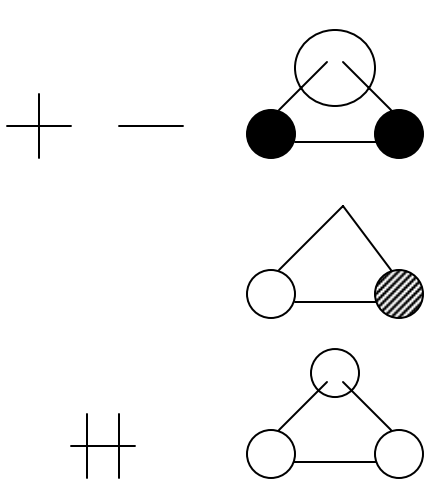
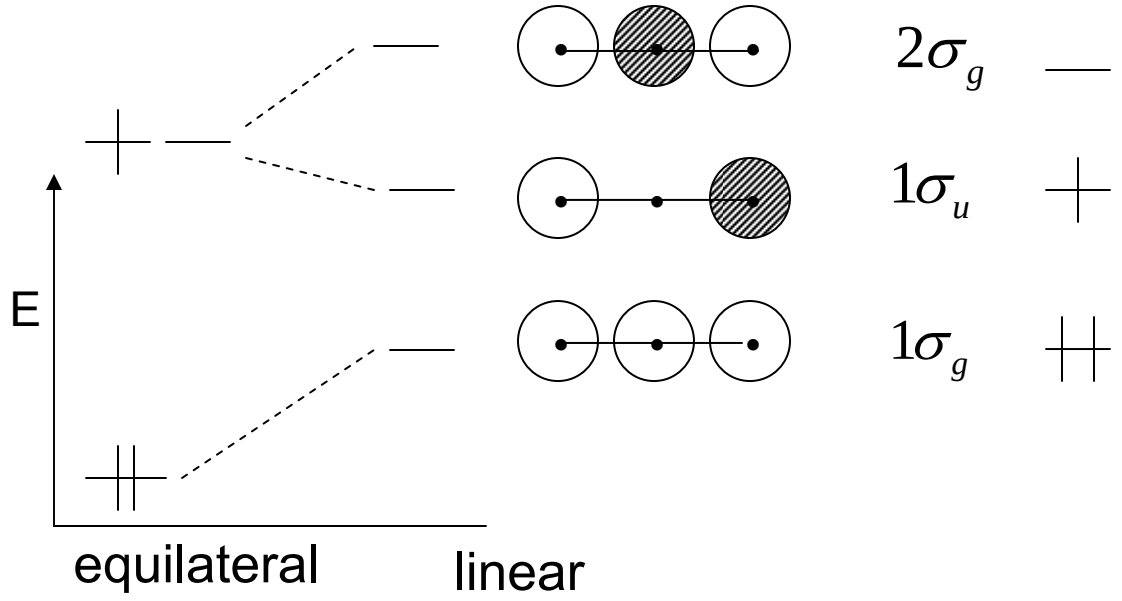
Chapter 14 – Polyatomics

Is H_3 linear or triangular?





If equilateral, 2nd and 3rd orbitals are degenerate

H_3^+ prefers triangular structure

H_3, H_3^- prefer linear structure

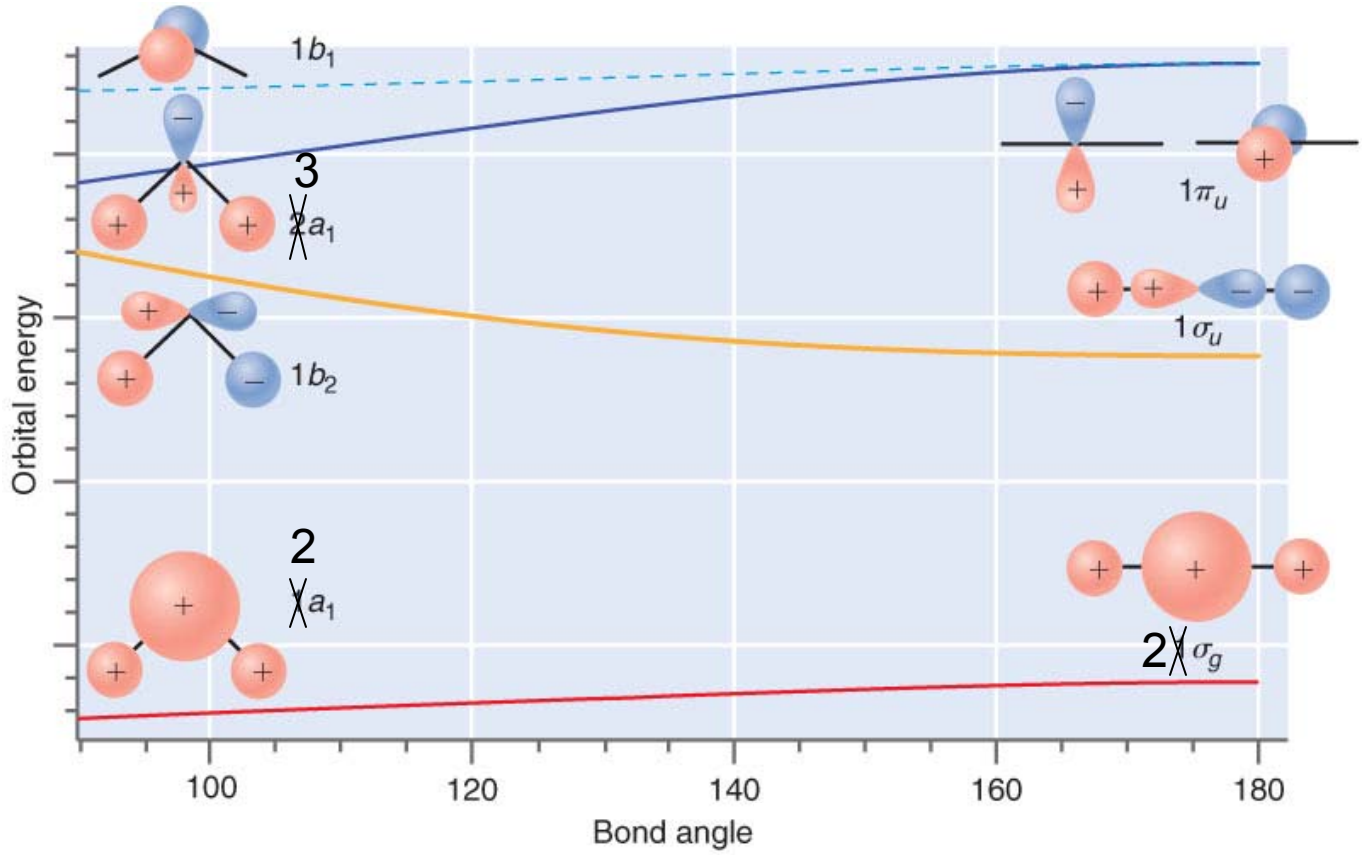
This is the simplest example of Walsh's rules.

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

can also apply to H_n clusters – one *s* orbital per *H* atom

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

$$\begin{pmatrix} H_{11} & H_{12} & \ldots & H_{1n} \\ H_{21} & H_{22} & \ldots & H_{2n} \\ \ldots & \ldots & & \ldots \\ H_{n1} & H_{n2} & \ldots & H_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix}$$

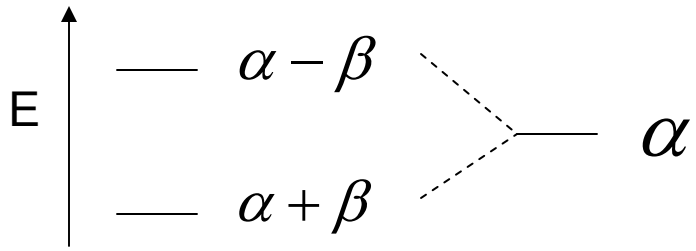
← Setting $S_{ij} = 0, \quad i \neq j$

Now set $H_{ii} = \alpha$

$H_{ij} = \beta$ ← nearest neighbor

$= 0$ ← otherwise

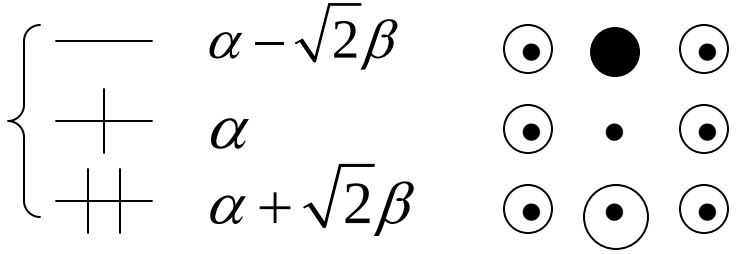
$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \qquad E = \alpha \pm \beta$$



β is a negative quantity

Model of H_2 or of pi orbitals of ethylene

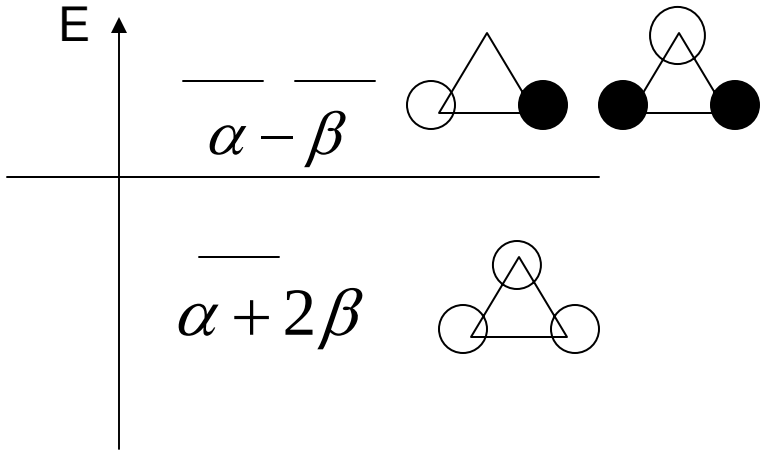
H_3 chain: $\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \longrightarrow$



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

H_3 equilateral Δ

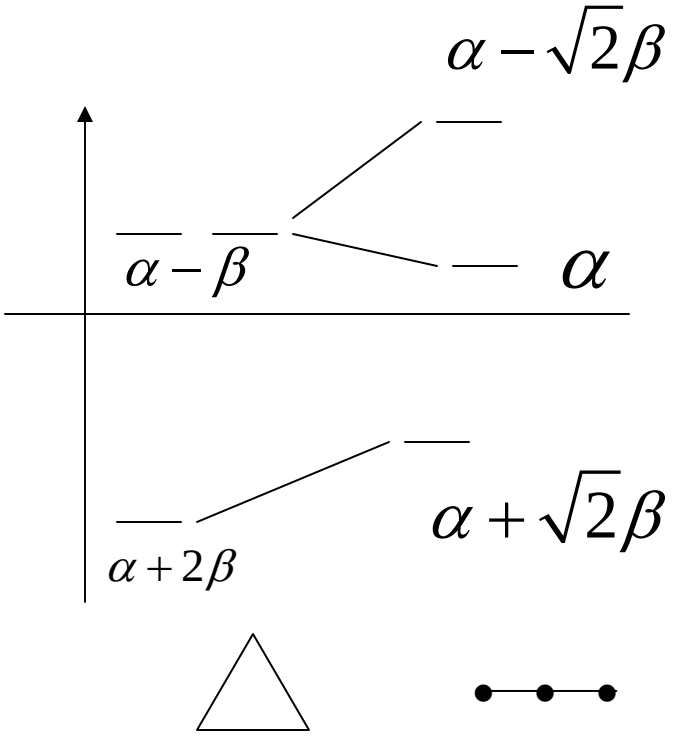
$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$



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

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

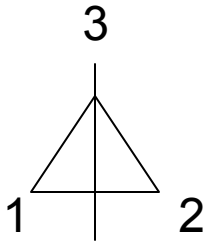
	linear	equil Δ
H_3^{2+}	$\alpha+1.4\beta$	$\boxed{\alpha+2\beta}$
H_3^{+}	$2\alpha+2.8\beta$	$\boxed{2\alpha+4\beta}$
H_3	$3\alpha+2.8\beta$	$\boxed{3\alpha+3\beta}$
H_3^{-}	$\boxed{4\alpha+2.8\beta}$	$4\alpha+2\beta$
$H_3^{=}$	$\boxed{5\alpha+1.4\beta}$	$5\alpha+\beta$



Use of symmetry to simplify

$$\psi_1=\frac{1}{\sqrt{2}}(\varphi_1+\varphi_2)$$
$$\psi_2=\varphi_3$$
$$\psi_3=\frac{1}{\sqrt{2}}(\varphi_1-\varphi_3)$$

$$H_{11}=\alpha+\beta \qquad H_{12}=\sqrt{2}\beta$$
$$H_{22}=\alpha \qquad H_{13}=0$$
$$H_{33}=\alpha-\beta \qquad H_{23}=0$$

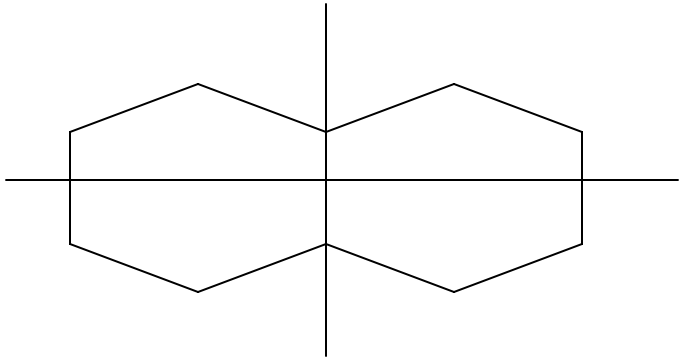


$$\left(\begin{array}{cc|c} \alpha+\beta & \sqrt{2}\beta & 0 \\ \sqrt{2}\beta & \alpha & 0 \\ \hline 0 & \alpha & \alpha\text{-}\beta \end{array}\right)$$

Block diagonal

2 x 2, 1 x 1

Naphthalene

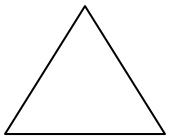


use these two symmetry planes to factorize
10 x 10 ⟶ 2(2 x 2), 2(3 x 3)

Butadiene: 4 x 4 ⟶ 2(2 x 2)

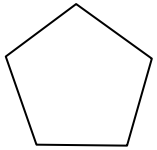
Connection between symmetry and degeneracies

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

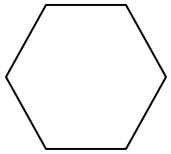


$n = 3$

$n = 4$



$n = 5$

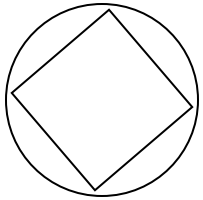


$n = 6$

•
•
•

cylinder (infinite-fold)

all have some doubly degenerate orbitals



$\alpha - 2\beta$

α

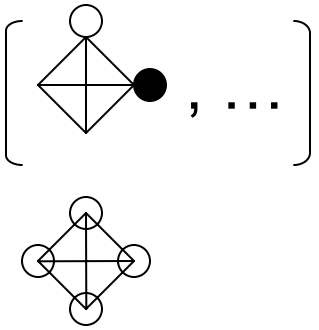
$\alpha + 2\beta$

Inscribe polygon inside circle of radius 2β.
Read off where corners touch the circle

Suppose we add another "dimension"

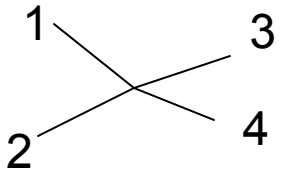
tetrahedron, cube, icosahedron, etc.

$$\begin{pmatrix} \alpha & \beta & \beta & \beta \\ \beta & \alpha & \beta & \beta \\ \beta & \beta & \alpha & \beta \\ \beta & \beta & \beta & \alpha \end{pmatrix} = H \longrightarrow \begin{array}{c} \text{— — —} \quad \alpha - \beta \\ \hline \text{—} \quad \alpha + 3\beta \end{array}$$



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

the tetrahedron is a good example for using symmetry



two perpendicular symmetry planes

$$x_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \qquad H_{11} = \alpha + \beta$$

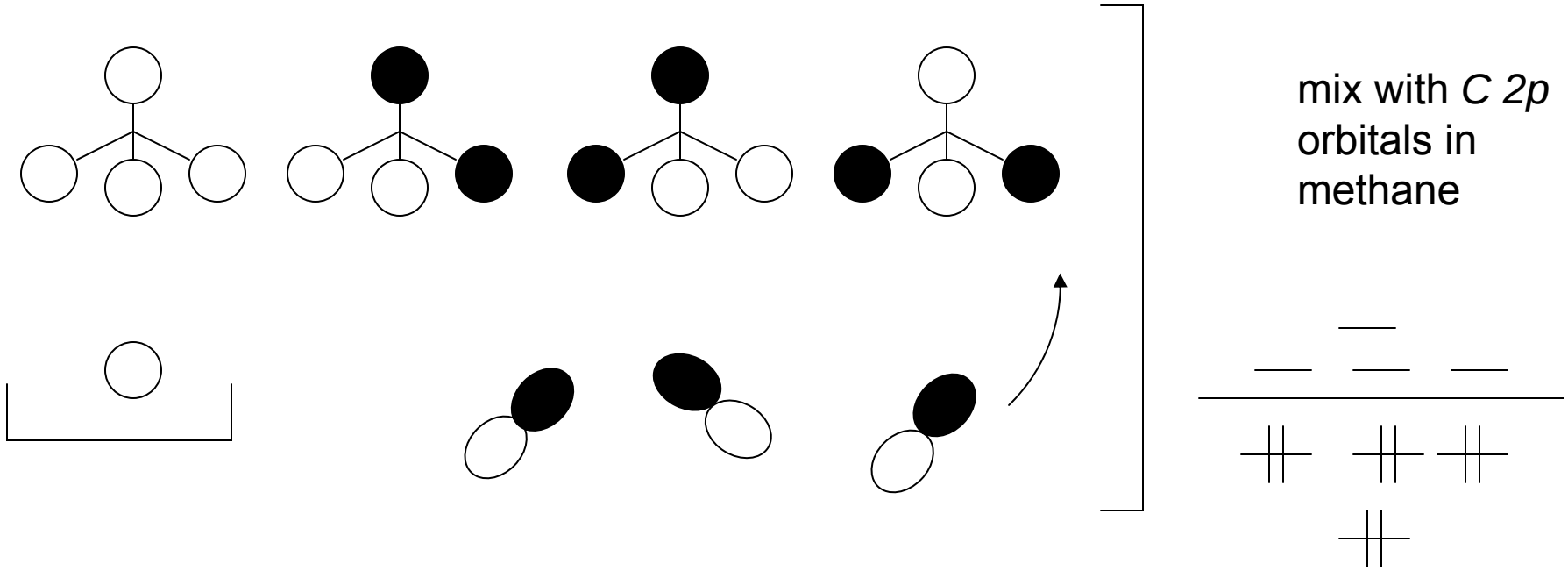
$$x_2 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4) \qquad H_{22} = \alpha + \beta$$

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

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

$$x_3 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \qquad H_{33} = \alpha - \beta$$

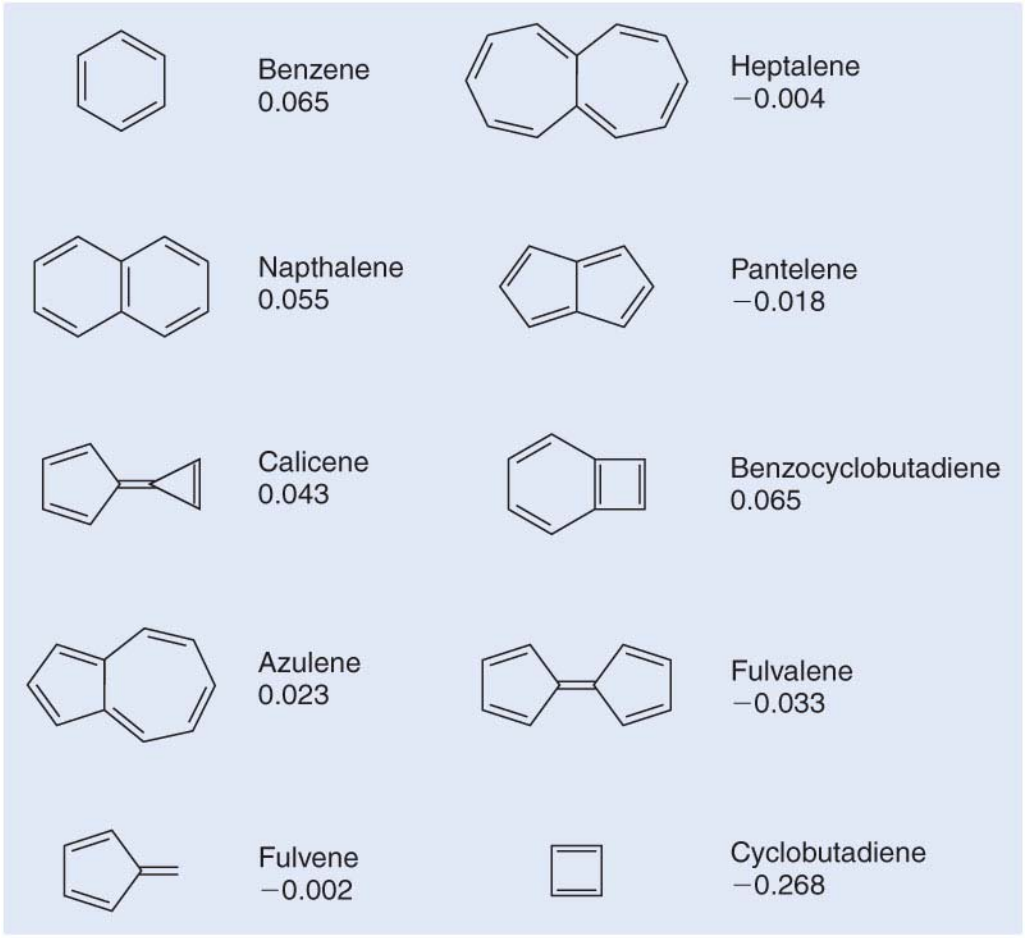
$$x_4 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3) \qquad H_{44} = \alpha - \beta$$



Interesting problem to think about

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

Resonance delocalization energy per π electron

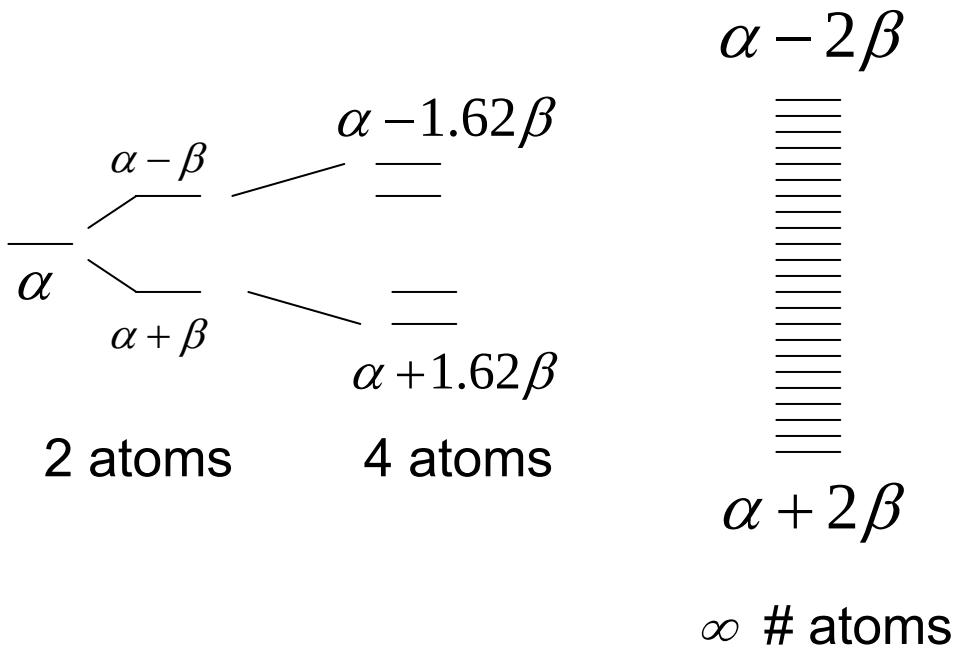


Reference molecule should be linear

Aromatic - stabilized

Antiaromatic - destabilized

Figure 14.20 correction



In reality, the ∞ has bond alternation, which opens up a band gap.