

# Chapter 13 – Electronic Structure of Polyatomics

Here we will learn:

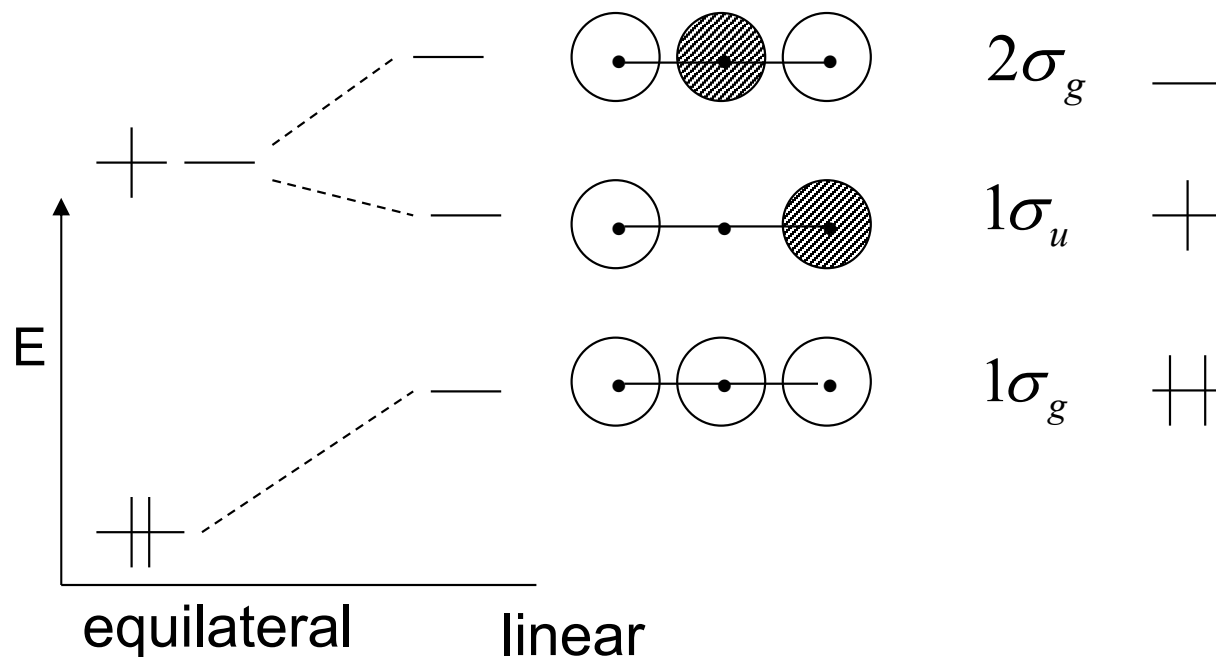
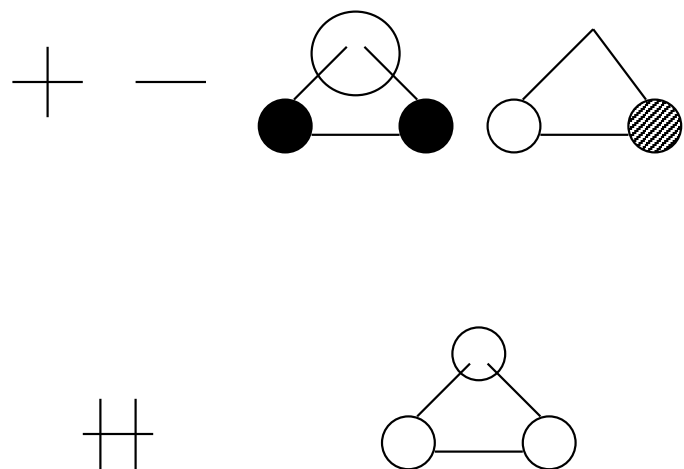
How to use bonding/antibonding nature of orbitals to make predictions about geometries

Huckel Model

Use of symmetry to simplify matrix eigenvalue problems

# Example of using bonding character to predict geometry

Is  $H_3$  linear or triangular?



If equilateral, 2<sup>nd</sup> and 3<sup>rd</sup> orbitals are degenerate

$H_3^+$  prefers triangular structure

$H_3^-$  prefers linear structure

This is the simplest example of **Walsh's rules**.

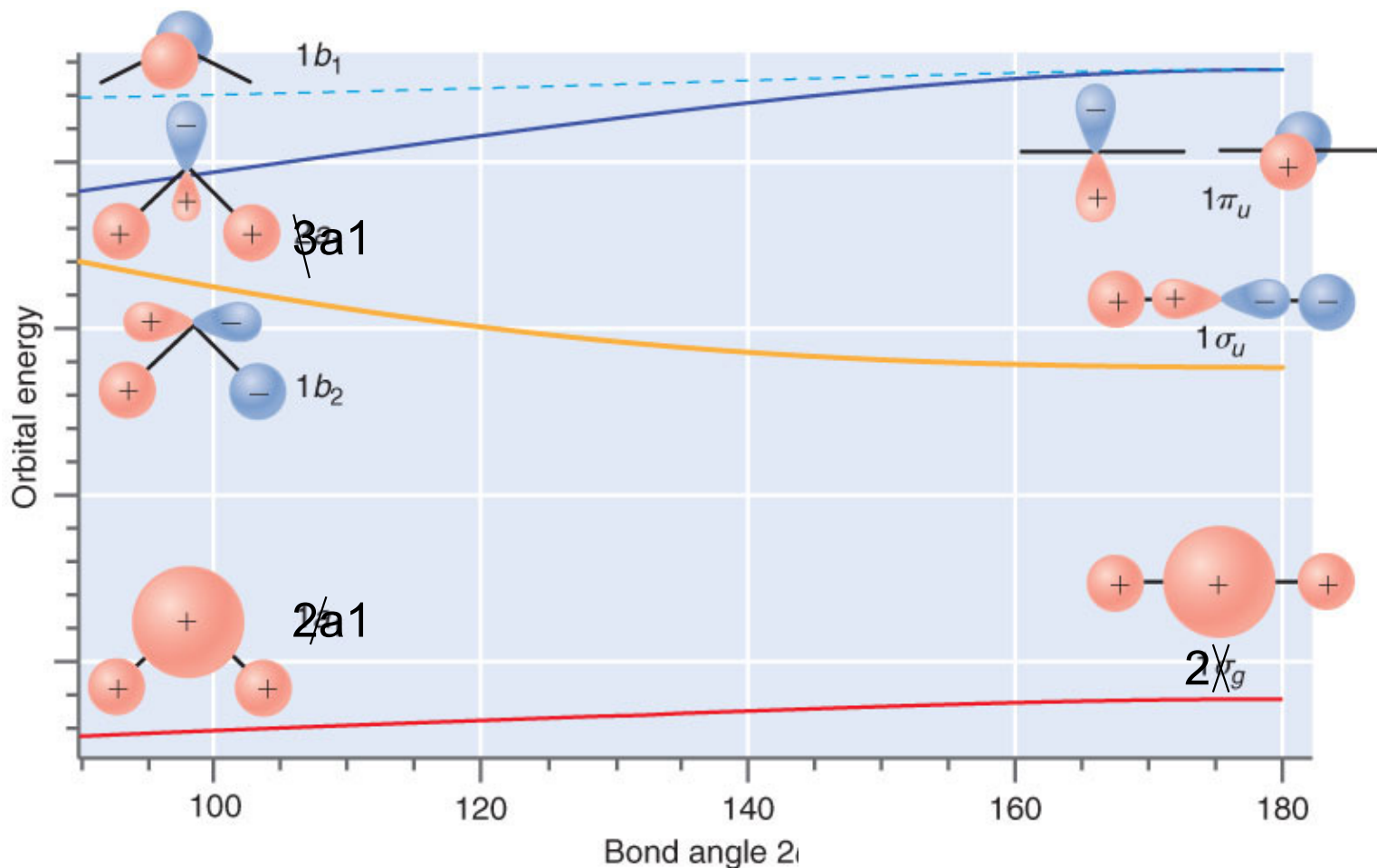
Less obvious whether  $H_3$  prefers linear or **triangular** structure

Now consider the bending of an  $XH_2$  triatomic molecule

$BeH_2$  : linear

$CH_2$  : bent

$OH_2^+$  almost the same geometry as  $OH_2$



## Huckel model

usual – one  $p_z$  orbital per C atom (conjugated pi electron systems)  
can also apply to  $H_n$  clusters – one s orbital per H atom

$$\psi = c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n$$

$$\begin{pmatrix} H_{11} - E & H_{12} & \dots & H_{1n} \\ H_{21} & H_{22} - E & \dots & H_{2n} \\ \dots & \dots & \dots & \dots \\ H_{n1} & H_{n2} & \dots & H_{nn} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0 \quad \leftarrow \text{Setting } S_{ij} = 0, i \neq j$$

Now set  $H_{ii} = \alpha$

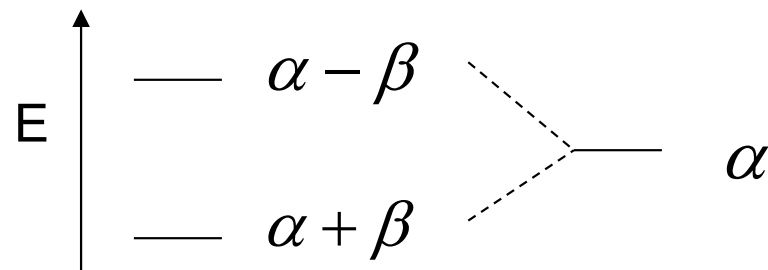
$H_{ij} = \beta$   $\leftarrow$  nearest neighbor

$= 0$   $\leftarrow$  otherwise

$\beta$  is a negative quantity

Model of  $H_2$  or of pi orbitals of ethylene

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad E = \alpha \pm \beta$$

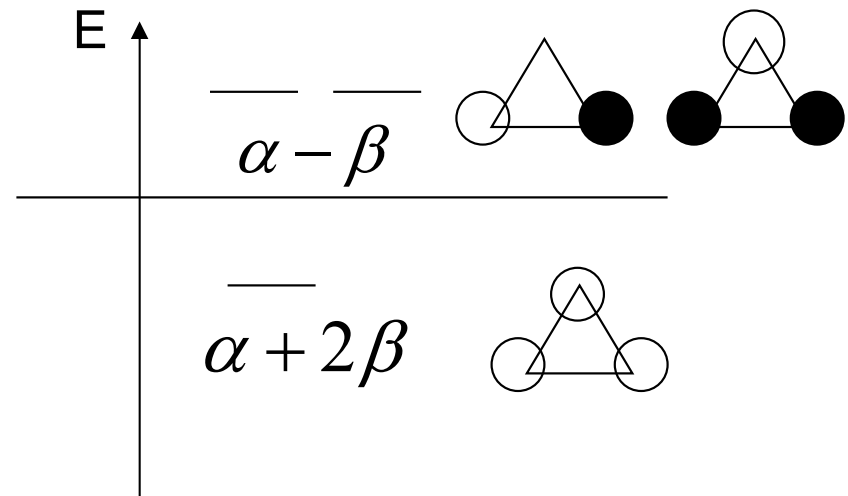


$$H_3 \text{ chain: } \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \rightarrow \begin{cases} \text{---} & \alpha - \sqrt{2}\beta & \odot \bullet \odot \\ \text{+} & \alpha & \odot \bullet \bullet \\ \text{++} & \alpha + \sqrt{2}\beta & \odot \odot \odot \end{cases}$$

$$E_{tot} = 3\alpha + 2\sqrt{2}\beta$$

$H_3$  equilateral  $\Delta$

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

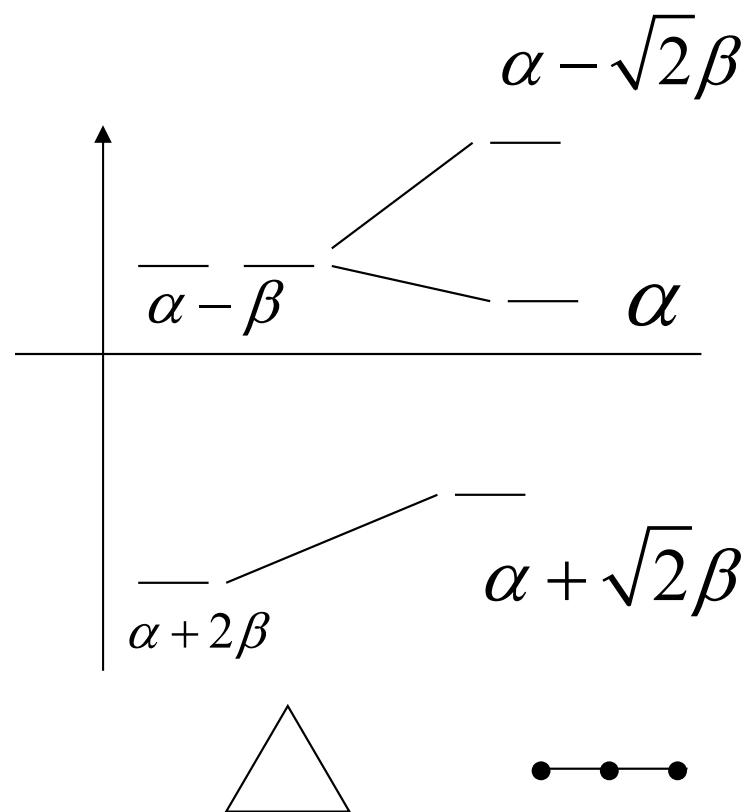


$$\longrightarrow (\alpha - E)^3 - 3\beta^2(\alpha - E) + 2\beta^3$$

$$\longrightarrow E = \alpha + 2\beta, \quad \alpha - \beta, \quad \alpha - \beta$$

# Total energies

	linear	equil $\Delta$
$H_3^{2+}$	$\alpha + 1.4\beta$	$\alpha + 2\beta$
$H_3^+$	$2\alpha + 2.8\beta$	$2\alpha + 4\beta$
$H_3$	$3\alpha + 2.8\beta$	$3\alpha + 3\beta$
$H_3^-$	$4\alpha + 2.8\beta$	$4\alpha + 2\beta$
$H_3^-$	$5\alpha + 1.4\beta$	$5\alpha + \beta$

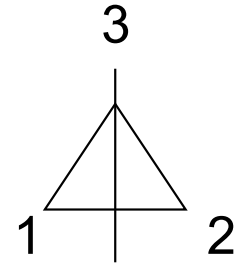


## Use of symmetry to simplify

Basic idea: make symmetry-adapted basis functions

Equilateral triangle using one symmetry plane

$$\left. \begin{aligned} \psi_1 &= \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2) \\ \psi_2 &= \varphi_3 \\ \psi_3 &= \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2) \end{aligned} \right\} \begin{aligned} H_{11} &= \alpha + \beta & H_{12} &= \sqrt{2}\beta \\ H_{22} &= \alpha & H_{13} &= 0 \\ H_{33} &= \alpha - \beta & H_{23} &= 0 \end{aligned}$$



$\psi_1$  and  $\psi_2$  same symmetry

The use of symmetry causes the matrix to become block-diagonal

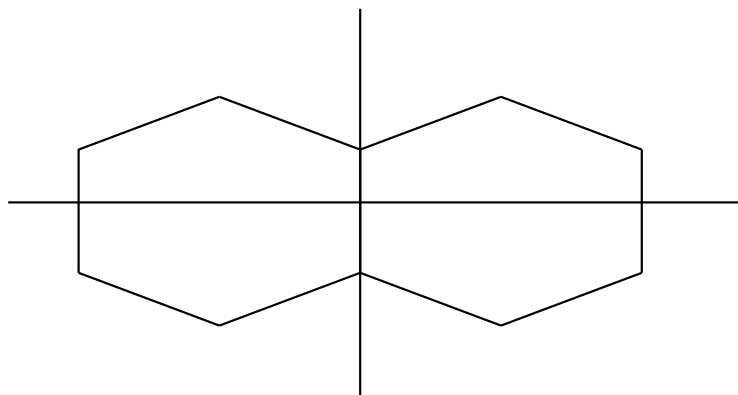
This is a consequence that only functions of the same symmetry can mix

$$\left( \begin{array}{cc|c} \alpha + \beta & \sqrt{2}\beta & 0 \\ \sqrt{2}\beta & \alpha & 0 \\ \hline 0 & 0 & \alpha - \beta \end{array} \right)$$

Block diagonal

2 x 2, 1 x 1

Naphthalene



use these two symmetry planes to factorize  
 $10 \times 10 \longrightarrow 2(2 \times 2), 2(3 \times 3)$

Butadiene:  $4 \times 4 \longrightarrow 2(2 \times 2)$

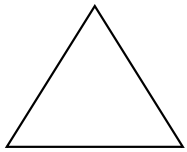
Using one symmetry operation



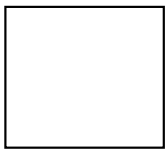
# Connection between symmetry and degeneracies

Need 3-fold or higher symmetry for degeneracies.

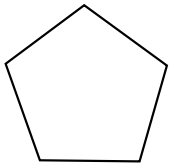
$(360/n)^\circ$  rotation  $\Rightarrow$   $n$ -fold symmetry axis



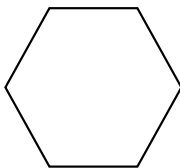
$n = 3$



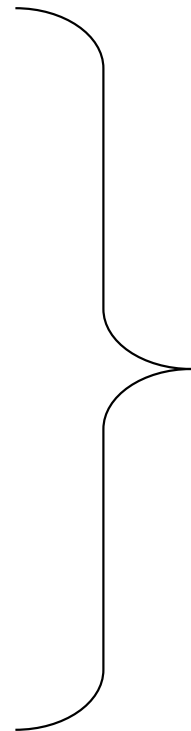
$n = 4$



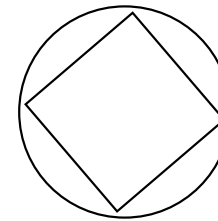
$n = 5$



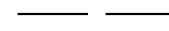
$n = 6$



all have some doubly degenerate orbitals



$\alpha - 2\beta$



$\alpha$



$\alpha + 2\beta$

Inscribe polygon inside circle of radius  $2\beta$ .

Read off where corners touch the circle

cylinder (infinite-fold)  
Note rectangle has only 2-fold symmetry

Suppose we add another “dimension”

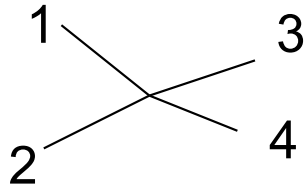
tetrahedron, cube, icosahedron, etc.

$$\begin{pmatrix} \alpha & \beta & \beta & \beta \\ \beta & \alpha & \beta & \beta \\ \beta & \beta & \alpha & \beta \\ \beta & \beta & \beta & \alpha \end{pmatrix} = H \quad \longrightarrow \quad \frac{\begin{array}{cccc} - & - & - & \alpha - \beta \end{array}}{-\alpha + 3\beta} \quad \left[ \begin{array}{c} \text{tetrahedron with one black dot} \\ \text{tetrahedron with four white dots} \end{array}, \dots \right]$$

**Note:** This could be a model for tetrahedral  $H_4$ , the arrangement of  $H$  atoms around the  $C$  atom in methane

In methane, these orbitals of the  $H$  atoms can only mix with  $C$  orbitals of the same symmetry. **What mixing is allowed?**

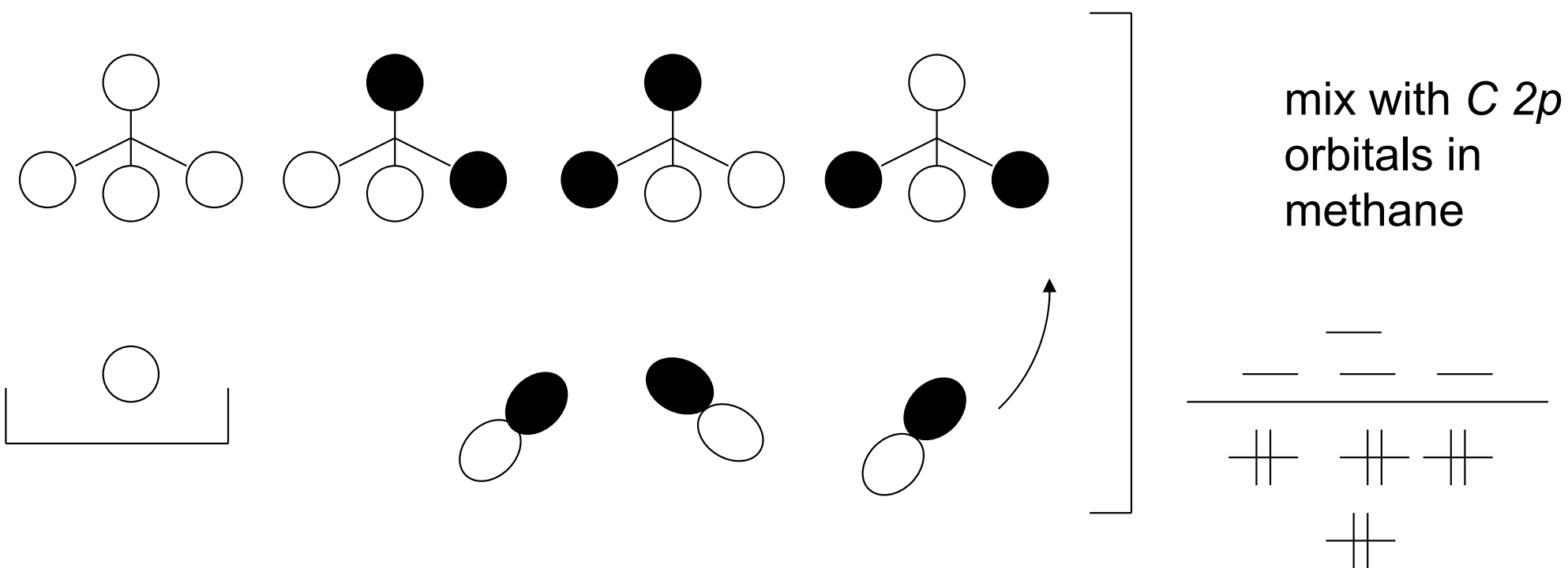
the tetrahedron is a good example the power of using symmetry



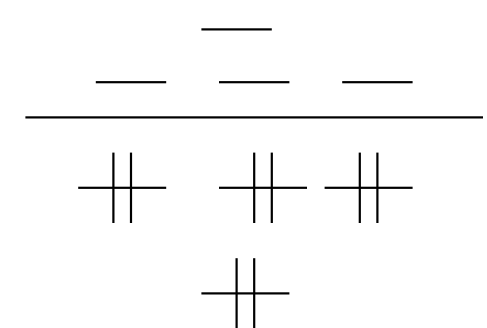
two perpendicular symmetry planes

$$\left[ \begin{array}{l} x_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \\ x_2 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4) \end{array} \right. \left. \begin{array}{l} H_{11} = \alpha + \beta \\ H_{22} = \alpha + \beta \\ H_{12} = 2\beta \end{array} \right\} \longrightarrow \alpha + 3\beta, \quad \alpha - \beta$$


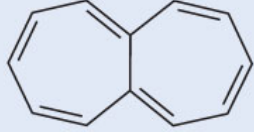
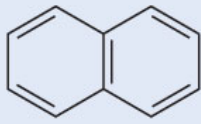
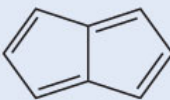
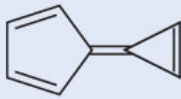
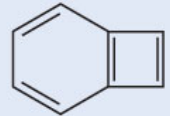
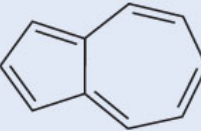
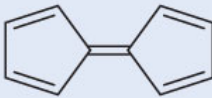
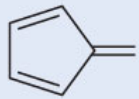

$$\begin{array}{l} x_3 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \\ x_4 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3) \end{array} \quad \begin{array}{l} H_{33} = \alpha - \beta \\ H_{44} = \alpha - \beta \end{array}$$



mix with C 2p  
orbitals in  
methane



# Resonance delocalization energy (units of $\beta$ , per $\pi$ electron)

	Benzene 0.065		Heptalene -0.004
	Naphthalene 0.055		Pantelene -0.018
	Calicene 0.043		Benzocyclobutadiene 0.065
	Azulene 0.023		Fulvalene -0.033
	Fulvene -0.002		Cyclobutadiene -0.268

Reference molecule should be linear

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Aromatic - stabilized

Antiaromatic - destabilized

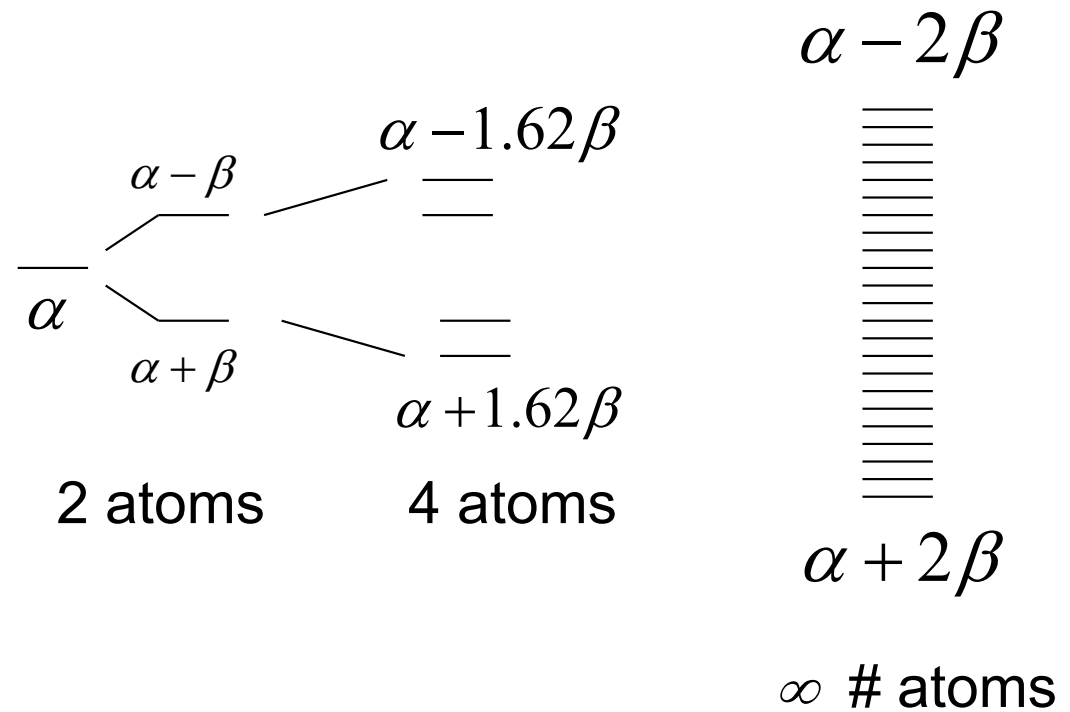
$$H = \begin{pmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{pmatrix}$$

What happens to the pattern of energy levels when we go from benzene to pyridine? To fluorobenzene? To 1,3,5 trifluorobenzene?

How can we model these chemical substitutions using Huckel theory?

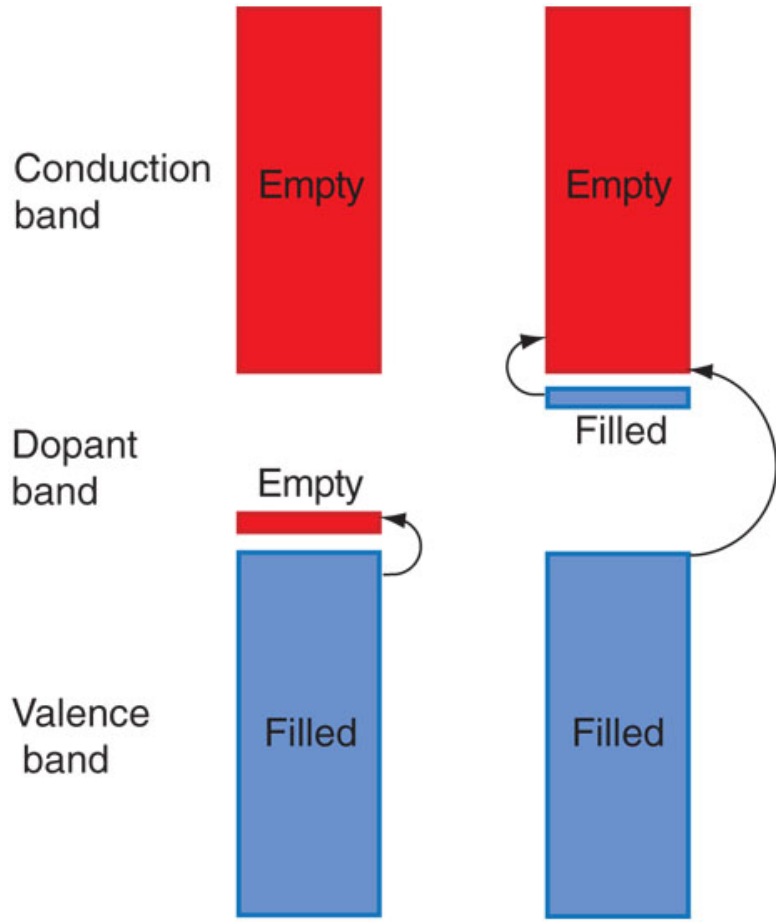
# Emergence of band structure as chain length grows

Figure 13.18  
correction



Actually, one cannot have long range order in 1 dimension, and as a results the bonds alternative long, short, long, which opens up a band gap.

Do you see why?



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*p*-type      *n*-type

Silicon

*B*      *P*      dopants