





- Molecular orbital (MO) theory uses the methods of group theory to describe the bonding in molecules.
- Symmetry properties and relative *E* of atomic orbital (AO) \rightarrow determine the way of forming MO
- Filling the MO w/ e⁻ follows three rules **1**) aufbau principle

2) Hund's rule

3) Pauli exclusion principle

If,,, total E of e⁻ in MO < total E of e⁻ in AO

 \subseteq molecule is stable

• if,,, total *E* of e⁻ in **MO** > total *E* of e⁻ in **AO**

 \subseteq molecule is unstable \rightarrow doesn't form

- In this chapter \rightarrow explain approaches to **describe bonding** using **group theory** & simpler

methods

 \rightarrow developing the symm. concept required for more complex cases

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- Schrödinger equation is used \rightarrow for approximate solutions to the molecules
 - ← by LCAO (linear combination of atomic orbitals): sum & differences of the atomic wave functions
 - e.g.) H_2 's wave function



 \triangleleft as distance b/w two atoms $\downarrow \rightarrow$ orbital overlap \rightarrow probability for e⁻ in the overlap region \uparrow

 \rightarrow \therefore molecular orbitals form

 \hookrightarrow e⁻ in bonding molecular orbitals \rightarrow space b/w nuclei



Three conditions for overlap to lead to bonding

- 1) the symm. of the orbitals must be such that regions w/ the same sign of ψ overlap
- 2) E of AO's must be similar
 - \hookrightarrow if great *E* difference \rightarrow *E* of e⁻ on formation of MO $\downarrow \rightarrow$ reduction in *E* of e⁻ is too small
- 3) distance b/w atoms { short enough to provide good overlap { not so short that repulsion forces interfere
 - \hookrightarrow if all conditions are met, then,,,
 - \rightarrow overall *E* of e⁻ in MO is lower than the *E* of e⁻ in the AO
 - \therefore The molecule has a lower *E* than the separate atoms!!





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\hookrightarrow AO wave functions: \psi(1s_a), \psi(1s_b)
```

two atoms approach each other

 \hookrightarrow MO \rightarrow linear combination of AO: sum & diff. b/w two orbitals



5.1.1 Molecular Orbitals from s Orbitals





- σ MO <u>sum</u> of two AO
 - e⁻ concentration b/w two nuclei \uparrow
 - both atomic wave functions contribute
 - <u>lower E</u>
 - ← bonding MO
 - \bigcirc e⁻ attract the nuclei, hold them together

- σ* MO <u>diff.</u> of two AO
 - a node (zero e⁻ density) b/w the nuclei
 - cancellation of the two functions
 - <u>higher E</u>
 - ← anti bonding MO
 - \hookrightarrow e⁻ causes a mutual repulsion b/w

atoms

5.1.1 Molecular Orbitals from s Orbitals





nonbonding orbitals - E of nonbonding orbitals = E of AOs

 \leftarrow if one AO of one atom does not have a counter part on the other atom.

 \leftarrow sometimes by coincidence \rightarrow just non-bonding

5.1.1 Molecular Orbitals from *s* Orbitals



- σ : orbitals that are <u>symmetric to rotation</u> about the line connecting the nuclei
- asterisk (*): anti bonding orbitals





 σ^* from p_z orbital

resulting MO = # initial AO

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• as two orbitals overlap $\begin{cases} 1 \end{pmatrix}$ if <u>same</u> signs $\rightarrow e^{-}$ probability in the overlap region \uparrow 2) if <u>opposite</u> signs $\rightarrow e^{-}$ probability in the overlap region \downarrow



5.1.2 Molecular Orbitals from p Orbitals





• π : a <u>change in sign</u> of the wave function w/ C₂ rotation

 $\subseteq p_x, p_y$



5.1.2 Molecular Orbitals from p Orbitals

- { Overlap of two regions w/ the same sign $\rightarrow e^{-}$ concentration \uparrow Overlap of two regions w/ the **opposite** sign \rightarrow node (zero e^{-} density)
- if there is nodes of AO \rightarrow nodes of MO

 $\begin{cases} p_z: \sigma, \sigma^* \text{ orbitals} \\ p_x, p_y: \pi, \pi^* \text{ orbitals} \end{cases}$

• Fig.5.2(c): if overlap equally w/ the same sign & the opposite sign

e.g.)
$$s + p_x \begin{cases} bonding \rightarrow cancel \rightarrow \underline{No MO results}!! \\ antibonding \end{cases}$$

in other description,,

 \leftarrow symm. do not match \rightarrow No combination!! -

(b)

 $p_{v}(a) p_{x}(b)$

no interaction

 $s(a) p_x(b)$

Fig.5.2(c) © 2014 Pearson Education, Inc.

5.1.3 Molecular Orbitals from d Orbitals



• in the heavier elements $(TM) \rightarrow \underline{d \text{ orbitals}}$ are involved



- two $d_z^2 \rightarrow \sigma$, σ^*

- d_{xz} , $d_{yz} \rightarrow \pi$, π^*



- $d_{x y}^{2}$, d_{xy} (two parallel planes) $\rightarrow \delta, \delta^*$
- δ : change in sign on C₄ rotation about the bond axis

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 $d_{x^2 - y^2}$ or d_{xz} orbitals in parallel planes

Fig. 5.3





- zero net overlap, cannot form MO



The # of nodes in orbitals

• Example 5.1)

- σ orbital: <u>no</u> node including the line of center
- π orbital: <u>one</u> node including the line of center
- δ orbital: <u>two</u> node including the line of center



Fig. 5.3





- if *E* of MO = *E* of AO \rightarrow nonbonding!!

 \subseteq can happen in larger molecules

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e.g.) 3 AO w/ same symm. \rightarrow 3 MO 1) bonding
similar E 3) Nonbonding 3) antibonding
```

- relative *E* of AO: Fig.5.4.



 \hookrightarrow The <u>closer</u> the *E* match, the <u>stronger</u> the interaction!!

5.2.1 Molecular Orbitals



- <u>MO description</u> is more in agreement w/ experiment than Lewis electron-dot diagram does.
- Fig.5.5: full set of MO for the homonuclear diatomic molecules of the first 10 elements

 \subseteq the order of *E* level for MO \rightarrow similar pattern



Fig. 5.5

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5.2.2 Orbital Mixing



- Orbitals w/ similar *E* can interact if they have the <u>same symm.</u>

 $\left\{ \begin{array}{l} \underline{lower} \text{ the } E \text{ of the } \underline{lower} \text{ orbitals} \\ \underline{raise} \text{ the } E \text{ of the } \underline{higher} \text{ orbitals} \\ \end{array} \right.$

e.g.) in the homonuclear diatomics $\sigma_{g}(s), \sigma_{g}(p)$ orbitals: same symm. σ_{g} $\int_{\tau_{g}} \left\{ \text{lower the } E \text{ of the } \sigma_{g}(2s) \right\}$ raise the E of the $\sigma_{g}(2p)$

$$\sigma_{u}^{*}(s), \sigma_{u}^{*}(p) \text{ orbitals: same symm. } \sigma_{u}$$

$$\left\{ \begin{array}{c} \text{lower the } E \text{ of the } \sigma_{u}^{*}(2s) \\ \text{raise the } E \text{ of the } \sigma_{u}^{*}(2p) \end{array} \right\}$$



- Mixing : molecular orbitals w/ similar E interact if they have appropriate symm.

5.2.2 Orbital Mixing



- Alternatively, 4 MO form 4 AO ($2 \times 2s$, $2 \times 2p_z$) w/ similar E.

$$\Psi=c_1\psi(2s_a)\pm c_2\psi(2s_b)\pm c_3\psi(2p_a)\pm c_4\psi(2p_b)$$

- (the lowest *E* MO: contains larger c_1 , c_2

 $\frac{1}{2}$ the largest *E* MO: contains larger c₃, c₄

two intermediate MO: contain intermediate values of all 4 coefficients

 \leftarrow The symm. of these four orbitals \rightarrow mixing!!

- *s*-*p* mixing have an important influence on *E* of the molecule.

e.g.) 1) Li_2 to N_2 : $E(\sigma_g, 2p_z) > E(\pi_u, 2p_x \& 2p_y)$ \leftarrow inverted order!!

2) B₂, C₂: magnetic properties of molecules







MO theory can explain para-vs. diamagnetic!!!

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• $B_2[\pi_u^1 \pi_u^1(2p)]$: example showing an <u>advantage of MO model</u> over Lewis dot picture

 \hookrightarrow <u>B₂ is paramagnetic!!!</u>

 $\begin{array}{c} : \underline{E \ level \ shifts \ by \ mixing \ of \ s \ \& \ p \ orbitals} \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$



 $\sigma_*(2p)$

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- two π bonds, no σ bond
- rarely encountered
- but, acetylide ion (C_2^{2-} w/ cations) is known. \leftarrow bond order = 3 ($\pi_u^2 \pi_u^2 \sigma_g^2$)

 C—C Distance (pm)

 C=C (gas phase)
 124.2

 H—C=C—H
 120.5

 CaC₂
 119.1









- $O_2 \left[\sigma_g^2 \pi_u^2 \pi_u^2 \pi_g^{*1} \pi_g^{*1} (2p)\right]$ paramagnetic (Fig.5.7)
 - liquid O_2 is held b/w the **poles of magnet** as it is poured.
 - O^{2+} , O^{2-} , O_2^{2-} are also known
 - bond order vs. bond distances
 - <u>small mixing</u> of $\sigma_g(2s)$ & $\sigma_g(2p)$ \leftarrow E ($\pi_u(2p)$) > E ($\sigma_g(2p)$)

	Bond Order	Internuclear Distance (pm)
O ₂ ⁺ (dioxygenyl)	2.5	111.6
O ₂ (dioxygen)	2.0	120.8
O ₂ ⁻ (superoxide)	1.5	135
O_2^{2-} (peroxide)	1.0	149

NOTE: Oxygen–oxygen distances in O_2^- and O_2^{2-} are influenced by the cation. This influence is especially strong in the case of O_2^{2-} and is one factor in its unusually long bond distance, which should be considered approximate.



- $F_2 [\sigma_g^2 \pi_u^2 \pi_u^2 \pi_g^{*2} \pi_g^{*2} (2p)]$ diamagnetic
 - N₂, O₂, F₂ \rightarrow the order of $\sigma_g(2p)$ & $\pi_u(2p)$ is diff.
 - *E* diff. b/w 2s & 2p for F = 21.5 eV
 - \hookrightarrow mixing \downarrow \rightarrow "normal" order of MO
- Ne₂ all MO are filled
 - # bonding e⁻ = # antibonding e⁻

← b.o = 0

• triumph of MO theory: 1) 2 unpaired e⁻ for O₂

paramagnetic (Lewis dot diagram cannot explains!!)
2) shifting of orbital *E*

$$\mathbf{A} \mid \mathbf{B}_2$$
: paramagnetic

C₂: diamagnetic





- B N (6 10 ve⁻): as # e⁻ $\uparrow \rightarrow$ # bonding orbitals $\uparrow \rightarrow$ bond strength $\uparrow \rightarrow$ bond length \downarrow
- O F: reversed trend
 - \hookrightarrow additional e⁻ \rightarrow antibonding orbitals





- As # ve^ $\uparrow \rightarrow$ nuclear charge $\uparrow \rightarrow$ covalent radii \downarrow

 \subseteq good agreement w/ the bond distance of the matching diatomic molecules

- but, beyond N $_{\rm f}$ covalent radii : N > O > F

bond distance in diatomic molecule: $N_2 < O_2 < F_2$

 \hookrightarrow $:e^{-}$ in antibonding orbitals



TABLE 5.1	Bond Distances in Diatomic Species ^a	
Formula	Valence Electrons	Internuclear Distance (pm)
H_{2}^{+}	1	105.2
H ₂	2	74.1
B ₂	6	159.0
C ₂	8	124.2
C ₂ ²⁻	10	119.1 ^b
N_2^+	9	111.6
N ₂	10	109.8
O ₂ +	11	111.6
O ₂	12	120.8
O_2^-	13	135
F ₂	14	141.2
CN	9	117.2
CN^{-}	10	115.9 ^c
СО	10	112.8
NO^+	10	106.3
NO	11	115.1
NO ⁻	12	126.7

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- one of the more direct ways of detecting orbital E

$$O_2 + hv \text{ (photons)} \rightarrow O_2^+ + e^-$$

(UV or X-ray)





- the order of the highest occupied orbitals: levels are very close for N_2

 \leftarrow less $\sigma_g(2s)$, $\sigma_g(2p)$ orbital mixing

: but, experiment shows σ_g above π_u

- Interaction $b/w e^{-} E$ & vibrational E
 - \hookrightarrow *E* levels of vibrational *E* \rightarrow closer than in *E*
- \subseteq *E* in many diff. vibrational levels
- \hookrightarrow transition of e⁻ level occurs from diff. vibrational levels
- \hookrightarrow resulting in multiple peaks

- Orbitals \int strongly involved in bonding \rightarrow multiple peaks

less involved bonding \rightarrow only a few peaks

e.g.) for $\begin{bmatrix} N_2: \pi_u \rightarrow \text{more involved in bonding than } \sigma, \\ \text{CO: Fig. 5.13} \end{bmatrix}$

- atomic *E* levels are diff. \rightarrow shifting the MO levels
 - Gestimate using the 'orbital potential *E*' (Table 5.2, Fig. 5.13)

 \subseteq attractive $E \rightarrow \therefore$ negative values



TABLE 5.2 Orbi	tal Potential	Energies							
		Orbital Potential Energy (eV)							
Atomic Number	Element	1 <i>s</i>	2 <i>s</i>	2p	35	Зр	4 <i>s</i>	4p	
1	Н	-13.61							
2	He	-24.59							
3	Li		-5.39						
4	Be		-9.32						
5	В		-14.05	-8.30					
6	С		-19.43	-10.66					
7	N		-25.56	-13.18					
8	0		-32.38	-15.85					
9	F		-40.17	-18.65					
10	Ne		-48.47	-21.59					
11	Na				-5.14				
12	Mg				-7.65				
13	AI				-11.32	-5.98			
14	Si				-15.89	-7.78			
15	Р				-18.84	-9.65			
16	S				-22.71	-11.62			
17	CI				-25.23	-13.67			
18	Ar				-29.24	-15.82			
19	К						-4.34		
20	Ca						-6.11		
30	Zn						-9.39		
31	Ga						-12.61	-5.93	
32	Ge						-16.05	-7.54	
33	As						-18.94	-9.17	
34	Se						-21.37	-10.82	
35	Br						-24.37	-12.49	
36	Kr						-27.51	-14.22	





- MO of heteronuclear diatomic molecules
 - : unequal contribution from AOs
 - \hookrightarrow diff. coefficients of AOs
- AO *E* diff. $\uparrow \rightarrow$ interaction \downarrow
- the closer the AO in *E* to MO, the stronger the contribution to the MO















- Why HOMO of CO have greater e^{-} density on <u>carbon</u>? Which orbital has the higher *E* level?
- \subseteq due to the AO contribution,,,

 $\begin{cases} p_z \text{ of } O \to \text{to } 2\sigma^*, \, 3\sigma, \, 3\sigma^* \text{ MOs } (\underline{\text{total } 3}) \to \text{relatively } \underline{\text{weaker}} \text{ contrib. to each one} \\ p_z \text{ of } C \to \text{to } 3\sigma, \, 3\sigma^* \text{ MOs } (\underline{\text{total } 2}) \to \text{relatively } \underline{\text{stronger}} \text{ contrib. to each one} \end{cases}$





- considered as the limiting form of polarity in heteronuclear diatomic molecules
- as electronegativity diff. $\uparrow \rightarrow$ orbital *E* diff. $\uparrow \rightarrow e^{-}$ concentration shifts toward the more electronegative atom

```
← at the limit: <u>complete e<sup>-</sup> transfer</u>
I negative ion + positive ion
↓
∴ ionic compound
```








in ionic crystal: ions are held together in 3-D lattice,,

 \hookrightarrow by electrostatic attraction + covalent bonding

 \leftarrow Li⁺ is surrounded by six F⁻

- LiF reaction
 - 1) formation of the ions

Li (s) \rightarrow Li (g)	161 KJ/mol (sul	blimation)
Li (g) \rightarrow Li ⁺ + e ⁻	531 KJ/mol (IE)	
$1/2F_2(g) \rightarrow F(g)$	79 KJ/mol (dis	sociation)
$F(g) + e^{-} \rightarrow F^{-}(g)$	-328 KJ/mol (-EA	A)
Li (s) + $1/2F_2$ (g) \rightarrow	Li ⁺ (g) + F ⁻ (g)	433 KJ/mol

2) crystal formation

 $Li^{+}(g) + F^{-}(g) \rightarrow LiF(g)$ -709 KJ/mol (ion pair)

 Li^+ (g) + F⁻ (g) \rightarrow LiF (s) -1239 KJ/mol (lattice enthalphy)



 \hookrightarrow more complex orbitals

 \subseteq start w/ linear molecules \rightarrow 'group orbital' concept

5.4.1 FHF⁻

• group orbitals: collections of matching orbitals on outer atoms

 \subseteq interact w/ <u>central-atom</u> orbitals w/ the proper symm.

- Fig.5.16: group orbitals of two F
 - ← potentially could interact w/ central orbitals









(3)*

 \odot



stronger interaction?

$$rightarrow$$
 potential *E* - H 1s : -13.61 eV
- F $\begin{cases} 2p_z : -18.65 eV \\ 2s : -40.17 eV \end{cases}$

 \therefore interaction w/ 2p_z of F

>> interaction w/ 2s of F



2p







• according to the MO diagram: bonding in FHF \rightarrow 3-center, 2-e⁻ bond

(2-e⁻ bond delocalized over three atoms)

 ↓ two e⁻ occupy a low-*E* orbital formed by the interaction of all three atoms

• in general: *E* of MO derived from <u>three or more atoms is lower</u> than that from two atoms.



- same procedure can be used for more complex molecules G more complex linear or non-linear
- General Procedure

1) Determine the <u>point group</u> of the molecule.

G if a linear molecule, use $\begin{cases} D_{2h} \text{ for } D_{\infty h} \\ C_{2h} \text{ for } C_{\infty v} \end{cases}$

2) Assign <u>x, y, z coordinates</u> to atoms.

highest order rotation axis \rightarrow choose as the <u>z axis</u> of the central atom for nonlinear molecule \rightarrow <u>y axes</u> of atoms: point toward the central atom

3) Construct a reducible representation

Astruct a reducible representation of the same procedure as in the case of the vector \longrightarrow $\begin{cases}
changing positions \\
remaining positions \\
reversing signs <math>\rightarrow -1
\end{cases}$



- General Procedure
 - 4) <u>Reduce</u> each representation
 - ← finding the symm. of the group orbitals or
 the symm.-adapted linear combinations (SALCS)

5) Identify the <u>AO of the central atom</u> w/ the same symm.

6) Form MO by combing $\int AO$ of the central atom w matching symm. & similar *E* group orbitals



• In CO₂ : $\begin{cases} group \text{ orbital of } O \to \text{ same as } F \text{ in } FHF^- \\ central C \to \text{ contain } s, p \end{cases}$

3) Reducible representation for outer atom orbitals

\rightarrow for oxygen \rightarrow <u>rour sets</u> : zs, zp _x , zp _y , zp _z	\hookrightarrow	for	oxygen -	→ <u>four</u>	sets:	2s,	2p _x ,	2p _y ,	$2p_z$
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D _{2h}	E	C ₂ (<i>z</i>)	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ (2 <i>s</i>)	2	2	0	0	0	0	2	2
D _{2h}	E	C ₂ (<i>z</i>)	C ₂ (<i>y</i>)	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ (2 <i>p_z</i>)	2	2	0	0	0	0	2	2
Γ (2 <i>p_x</i>)	2	-2	0	0	0	0	2	-2
Γ (2 <i>p_y</i>)	2	-2	0	0	0	0	-2	2



4) Group orbitals from reducible representation

 \hookrightarrow Reduce step 3

e.g)
$$\Gamma(2s) = A_{g} + B_{1u}$$

D _{2h}	E	C ₂ (<i>z</i>)	C ₂ (<i>y</i>)	C ₂ (<i>x</i>)	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
A_g	1	1	1	1	1	1	1	1
B _{1u}	1	1	-1	-1	-1	-1	1	1

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Graph Repeat the process for all sets



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5) Matching orbitals on the <u>central atoms</u>

 \subseteq determine AOs of C, which interact w/ the group orbitals

 \subseteq use the character table of D_{2h}





6) Formation of molecular orbitals







-The more <u>the similar *E* b/w orbitals</u> \rightarrow <u>the stronger</u> the interaction is!! $\leftarrow E_{\text{match b/w group 3 & 2s of C} \rightarrow E \text{ diff.:} \underbrace{3.58 \text{ eV}}_{\text{match b/w group 1 & 2s of C} \rightarrow E \text{ diff.:} \underbrace{12.95 \text{ eV}}_{\text{match b/w group 3 & 2s of C}}$ <u>Group 3 & 2s of C is better match!!</u>



6) Formation of Molecular Orbitals

- electron filling: 16 e⁻ $\rightarrow \int_{\Gamma} two nonbonding \sigma orbitals two bonding \sigma orbitals two bonding <math>\pi$ orbitals two bonding π orbitals two nonbonding π orbitals \leftarrow four bonds in the molecules





- Numerical values of the coefficients of the AO in the MO can be obtained

 \rightarrow using computer software





3) hydrogen atoms \rightarrow used as <u>basis</u> & conduct operations

3) hydrogen atoms \rightarrow used as basis & conduct operations

TABLE	5.3	Representations	s for $C_{2\nu}$ Symm	netry Operation	ns for Hydrog	en Atoms in Water				
C ₂ Character Table										
$C_{2\nu}$	E	<i>C</i> ₂	$\sigma_{ u}$ (xz)	$\sigma_{ u}{}'(yz)$						
A ₁	1	1	1	1	Ζ	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				
<i>B</i> ₂	1	-1	-1	1	y, R _x	yz				
$\begin{bmatrix} H_{a'} \\ H_{b'} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} H_{a} \\ H_{b} \end{bmatrix}$ for the identity operation										

 $\begin{bmatrix} H_{b'} \\ H_{b'} \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} H_{a} \\ H_{b} \end{bmatrix}$ for the $C_{2\nu}$ operation $\begin{bmatrix} H_{a'} \\ H_{b'} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} H_{a} \\ H_{b} \end{bmatrix}$ for the σ_{ν} reflection (*xz* plane) $\begin{bmatrix} H_{a'} \\ H_{b'} \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} H_{a} \\ H_{b} \end{bmatrix}$ for the σ_{ν} ' reflection (*yz* plane)

The reducible representation $\Gamma = A_1 + B_1$:

$C_{2\nu}$	E	<i>C</i> ₂	$\sigma_{ u}$ (xz)	$\sigma_{ u}{}'(yz)$		
Г	2	0	2	0		
A ₁	1	1	1	1	Z	
<i>B</i> ₁	1	-1	1	-1	x	





4) Reduce it, $\Gamma = A_1 + B_1$

5) Match group orbitals w/ symmetries of oxygen

 $\begin{cases} A_1: 1/J2[(\Psi(H_a) + \Psi(H_b)] \leftarrow \text{group orbitals of 1s w/ matching signs} \\ B_1: 1/J2[(\Psi(H_a) - \Psi(H_b)] \leftarrow \text{group orbitals of 1s w/ opposite signs} \\ & & & \leftarrow \text{normalizing factor: N} = 1/J(\Sigma C_i^2) \end{cases}$

c_i: the coefficients on the AO



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5) Match group orbitals w/ symmetries of oxygen

Hydrogen orbitals	E	C_2	$\sigma_{_{\mathcal{V}}}$	σ_{v}'
B_1 $H_a - H_b$	$\bigcirc \bigcirc$	$\bigcirc \bigcirc$	$\bigcirc \bigcirc$	$\bigcirc \bigcirc$
Characters	1	—l	1	—l
$\begin{array}{c} A_1 \\ H_a + H_b \end{array}$	$\bigcirc \bigcirc$	$\bigcirc \bigcirc$	$\bigcirc \bigcirc$	$\bigcirc \bigcirc$
Characters	a b	a b	l a b	a b
Oxygen orbitals	E	<i>C</i> ₂	σ_{v}	σ_{v}'
p _y B ₂	\bigcirc	\bigcirc	\bigcirc	\bigcirc
Characters	1	—l	—l	1
$p_x B_1$ Characters	\bigcirc		\bigcirc	
$p_z A_1$	\bigcirc	\bigcirc	\bigcirc	\bigcirc
Characters	1	1	1	1
s A ₁	\bigcirc	\bigcirc	\bigcirc	\bigcirc
Characters	1	1	1	1



6) AO + group orbital w/ the same symm. is combined.

molecular orbitals (Table 5.4)

Molecular Orbitals for Water TABLE 5.4 Molecular **Oxygen Atomic Group Orbitals from Orbitals** Orbitals Description **Symmetry** Hydrogen Atoms Antibonding (c_{10} is negative) B_1 Ψ_6 $C_9 \psi(p_x)$ + $c_{10} \left[\psi(H_a) - \psi(H_b) \right]$ =Antibonding (c_8 is negative) $C_7 \psi(s)$ $c_8 \left[\psi(H_a) + \psi(H_b) \right]$ A_1 Ψ_5 +=Nonbonding B_2 Ψ_4 $\psi(p_v)$ =Nearly nonbonding (slightly Ψ_3 A_1 $C_5 \psi(p_z)$ + $c_6 \left[\psi(H_a) + \psi(H_b) \right]$ =bonding; c_6 is very small) Bonding (c_4 is positive) B_1 Ψ_2 + $c_4 \left[\psi(H_a) - \psi(H_b) \right]$ $c_3 \psi(p_x)$ =Bonding (c_2 is positive) Ψ_1 $c_2 \left[\psi(H_a) + \psi(H_b) \right]$ A_1 $C_1 \psi(s)$ +=





- NH_3 : pyradimal shape w/ a lone pair e^-



- looking down on the lone pair
- yz plane passing through one of the H
- reducible representation for three H 1s

TABLE 5.5 Representations for Atomic Orbitals in Ammonia									
$C_{3\nu}$ Character Table									
$C_{3\nu}$	E	2 C ₃	З $\sigma_{ u}$						
A_1	1	1	1	Ζ	$x^2 + y^2, z^2$				
A_2	1	1	-1						
Ε	2	-1	0	(x, y), (R _x , R _y)	$(x^2 - y^2, xy) (xz, yz)$				
The redu	cible rep	resentation	$\Gamma = A_1 +$	E:	I				
$C_{3\nu}$	E	2 C ₃	3 $\sigma_{ u}$						
Г	3	0	1						
<i>A</i> ₁	1	1	1	Ζ	$x^2 + y^2, z^2$				
Ε	2	-1	0	(x, y,), (R _x , R _y)	$(x^2 - y^2, xy) (xz, yz)$				
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- three group orbitals are generated $\begin{cases} \text{ one } A_1 \text{ symm.} \to \text{easily seen} \\ \text{ two E symm.} \to \text{more difficult to see} \end{cases}$
- Two conditions to describe MO equation:
 - 1) Σ of the square of the coefficients of each of the AO in the LCAO \rightarrow 1/each AO
 - 2) symm. of the central AO ↔ symm. of group orbitals

e.g.) E symm. of SALCs
$$\leftrightarrow$$
 E symm. of N p_x, p_y
 \downarrow
one node/each *E* group orbitals





- E symm. group orbital combinations of NH_3 : $\begin{cases}
 1/\int 6[2\Psi(H_a) - \Psi(H_b) - \Psi(H_c)] & \\
 1/\int 2[\Psi(H_b) - \Psi(H_c)]
 \end{cases}$
- A_1 symm. group orbital combinations of NH_3 : 1/ $\int 3[2\Psi(H_a) + \Psi(H_b) + \Psi(H_c)]$

1) condition #1:
E
$$\begin{cases} H_a \rightarrow (2/\int 6)^2 = 2/3 \\ H_b, H_c \rightarrow (1/\int 6)^2 + (1/\int 2)^2 = 2/3 \end{cases}$$



$$A_1 \begin{cases} H_a, H_b, H_c \rightarrow 1/\sqrt{3}[\Psi(H_a) + \Psi(H_b) + \Psi(H_c)] \\ \rightarrow (1/\sqrt{3})^2 = 1/3 \text{ each} \end{cases}$$

:
$$H_a = 2/3 + 1/3 = 1$$
; H_b , $H_c = 2/3 + 1/3 = 1$

- Central N:

$$\begin{cases} s, p_z \to A_1 \text{ symm.} \\ p_x, p_y \to E \text{ symm.} \end{cases} \xrightarrow{\text{matching}} 1s \text{ of H group orbitals } (A_1 + E) \end{cases}$$



- Fig. 5.30

- Fig. 5.31









- e^{-} filling: 8 e^{-} from the lowest *E* level

{ three bonds
 one lone-pair

- *E* level:
$$\begin{cases} H \ 1s \rightarrow -13.6 \ eV \\ N \ 2p \rightarrow -13.18 \ eV \end{cases}$$
 generate a large diff. b/w bonding & antibonding $N \ 2p \rightarrow -13.18 \ eV \end{cases}$ generate a large diff. b/w bonding & antibonding $N \ 2s \rightarrow -25.56 \ eV \rightarrow$ quite small interaction w/ H

- HOMO of NH₃: slightly bonding of a result of $2p_z(N)$ & 1s (H) interactions but nearly-nonbonding \rightarrow act as the lone-pair

← Lewis base

5.4.5 BF₃



- BF₃: Lewis acid

e⁻-pair acceptor \rightarrow MO acting as an acceptor trigonal shape

- F contains 2s, 2p
- coordinates: $\begin{cases} C_3 \to z \text{ axis} \\ p_y \text{ of } F \to \text{ point toward } B \\ p_x \to \text{ plane of molecule} \end{cases}$
- BF₃: B-F bonds contain double-bond character



5.4.5 BF₃





- LUMO of BF₃: antibonding b/w 2p_z of B & 2p_z of F - $\frac{1}{2p}$

- \subseteq empty π orbital (a₂")
- \leftarrow can act as an e⁻-pair acceptor





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в

5.4.5 BF₃





- E diff. b/w bonding orbitals: e.g) single bond b/w the same atom can be diff.

← C-C bond: 345 kJ/mol (avg.)

 \checkmark but, can be tremendously diff. for each individual bond

```
1) hexaphenyl ethane: (C_6H_5)_3C-C(C_6H_5)_3
```

 $\begin{array}{c} & \textbf{ 63 kJ/mol} \\ \textbf{ 2) diacetylene: H-C} \equiv \textbf{ C-C} \equiv \textbf{ C-H} \end{array}$

€ 628 kJ/mol



- hybrid orbitals, hybrids: combined AO to form MO

- \mathcal{G} sets of equivalent hybrids of the central atom
- : localized, directional
- : point from a central atom \rightarrow to surrounding atom
 - \triangleleft symm. properties \rightarrow identical to the vectors used as basis sets

- methane: vectors point at the corner of a cube



Generating reducible representation using four vectors Generating $\Gamma = A_1 + T_2$

T _d	E	8 C ₃	3 C ₂	6 <i>S</i> ₄	6 σ_d		
Г	4	1	0	0	2		
A ₁	1	1	1	1	1		$x^2 + y^2 + z^2$
<i>T</i> ₂	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)





5.4.6 Hybrid orbitals

- ammonia: sp³ hybrid (one s + three p)
 - : tetrahedral symm.
 - : \angle HNH = 106.6° (narrower than the predicted 109.5°)
 - \mathbf{G} : repulsion from the lone pair
- H_2O : two alternative approaches
 - 1) tetrahedral symm. (two lone-pair + two bonds)
 - sp³ hybrid
 - 104.5° (\because repulsion from the lone pairs)
 - 2) bent planar symm.
 - 2s, $2p_x$, $2p_y$ are used $\rightarrow sp^2$
 - 104.5° (\therefore repulsion by one pair in an sp² & one pair in the remaining p_y)

5.4.6 Hybrid orbitals





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- Fig.5.35 Hybrid orbitals

T.-S.You


- Example: determine the types of hybrids orbitals for boron in BF₃
 - Step 1: determine the shape of the molecule & vectors
 - Step 2: determine the <u>reducible representation</u> & <u>reduce</u> it
 - Step 3: the <u>AO that match</u> the irreducible representation are those used in the hybrid orbitals

D _{3h}	E	2 <i>C</i> ₃	3 <i>C</i> ₂	σ_h	2 <i>S</i> ₃	$3\sigma_{ u}$		
Г	3	0	1	3	0	1		
A ₁ '	1	1	1	1	1	1		$x^2 + y^2, z^2$
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$

$$\Gamma = A_1' + E^2$$

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← AO in the hybrids: $\begin{cases} one \text{ orbital} \rightarrow A_1' \\ two \text{ orbitals} \rightarrow E' \end{cases}$

5.4.6 Hybrid orbitals



- AO in the hybrids: $\begin{cases} one \text{ orbital} \rightarrow A_1' \\ two \text{ orbitals} \rightarrow E' \end{cases}$

- hybrid approaches: deals w/ σ bonding only

 \checkmark then, π bonding is added

(use orbitals that <u>do not</u> participated in the hybridization!!)

: quicker than MO (\because MO approach uses all AO)