



# **Part III** Symmetry and Bonding

#### **Chapter 5** Molecular Orbitals (分子轨道)

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## **Reviewing**—direct products



- 如果两个函数分别按不可约表示 「<sup>(i)</sup> 和 「<sup>(i)</sup> 空换, 那么他们的乘积函数当按这两个不可约表示的直积「<sup>(i)</sup> ※」「<sup>(i)</sup> 空换.
- 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, ...) Ø (p, q, r, ...) = (a × p, b × q, c × r, ...)
- •每个点群必有一个全对称不可约表示[<sup>rtot. sym.</sup>-- 所有操作的特征标均为 +1。
- •任一不可约表示**Г<sup>(i)</sup>与全对称不可约表示的直积就是该表示本身**:**Г<sup>(i)</sup>⊗Г<sup>tot. sym.</sup>=Г<sup>(i)</sup>**.
- 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: **Г<sup>(i)</sup> 🖉 Г<sup>(i)</sup> = Г<sup>tot. sym.</sup>**
- 任意高维不可约表示和它自身的直积**Г<sup>(i)</sup> ⊗Г<sup>(i)</sup>**必包含全对称不可约表示**Г<sup>tot. sym.</sup>。**
- 标量(数字) (numbers) 按全对称不可约表示变换。



# Reviewing—vanishing integrals



- 1. 若函数 $\psi$ 不按全对称不可约表示变换,则其积分 $I = \int \psi d\tau$  必为 $\overline{\phi}$ .
- 2. 若两个原子的AO波函数 $\psi_i$ 和  $\psi_j$ 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,<u>对称性相同(依同一不可约表示变换)的原子轨道间才</u>可以有效重叠。

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  $\Gamma^{(i)} \otimes \Gamma^{(i)} \otimes \Gamma^{(j)}$ 不含全对称不可约表示。

4. 哈密顿算符必然按全对称不可约表示变换(?!),若两个原子的AO波函数 $\psi_i$ 和 $\psi_j$ 不依同一不可约表示变换,则交换积分 $\beta_{ij} = \int \psi_i^* \hat{H} \psi_j d\tau$ 必为零。即<u>对称性相同(依</u>同一不可约表示变换)的原子轨道间才可以有效成键,形成分子轨道。



#### 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, CMO) 图像,而非大一时学过的定域分子轨道(LMO)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, SOs.
- 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.)



# 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.





# 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.





#### **5.2 MO diagram for water**

- Example:  $H_2O$  (point group  $C_{2v}$ )
- The O *Is* AO is too contracted and too low in energy, transforming as *A*<sub>1</sub>.
- *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  $B_2$

 $C_2^z \sigma^{xz}$  $C_{2v}$  $\sigma^{yz}$ E $x^2; y^2; z^2$ 1  $A_1$ 1 Z  $A_2$ 1 -1 -1  $R_z$ xy -1 1 -1  $x R_v xz$  $B_1$ -1 -1 1  $y R_x$  $B_2$ 1 *yz* 2 0 2 0  $\Gamma = A_1 \oplus B_1$  $(s_a, s_b)$ By inspection! (For AOs without equivalent AOs)



• 2H:  $(s_a, s_b) A_1 \bigoplus B_1$  (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)  $O2p_x(\boldsymbol{B_1}) + \text{the } \boldsymbol{B_1} SO(\boldsymbol{\theta_2}) \text{ of } H1s.$ 

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

→ Two MOs with  $B_1$  symmetry! (in-phase & out-of-phase) 2) O2s,  $2p_z(A_1)$  + the  $A_1$  SO.  $\psi(A_1) = d_1 2s + d_2 p_z + d_3 \theta_1$  ( $d_1 \sim d_3 \sim \text{coefficients}$ )

 $\rightarrow$  Three MOs with  $A_1$  symmetry!

3)  $O2p_y$  gives a non-bonding MO with  $B_2$  symmetry !  $\rightarrow$  A total of six VMOs (valence molecular orbitals)





# 5.2 MO diagram for water Labelling the MOs

- The inner **O1s** gives the lowest-energy, nonbonding *MO* of *A*<sub>1</sub>*IR*, therefore labelled *1a*<sub>1</sub>.
- The O2p<sub>y</sub> gives a non-bonding *MO* of *B*<sub>2</sub>*IR*, labelled *1b*<sub>2</sub>.
- The O2p<sub>x</sub> interacts with the **B**<sub>1</sub> SO to form a bonding MO 1b<sub>1</sub> and an anti-bonding MO 2b<sub>1</sub>.
- The O2p<sub>z</sub> and 2s interact with the A<sub>1</sub> SO to give *three MO*s, labelled 2a<sub>1</sub>, 3a<sub>1</sub> and 4a<sub>1</sub>.
- Computer calculation is needed to determine the position of  $3a_1$  in relation to  $1b_1$  and  $1b_2$ .
- 8 VEs  $\rightarrow$  The lowest four VMOs are occupied.
- Electronic configuration:  $2a_1^2 1b_1^2 3a_1^2 1b_2^2$

Molecular-orbital diagram of H<sub>2</sub>O

 $(C_{2v})$ 







#### Form of the MOs

• We can also make some educated guesses about *the form of the MOs*.

 $B_2$ 

 $B_1$ 

 $A_1$ 

- The  $lb_2$  MO is solely the O2p<sub>y</sub> AO.
- The interaction of the O  $2p_x$  and  $\theta_2$  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*<sub>1</sub> gives *three* MOs:
- ➤ The A₁ MO, 2a₁, arises from in-phase combination of the O2s, O2p₂ (minor) and the θ₁ SO.
- ➢ The 3a₁ MO arises from out-of-phase combination of O2s (minor) and in-phase combination of O2p₂ (major) with the θ₁ SO.







#### Form of the MOs

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





#### $H_2$ O的占据分子轨道 & PES







# 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 <mark>SO</mark>s:

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

(2) by use of the *projection formula* (投影公式).

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	$2C_{3}$	$3C_{2}$	$\sigma_h$	2 <i>S</i> <sub>3</sub>	$3\sigma_v$	
$A'_1$	1	1	1	1	1	1	$x^2 + y^2; z^2$
$A'_2$	1	1	-1	1	1	-1	$R_z$
$E^{\overline{\prime}}$	2	-1	0	2	-1	0	$(x, y)$ $(x^2 - y^2, 2xy)$
$A_1^{\prime\prime}$	1	1	1	-1	-1	-1	
$A_2^{\prime\prime}$	1	1	-1	-1	-1	1	Ζ.
$E^{\prime\prime}$	2	-1	0	-2	1	0	$(R_x, R_y)$ $(xz, yz)$
Г	3	0	1	3	0	1	$= \mathbf{A_1'} \oplus \mathbf{E'}$
(S <sub>A</sub> (S <sub>C</sub> )	S <sub>B</sub>	) . Sc <sup>1</sup>	(SA)	 S <sub>B</sub>	(S <sub>P</sub> S <sub>C</sub> )	A) SB	S <sub>A</sub> S <sub>A</sub> S <sub>C</sub> S <sub>B</sub> S <sub>C</sub> S <sub>B</sub>
C <sub>3</sub>	3		<i>C</i> <sub>2</sub>		σι	b	$S_3$ $\sigma_v$

 Obviously, the combination of the hydrogen *Is* AOs which transforms as the totally symmetric *IR A*<sup>'</sup><sub>1</sub> 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*',







#### **5.3.1** SOs in BH<sub>3</sub>



• Hence the three H 1s AOs in  $BH_3$  give the following three SOs,

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

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





# 5.3.2 Normalization of symmetry orbitals

- In quantum mechanics a wavefunction  $\psi$  is normalized if
- If a wavefunction  $\psi$  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  $\Phi_i$ :

 $\boldsymbol{\theta} = \boldsymbol{c}_1 \boldsymbol{\Phi}_1 + \, \boldsymbol{c}_2 \boldsymbol{\Phi}_2 + \, \boldsymbol{c}_3 \boldsymbol{\Phi}_3 + \cdots$ 

If the AO wavefunctions are themselves normalized, and if we assume that the AOs on different (but symmetrically equivalent) atoms *do not overlap*, i.e.,  $\int \Phi_i \Phi_j d\tau = \delta_{ij} = \theta$  ( $i \neq j$ ) the SO can be normalized as  $\theta = \frac{c_1 \Phi_1 + c_2 \Phi_2 + c_3 \Phi_3 + \dots}{\sqrt{c_1^2 + c_2^2 + c_3^2 + \dots}}$ 

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



 $\psi^*\psi d\tau = 1$ 





# 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  $\theta_{E',y} = \frac{1}{\sqrt{6}}(2s_A s_B s_C)$
- By 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<sub>3</sub>

$D_{3h}$	E	$2C_{3}$	$3C_2$	$\sigma_h$	2 <i>S</i> <sub>3</sub>	$3\sigma_v$	
$A'_1$	1	1	1	1	1	1	
$A'_2$	1	1	-1	1	1	-1	
$E^{\tilde{\prime}}$	2	-1	0	2	-1	0	(x, y)
$A_1^{\prime\prime}$	1	1	1	-1	-1	-1	
$A_2^{\prime\prime}$	1	1	-1	-1	-1	1	z
$E^{\tilde{\prime}\prime}$	2	-1	0	-2	1	0	

- H:  $(s_A, s_B, s_C) \rightarrow SOs: A'_1, E'$
- 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  $A_I$ '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<sub>x</sub> and SO<sub>y</sub>, respectively.



• 6 VEs





#### 5.3.4 SOs in 'OH<sub>4</sub>'

• Example: a hypothetic molecule  $OH_4$  in a square planar geometry  $(D_{4h})$ .  $4xH1s \rightarrow 4$  SOs

$D_{4h}$	E	$2C_4$	$C_4^2$	$2C_2$	$2C'_2$	i	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$			• We encounter 2-dimensional IR
$A_{1g}$ $A_{2g}$ $B_{1g}$ $B_{2g}$ $E_g$ $A_{1u}$ $A_{2u}$ $B_{1u}$ $B_{2u}$	$     \begin{array}{c}       1 \\       1 \\       1 \\       2 \\       1 \\       1 \\       1 \\       1 \\       1 \\       1 \\       1 \\       1   \end{array} $	$ \begin{array}{c} 1 \\ -1 \\ -1 \\ 0 \\ 1 \\ -1 \\ -1 \\ -1 \\ -1 \end{array} $	$     \begin{array}{c}       1 \\       1 \\       1 \\       -2 \\       1 \\       1 \\       1 \\       1 \\       1 \\       1 \\       1   \end{array} $	$ \begin{array}{c} 1 \\ -1 \\ 1 \\ -1 \\ 0 \\ 1 \\ -1 \\ 1 \\ -1 \\ 1 \end{array} $	$ \begin{array}{c} 1 \\ -1 \\ -1 \\ 1 \\ 0 \\ 1 \\ -1 \\ -1 \\ 1 \end{array} $	$ \begin{array}{c} 1 \\ 1 \\ 1 \\ 2 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 \end{array} $	$ \begin{array}{c} 1 \\ -1 \\ -1 \\ 0 \\ -1 \\ -1 \\ 1 \\ 1 \end{array} $	$ \begin{array}{c} 1 \\ 1 \\ 1 \\ -2 \\ -1 \\ -1 \\ -1 \\ -1 \\ -1 \end{array} $	$ \begin{array}{c} 1 \\ -1 \\ 1 \\ -1 \\ 0 \\ -1 \\ 1 \\ -1 \\ 1 \end{array} $	$ \begin{array}{c} 1 \\ -1 \\ -1 \\ 1 \\ 0 \\ -1 \\ 1 \\ 1 \\ -1 \end{array} $	$R_z$ $(R_x, R_y)$ $z$	$x^{2} + y^{2}; z^{2}$ $x^{2} - y^{2}$ $xy$ $(xz, yz)$	again. • $A_{1g}$ ~ totally symmetric IR. • $\theta_{A_{1g}} = s_A + s_B + s_C + s_D$ (Note: $(x^2+y^2)$ transforms as $A_{1g}$ .)
$\frac{E_u}{E_u}$	<u>2</u> 4	0 0	-2 0	0	<u>0</u> 2	-2 0	0 0	2	0 0	<u>0</u> 2	$(x, y)$ $A_{1g} \oplus$	$\overline{B_{2g} \oplus E_u}$	• ( <i>x</i> , <i>y</i> ) transforms like <i>E<sub>u</sub></i> and <i>xy</i> transforms like <i>B<sub>2g</sub></i> .
B z(		A D		$C_4, S_4$		)		)	(	$C_2$	σ <sub>ν</sub> <i>c</i> <sub>2</sub> ', σ <sub>d</sub>		• Now make the coefficients match the corresponding functions.



# 5.3.4 SOs in 'OH<sub>4</sub>'



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







# 5.3.5 Constructing SOs in an intelligent way

- Example: BF<sub>3</sub> (point group  $D_{3h}$ ). F: 2s,  $2p_x$ ,  $2p_y$ ,  $2p_z$
- Three F 2s AOs  $\rightarrow$  three SOs (A<sub>1</sub>'  $\oplus$  E'); three F 2p<sub>z</sub> AOs  $\rightarrow$  three SOs. (Q11!)
- However, the  $2p_x$  and  $2p_y$  AOs are all mixed together in a rather complicated way by the operations of the group,  $2p_{y}$ 2p<sub>7</sub> producing an annoying ?-D rep.! How to simplify the situation? • The situation can be simplified by Set 1 Set 2 using a different *local axis system*. • Now the **SO**s for **set 1** is similar to those for the 2s AOs.





 $D_{3h}$ 

 $\begin{array}{c} A_1'\\ A_2'\\ E' \end{array}$ 

 $A_1^{\prime\prime}$ 

 $A_2^{\prime\prime}$ 

 $E^{\prime\prime}$ 

E

2

2

 $2C_3$ 

Finding the SOs

 $\sigma_h$ 

2

-1

-2

 $3C_2$ 

0

0



• Now find the characters of the  $x^2 + y^2; z^2$  • Now find the characters of the representation in the basis of the three  $2p_z$  AOs. (Q11) ( $x^2 - y^2, 2xy$ ) •  $\theta_{A_2}'' = p_{z,A} + p_{z,B} + p_{z,C}$ (xz, yz) •  $\theta_{E''xz} = p_{z,B} - p_{z,C}$ 



 $^{-1}$ 



 $2S_3$ 

-1

-1

 $3\sigma_v$ 

-1

-1

0

0

(x, y)

 $\mathcal{Z}$ 

 $p_{z,A}$ 

 $R_z$ 

 $(R_x, R_y)$ 

 $\sigma_h$ 

 $= A_2'' \oplus E''$ 

 $-\overline{p}_{z,C}$ 

-p<sub>z.A</sub>

 $-p_{z,B}$ 







Finding the SOs



**Ex. 18** 





#### 5.3.6 One last example



 $- C_2^x$ 

 $C_2^z$ 

•  $C_2H_4$ , point group  $D_{2h}$ 

 $\sigma^{xy}$ 



• Constructing the SOs arising from the four hydrogen *Is* AOs in  $C_2H_4$ .





#### 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 <u>it does not work</u> <u>straightforwardly for two- and higher-dimensional *IRs*.</u>
- 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,

$$\boldsymbol{\theta}^{(k)} = \widehat{\boldsymbol{P}}^{(k)} \boldsymbol{\phi}_{\boldsymbol{i}} \qquad \sim Projection \ formula$$

in which *the projection operator* is

$$\widehat{P}^{(k)} = \frac{1}{h} \sum_{\widehat{R}} \left[ \chi^{(k)}(\widehat{R}) \right]^* \widehat{R}$$
Sum over all symmetry operations



# 5.4.1 SOs in H<sub>2</sub>O

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







- For the SO that transforms as  $A_1$ ,  $\widehat{P}^{(A_1)}s_A = (s_A + s_B)/2$
- For the SO that transforms as  $B_1$ ,

$$\widehat{\boldsymbol{P}}^{(B_1)}\boldsymbol{s}_A = (\mathbf{s}_A - \mathbf{s}_B)/2$$

• Using the projection operator for the IR  $A_2$  gives

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



В

#### 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  $s_A$

 $S_A$ 

effect of E

 $\widehat{E}s_A = s_A$ 

effect of *i* 

 $is_{A}$ 





#### 5.4.2 SOs in ethene



ERSITAS AMOUNT					$D_2$	$\sim a si$	ubgrou	$p of D_{2h}$	1921 The state of the state of
Operation	E	$C_2^{z}$	$C_2^{v}$	$C_2^x$	i	$\sigma^{xy}$	$\sigma^{xz}$	$\sigma^{yz}$	
Effect on s <sub>A</sub>	<u>s</u>	s <sub>C</sub>	<u> </u>	<u> </u>	s <sub>C</sub>	S <sub>A</sub>	s <sub>D</sub>	s <sub>B</sub>	
Characters for $A_{g}$	1	1	1	1	1	1	1	1	
Result	S <sub>A</sub>	s <sub>C</sub>	s <sub>B</sub>	s <sub>D</sub>	s <sub>C</sub>	S <sub>A</sub>	s <sub>D</sub>	s <sub>B</sub>	$=(2s_A + 2s_B + 2s_C + 2s_D)/8$
Characters for $B_{1g}$	1	1	-1	-1	1	1	-1	-1	
Result	s <sub>A</sub>	s <sub>C</sub>	-s <sub>B</sub>	-s <sub>D</sub>	s <sub>C</sub>	S <sub>A</sub>	-s <sub>D</sub>	-s <sub>B</sub>	$=(2s_A - 2s_B + 2s_C - 2s_D)/8$
Characters for $B_{2u}$	1	-1	1	-1	-1	1	-1	1	
Result	s <sub>A</sub>	-s <sub>C</sub>	S <sub>B</sub>	-s <sub>D</sub>	-s <sub>C</sub>	S <sub>A</sub>	-s <sub>D</sub>	s <sub>B</sub>	$=(2s_A + 2s_B - 2s_C - 2s_D)/8$
Characters for $B_{3u}$	1	-1	-1	1	-1	1	1	-1	
Result	S <sub>A</sub>	-s <sub>C</sub>	-s <sub>B</sub>	s <sub>D</sub>	-s <sub>C</sub>	S <sub>A</sub>	s <sub>D</sub>	-s <sub>B</sub>	$=(2s_A - 2s_B - 2s_C + 2s_D)/8$

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	$2C_{3}$	$3C_{2}$	$\sigma_h$	2 <i>S</i> <sub>3</sub>	$3\sigma_v$
$\begin{array}{c} A_1'\\ E' \end{array}$	1	1	1	1	1	1
	2	-1	0	2	-1	0



• The three hydrogen 1s AOs in BH<sub>3</sub> (point group  $D_{3h}$ ) transform as  $A'_1 \oplus E'$ .

Operation	E	$C_3$	$C_{3}^{2}$	$C_{2}^{(a)}$	$C_{2}^{(b)}$	$C_{2}^{(c)}$	$\sigma_h$	<b>S</b> <sub>3</sub>	$S_{3}^{5}$	$\sigma^{(a)}$	$\sigma^{(b)}$	$\sigma^{(c)}$	
Effect on s <sub>A</sub>	S <sub>A</sub>	s <sub>C</sub>	s <sub>B</sub>	S <sub>A</sub>	s <sub>B</sub>	s <sub>C</sub>	s <sub>A</sub>	s <sub>C</sub>	s <sub>B</sub>	s <sub>A</sub>	s <sub>B</sub>	s <sub>C</sub>	
Characters for $A_1'$	1	1	1	1	1	1	1	1	1	1	1	1	
Result	S <sub>A</sub>	s <sub>C</sub>	S <sub>B</sub>	S <sub>A</sub>	s <sub>B</sub>	s <sub>C</sub>	S <sub>A</sub>	s <sub>C</sub>	S <sub>B</sub>	S <sub>A</sub>	s <sub>B</sub>	s <sub>C</sub>	
Characters for <i>E'</i>	2	-1	-1	0	0	0	2	-1	-1	0	0	0	
Result	$2s_A$	-s <sub>C</sub>	-s <sub>B</sub>	0	0	0	$2s_A$	-s <sub>C</sub>	-s <sub>B</sub>	0	0	0	
	······································	2 <sup>(a)</sup>	$C_2^{(b)}$	<ul> <li><i>θ</i><sub>A</sub></li> <li><i>θ</i><sub>E</sub></li> <li>An</li> <li>Sin</li> </ul>	y = (4) y =	$(4s_A + 4s_A - 2)$ SO coroble	4s <sub>B</sub> 2s <sub>B</sub> – of E' em v	+ 4s <sub>c</sub> - 2s <sub>c</sub> ) can vill b	-)/12 /12 not b e end	<i>(like</i> be four counte	'y') nd by ered fo	using or 3-D	the PO! IRs.


#### PO problem with a degenerate IR: the way-out



C3	$E$ $C_3$ $C_3^2$			$\omega = ex$	κp(2πi/	3)	•	Alternatively, lower the symmetry of the molecule from D to its pure rotation				
$ \begin{array}{c} A \\ E \end{array} \Big\{ \end{array} $	1 1 1	$\frac{1}{\omega}{\omega^2}$	$\frac{1}{\omega^2}$	$\begin{vmatrix} z & R_z \\ x - iy & R_x - iR_y & x \\ x + iy & R_x + iR_y & x \end{vmatrix}$	$x^{2}$ $z - iyz;$ $z + iyz;$	$+y^{2}; z^{2}$ $x^{2} + 2i$ $x^{2} - 2i$	$2  xy - y^2  xy - y^2$	subgroup, $C_n$ , for which the degenerate $E$ IR becomes <i>two associate 1-D representations</i> .				
Γ	3	0	0	(note:	ω* = (	ω <sup>2</sup> )		• Again for $BH_3$ , 3H 1s SOs $\Gamma = A \otimes E$				
$\subset$				Operation Effect on <i>s<sub>A</sub></i>	E s <sub>A</sub>	C <sub>3</sub> s <sub>C</sub>	$C_3^2$ $s_B$	$\widehat{P}^{(k)}s_{A} = \frac{1}{h} \left\{ \sum_{R} \left[ \chi^{(k)}(R) \right]^{*} \widehat{R} \right\} s_{A}$				
C	B	$\supset$		Characters for <i>E</i> <sup>(1)</sup> Result	1 <i>s</i> <sub>A</sub>	ω <i>ω</i> *s <sub>C</sub>	$\omega^*$ $\omega_B$	$\boldsymbol{\theta}_{E,1} = (s_A + \omega^* s_C + \omega s_B)/3$				
				Characters for <i>E</i> <sup>(2)</sup> Result	1 s <sub>A</sub>	യ* ഡ്യ <sub>്</sub>	ω Ø <sup>*</sup> S <sub>B</sub>	$\theta_{E,2} = (s_A + \omega s_C + \omega^* s_B)/3$				
			→ (	$\boldsymbol{\theta}_{E,a} = N(\boldsymbol{\theta}_{E,1} + \boldsymbol{\theta}_{E,2})$	(2) = N(	$2s_A - s_B$	$s - s_C$	$\boldsymbol{\theta}_{E,b} = N(\boldsymbol{\theta}_{E,1} - \boldsymbol{\theta}_{E,2}) = N(s_B - s_C)$				



#### 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  $CI^-$ , or small molecules, such as  $H_2O$  and CO.
- Some frequently encountered coordination geometries: (a) is *tetrahedral* (point group T<sub>d</sub>), (b) is *square planar* (point group D<sub>4h</sub>) and if we concentrate on just the ligating atoms, (c) is *octahedral* (point group O<sub>h</sub>).





#### 5.5.1 MO diagram of an octahedral complex with $\sigma$ -only ligands



HOMO of NH<sub>3</sub>

- Suppose an *octahedral* complex in which the central metal ion is surrounded by six *structureless ligands*, each directing a  $\sigma$ -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:





A STATE	SIS	<b>J.1</b> 1		ungi		'j ul		nicu		ompi		<i>Uniy ii</i> g		Lannersity
SITAS AMOL				Carte	esian f	uncti	on	orbit	al			IR	24 Character England	/
				$r^2 = x^2$	$^{2}+y^{2}+$	$-z^2$		4s				$A_{lg}$		
VAOs of the central metal			e	( <i>x</i> , <i>y</i> , <i>z</i>			$4p_x$ , $4p_y$ , $4p_z$							
			(xz,xy)			$3d_{xz}$ , $3d_{xy}$ , $3d_{yz}$								
				$(2z^2-z^2)$	$x^2 - y^2$ ,	$\sqrt{3}(x)$	$^{2}-y^{2}))$	$3d_{z^2}$	, 3d,	$x^2-y^2$		$E_g^{\circ}$		
$O_h$	E	8 <i>C</i> <sub>3</sub>	$3C_{4}^{2}$	$6C_4$	$6C_2$	i	8 <i>S</i> <sub>6</sub>	$3\sigma_h$	$6S_4$	$6\sigma_d$				_
$A_{1g}$	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				
$E_g$	2	-1	2	0	0	2	-1	2	0	0		$((2z^2 - x^2))$	$(x^2 - y^2), \sqrt{3}(x^2 - y^2)$	)
$T_{1g}$	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	(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 $\sigma$ -only ligands









#### MO diagram for an ML<sub>6</sub> 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*,  $\Delta_o$ .
- <u>The size of  $\Delta_{\underline{o}}$  depends on the</u> <u>strength of the M-L bonding</u> <u>interaction. *why*?</u>





### Ligand-field splitting

For a fixed set of ligands, Δ<sub>o</sub> 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  $\sigma$ -interaction, and hence a greater shift of the antibonding MOs ( $2e_g$ ).

• The way in which  $\Delta_o$  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 *lt<sub>2g</sub>* MOs is *θ*, the energy of the *2e<sub>g</sub>* MOs is *Δ<sub>0</sub>*, and each pair of electrons of parallel spins lowers the energy by an amount of *K* (*exchange energy*).
   (Note: for d<sup>1</sup>-d<sup>3</sup> or d<sup>8</sup>-d<sup>10</sup>, there is only one electronic configuration!)





#### 5.5.2 High- and low-spin complexes



 $2e_{o}$ 

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

		d <sup>0</sup>	d1	d <sup>2</sup>	d <sup>3</sup>	d <sup>4</sup>	<b>d</b> <sup>5</sup>	d <sup>6</sup>	d <sup>7</sup>	d <sup>8</sup>	d <sup>9</sup>	<b>d</b> <sup>10</sup>
High-spin	Orbital ( $\Delta_0$ )											
	Exchange(K)											
Low-spin	Orbital( $\Delta_0$ )											
	exchange(K)											

#### i) For small $\Delta_0$ , exchange contribution dominates.

ii) For large  $\Delta_0$ , orbital contribution dominates.





### 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  $\Delta_o$ .
- 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.

 $v \sim Visible light$ 



We observe the complementary color of light absorbed!







- 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,  $\mu_{eff}$ , which is a measure of the degree of paramagnetism, is given by

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

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 rewritten as

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

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





- This figure shows how the **hydration enthalpies** (水合热) of M<sup>2+</sup> and M<sup>3+</sup> ions and **the lattice energies** (晶格能) of divalent chlorides vary along the first transition series.
- (a) (b) number of d electrons number of d electrons • If on the plot we connect the values у от hydration kJ mol<sup>-1</sup> -3800 -1600  $M^{2+}$ -4000 M<sup>3+</sup> for  $d^0$ ,  $d^5$  and  $d^{10}$  configurations we -1800 -4200 see that all the other data fall beneath 5 -4400 -2000 these lines in *two dips*, one between -4600 -4800 l -2200L  $d^0$  and  $d^5$ , and the second between  $d^5$ and  $d^{10}$ . number of d electrons (c) (d) 2.20 -2200 distance MCl<sub>2</sub> lattice enthalpy / kJ mol<sup>-1</sup> 2.15 -2400 2.10 -2600 2.05 Ś 2.00 -2800L

number of d electrons

0





• The predominately ligand-based  $la_{1g}$ ,  $lt_{1u}$  and  $le_g$  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  $E_{\sigma}$ .

- Then overall the energy change upon forming the complex is  $-E_L + n_{E_{\sigma}} \times E_{\sigma} (n_{E_{\sigma}} \sim \text{the number of electrons in the } 2eg$ MOs).
- For high-spin complex, the energy change solely depending on the occupation in the  $2e_g$  MOs is given here.







- 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).







- We have assumed that  $E_{\sigma}$  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 $\pi$ 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<sub>1g</sub> ⊕T<sub>2g</sub> ⊕T<sub>1u</sub> ⊕T<sub>2u</sub>. (*after-class Ex.: prove this!*)





# 5.5.5 Effect of $\pi$ 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.





# 5.5.5 Effect of $\pi$ -interactions with the ligands



- Such  $\pi$ -interaction gives bonding  $l_{t_{2g}}$  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.  $\Delta_o$  is decreased.
- The ligand  $T_{2g}$  SOs are filled, so in the complex the  $lt_{2g}$  bonding MOs are filled as well.
- The extent to which the antibonding 2t<sub>2g</sub> are occupied depends on the number of 3d electrons present.
- Ligands which interact in this way so as to decrease  $\Delta_o$  are called  $\pi$  *donors*.





#### $\pi$ -acceptor ligands

- Ligands such as CO and CN<sup>-</sup> also have *empty*  $\pi$ -type orbitals, generally the  $\pi^*$  MOs, available for interacting with the metal.
- Such type of π-interactions results in an *increase in* Δ<sub>o</sub>, and *transfer of electron density* from the metal to the π-acceptor ligands.
   (d)
- The aforementioned  $\sigma$  and  $\pi$ -bonding between transition metal and  $\pi$ -acceptor ligands (e.g., CO, CN<sup>-</sup>, *alkene*, and *alkyne*) thus result in  $\sigma$ -donation of electron density from the ligands to mental and  $\pi$ *backdonation* of electron density from metal to the ligands! (i.e., Dewar-Chatt-Duncanson model -- widely used in organometallics and catalysis!)



**Ex. 24** 



#### 5.5.6 Spectrochemical series



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

Resulting from a subtle balance between  $\sigma$ - and  $\pi$ -type interactions:

- *The stronger*  $\sigma$ -type interaction  $\rightarrow$  *the greater* the value of  $\Delta_o$ .
- The ligating atom going from  $O \rightarrow N \rightarrow C \rightarrow$  increasing energy of ligand  $\sigma$  orbital  $\rightarrow$  better matching the energy of metal 3d AOs  $\rightarrow$  stronger  $\sigma$ -type interaction.
- Enhanced  $\sigma$ -type interaction leads to shorter M-L bond length and thus facilitates a stronger  $\pi$ -backbonding interaction, further increasing  $\Delta_o$ .
- CN<sup>-</sup> and CO lead to particularly large values of  $\Delta_o$ : strong  $\sigma$  donor & strong  $\pi$  acceptor.



### 5.5.7 Eighteen-electron rule

- In an octahedral complex with  $\pi$ -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*  $\pi$  *acceptors* are not likely to obey the eighteen electron rule since the metal-based  $t_{2g}$  MOs are either non-bonding or antibonding.





#### MO diagram of tetrahedral metal complex, ML<sub>4</sub>







#### 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 metalbased orbitals is denoted  $\Delta_t$ .  $\Delta_t \approx 0.44 \Delta_o$
- This smaller value for Δ<sub>t</sub> means that the exchange term dominates and high-spin complexes are invariably found, e.g., [FeCl<sub>4</sub>]<sup>2-</sup>.

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?





Ε

2

2

4

cartesian function

 $2C_4$ 

-1

-1

 $^{-1}$ 

0

0

 $D_{4h}$ 

 $\frac{A_{1g}}{A_{2g}}$ 

 $B_{1g}$ 

 $B_{2g}$ 

 $E_g$ 

 $A_{1u}$ 

 $A_{2u}$ 

 $B_{1u}$ 

 $B_{2u}$ 

 $E_u$ 

 $\Gamma(4\sigma)$ 

(x, y)

(xz, yz)

 $x^2 - y^2$ 

Z.

xy

 $z^2$ 

Square-planar coordination

 $2C_2$ 

0

 $^{-1}$ 

 $^{-1}$ 

0

2

 $4p_x, 4p_y$ 

 $3d_{xz}, 3d_{yz}$ 

 $2C'_2$ 

0

0

0

corresponding orbital(s)

 $^{-1}$ 

 $^{-1}$ 

-2

0

 $i \quad 2S_4$ 

-1

0

0

 $2\sigma_{\nu}$ 

0

0

2

 $A_{lg}$ 

 $E_u$ 

 $A_{2u}$ 

 $E_{g}$ 

 $B_{2g}$  -

 $B_{1g}$ 

 $A_{lg}$ 

 $\sigma_h$ 

-2

 $^{-1}$ 

-1

-1

 $^{-1}$ 

4

 $2\sigma_d$ 

 $^{-1}$ 

 $^{-1}$ 

0

-1

 $^{-1}$ 

0

0

IR of metal AOs

 $C_{4}^{2}$ 

-2

-2

0

4s

 $4p_z$ 

 $3d_{xy}$ 

 $3d_{z^2}$ 

 $3d_{x^2-y^2}$ 

• The point group  $D_{4h}$ :

 $x^2 + y^2; z^2$ 

 $x^2 - y^2$ 

xy

(xz, yz)

IR of ligand SOs

 $R_z$ 

 $(R_x, R_y)$ 

Z,

(x, y)

non-bonding

 $=A_{1g} \oplus B_{1g} \oplus E_u$ 

 $A_{lg}$ 

 $E_u$ 

 $B_{1g}$ 



• The four σ-type ligand orbitals.

MOs & main contribution  $1a_{1g}$  bonding, ligand-based  $2a_{1g}$  wab/nb, M (n-1)d<sub>z</sub><sup>2</sup>-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<sub>x</sub><sup>2</sup>-y<sup>2</sup>-based



#### Square-planar coordination

**Ex. 26** 



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



- 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  $\pi$  interactions with the ligands are also present, the  $le_g$  and  $lb_{2g}$  orbitals separate, with the  $lb_{2g}$  moving higher in energy, possibly above the  $2a_{1g}$ .
- $\equiv 1e_g + 1b_{2g}$  (Is the ligand  $\pi$ -donor or  $\pi$ -acceptor?)

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





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.







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.
- $\pi$  donor ligands generally reduce  $\Delta_o$ , whereas  $\pi$  acceptor ligands generally increase  $\Delta_o$ .
- Ligands can be arranged into a spectrochemical series according to the  $\Delta_0$  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 <sub>i</sub>	i	VO's	Examples
<b>2</b> e	1	2	S	LiH, LiR, Li2
<b>4</b> e	2	4	sp	BeR <sub>2</sub> , R-Mg-Cl
<u>6e</u>	3	6	sp²	BEt <sub>3</sub> , La(Ph) <sub>3</sub>
<mark>8</mark> e	4	8	sp <sup>3</sup>	$CH_4$ , $NF_3$ , $H_2O$
<b>10e</b>	5	10	sp³d	PF <sub>5</sub> , SF <sub>4</sub> , XeF <sub>2</sub>
<b>12</b> e	6	12	sp <sup>3</sup> d <sup>2</sup>	SF <sub>6</sub> , MoF <sub>6</sub> , PF <sub>6</sub> <sup>-</sup> , SiF <sub>6</sub> <sup>2-</sup>
<b>14</b> e	7	14	sp <sup>3</sup> d <sup>3</sup> /d <sup>5</sup> sp	IF <sub>7</sub> / Agl <sub>2</sub> <sup>-</sup> , Au(CN) <sub>2</sub> <sup>-</sup>
<b>16e</b>	8	16	d <sup>5</sup> sp <sup>2</sup>	Cp <sub>2</sub> Cr, Au(CN) <sub>4</sub> <sup>-</sup>
<b>18e</b>	9	18	d <sup>5</sup> sp <sup>3</sup>	$Ni(CO)_4$ , $Fe(CO)_5$ , $Cr(CO)_6$



#### 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<sub>a</sub>* = *VE<sub>b</sub>-10*) and *similar frontier orbitals* are *isolobal*.
- A fragment in a molecule can be substituted with an isolobal fragment. e.g.,  $CR_2 vs$  $Fe(CO)_4$ ,  $\rightarrow$  Metal-carbene complexes:  $(L)_n M = CR_2$
- *Isolobal analogy* has been widely exploited in synthetic chemistry and led to the production of numerous cluster compounds.



we experimental evidences of isolobal  $AuPR_3 \sim H$  analogy.

- isostructural [Co(CO)<sub>4</sub>X] (X=H, AuPR<sub>3</sub>)
- isostructural [FeCo<sub>3</sub>(CO)<sub>12</sub>( $\mu_3$ -X)] (X=H, AuPR<sub>3</sub>) 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 <u>carborane</u> 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




• A: 1s $\sim \Sigma_g^+$ (core AO)	$D_{\infty \mathrm{h}}$	Ε	$2C_{\phi}$	$\infty C'_2$	i	$2iC_{\infty}$	$iC'_2$	$h = \infty$
$2s \sim \Sigma_{g}^{+}$	$\overline{A_{1q}(\Sigma_q^+)}$	1	1	1	1	1	1	$z^2, x^2 + y^2$
$2p_z \sim \Sigma_u^+$	$A_{1u}(\Sigma_u^+)$	1	1	1	-1	-1	-1	z
$(2p_x, 2p_y) \sim \Pi_u$	$A_{2g}(\Sigma_{g}^{-})$	1	1	-1	1	1	-1	
2H 1s:	$A_{2u}(\Sigma_{u}^{-})$	1	1	-1	-1	1	1	
$(s_{\perp} + s_{p}) \sim \Sigma_{p}^{+}$	$E_{1g}(\Pi_g)$	2	$2\cos\phi$	0	2	$-2\cos\phi$	0	(xz, yz)
$(\mathbf{a}_{\mathrm{A}} + \mathbf{a}_{\mathrm{B}}) - \mathbf{g}$	$E_{1u}(\Pi_u)$	2	$2\cos\phi$	0	-2	$2\cos\phi$	0	(x, y)
$(s_A - s_B) \sim \Sigma_u^+$	$E_{2g}(\Delta_g)$	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. $bent(C_{2\nu})$
------------------------------------	----------------------

- BH<sub>2</sub>: 4 VEs L:  $2\sigma_g^2 1\sigma_u^2$ 
  - B: 2a<sub>1</sub><sup>2</sup>3a<sub>1</sub><sup>2</sup>
  - BH<sub>2</sub> prefers the linear structure.
- $H_2O$ : 8 Ves  $\rightarrow$  4 occupied VMOs.

The bent structure has 3 bonding MOs.





 $2\sigma_{\mu}$ 

 $3\sigma_g$ 

 $1\sigma_{u}$ 

 $2\sigma_{g}$ 

 $H = 1\pi_u, 1\pi_u$ 







•  $C_6H_6$ 

## PO problem with a degenerate IR: the way-out

•  $\pi$ -MOs formed by six  $p_z$  AOs



$\mathcal{G}_6$	$\mathcal{C}_6$	Ε	$C_6$	<i>C</i> <sub>3</sub>	$C_2$	$C_{3}^{2}$	$C_6^5$
R <sub>0</sub>	А	1	1	1	1	1	1
$R_3$	В	1	-1	1	-1	1	-1
$R_1$	$\mathbf{E}_1^a$	1	ω	$\omega^2$	$\omega^3$	$\omega^4$	$\omega^5$
$R_5$	$\mathbf{E}_1^{\tilde{b}}$	1	$\omega^5$	$\omega^4$	$\omega^3$	$\omega^2$	ω
$R_2$	$E_2^a$	1	$\omega^2$	$\omega^4$	1	$\omega^2$	$\omega^4$
$R_4$	$\mathrm{E}_2^{ ilde{b}}$	1	$\omega^4$	$\omega^2$	1	$\omega^4$	$\omega^2$
					Ø	= exp(	2 <i>π</i> i/6)

 $D_{6h}$ 

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

 $\Psi_{A} = \theta_{A} = (\phi_{1} + \phi_{2} + \phi_{3} + \phi_{4} + \phi_{5} + \phi_{6})/6$  $\Psi_{B} = \theta_{B} = (\phi_{1} - \phi_{2} + \phi_{3} - \phi_{4} + \phi_{5} - \phi_{6})/6$ 

• For cyclic group, the six equivalent AOs span as -  $\Gamma = A \oplus B \oplus E_1 \oplus E_2$ 

Operation	E C	$C_6  C_3  C_2$	$C_{3}^{2}$	$C_{6}^{5}$	
Effect on $p_{z,1}$	$\phi_1 \phi_2$	$\phi_3 \phi_4$	$\phi_5$	$\phi_6$	
$\theta(E_1^a) = (\phi_1 + \omega^5 \phi)$	$\phi_2 + \omega^4 \phi_3 + \phi_3$	$\omega^3 \phi_4 + \omega^2 \phi_4$	$\phi_5 + \omega \phi$	<sub>6</sub> )/6	
$\theta(\mathbf{E}_1^{\mathbf{b}}) = (\phi_1 + \omega \phi_2$	$+\omega^2\phi_3 + \omega$	$\phi^{3}\phi_{4} + \omega^{4}\phi_{4}$	$_{5} + \omega^{5} \phi$	<sub>6</sub> )/6	
$\Psi(E_1^{a}) = N[\theta(E_1^{a})]$	$+ \theta(E_1^{b})] =$	$(2\phi_1 + \phi_2 -$	$\phi_3 - 2\phi_4$	- φ <sub>5</sub> +φ <sub>6</sub> )/γ	1
$\Psi(\mathbf{E}_1{}^{\mathbf{b}}) = \mathbf{N}[\theta(\mathbf{E}_1{}^{\mathbf{a}})$	$-\theta(E_1^b)]=$	$(\phi_2 + \phi_3 - \phi)$	$(5-\phi_6)/2$		
$\theta(\mathbf{E}_2^{\mathbf{a}}) = (\phi_1 + \omega^4 \phi_2)$	$_{2} + \omega^{2} \phi_{3} + \phi$	$\phi_4 + \omega^4 \phi_5 - \phi_5$	+ ω <sup>2</sup> φ <sub>6</sub> )	/6	
$\theta(\mathbf{E}_2^{\mathbf{b}}) = (\phi_1 + \omega^2 \phi_2)$	$_{2} + \omega^{4}\phi_{3} + \phi$	$\phi_4 + \omega^2 \phi_5 - \phi_5$	+ ω <sup>4</sup> φ <sub>6</sub> )	/6	
$\Psi(\mathbf{E}_2^{\mathbf{a}}) = \mathbf{N}[\theta(\mathbf{E}_2^{\mathbf{a}}) +$	$+ \theta(E_2^b)] =$	$(2\phi_1 - \phi_2 - \phi_2)$	$\phi_3 + 2\phi_4$	- φ <sub>5</sub> -φ <sub>6</sub> )/√	12
$\Psi(E_2^{b}) = N[\theta(E_2^{a}) -$	$-\theta(E_2^b)] =$	$(\phi_2 - \phi_3 + \phi)$	$(\phi_{5}-\phi_{6})/2$		









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

 $\Psi(E_2^{a1}) = (2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6)/\sqrt{12}$  $\Psi(E_2^{b1}) = (\phi_2 - \phi_3 + \phi_5 - \phi_6)/2$ 

 $\Psi(E_1^{a1}) = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6)/\sqrt{12}$  $\Psi(E_1^{b1}) = (\phi_2 + \phi_3 - \phi_5 - \phi_6)/2$ 

 $\Psi_{A} = \theta_{A} = (\phi_{1} + \phi_{2} + \phi_{3} + \phi_{4} + \phi_{5} + \phi_{6})/\sqrt{6}$ 





## 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.

