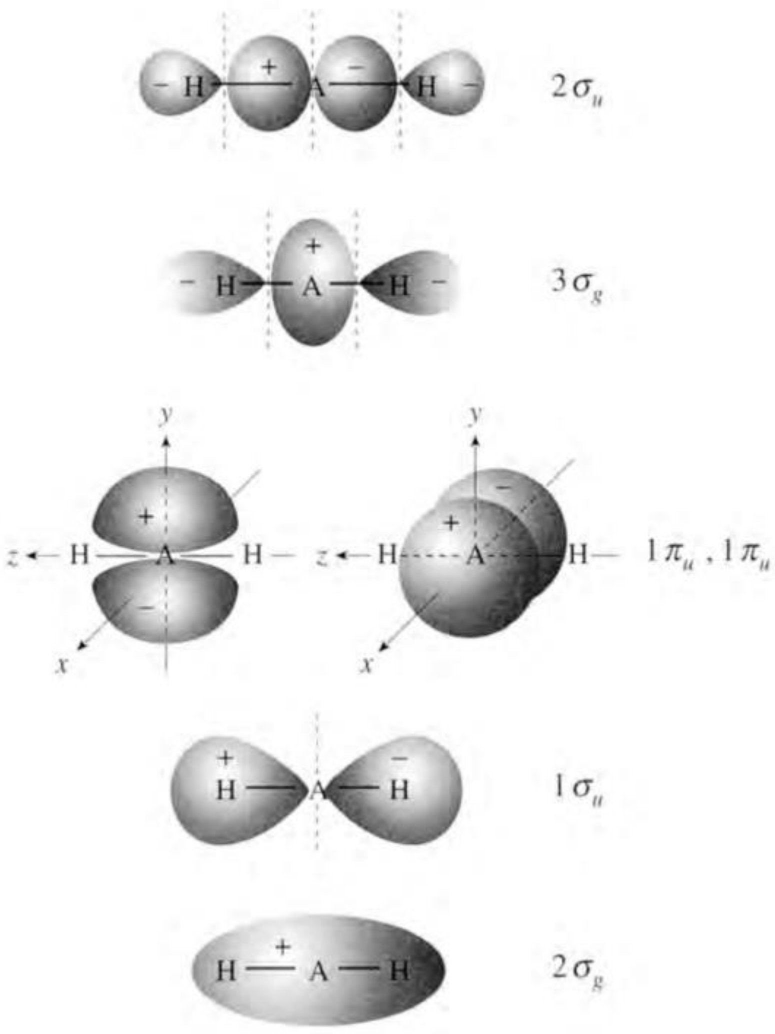
- H_2O: 8 Ves

→ 4 occupied VMOs.

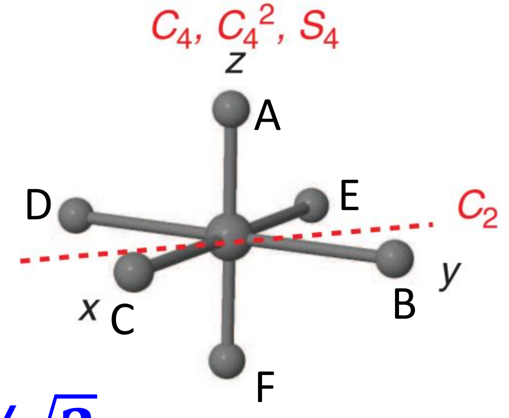
The bent structure has 3 bonding MOs.







SOs arising from the six *s*-type ligand orbitals.



$$\theta_{A_{1g}} = (s_A + s_B + s_C + s_D + s_E + s_F)/\sqrt{6}$$

$$\theta_{T_{1u},x} = (s_C - s_E)/\sqrt{2} \qquad \theta_{T_{1u},y} = (s_B - s_D)/\sqrt{2} \qquad \theta_{T_{1u},z} = (s_A - s_F)/\sqrt{2}$$

$$\theta_{E_g,1} = (s_C + s_E - s_B - s_D)/2 \qquad \theta_{E_g,2} = (2s_A + 2s_F - s_C - s_E - s_B - s_D)/\sqrt{12}$$

PO problem with a degenerate IR: the way-out

- C_6H_6 D_{6h}
- π–MOs formed by six p_z AOs

- Reduce the symmetry of the molecule to pure rotational symmetry C_6.

$\mathcal{G}_6$	$\mathcal{C}_6$	E	C_6	C_3	C_2	C_3^2	C_6^5
R_0	A	1	1	1	1	1	1
R_3	B	1	-1	1	-1	1	-1
R_1	E_1^a	1	ω	ω^2	ω^3	ω^4	ω^5
R_5	E_1^b	1	ω^5	ω^4	ω^3	ω^2	ω
R_2	E_2^a	1	ω^2	ω^4	1	ω^2	ω^4
R_4	E_2^b	1	ω^4	ω^2	1	ω^4	ω^2

$\omega = exp(2\pi i/6)$

$$\hat{P}^{(k)} s_A = \frac{1}{h}\left\{\sum_R [\chi^{(k)}(R)]^* \hat{R}\right\} s_A$$

$\Psi_A = \theta_A = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/6$

$\Psi_B = \theta_B = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)/6$

- For cyclic group, the six equivalent AOs span as

$\Gamma = A \oplus B \oplus E_1 \oplus E_2$

Operation	E	C_6	C_3	C_2	C_3^2	C_6^5
Effect on $p_{z,1}$	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6

$\theta(E_1^a) = (\phi_1 + \omega^5\phi_2 + \omega^4\phi_3 + \omega^3\phi_4 + \omega^2\phi_5 + \omega\phi_6)/6$

$\theta(E_1^b) = (\phi_1 + \omega\phi_2 + \omega^2\phi_3 + \omega^3\phi_4 + \omega^4\phi_5 + \omega^5\phi_6)/6$

$\Psi(E_1^a) = N[\theta(E_1^a) + \theta(E_1^b)] = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$

$\Psi(E_1^b) = N[\theta(E_1^a) - \theta(E_1^b)] = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2$

$\theta(E_2^a) = (\phi_1 + \omega^4\phi_2 + \omega^2\phi_3 + \phi_4 + \omega^4\phi_5 + \omega^2\phi_6)/6$

$\theta(E_2^b) = (\phi_1 + \omega^2\phi_2 + \omega^4\phi_3 + \phi_4 + \omega^2\phi_5 + \omega^4\phi_6)/6$

$\Psi(E_2^a) = N[\theta(E_2^a) + \theta(E_2^b)] = (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/\sqrt{12}$

$\Psi(E_2^b) = N[\theta(E_2^a) - \theta(E_2^b)] = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2$

PO problem with a degenerate IR: the way-out

- C_6H_6 D_{6h}
- π–MOs formed by six p_z AOs $\Gamma = A \oplus B \oplus E_1 \oplus E_2$

$$\Psi_B = \theta_B = (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)/\sqrt{6}$$

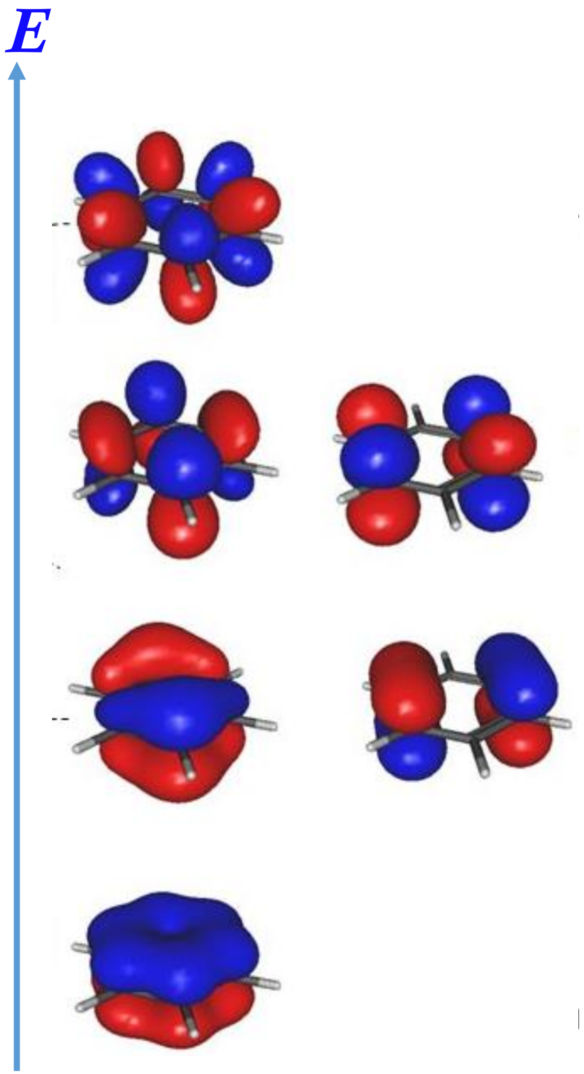
$$\Psi(E_2^{a1}) = (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/\sqrt{12}$$

$$\Psi(E_2^{b1}) = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2$$

$$\Psi(E_1^{a1}) = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$$

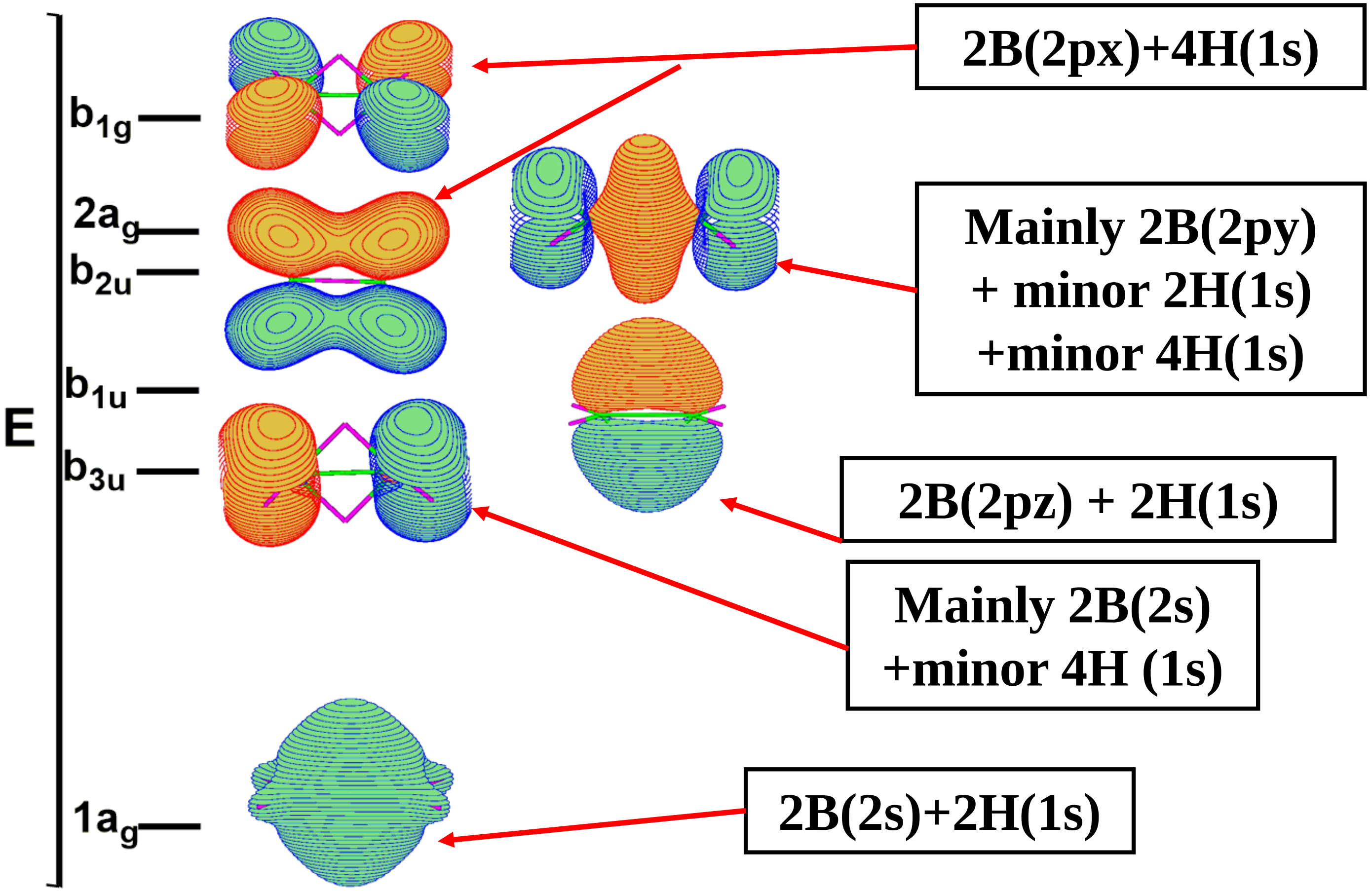
$$\Psi(E_1^{b1}) = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2$$

$$\Psi_A = \theta_A = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)/\sqrt{6}$$



More considerations:

1. Use the MO theory to understand the bonding in electron-deficient boranes and carboranes, e.g., B_2H_6 , as well as the topological rules, e.g., Lipcomb's ***styx*** method and Tang's rule for boranes, Wade's ***(n+1)*** rule for closo-boranes and carboranes.



2B(2px)+4H(1s)

Mainly 2B(2py)
+ minor 2H(1s)
+minor 4H(1s)

2B(2pz) + 2H(1s)

Mainly 2B(2s)
+minor 4H (1s)

2B(2s)+2H(1s)

MOs of fragmental molecular orbitals: LMO view

- CH_2 in $CH_2{=}CH_2$

C sp^2