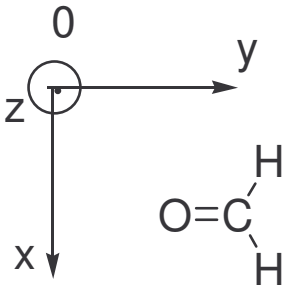
Plan du cours

Le formaldéhyde en Hückel simple

Systèmes conjugués en Hückel simple

Applications des diagrammes orbitalaires

Le formaldéhyde $CH_2=O$



Déterminant séculaire

$$\begin{array}{c|cc} & 2p_{zO} & 2p_{zC} \\ 2p_{zO} & \alpha_O - E & \beta_{CO} \\ 2p_{zC} & \beta_{CO} & \alpha - E \end{array}$$

$$\alpha = \langle \varphi_1 | H | \varphi_1 \rangle$$

paramétré en fonction de α pour les hétéroatomes

$$\beta = \langle \varphi_1 | H | \varphi_2 \rangle$$

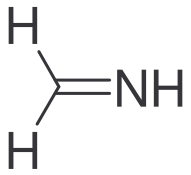
- β = 0 si 2 atomes non liés directement
- paramétré en fonction de $\beta_{C\text{-}C}$ pour les liaisons C=X

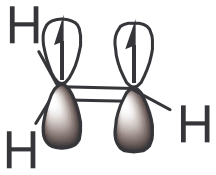
Paramètres Hückel

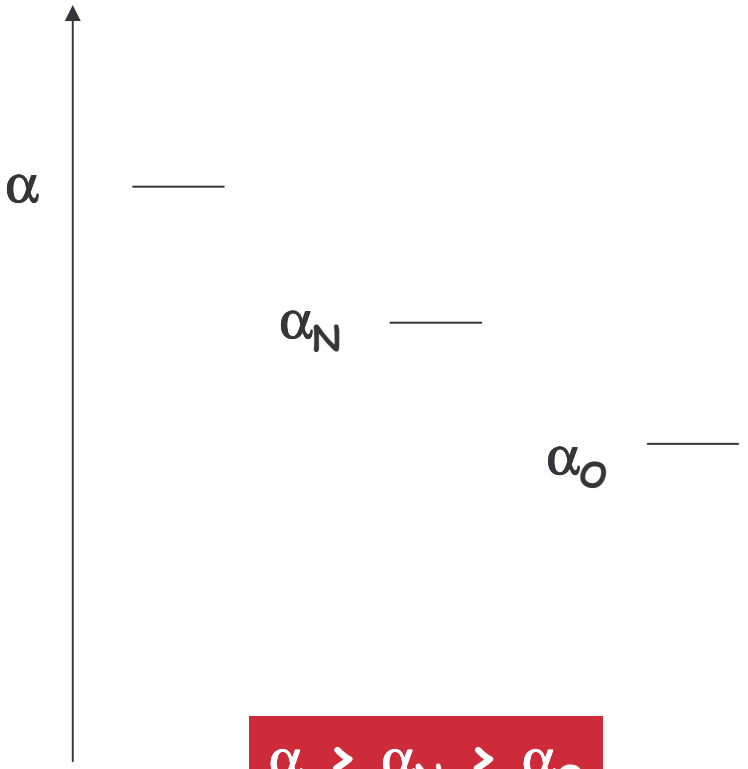
Atome ou groupement		Intégrale coulombienne	Intégrale de résonance
O	1 électron	$\alpha_O = \alpha+\beta$	$\beta_{C-O} = \beta$
	2 électrons	$\alpha_O = \alpha+2\beta$	$\beta_{C-O} = 0,8\beta$
S	1 électron	$\alpha_S = \alpha+0,2\beta$	$\beta_{C-S} = 0,6\beta$
	2 électrons	$\alpha_S = \alpha+0,5\beta$	$\beta_{C-S} = 0,4\beta$
N	1 électron	$\alpha_N = \alpha+0,5\beta$	$\beta_{C-N} = \beta$
	2 électrons	$\alpha_N = \alpha+1,5\beta$	$\beta_{C-N} = 0,8\beta$
F		$\alpha_F = \alpha+3\beta$	$\beta_{C-F} = 0,7\beta$
Cl		$\alpha_{Cl} = \alpha+2\beta$	$\beta_{C-Cl} = 0,4\beta$
Br		$\alpha_{Br} = \alpha+1,5\beta$	$\beta_{C-Br} = 0,3\beta$
Me		$\alpha_{Me} = \alpha+2\beta$	$\beta_{C-Me} = 0,7\beta$

Un hétéroatome en Hückel

Hétéroatome donneur d'un électron







$\alpha > \alpha_N > \alpha_O$

Si X impliqué dans une double liaison

X apporte 1 électron au système π

Paramètres Hückel

Atome ou groupement		Intégrale coulombienne	Intégrale de résonance
O	**1 électron**	$\alpha_O = \alpha+\beta$	$\beta_{C-O} = \beta$
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	2 électrons	$\alpha_S = \alpha+0,5\beta$	$\beta_{C-S} = 0,4\beta$
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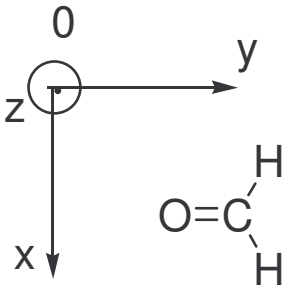
Le formaldéhyde $CH_2=O$



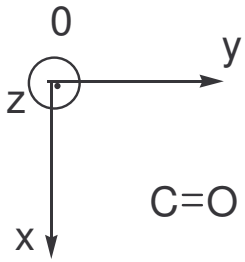
Déterminant séculaire

$$\begin{array}{c|cc} & 2p_{zO} & 2p_{zC} \\ 2p_{zO} & \alpha_O - E & \beta_{CO} \\ 2p_{zC} & \beta_{CO} & \alpha - E \end{array} = \begin{vmatrix} \alpha+\beta-E & \beta \\ \beta & \alpha-E \end{vmatrix} = 0$$

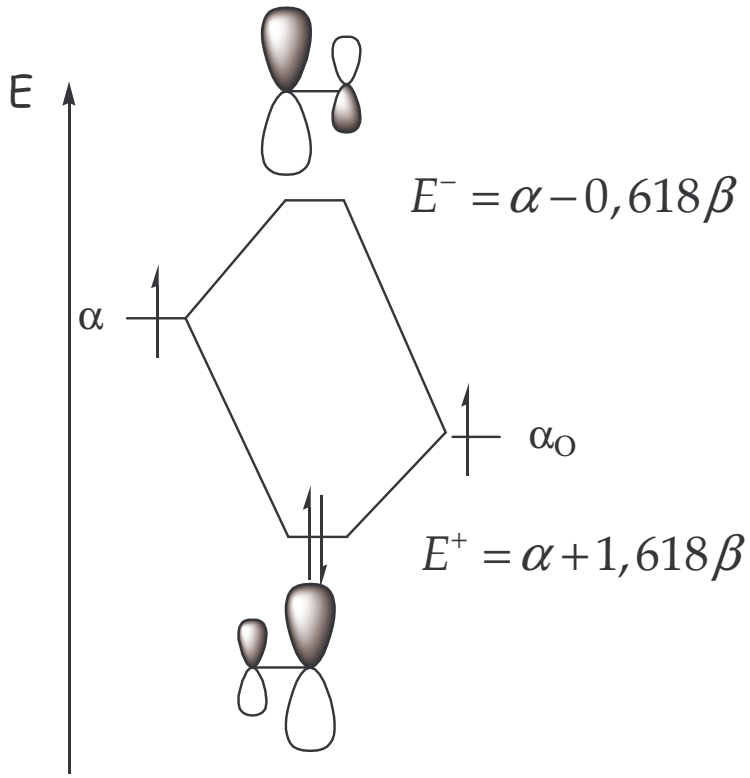
$$(\alpha+\beta-E)(\alpha-E)-\beta^2=0$$

$$\begin{cases} E^+ = \alpha + 1{,}618\beta \\ E^- = \alpha - 0{,}618\beta \end{cases} \Rightarrow \begin{cases} \psi^+ = 0{,}85\varphi_O + 0{,}53\varphi_C \\ \psi^- = 0{,}53\varphi_O - 0{,}85\varphi_C \end{cases}$$

Le formaldéhyde $CH_2=O$



$$\psi^- = 0,53\varphi_O - 0,85\varphi_C$$



$$\psi^+ = 0,85\varphi_O + 0,53\varphi_C$$

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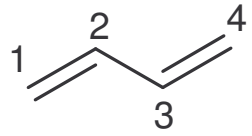
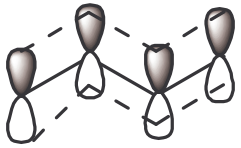
Le butadiène





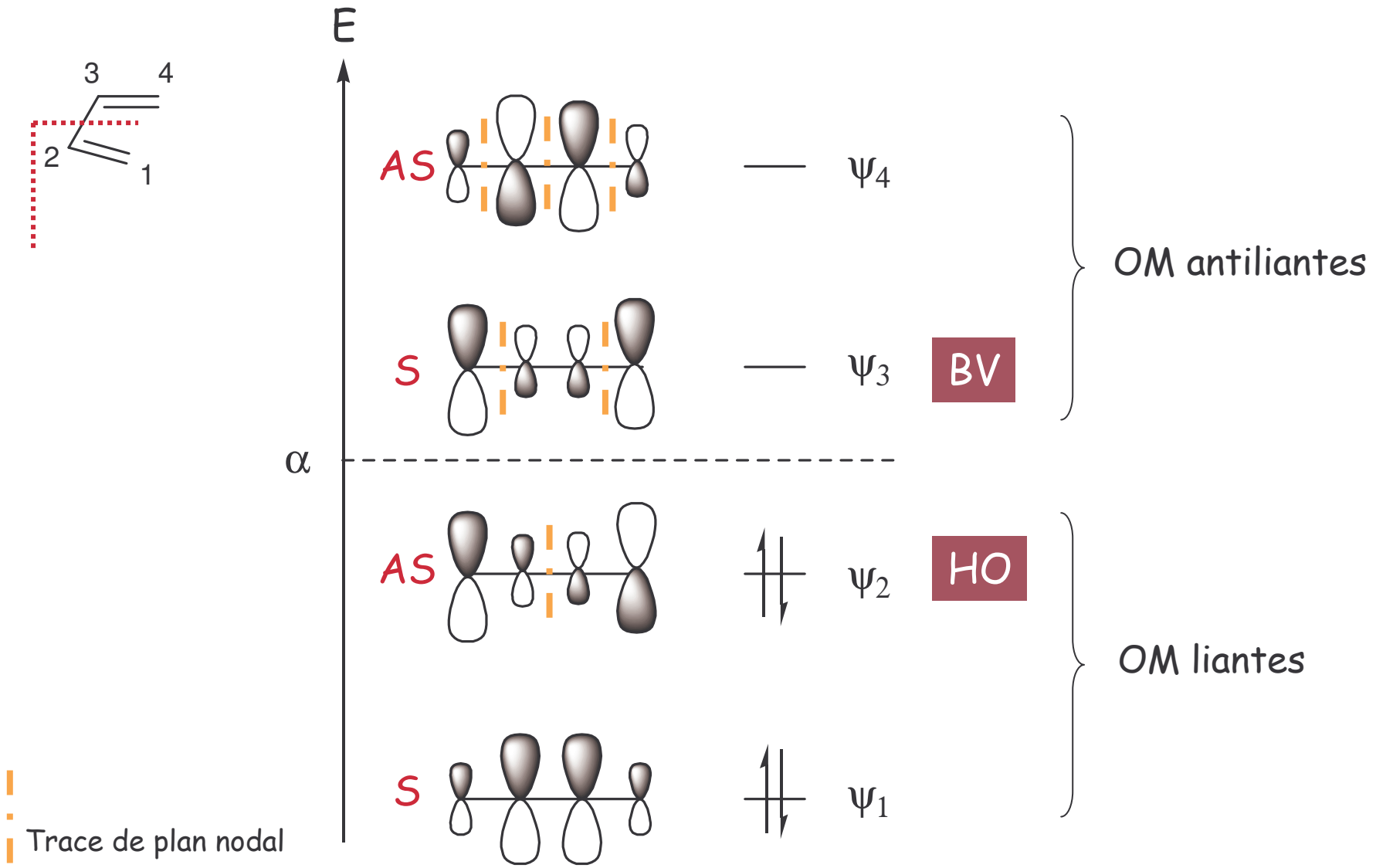
En Hückel simple,
le déterminant séculaire s'écrit :

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

4 racines pour l'énergie

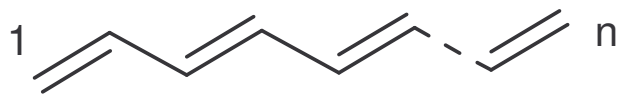
$$\begin{cases} E_4 = \alpha - 1{,}618\beta \\ E_3 = \alpha - 0{,}618\beta \\ E_2 = \alpha + 0{,}618\beta \\ E_1 = \alpha + 1{,}618\beta \end{cases}$$

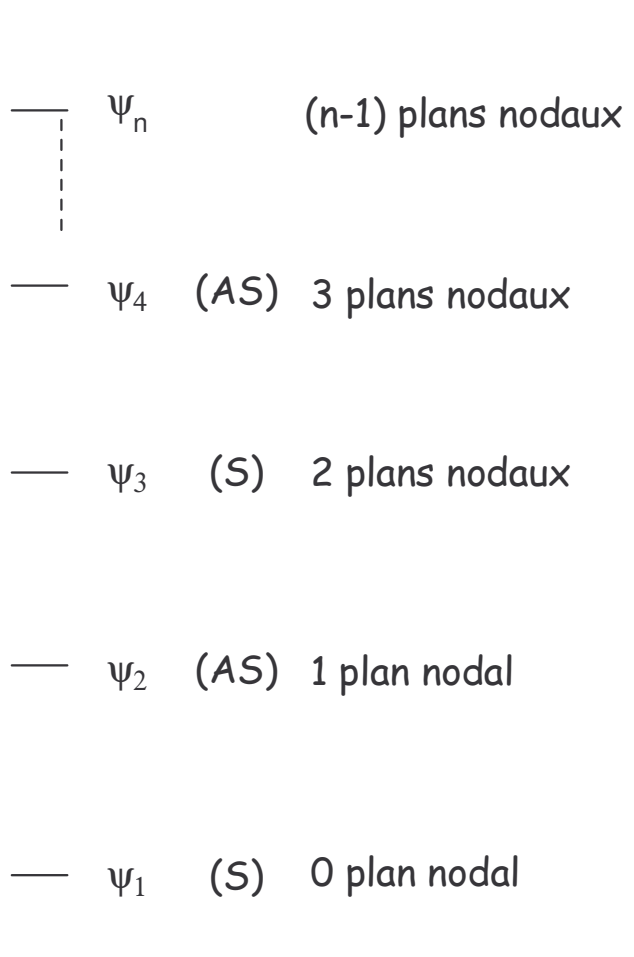
Diagramme orbitalaire



Généralisation

Polyène linéaire de degré *n*





Méthode Hückel simple ⇨ Détermination rapide de l'allure des OM de systèmes conjugués

Généralisation : formules de coulson

Energie

$$E_p = \alpha + 2\beta \cos\left(\frac{p\pi}{n+1}\right)$$

⇒ Nombre de niveaux = nombre d'atomes

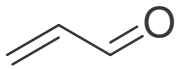
variant entre $\alpha+2\beta$ et $\alpha-2\beta$

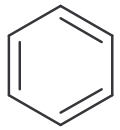
Coefficients

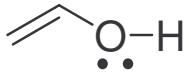
$$c_k^p = \sqrt{\frac{2}{n+1}} \sin\left(\frac{pk\pi}{n+1}\right)$$

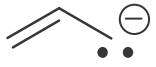
Systèmes conjugués

systèmes conjugués

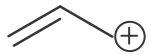
acroléine 

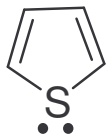
benzène 

énol 

anion allyle 

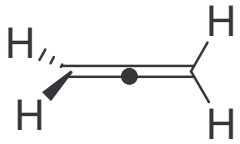
anion penta-1,4-diènique 

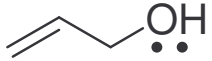
cation allyle 

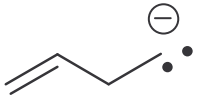
thiofurane 

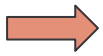
systèmes non conjugués


penta-1,4-diène


allène


alcool allylique

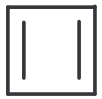

anion but-3-ènique



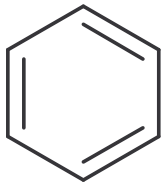
enchaînement $\pi-\sigma-\pi$ ou $n-\sigma-\pi$

Polyènes cycliques

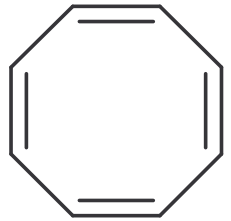
Annulènes



cyclobutadiène

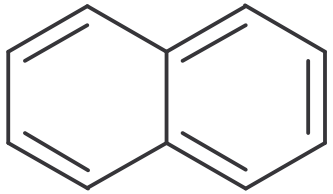


benzène

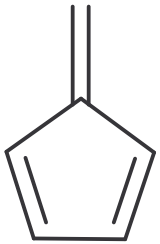


cyclooctatétraène

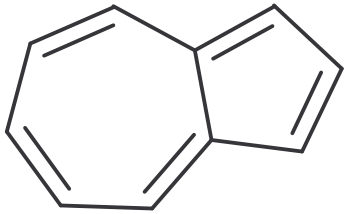
Et ceux qui n'en sont pas…



naphtalène



fulvalène



azulène

Formules de coulson

Energie

$$E_p = \alpha + 2\beta \cos\left(\frac{2p\pi}{n}\right)$$

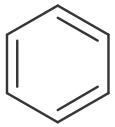
⇒ Varie entre $\alpha+2\beta$ et $\alpha-2\beta$

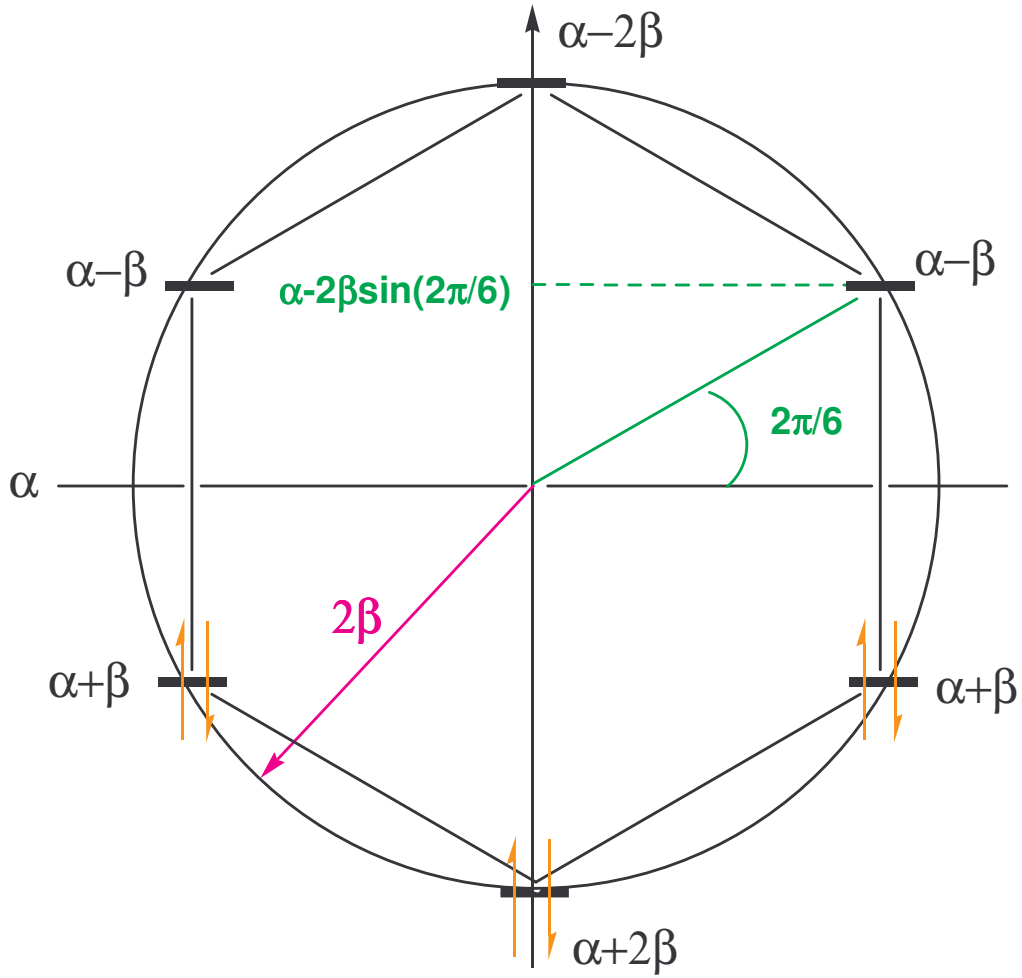
Coefficients

$$c_k^p = \sqrt{\frac{1}{n}} \exp\left(\frac{(2\pi i)(k-1)p}{n}\right)$$

⇒ Construction géométrique

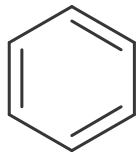
Diagramme de Frost du benzène

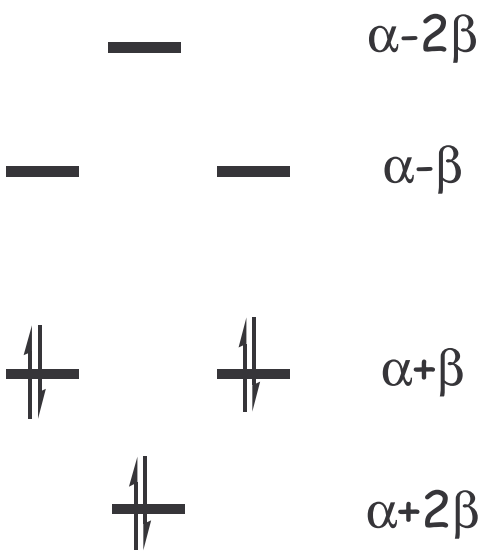




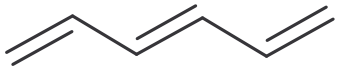
Energies des OM
du benzène

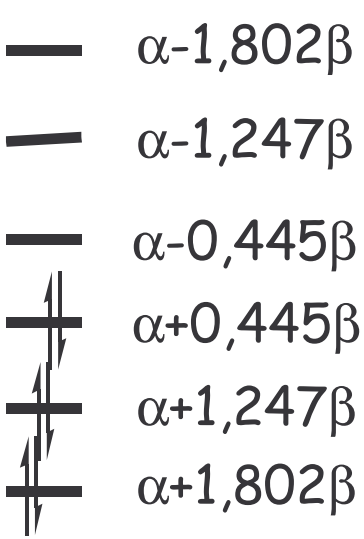
Stabilité comparée des formes ouvertes et fermées





E=6α+8β



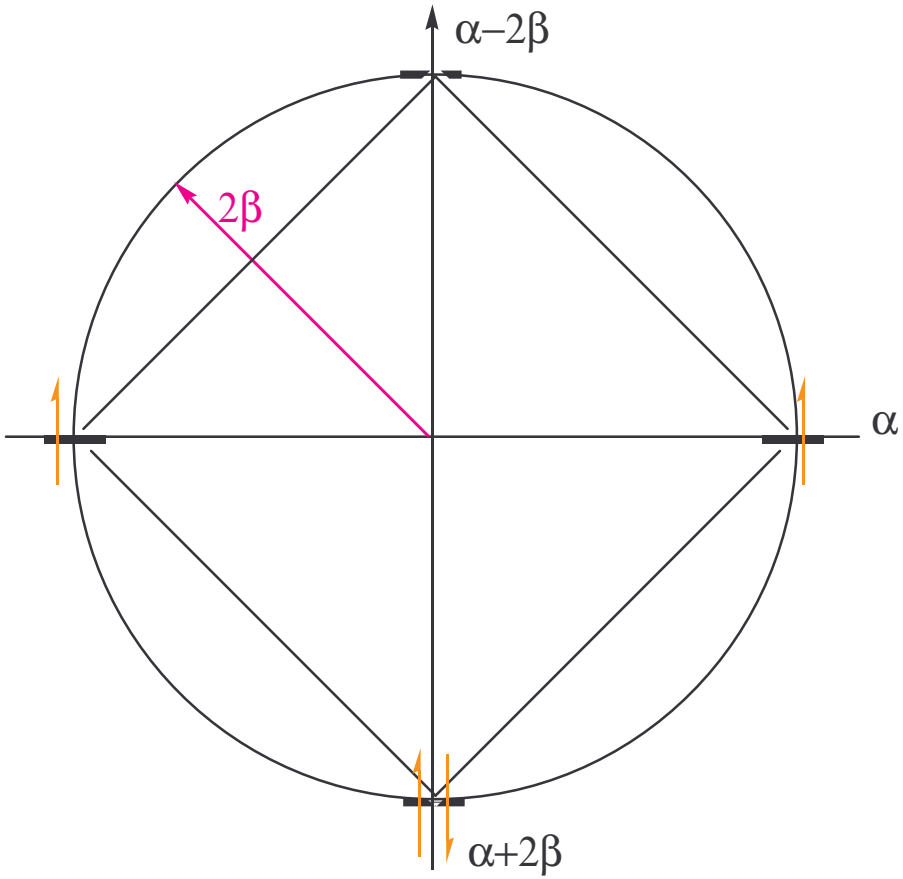


E=6α+6,988β

$\Delta E \approx \beta < 0$

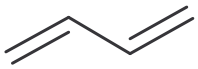
Le benzène est aromatique

Energies du cyclobutadiène



Energies des OM
du cyclobutadiène

Stabilité comparée des formes ouvertes et fermées



157,8 pm

133,4 pm

α-1,618β

α-0,618β

α+0,618β

α+1,618β

α-2β

α

α+2β

$E_{bu}=4\alpha+4,472\beta$

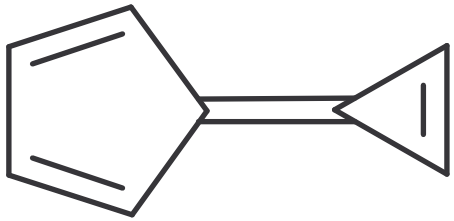
$E_{cy}=4\alpha+4\beta$

$\Delta E \approx -0,5\beta > 0$ **cyclobutadiène antiaromatique**

Critères d'aromaticité

Enoncé selon Hückel

- Molécule monocyclique insaturée plane
- 4n+2 électrons π



$\mu = 9$ D

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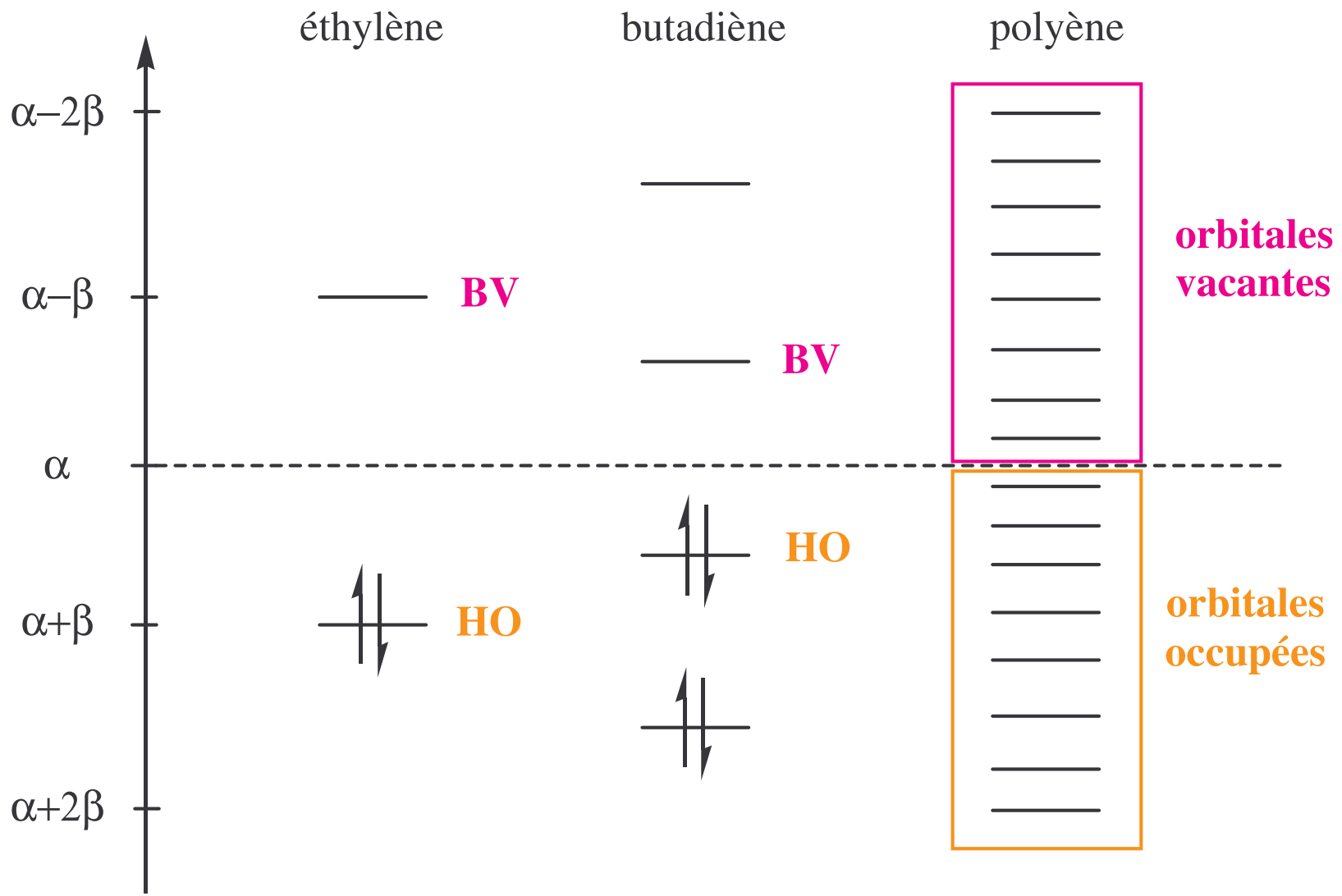
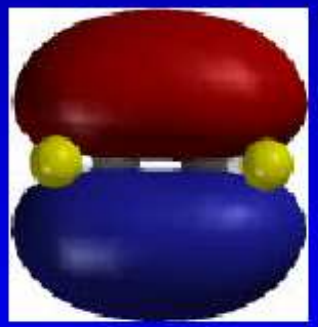
Systèmes conjugués



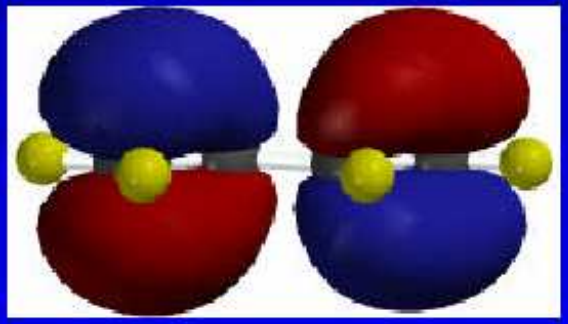
Longueurs d'onde absorbées

$H_2C=CH_2$



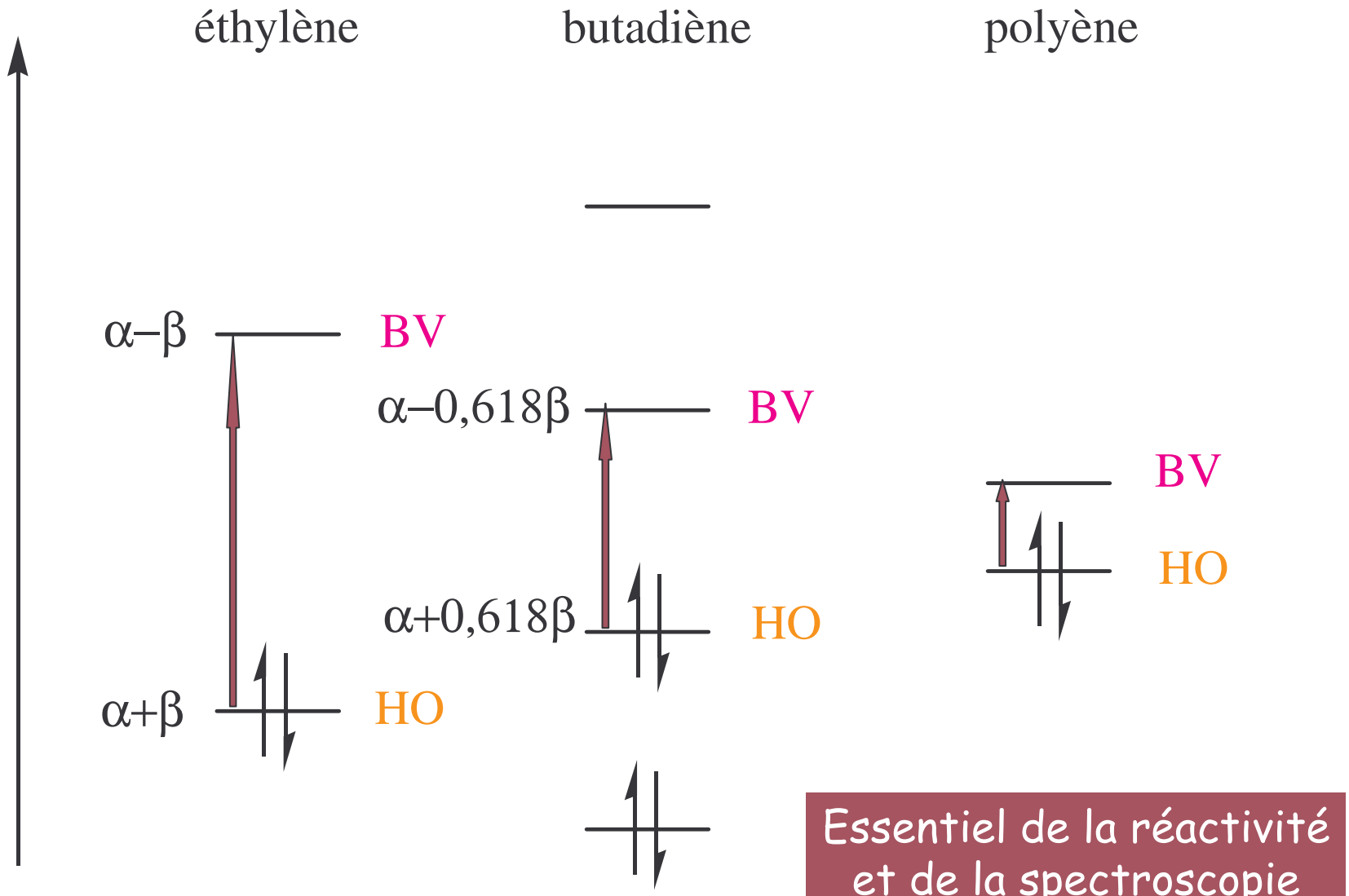
λ_{max}
165 nm

$H_2C=CH–CH=CH_2$



λ_{max}
217 nm

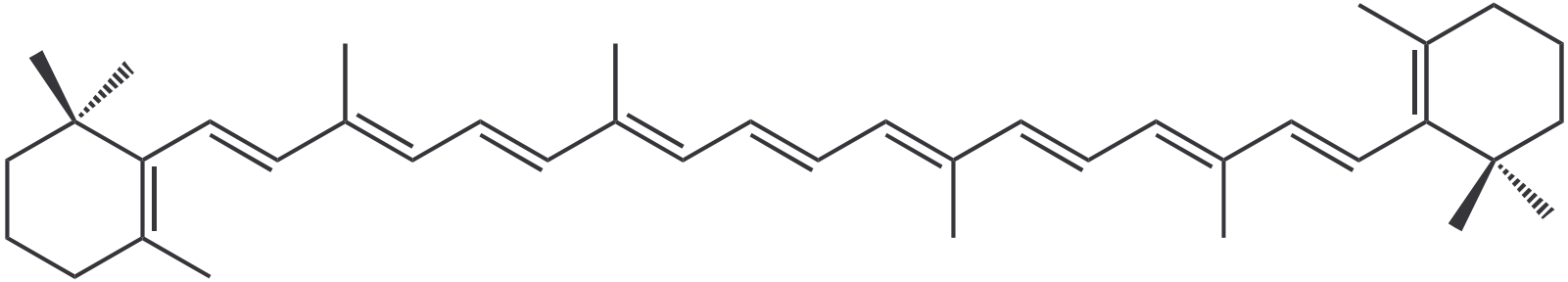
Systèmes conjugués



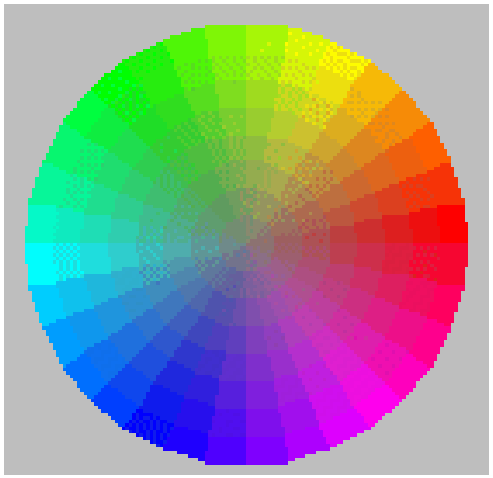
Essentiel de la réactivité et de la spectroscopie

LA CHIMIE DES COULEURS DE L'AUTOMNE

Les carotènes

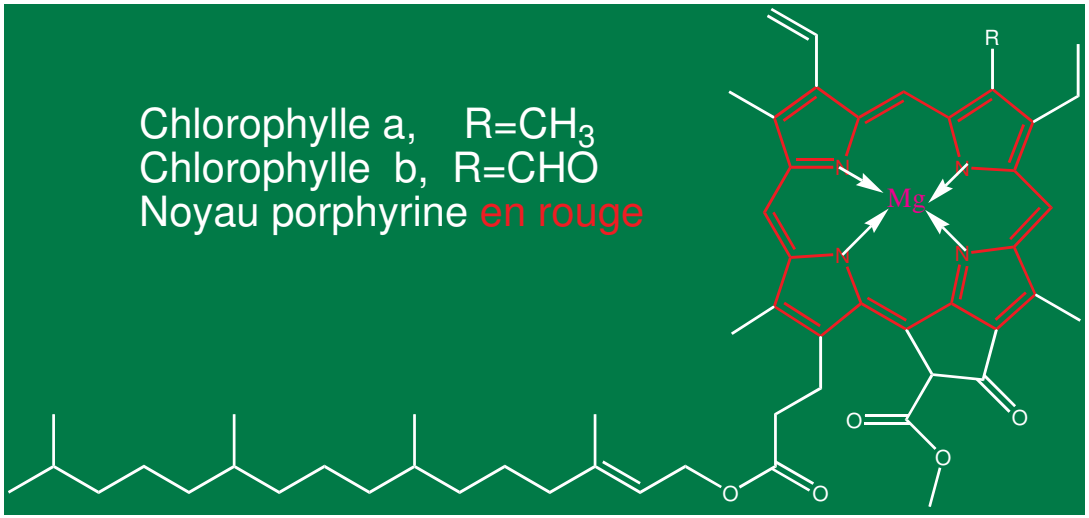


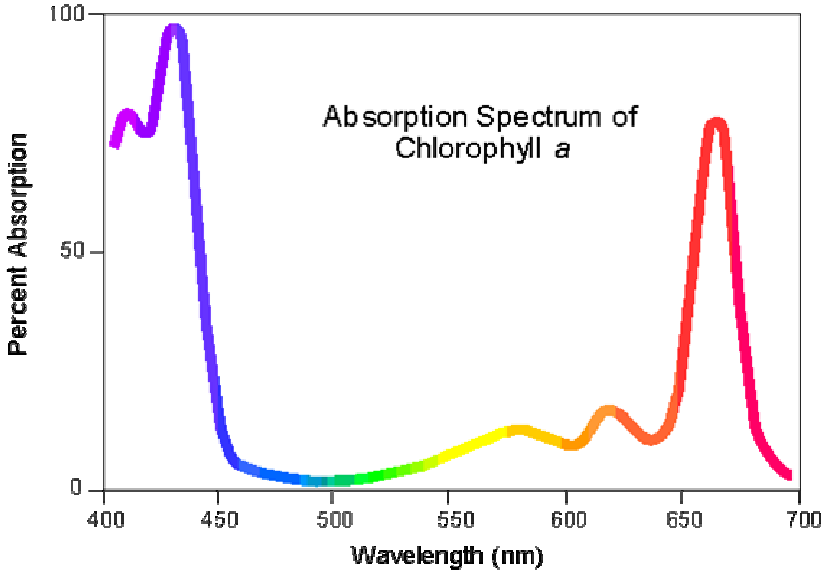
β-carotene λ_{max} 452 nm



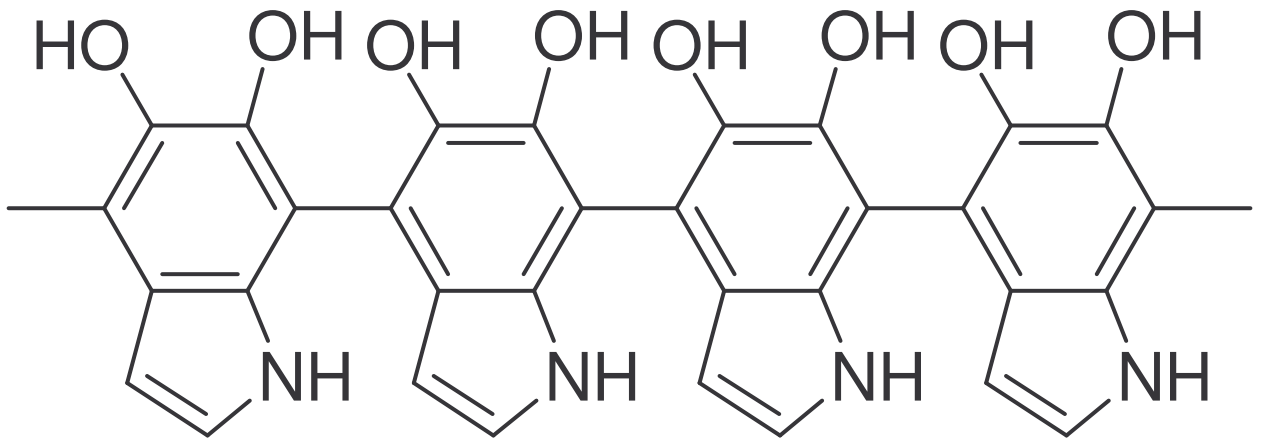
La chlorophylle

Chlorophylle a, R=CH_3
Chlorophylle b, R=CHO
Noyau porphyrine en rouge

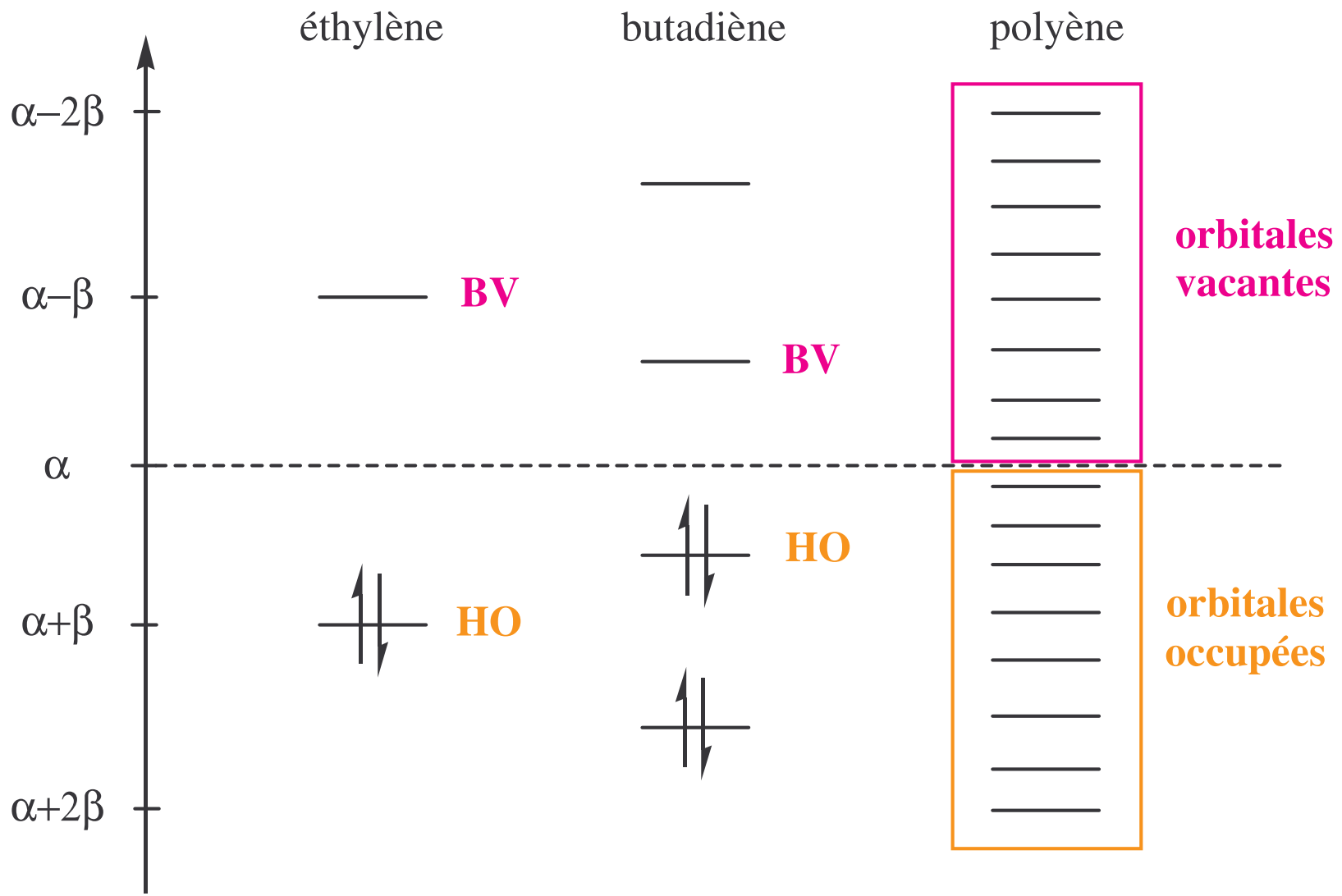




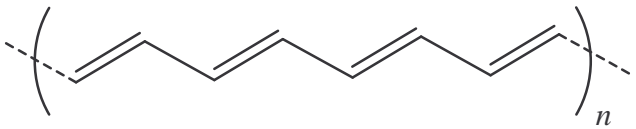
La mélanine

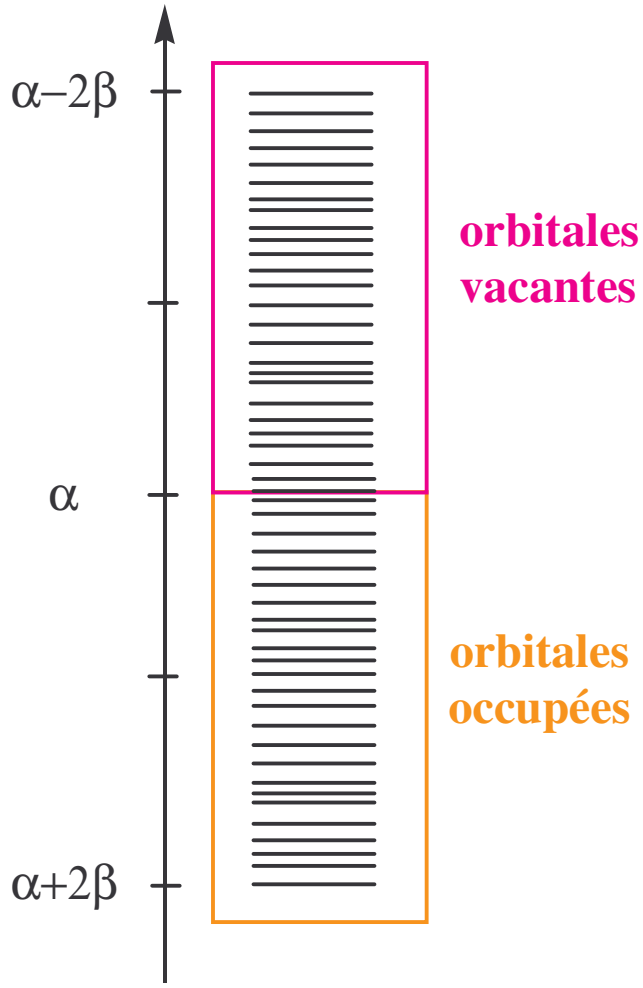


Systèmes conjugués



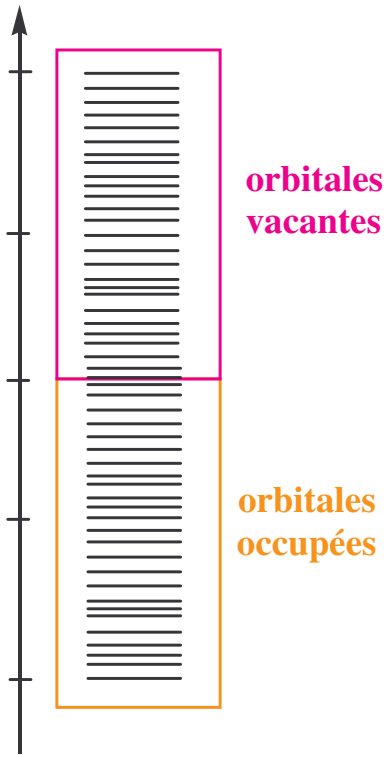
Le polyacétylène





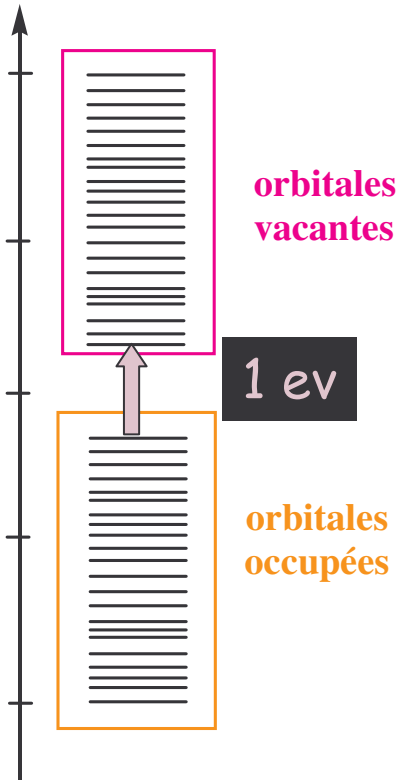
D'après les calculs Hückel, c'est un conducteur électrique !

Exemples



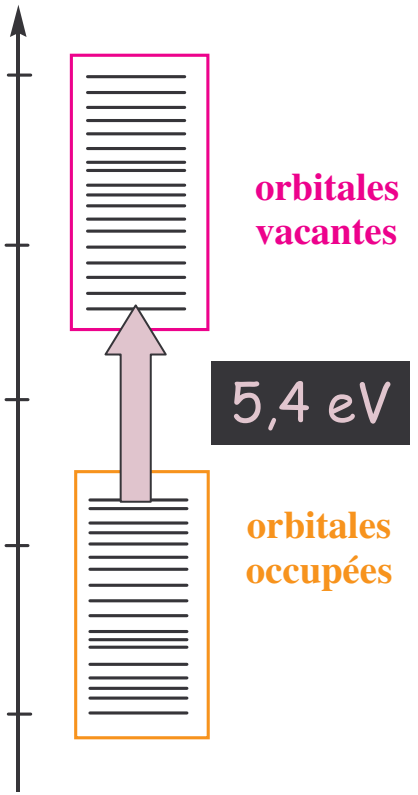
Cu, Graphite

conducteur



Silicium

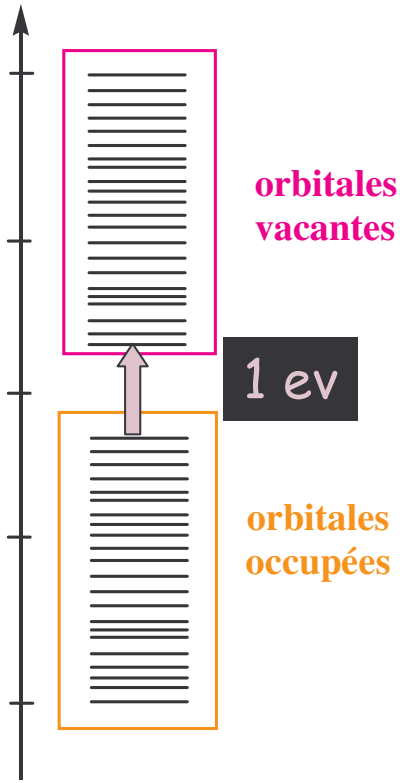
semi-conducteur



Diamant

isolant

Applications des semi-conducteurs



Silicium

Energie ambiante : 3 kJ.mol^{-1} ≈ 0,03 eV

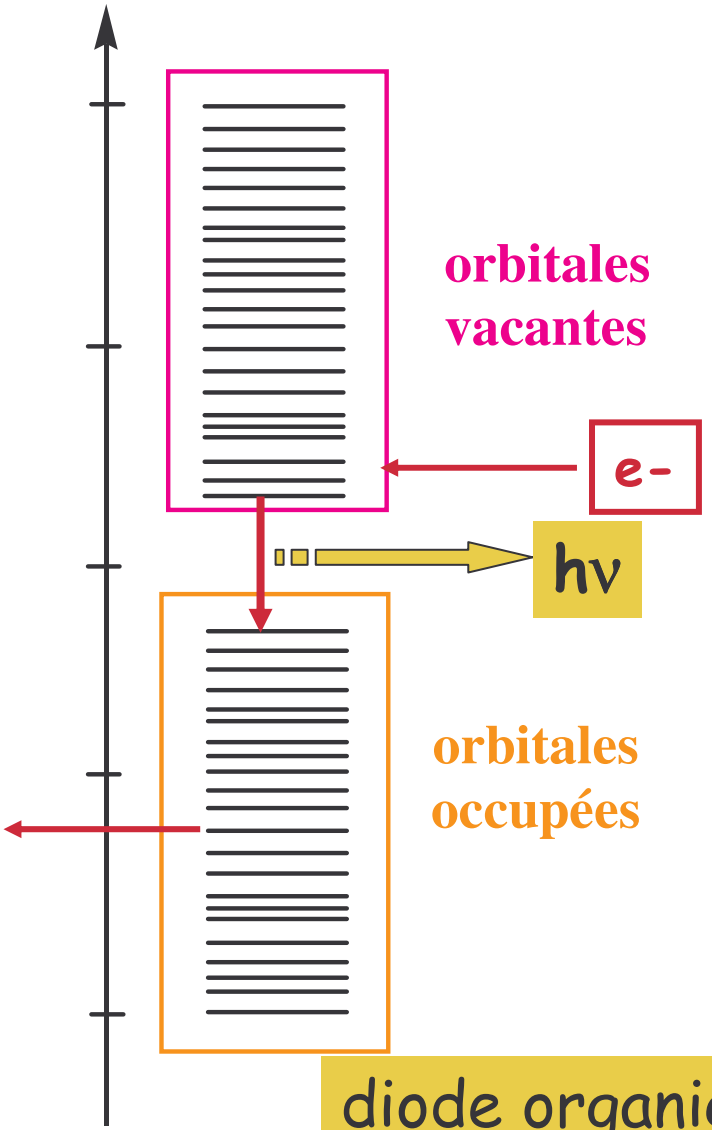
↪ Pas de conduction à l'ambiante

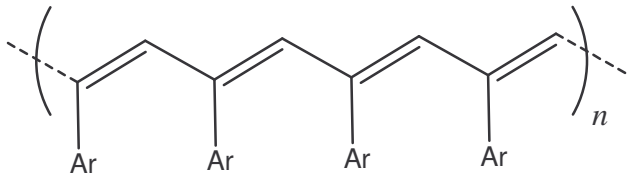
1 eV ⟷ 1200 nm (I.R.)

↪ Cellules photovoltaïques

Pour applications électroniques : dopage nécessaire

Semi-conducteurs organiques

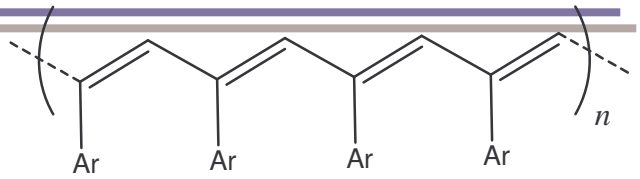




polyéthylène vinylène

diode organique électroluminescente jaune

Applications multiples



Les polymères organiques conducteurs ont de multiples applications…

Ecrans OLED

Films d'emballage contre l'électricité statique

Verres électrochromes…