第7-9章

Key points/concepts

1. Lattice of crystal structure: translation symmetry

   a lattice point = a structure motif   -- unit cell
2. Crystal systems (7), Bravais Lattice (14)
3. Symmetry operations (point & translation) Crystallographic point groups(32), space groups (230), miller index of crystal plane， d-spacing etc.
4. X-ray diffraction, Laue equation, Bragg’s Law, reciprocal lattice, Ewald sphere, structural factor, system absence, general process of x-ray crystal structure determination.
5. Close-packing of spheres (ccp/A1,hcp/A3,bcp/A2) in metals and ionic compounds, coordination of cations.
6. Crystal structures of some typical ionic compounds.

Example: p224, 7.2 -- concept of lattice

- A structure motif （+ occupying space) = a lattice point
- Each lattice point has identical surroundings.
- A lattice fulfills translation symmetry.
- Differences between a real crystal structure and its lattice.

Key point is to find the structure motif (basis) that fulfills translation symmetry!

p.227, 7.26

Sn: (0,0,0), (1/2,1/2,1/2)

F: (0,1/2,0), (1/2,0,0)

(0,0,0.237), (0,0,-0.237)

1) body-centred tetragonal

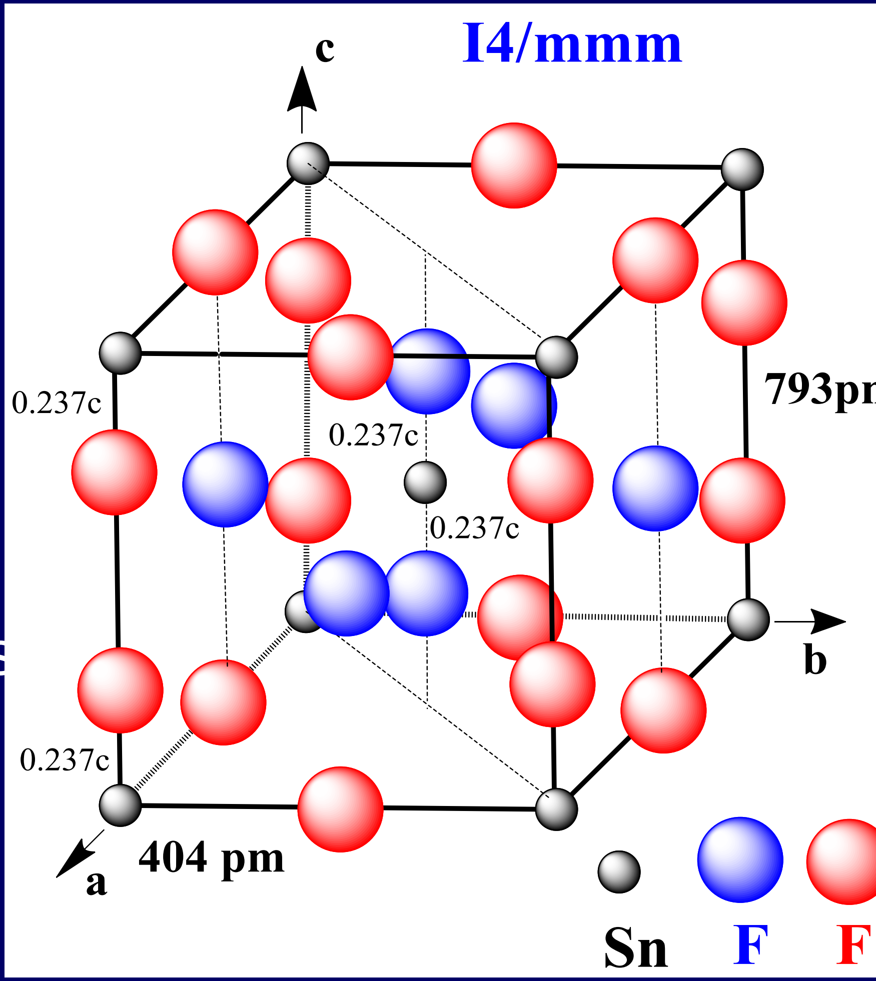
2 lattice point within a unit cell.

The black dots (2 Sn) and red balls (4 F) are defined by the coordinates given!

Other 4 F atoms can be obtained by translation operation (2 LP).

2) Each Sn atom is located in a distorted octahedral hole.

SnF_4

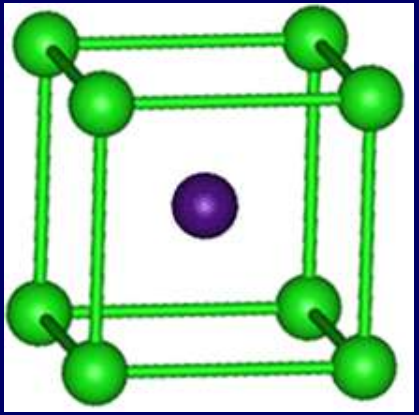


R(Sn-F)$_1$ =0.237x 793 = 187.9pm; R(Sn-F)$_2$ = 0.5x404=202 pm

Key: Figure out the atoms within a LP!

Simple cubic crystal – example: CsCl

p.286 9.13



- Only one lattice point within a unit cell.
- Each lattice point contains ***2*** atoms,

  Cl (0,0,0), Cs(1/2,1/2,1/2);
- The structural factor is

$$F_{hkl} = \sum_{i=1}^{2} f_i e^{2\pi i(hx_i + ky_i + lz_i)}$$

$$= f_{Cl} + f_{Cs} e^{\pi i(h+k+l)}$$

Therefore, all possible diffractions are observable without system absence! However,

If $h+k+l = 2n$, $F_{hkl} = f_{Cl} + f_{Cs}$ ***Strongest diffraction***

If $h+k+l = 2n+1$, $F_{hkl} = f_{Cl} - f_{Cs}$ ***Weakest diffraction***

Face-centered cubic crystal – general case p227, 7.21

- Lattice points (**LPs**): (0,0,0), (1/2,1/2,0), (0,1/2,1/2), (1/2,0,1/2)
- Suppose each lattice point contains ***n*** atoms, $\{(x_j,y_j,z_j)\}$ (j=*1*,…,***n***)
- Each unit cell contains N=***4n*** atoms, e.g., an atom $A(x_i,y_i,z_i)$ in one LP has other three equivalent A atoms within the same unit cell!
- Then the structure factor is

Sum up over all atoms within a unit cell!

$$F_{hkl} = \sum_{i=1}^{N} f_i e^{2\pi i(hx_i+ky_i+lz_i)} \rightarrow$$

$$F_{hkl} = [1+e^{2\pi i(\frac{h}{2}+\frac{k}{2})}+e^{2\pi i(\frac{h}{2}+\frac{l}{2})}+e^{2\pi i(\frac{k}{2}+\frac{l}{2})}]\times\sum_{j=1}^{n} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

From translation symmetry of fcc!

Now sum up over all atoms within a LP!

- Thus, when *h,k,l* are neither all even nor all odd,

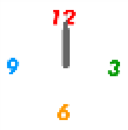
$$F_{hkl} = 0$$

system absence!

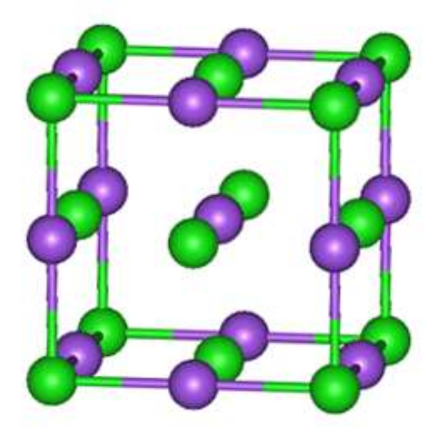
- Furthermore, when *h,k,l* are all even or all odd,

$$F_{hkl} = 4\sum_{j=1}^{n} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

diffraction observable!



Face-centered cubic crystal – Special case: NaCl p227, 7.23



- Unit cell contains 4 lattice points, or 4NaCl
- Each lattice point (LP) corresponds to a NaCl.
- Put Cl at (0,0,0), then a neighboring Na at (1/2,0,0).
- Only when h,k,l are all even or all odd can diffractions be observed!

$$\mathrm{F_{hkl}} = 4\sum_{j=1}^{2} f_j e^{2\pi i(hx_j+ky_j+lz_j)} = 4[\,f_{Cl} + f_{Na}e^{\pi hi}\,]$$

Now sum up over all atoms within a LP!

Case 1: if *h* = 2n (note we also have *l*=2n and *k*=2n)

$$\mathrm{F_{hkl}} = 4[\,f_{Cl} + f_{Na}\,]$$

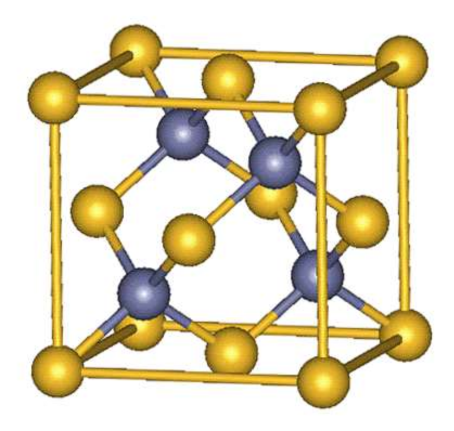
Strong diffraction!

Case 2: if *h* = 2n+1 (note we also have *l*=2n+1, *k*=2n+1)

$$\mathrm{F_{hkl}} = 4[\,f_{Cl} - f_{Na}\,]$$

Weak diffraction!

Face-centered cubic crystal – Special case: ZnS (sphalerite)



- Unit cell contains 4 lattice points, or 4ZnS
- Each lattice point corresponds to a ZnS.

  S(0,0,0), Zn(1/4,1/4,1/4) (different elements!)
- When h,k,l are all even or all odd, diffractions observable,

$$F_{hkl} = 4\sum_{j=1}^{2} f_j e^{2\pi i(hx_j+ky_j+lz_j)} = 4[\,f_S + f_{Zn} e^{\pi i(h+k+l)/2}\,]$$

→ (111),(200),(220),(311),(222),(400),(331),(420),(422),…

Case 1: if $h+k+l = 4n$, e.g., (220),(400),(440)…

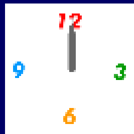
$$F_{hkl} = 4[\,f_S + f_{Zn}\,]$$

Strongest diffraction!

Case 2: if $h+k+l = 4n+2$, e.g., (200),(222),(420),(442)…..

$$F_{hkl} = 4[\,f_S - f_{Zn}\,]$$

Weakest diffraction!



Face-centred cubic crystal -- Special case: Diamond O_h^7- $Fd\bar{3}m$

Derive the system absence of diamond!

- Lattice points: (0,0,0)+, (1/2,1/2,0)+, (0,1/2,1/2)+, (1/2,0,1/2)+
- Each LP contains two C atoms (i.e., structure motif =2C)

C1-- (0,0,0), C2-- (1/4,1/4,1/4) (the same element)

- The other six C atoms within a unit cell can be derived as
  (1/2,1/2,0), (3/4,3/4,1/4) ; (0,1/2,1/2), (1/4,3/4,3/4) ;
  (1/2,0,1/2), (3/4,1/4,3/4)

- Such an arrangement of C atoms produces new translation symmetry elements, i.e., screw axes and d glide planes, which in turn introduce special system absence of diffractions (in addition to the system absence from normal FCC lattice !!!!!!!

Face-centred cubic crystal --
Special case: Diamond O_h^7- $Fd\bar{3}m$

Derive the system absence of diamond!

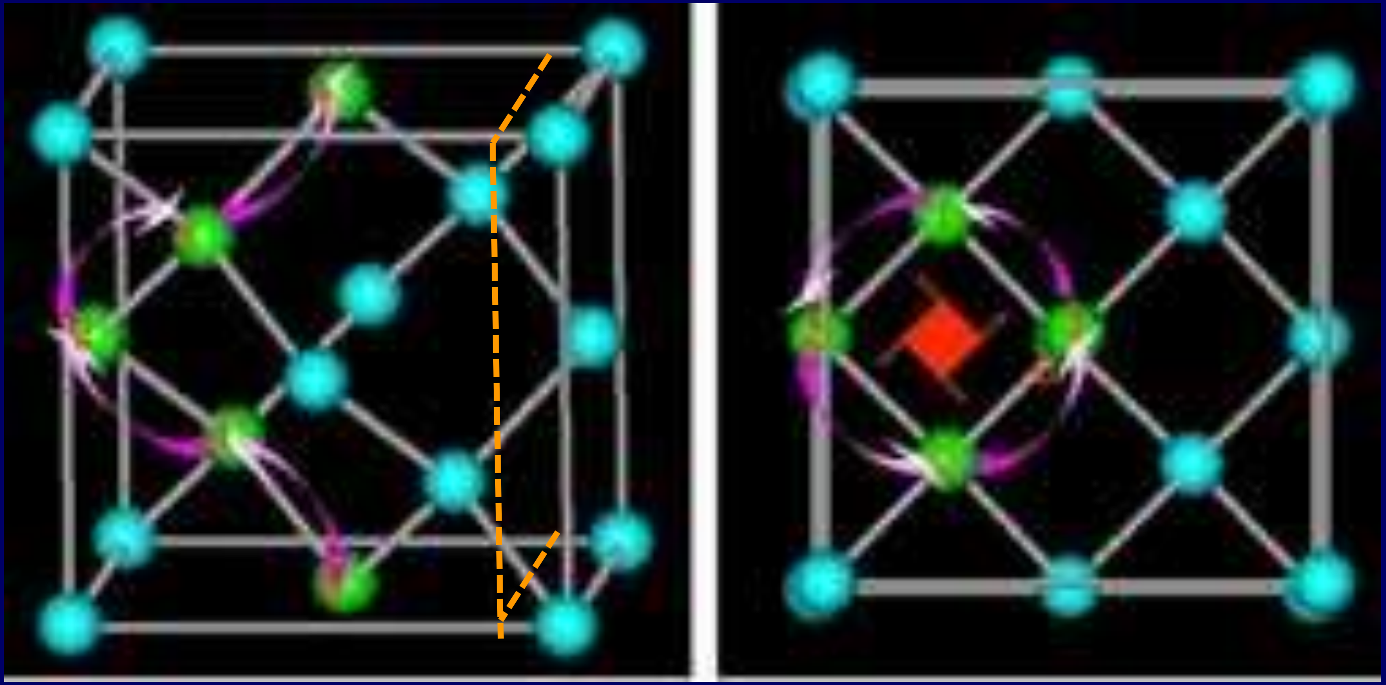
- Such an arrangement of C atoms produces new translation symmetry elements, i.e., screw axes and d glide planes, which in turn introduce special system absence of diffractions (in addition to the system absence from normal FCC lattice !!!!!!!

4_1

d glide plane

1/8,3/8,

5/8,7/8



- Let’s derive the structural factor of diamond to unravel its system absence.

Face-centered cubic crystal – Special case: Diamond

Now sum up over all atoms within a unit cell!

$$F_{hkl} = \sum_{i=1}^{8} f_C e^{2\pi i(hx_i+ky_i+lz_i)}$$

Now sum up over all atoms within a LP!

$$= f_C[1+e^{2\pi i(\frac{h}{2}+\frac{k}{2})}+e^{2\pi i(\frac{h}{2}+\frac{l}{2})}+e^{2\pi i(\frac{k}{2}+\frac{l}{2})}]\times\sum_{j=1}^{2} e^{2\pi i(hx_j+ky_j+lz_j)}$$

$$= f_C[1+e^{2\pi i(\frac{h}{2}+\frac{k}{2})}+e^{2\pi i(\frac{h}{2}+\frac{l}{2})}+e^{2\pi i(\frac{k}{2}+\frac{l}{2})}](1+e^{\pi i(h+k+l)/2})$$

(Note: two carbon atoms within a lattice point: (0,0,0), (1/4,1/4,1/4))

→System absence:

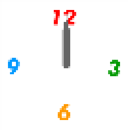
$$a)\quad [1+e^{2\pi i(\frac{h}{2}+\frac{k}{2})}+e^{2\pi i(\frac{h}{2}+\frac{l}{2})}+e^{2\pi i(\frac{k}{2}+\frac{l}{2})}]=0 \quad \text{or}$$

$$\text{b)}\quad (1+e^{\pi i(h+k+l)/2})=0$$

i.e., **a) *h,k,l* are neither all even nor all odd! & b) h+k+l = 4n+2**

→ Observable diffractions: (111), (220),(311),(400),(331),(422) &

If h+k+l=4n, $F_{hkl} = 8f_C$, (220),(400)… strongest diffraction!



Body-center crystal – p227, 7.22

General case: each lattice point contains ***n*** atoms

- The total number of atoms within a unit cell is ***2n***;
- For jth atom in a structure motif (a lattice point): **(x_j,y_j,z_j)**
- Its body-center equivalent is: (**0.5+x_j, 0.5+y_j, 0.5+z_j**)

$$F_{hkl} = \sum_{i=1}^{2n} f_i e^{2\pi i(hx_i+ky_i+lz_i)}$$

Sum up over all atoms within a unit cell!

$$= \sum_{j=1}^{n} \{ f_j e^{2\pi i(hx_j+ky_j+lz_j)} + f_j e^{2\pi i[h(\frac{1}{2}+x_j)+k(\frac{1}{2}+y_j)+l(\frac{1}{2}+z_j)]} \}$$

From translation-symmetry

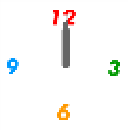
$$= [1+e^{\pi i(h+k+l)}] \sum_{j=1}^{n} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

Sum up over all atoms in a LP!

While $h+k+l$ =2n+1,

$$e^{\pi i(h+k+l)} = e^{(2n+1)\pi i} = -1 \Rightarrow F_{hkl} = 0$$

System absence



Body-center crystal – special case (p.227, 7.24)

- Each lattice point (LP) contains ***2*** atoms, A (0,0,0), B(x,y,z);
- Thus in another LP, A (1/2,1/2,1/2), B (x+1/2,y+1/2,z+1/2)
- The structural factor is

$$F_{hkl} = \sum_{i=1}^{4} f_i e^{2\pi i(hx_i+ky_i+lz_i)}$$

$$= [1+e^{\pi i(h+k+l)}]\times\sum_{j=1}^{2} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

$$= [1+e^{\pi i(h+k+l)}]\times[f_A + f_B e^{2\pi i(hx+ky+lz)}]$$

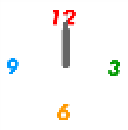
Translation-symmetry term!

Sum up over all atoms in a LP!

While $h+k+l$ =2n+1,

$$e^{\pi i(h+k+l)} = e^{(2n+1)\pi i} = -1 \Rightarrow F_{hkl} = 0$$

System absence



Example: diffraction data → indexing → cell parameter!

- 钨为立方晶系，其粉末衍射线指标为: 110,200,211,220, 310, 222,321,400,…. 属何种点阵类型？若X射线λ=154.4 pm，220衍射角43.6°，试计算晶胞参数。 p.226, 7.18
- Answer: $h+k+l$ =2n diffractions observed! =2n+1 system absence!

or $(h^2+k^2+l^2)$: 2:4:6:8:10:12:14:16….. → bcc lattice!

Bragg law: $2d_{hkl} \cdot \sin\theta = \lambda \rightarrow d_{hkl} = \lambda/(2\sin\theta)$

since $\theta_{220} = 43.6°$

cell parameter:

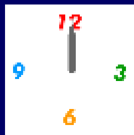
$$a = d_{hkl} \times \sqrt{h^2+k^2+l^2} = \lambda\sqrt{h^2+k^2+l^2}\,/\,2\sin\theta_{hkl}$$

$$= 154.4 \times \sqrt{8}\,/\,2\sin(43.6) \approx 316.6\,pm$$

The answer given in p. 317 is wrong!

Atomic radius of W atom: (bcc)

$$\because 4R = \sqrt{3}a \Rightarrow R = \sqrt{3}a/4 = 316.6x\sqrt{3}/4 \approx 137.1\,ppm$$



P227, 7.27 Bragg's law, *d-spacing*

- Number of S_8 in a unit cell of orthorhombic crystal:

$$n_{S8} = \tilde{N}_0 V\rho / M_{S8} = \tilde{N}_0 (abc)\rho / M_{S8}$$
$$= 6.022\times 10^{23}\times(1048\times1292\times2455)\times10^{-30}\times2.07/(32\times8)\approx 16$$

For orthohombic crystal, $1/d_{hkl}=[(h/a)^2 + (k/b)^2 + (l/c)^2]^{1/2}$ p.200

According to Bragg's Law, we have

$$\sin\theta = \lambda/2d_{hkl} = [(h/a)^2 + (k/b)^2 + (l/c)^2]^{1/2}\times\lambda/2$$
$$= [(2/1048)^2 + (2/1292)^2 + (4/2455)^2]^{1/2}\times 154.18/2$$
$$= [(1/1048)^2 + (1/1292)^2 + (2/2455)^2]^{1/2}\times 154.18 = 0.2273$$
$$\rightarrow \theta = 13.1^{o}$$

(Cu $K\alpha_1$ x-ray, $\lambda = 154.18$ pm)

Note: the value of λ is not given in question 7.27! !!!

p.257, 8.8 indexing of diffraction data!

Ta metal's x-ray diffraction data, ($\sin^2\theta$) is known.

1) Indexing:

$\sin^2\theta_1:\sin^2\theta_2:\sin^2\theta_3:\sin^2\theta_4:\sin^2\theta_5:\sin^2\theta_6:\sin^2\theta_7:\sin^2\theta_8:\sin^2\theta_9\ldots$

$= 1:2:3:4:5:6:7:8:9:\ldots = 2:4:6:8:10:12:14:16:18:\ldots$

➔ body-centered cubic lattice, $h+k+l = 2n+1$ system absence!

Observed hkl: (110)(200)(211)(220)(310)(222)(321)(400)(330)…

2) Cell parameter: $d_{hkl} = a/(h^2+k^2+l^2)^{1/2} \Rightarrow a = d_{hkl}(h^2+k^2+l^2)^{1/2}$

According to Bragg's Law, we have $d_{hkl} = \lambda/2\sin\theta$

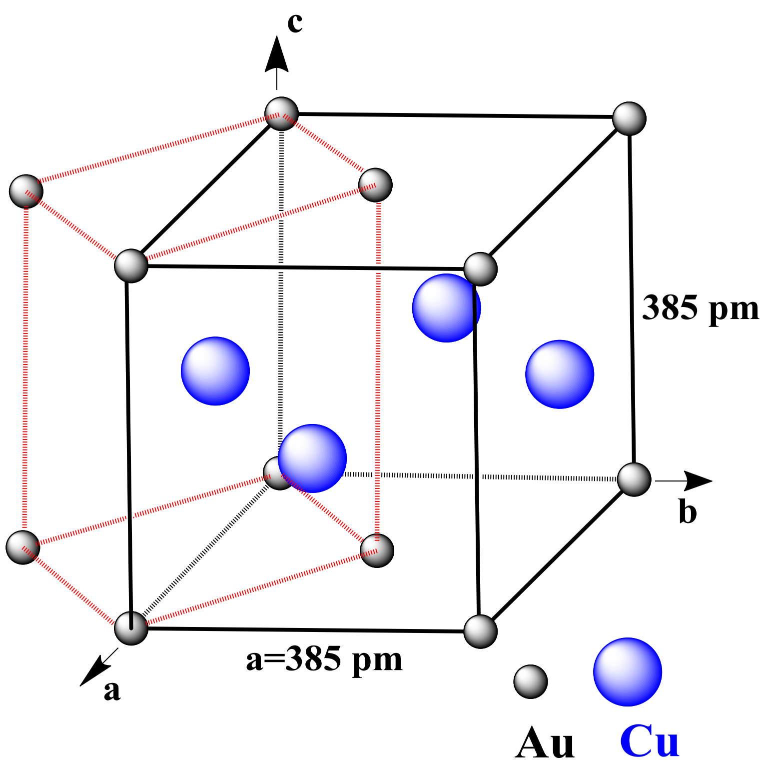
➔ $a = \lambda(h^2+k^2+l^2)^{1/2}/2\sin\theta$

Choosing the (330) diffraction with $\sin^2\theta=0.97826$ ($\lambda=154.1$ pm), we have $a = \lambda(h^2+k^2+l^2)^{1/2}/2\sin\theta$

$= 154.1 \times (18)^{1/2}/(2\times0.98907) = 330.5$ pm

p.259, 8.21

1) Statistically, the probability for a Cu atom to appear at a lattice point is equal to the percentage (x) of Cu doping. Thus the AuCu alloy belongs to face-centered cubic lattice system. Each unit cell contains 4 lattice points and each of them is a statistic atom ($Au_{1-x}Cu_x$).



2) The ordered phase belongs to simple tetragonal lattice; each unit cell/lattice point contains AuCu. Au(0,0,0), Cu (1/2,1/2,1/2);

3) Cell parameter for the ordered phase:

$$\mathbf{a' = b' = a/\sqrt{2} = 272.23\ pm, \qquad c' = a = 385\ pm}$$

The first observed diffraction is (001)

$$d_{001} = 1/((h/a')^2+(k/a')^2+(l/c')^2)^{1/2} = c' = a$$

According to Bragg's Law, we have

$$\sin\theta_{001} = \lambda/2d_{001} = \lambda/2a = 0.2 \rightarrow \theta = 11.5°$$

p.259, 8.21

The randomly doping phase belongs to fcc lattice. Hence its first observable diffraction is (111).

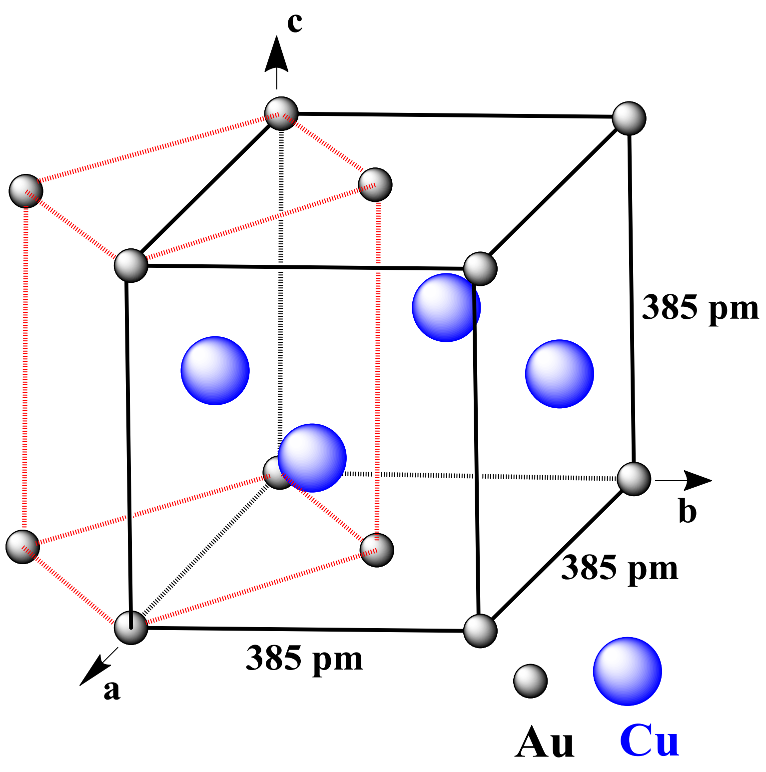
$$d_{111} = a/(h^2+k^2+l^2)^{1/2} = a/3^{1/2}$$

According to Bragg's Law,

$$\sin\theta_{111} = \lambda/2d_{111}$$

$$= 3^{1/2}\lambda/2a = 0.3464$$

$$\theta = 22.3°$$



Note: in some cases, random/multiple orientations/rotations of structural units (clusters, molecules, or groups) exist within a single crystal, which poses difficulty in the structural determination based on X-ray diffraction data!

Example:

- 银为立方晶系，用CuK_α射线(λ=154.18 pm)作粉末衍射，在*hkl*类型衍射中，*hkl*奇偶混合的系统消光。衍射线经指标化后，选取333 衍射线，θ = 78.64 °，试计算晶胞参数。已知Ag 的密度为10.507 g cm^{-3}，相对原子质量为107.87，问晶胞中有几个Ag 原子; 试写出Ag 原子的分数坐标。

Answer: when h,k,l are neither all odd nor all even, system absence!

→ Cubic F-centred.

Bragg law: **$2d_{hkl} \cdot \sin\theta = \lambda \rightarrow d_{hkl} = \lambda/2\sin\theta$**

cell parameter:

$$a = d_{hkl} \times \sqrt{h^2+k^2+l^2} = \lambda\sqrt{h^2+k^2+l^2}\,/\,2\sin\theta$$

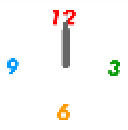
$$= 154.18 \times \sqrt{27}\,/\,2\sin(78.64) = 408.58\,pm$$

atoms in a unit cell:

$$n_{Ag} = \tilde{N}_0 V\rho / M_{Ag} = \tilde{N}_0 a^3 \rho / M_{Ag}$$

$$= 6.022 \times 10^{23} \times (408.58 \times 10^{-10})^3 \times 10.507 / 107.87 = 4$$

Thus each atom corresponds to one lattice point, atomic coordinates: **(0,0,0) (1/2,1/2,0) (1/2,0,1/2) (0,1/2,1/2)**



Example:

- 金属Mg是由Mg原子按*A*3型堆积而成，已知Mg的原子半径是160 pm，求晶胞参数。

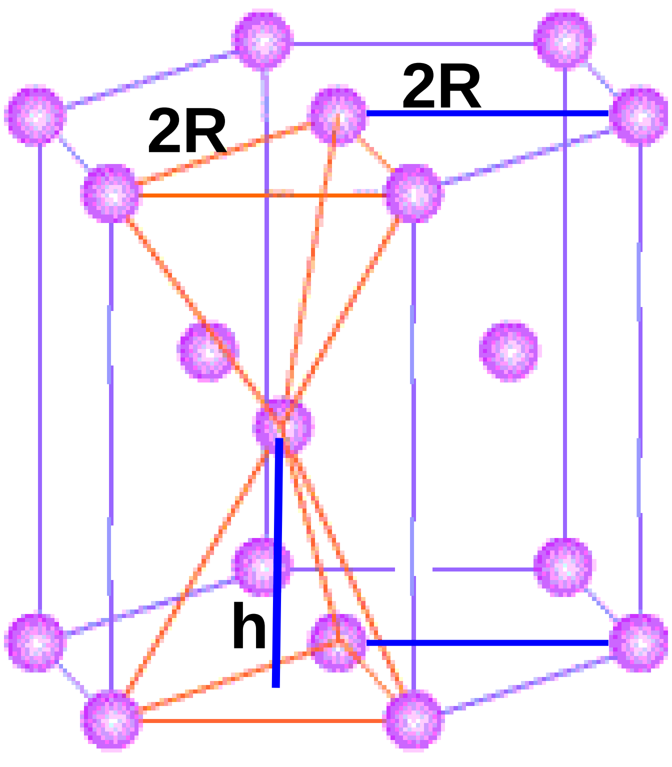
Answer: Hexagonal close-packing mode

→ ***a = b = 2R = 320 pm***,

The height of a tetrahedron with an edge length of 2R is

$$\boxed{h = 2R \times \sqrt{6}/3}$$

$$\rightarrow \boxed{\begin{aligned} c &= 2h = 4R \times \sqrt{6}/3 \\ &= 522.6\,pm \end{aligned}}$$



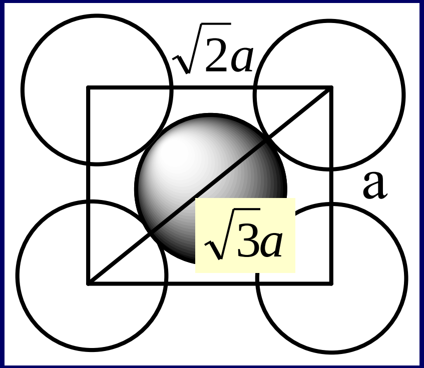
Example: p.286, 9.9

- **KF crystal– cubic system, Mo Kα λ=70.8 pm, diffraction $\sin^2\theta$: 0.0132, 0.0256, 0.0391, 0.0514, 0.0644, 0.0769, 0.102, 0.115, 0.127, 0.139, ……, 1) plz derive its lattice type and cell parameter; 2) Suppose the F^- adopts the simple cubic packing with cubic interstices being occupied by K^+; R_K =133 pm and R_F = 136 pm. plz derive the cell parameter.**

Answer:

1) indexing: **$\sin^2\theta$ = 1:2:3:4:5:6:8:9:10:11… → simple cubic**

Bragg law: ***$2d_{hkl}\cdot\sin\theta = \lambda$ → $d_{hkl} = \lambda/2\sin\theta$***



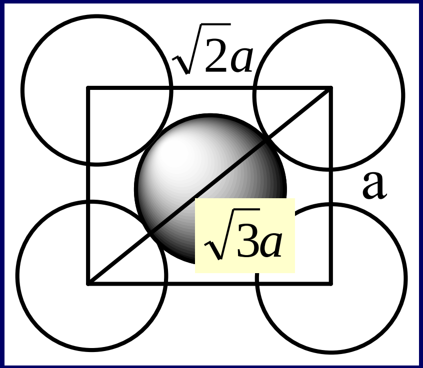
$$a = d_{hkl} \times \sqrt{h^2+k^2+l^2} = \lambda\sqrt{h^2+k^2+l^2}\,/\,2\sin\theta$$
$$= 70.8 \times \sqrt{11}/(2\sqrt{0.139}) = 314\,pm$$

Or $\because \lambda^2/4a^2 = \sin^2\theta/(h^2+k^2+l^2)$ 取四条高指标衍射线求该式的平均值得

$$\lambda^2/4a^2 = 0.012716 \Rightarrow a = 313.9\,pm$$

2) For simple cubic packing of anions, cations occupy the cubic interstices. As such, both types of ions directly contacts with each other along the diagonals of a cube, i.e.,

$$2(R_F + R_K) = \sqrt{3}a \Rightarrow a = 2(R_F + R_K)/\sqrt{3} = 310.6pm$$



Example: p.286, 9.14

- **Cell parameters of NaCl-type KBr, LiBr, KF, and LiF are 658, 550, 534, 402 pm, respectively. Please derive the ionic radii of K, Li, F, and Br.**

Answer:

1. Br anion is the largest and Li cation is the smallest! For LiBr, the anions adopt ccp structure with Li cations occupying the octahedral holes. Thus,

$$\sqrt{2}a_{LiBr} = 4R_{Br} \Rightarrow R_{Br} = \sqrt{2}a_{LiBr}/4 = 194.5pm$$

For KBr, the K cation is large, thus, the anions may not closely contact with each other. Instead, the cations and anions closely contact with each other. Thus,

$$R_{Br} + R_{K} = a_{KBr}/2 \Rightarrow R_{K} \approx 134.5pm$$

Similarly, for KF,

$$R_{F} + R_{K} \approx a_{KF}/2 \Rightarrow R_{F} \approx 132.5pm$$

For LiF, the ultimate case is Li-F closely contact with each other,

$$R_{F} + R_{Li} \leq a_{LiF}/2 \Rightarrow R_{Li} \approx 68.5pm$$

Example: p.288, 9.32

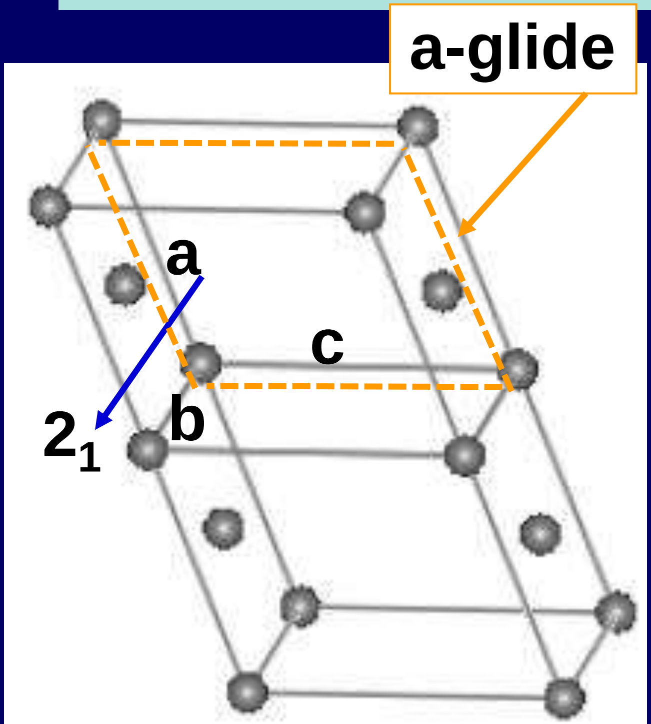
- The cell parameters of monoclinic crystal of biphenyl: a = 824 pm, b= 573 pm, c= 951pm, β = 94.5°; ρ= 1.16 gcm^{-3}.

Answer: 1) Number of molecules within a cell,

$$n_{bp} = \tilde{N}_0 V\rho / M_{bp} = \tilde{N}_0 \rho[b \times a \times c \times \cos(\beta - 90^\circ)] / M_{bp}$$

$$= (6.022 \times 10^{-23}) \times 1.16 \times (573 \times 824 \times 951 \times \cos 4.5 \times 10^{-30}) / 154.2$$

$$= 2$$



2) When *h* is odd, *h0l* system absence

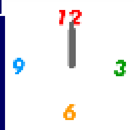
→ a-glide (a/2) perpendicular to b-axis.

When *k* is odd, *0k0* system absence

→ 2_1 screw axis parallel to b-axis. (P.215)

→ c-centered monoclinic or $P2_1/c$.

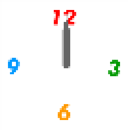
3) The molecule is D_{2d} symmetric. Each molecule corresponds to a lattice point, i.e. centering at (0,0,0), (1/2,1/2,0).



- From this example, we know that some special translation symmetry, elements e.g., screw axes or glide planes, do introduce specific system absence in x-ray diffraction. So you need to keep in mind the rules of system absence related to these translation symmetry elements (see Table 7-6, p.214-215)!

systematic absence and symmetry (p214-215)

Types of reflection	Conditions for extinction	Cause of extinction	Centering and symmetry elements
hkl	$h+k+l$ = odd $h+k$ = odd $h+l$ = odd $k+l$ = odd h,k,l not all even and not all odd $-h+k+l$ not multiples of 3	I-centred C-centred B-centred A-centred Face-centred R-centred	I C B A F R(hexagonal)
$0kl$ (or $h0l$, $hk0$)	k =odd l =odd $k+l$ =odd $k+l$ not multiples of 4	Translation in (100) b/2 c/2 (100) glide (b+c)/2 planes (b+c)/4	b-glide ⊥a (b,c) c-glide⊥a (b,c) n-glide⊥a (b,c) d-glide⊥a (b,c)
$00l$ (or $h00$, or $0k0$)	l =odd l not multiples of 3 l not multiples of 4 l not multiples of 6	Translation c/2 Along c/3 (001) c/4 Screw axis c/6	2_1, 4_2, 6_3 3_1, 3_2, 6_2, 6_4 4_1, 4_3 6_1, 6_5



Example: p.288, 9.30

SiP_2O_7.

Answer: 1) Each Si(4+) is surrounded by 6 Oxygen anions.

→ $s(\text{Si-O}_1) = +4/6 = +2/3$

→ $s(\text{P-O}_1) = 2 - (4/6) = +4/3$

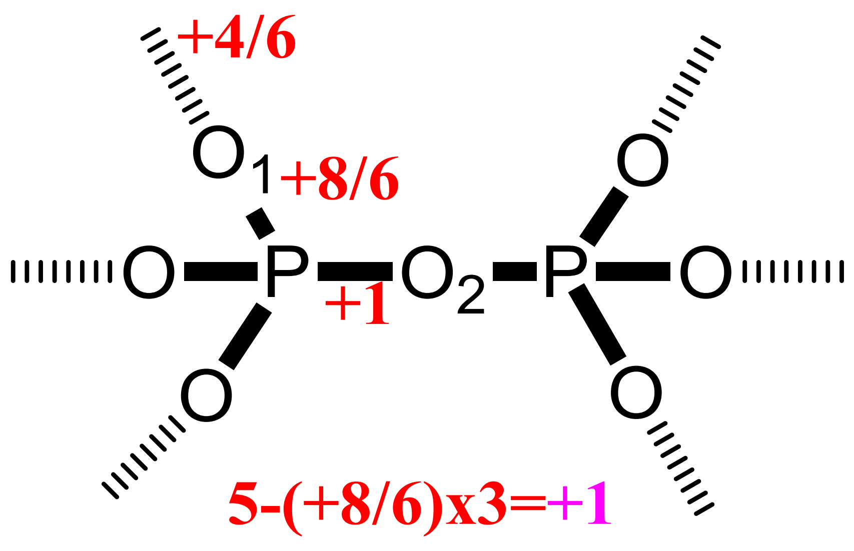
→ $s(\text{P-O}_2) = 5 - (4/3)\text{x}3 = +1$

→ $Z(\text{O}_2) = 2\text{x}(+1) = 2$

→ $P_2O_7^{4-}$ in SiP_2O_7 solid is stable!

2) $s(\text{P-O}_1) > s(\text{P-O}_2)$

→ $R(\text{P-O}_1) < R(\text{P-O}_2)$



$$Z_- = \sum_i s_i = \sum_i \frac{Z_i}{\nu_i}$$

3) Free $P_2O_7^{4-}$ anion is unstable!

$s(\text{P-O}_2) = +5/4$

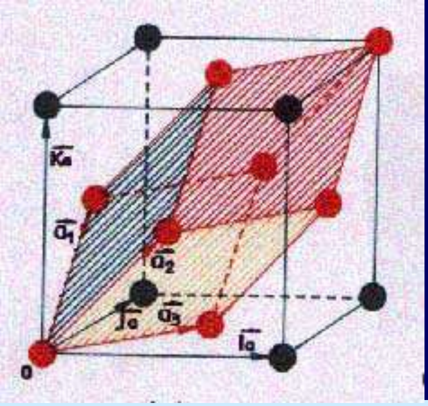
→ $Z(\text{O}_2) = 2\text{x}(+5/4) = 2.5 > 2$!

面心立方点阵的倒易点阵为体心立方点阵，反之亦然！

- 若面心立方点阵单胞的边长为a, 其三个正交的单位矢量为 $\hat{x},\hat{y},\hat{z}$

注意到面心立方点阵的素原胞为棱方单胞，其基矢为:

$$\vec{a}_1=\frac{a}{2}(\hat{x}+\hat{y});\vec{a}_2=\frac{a}{2}(\hat{y}+\hat{z});\vec{a}_3=\frac{a}{2}(\hat{x}+\hat{z})$$

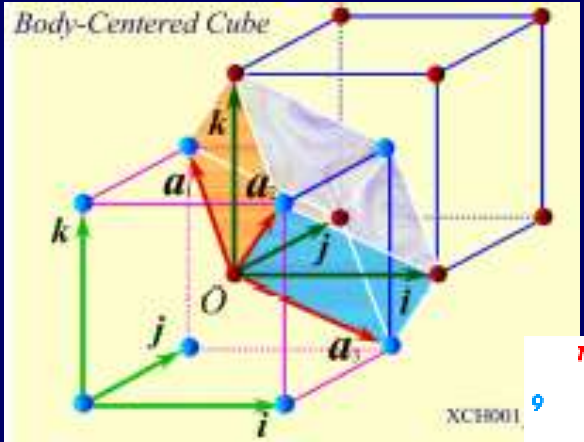


其体积为： $V_c=\vec{a}_1\bullet(\vec{a}_2\times\vec{a}_3)=a^3/4$

则其倒易点阵的基矢为:

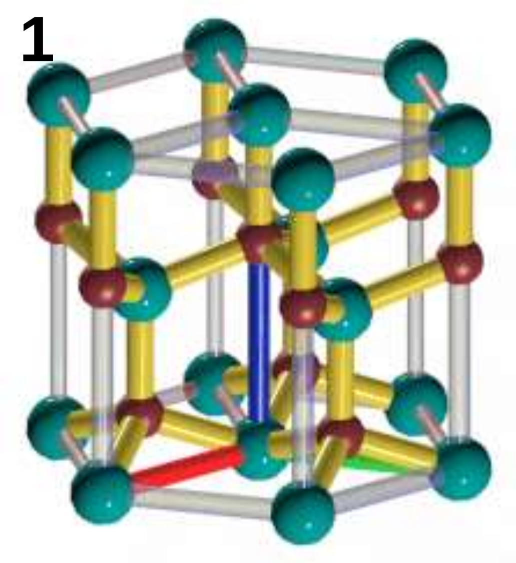
$$\vec{b}_1=\frac{\vec{a}_2\times\vec{a}_3}{V_c}=\frac{1}{a}(\hat{x}+\hat{y}-\hat{z});\vec{b}_2=\frac{\vec{a}_1\times\vec{a}_3}{V_c}=\frac{1}{a}(\hat{y}+\hat{z}-\hat{x});\vec{b}_3=\frac{\vec{a}_1\times\vec{a}_2}{V_c}=\frac{1}{a}(\hat{x}+\hat{z}-\hat{y})$$

此为体心立方点阵素单胞的三个基矢，该体心立方点阵单胞的边长为 2/a.

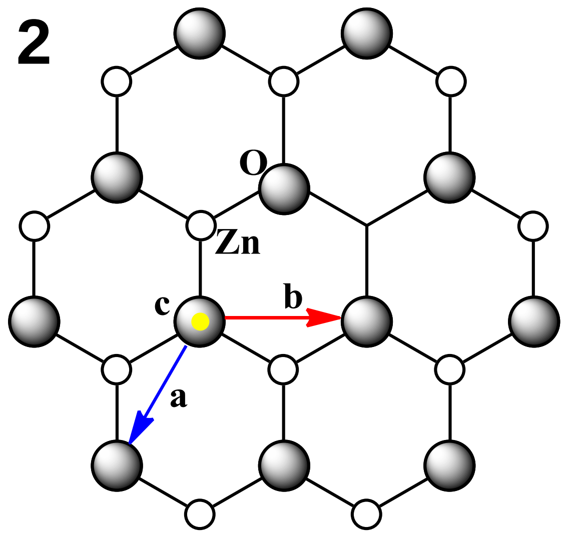


故单胞参数为a的面心立方点阵, 其倒易点阵为体心立方点阵(单胞参数为2/a)！

- 已知ZnO晶体具有六方ZnS结构(如下图1)， 试画出其符合化学配比的(10-10)、(0001)和 (000-1)晶面的原子排列的平面示意图(通常包含次表面层原子，用球棍模型表示), 并说明其表面原子的配位数。



⑩ **(0001)和(000-1)晶面和c轴垂直这两个表面均可用下图2表示.**



(0001):

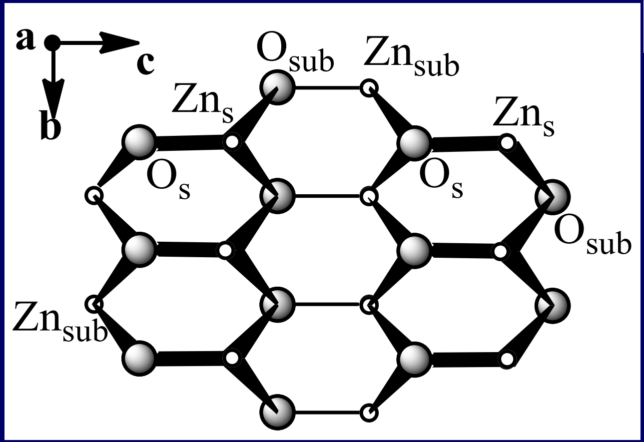
Zn_s CN=3

O_{sub} CN = 4

(000-1) :

O_s CN=3

Zn_{sub} CN=4



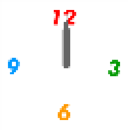
⑩ (10-10) 晶面实际上就是(100)面，与b、c两轴平行 (图3)。

Zn_s/O_s: CN=3, Zn_{sub}/O_{sub}: CN =4

第5-6章

Key points/concepts

1. Hybrid orbital theory and VSEPR
2. HMO, HMO treatment of π-conjugated systems and graphical method to predefine coefficients of HMO of π-conjugated systems.
3. Symmetry rules for molecular reactions.
4. Chemical bonds in electron-deficient molecules (boranes and carboranes etc), styx method & Wade' (N+1) rules
5. Chemical bonding in coordination complexes, crystal-field theory, ligand-field theory; 18e rule and its application in transition-metal cluster compounds.



VSEPR and Hybrid orbital theory p.149, 5.8, 5.12

1) SCl_3^+: S^+ (5Ve), each Cl provides 1e to form a S-Cl bond; thus SCl_3^+ has a lone pair on S. Pyramidal structure like PCl_3. S sp^3 hybridization. S(4+)
2) ICl_4^-: I^- (8Ve), each Cl provides 1e to form a I-Cl bond; thus ICl_4^- has two lone-pairs on I with a square planar structure. I atom adopts sp^3d^2 hybridization. I(3+).
3) ICl_3: I (7 Ve), each Cl provides 1e to form a I-Cl bond; thus ICl_3 has two lone-pairs on I with a T-shaped structure. I atom adopts sp^3d hybridization. I(3+), non-polar
4) SO_3: S (6 ve), sp^2 hybridization, trigonal planar; three S-O sigma bond, and a Π_4^6
5) SO_3^{2-}: S (6 ve), sp^3 hybridization, Pyramidal structure like PCl_3; three S-O sigma bond.
6) CO_3^{2-}: C(4 ve), sp^2 hybridization, trigonal planar; a Π_4^6

MO theory p.149, 5.12

Suppose the bonding MO of AB is

$$\psi_{\mathrm{AB}} = \mathrm{c}_{\mathrm{a}}\varphi_a + c_b\varphi_b$$

$$\because \int \varphi^*_{\mathrm{a}}\, \varphi_{\mathrm{b}} d\tau = \int \varphi^*_{\mathrm{b}}\, \varphi_{\mathrm{a}} d\tau = 0$$

$$\therefore \int \psi^*_{\mathrm{AB}}\, \psi_{\mathrm{AB}} d\tau = \int c_a{}^2 \varphi^*_{\mathrm{a}}\, \varphi_{\mathrm{a}} d\tau + \int c_b{}^2 \varphi^*_{\mathrm{b}}\, \varphi_{\mathrm{b}} d\tau$$

$$= c_a{}^2 + c_b{}^2 = 1$$

$$\because c_a{}^2 = 90\%, c_b{}^2 = 10\% \Rightarrow c_a \approx \pm 0.95; c_b \approx \pm 0.32$$

$$\Rightarrow \psi_{\mathrm{AB}} = 0.95\varphi_a \pm 0.32\varphi_b$$

Possible structures of XeO_nF_m (n,m=1,2,3)? P.150, 5.19

- Any stable XeO_nF_m (n,m=0,1,2,3) compound should have even number of valence electrons. So m =even.

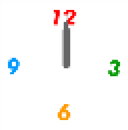
- If n=0, a) m=2, XeF_2, Xe has three lone pairs, linear structure of $D_{\infty h}$; b) m=4, XeF_4, Xe has two lone pairs, planar square D_{4h}; c) m=6, XeF_6, Xe has one lone pair, thus being C_3; d) m=8, XeF_8, tetragonal antiprism structure of D_{4d} symmetry.

- If m=0, a) n=1, XeO, Xe has 3 lone pairs, $C_{\infty v}$; b) n=2, XeO_2, Xe has 2 lone pairs, H_2O-like structure of C_{2v}; c) n=3, XeO_3, Xe has one lone pair, C_{3v}; c) n=4, XeO_4, tetrahedral structure, T_d;

- If n=1, a) m=2, $XeOF_2$, Xe has two lone pairs, C_{2v} symmetry; b) m=4, $XeOF_4$, Xe has one lone pair, C_{4v}; c) m=6, $XeOF_6$, Xe has no lone pair, C_3.

- If n=2, a) m=2, XeO_2F_2 , Xe has one lone pair, C_{2v} symmetry; b) m=4, XeO_2F_4, Xe has no lone pair, D_{4h};

- If n=3, a) m=2, XeO_3F_2, Xe has no lone pair, D_{3h}.



P.150, 5.20

1) 第一种解释（杂化轨道理论）：中心元素为主族元素(如P)时，中心元素和配位原子间通常形成共价键，中心原子成键时采取$sp^3d(z^2)$杂化形式，轴向杂化轨道包含了大量的$nd(z^2)$的组分，而赤道平面轨道则只包含ns和np轨道组分，故轴向键比赤道面内的键来得长。第二种解释（VSEPR）：轴向键和赤道面键的夹角为直角，比赤道面键角(120度) 小，因此 轴向键电子对受到的排斥大于赤道面键电子对，轴向键比赤道面键来得长。

2) 第一种解释（VSEPR）：当中心原子为过渡金属原子时,过渡金属原子上d轨道的电子对会与配体的电子对互相排斥。a)$[Ni(CN)_5]^{3-}$为四角锥构型，中心离子Ni^{2+}的$3d(x^2-y^2)$轨道（赤道面内）上没有电子占据，其它3d原子轨道满占据，因此，赤道平面内配体受到的排斥比轴向配体受到的排斥小，所以轴向配位键长于赤道面键。b) $[Cu(Cl)_5]^{3-}$为三角双锥，中心原子$3d(z^2)$轨道为单占据，其它3d原子轨道满占据，因此，轴向配体受到的排斥比赤道面内配体受到的排斥小，所以轴向配位键短于赤道面键。

同样地，可以解释当 $[Cu(Cl)_5]^{3-}$为四角锥时，轴向键比赤道
内键长！

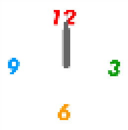
P.150, 5.20

2）第二种解释（杂化轨道理论）：a)$[Ni(CN)_5]^{3-}$为四角锥构型时，中心离子Ni^{2+}的$3d(x^2-y^2)$轨道（赤道面内）上没有电子占据，其它3d原子轨道满占据，中心离子采取dsp^3杂化，因此，赤道平面内的杂化轨道有较多$3d(x^2-y^2)$成分，轴向键没有$3d(x^2-y^2)$ 成分, 因此轴向配位键长于赤道面键。b) $[Cu(Cl)_5]^{3-}$为三角双锥，中心原子$3d(z^2)$轨道为单占据，其它3d原子轨道满占据，中心原子取$sp^3d(4dz^2)$杂化，但轴向配体受到的内层3d电子的排斥比赤道面内配体受到的排斥小，所以轴向配位键短于赤道面键。

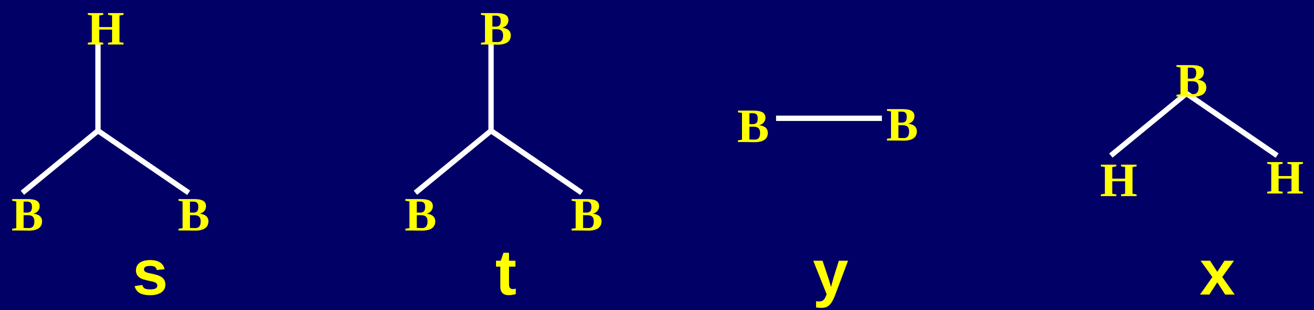
From 2e, 8e, 18e rules to electron counting rules for metal cluster compounds and styx method for electron-deficient molecules.

- 2e, 8e, 18e rules govern the stability of such molecules/groups AX_n and accounts for their geometries in combination with the VSEPR or hybrid orbital theory.
- Yet, there are exceptions of these rules, e.g., PCl_5, and $PtCl_4^{2-}$, whose structures can be well-understood with use of the VSEPR and hybrid orbital theory (or more precisely the generalized octet rule).
- The electron counting rule for transition-metal cluster compounds is actually a natural extension of the 18e rule, which states that when the valence electrons provided by the ligands of a TM center are not enough to fulfill the 18e rule, valence electrons from neighboring TM center(s) should be involved to maintain the TM center to have 18 VE.

$$b = \frac{1}{2}(18n - g)$$



- For electron-deficient molecules/ions, the (styx) method is also a natural extension of the 8e/2e rule. In case that the total valence electrons of a molecule are inadequate to maintain the essential number of 2c-2e bonds, formation of one or more 3c-2e (or nc-ne) bonds can make all component atoms fulfilling the 8e/2e rule.



$x = m - s$

$t = n - s$

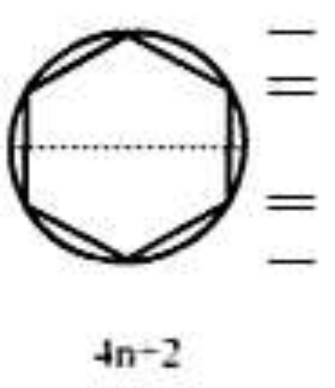
$y = (2s - m)/2$

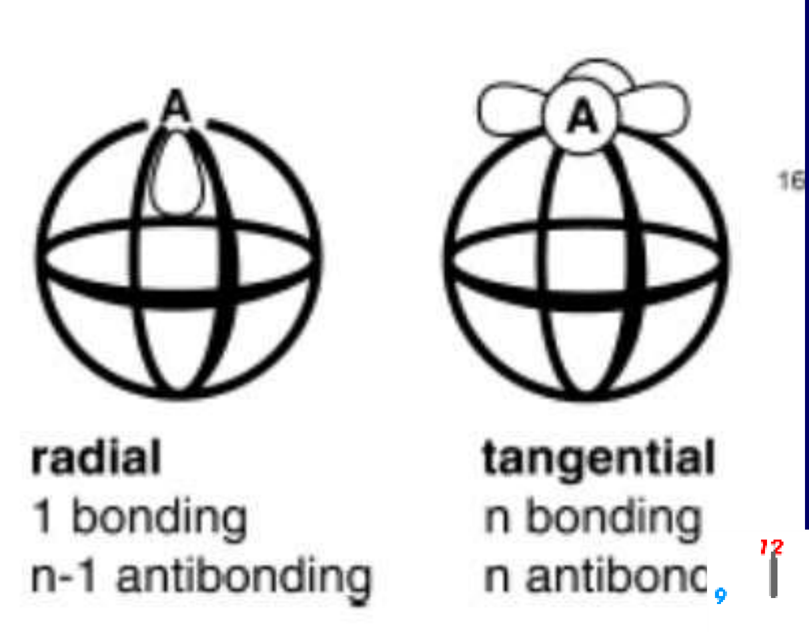
⇨ *p* sets of *styx* ⇨ *p* isomers

Styx method

General rule for stability of molecules/ions

- The molecules/ions should have a large HOMO-LUMO gap to enforce kinetic stability!
- The 2e/8e/18e rules work well because molecules adopting such electron configurations always have a large HOMO-LUMO gap.
- Following this general rule, the Wade's (n+1) rule accounts for the stability of closo-boranes/carboranes, whose skeletal bonding electrons are actually delocalized over the whole molecule.
- Similarly, the Huckel (4n+2) rule accounts for the stability of cyclic π-conjugated systems that have delocalized electrons.





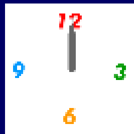
The chemical bonding in $B_nH_n^{2-}$ (n=5,6,7)? P.184, 6.4

According to Wade's (n+1) rule,

- In $B_5H_5^{2-}$, there are 5 B-H σ-bonds, one radial bonding skeletal MO and 5 tangential bonding skeletal MOs.
- In $B_6H_6^{2-}$, there are 6 B-H σ-bonds, one radial bonding skeletal MO and 6 tangential bonding skeletal MOs.
- In $B_7H_7^{2-}$, there are 7 B-H σ -bonds, one radial bonding skeletal MO and 7 tangential bonding skeletal MOs.

It is known that $[Co(NH_3)Cl_2]$ has two isomers. P.184, 6.9

- If the complex has a planar hexagonal structure, there should be 3 isomers depending on the relative position of two Cl ligands.
- If the complex has a trigonal prismatic structure, there should be three isomers.
- If the complex has a trigonal antiprismatic structure (or octahedral structure), there should be only two isomers. Therefore the complex has this structure.



Examples p.185, 6.17, 6.24,

- **18-e rule, TM cluster**

b=(18n-g)/2 b= number of M-M bonds.

Or b = (18n + 8m –g)/2 (m = non-metal in-cluster atom).

- **$Ni(CO)_4$**:

1) Ni (10ve) + 4(CO) (8ve) = 18ve; sp^3 hybridization. Tetrahedral structure, T_d-symmetry.

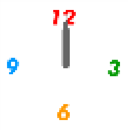
2) Ni ($3d^{10}$), 3d orbitals split into $(3d_{z2}, 3d_{x2-y2})^4(3d_{xy},3d_{yz},3d_{xz})^6$

3) no d-d excitation can be observed in such a case.

- **$Fe_5C(CO)_{15}$**: g= 5x8 + 4 + 15x2 = 74; b= (18n-g)/2 = 8

Square pyramid with 8 Fe-Fe bonds. (in-cluster C atom?!)

- **$Ru_6C(CO)_{16}$**: g= 6x8 + 4 + 16x2 = 84; b= (18n-g)/2 = 12
Octahedron with 12 Ru-Ru bonds!



Examples p.185, 6.17, 6.24,

- **$[Rh_6C(CO)_{15}]^{2-}$**: g= 6x9 + 4 + 15x2 +2 = 90; b= (18n-g)/2 = 9 trigonal prism with 9 Rh-Rh bonds!
- **$[Ni_8C(CO)_{16}]^{4-}$**: g =8x10 + 4 +16x2+ 4 = 120, b = (18n-g)/2 = 12 cube-shaped with 12 Ni-Ni bonds.
- **$[Ni_8C(CO)_{16}]^{2-}$**: g = 8x10 + 4 +16x2 + 2 = 118, b = (18n-g)/2 =13 square antiprism. (actually synthesized!)

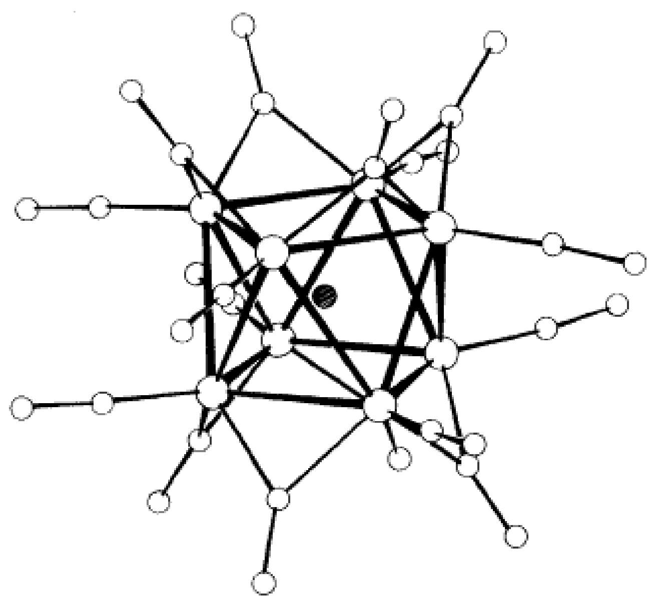


FIGURE 4. Structure of $[Ni_8C(CO)_{16}]^{2-}$.

Examples p.185, 6.26,

- $Fe_6(CO)_{18}$: g= 6x8 + 18x2 = 84; b= (18n-g)/2 = 12

  Octahedron with 12 Fe-Fe bonds.

- $[Fe_4RhC(CO)_{14}]^-$: g= 4x8+9+4 +14x2+1 = 74; b= (18n-g)/2 = 8

  square pyramid with 8 M-M bonds!

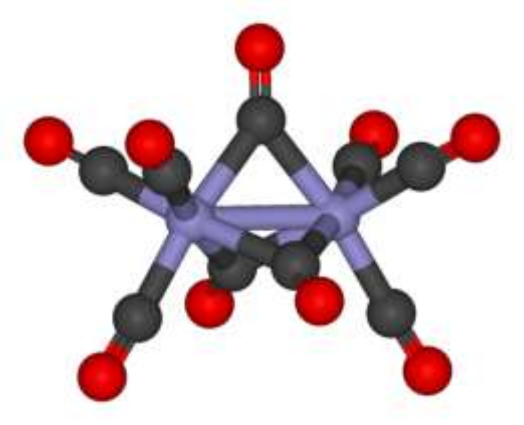
- $[Co_6N(CO)_{15}]^-$: g= 6x9 + 5 + 15x2 +1 = 90; b= (18n-g)/2 = 9

  trigonal prism with 9 Rh-Rh bonds!

- **$Ni_8(CO)_8(PPh_3)_{12}$**: g = 8x10 + 8x2+12x2 = 120, b = (18n-g)/2 =12
  cube-shaped with 12 Ni-Ni bonds. (wrong ligand in text book!)

- **$Ni_8(PPh)_6\,(CO)_8$**: g = 8x10 + **6x4** + 8x2 = 120, b = (18n-g)/2 =12
  cube-shaped with 12 Ni-Ni bonds. Each PPh ligand is μ_4-ligated!

Examples p.185, 6.25,



- **$Fe_2(\mu_2\text{-}CO)_3(CO)_6$:**

1) g= 2x8 + 9x2 = 34; b= (18n-g)/2 = 1

There exists one Fe-Fe bond.

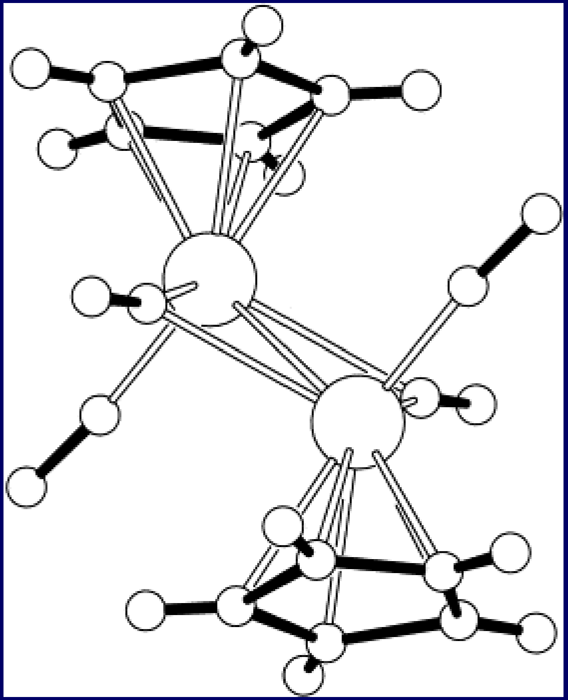
2) The CO(μ_2) forms two Fe-C bonds with the Fe atoms, adopting C=O double bond. On the contrary, a terminal CO forms a donative Fe-CO σ-bond and, meanwhile, get backdonation from Fe(3dπ) arising from the 3dπ(Fe)→2π*(CO) bonding, which results in a partially weakened C≡O triple bond. Thus the C-O bond in a terminal CO is strong than that in a bridging CO(μ_2).

3) **Why are there three μ_2-CO ligands?** To fulfill the 18e rule, all valence AOs of a Fe center should be involved, demanding each Fe center being 6-fold coordinated (excluding Fe-Fe bond). Thus for $Fe_2(CO)_9$, three μ_2-CO ligands are required to keep both Fe centers being 6-fold coordinated.

Example: $Re_2(CO)_4(\eta_5\text{-}C_5H_5)_2$
Re-Re bond order =? Why are there two μ_2-CO ligands?

1) $g = 2 \times 7 + 4 \times 2 + 2 \times 5 = 32$; $b = (18n - g)/2 = 2$

Re-Re bond order is 2.



2) For a TM complex fulfilling the 18e rule, all the valence AOs of a TM center should be involved in the chemical bondings. As such the coordination number of a Re center should be 6 (excluding the Re-Re bond). As a C_5H_5 ligand makes use of 3 valence AOs of Re, there should be 3 CO ligands coordinated to a Re center. Thus, two μ_2-CO ligands are required to keep both Re center being 6-fold coordinated!

根据Hückel近似，写出下列分子的π电子分子轨道久期行列式：

p.150, 5.21

Answer: Generally, these three molecules all have a $\prod_4^4$ bond, the MO of which can be expressed as

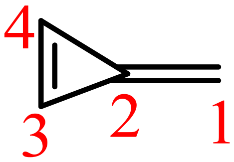
$$\psi = \sum_{i=1}^{4} c_i \varphi_i$$

Accordingly to HMO, the seqular determinant of molecule a is

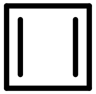
$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & \beta \\ 0 & \beta & \alpha - E & \beta \\ 0 & \beta & \beta & \alpha - E \end{vmatrix} = 0$$

Key point: In the framework of HMO, the resonance integral β exists only when two centers are directly connected!

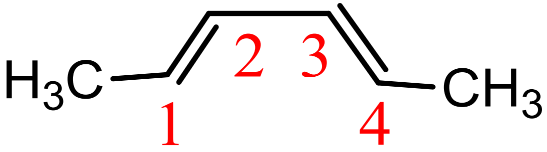
a)



b)



c)



The seqular determinant of molecule b is

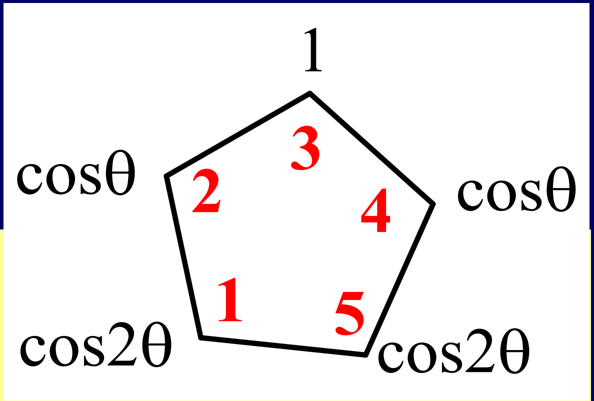
$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

The seqular determinant of molecule c is

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

C_5H_5 and its anion: **p.150, 5.24**

symmetric MOs, boundary condition



$$2\cos\theta\cos(2\theta)=\cos(2\theta)+\cos(\theta)$$

$$\Rightarrow \cos 3\theta = \cos 2\theta$$

$$\Rightarrow 2\sin(5\theta/2)\sin(\theta/2)=0 \Rightarrow \theta = 2m\pi/5 \quad (\mathrm{m}=0,1,2)$$

$$E_{s1}=\alpha+2\beta, \psi_{s1}=A\sum_{k=1}^{5}\varphi_k$$

$$E_{s2}=\alpha+2\beta\cos(2\pi/5),$$

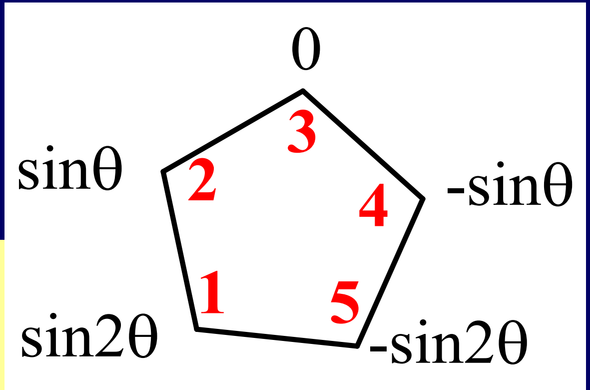
$$\psi_{s2}=A[\varphi_3+\cos(2\pi/5)(\varphi_2+\varphi_4)+\cos(4\pi/5)(\varphi_5+\varphi_1)]$$

$$E_{s3}=\alpha+2\beta\cos(4\pi/5),$$

$$\psi_{s3}=A[\varphi_3+\cos(4\pi/5)(\varphi_2+\varphi_4)+\cos(2\pi/5)(\varphi_5+\varphi_1)]$$

C_5H_5 radical and its anion:

asymmetric MOs, boundary condition



$$2\cos\theta\sin(2\theta)=\sin(-2\theta)+\sin(\theta)$$

$$\Rightarrow \sin 3\theta = -\sin 2\theta$$

$$\Rightarrow 2\sin(5\theta/2)\cos(\theta/2)=0 \Rightarrow \theta = 2m\pi/5 \quad (\mathrm{m}=1,2)$$

$$E_{as1}=\alpha+2\beta\cos(2\pi/5),$$

$$\psi_{as1}=A[\sin(2\pi/5)(\varphi_2-\varphi_4)+\sin(4\pi/5)(\varphi_1+\varphi_5)]$$

$$E_{as2}=\alpha+2\beta\cos(4\pi/5),$$

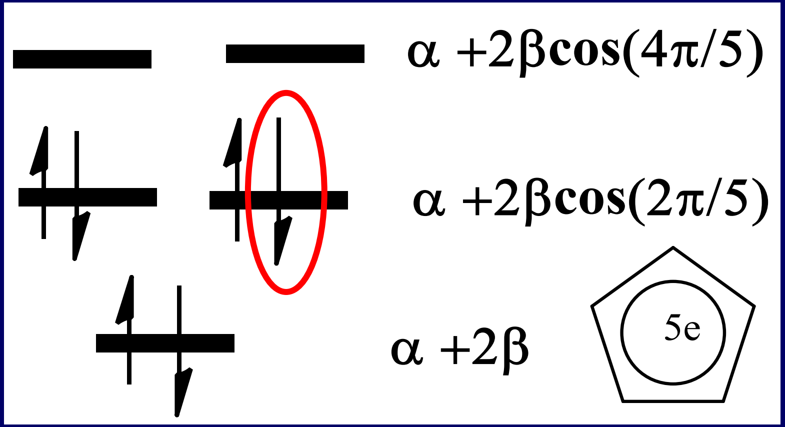
$$\psi_{as2}=A[\sin(4\pi/5)(\varphi_2-\varphi_4)+\sin(2\pi/5)(\varphi_1-\varphi_5)]$$

→ **Three symmetric and two asymmetric MOs!**

→ **s1 is the lowest occupied MO (LOMO) with $E_{s1} = \alpha + 2\beta$**

→ **$E_{as1} = E_{s2}$, $E_{as2} = E_{s3}$ (doubly degenerate MOs)**

C_5H_5 and its anion:

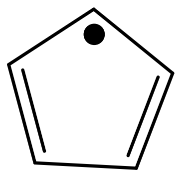


1) For neutral C_5H_5, 5πe in total.

$$E_{total} = 2(\alpha + 2\beta) + 3[\alpha + 2\beta\cos(2\pi/5)]$$

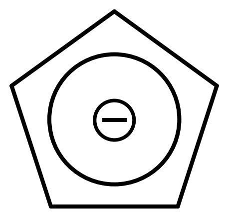
$$= 5\alpha + 4\beta + 6\beta\cos(2\pi/5)$$

For the localized system: $E_{loc} = 2\text{x}2(\alpha + \beta) + \alpha = 5\alpha + 4\beta$



→ $E_{deloc} = E_{total} - E_{loc} = 6\beta\cos(2\pi/5) \approx 1.85\beta$

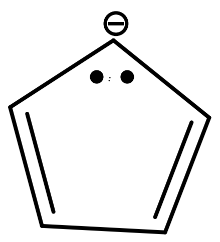
2) For C_5H_5 anion, 6e in total.



The s1,s2 and as1 MOs are fully occupied.

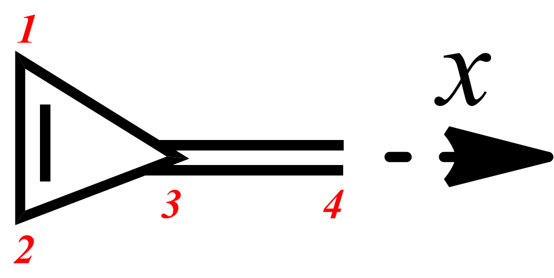
$$E_{total} = 6\alpha + 4\beta[1+2\cos(2\pi/5)]$$

For the localized system: $E_{loc} = 6\alpha + 4\beta$



→ $E_{deloc} = E_{total} - E_{loc} = 8\beta\cos(2\pi/5) \approx 2.47\beta$

HMO---More complex systems (p.138,)



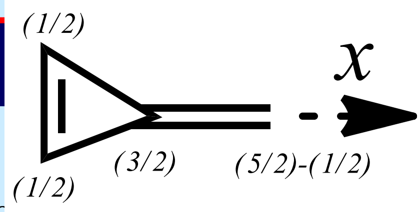
The seqular determinant of this molecule:

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

$$(\alpha-E)/\beta = -2\cos\theta$$

$$c_1\beta + c_2\beta + c_3(\alpha-E) + c_4\beta = 0 \Rightarrow 2\cos\theta c_3 = \mathrm{c}_1 + \mathrm{c}_2 + \mathrm{c}_4$$

For symmetric MOs



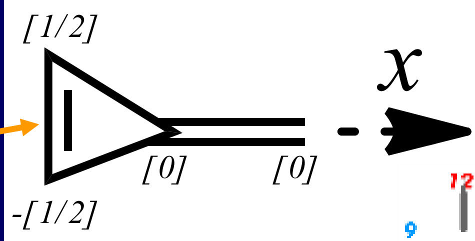
$$c_1 = c_2 = cos(\theta/2); c_3 = cos(3\theta/2);$$

$$\therefore c_4 = 2\cos\theta c_3 - \mathrm{c}_1 - \mathrm{c}_2 = 2\cos\theta\cos\frac{3\theta}{2} - 2\cos\frac{\theta}{2} = \cos\frac{5\theta}{2} - \cos\frac{\theta}{2}$$

$$\Rightarrow 2\cos\theta[\cos\frac{5\theta}{2} - \cos\frac{\theta}{2}] = \cos\frac{3\theta}{2} \qquad (\text{boundary condition!})$$

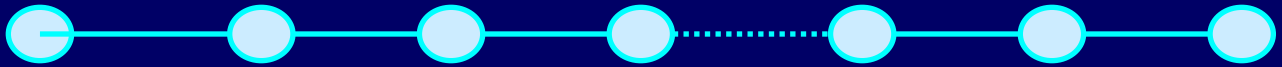
For asymmetric MO

It is the antibonding π-MO of a C=C bond!



cosθ=-1

Linear carbon chain with 2n carbon atoms: HOMO and LUMO



$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \qquad\qquad \sin(2n-1)\theta \quad \sin 2n\theta$

$$E = \alpha + 2\beta\cos\theta, \text{ where } \theta = \frac{m\pi}{2n+1} \qquad (\mathrm{m} = 1,2,3,\ldots,2\mathrm{n})$$

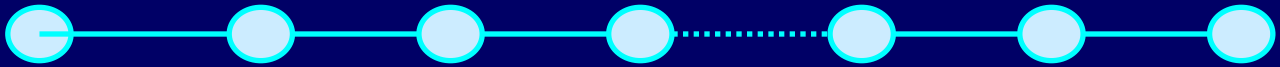
$$\psi_m = \sqrt{\frac{2}{2n+1}} \sum_{k=1}^{2n} \sin\frac{km\pi}{2n+1}\varphi_k \qquad (\mathrm{m} = 1,2,3,\ldots,2\mathrm{n})$$

$2ne_\pi$, n occupied π-MOs; so HOMO (m=n), LUMO (m=n+1).

$$\psi_{HOMO} = \sqrt{\frac{2}{2n+1}} \sum_{k=1}^{2n} \sin\frac{kn\pi}{2n+1}\varphi_k, \qquad \mathrm{E}_{\mathrm{HOMO}} = \alpha + 2\beta\cos\frac{n\pi}{2n+1}$$

$$\psi_{LUMO} = \sqrt{\frac{2}{2n+1}} \sum_{k=1}^{2n} \sin\frac{k(n+1)\pi}{2n+1}\varphi_k, \qquad \mathrm{E}_{\mathrm{LUMO}} = \alpha + 2\beta\cos\frac{(n+1)\pi}{2n+1}$$

Linear carbon chain with 2n carbon atoms: HOMO



$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \qquad \sin(2n-1)\theta \quad \sin 2n\theta$

$$\psi_{HOMO} = \sqrt{\frac{2}{2n+1}}\sum_{k=1}^{2n}\sin\frac{kn\pi}{2n+1}\varphi_k, \qquad \mathrm{E}_{\mathrm{HOMO}} = \alpha + 2\beta\cos\frac{n\pi}{2n+1}$$

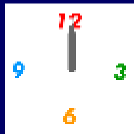
$$c_{2n} = \sin\frac{2n^2\pi}{2n+1} = \sin[\frac{n(2n+1)\pi - n\pi}{2n+1}] = \sin(n\pi - \frac{n\pi}{2n+1})$$

If *2n=4l*, $$c_{2n} = \sin(n\pi - \frac{n\pi}{2n+1}) = -\sin\frac{n\pi}{2n+1} = -c_1$$

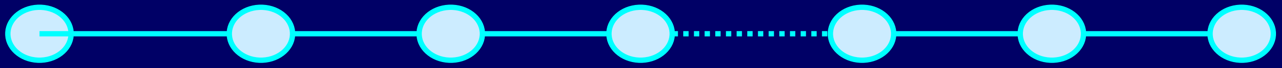
Similarly, $c_{2n-1} = -c_2, \ldots, c_{n+1} = -c_n$ **→ HOMO is asymmetric!**

If *2n=4l+2*, $$c_{2n} = \sin(n\pi - \frac{n\pi}{2n+1}) = \sin\frac{n\pi}{2n+1} = c_1$$

Similarly, $c_{2n-1} = c_2, \ldots, c_{n+1} = c_n$ **→ HOMO is symmetric!**



Linear carbon chain with 2n carbon atoms: LUMO



$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \qquad \sin(2n-1)\theta \quad \sin 2n\theta$

$$\psi_{LUMO} = \sqrt{\frac{2}{2n+1}} \sum_{k=1}^{2n} \sin\frac{k(n+1)\pi}{2n+1}\varphi_k , \qquad \mathrm{E}_{\mathrm{LUMO}} = \alpha + 2\beta\cos\frac{(n+1)\pi}{2n+1}$$

$$c_{2n} = \sin\frac{(2n^2+2n)\pi}{2n+1} = \sin[\frac{n(2n+1)\pi + n\pi}{2n+1}] = \sin(n\pi + \frac{n\pi}{2n+1})$$

If $2n=4l$, $$c_{2n} = \sin(n\pi + \frac{n\pi}{2n+1}) = \sin\frac{n\pi}{2n+1} = \sin\frac{(n+1)\pi}{2n+1} = c_1$$

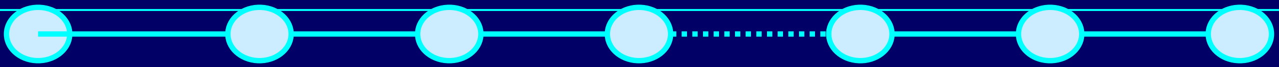
Similarly, $c_{2n-1} = c_2 ,\ldots, c_{n+1} = c_n$ → **LUMO is symmetric!**

If $2n=4l+2$,

$$c_{2n} = \sin(n\pi - \frac{n\pi}{2n+1}) = -\sin\frac{n\pi}{2n+1} = -\sin\frac{(n+1)\pi}{2n+1} = -c_1$$

Similarly, $c_{2n-1} = -c_2 ,\ldots, c_{n+1} = -c_n$ → **LUMO is asymmetric!**

Linear carbon chain with 2n carbon atoms: HOMO and LUMO



$$\sin\theta \quad \sin 2\theta \quad \sin 3\theta \qquad\qquad \sin(2n-1)\theta \quad \sin 2n\theta$$

If *2n=4l*,

HOMO: $c_{2n} = -c_1, c_{2n-1} = -c_2, \ldots, c_{n+1} = -c_n$ **asymmetric!**

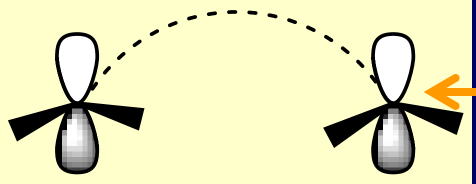
LUMO: $c_{2n} = c_1, c_{2n-1} = c_2, \ldots, c_{n+1} = c_n$ **symmetric!**

If *2n=4l+2*,

HOMO: $c_{2n} = c_1, c_{2n-1} = c_2, \ldots, c_{n+1} = c_n$ **symmetric!**

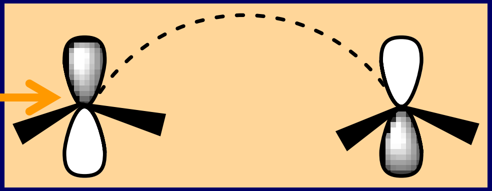
LUMO: $c_{2n-1} = -c_2, \ldots, c_{n+1} = -c_n$ **asymmetric!**

Simplified motif of symm. & asymm. π-MOs:



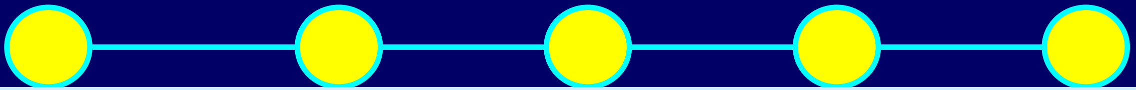
Symmetric!

p_π-AO of terminal carbon atom



Asymmetric with respect to Cs operation!

Linear carbon chain with (2n+1) p_π-orbitals.



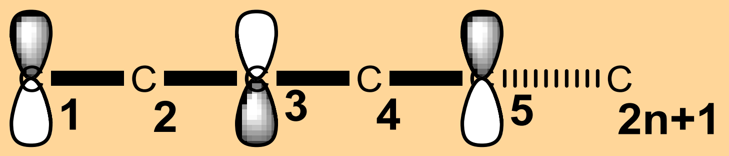
$$\sin\theta, \quad \sin 2\theta, \quad \sin 3\theta, \quad \sin 4\theta, \quad .....\sin(2n+1)\theta$$

$$E = \alpha + 2\beta\cos\theta \qquad \theta = m\pi/(2n+2) \quad (m = 1,2,3,...,2n+1)$$

$$\psi_m = \sqrt{\frac{2}{2n+2}} \sum_{k=1}^{2n+1} \sin\frac{km\pi}{2n+2}\varphi_k \qquad (m = 1,2,3,...,2n+1)$$

$N_{e\pi}$=2n+1 → n doubly occupied MOs (m=1,..,n), and a singly occupied MO (SOMO, m= n+1). $\theta_{SOMO}=\pi/2$, $E_{SOMO}=\alpha$, non-bonding!

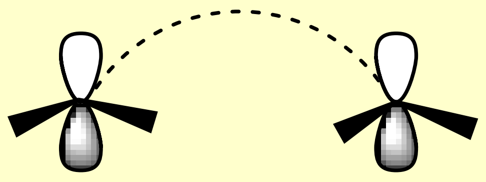
$$\Psi_{somo} = \sqrt{\frac{2}{2n+2}} \sum_{k=1}^{2n+1} c_k\varphi_k \quad \text{where} \quad c_k = \sin\frac{k\pi}{2}$$



If 2n+1 = 4*l* +1 (e.g., 5),

$$c_1 = \sin\frac{\pi}{2} = 1; c_{2n+1} = \sin\frac{(4l+1)\pi}{2} = 1$$

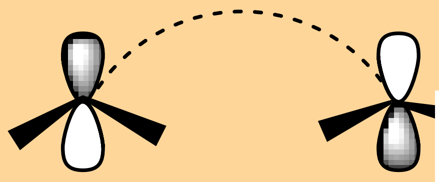
symmetric



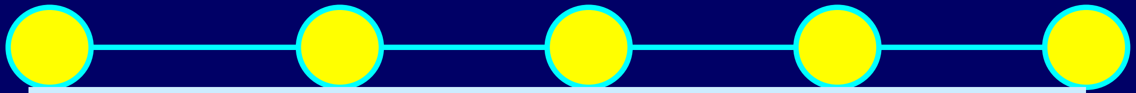
If 2n+1 = 4*l* +3 (e.g., 7),

$$c_1 = \sin\frac{\pi}{2} = 1; c_{2n+1} = \sin\frac{(4l+3)\pi}{2} = -1$$

asymmetric



linear system, C5H7 anion. P.150, 5.24

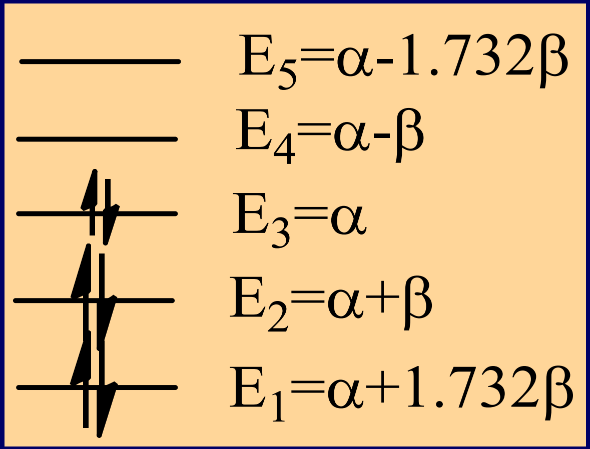


$\sin\theta,\quad \sin 2\theta,\quad \sin 3\theta,\quad \sin 4\theta,\quad \sin 5\theta$

$$Boundary: \sin 6\theta = 0 \Rightarrow \theta = \mathrm{m}\pi/6 \quad (\mathrm{m} = 1,2,3,\ldots,5)$$

$$E_m = \alpha + 2\beta\cos\theta \qquad \theta = \mathrm{m}\pi/6 \quad (\mathrm{m} = 1,2,3,\ldots,5)$$

$$\psi_m = \sqrt{\frac{2}{6}}\sum_{k=1}^{2n+1}\sin\frac{km\pi}{6}\phi_k \qquad (\mathrm{m} = 1,2,3,\ldots,5)$$



$E_5=\alpha-1.732\beta$

$E_4=\alpha-\beta$

$E_3=\alpha$

$E_2=\alpha+\beta$

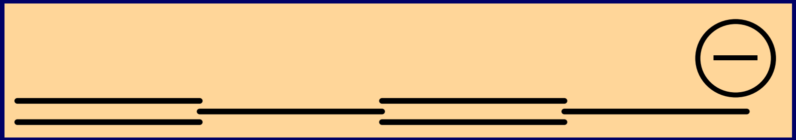
$E_1=\alpha+1.732\beta$

6e, three doubly occupied MOs (m=1-3)

$$E_{total} = 2(E_1 + E_2 + E_3) = 6\alpha + 4\beta[\cos(\pi/6) + \cos(2\pi/6) + \cos(\pi/2)]$$
$$= 6\alpha + 5.464\beta$$

For localized system,

$$E_{local} = 2\times 2(\alpha+\beta) + 2\alpha = 6\alpha + 4\beta$$

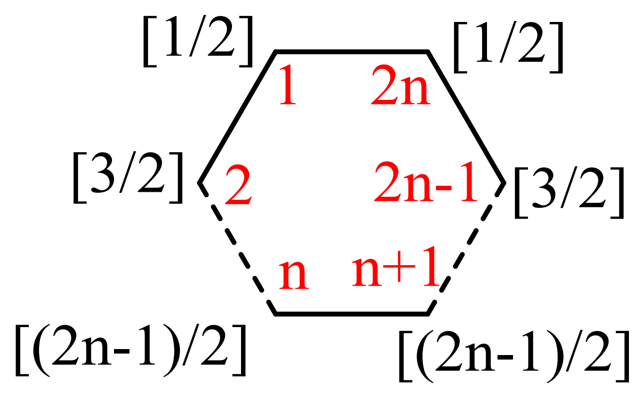


Delocalization energy

$$E_{local} = E_{total} - E_{local} = 1.464\beta$$

Cyclic system with 2n carbon atoms: HOMO and LUMO

Symmetric MOs



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

$$\Rightarrow 2\sin(n\theta)\sin\frac{\theta}{2} = 0$$

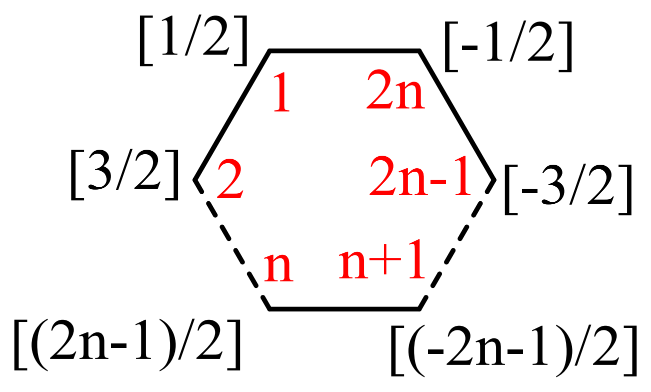
$$\Rightarrow \theta = m\pi / n(m = 0,1,2,\ldots,n-1)$$

$$E_{sm} = \alpha + 2\beta\cos(m\pi / n) \qquad (m = 0,1,2,\ldots,n-1)$$

$$\psi_{sm} = A\sum_{k=0}^{n-1}(\varphi_{1+k} + \varphi_{2n-k})\cos[(2k+1)m\pi / 2n] \qquad (m = 0,1,2,\ldots,n)$$

Cyclic system with 2n carbon atoms: HOMO and LUMO

Asymmetric Mos, boundary condition:



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

$$\Rightarrow 2\sin(n\theta)\cos\frac{\theta}{2}=0$$

$$\Rightarrow \theta=m\pi/n(m=1,2,\ldots,n)$$

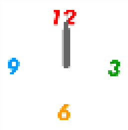
$$E_{as}=\alpha+2\beta\cos(m\pi/n)\qquad(m=1,2,\ldots,n)$$

$$\psi_{asm}=A\sum_{k=0}^{n-1}(\varphi_{1+k}-\varphi_{2n-k})\sin[(2k+1)m\pi/2n]\qquad(m=1,2,\ldots,n)$$

So the π-conjugated molecule has 1 LOMO(s), 1 HUMO(as) and (n-1) doubly degenerate MOs. HOMO --doubly degenerated!

For 2n = 4l +2, the two degenerate HOMOs are fully occupied!

$$E_{HOMO}=\alpha+2\beta\cos[(n-1)\pi/2n]$$



Cyclic system with 2n carbon atoms: HOMO and LUMO

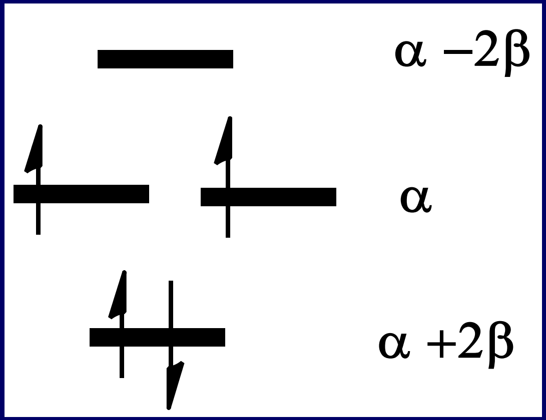
For 2n = 4l , the two degenerate HOMOs are singly occupied!

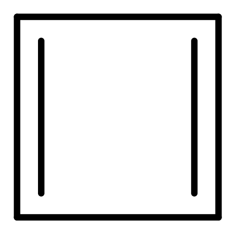
$$E_{HOMO} = \alpha + 2\beta \cos[n\pi / 2n] \quad = \alpha$$

e.g., cyclobutadiene, the HOMOs are singly occupied!

$$E_{HOMO} = \alpha$$

$$E_{LOMO} = \alpha + 2\beta$$





Thus,

$E_{total} = 2(\alpha + 2\beta) + 2\alpha = 4(\alpha + \beta)$

For localized system: $E_{loc} = 4(\alpha + \beta)$

→ $E_{deloc} = E_{total} - E_{loc} = 0$

No delocalization stability! Antiaromatic!

Cyclic system with 2n+1 carbon atoms: HOMO and LUMO

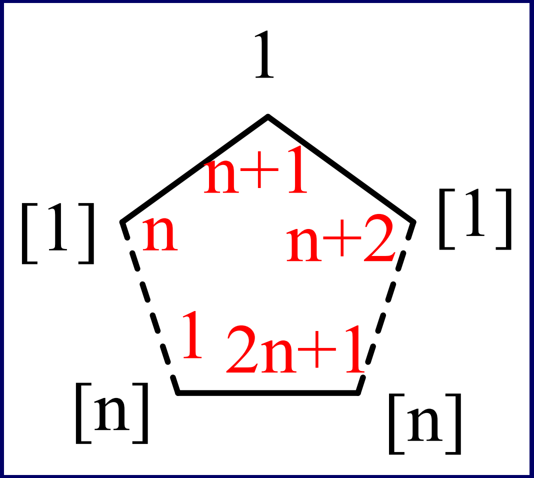
Symmetric MOs

Boundary:

$$\cos n\theta = \cos(n+1)\theta$$

$$\Rightarrow 2\sin\frac{(2n+1)\theta}{2}\sin\frac{\theta}{2} = 0$$

$$\Rightarrow \theta = 2m\pi/(2n+1) \quad (m = 0,1,2,\ldots,n)$$

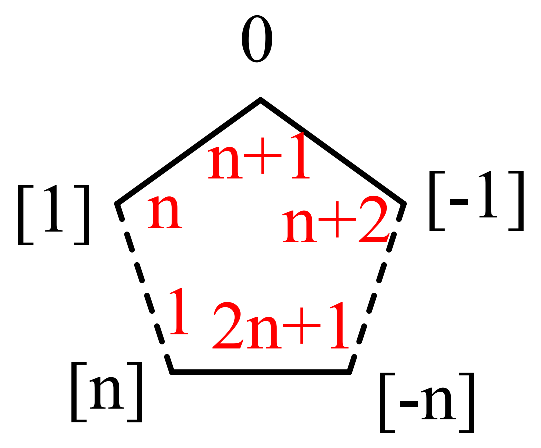


$$E_{sm} = \alpha + 2\beta\cos[2m\pi/(2n+1)] \qquad (m = 0,1,2,\ldots,n)$$

$$\psi_{sm} = A\sum_{k=1}^{n}\varphi_{n+1} + (\varphi_{n-k+1} + \varphi_{n+k+1})\cos[2km\pi/(2n+1)]$$

Cyclic system with 2n+1 carbon atoms: HOMO and LUMO

Asymmetric MOs



$$\sin n\theta = -\sin(n+1)\theta$$

$$\Rightarrow 2\sin\frac{(2n+1)\theta}{2}\cos\frac{\theta}{2} = 0$$

$$\Rightarrow \theta = 2m\pi/(2n+1) \quad (m = 1,2,\ldots,n)$$

$$E_{asm} = \alpha + 2\beta\cos[2m\pi/(2n+1)] \qquad (m = 1,2,\ldots,n)$$

$$\psi_{asm} = A\sum_{k=1}^{n}(\phi_{n-k+1} - \phi_{n+k+1})\cos[2km\pi/(2n+1)]$$

- **So the π-conjugated molecule has 1 LOMO, and n doubly-degenerate MOs (one is symmetric, one is asymmetric).**
- **HOMO – doubly-degenerate!**

Cyclic system with 2n+1 carbon atoms: HOMO and LUMO

- **HOMO –doubly-degenerate!**

a) For 2n+1 = *4l* +1, the doubly degenerate HOMOs hold 3 electrons!

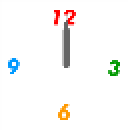
$$E_{HOMO} = \alpha + 2\beta \cos[n\pi/(2n+1)]$$

Thus, such type of cyclic pi-conjugation systems tends to accept one more electron to have a stable closed-shell electronic configuration, which also fulfills the (4N+2) Huckel rule of aromaticity!

b) For 2n+1 = *4l* +3, the doubly degenerate HOMOs hold 1 electrons!

$$E_{HOMO} = \alpha + 2\beta \cos[(n+1)\pi/(2n+1)]$$

Thus, such type of cyclic pi-conjugation systems tends to lose one electron to have a stable closed-shell electronic configuration, which also fulfills the (4N+2) Huckel rule of aromaticity!



Cyclic system with 2n+1 carbon atoms: HOMO and LUMO

e.g., C_3H_3, MOs! p.150 5.23

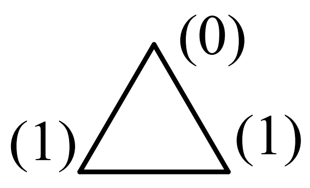
Symmetric MOs,

$$\cos 2\theta = \cos\theta \Rightarrow \theta = 0, 2\pi/3; E_{s1} = \alpha + 2\beta, E_{s2} = \alpha - \beta$$

$$\psi_{s1} = \mathrm{A}(\varphi_1 + \varphi_2 + \varphi_3) \quad (\mathrm{A} = 1/\sqrt{3})$$

$$\psi_{s2} = \mathrm{A}[\varphi_1 \cos(2\pi/3) + \varphi_2 + \varphi_3 \cos(2\pi/3)]$$

$$= \frac{1}{\sqrt{6}}(\varphi_1 - 2\varphi_2 + \varphi_3)$$

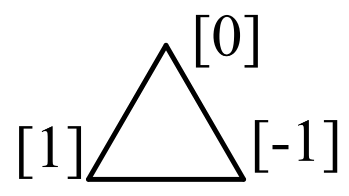


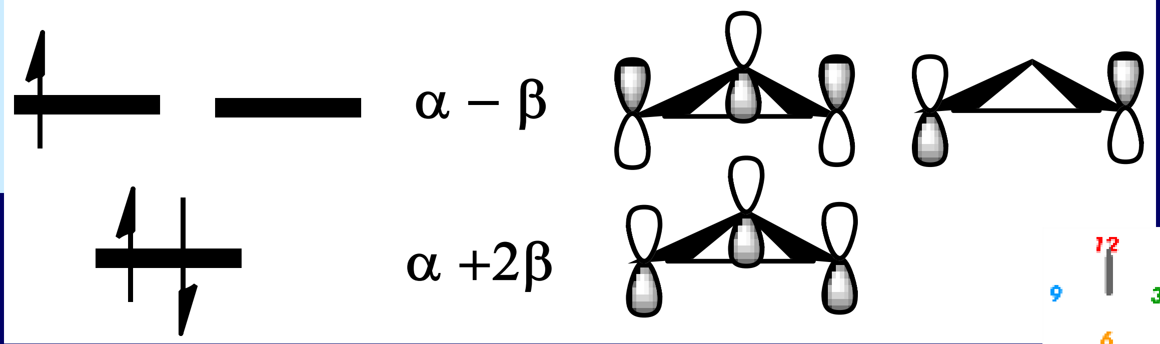
Asymmetric MOs,

$$\sin 2\theta = -\sin\theta \Rightarrow \theta = \pi/3; E_{as1} = \alpha - \beta$$

$$\psi_{as1} = \mathrm{A}[\varphi_1 \sin(2\pi/3) - \varphi_3 \sin(2\pi/3)]$$

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



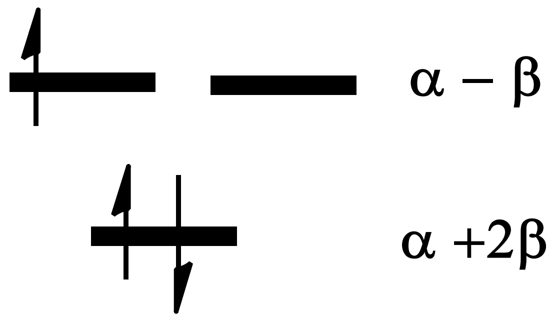


e.g., C_3H_3, the HOMO is singly occupied!

p.150
5.23

$$E_{HOMO} = \alpha - \beta$$

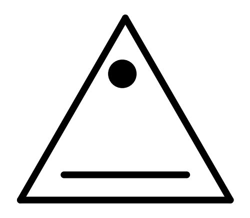
$$E_1 = \alpha + 2\beta$$



Thus, $E_{total} = 2(\alpha + 2\beta) + (\alpha - \beta) = 3(\alpha + \beta)$

For localized system: $E_{loc} = 2(\alpha + \beta) + \alpha = 3\alpha + 2\beta$

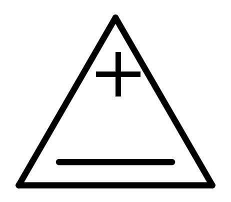
→ $E_{deloc} = E_{total} - E_{loc} = \beta$



For C_3H_3 cation, $E_{total} = 2(\alpha + 2\beta)$

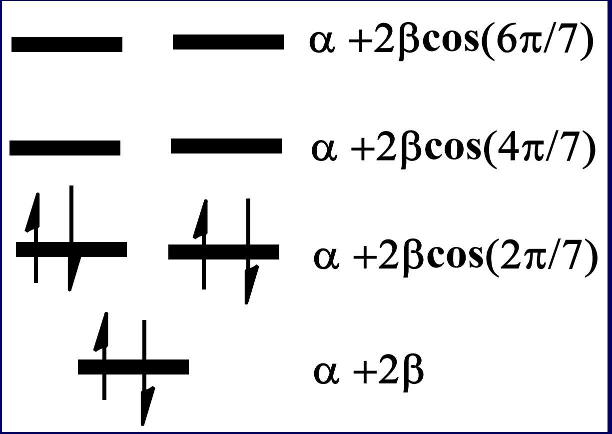
For localized system: $E_{loc} = 2(\alpha + \beta)$

$E_{deloc} = E_{total} - E_{loc} = 2\beta$



Enhanced delocalization fulfilling the Hückel rule!

Cyclic system with 2n+1 carbon atoms: HOMO and LUMO



e.g., C_7H_7 cation,

Delocalized system

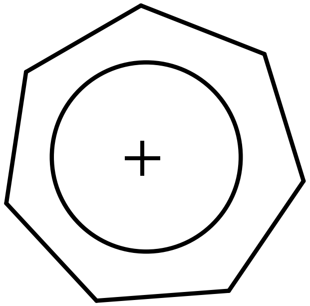
$$E_{total} = 2x(\alpha+2\beta) + 4(\alpha+2\beta\cos(2\pi/7))$$

$$= \quad 6\alpha + 4\beta(1+2\cos(2\pi/7))$$

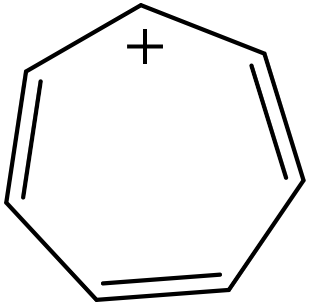
For localized system: $E_{loc} = 3x2(\alpha + \beta)$

→ Delocalization energy:

$$E_{deloc} = E_{total} - E_{loc} = 8\beta\cos(2\pi/7) - 2\beta = 2.99\beta$$



delocalized structure



localized structure

O_3 - cyclic or linear geometry?

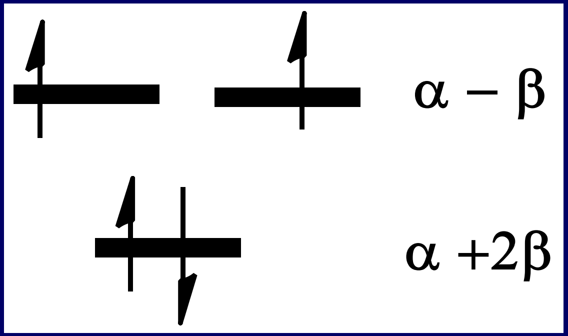
Suppose either geometry has a Π_3^4 conjugation system.

For cyclic form, the three π-MOs,

$$E_1 = \alpha + 2\beta$$

$$E_2 = E_3 = \alpha - \beta$$

$$E_{cyc}^{total} = 2E_1 + 2E_2 = 4\alpha + 2\beta$$



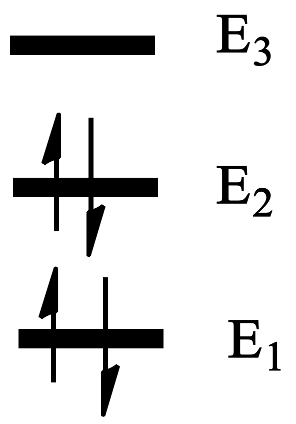
For linear form, the three π-MOs,

$$E_1 = \alpha + \sqrt{2}\beta$$

$$E_2 = \alpha, E_3 = \alpha - \sqrt{2}\beta$$

$$E_{linear}^{total} = 2E_1 + 2E_2 = 4\alpha + 2\sqrt{2}\beta$$

$$E_{linear}^{total} - E_{cyclic}^{total} = 2\beta(\sqrt{2}-1) < 0$$



So the linear form is more stable than the cyclic form.

Note: such a treatment is not too reasonable as there are acturally 6 pi-electrons in the cyclic form!

H_3^+ - cyclic or linear geometry?

- Let’s consider the MOs consisting of three H1s AO by using the HMO theory!
- Similar to the O_3 case, we have the following MO energies for the cyclic and linear forms of the H_3 system.

For the cyclic form, $E_1 = \alpha + 2\beta$ $E_2 = E_3 = \alpha - \beta$

$$E_{cyc}^{total} = 2E_1 = 2\alpha + 4\beta$$

For the linear form, $E_1 = \alpha + \sqrt{2}\beta$ $E_2 = \alpha, E_3 = \alpha - \sqrt{2}\beta$

$$E_{linear}^{total} = 2E_1 = 2\alpha + 2\sqrt{2}\beta$$

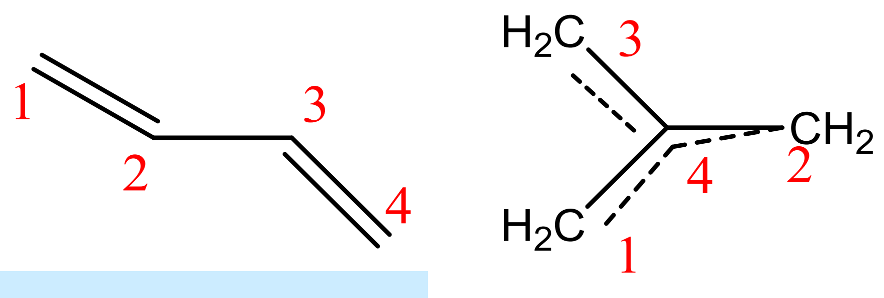
$$E_{linear}^{total} - E_{cyclic}^{total} = 2\beta(2 - \sqrt{2}) > 0$$

So H_3^+ prefers the cyclic form!

How about H_3 and H_3^-?

Which isomer of C_4H_6 is more stable, 1,3-butadiene (BD) or trimethylenemethane(TMM)?

Π_4^4

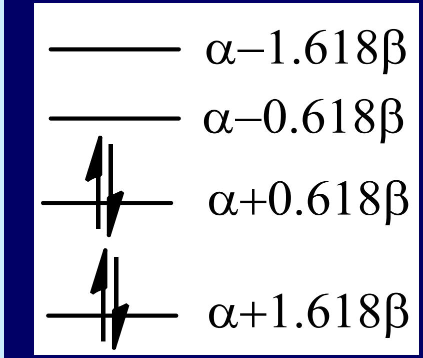


1) For BD (see textbook),

$$E=\alpha+2\beta\cos\theta,\ \text{where}\ \ \theta=\frac{m\pi}{5}\qquad (\mathrm{m}=1,2,3,4)$$

$$\psi_m=\sqrt{\frac{2}{5}}\sum_{k=1}^{4}\sin\frac{km\pi}{5}\phi_k\qquad (\mathrm{m}=1,2,3,.4)$$

$$\Rightarrow \mathrm{E}^{\mathrm{BD}}_{\mathrm{totaltotal}}=2E_1+2E_2=4\alpha+4.472\beta$$



2) For TMM, the seqular determinant is

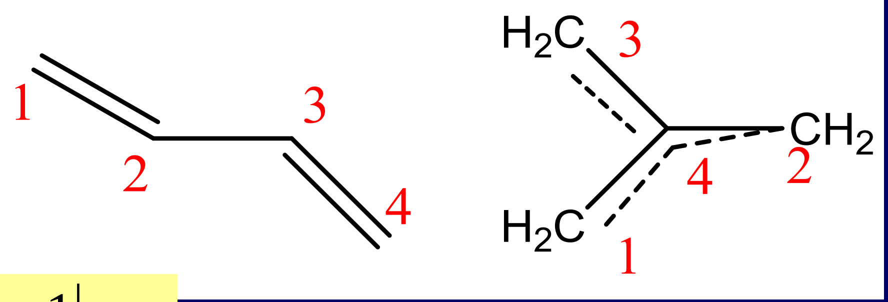
$$\begin{vmatrix}\alpha-E & 0 & 0 & \beta\\ 0 & \alpha-E & 0 & \beta\\ 0 & 0 & \alpha-E & \beta\\ \beta & \beta & \beta & \alpha-E\end{vmatrix}=\begin{vmatrix}x & 0 & 0 & 1\\ 0 & x & 0 & 1\\ 0 & 0 & x & 1\\ 1 & 1 & 1 & x\end{vmatrix}=0$$

$$x=(\alpha-E)/\beta$$

or $E=\alpha-x\beta$

$$\Rightarrow x^2(x^2-3)=0\qquad \Rightarrow x=\pm\sqrt{3},0,0$$

Which isomer of C_4H_6 is more stable, 1,3-butadiene (BD) or trimethylenemethane(TMM)?



Π_4^4

2) For TMM,

$$\begin{vmatrix} \alpha-E & 0 & 0 & \beta \\ 0 & \alpha-E & 0 & \beta \\ 0 & 0 & \alpha-E & \beta \\ \beta & \beta & \beta & \alpha-E \end{vmatrix} = \begin{vmatrix} x & 0 & 0 & 1 \\ 0 & x & 0 & 1 \\ 0 & 0 & x & 1 \\ 1 & 1 & 1 & x \end{vmatrix} = 0$$

$x = (\alpha - E)/\beta$

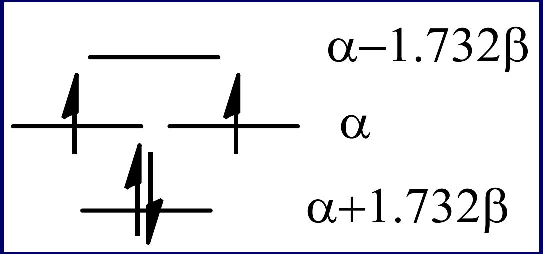
or $E = \alpha - x\beta$

$$\Rightarrow x^2(x^2-3)=0 \quad \Rightarrow x = \pm\sqrt{3},0,0$$

$$\Rightarrow E_1 = \alpha + \sqrt{3}\beta, \mathrm{E}_2 = \mathrm{E}_3 = \alpha, E_4 = \alpha - \sqrt{3}\beta$$

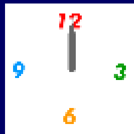
$$\Rightarrow x^2(x^2-3)=0 \quad \Rightarrow x = \pm\sqrt{3},0,0$$

$$\Rightarrow E_1 = \alpha + \sqrt{3}\beta, \mathrm{E}_2 = \mathrm{E}_3 = \alpha, E_4 = \alpha - \sqrt{3}\beta$$



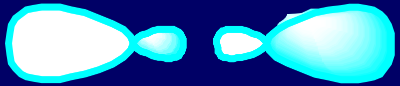
$$E_{total}^{TMM} = 2E_1 + \mathrm{E}_2 + \mathrm{E}_3 = 4\alpha + 2\sqrt{3}\beta = 4\alpha + 3.464\beta$$

$$\Rightarrow E_{total}^{BD}(\Pi_4^4) < E_{total}^{TMM}(\Pi_4^4) \Rightarrow BD \text{ is more stable than TMM!}$$

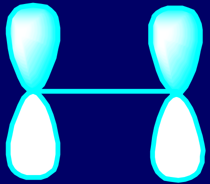


$C_2H_4 + Br_2 \rightarrow CH_2Br\text{-}CH_2Br$ is not an elementary rxn! P.150, 5.29

LUMO (Br_2) $-\sigma_u{}^*$

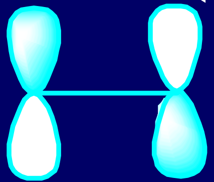


Symmetry incompatible!
Overlap=0



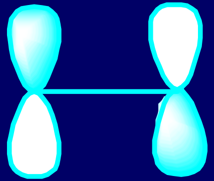
HOMO(C_2H_4) $-\pi_u$

HOMO(Br_2) $-\pi_g{}^*$



e

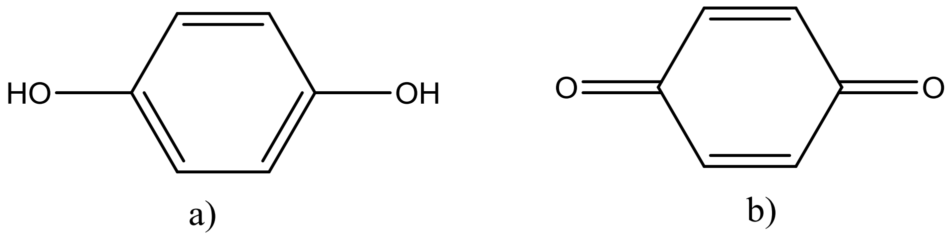
Symmetry compatible! Wrong direction of electron transfer!



LUMO(C_2H_4) $-\pi_g{}^*$

- LUMO (Br_2) and HOMO(C_2H_4) are symmetry-incompatible!
- The interaction between HOMO (Br_2) and LUMO(C_2H_4), though being symmetry-compatible, leads to electron transfer incompatible with the relative electronegativity of the reactants!
- The reaction can not be an elementary rxn.

p.150, 5.32



Key points:

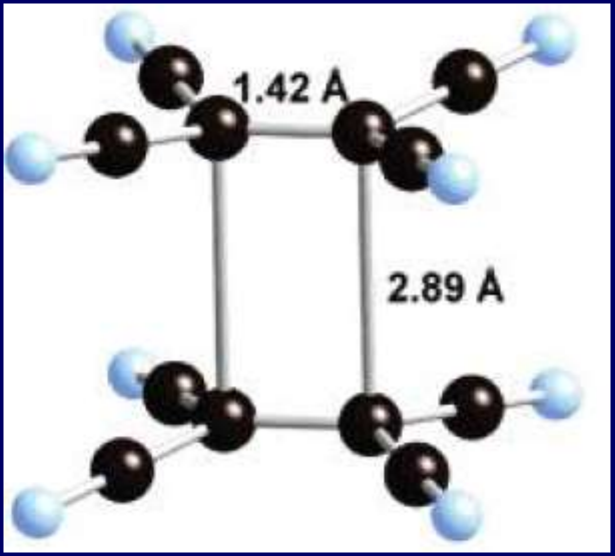
1. **Frontier molecular orbital theory.**
2. **HOMO of hydroquinone interacts with LUMO of quinone!**

- Both molecules have similar 8-center π-conjugations, i.e. 8c-10e in molecule a and 8c-8e in molecule b.
- Thus, the LUMO of molecule b resembles the HOMO of molecule a, i.e., both are symmetry-compatible!
- Hence, the LUMO of molecule b can interact effectively with the HOMO of molecule a, leading to electron-transfer from a to b.

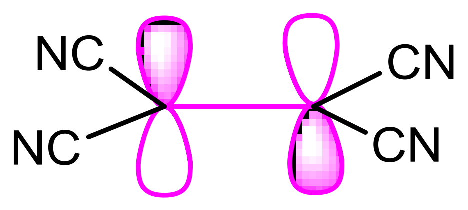
(You may figure out the diagrams of these MOs with use of the HMO theory)

Let’s consider a simpler case in the next page!

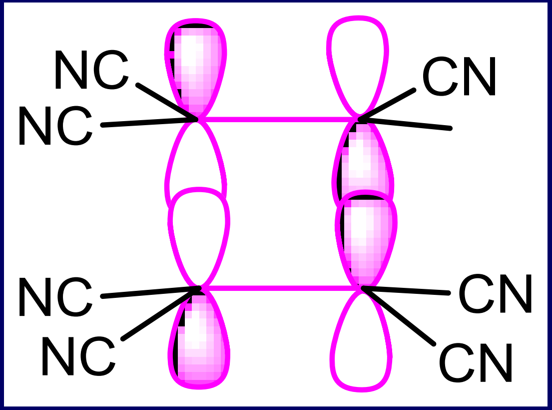
The reaction of [Et4N]I and tetracyanoethylene (TCNE) forms $[Et4N]_2[TCNE]_2$, which possesses $[TCNE]_2^{2-}$ with a 2.827(3) Å intradimer CC bond distance (CrystEngComm, 2001, 47,1). Plz analyze the intradimer bonding.



- The LUMO of neutral TCNE is the π^* MO of the C=C moiety.
- This MO becomes the SOMO of TCNE monoanion!

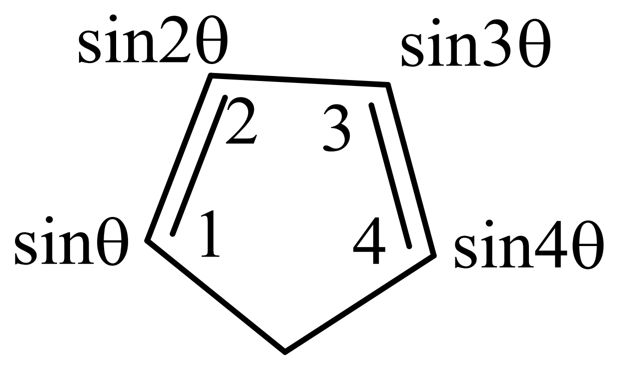


- So the SOMOs of two $[TCNE]^-$ are symmetry-compatible and can effectively interact with each other!



Please derive the π-MOs of cyclopentadiene and explain why the reaction of two cyclopentadienes gives rise to [4+2] cycloaddition product, but not the [2+2] or [4+4] cycloaddition product.

Answer: 1) The π-MOs of cyclopentadiene are similar to those of 1,3-butadiene; the MO coefficients are given in the diagram. Thus



The boundary condition is

$$sin 5\theta = 0 \Rightarrow \theta = m\pi / 5 \quad (\mathrm{m} = 1,2,3,4)$$

The four π-MOs are

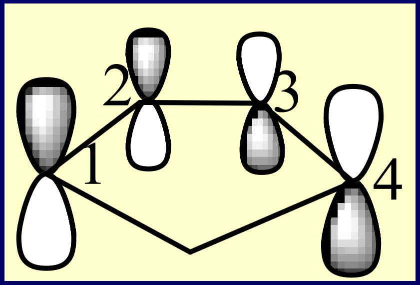
$$m = 1, \psi_1 = (1/2)\sum_{k=1}^{4} \sin(k\pi/5)\phi_k, E_1 = \alpha + 1.618\beta$$

$$m = 2, \psi_2 = (1/2)\sum_{k=1}^{4} \sin(2k\pi/5)\phi_k, E_2 = \alpha + 0.618\beta$$ HOMO

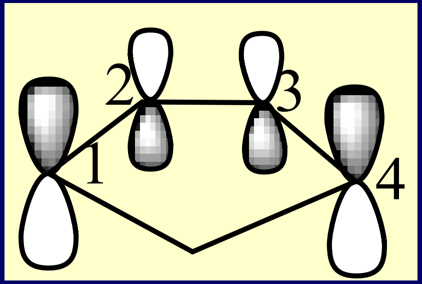
$$m = 3, \psi_3 = (1/2)\sum_{k=1}^{4} \sin(3k\pi/5)\phi_k, E_3 = \alpha - 0.618\beta$$ LUMO

$$m = 4, \psi_4 = (1/2)\sum_{k=1}^{4} \sin(4k\pi/5)\phi_k, E_1 = \alpha - 1.618\beta$$

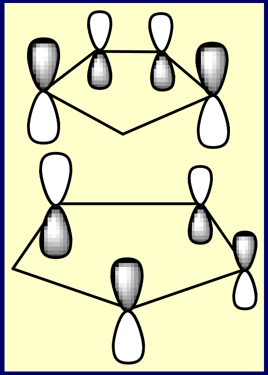
2)



HOMO



LUMO



Symmetry-allowed [4+2]

A) For [4+2] cycloaddition of two cyclopentadienes, the 1,4-site of molecule **a** interacts with the 1,2-site of molecule b. The 1,4-site of HOMO (a) is compatible with the 1,2-site of LUMO(b); meanwhile, the 1,4-site of LUMO(a) is compatible with the 1,2-site of HOMO(b). So the [4+2] cycloaddition is symmetry-allowed.

B) For [4+4] cycloaddition, the 1,4-site of molecule **a** should interact with the 1,4-site of molecule b. However, the 1,4-site of HOMO (a) is not compatible with the 1,4-site of LUMO(b); likewise, the 1,4-site of LUMO(a) is not compatible with the 1,4-site of HOMO(b). So the [4+4] cycloaddition is symmetry-forbidden. Similarly, the [2+2] cycloaddition is symmetry-forbidden and could not occur!

More exercises of chapter 5-9 can be found at:

http://ctc.xmu.edu.cn/jiegou/wlkch/Chapter5/exercise.htm

http://ctc.xmu.edu.cn/jiegou/wlkch/Chapter6/exercise.htm

http://ctc.xmu.edu.cn/jiegou/wlkch/Chapter7/exercise.htm

http://ctc.xmu.edu.cn/jiegou/wlkch/Chapter8/exercise.htm

http://ctc.xmu.edu.cn/jiegou/wlkch/Chapter9/exercise.htm

止于至善！

这不只是做事的态度，

还是成功者的必要素质，

更是科学精神！

----谨以此校训与各位学生共勉！