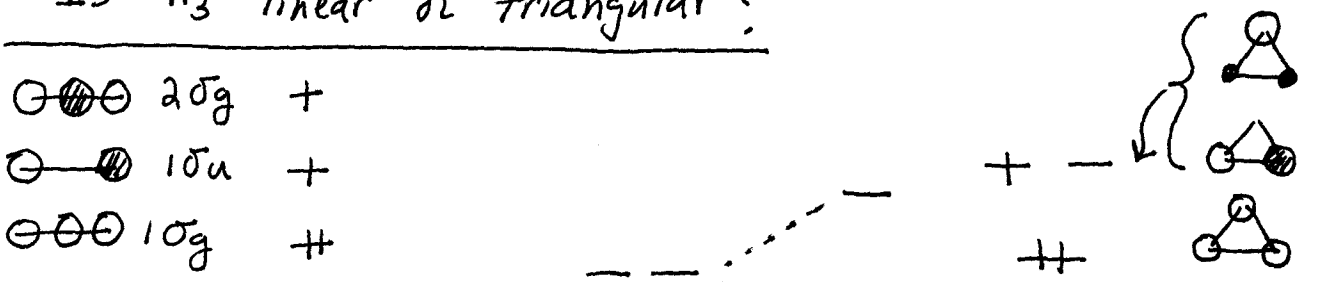
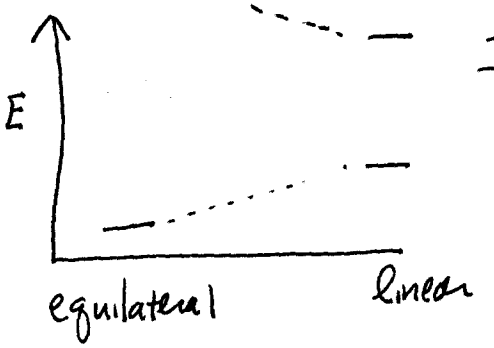
Is H_3 linear or triangular?



Now construct a correlation diagram



If an equilateral 2nd + 3rd orbitals are degenerate

H_2^+ prefers triangular structure
H_2, H_2^- prefer linear structure

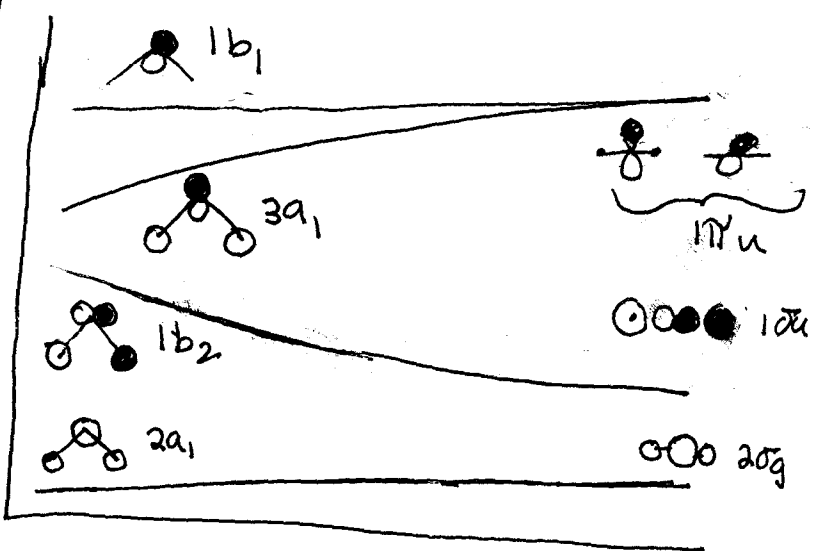
This is the simplest example of Walsh's rules.

Now consider the bending of an XH_2 triatomic.

BeH_2 : linear

CH_2 : bent

OH_2^+ – almost the same geometry as OH_2.



Huckel model

usual - 1 p_z orbital per C atom

can also apply to H_n clusters - 1 s orbital per H atom.

$$\psi = c_1\phi_1 + c_2\phi_2 + \cdots + c_N\phi_N$$

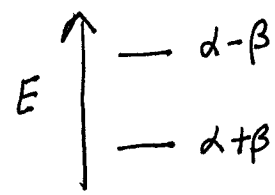
$$\begin{pmatrix} H_{11}-E & H_{12} \cdots & H_{1n} \\ H_{21} & H_{22}-E \cdots & H_{2n} \\ \vdots & \vdots & \vdots \\ H_{n1} & H_{n2} & H_{nn}-E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix} \longleftarrow \text{Setting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

Now set $H_{ii} = \alpha$

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

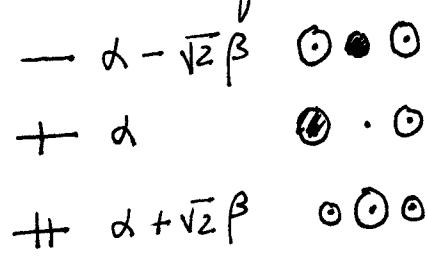
$= 0 \leftarrow$ otherwise

H_2 $\begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix} = 0 \quad E = \alpha \pm \beta$



β is a negative quantity

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



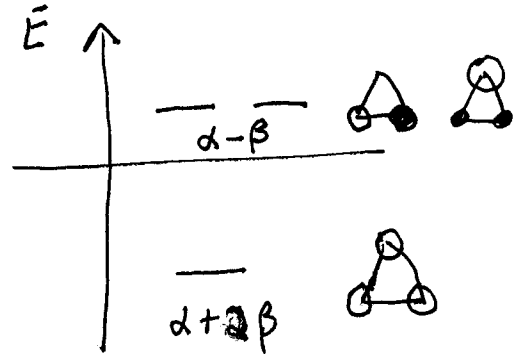
$E_{tot} = 3\alpha + 2\sqrt{2}\beta$

H_3 equilateral Δ

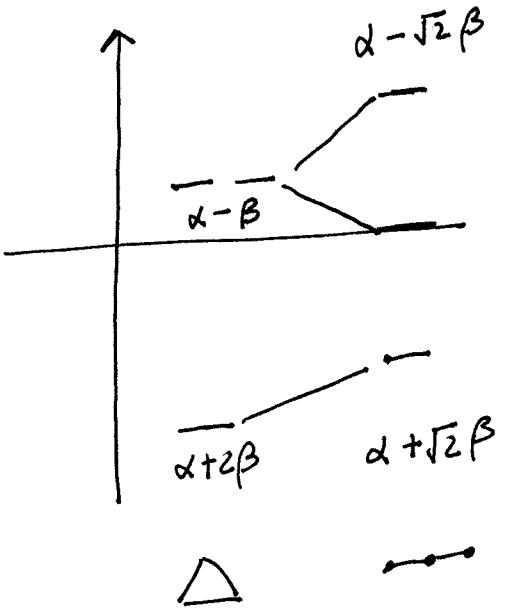
$$\begin{vmatrix} \alpha-E & \beta & \beta \\ \beta & \alpha-E & \beta \\ \beta & \beta & \alpha-E \end{vmatrix} = 0$$

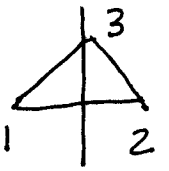
$\rightarrow (\alpha-E)^3 - 3\beta^2(\alpha-E) + 2\beta^3$

$\rightarrow E = \alpha+2\beta,\ \alpha-\beta,\ \alpha-\beta$



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





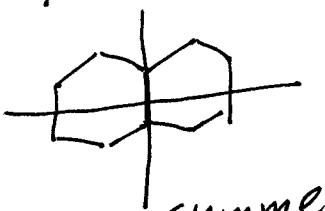
Use of symmetry to simplify

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

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

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

$\leftarrow$ Block diagonal 2×2, 1×1

Naphthalene 

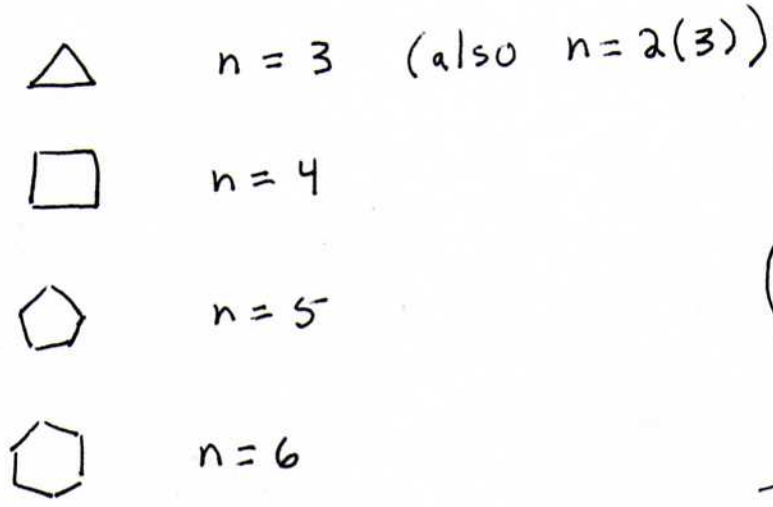
use these two symmetry planes to factorize
$10\times 10 \rightarrow 2(2\times 2)$, $2(3\times 3)$

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

Symmetry — degeneracies.

Need 3-fold or higher symmetry for degeneracies.

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



$n = 3$ (also $n = 2(3)$)

$n = 4$

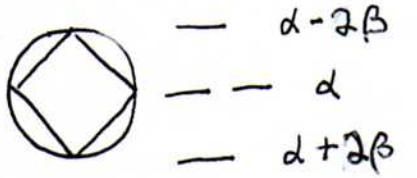
$n = 5$

$n = 6$

⋮

cylinder (infinite fold)

all have some doubly degenerate orbitals

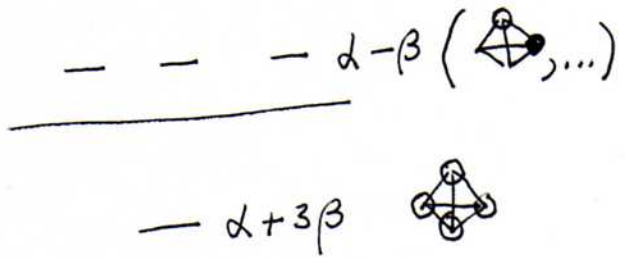


Inscribe polygon inside circle of radius 2β.
Read off where edges touch the circle

Suppose we add another "dimension"

tetrahedron, cube, icosahedron, etc

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



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

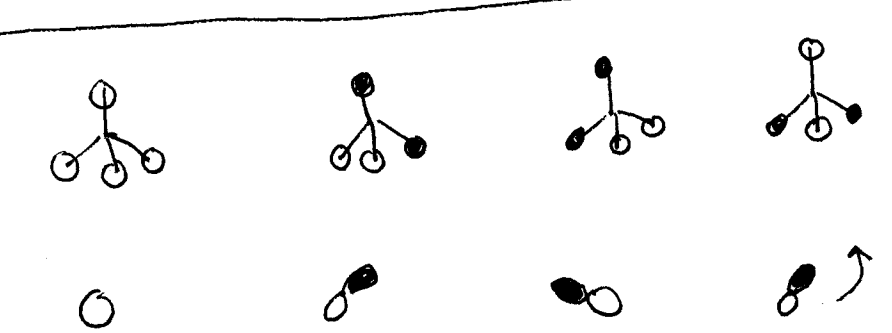
The tetrahedron is a good example for using symmetry

two perpendicular symmetry planes

$$\left[\begin{array}{l} \chi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \\ \chi_2 = \frac{1}{\sqrt{2}}(\phi_3 + \phi_4) \end{array}\right. \qquad \left.\begin{array}{l} H_{11} = \alpha + \beta \\ H_{22} = \alpha + \beta \\ H_{12} = 2\beta \end{array}\right\} \rightarrow \alpha + 3\beta,\ \alpha - \beta$$

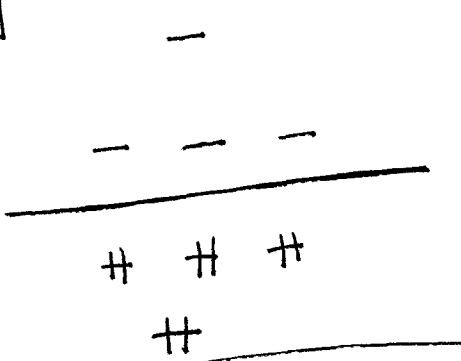
$$\chi_3 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \qquad H_{33} = \alpha - \beta$$

$$\chi_4 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3) \qquad H_{44} = \alpha - \beta$$



mixes with C 2s orbital in methane

mix with C 2p orbitals in methane



Interesting problem to think about.

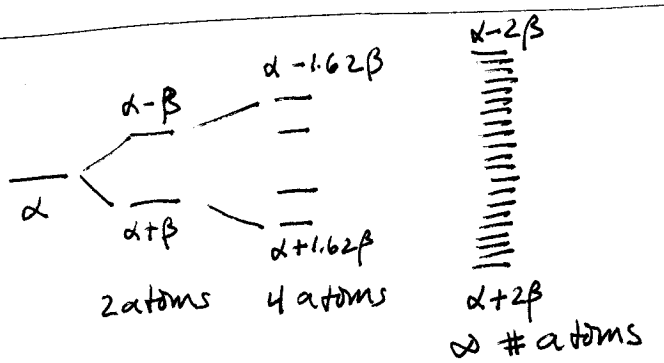
Bonding in dibenzenechromium, a sandwich compound with the Cr between two benzene rings

Resonance delocalization energy per π electron

benzene:	+0.065	aromatic
naphthalene:	+0.055	aromatic
azulene:	+0.023	aromatic
fulvene:	−0.002	
cyclobutadiene:	−0.268	antiaromatic
pentalene:	−0.018	antiaromatic

Reference molecule should be linear

Figure 14.20 correction



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