

# شیمی فیزیک آلی

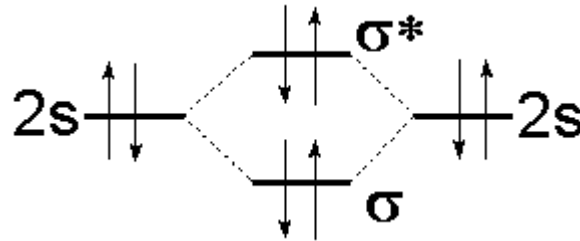
(مبانی مکانیسم واکنشهای آلی)

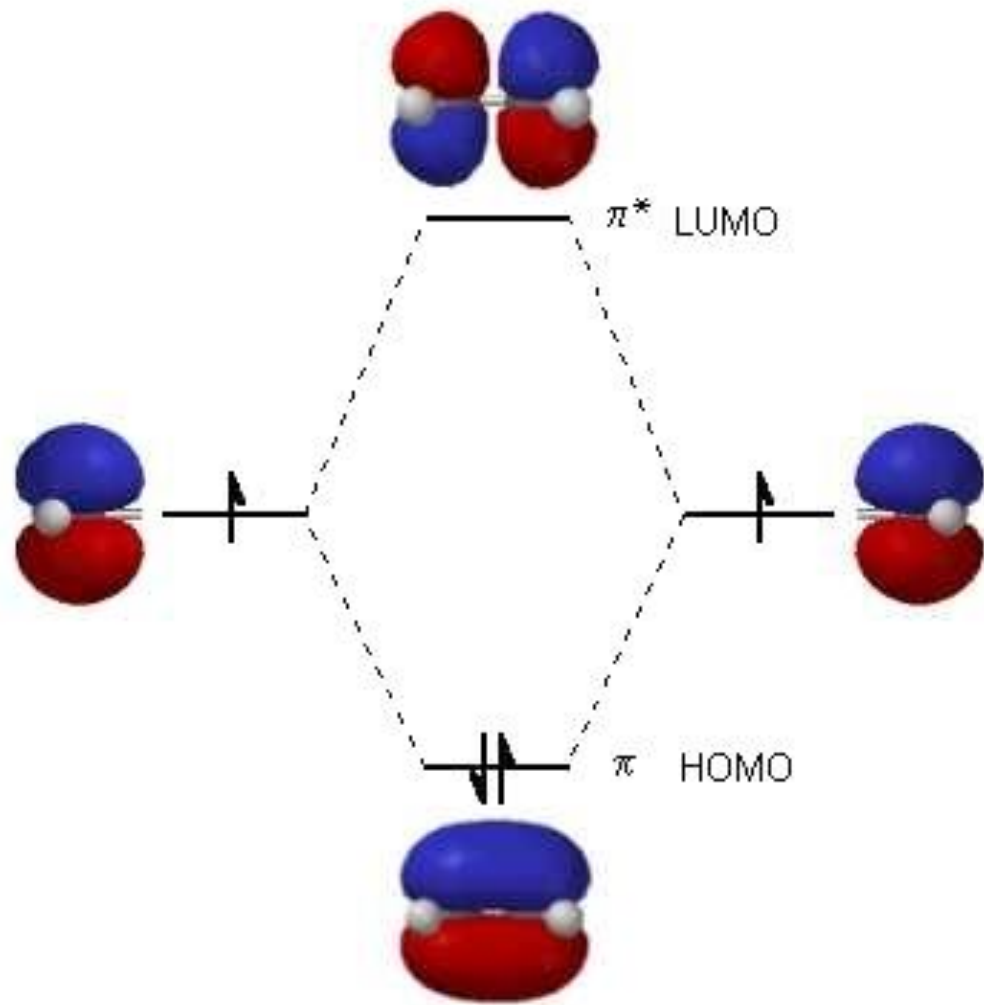
## هدفهای کلی :

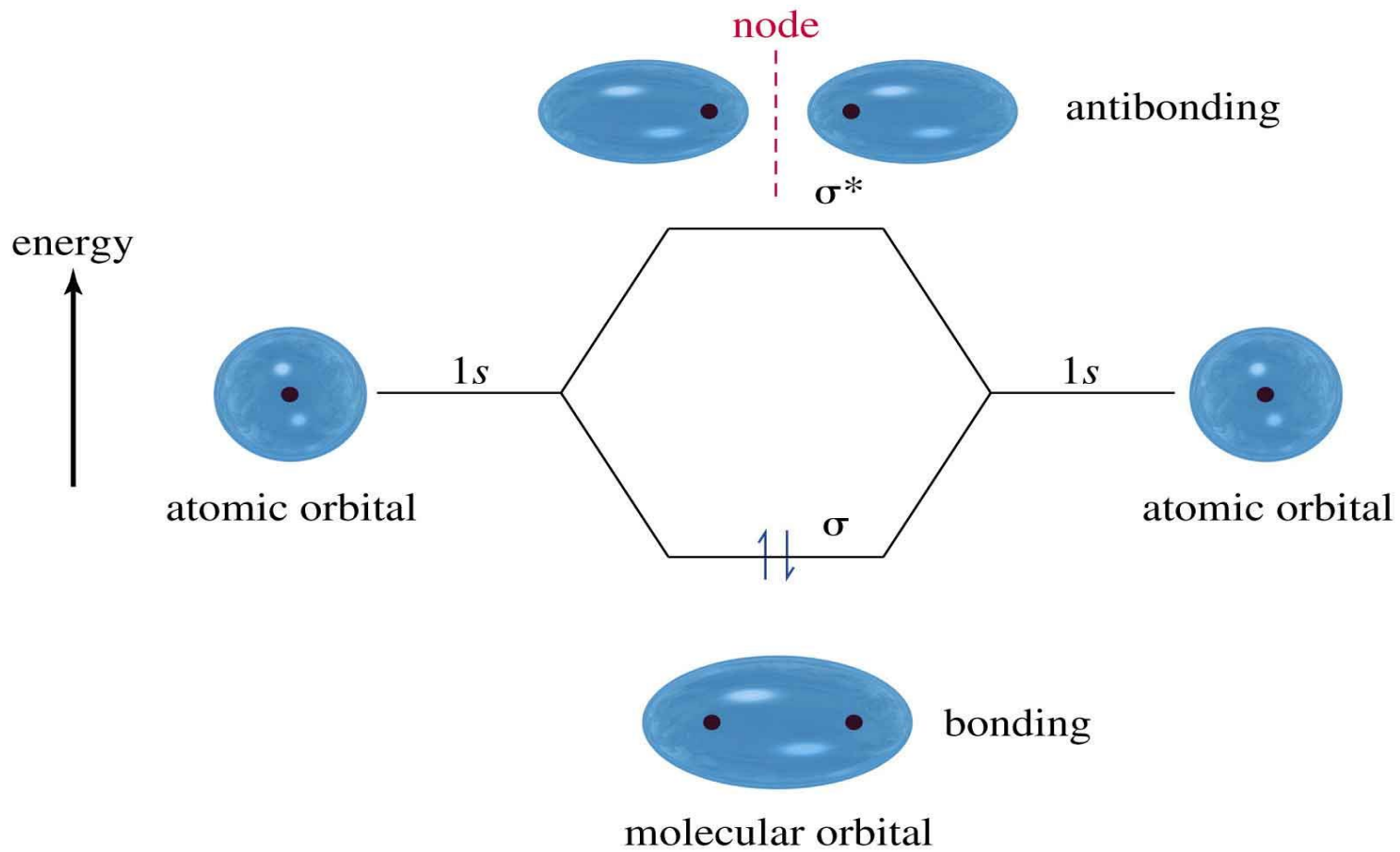
در این مبحث دانشجویان با توجه به مطالب شیمی کوانتوم ، مبحث اوربیتال مولکولی را منطبق با معادلات بکار رفته در شیمی کوانتوم ( معادله شرودینگر) فرا گرفته و برای مولکولهای بزرگتر انرژی سیستم را محاسبه می کنند .

# نظريه اوربیتال مولکولي:

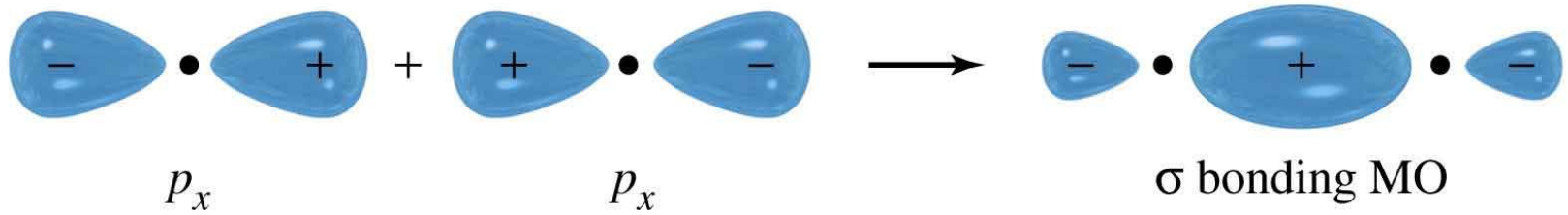
از همپوشانی اوربیتالهای اتمی، اوربیتالهای مولکولی به وجود می آید این اوربیتالها وضعیت الکترونها را در يك محیط مولکولي که تحت تاثیر بیش از يك هسته هستند، توصیف می کنند.



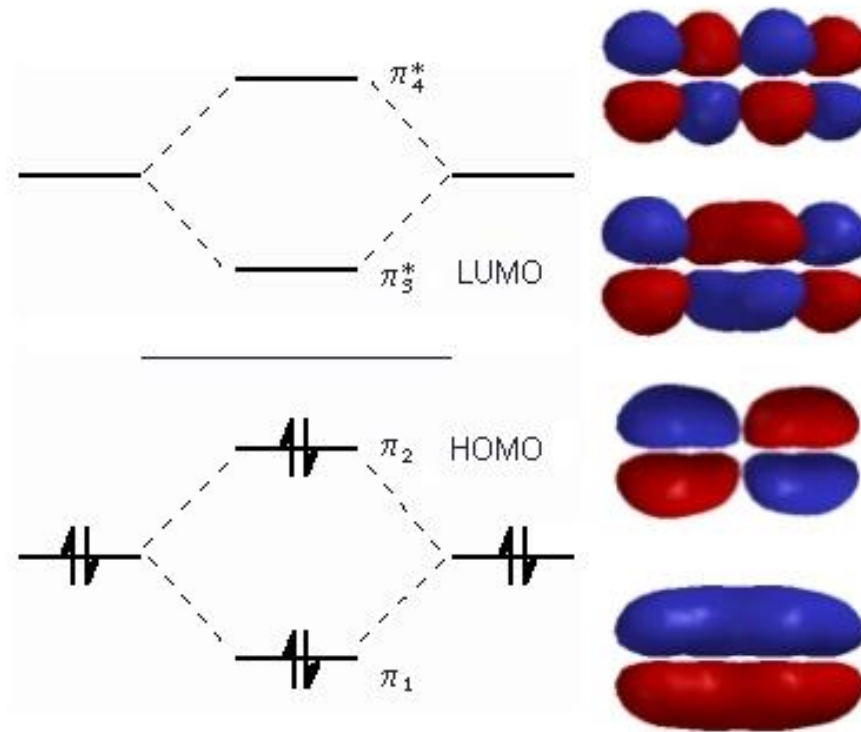




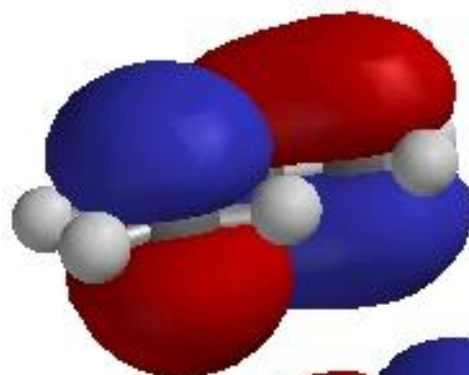
# همپوشانی اوربیتال های p



# ترازهای انرژی بوتادی ان :

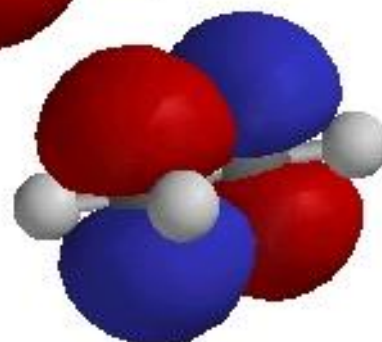


1,3-butadiene HOMO



Bonding interaction

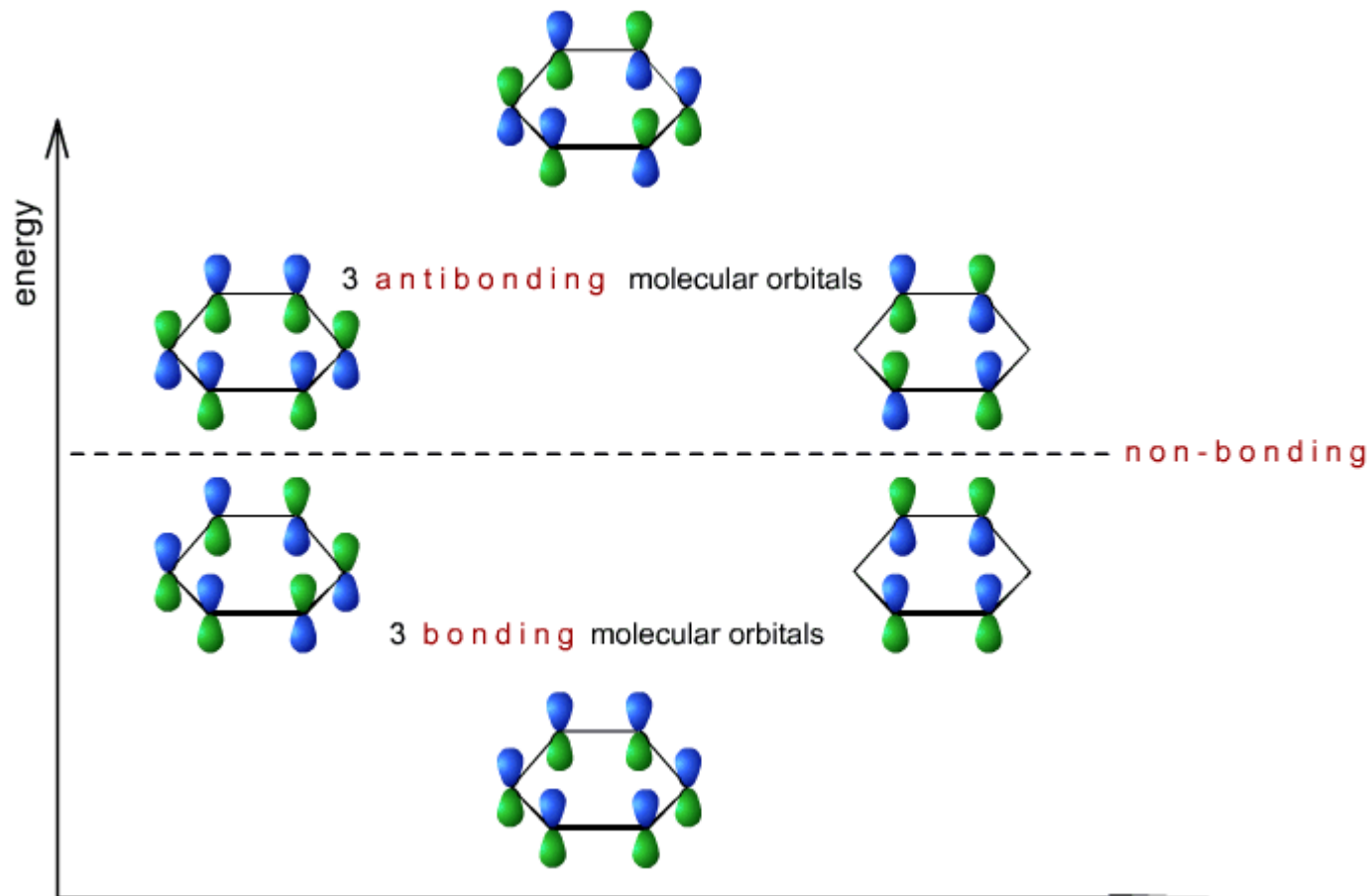
Bonding interaction



ethene LUMO



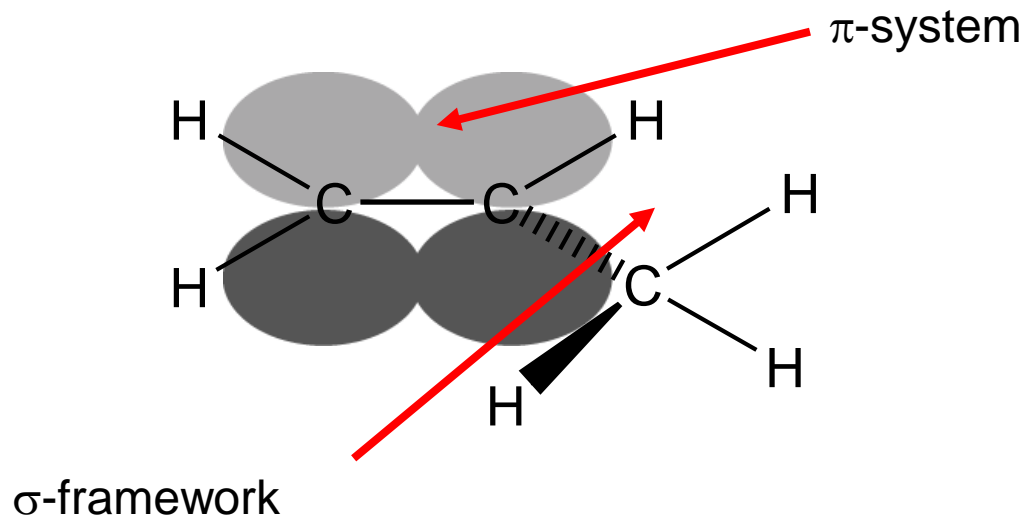
# سیستم بنزن:



# نظریه اربیتال مولکولی هوکل :

## Hückel Molecular Orbital Theory

نظریه اربیتال مولکولی هوکل (HMO) در سال ۱۹۳۱ عرضه شد و کاربرد آن به همراه نظریه پیوند ظرفیتی عامل اصلی استفاده از نظریه کوانتوم به عنوان ابزار در مطالعه شیمی آلی بوده است.



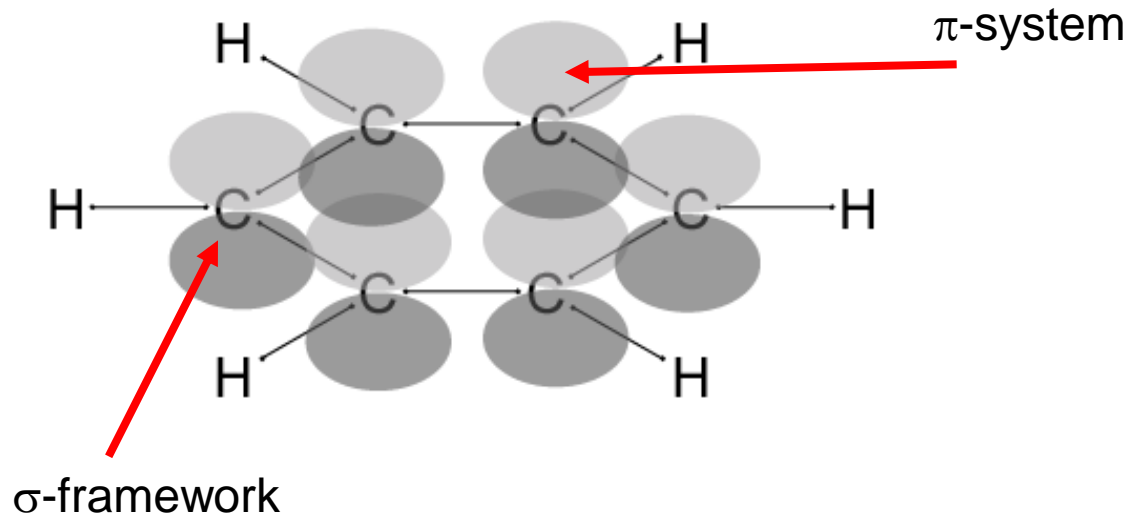
Erich Hückel (1896-1980)

# Benzene

سیستم بنزن شامل ۶ الکترون غیر مسقر

این شش الکترون تشکیل ۳ پیوند

$\pi$



معادلات عام براي سيستم هاي ۲ اتمي :

$$H_{ij} = \int \Phi_i H \Phi_j d\tau$$

$$S_{ij} = \int \Phi_i \Phi_j d\tau$$

$$\sum_J a_j (H_{ij} - ES_{ij}) = 0$$

$$ij = 1, 2, \dots, n$$

## دترمینان عام :

$$\left| H_{ij} - E_{ij} \right| = 0$$

$$\begin{array}{cccc} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots\dots\dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots\dots\dots & H_{2n} - ES_{2n} \end{array}$$

$$\left| H_{ij} - E_{ij} \right| = \begin{array}{cccc} \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots\dots\dots & H_{nn} - ES_{nn} \end{array} = 0$$

## روش هوکل :

به جاي حل دترمینان عام و انتگرالهاي  $H_{ij}, S_{ij}$  انتگرالها به صورت پارامتر در نظر گرفته مي شوند.

۱.

$$H_{ij} = \alpha$$

و اگر نباشند

۲. اگر  $H_{ij} = 0$  بهم متصل باشند

$$H_{ij} = \beta$$

$i, j$

و براي

۳. براي

$$S_{ii} = 0, i \neq j$$

$$S_{ii} = 1, i = j$$

۴. پیوند هاي سیگما متمرکز بوده , مي توان آنها را به عنوان يك چهار چوب براي الكترونهاي پي در نظر گرفت

دترمینان عام برای سیستم های ۲ اتمی:

$$\begin{pmatrix} \alpha - \varepsilon & \beta \\ \beta & \alpha - \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

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

محاسبه انرژی برای سیستم های ۲ اتمی:

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

$$(\alpha - \varepsilon)^2 - \beta^2 = 0$$

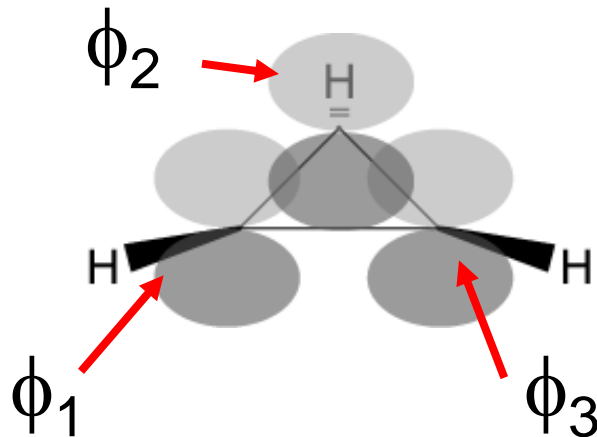
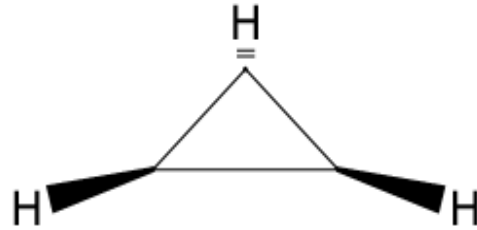
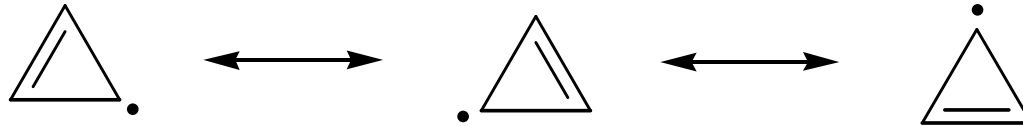
$$(\alpha - \varepsilon - \beta)(\alpha - \varepsilon + \beta) = 0$$

$$\varepsilon = \alpha \pm \beta$$

This is the energy of an isolated  $\pi$ -bond



Cyclopropenyl radical –  $C_3H_3$  سیسٹم رادیکال سیکلوپروپیل:



$$\hat{H}(c_1\phi_1 + c_2\phi_2 + c_3\phi_3) = \epsilon(c_1\phi_1 + c_2\phi_2 + c_3\phi_3)$$

Left multiplying by  $\phi_1$  and integrating gives us

$$c_1 \int \phi_1 \hat{H} \phi_1 d\tau + c_2 \int \phi_1 \hat{H} \phi_2 d\tau + c_3 \int \phi_1 \hat{H} \phi_3 d\tau = \epsilon \left( c_1 \int \phi_1 \phi_1 d\tau + c_2 \int \phi_1 \phi_2 d\tau + c_3 \int \phi_1 \phi_3 d\tau \right)$$

assuming no overlap ( $\int \phi_1 \phi_2 d\tau = 0$ ) and normalization ( $\int \phi_1 \phi_1 d\tau = 1$ ), this may be simplified to

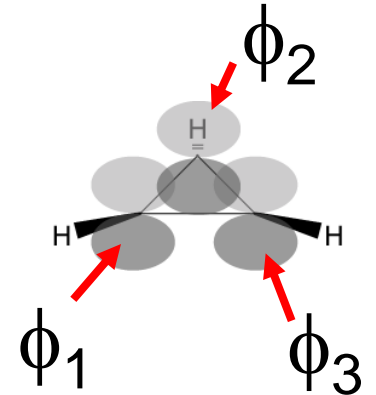
$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon.$$

We now have three equations

$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon$$

$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon$$

$$c_1\beta + c_2\beta + c_3\alpha = c_3\epsilon$$



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

Dividing the matrix by  $\beta$  and substituting  $x = (\alpha - \epsilon)/\beta$  we get

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

$$x(x^2 - 1) - 1(x - 1) + 1(1 - x) = 0$$

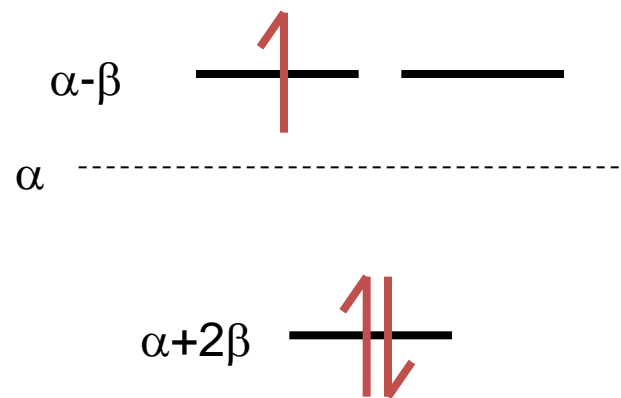
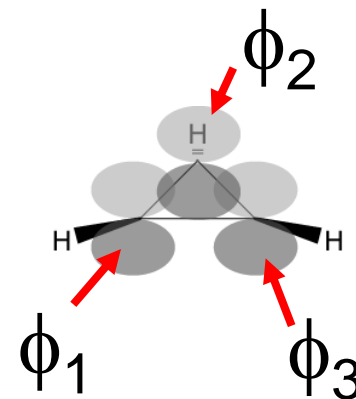
$$x^3 - 3x + 2 = 0$$

$$(x - 1)(x - 1)(x + 2) = 0$$

$$x = 1, 1, -2$$

$$(\alpha - \epsilon)/\beta = 1, 1, -2$$

$$\epsilon = \alpha + 2\beta, \alpha - \beta, \alpha - \beta$$



We have three equations

$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon \quad (1)$$

$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon \quad (2)$$

$$c_1\beta + c_2\beta + c_3\alpha = c_3\epsilon \quad (3)$$

(1)-(2) and (1)-(3)

$$(\alpha - \epsilon - \beta)c_1 + (\beta - \alpha + \epsilon)c_2 = 0$$

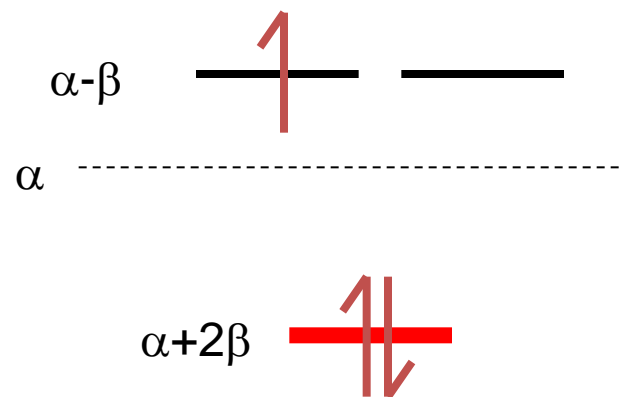
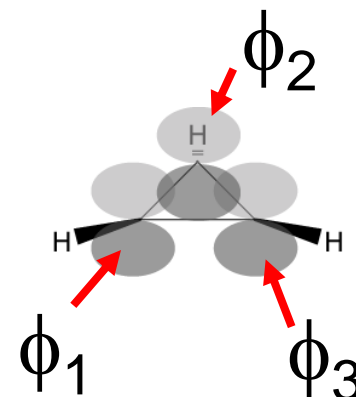
$$(\alpha - \epsilon - \beta)c_1 + (\beta - \alpha + \epsilon)c_3 = 0$$

substitute  $\epsilon = \alpha + 2\beta$

$$-3\beta c_1 + 3\beta c_2 = 0$$

$$-3\beta c_1 + 3\beta c_3 = 0$$

$$c_1 = c_2 = c_3$$

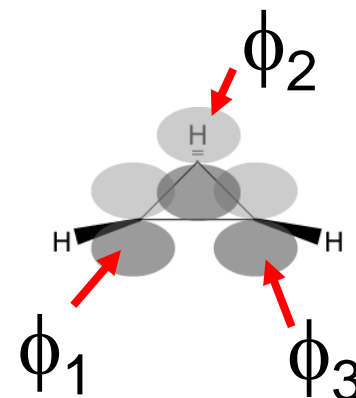


We have three equations

$$c_1\alpha + c_2\beta + c_3\beta = c_1\epsilon \quad (1)$$

$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon \quad (2)$$

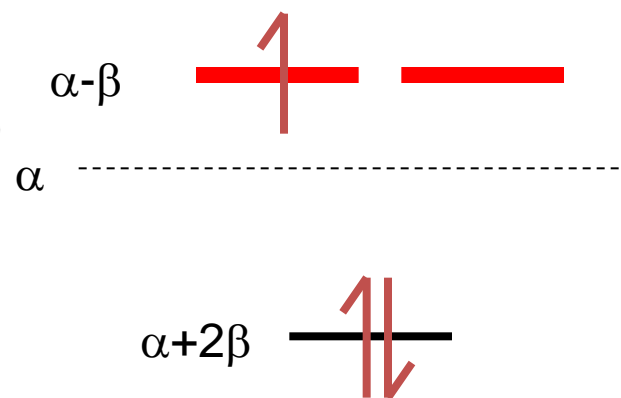
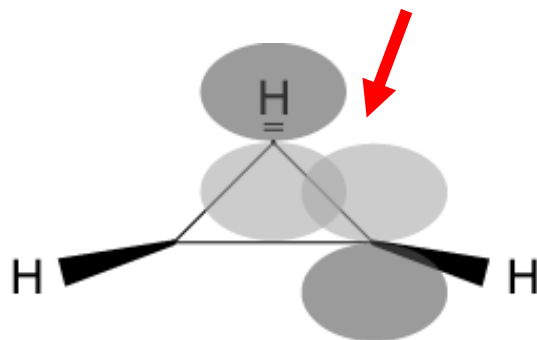
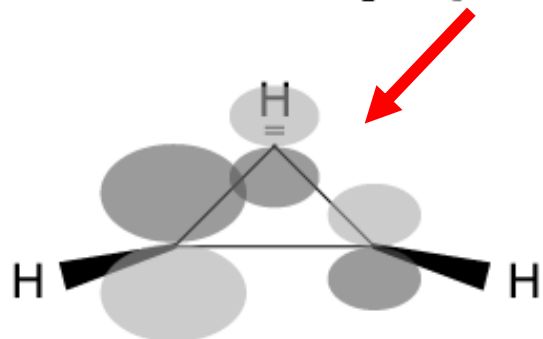
$$c_1\beta + c_2\beta + c_3\alpha = c_3\epsilon \quad (3)$$



Substitute  $\epsilon = \alpha - \beta$  into (1)

$$c_2\beta + c_3\beta = -c_1\beta$$

If one solution has  $c_2 = c_3 = -\frac{1}{2}c_1$ . The other has  $c_1 = 0, c_2 = -c_3$ .



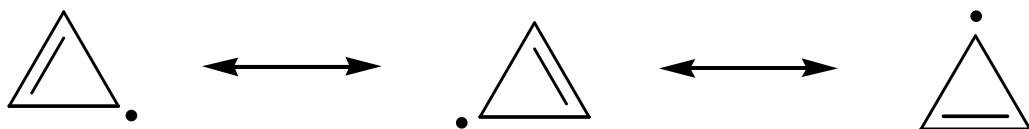
$$E_{\pi} = 2 \times (\alpha + 2\beta) + 1 \times (\alpha - \beta)$$

$$= 3\alpha + 3\beta$$

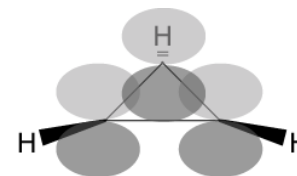
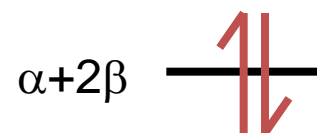
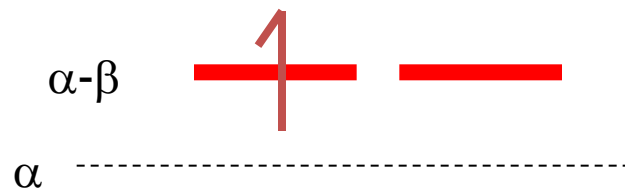
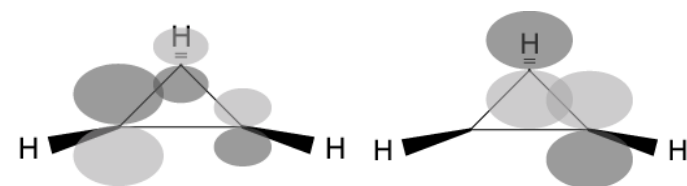
The energy of a normal double bond is  $2\alpha + 2\beta$  (2 electrons in  $\alpha + \beta$ )

The energy of a lone p-orbital is  $\alpha$

Therefore, the energy of each resonance form is  $3\alpha + 2\beta$



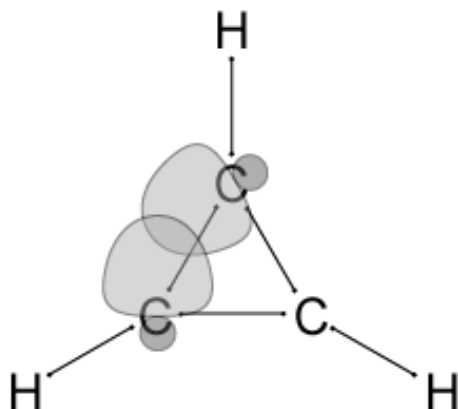
Cyclopropenyl is resonance stabilized! (by  $\beta$ )



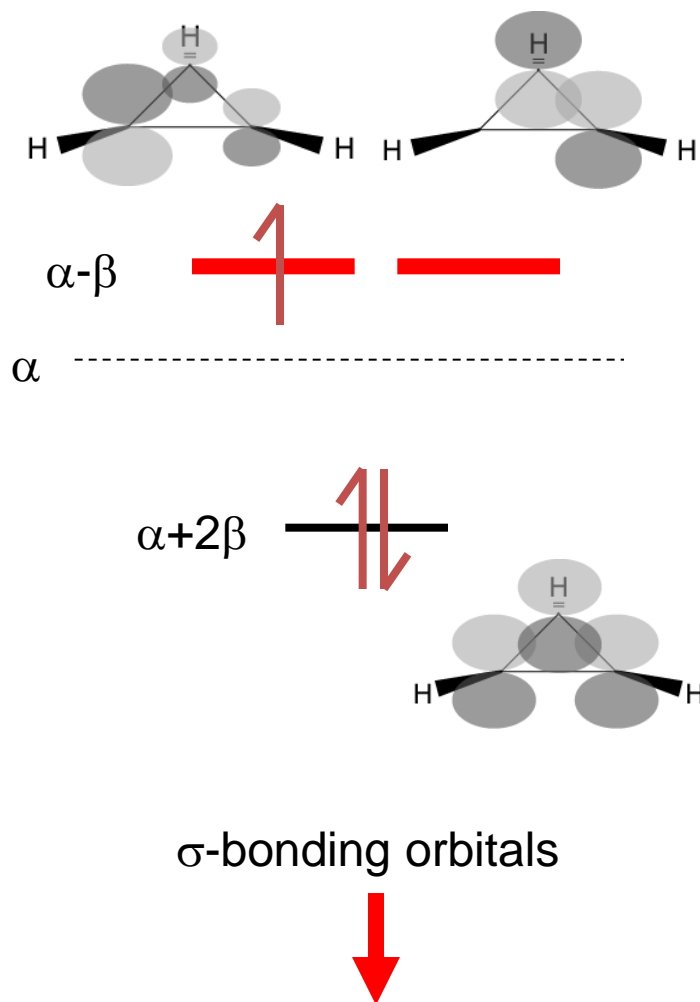
*i.e.* its resonance energy is  $\beta$

While the cyclopropenyl molecule is stable, its  $\sigma$ -bonds are not as strong as they would be in, say, benzene. This is because the overlap between the  $sp^2$  hybrids is reduced due to the strained geometry of the radical.

This is called  $\sigma$ -strain



This should be taken into account when comparing the stabilities of various isomers



The lowest energy transition between the  $\pi$ -orbitals in this system has an energy of  $-3\beta$ .

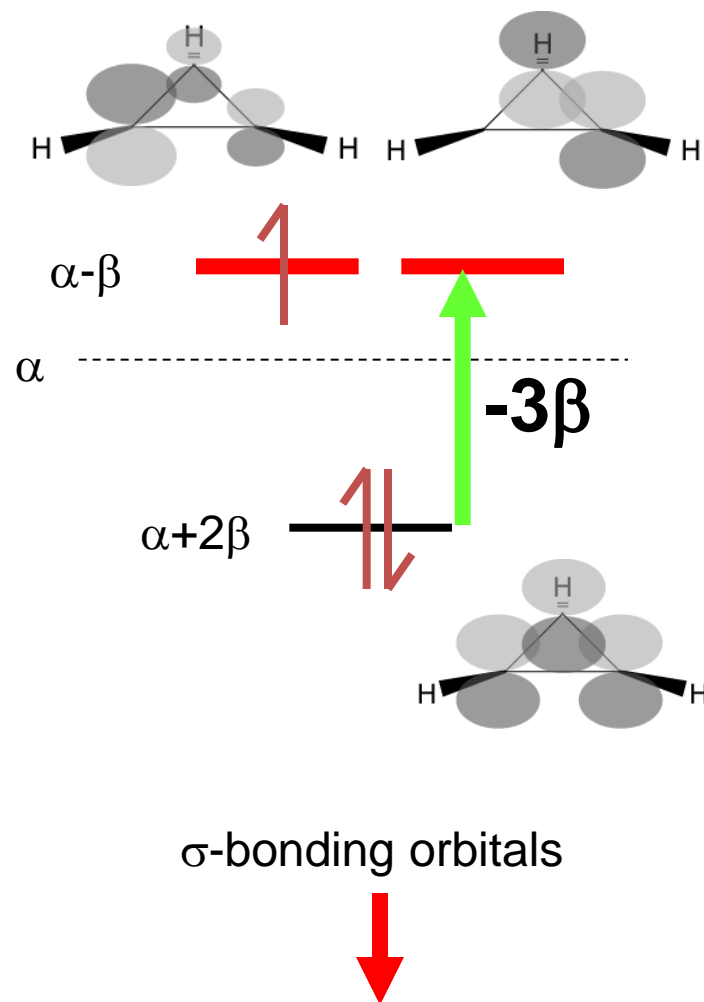
This transition is well into the UV

The cation is stable and symmetric ( $2e^-$ ) and has  $2\beta$  of resonance stability (prove yourself)

(not examinable)

A note on Jahn-Teller distortion:

The singly occupied MO as drawn on the right may be lowered in energy by decreasing the distance between carbons 2 and 3 while increasing the other two bond lengths. This is energetically favourable and will happen. This is known as Jahn-Teller distortion.





# Cyclobutadiene – $C_4H_4$

سیستم بوتادی ان:

$$\hat{H}(c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4) = \epsilon(c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4)$$

Left multiplying by  $\phi_1$  and integrating gives us

$$\begin{aligned} c_1 \int \phi_1 \hat{H} \phi_1 d\tau + c_2 \int \phi_1 \hat{H} \phi_2 d\tau + c_3 \int \phi_1 \hat{H} \phi_3 d\tau + c_4 \int \phi_1 \hat{H} \phi_4 d\tau \\ = \epsilon \left( c_1 \int \phi_1 \phi_1 d\tau + c_2 \int \phi_1 \phi_2 d\tau + c_3 \int \phi_1 \phi_3 d\tau + c_4 \int \phi_1 \phi_4 d\tau \right) \end{aligned}$$

assuming no overlap ( $\int \phi_1 \phi_2 d\tau = 0$ ) and normalization ( $\int \phi_1 \phi_1 d\tau = 1$ ), this may be simplified to

$$c_1\alpha + c_2\beta + c_4\beta = c_1\epsilon.$$

There is no bonding between carbons 1 and 3!

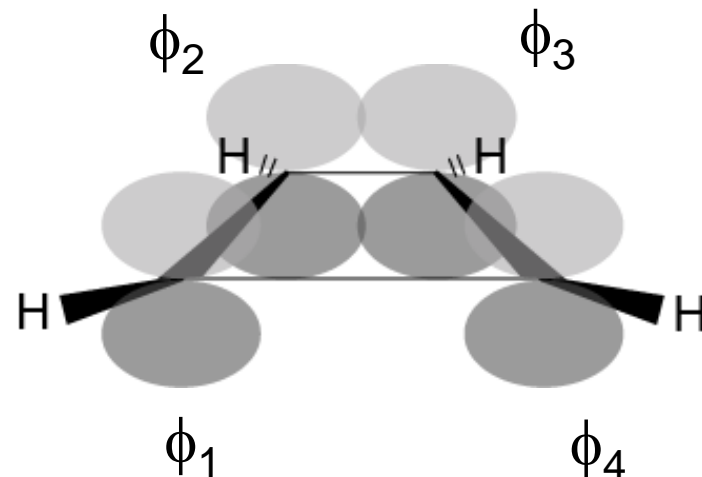
We now have four equations

$$c_1\alpha + c_2\beta + c_4\beta = c_1\epsilon$$

$$c_1\beta + c_2\alpha + c_3\beta = c_2\epsilon$$

$$c_2\beta + c_3\alpha + c_4\beta = c_3\epsilon$$

$$c_1\beta + c_3\beta + c_4\alpha = c_4\epsilon$$



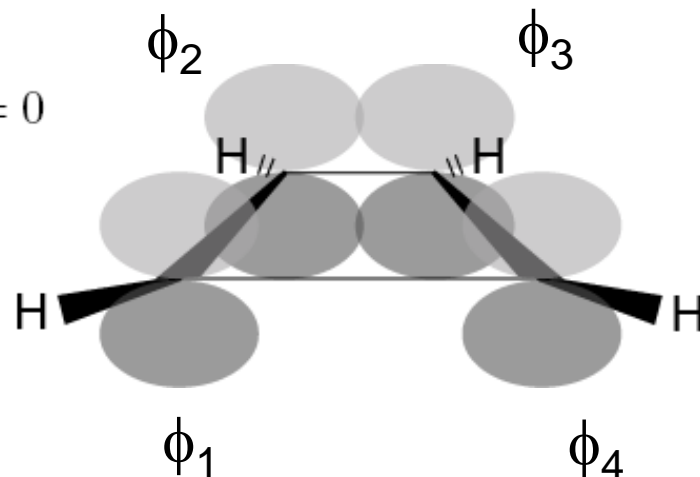
Dividing the matrix by  $\beta$  and substituting  $x = (\alpha - \epsilon)/\beta$  we get

$$\begin{array}{l} \text{1 off diagonal where there} \\ \text{is bonding interaction} \end{array} \begin{array}{c} \begin{array}{c} \text{x on diagonal} \\ \text{1 off diagonal where there} \\ \text{is bonding interaction} \end{array} \end{array} \begin{array}{c} \left| \begin{array}{cccc} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{array} \right| = 0 \end{array} \begin{array}{l} \leftarrow 1 \\ \leftarrow 0 \end{array} \begin{array}{l} \text{0 off diagonal where there is no} \\ \text{Bonding interaction; i.e. 1 \& 3, 2\&4} \end{array}$$

$$x(x(x^2 - 1) - x) - ((x^2 - 1) + 1) - (1 - x(-x) - 1) = 0$$

$$x = -2, 0, 0, +2$$

$$\epsilon = \alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$$



$$E_{\pi} = 2 \times (\alpha + 2\beta) + 2 \times \alpha$$

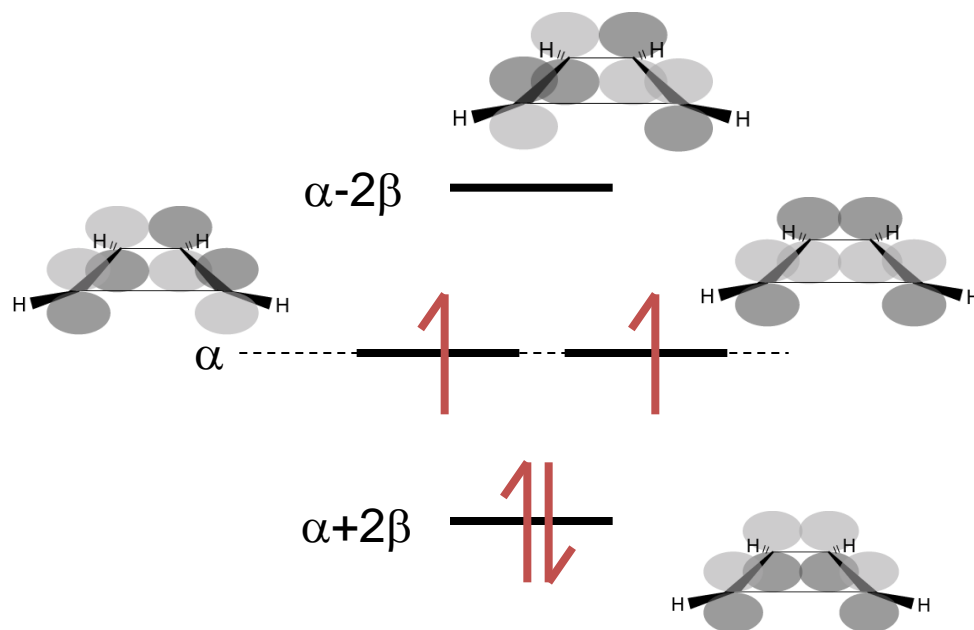
$$= 4\alpha + 4\beta$$

The energy of a normal double bond is  $2\alpha + 2\beta$  (2 electrons in  $\alpha + \beta$ )

Therefore, the energy of each resonance form is  $4\alpha + 4\beta$

Cyclobutadiene is not resonance stabilized! *i.e.* its *resonance energy* is 0

$4e^{-}$  system is *anti-aromatic* and  $\sigma$ -strained

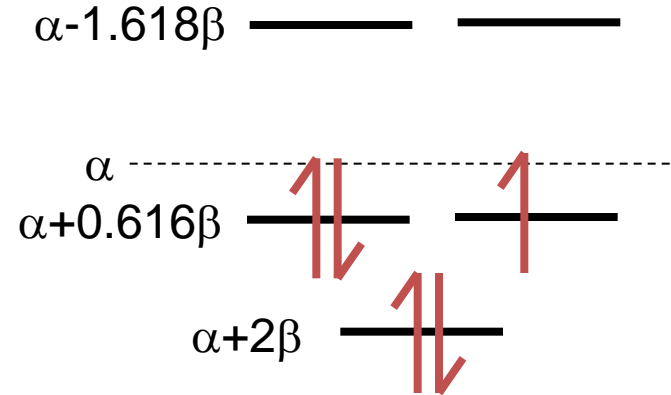


$\sigma$ -bonding orbitals



Cyclopentadienyl radical –  $C_5H_5$ : سیستم رادیکال سیکلو پنتا دی ان

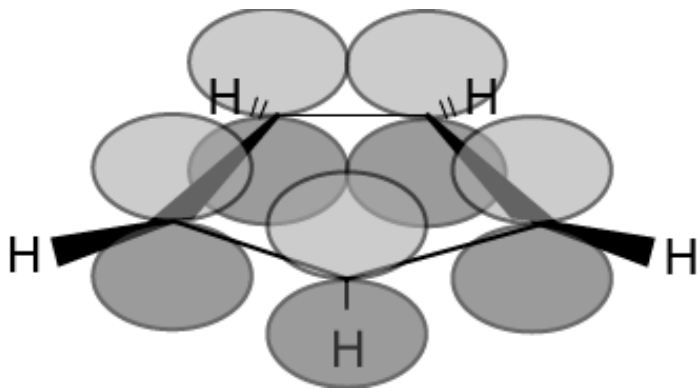
$$\begin{vmatrix} x & 1 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 1 & x \end{vmatrix} = 0$$



Lowest orbital has no node

Second lowest has 1 node

Highest has two nodes



This radical suffers from Jahn-Teller distortion...  
not a true pentagon

*Cyclopentadienyl anion – C<sub>5</sub>H<sub>5</sub><sup>-</sup>*

سیستم آنیون سیکلو پنتادی ان :

This system readily accepts an extra electron

As it does so it can no longer lower its energy by distortion

This anion is perfectly pentagonal

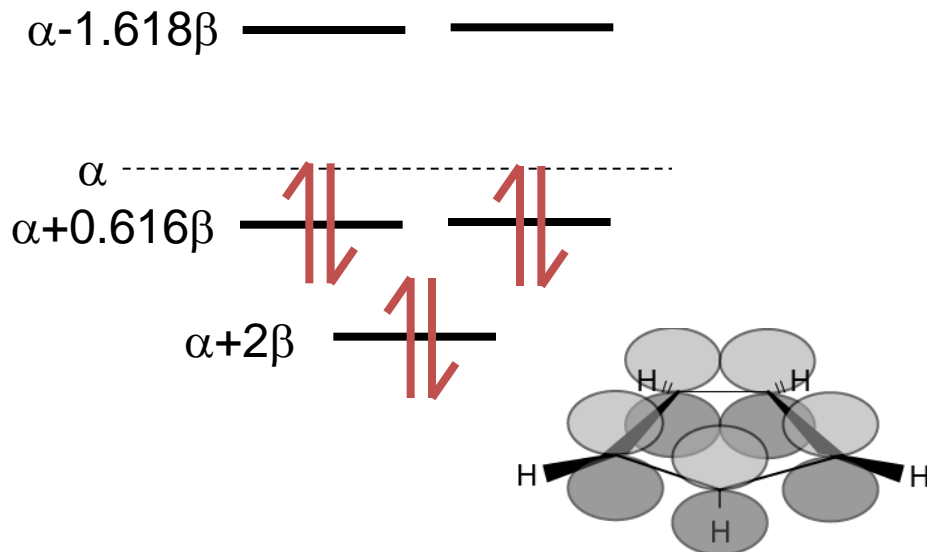
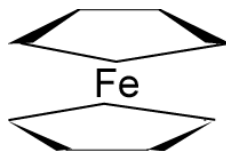
It is resonance stabilized!

$E_{\pi} = 6\alpha + 5.232\beta$  (Compare to energy of two double bonds and a p-orbital :  $6\alpha + 4\beta$ )

6e<sup>-</sup> system nicely aromatic

Will ligate to transition metal ions to make metallocenes e.g.

Ferrocene



cp<sup>-</sup> is a closed shell singlet

cp<sup>+</sup> is also stable as a triplet

# Benzene – $C_6H_6$

بنزن:

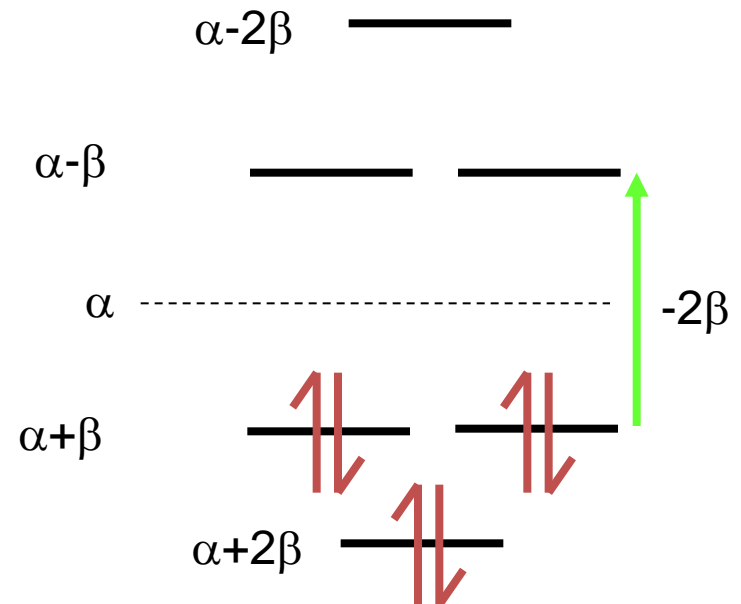
Benzene is the archetypal aromatic molecule

It has no  $\sigma$ -strain – it is a perfect hexagon

You may wish to compute its stability compared to the mythical beast – 1,3,5-hexatriene (it's a quiz question!)

Its energy levels and orbitals are readily computed by a program on my website.

Benzene cation is Jahn-Teller distorted and is not a perfect hexagon



Benzene absorbs in UV at 260nm

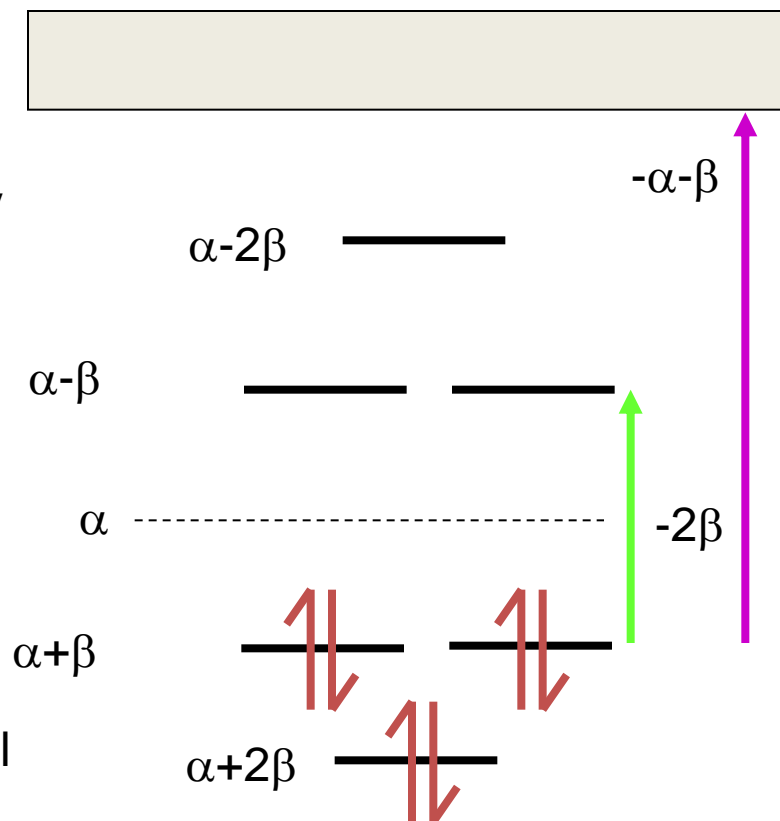
This corresponds to 460 kJ/mol

We can parametrize the  $\beta$  in Hückel theory by setting  $-2\beta$  equal to this energy!

Benzene's ionization potential is 730 kJ/mol

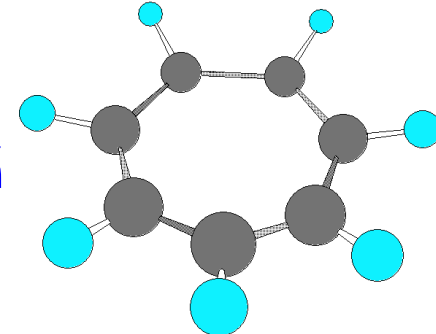
We can parametrize the  $\alpha$  integral by setting this to be  $-\alpha-\beta$ .

Doing this....  $\alpha = -500$  kJ/mol,  $\beta = -230$  kJ/mol



## Tropyl – $C_7H_7$

تروپولیوم:



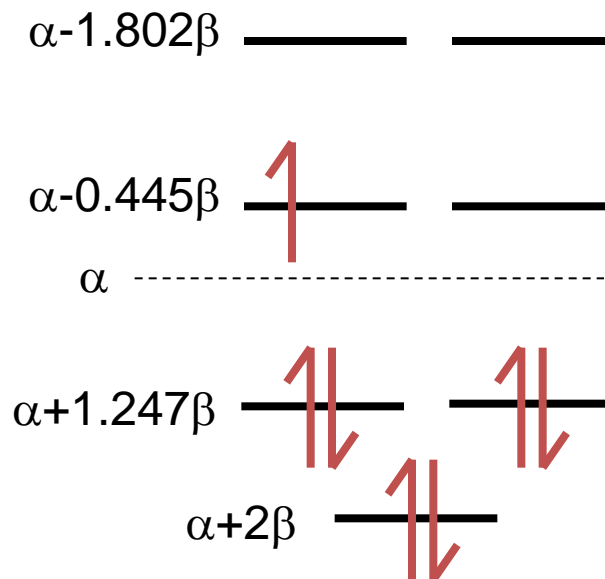
Tropyl radical is a Jahn-Teller distorted heptagon

It is easily ionized – its experimental IP is  $48000\text{cm}^{-1}$  or  $570\text{ kJ/mol}$

Hückel theory predicts  $\alpha - 0.445\beta$  or  $397\text{ kJ/mol}$ ... but there is  $\sigma$ -strain &c.

Tropyl anions and cations are both perfect heptagons

Tropyl cation is very stable...  $6e^-$  system!





# Cyclooctatetraene – $C_8H_8$ : سيكلو اکتاتتران

$$E_{\pi} = 8\alpha + 9.656\beta$$

But planar structure is highly strained.

Ring puckers to relieve bond strain at the expense of slight delocalization energy

The molecule is not flat – it is not aromatic

