Part III Symmetry and Bonding

Graphical Method in Hückel Molecular Orbitals

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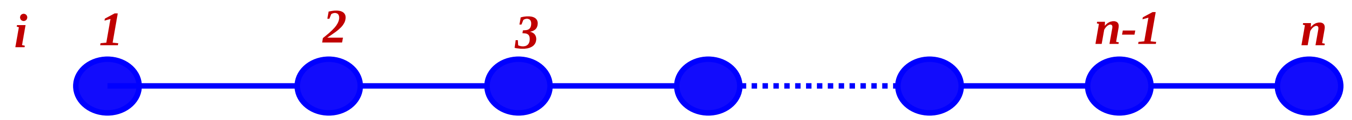
http://pcossgroup.xmu.edu.cn/old/users/xlu/group/courses/theochem/

6.6.1 General process for linear [n]polyenes

Graphical method to predefine the coefficients of HMOs for conjugated systems (developed by ***Qianer Zhang*** et al.)



$$\psi^{\pi} = \sum_{i=1}^{n} c_i \phi_i$$

- For a linear [n]polyene, we have n secular equations ($x = (\alpha - E)/\beta$) :

$$\begin{pmatrix} x & 1 & \dots & 0 & 0 \\ 1 & x & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & x & 1 \\ 0 & 0 & \dots & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \dots \\ c_{n-1} \\ c_n \end{pmatrix} = 0 \Rightarrow \begin{cases} xc_1 + c_2 = 0 \\ c_1 + xc_2 + c_3 = 0 \\ \dots\dots \\ c_{i-1} + xc_i + c_{i+1} = 0 \\ \dots\dots \\ c_{n-2} + xc_{n-1} + c_n = 0 \\ c_{n-1} + xc_n = 0 \end{cases}$$

(cyclic formula)

$$c_{i+1} + c_{i-1} = -xc_i$$

$$\sin A + \sin B = 2\sin\frac{A+B}{2}\cos\frac{A-B}{2}$$

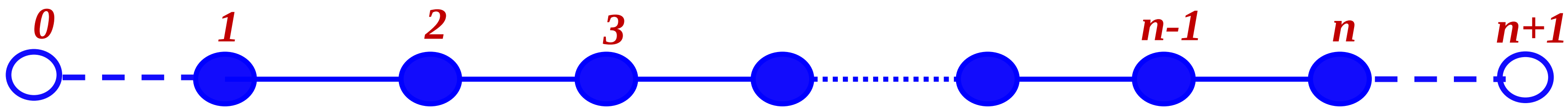
$$\text{if } A = (i+1)\theta, \quad B = (i-1)\theta$$

$$\text{then } \quad x = -2\cos\theta$$

$$\& \quad c_i = \sin i\theta$$

6.6.1 General process for [n]polyenes

Graphical method to predefine the coefficients of HMOs for conjugated systems (developed by ***Qianer Zhang*** et al.)



$$\psi^{\pi} = \sum_{i=1}^{n} c_i \phi_i$$

For a linear [n]polyene, we have ***n*** secular equations ($x = (\alpha - E)/\beta$) :

$xc_1 + c_2 = 0$;

$c_1 + xc_2 + c_3 = 0$; ……

$c_{i-1} + xc_i + c_{i+1} = 0$;

(cyclic formula)

……; $c_{n-1} + xc_n = 0$

$$\xrightarrow[c_1 = \sin\theta]{\text{set } x = -2\cos\theta}
\left[\begin{array}{l}
c_2 = \sin 2\theta \\
c_3 = \sin 3\theta \\
\dots \\
c_i = \sin i\theta \\
\dots \\
c_n = \sin n\theta
\end{array}\right.$$

Boundary condition:

$c_{n+1} = \sin(n+1)\theta = 0$

$\theta_k = 2k\pi/(n+1)$ $(k=1,\dots,n)$

$E_k = \alpha + 2\beta\cos\theta_k$

$$\psi_k^{\pi} = \sum_{i=1}^{n} \phi_i \sin(i\theta_k)$$

(***k*** defines the energy level!)

Now recall the sine wave rule we learnt in the 1st semester!

- The method can be used for dealing with more complicated systems.
- Recent work developed by Prof. Zhenhua Chen can be found as "*Graphical representation of Hückel Molecular Orbitals*" in *J. Chem. Educ.* 2020, 97(2), 448-456.

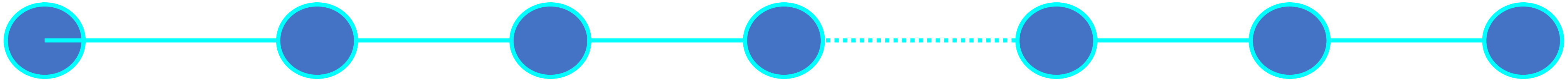
(https://pubs.acs.org/doi/10.1021/acs.jchemed.9b00687)

- FYI： "Introduction to Computational Chemistry: Teaching Hückel Molecular Orbital Theory Using an Excel Workbook for Matrix Diagonalization"

in *J. Chem. Educ.* 2015, 92(2), 291-295.
(https://pubs.acs.org/doi/full/10.1021/ed500376q)

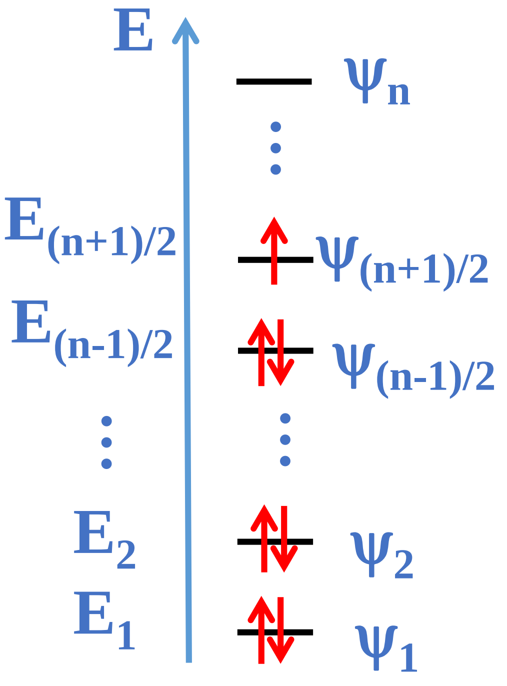
- after-class assignment 2: Please figure out the trends in the energies and compositions of LUMO and HOMO for linear and cyclic [n]ployenes, respectively! (n = 4k,4k+1,4k+2,4k+3)
- After-class assignment 3: Ex. 29

Frontier MO′s of [n]polyene

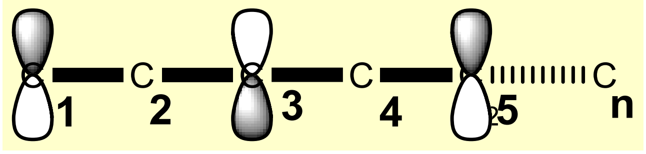


$\theta_k = \frac{k\pi}{n+1}$ $E_k = \alpha + 2\beta\cos(\theta_k)$ $\psi_k = A\sum_{m=1}^{n} \sin(m\theta_k)$ $(k=1,2,\ldots,n;\ A = [2/(n+1)]^{1/2})$

a) When *n=odd*, **SOMO** with $k = (n+1)/2$, $\theta_{SOMO} = \pi/2$, $E_{SOMO} = \alpha$ Non-bonding!



$\psi_{SOMO} = A(\phi_1 - \phi_3 + \phi_5 - \ldots)$ with $C_1 = C_{4i+1} = -C_{4i+3} = A,\ C_2 = C_{2i} = 0$

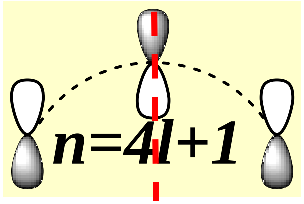


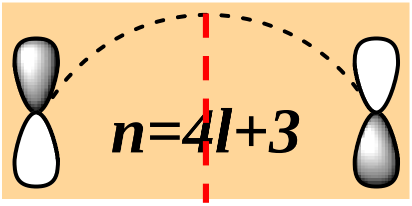
coefficients of AOs in SOMO

$n = 4l+1$ symmetric

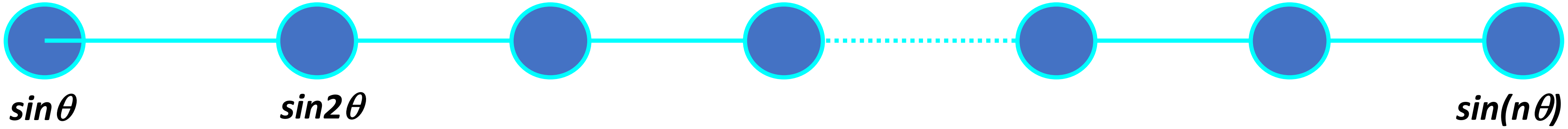
$n = 4l+3$ asymmetric

Simplified diagram of SOMO:



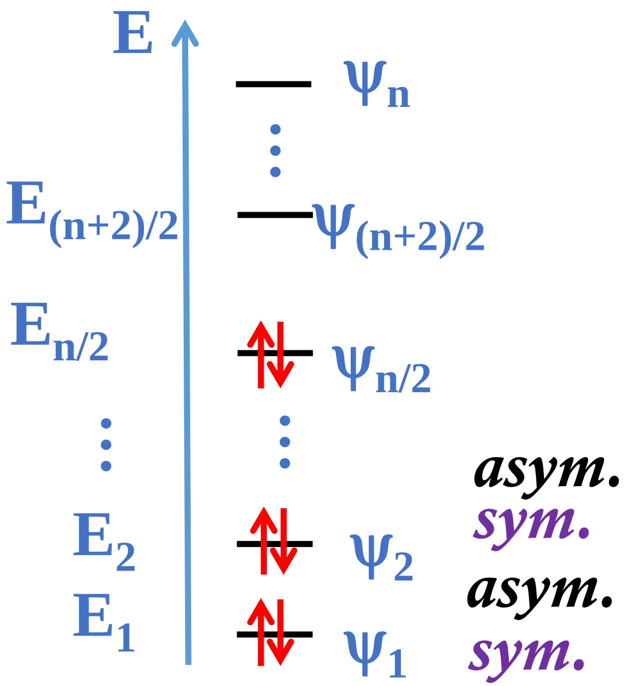


Frontier MO′s of [n]polyene



$$\theta_k = \frac{k\pi}{n+1} \qquad E_k = \alpha + 2\beta\cos\theta_m \qquad \psi_k = A\sum_{m=1}^{n} \sin m\theta_k \quad (k=1,2,\ldots,n;\ A = [2/(N+1)]^{1/2})$$

a) When *n=even*, n/2 bonding MOs, **HOMO** with ***k = n/2***, **LUMO** with ***k = (n+2)/2***,



$$\theta_{HOMO} = \frac{n\pi}{2(n+1)} = \frac{\pi}{2} - \frac{\pi}{2(n+1)} \qquad \theta_{LUMO} = \frac{(n+2)\pi}{2(n+1)} = \frac{\pi}{2} + \frac{\pi}{2(n+1)}$$

i) n = 4l+2

HOMO: $C_n = C_1 \quad C_{n-1} = C_2$ *…, symmetric*

LUMO: $C_n = -C_1 \quad C_{n-1} = -C_2$ *…, anti-symmetric*

ii) n = 4l

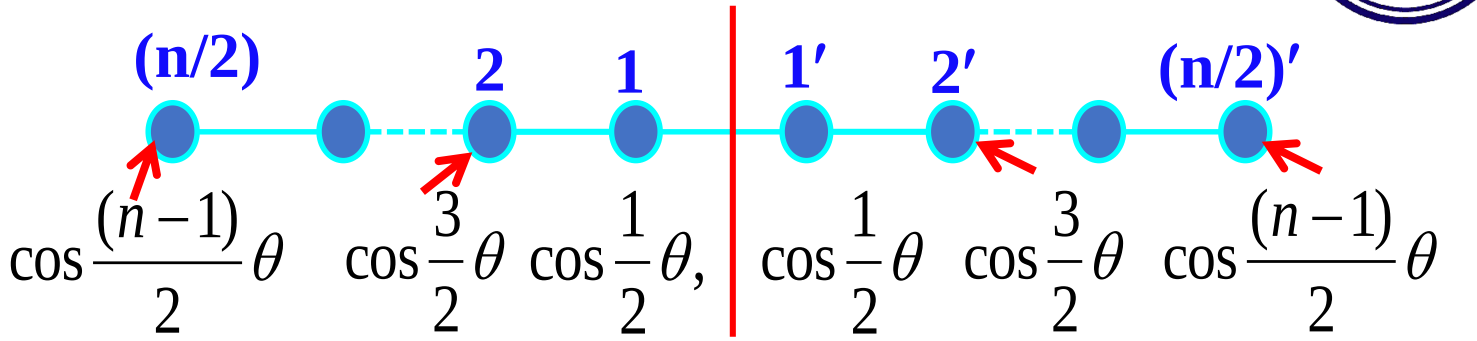
HOMO: $C_n = -C_1 \quad C_{n-1} = -C_2$ *…, anti-symmetric*

LUMO: $C_n = C_1 \quad C_{n-1} = C_2$ *…, symmetric*

Odd-numbered MO: coeff. sym.

Even-numbered MOs: coeff. asym.

6.6.2 Symmetry classification: a. [n]polyenes with n=even



Symmetric MOs:

$\because C_1 = C_{1'}$

$C_2 = C_{2'}$ ...,

$C_{n/2} = C_{(n/2)'}$ $\quad \& \; C_{k-1} + C_{k+1} = 2C_k \cos\theta$ *(Cyclic formula)*

Let coefficients of central atoms (**1** & **1′**) be $\boldsymbol{cos(\theta/2)}$

$$\Rightarrow C_2 = C_{2'} = 2\cos\frac{\theta}{2}\cos\theta - \cos\frac{\theta}{2} = (\cos\frac{3\theta}{2} + \cos\frac{\theta}{2}) - \cos\frac{\theta}{2} = \cos\frac{3\theta}{2}$$

$$C_3 = C_{3'} = 2\cos\frac{3\theta}{2}\cos\theta - \cos\frac{\theta}{2} = (\cos\frac{5\theta}{2} + \cos\frac{\theta}{2}) - \cos\frac{\theta}{2} = \cos\frac{5\theta}{2}$$

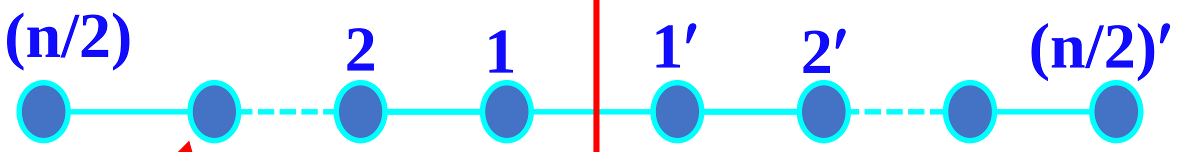
$$\ldots, C_{(n/2)} = C_{(n/2)'} = \cos\frac{(n-1)\theta}{2}$$

→ Boundary condition: $cos[(n+1)\theta/2]=0$

→ $\theta_m = \frac{2m+1}{n+1}\pi$ (m=0, 1,2,…, (n-2)/2) $\qquad E_m^{sym} = \alpha + 2\beta cos\,\boldsymbol{\theta_m}$

6.6.2 Symmetry classification: a. [n]polyenes with n=even

Asymmetric MOs:



$$C_i \quad -\sin\frac{n-1}{2}\theta,\ -\sin\frac{n-3}{2}\theta \quad -\boldsymbol{sin}(\theta/2),\ \boldsymbol{sin}(\theta/2)\ \sin\frac{n-3}{2}\theta,\ \sin\frac{n-1}{2}\theta$$

$$\because C_1 = -C_{1'}, C_2 = -C_{2'}, \ldots, \quad \& \; C_{k-1} + C_{k+1} = 2C_k \,\boldsymbol{cos}\,\theta$$

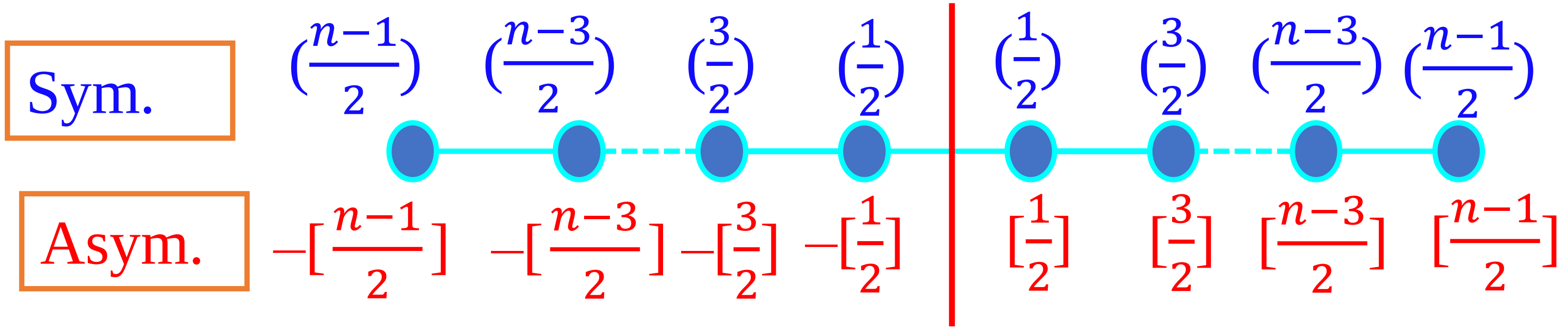
Let coefficients for central atoms be $-\boldsymbol{sin}(\theta/2),\ \boldsymbol{sin}(\theta/2)$

Then coefficients for terminal atoms are $-\sin\frac{n-1}{2}\theta$ and $\sin\frac{n-1}{2}\theta$

→ Boundary condition: *sin*[(n+1)θ/2]=0

→ $\theta_m = \frac{2m}{n+1}\pi$ (m=1,2,…, n/2) $\qquad E_m^{asym} = \alpha + 2\beta cos\,\boldsymbol{\theta_m}$

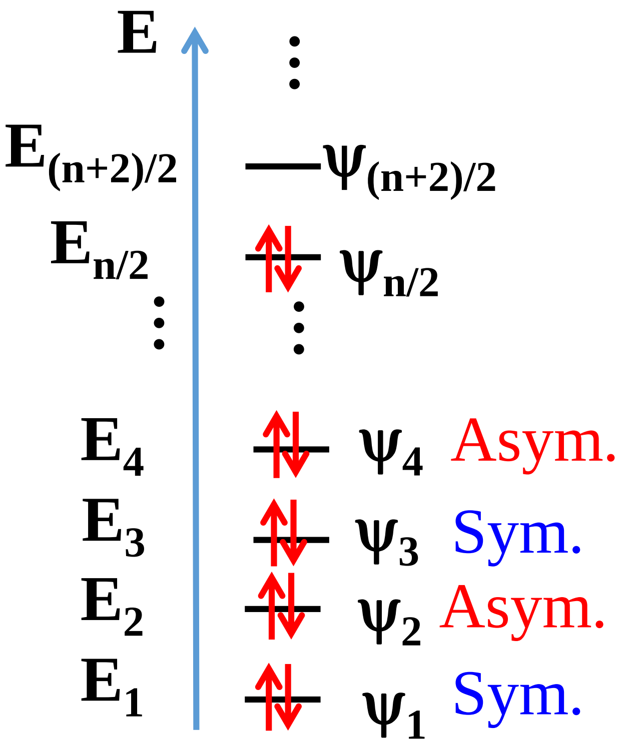
6.6.2 Symmetry classification: a. [n]polyenes with n=even



$\theta_m = \frac{2m+1}{n+1}\pi$ (m=0, 1,2,…, <n/2)

$$E_m = \alpha + 2\beta\cos\boldsymbol{\theta_m}$$

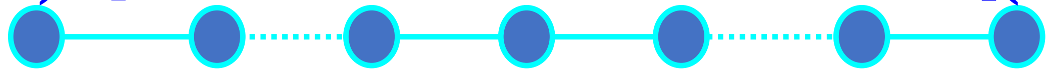
$\theta_m = \frac{2m}{n+1}\pi$ (m=1,2,…, n/2)



Thus the lowest n/2 MOs with $\boldsymbol{\theta_m} < \pi/2$ are bonding MOs.

	n= 4k, ***n/2= 2k*** ***(n+2)/2= 2k+1***	n= 4k+2, ***n/2= 2k+1*** ***(n+2)/2= 2k+2***
LUMO **No.(n+2)/2**	Sym., $m=\frac{n}{4}$, $\theta_m=\frac{n+2}{2(n+1)}\pi$	Asym., $m=\frac{n+2}{4}$, $\theta_m=\frac{n+2}{2(n+1)}\pi$
HOMO **No. n/2**	Asym. $m=\frac{n}{4}$, $\theta_m=\frac{n}{2(n+1)}\pi$	Sym., $m=\frac{n-2}{4}$, $\theta_m=\frac{n}{2(n+1)}\pi$

b. [n]polyenes with n=odd



$$\cos\frac{n-1}{2}\theta \quad \cos\frac{n-3}{2}\theta \quad \cos\theta,\ 1,\ \cos\theta \quad \cos\frac{n-3}{2}\theta \quad \cos\frac{n-1}{2}\theta$$

Symmetric MO′s:

$$\because C_{k-1} + C_{k+1} = 2C_k \cos\theta$$

$$\& C_0 = 1, C_1 = C_{1'}, \ldots, C_{[(n-1)/2]} = C_{[(n-1)/2]'} \qquad \Rightarrow C_1 = C_{1'} = \cos\theta$$

$$\Rightarrow C_2 = 2C_1 \cos\theta - 1 = \cos 2\theta \qquad \Rightarrow \ldots, C_{(n-3)/2} = \cos\frac{n-3}{2}\theta \qquad \Rightarrow C_{(n-1)/2} = \cos\frac{n-1}{2}\theta$$

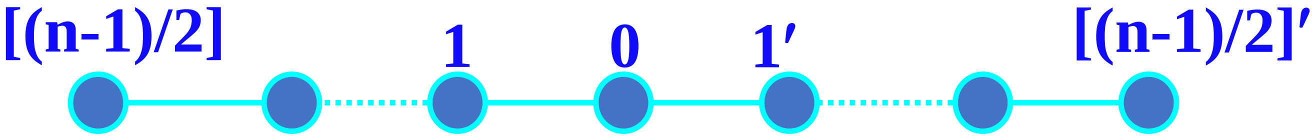
Boundary conditions:

$$\cos\frac{n+1}{2}\theta = 0 \Rightarrow \frac{n+1}{2}\theta = \frac{2m+1}{2}\pi$$

$$\rightarrow \theta_m = \frac{2m+1}{n+1}\pi \ (m=0, 1, 2, \ldots, (n-1)/2)$$

$$E_m^{sym} = \alpha + 2\beta\cos\boldsymbol{\theta_m}$$

b. [n]polyenes with n=odd



Asymmetric MO′s:

$$\boldsymbol{sin}\frac{n-1}{2}\theta \quad \boldsymbol{sin}\frac{n-3}{2}\theta \quad \boldsymbol{sin}\theta, 0, \text{-}\,\boldsymbol{sin}\theta \quad -\boldsymbol{sin}\frac{n-3}{2}\theta \quad -\boldsymbol{sin}\frac{n-1}{2}\theta$$

$$\because C_{k-1}+C_{k+1}=2C_k\cos\theta \;\; \& \; C_0=0, C_1=\text{-}C_{1'}, ..., C_{[(n-1)/2]}=\text{-}C_{[(n-1)/2]'}$$

$$\text{Let } \; C_1=\text{-}C_{1'}=\sin\theta \qquad \Rightarrow \; C_2=2C_1\boldsymbol{cos}\,\theta=\sin2\theta$$

$$...\Rightarrow \; C_{[(n-3)/2]}=\sin[(\mathrm{n}-3)\theta/2]=\text{-}C_{[(n-3)/2]'}$$

$$\Rightarrow \; C_{[(n-1)/2]}=\sin[(\mathrm{n}-1)\theta/2]=\text{-}C_{[(n-1)/2]'}$$

Boundary condition: $\boldsymbol{sin}\frac{n+1}{2}\theta=0$ $\rightarrow \theta_m=\frac{2m}{n+1}\pi$ (m=1,2,…, $\frac{n-1}{2}$)

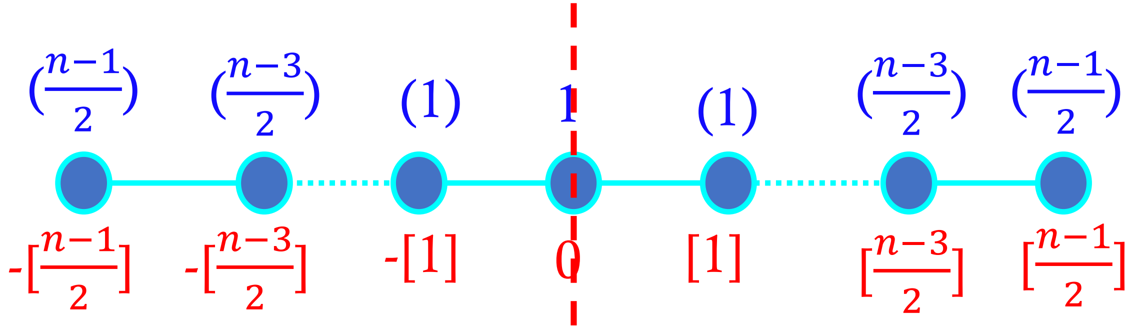
$$E_m^{asym}=\alpha+2\beta cos\,\boldsymbol{\theta_m}$$

FMOs of [n]polyenes with odd-number carbon atoms

$$E_m = \alpha + 2\beta\cos\theta_m$$

Sym.

Asym.



$$\theta_m^{sym} = \frac{2m+1}{n+1}\pi \ (\text{m}=0,\ 1,2,\ldots,\ \frac{n-1}{2})$$

$$\theta_m^{asym} = \frac{2m}{n+1}\pi \ (\text{m}=1,2,\ldots,\ \frac{n-1}{2})$$

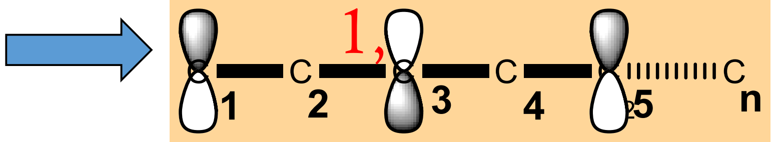
i) n = 4l+1, n-1= 4l, (n+1)/2=2l+1; Let m = l, $\theta_l^{sym} = \frac{2l+1}{n+1}\pi = \frac{\pi}{2} > \theta_m^{asym} = \frac{2l}{n+1}\pi$

SOMO, sym. MO, $\theta = \pi/2,\ \ E = \alpha$ $\quad C_{2l+1} = 1, C_{2l} = C_{2l+2} = 0,$

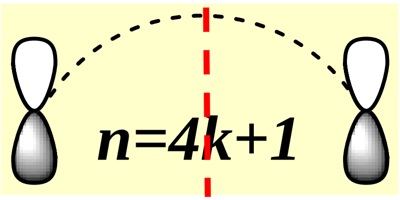
$C_{2l-1} = C_{2l+3} = \text{-}1, \quad \ldots C_1 = C_n = \text{-}1,$

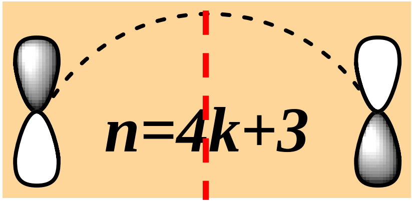
i) n = 4l+3, n-1= 4l+2, (n+1)/2=2l+2; **SOMO ~ asym. MO with m = l+1,** $\theta_{l+1}^{asym} = \frac{\pi}{2}$

$E = \alpha \quad C_{2l+2} = 0, -C_{2l+1} = C_{2l+3} = \text{-}-C_{2l} = C_{2l+4} = 0, \quad \ldots - C_1 = C_n = 1$

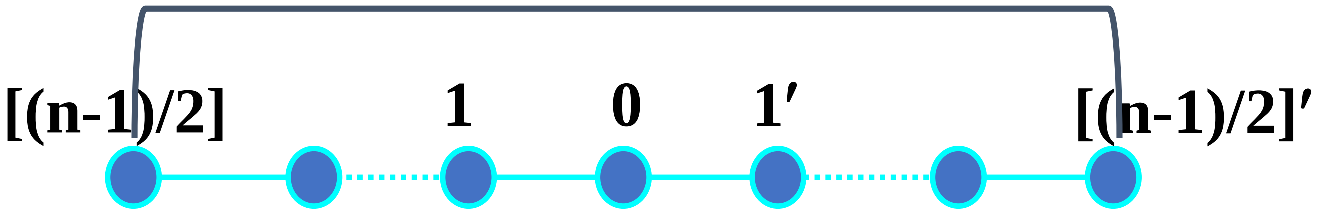


Simplified diagram of SOMO:





c. Cyclic [n]polyenes with odd-number carbon atoms: (n=odd)



Symmetric MO′s:

$$\cos\frac{n-1}{2}\theta \quad \cos\frac{n-3}{2}\theta \quad \cos\theta,\ 1,\ \cos\theta \quad \cos\frac{n-3}{2}\theta \quad \cos\frac{n-1}{2}\theta$$

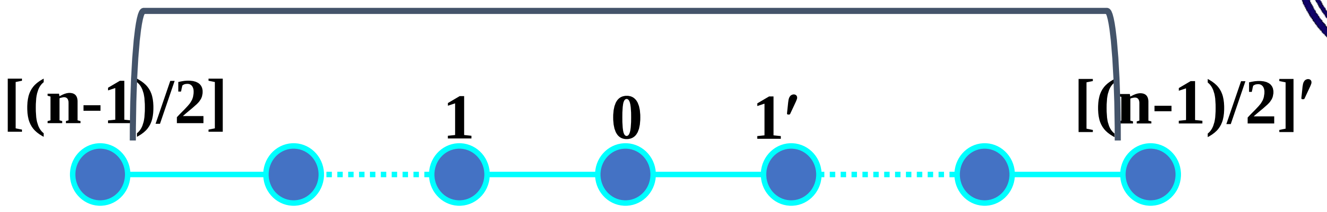
Boundary conditions:

$$\cos\frac{n+1}{2}\theta = \cos\frac{n-1}{2}\theta \quad \rightarrow -\sin\frac{n}{2}\theta\sin\frac{\theta}{2} = 0$$

$$\rightarrow \theta_m^{sym} = \frac{2m}{n}\pi \ \ (m=0,1,2,\ldots,\frac{n-1}{2})$$

$$E_m^{sym} = \alpha + 2\beta\cos\theta_m^{sym}$$

Asymmetric MO′s:



$$\sin\frac{n-1}{2}\theta \quad \sin\frac{n-3}{2}\theta \quad \sin\theta, 0, -\sin\theta \quad -\sin\frac{n-3}{2}\theta \quad -\sin\frac{n-1}{2}\theta$$

Boundary conditions:

$$-\sin\frac{n+1}{2}\theta = \sin\frac{n-1}{2}\theta \quad \rightarrow \sin\frac{n}{2}\theta\cos\frac{\theta}{2} = 0$$

$$\rightarrow \theta_m^{asym} = \frac{2m}{n}\pi \ \ (\mathrm{m}=1,2,\ldots,\frac{n-1}{2}) \qquad E_m^{asym} = \alpha + 2\beta\cos\theta_m^{sym}$$

MOs of cyclic [n]polyenes with odd-number carbon atoms

Sym. MOs: $\theta_m^{sym} = \frac{2m}{n}\pi$ (m=0,1,2,…, $\frac{n-1}{2}$) $\quad E_m^{sym} = \alpha + 2\beta cos\theta_m^{sym}$

Asym. MOs: $\theta_m^{asym} = \frac{2m}{n}\pi$ (m=1,2,…, $\frac{n-1}{2}$) $\quad E_m^{asym} = \alpha + 2\beta cos\theta_m^{asym}$

→ m = 0, non-degenerate MO; m > 0, doubly degenerate MOs.

i) ***n*= 4*l* + 1,** → **m**$_{\mathrm{HOMO}}$ = ***(n-1)/4=l***, triply occupied! → **m**$_{\mathrm{LUMO}}$ = ***l*+1**!

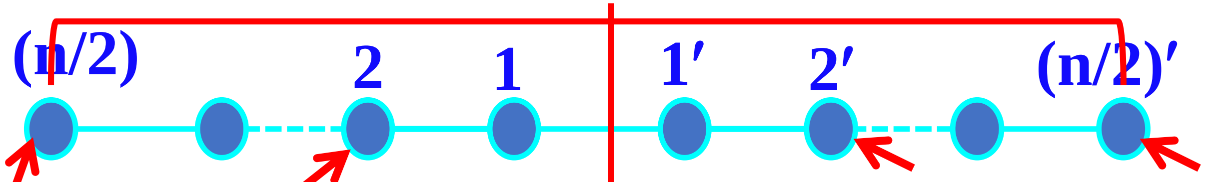
$$E_{HOMO} = \alpha + 2\beta cos\frac{(n-1)}{2n}\pi = \alpha + 2\beta sin\frac{\pi}{2n} \qquad E_{LUMO} = \alpha + 2\beta cos\frac{(n+3)}{2n}\pi = \alpha - 2\beta sin\frac{3\pi}{2n}$$

ii） *n*= 4*l*+ 3 → m$_{\mathrm{SOMO}}$ **= (n+1)/4=*l*+1, singly occupied.**

$$E_{SOMO} = \alpha + 2\beta cos\frac{(n+1)}{2n}\pi = \alpha - 2\beta sin\frac{\pi}{2n}$$

d. cyclic [n]polyenes with n=even

Symmetric MOs:



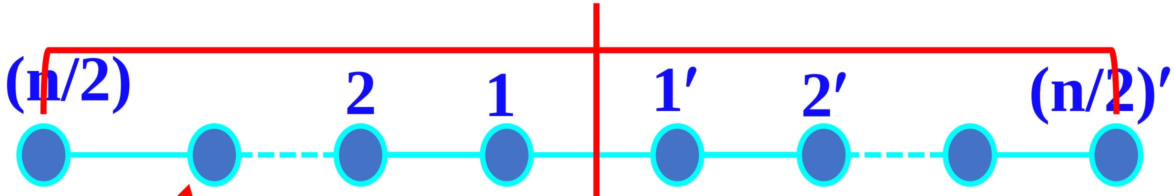
$$\cos\frac{(n-1)}{2}\theta \quad \cos\frac{3}{2}\theta \quad \cos\frac{1}{2}\theta, \quad \cos\frac{1}{2}\theta \quad \cos\frac{3}{2}\theta \quad \cos\frac{(n-1)}{2}\theta$$

Boundary condition:

$$cos\frac{n+1}{2}\theta = cos\frac{n-1}{2}\theta \rightarrow -sin\frac{n}{2}\theta sin\frac{\theta}{2} = 0$$

$$\rightarrow \theta_m^{sym} = \frac{2m}{n}\pi \ \ (\text{m}=0,1,2,\ldots,\frac{n-2}{2}) \qquad E_m^{sym} = \alpha + 2\beta cos\theta_m^{sym}$$

Asymmetric MOs:



$$-\sin\frac{n-1}{2}\theta, \ -\sin\frac{n-3}{2}\theta \ \ -\boldsymbol{sin}(\theta/2), \ \boldsymbol{sin}(\theta/2) \ \sin\frac{n-3}{2}\theta, \ \sin\frac{n-1}{2}\theta$$

Boundary condition:

$$sin\frac{n+1}{2}\theta = -sin\frac{n-1}{2}\theta \rightarrow sin\frac{n}{2}\theta cos\frac{\theta}{2} = 0$$

$$\rightarrow \theta_m^{asym} = \frac{2m}{n}\pi \ \ (\text{m}=1,2,\ldots,\frac{n}{2}) \qquad E_m^{sym} = \alpha + 2\beta cos\theta_m^{sym}$$

FMOs of cyclic [n]polyenes with n=even

Sym. MOs: $\theta_m^{sym} = \frac{2m}{n}\pi$ (m=0,1,2,…, $\frac{n-2}{2}$) $E_m^{sym} = \alpha + 2\beta cos\theta_m^{sym}$

Asym. MOs: $\theta_m^{asym} = \frac{2m}{n}\pi$ (m=1,2,…, $\frac{n}{2}$) $E_m^{asym} = \alpha + 2\beta cos\theta_m^{asym}$

→ m = 0, non-degenerate sym. MO; m= n/2, non-degenerate asym. MOs.

0 < m < (n-2)/2, a total of (n-2)/2 doubly degenerate MOs.

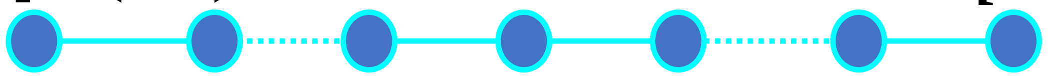
i) ***n*= 4*l* + 2,** ***m***$_{\text{HOMO}}$ = ***(n-2)/4=l***, $\theta_{\text{HOMO}} = \frac{n-2}{2n}\pi$, ***m***$_{\text{LUMO}}$ **=*(n+2)/4 = l+1*!**, $\theta_{\text{LUMO}} = \frac{n+2}{2n}\pi$,

$E_{HOMO} = \alpha + 2\beta cos\frac{(n-2)}{2n}\pi = \alpha + 2\beta sin\frac{\pi}{n}$ $E_{LUMO} = \alpha + 2\beta cos\frac{(n+2)}{2n}\pi = \alpha - 2\beta sin\frac{\pi}{n}$

ii） ***n*= 4*l*,** doubly degenerate SOMO with ***m***$_{\text{SOMO}}$ = ***n/4=l***, $\theta_{\text{SOMO}} = \pi/2$, $E_{SOMO} = \alpha$

e. Cyclic [n]polyenes with even-number carbon atoms: (n=even)

[n/2] [(n-2)/2] 1 0 1′ [n/2]′



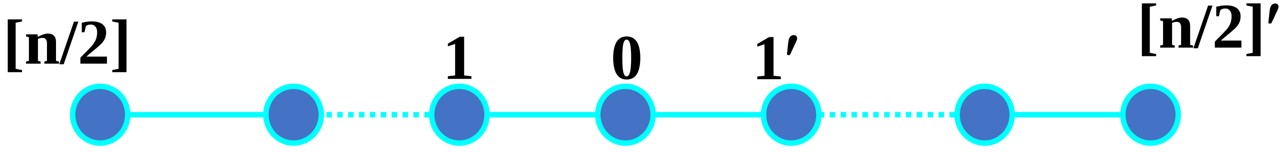
Symmetric MO′s: 两端点重合！

$$\cos\frac{n\theta}{2} \qquad \cos\theta,\ 1,\ \cos\theta \qquad \cos\frac{n\theta}{2}$$

$$\cos\frac{n+2}{2}\theta \ \cos(n-1)$$ (Note: cyclic formula)

Boundary conditions:
$$cos\frac{n+2}{2}\theta = cos\frac{n-2}{2}\theta \rightarrow -sin\frac{n}{2}\theta sin\frac{\theta}{2} = 0$$

$$\rightarrow \theta_m^{sym} = \frac{2m}{n}\pi \ \ (m=0,1,2,\ldots,\frac{n}{2}) \qquad E_m^{sym} = \alpha + 2\beta cos\theta_m^{sym}$$



Asymmetric MO′s:

两端点重合！

$\sin\frac{n\theta}{2}$ $\sin\frac{n-2}{2}\theta$ $\boldsymbol{\sin}\theta, 0, -\boldsymbol{\sin}\theta$ $-\sin\frac{n-2}{2}\theta$ $-\sin\frac{n\theta}{2}$

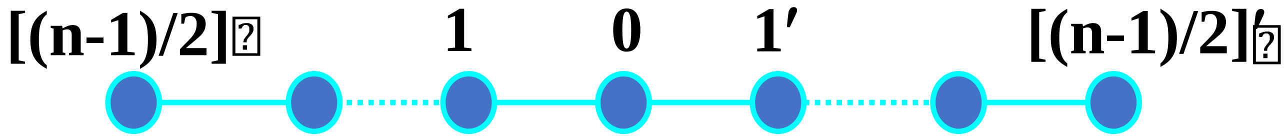
$\sin(n-1)$ $\sin\frac{(n+2)}{2}$

Boundary conditions:

$$\sin\frac{n}{2}\theta = -\sin\frac{n}{2}\theta \quad \rightarrow \sin\frac{n}{2}\theta = 0$$

$$\rightarrow \theta_m^{asym} = \frac{2m}{n}\pi \ \ (\mathrm{m}=1,2,\ldots,\frac{n-2}{2}) \qquad E_m^{asym} = \alpha + 2\beta cos\theta_m^{sym}$$

f. Cyclic [n]polyenes with odd-number carbon atoms: (n=odd)



Symmetric MO′s: 两端点相连！

$\cos\frac{(n-1)}{2}\theta$ ... $\cos\theta,\ 1,\ \cos\theta$ ... $\cos\frac{(n-1)}{2}\theta$

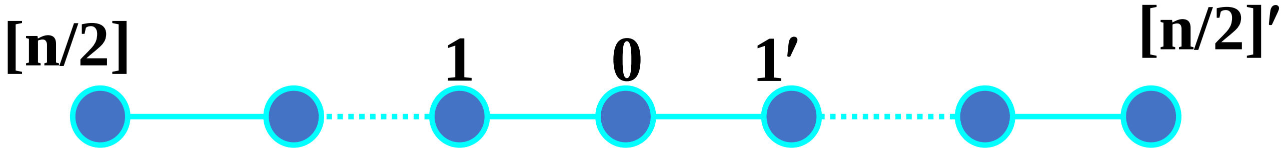
$\cos\frac{(n+3)}{2}\theta = \cos\frac{(n-3)\theta}{2}$ $\quad \cos\frac{(n+1)}{2}\theta$

Boundary conditions: $cos\frac{n+1}{2}\theta = cos\frac{n-1}{2}\theta \quad \rightarrow -sin\frac{n}{2}\theta sin\frac{\theta}{2} = 0$

$\rightarrow \theta_m^{sym} = \frac{2m}{n}\pi$ (m=0,1,2,…, $\frac{n-1}{2}$) $\qquad E_m^{sym} = \alpha + 2\beta cos\theta_m^{sym}$

Asymmetric MO′s:

两端点重合！



$\sin\frac{n\theta}{2}$ $\sin\frac{n-2}{2}\theta$ $\boldsymbol{sin}\theta, 0, \text{-}\,\boldsymbol{sin}\theta$ $-\sin\frac{n-2}{2}\theta$ $-\sin\frac{n\theta}{2}$

Boundary conditions:

$$sin\frac{n}{2}\theta = -sin\frac{n}{2}\theta \quad \rightarrow sin\frac{n}{2}\theta = 0$$

$$\rightarrow \theta_m^{asym} = \frac{2m}{n}\pi \ \ (\mathrm{m}=1,2,\ldots,\frac{n-2}{2})$$

$$E_m^{asym} = \alpha + 2\beta cos\theta_m^{sym}$$

cyclic [n]polyenes

$\theta = 2\pi/n$

k= 0, 1, …, (n-1)/2 (for n =odd) or n/2 (for n= even)

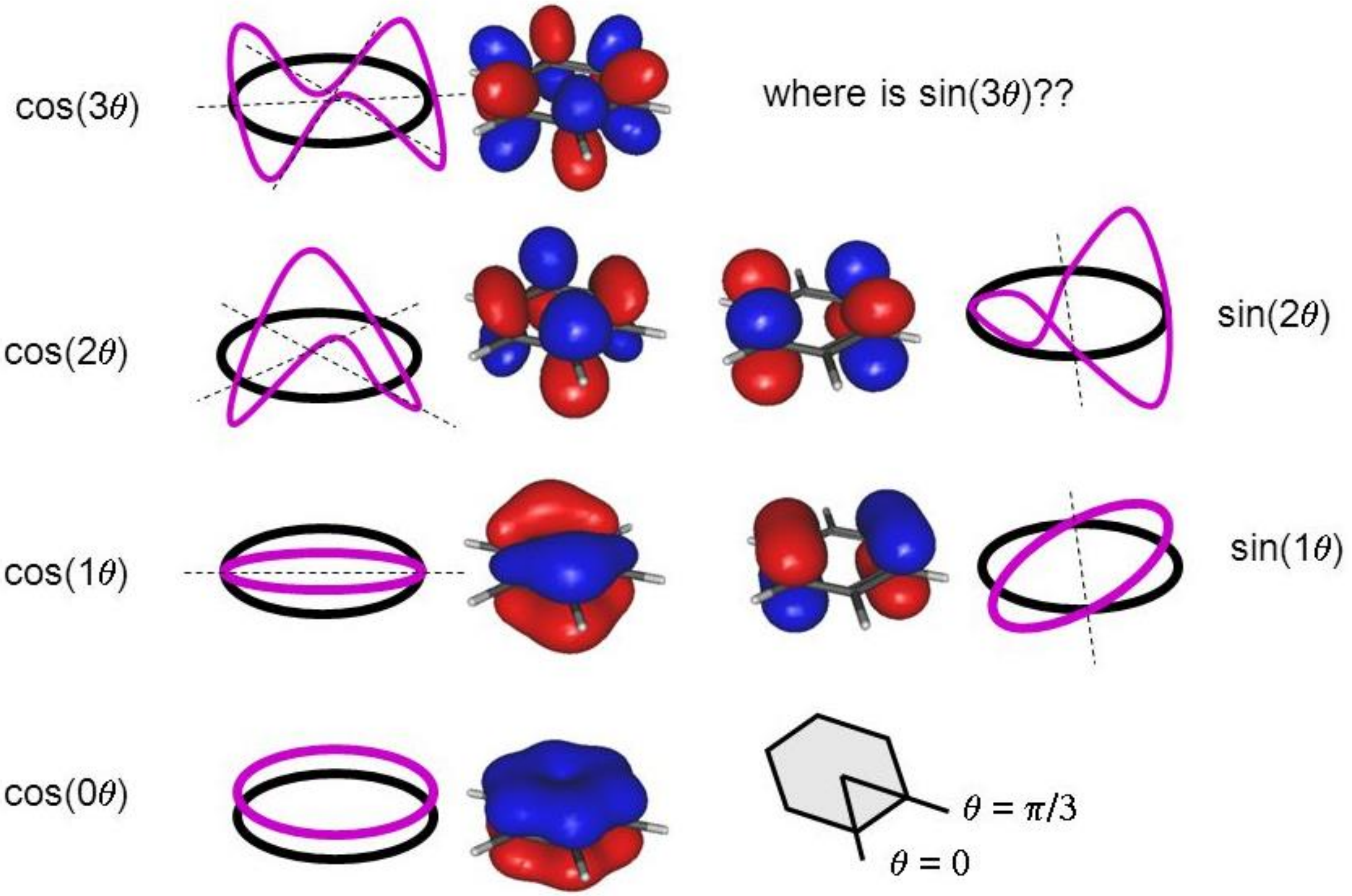
$$E_k = \alpha + 2\beta\cos(k\theta)$$

$$\psi_k^{cos} = \sum_{m=1}^{n} \phi_m \cos[(m-1)k\theta]$$

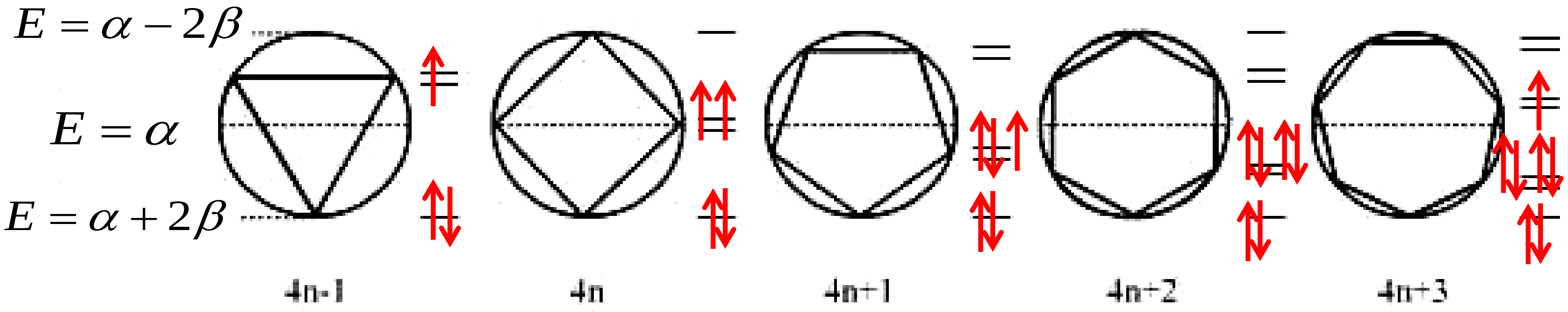
$$\psi_k^{sin} = \sum_{m=1}^{n} \phi_m \sin[(m-1)k\theta]$$

(*when* $k\theta = 0$ or π, no ψ_k^{sin})

π MOs of Benzene

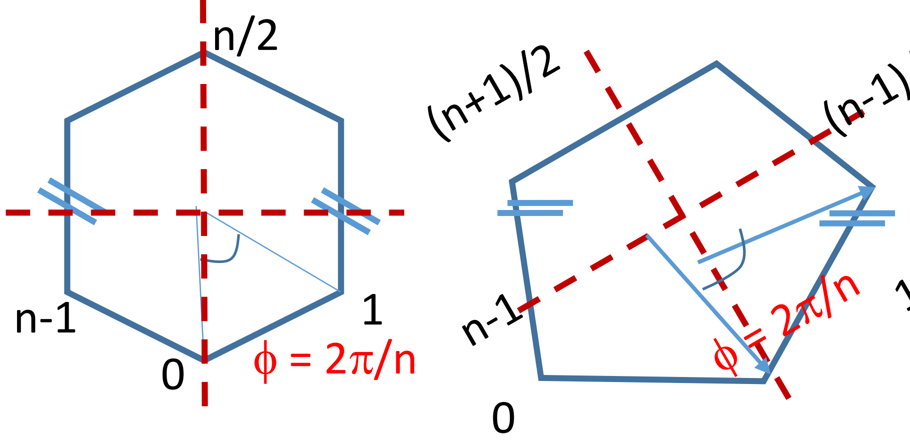


General HMO solutions for cyclic [n]polyenes (C_nH_n)



- **When *n=4m+1* or *4m+3*, the system has a singly occupied HOMO, being radicaloid.**
- **When *n=4m*, the system has two degenerate singly-occupied HOMOs (non-bonding), thus being diradicaloid.**
- **Only when *n= 4m+2* can a cyclically conjugated system has fully occupied HOMOs and be chemically stable. (fulfilling the Hückel rule of aromaticity!)**
- Can we use the representations for cyclic groups to obtain the aforementioned trends?

cyclic [n]polyenes with n=even、odd



MO level	$\theta_m = m\phi$	$E_m = \alpha + 2\beta\cos\theta_m$	$\psi_m = A\sum_{k=0}^{n-1} c_k^m p_k$	N_{Node}
m=n/2 (n=even) m=(n-1)/2 (n=odd)	π $(n-1)\pi/n$	$\alpha - 2\beta$ $\alpha - 2\beta\cos(\phi/2)$	$C_k^{n/2} = \cos(k\pi)$ $C_k^m = \cos(km\phi)$ $C_k^{m\prime} = \sin(km\phi)$	n/2 (n-1)/2
· m ·	$m\phi$	$\alpha + 2\beta\cos(m\phi)$	$C_k^m = \cos(km\phi)$ $C_k^{m\prime} = \sin(km\phi)$	m
m=1	ϕ	$\alpha + 2\beta\cos\phi$	$C_k^1 = \cos(k\phi)$ $C_k^{1\prime} = \sin(k\phi)$	1
LEMO m=0	0	$\alpha + 2\beta$	$C_k^0 = 1$	0