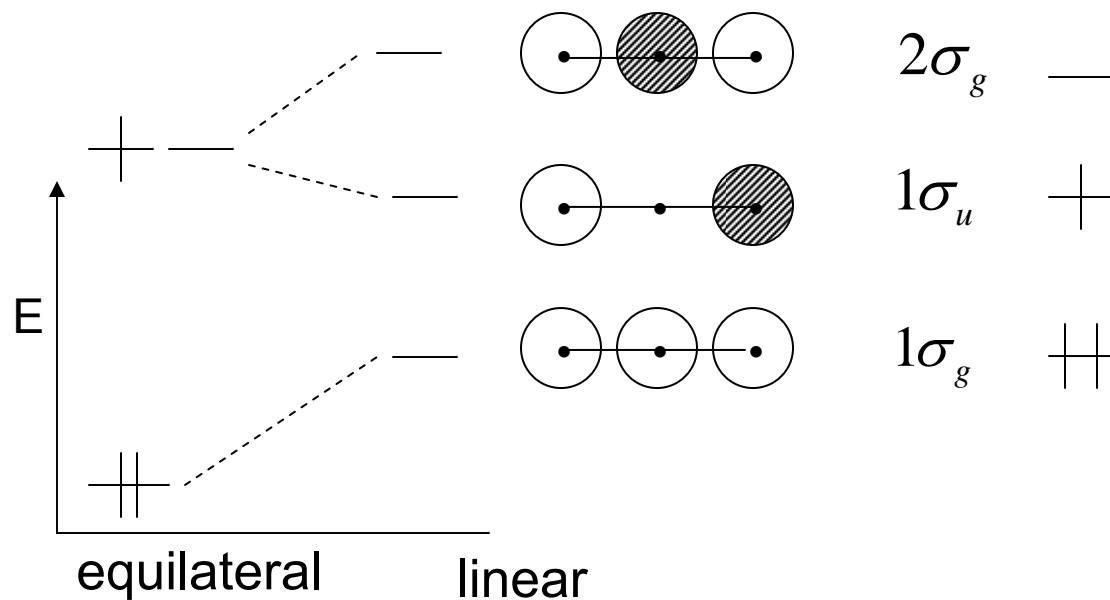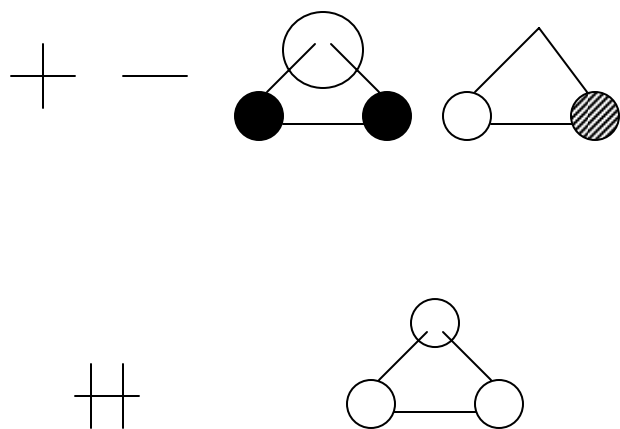# Chapter 14 – Polyatomics

Is H_3 linear or triangular?

If equilateral, 2nd and 3rd orbitals are degenerate

H_3^+ prefers triangular structure

H_3^- prefers linear structure
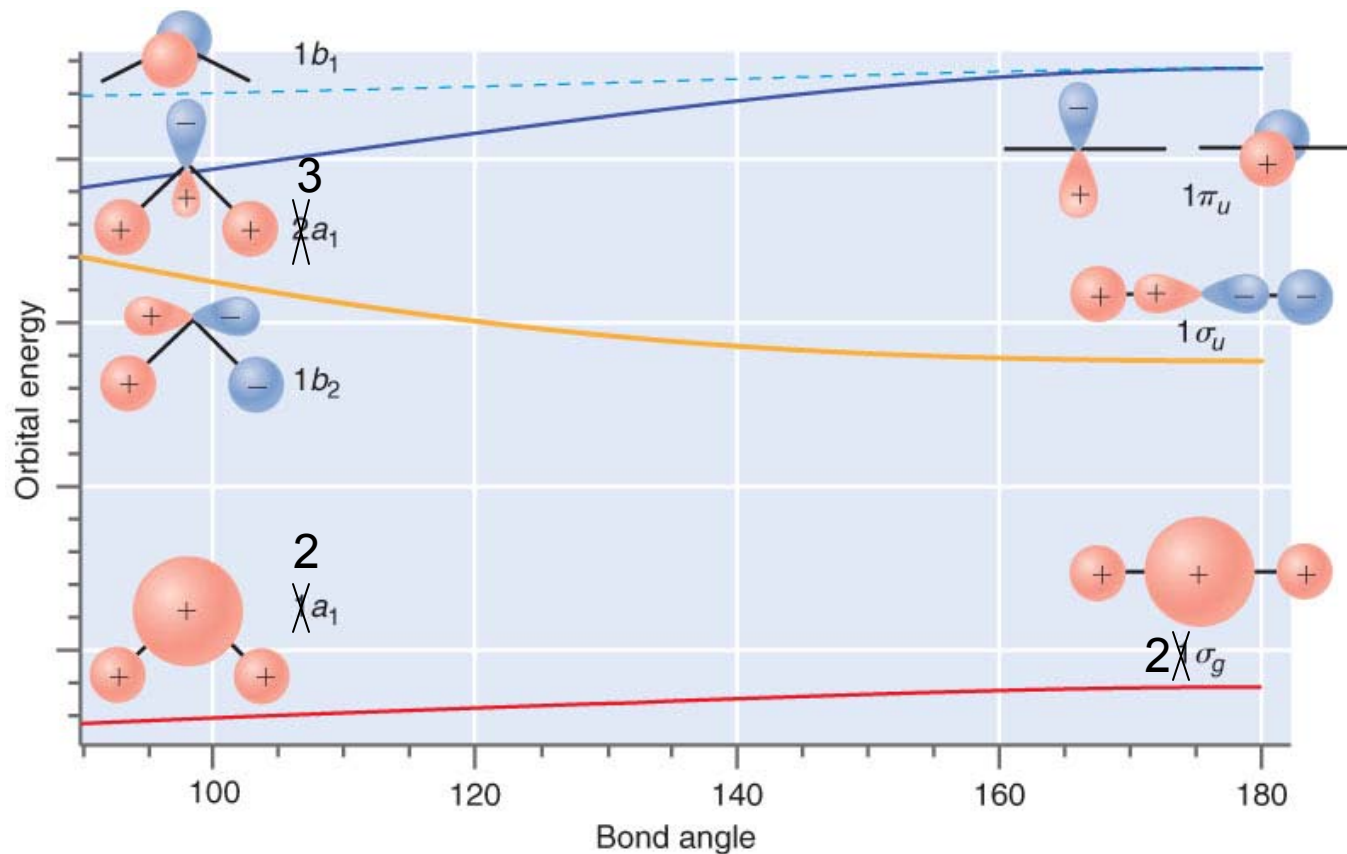
This is the simplest example of Walsh's rules.

Less obvious whether H_3 will 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

Note: the text sips over the numbers associated with orbitals derived from core 1s.

This is non-standard. It is better to account for these AOs when labeling MOs.

Orbital energy

$1b_1$

3

$\cancel{2}a_1$

$1b_2$

2

$\cancel{X}a_1$

$1\pi_u$

$1\sigma_u$

$2\cancel{X}\sigma_g$

100   120   140   160   180

Bond angle

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

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

$$\begin{pmatrix} H_{11} - E & H_{12} ... & H_{1n} \\ H_{21} & H_{22} - E ... H_{2n} \\ ... & ... & ... \\ H_{n1} & H_{n2} & H_{nn} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = 0$$
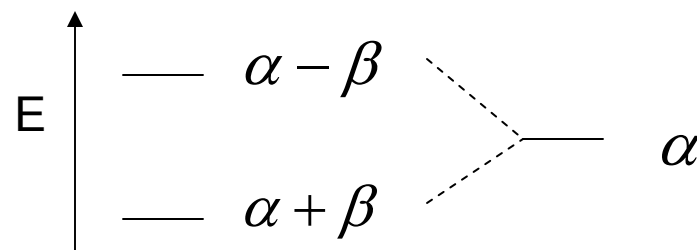
⟵ Setting $S_{ij} = 0,$

$$i \neq j$$

Now set $H_{ii} = \alpha$

$H_{ij} = \beta$ ⟵ nearest neighbor

$= 0$ ⟵ otherwise

E —— $\alpha - \beta$

—— $\alpha + \beta$

α

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

β is a negative quantity

Model of H_2 or of pi orbitals of ethylene

H_3 chain:
$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \longrightarrow$$

$$\begin{cases} \text{---} & \alpha - \sqrt{2}\beta \\ + & \alpha \\ ++ & \alpha + \sqrt{2}\beta \end{cases}$$
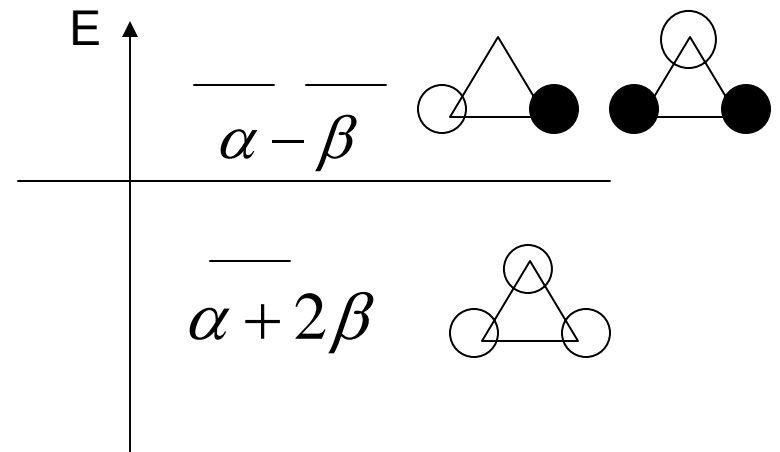
$$E_{tot} = 3\alpha + 2\sqrt{2}\beta$$

H_3 equilateral Δ

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$
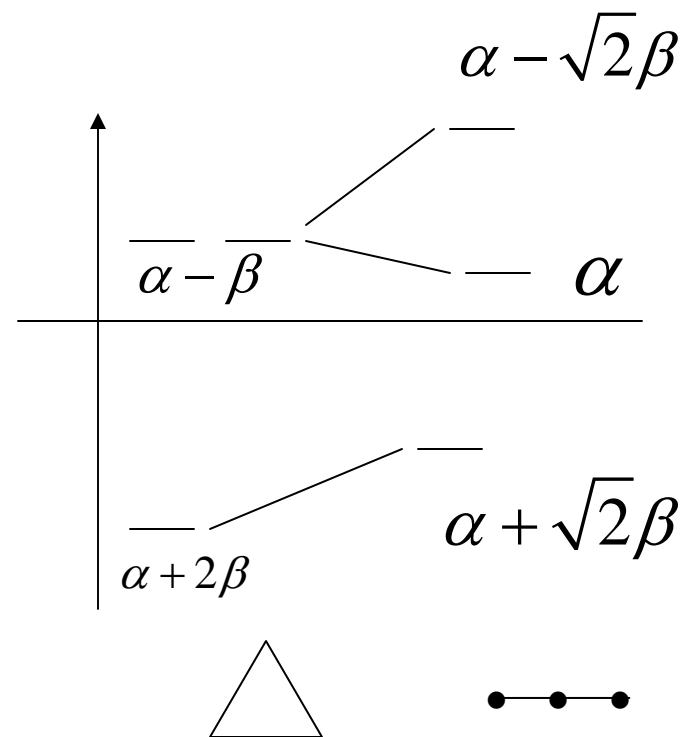
$\longrightarrow \quad (\alpha - E)^3 - 3\beta^2(\alpha - E) + 2\beta^3$

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

E

$$\alpha - \beta$$

$$\alpha + 2\beta$$

Actually, when one does the cofactor expansion it is clear that $E = \alpha - \beta$ factorizes out

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

$$\alpha - \sqrt{2}\beta$$

$$\alpha - \beta \qquad \alpha$$

$$\alpha + \sqrt{2}\beta$$

$$\alpha + 2\beta$$

Use of symmetry to simplify – use of one symmetry plane

$$\psi_1 = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$$

$$\psi_2 = \varphi_3$$

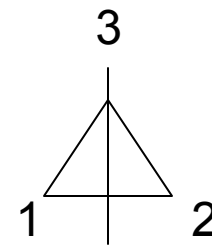$$\psi_3 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3)$$

$$H_{11} = \alpha + \beta \qquad H_{12} = \sqrt{2}\beta$$

$$H_{22} = \alpha \qquad H_{13} = 0$$

$$H_{33} = \alpha - \beta \qquad H_{23} = 0$$

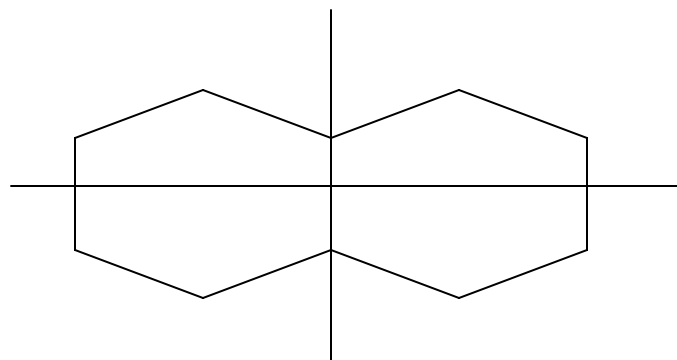ψ_1 and ψ_2 same symmetry

$$\begin{pmatrix} \alpha + \beta & \sqrt{2}\beta & 0 \\ \sqrt{2}\beta & \alpha & 0 \\ 0 & 0 & \alpha - \beta \end{pmatrix}$$
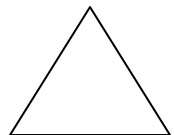
Block diagonal

2 x 2,   1 x 1

Naphthalene

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

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

Connection between symmetry and degeneracies
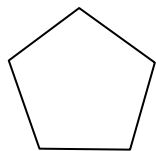
Need 3-fold or higher symmetry for degeneracies.
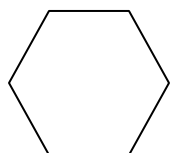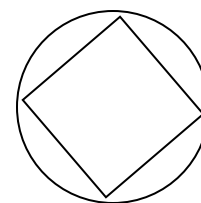$(360/n)°$ rotation $\Rightarrow$ n-fold symmetry axis

$n = 3$

$n = 4$

$n = 5$

$n = 6$

all have some
doubly degenerate
orbitals

— $\alpha - 2\beta$

– – α

— $\alpha + 2\beta$

Inscribe polygon
inside circle of
radius 2β.
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.

$$\begin{pmatrix} \alpha & \beta & \beta & \beta \\ \beta & \alpha & \beta & \beta \\ \beta & \beta & \alpha & \beta \\ \beta & \beta & \beta & \alpha \end{pmatrix} = H \qquad \longrightarrow \qquad \begin{matrix} - - - \quad \alpha - \beta \\ \rule{5cm}{0.4pt} \\ - \quad \alpha + 3\beta \end{matrix}$$

Note: This could be a model for tetrahedral H_4, precisely 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?
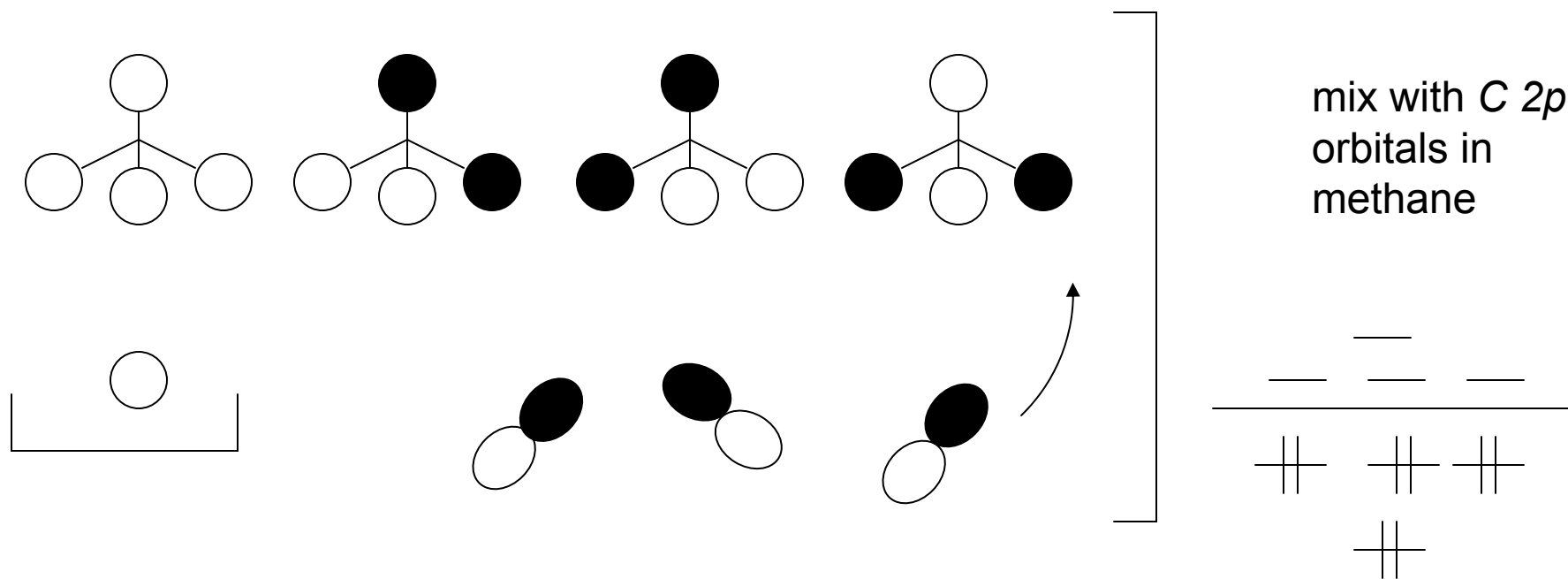
the tetrahedron is a good example for using symmetry

1   3

2   4
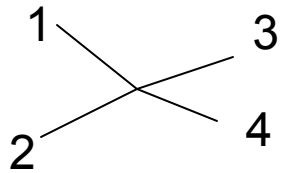
two perpendicular symmetry planes

$$x_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$$x_2 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4)$$

$$x_3 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

$$x_4 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3)$$

$$H_{11} = \alpha + \beta$$

$$H_{22} = \alpha + \beta$$

$$H_{12} = 2\beta$$

$$H_{33} = \alpha - \beta$$

$$H_{44} = \alpha - \beta$$

$$\longrightarrow \quad \alpha + 3\beta, \quad \alpha - \beta$$

mix with *C 2p*
orbitals in
methane
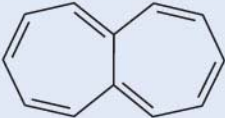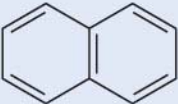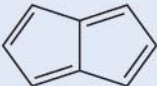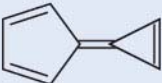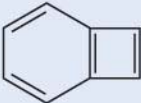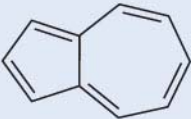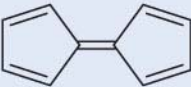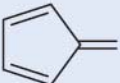
Interesting problem to think about

Bonding in dibenzenechromium, a sandwich
compound with the *Cr* between two benzene rings

Resonance delocalization energy per π electron

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

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Reference molecule should be linear

-0.12

Aromatic - stabilized

Antiaromatic - destabilized

Figure 13.18
correction

$\alpha - \beta$

α

$\alpha + \beta$

$\alpha - 1.62\beta$

$\alpha + 1.62\beta$

$\alpha - 2\beta$

$\alpha + 2\beta$

2 atoms

4 atoms

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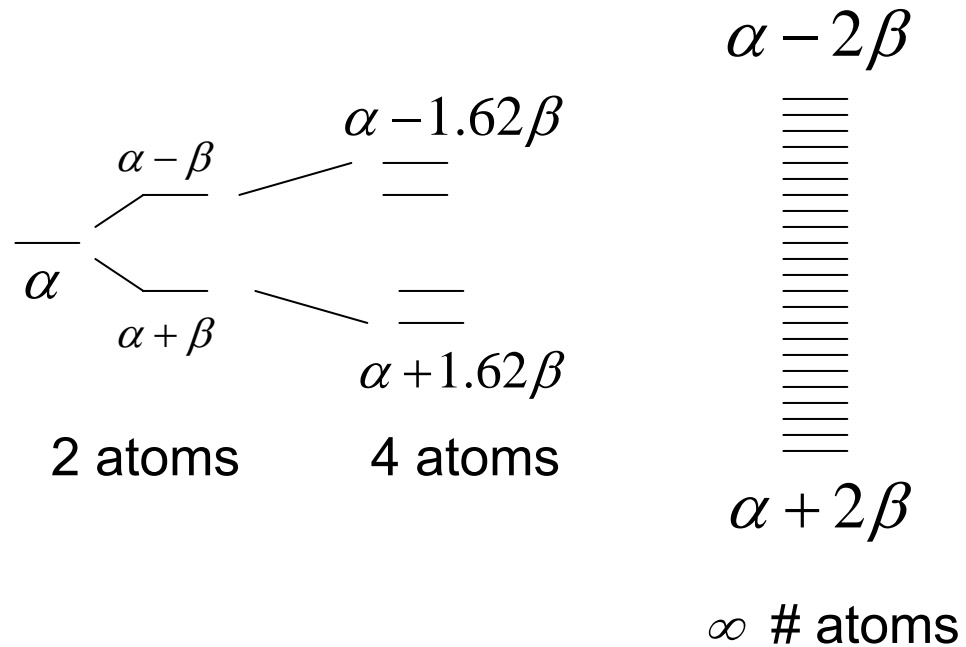
Actually, one cannot have long range order in 1 dimension, and as a results the bonds alternative long, short, long, which opens up a band gap.

Do you see why?

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

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?

Conduction band — Empty (p-type), Empty (n-type)

Dopant band — Empty (p-type), Filled (n-type)

Valence band — Filled (p-type), Filled (n-type)

p-type   *n*-type

Silicon

B   P   dopants