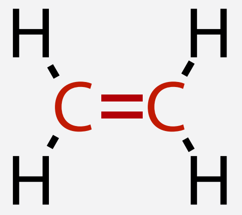
2.3 Molecular Orbitals in π-Conjugated Systems

Molecules with Several Multiple Bonds

- bond lengths and energy barriers for rotation for single bonds in dienes/trienes

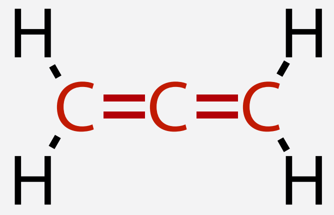
ethene

1.33 Å



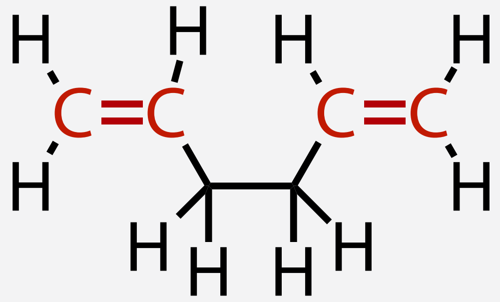
1,2-propadiene

1.33 Å 1.33 Å



1,5-hexadiene

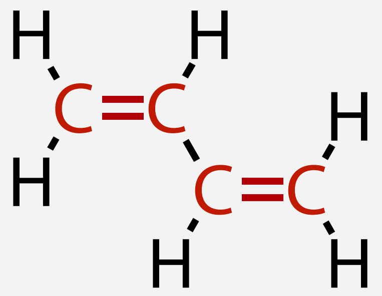
1.33 Å 1.33 Å



1.54 Å ⟳ 3 kJ/mol

1,3-butadiene

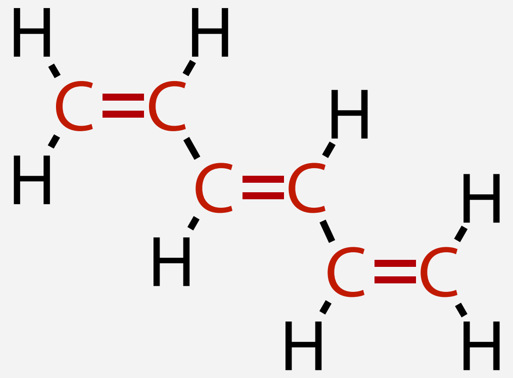
1.34 Å 1.34 Å



1.47 Å ⟳ 30 kJ/mol

1,3,5-hexatriene

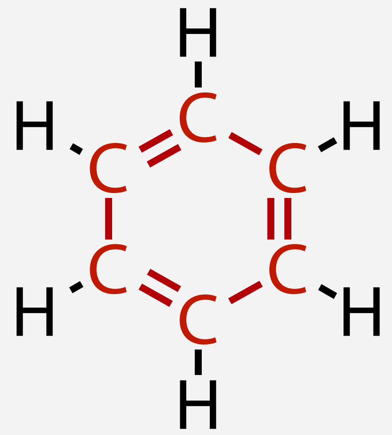
1.34 Å 1.37 Å 1.34 Å



1.46 Å 1.46 Å ⟳ 30 kJ/mol

benzene

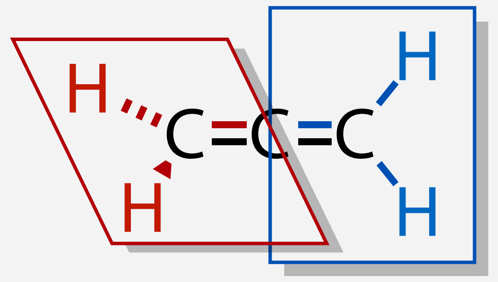
1.45 Å (all bonds)



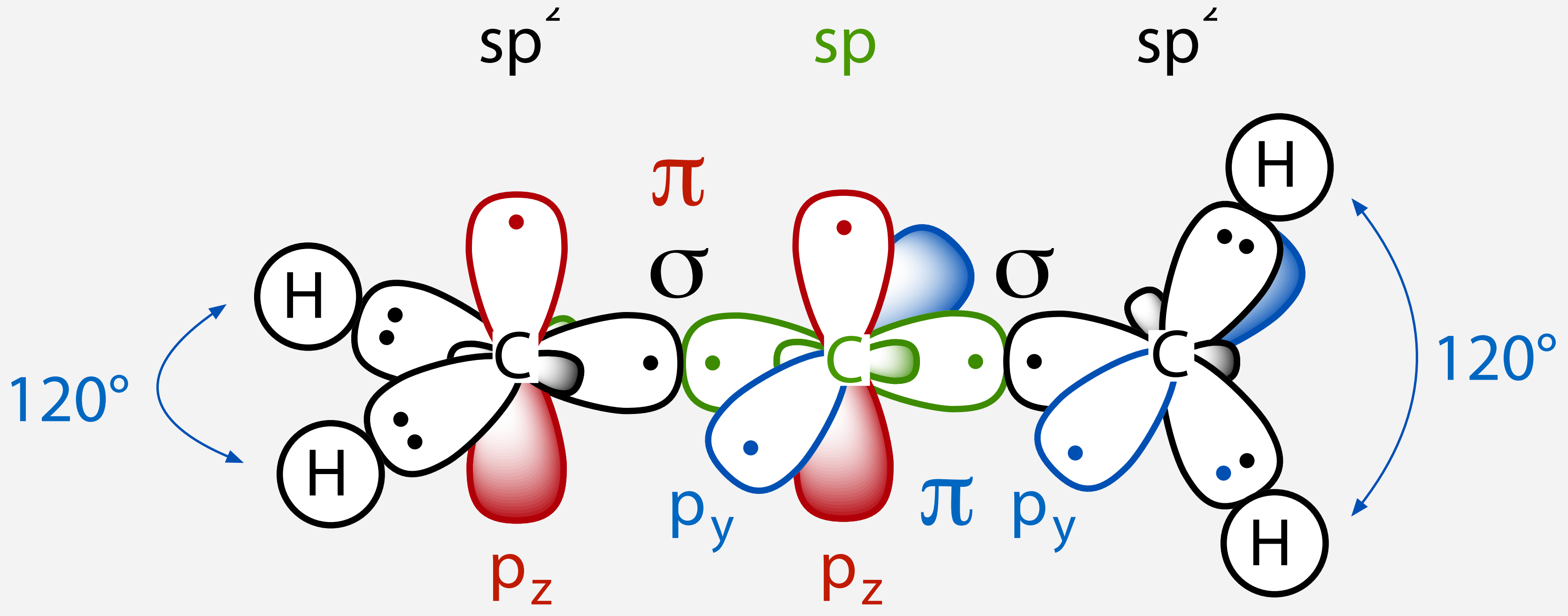
- **alternating double and single bonds are called “conjugated” double bonds**
- **conjugated double bonds longer than normal, single bonds shorter, higher rotation barrier**

Molecules with Cumulated and Isolated Double Bonds

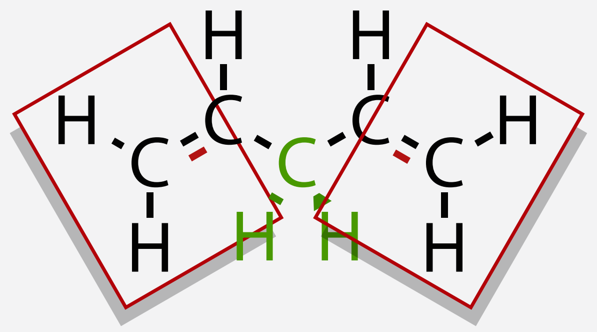
- “cumulated double bonds” are in orthogonal planes, do not interact electronically



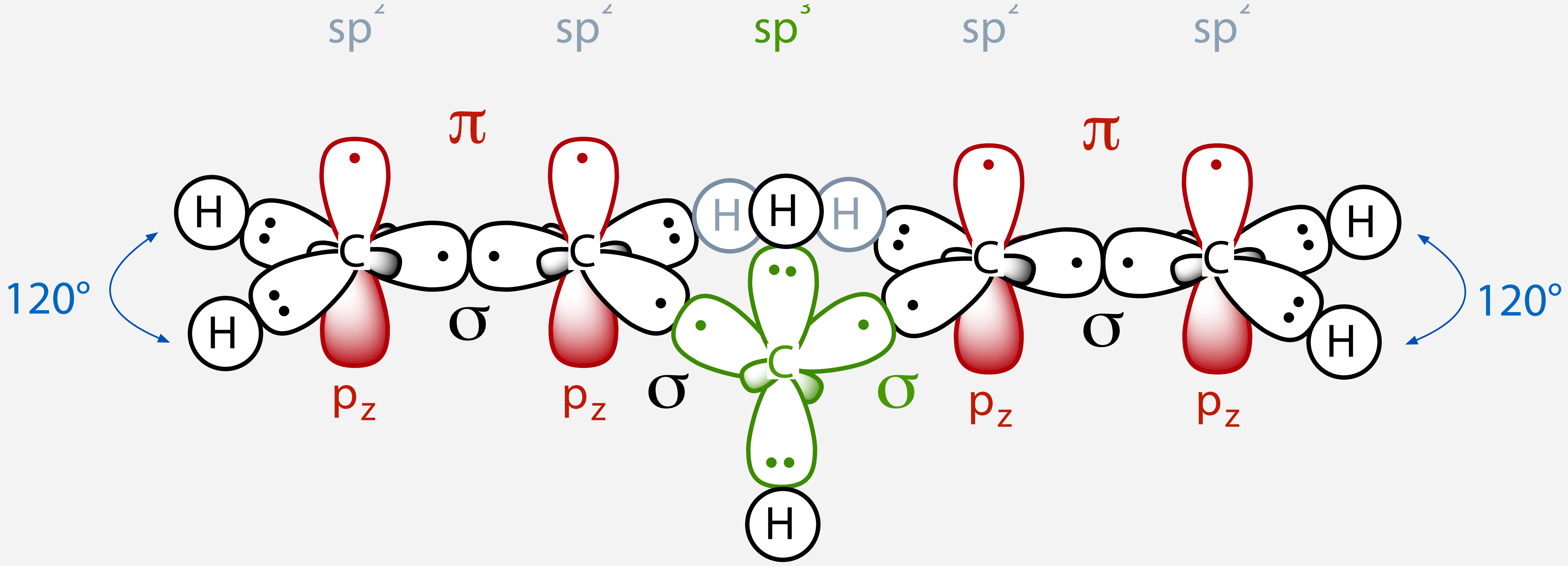
1,2-propadiene



- isolated double bonds separated are in arbitrary planes, do not interact



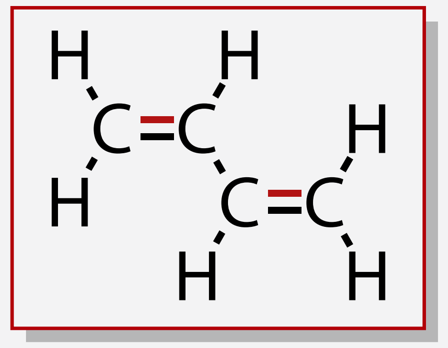
1,4-pentadiene



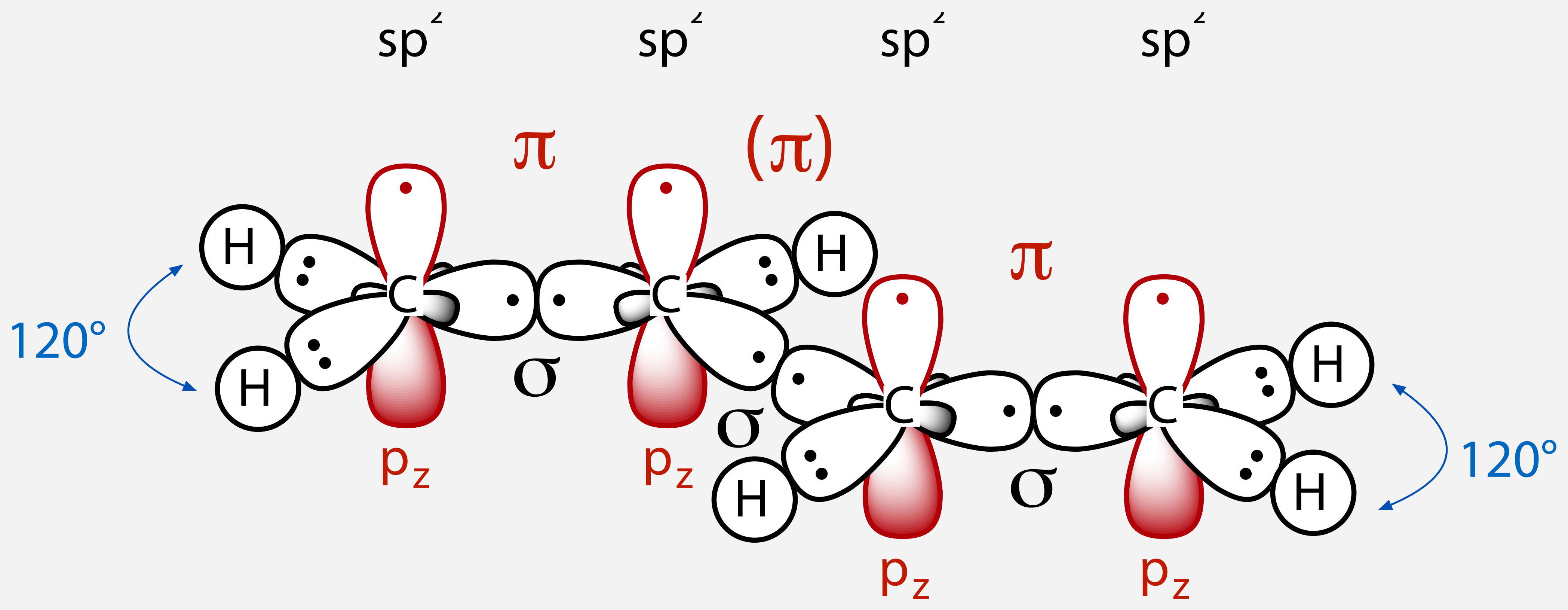
- **neither cumulated nor isolated multiple bonds “communicate”, i.e., interact electronically**

Molecules with Conjugated Multiple Bonds

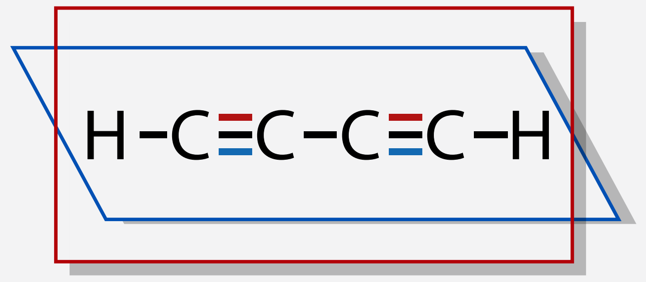
- alternating multiple and single bonds are called “conjugated multiple bonds”



1,3-butadiene

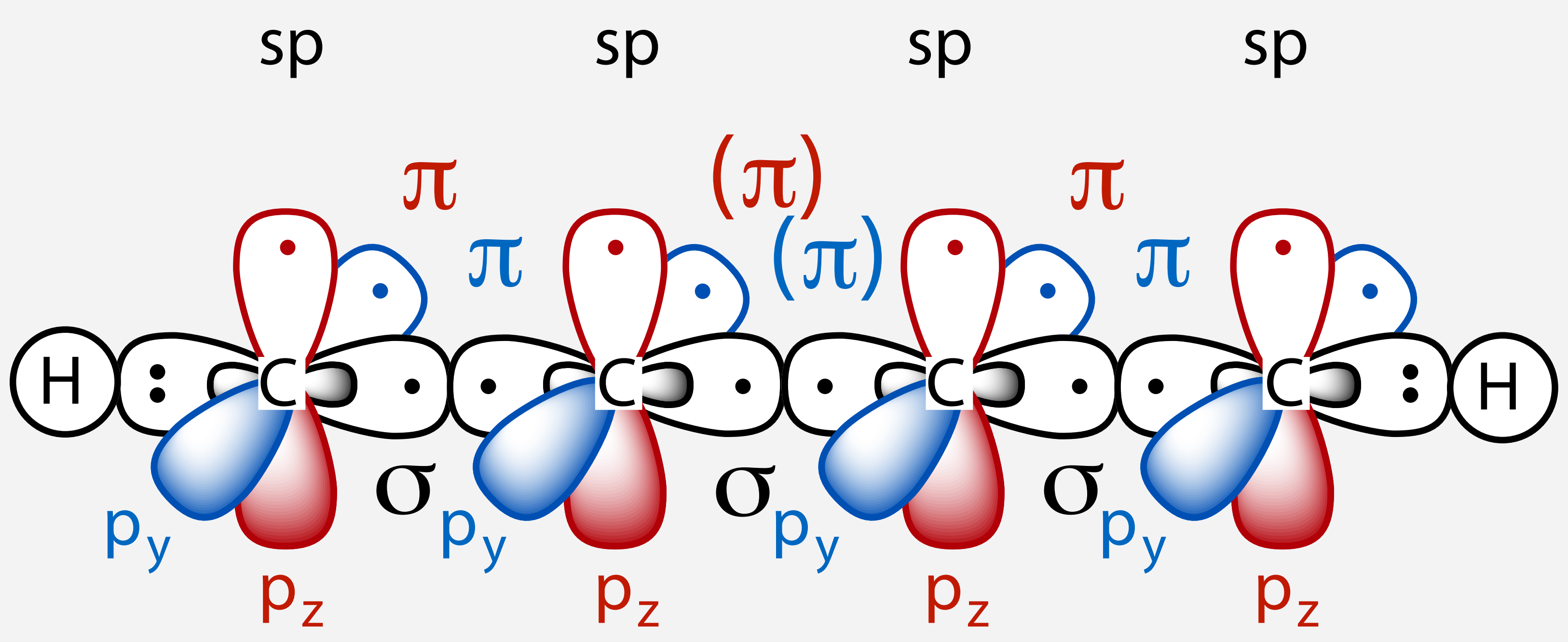


- “conjugated triple bonds” are in the same planes, pz and py orbitals are in direct contact



H−C≡C−C≡C−H

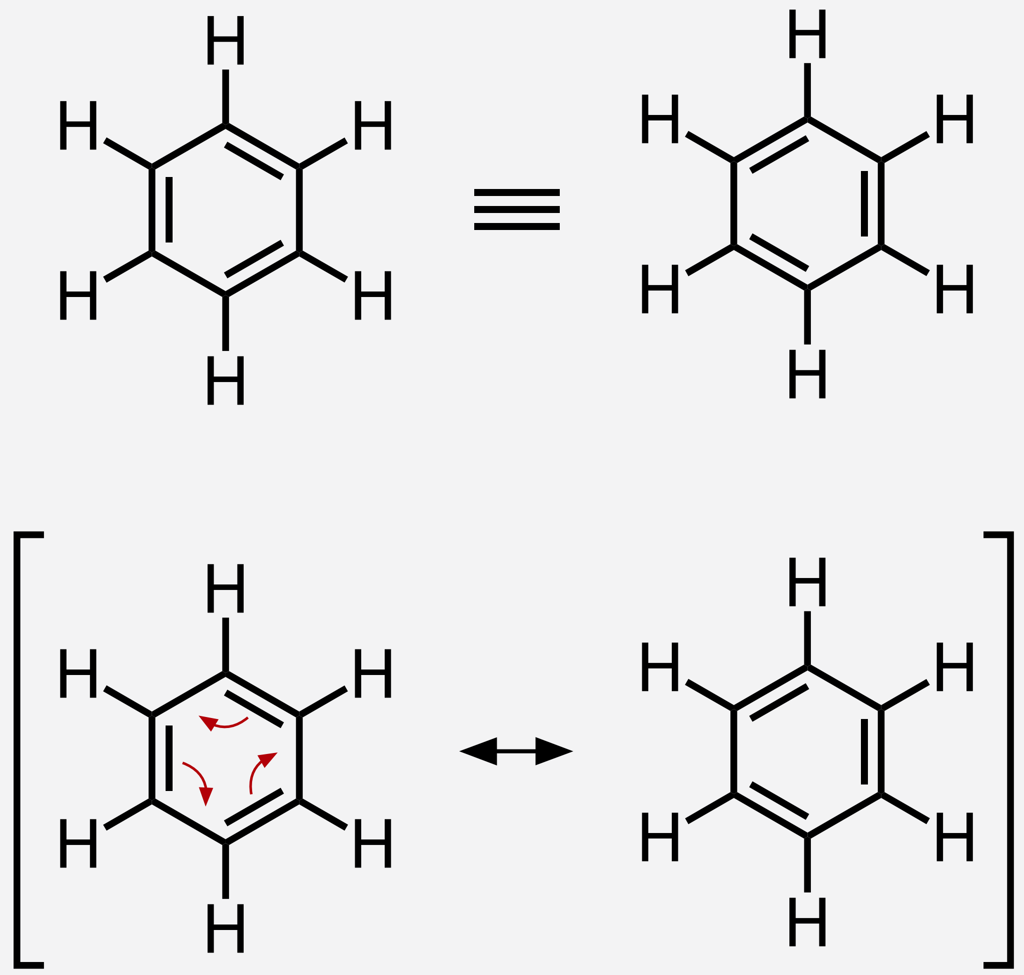
1,3-butadiyne

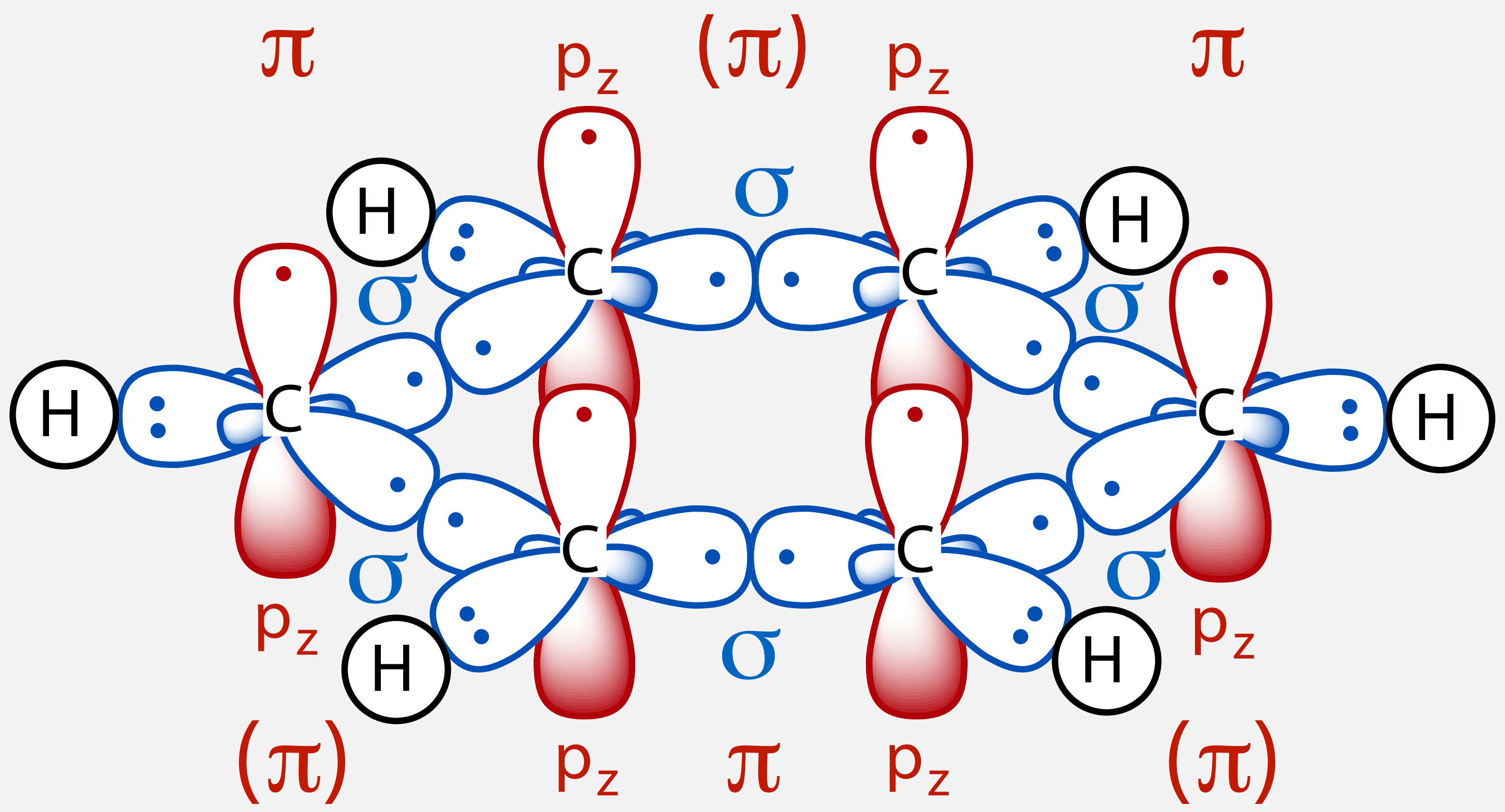


- **conjugated multiple bonds interact with each other electronically, and electrons are delocalized across the whole system of π bonds**

Cyclic π-Conjugated Multiple Bonds

- molecules with cyclic conjugated double bonds can be represented by two neutral canonical formulae (resonance structures)

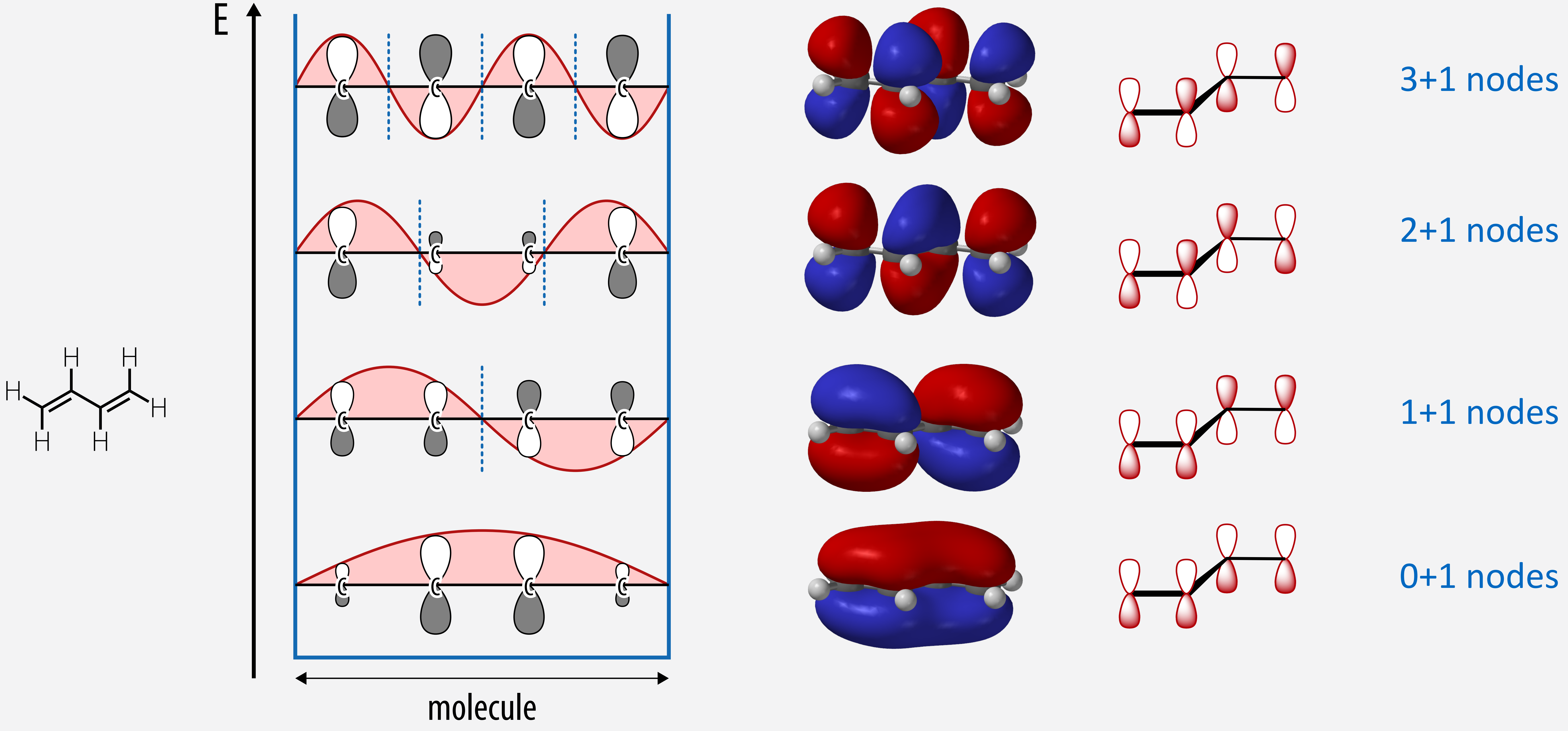




- **molecules with 2*n*+1 cyclic conjugated double bonds are particularly stable (Hückel rule)**
- **compounds are called aromatic, all bonds are symmetrically equivalent, bond order 1.5**

“Electron in a 1D Box” Model for a Linear π-Conjugated Systems

- electron in 1D Box with infinite potential is a simple model for linear π systems



3+1 nodes

2+1 nodes

1+1 nodes

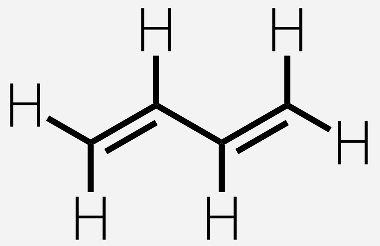
0+1 nodes

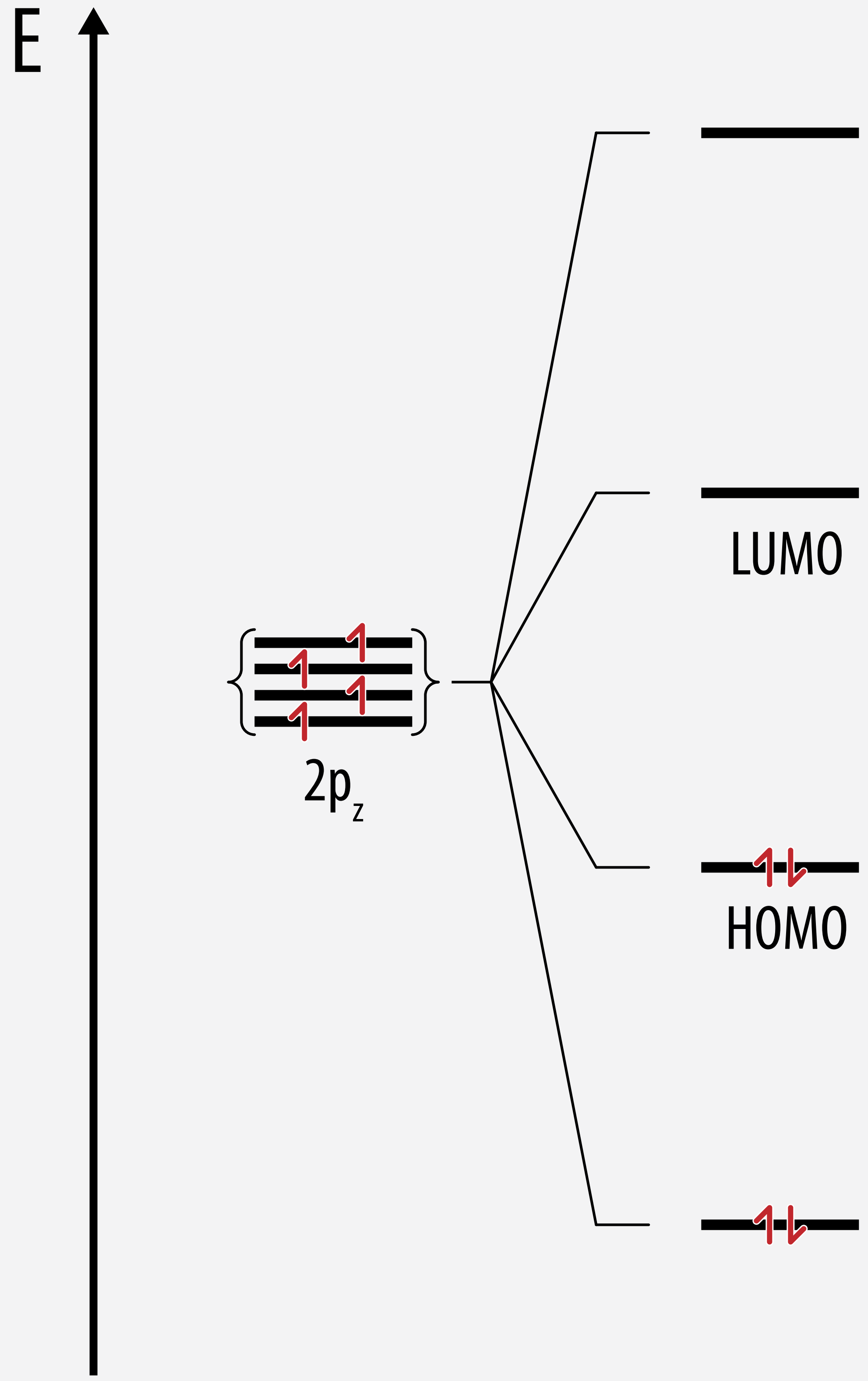
- 4 p_z orbitals result in 4 linearly independent MO states
- ***all* resulting molecular π-orbitals are delocalized over all four carbon atoms (despite nodes)**

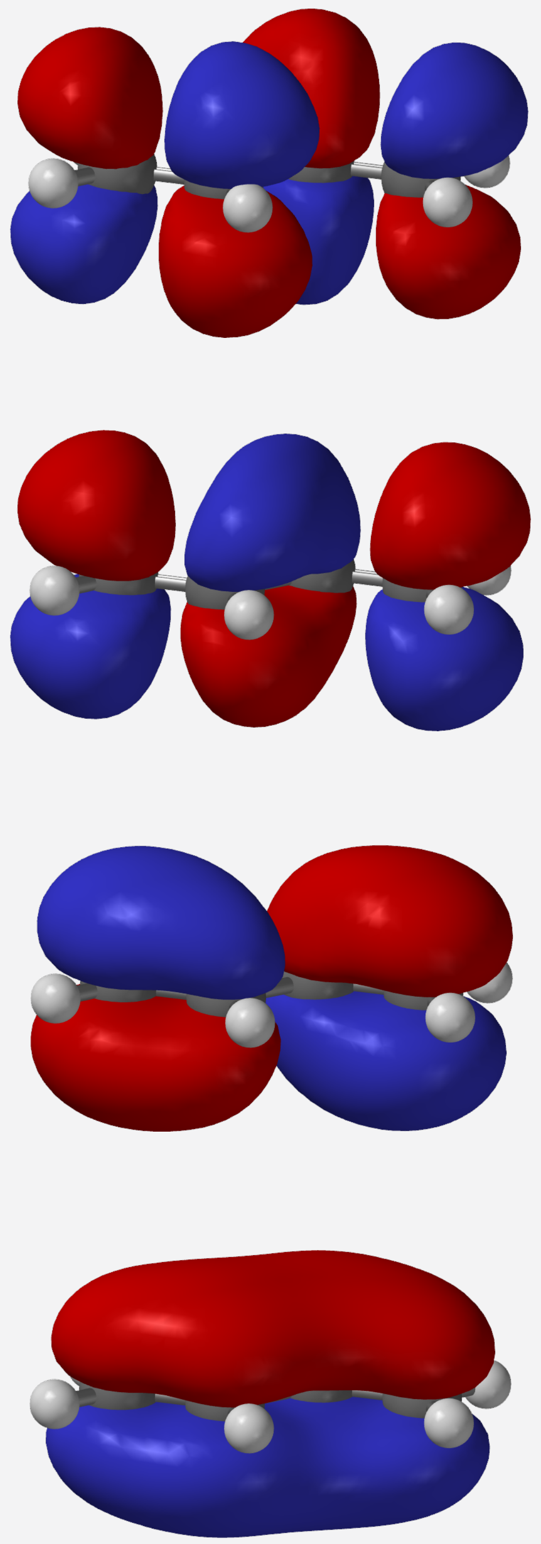
KEY CONCEPT: see reader *“Quantum States of π-Electrons in Polyacetylene”* for details

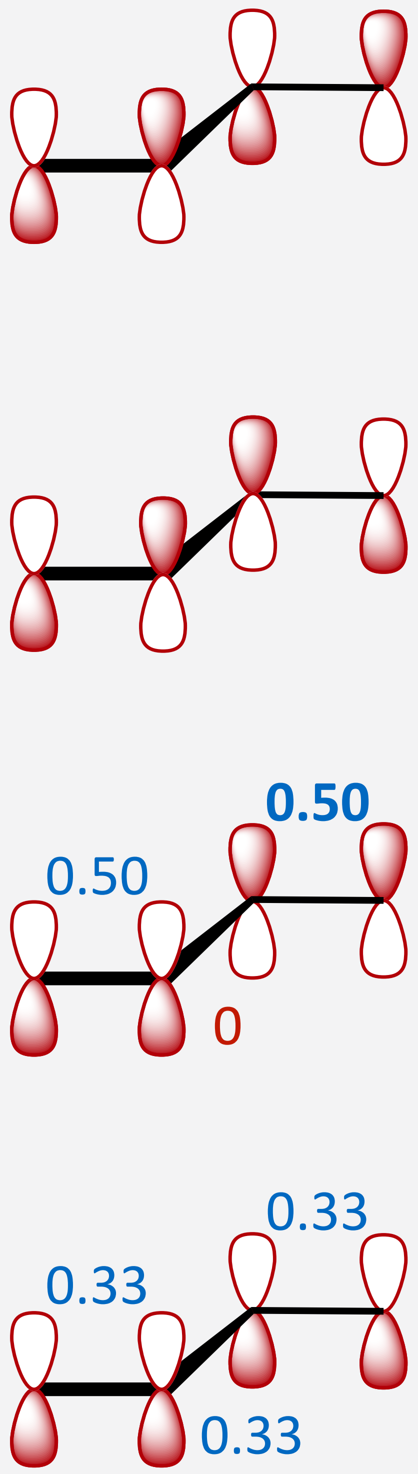
Frontier Orbitals and Bond Orders in 1,3-Butadiene

- simplified schematic MO energy diagram of the frontier orbitals of 1,3-butadiene







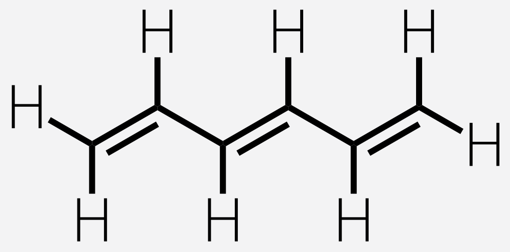


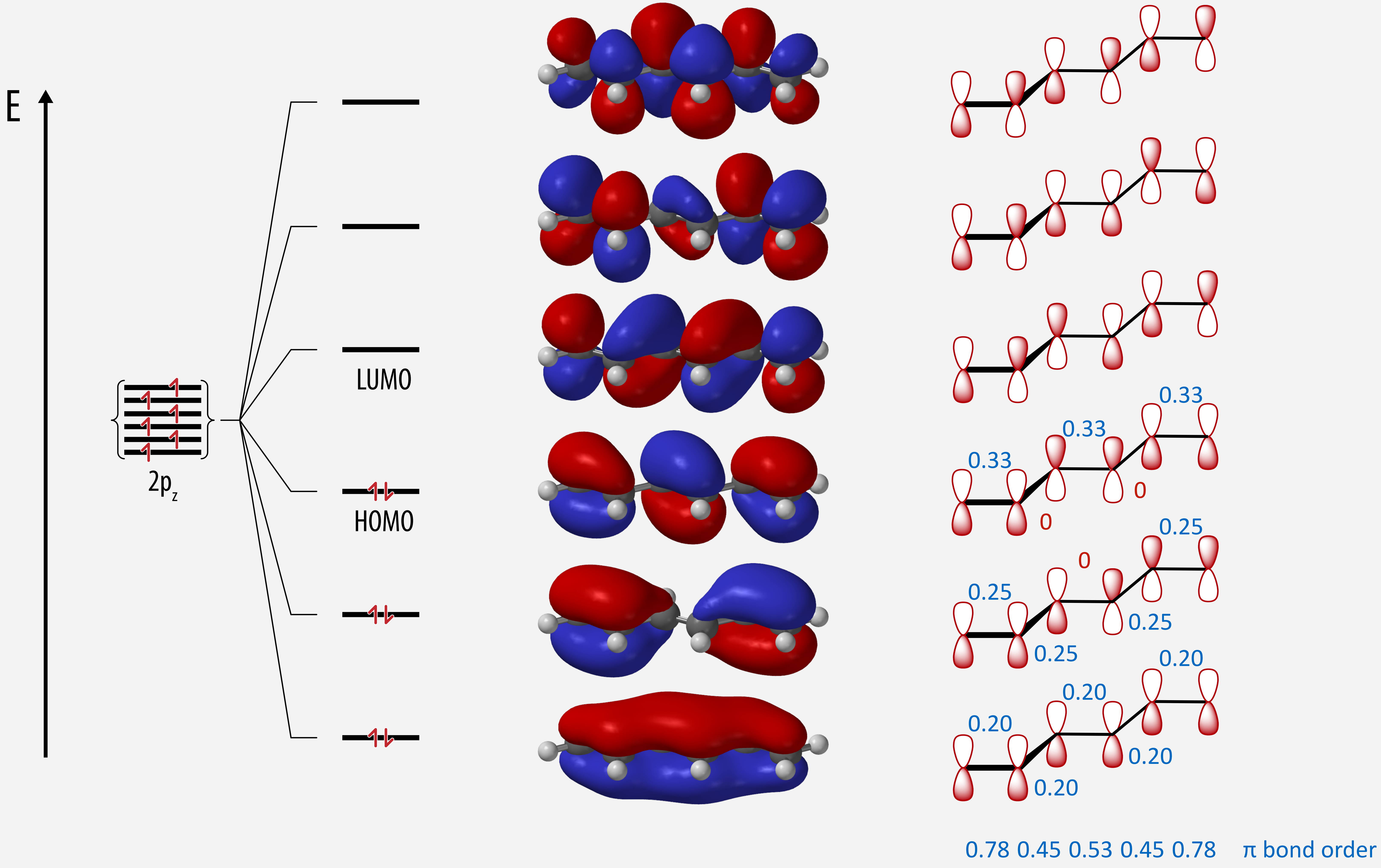
0.83 0.33 0.83	π bond order
1.83 1.33 1.83	bond order

- **double bonds have bond order <2, central single bond >1, restricted rotation (30 kJ/mol)**

see reader *"Quantum States of π-Electrons in Polyacetylene"* for details

Frontier Orbitals and Bond Orders in 1,3,5-Hexatriene



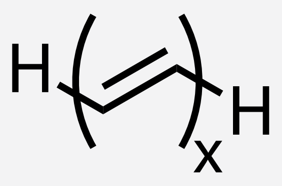


- **all π-electrons delocalized over entire molecule**
- **HOMO/LUMO gap decreases, bond order of bonds converges to 1.5**

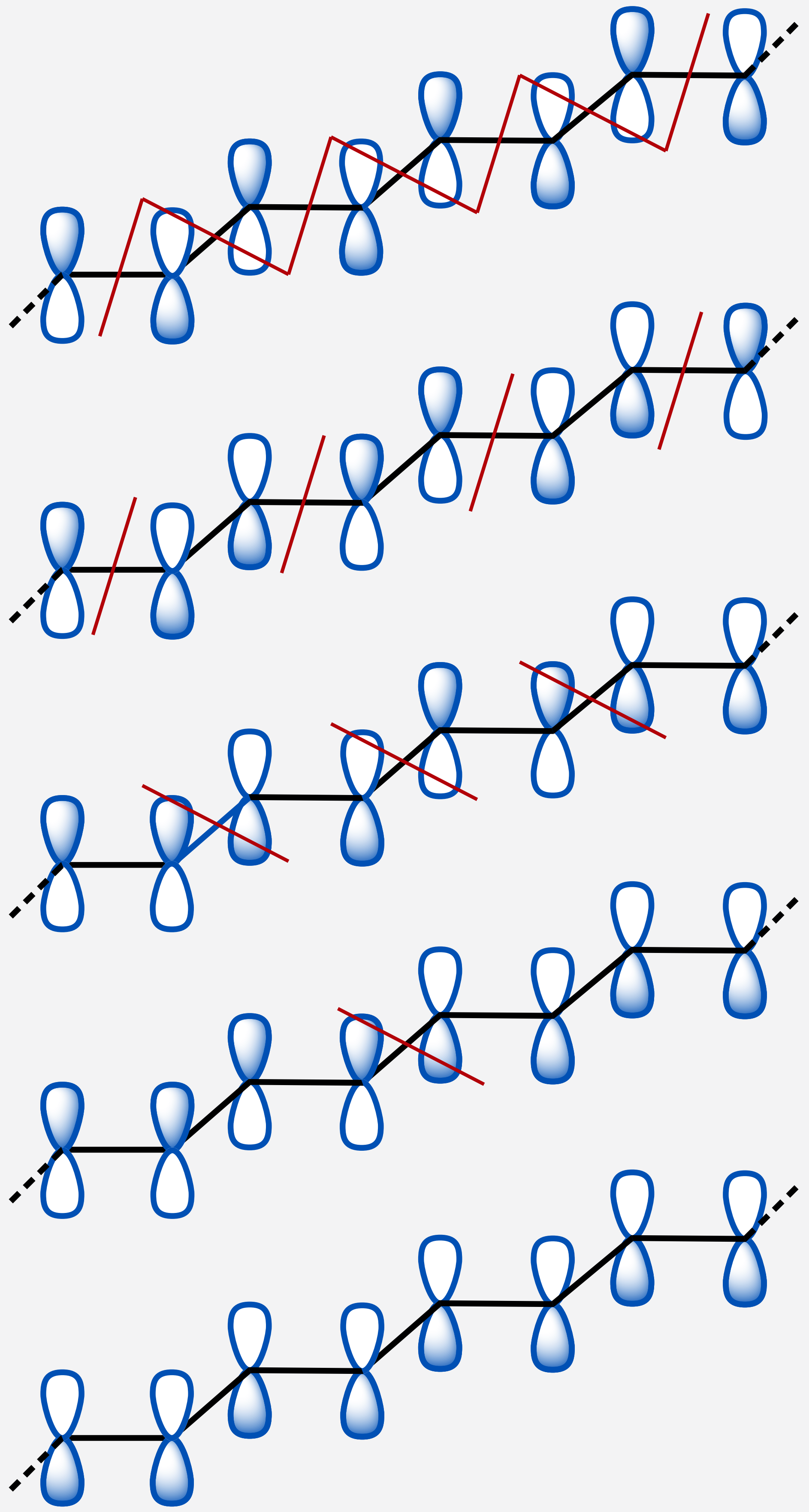
see reader *“Quantum States of π-Electrons in Polyacetylene”* for details

Expanding the Model to Poly(acetylene)

- poly(acetylene) is an “infinite” linear chain of conjugated double bonds



molecular orbital	**energy level *n***
highest	*n*
LUMO	*n*/2 + 1
HOMO	*n*/2
2nd lowest	2
lowest	1



- **if chains were extended and coplanar, all MO would be delocalized over the whole chain**
- **however, deviation from coplanarity by “random coil” formation breaks delocalization**

see reader *“Quantum States of π-Electrons in Polyacetylene”* for details

Electron in a 1D Box Model of Poly(acetylene)

- energy level E_n for poly(acetylene) with N carbon atoms, bond length d, for large N, scales with n^2

$$E_n = \frac{\hbar^2\pi^2 n^2}{2md^2(N-1)^2} \approx \frac{\hbar^2\pi^2 n^2}{2md^2N^2} \propto n^2$$

- HOMO and LUMO energy levels (for N electrons in N MO) at $n = N/2$ and $n = N/2 + 1$

$$E_{HOMO} = \left(\frac{N}{2}\right)^2 \frac{\hbar^2\pi^2}{2md^2N^2} \quad \text{and} \quad E_{LUMO} = \left(\frac{N}{2}+1\right)^2 \frac{\hbar^2\pi^2}{2md^2N^2}$$

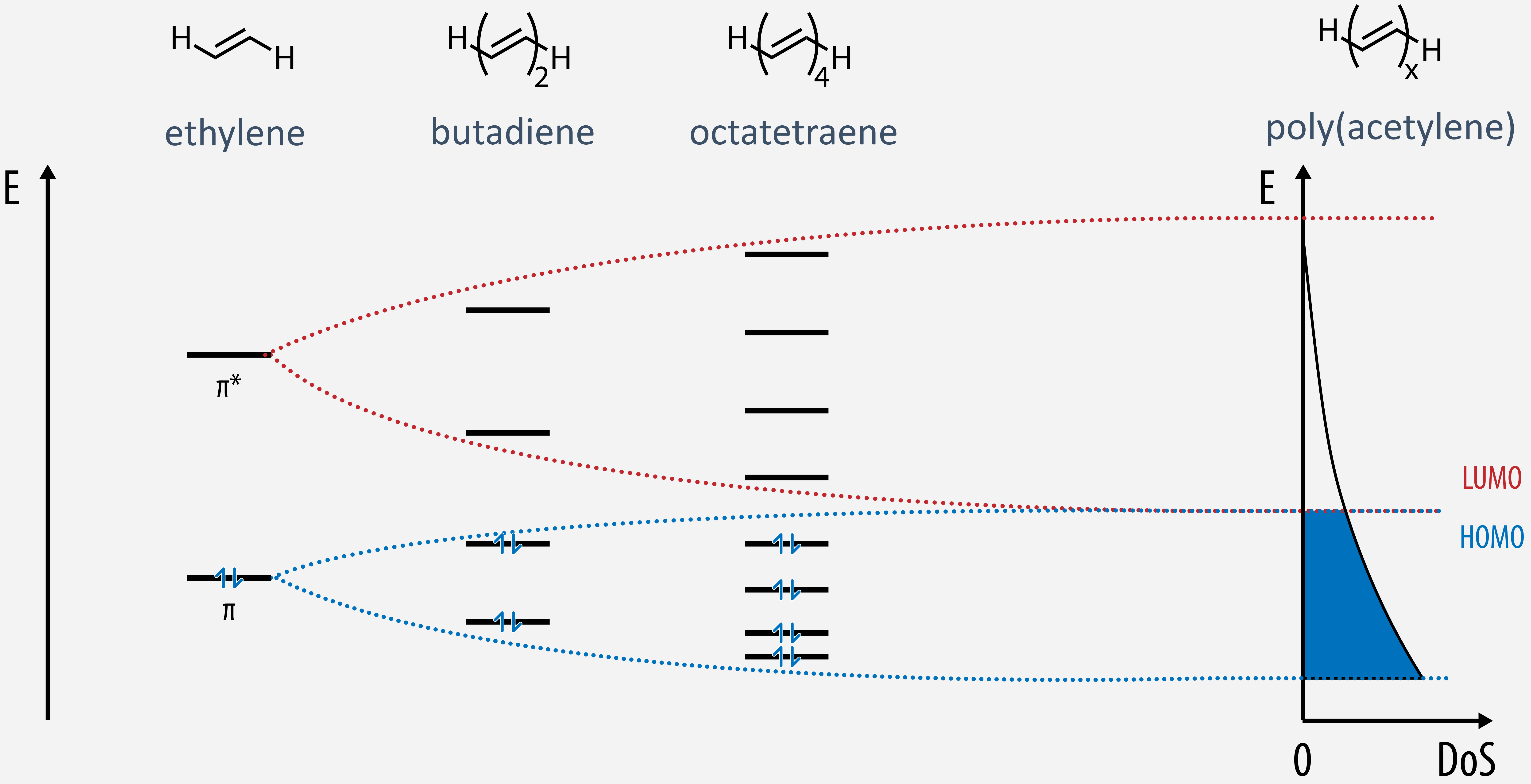
- HOMO-LUMO gap, and its limit for large N

$$E_g = E_{LUMO} - E_{HOMO} = (N+1)\frac{\hbar^2\pi^2}{2md^2N^2} \approx \frac{1}{N}\frac{\hbar^2\pi^2}{1md^2} \propto \frac{1}{N}$$

- **for an “infinite” linear π-conjugated system, the HOMO-LUMO gap converges to zero!**

KEY CONCEPT: see reader *“Quantum States of π-Electrons in Polyacetylene”* for details

Electronic Structure of Extended Linear π-Conjugated Systems



- set of MO with energy differences $\Delta E \sim 1/N$ much smaller than thermal energy $k_B T$
- **partially filled band**, so **poly(acetylene) would be a metallic conductor! (it is not!)**
- but **energy levels** $\propto n^2$; so **density of states (DoS) decreases** with inreasing energy! **(it does not!)**

Hückel Theory of Linear π-Conjugated Systems

- optoelectronic properties of molecules determined by “frontier orbitals”, HOMO and LUMO
- in π-conjugated molecules, HOMO and LUMO are π-orbitals from interaction of $2p_z$ orbitals

- **Hückel theory provides simple and fast solutions, in good agreement with precise calculations, further approximations: over molecular orbital theory (MOT)**

1. Born Oppenheimer approximation
2. independent electrons approximation
3. LCAO approximation
4. **no spatial overlap between distinct p_z orbitals, $S = 0$**

   diagonal matrix elements $\alpha_{ii} - E$, all others β_{ij}

5. **interactions only between direct neighbors**

   diagonal matrix elements $\alpha_{ii} - E$, between neighbors β_{ij} for $i - j = \pm 1$, all others 0

6. **all similar interactions are equal for all the $2p_z$ orbitals**

   diagonal matrix elements $\alpha - E$, elements between neighbors β, all others 0

KEY CONCEPT: see reader *“Quantum States of π-Electrons in Polyacetylene”* for details

Hückel Theory of Linear π-Conjugated Systems

- Hückel theory results in more simplified secular determinant than LCAO, easier to calculate
- model can be straightforwardly extended to linear π-conjugated systems with *N* carbons

LCAO, *N* = 2

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

Hückel, *N* = 2

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

Hückel, *N* = 6

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

- Eigenvalues for Schrödinger equation for Hückel model of linear system with N carbons:

$$E_n = \alpha + 2\beta \cdot \cos\left(\frac{n \cdot \pi}{N+1}\right)$$

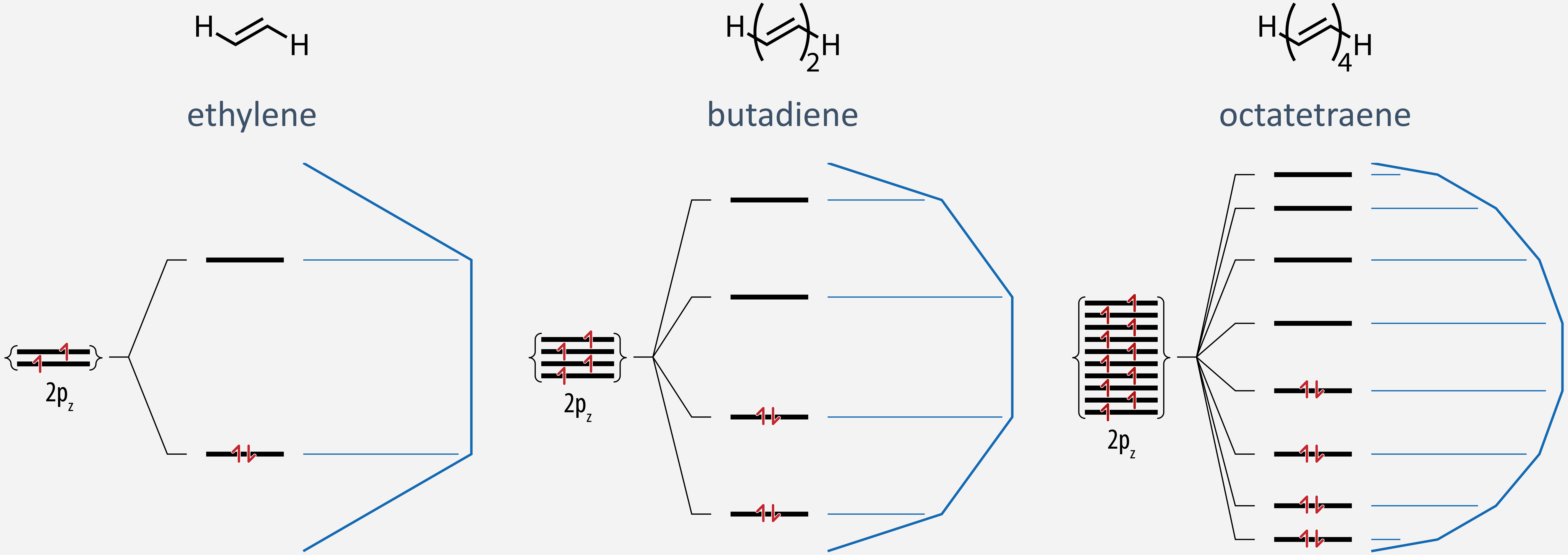
- **also energy level differences from Hückel theory approximately scale with** $\Delta E \sim 1/N$

C.A. Coulson, *Proc. Poy. Soc.* **1938**, A164, 383; **1939**, A169, 413; **1947**, A192, 16.

Energy Levels in Hückel Theory of Linear π-Conjugated Systems

- a graphical method to draw the relative energy levels in linear π-conjugated systems

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

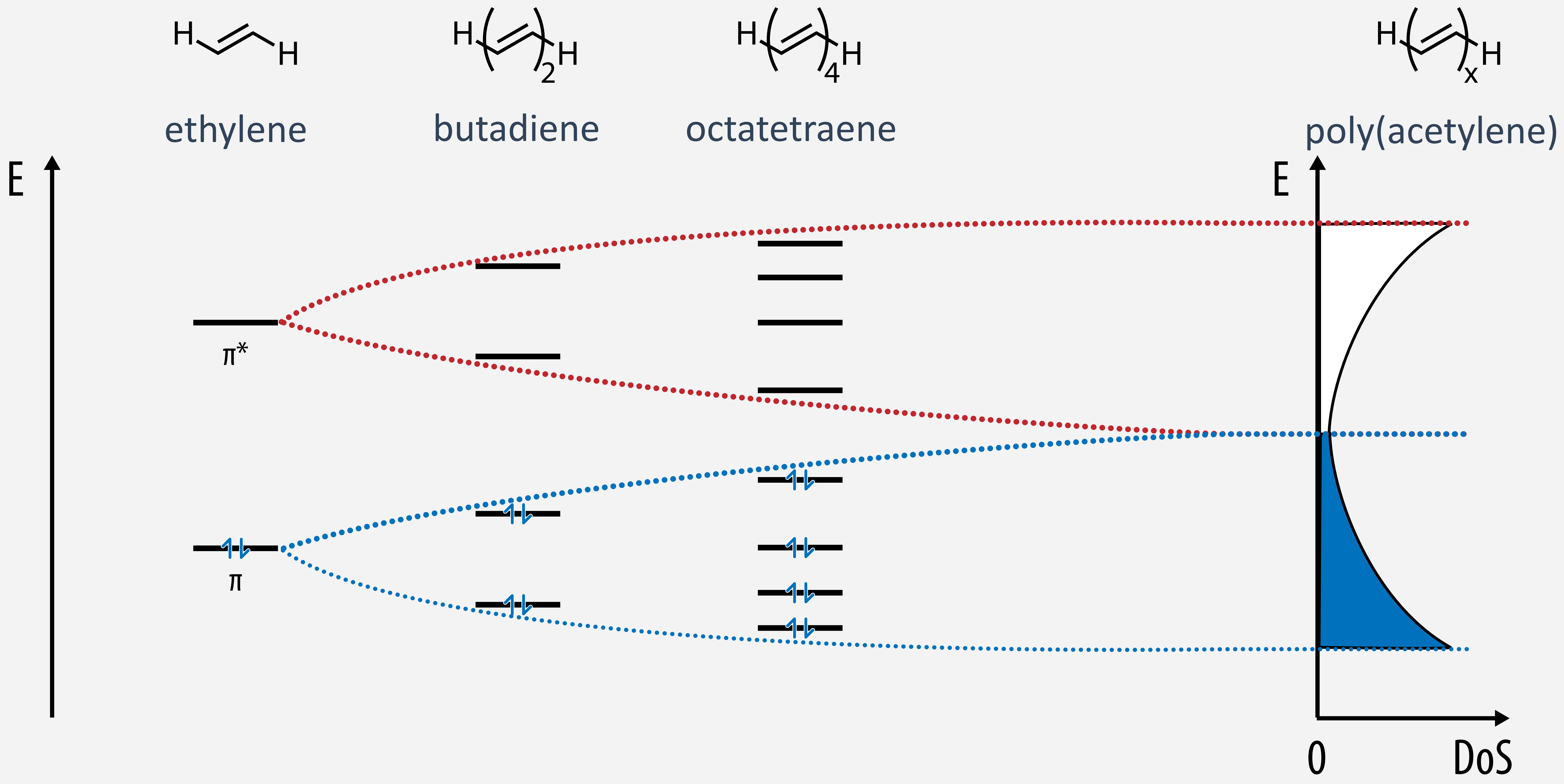


- **due to *S* = 0, symmetric energy splitting centered around p_z orbital level**
- **isolated, not evenly spaced MO levels, but energy differences scale with** $\Delta E \sim 1/N$
- **higher density of states at the top and the bottom of the energy diagram**
- **entire π system thermodynamically more stable (delocalization), but HOMO/LUMO more reactive**

see reader *"Quantum States of π-Electrons in Polyacetylene"* for details

Electronic Structure of Extended Linear π-Conjugated Systems

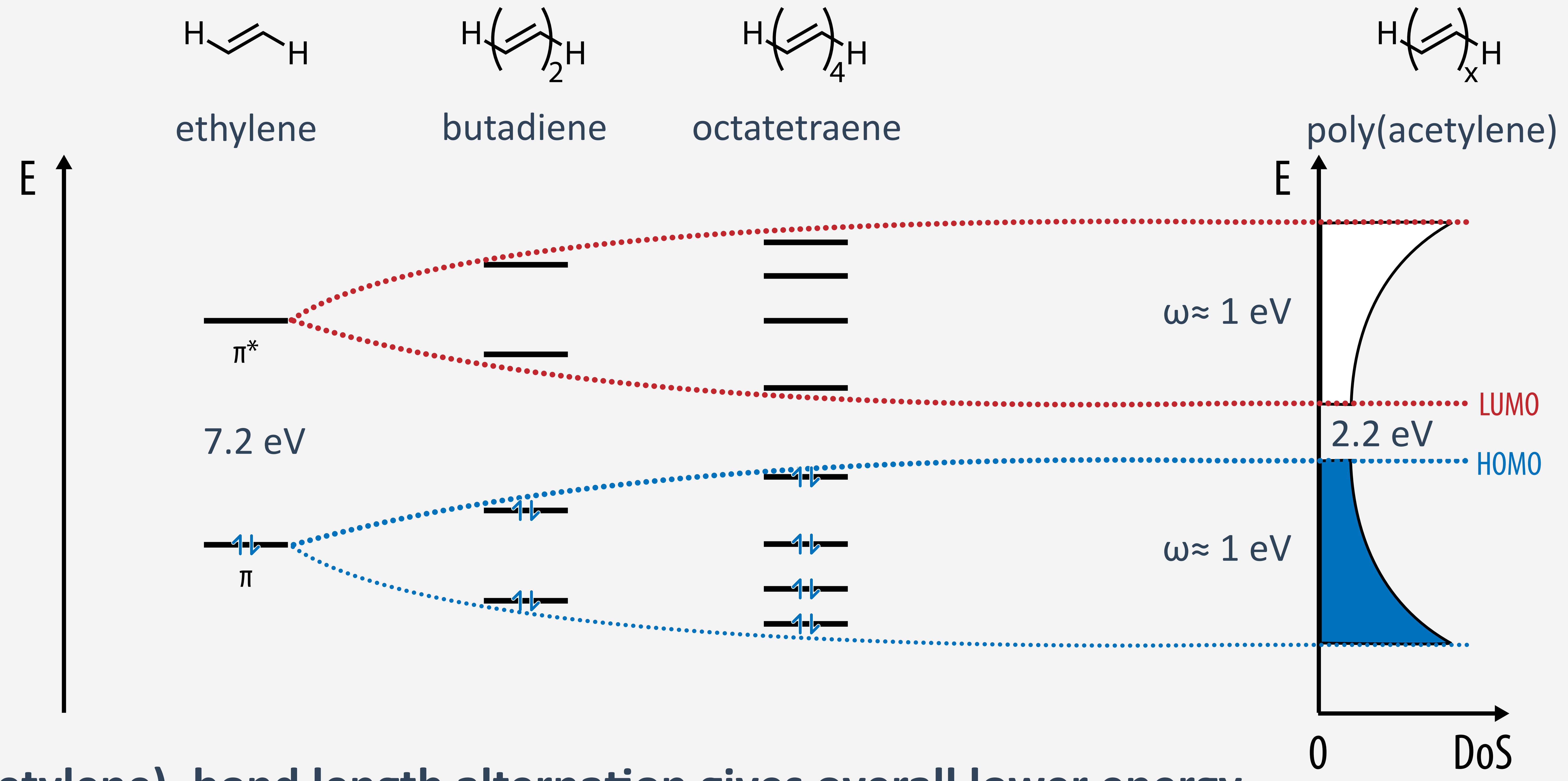
- schematic MO energy diagram of frontier orbitals according to Hückel theory



- **discrete, unevenly spaced MO levels, but energy differences $\Delta E \sim 1/N < k_b T$**
- **partially filled band, so Hückel model predicts poly(acetylene) to be a metallic conductor!**
- **different from electron in a 1D box model, lower density of states in the middle of the band**

Electronic Structure of Extended Linear π-Conjugated Systems

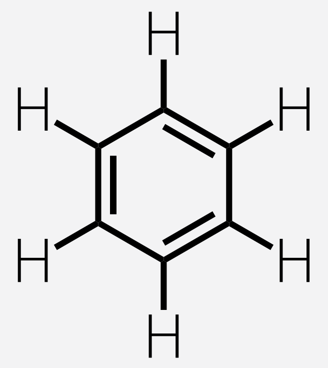
- Peierl's distortion: 1D metals are not thermodynamically stable, undergo geometry distortion

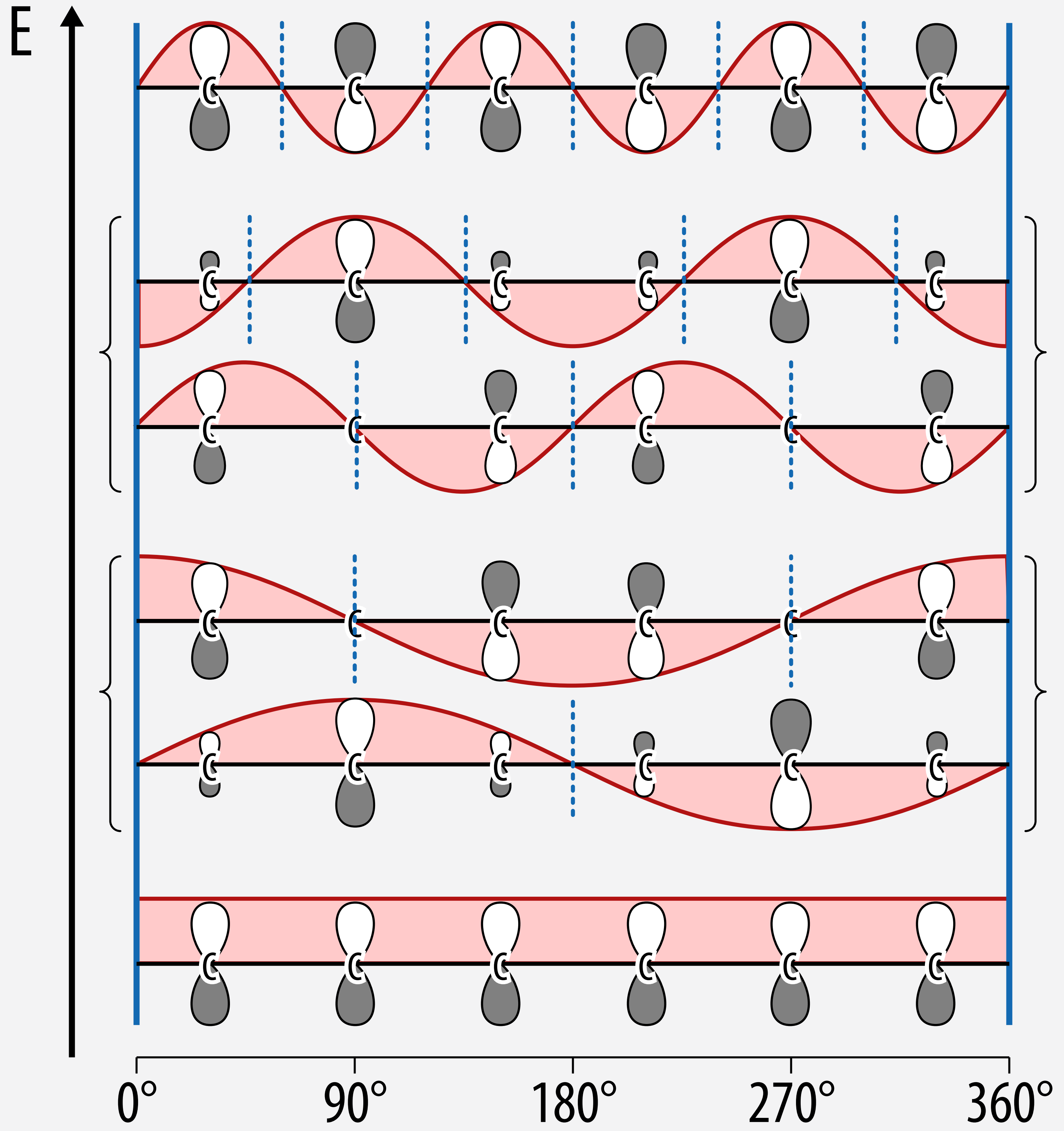


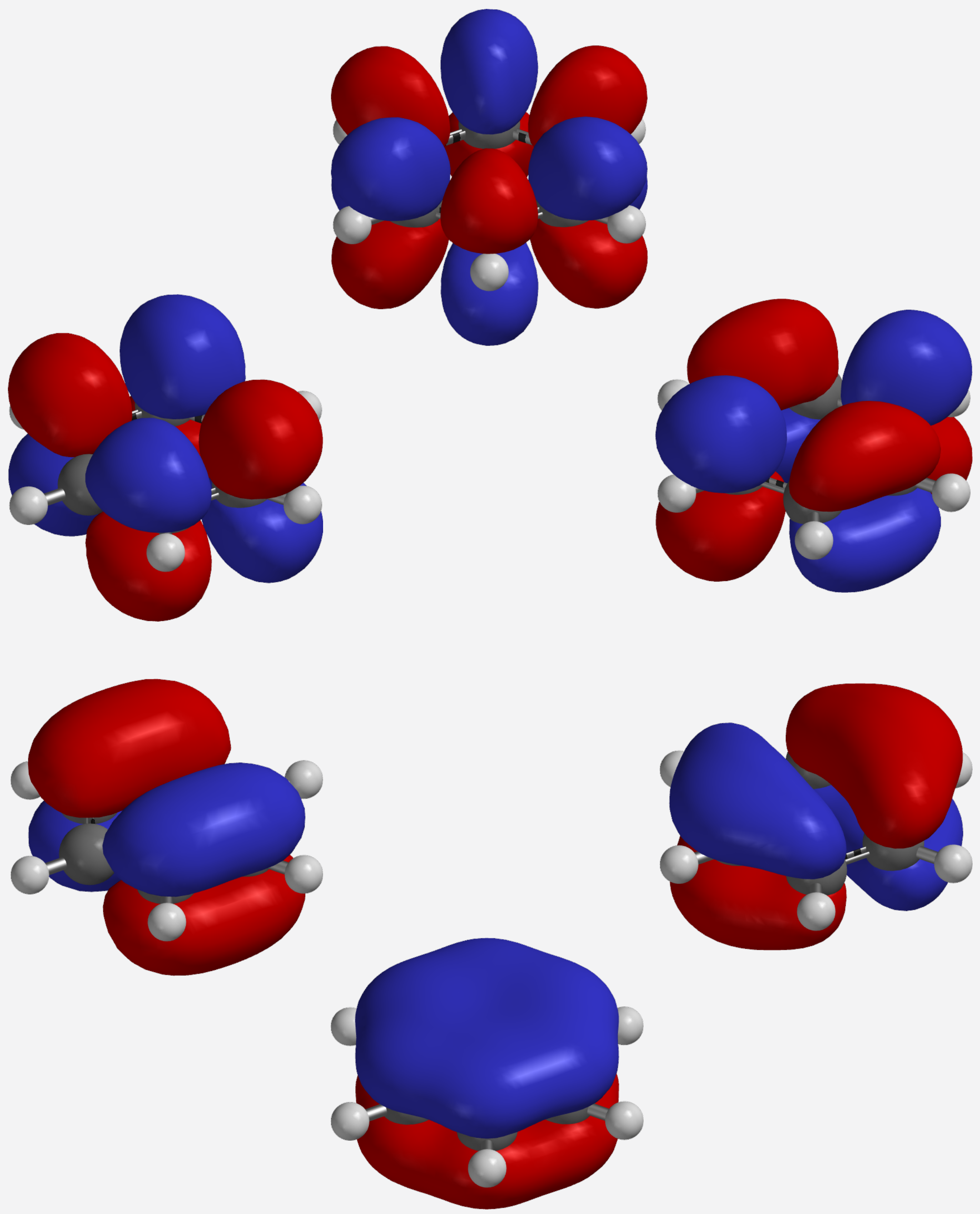
- **for poly(acetylene), bond length alternation gives overall lower energy**
- **central density of states not only lower but reduced to 0, which opens band gap (of about 2.2 eV)**
- **indeed all states fully delocalized on the molecular level (in single-crystalline state)**
- **polyacetylene is a poor semiconductor, very few charge carriers and $\mu = 10^{-6}$ cm^2 V^{-1} s^{-1}**

Electron in a Box Model for Cyclic π-Conjugated Systems

- electron in a box with steady boundary condition is a simple model for cyclic systems

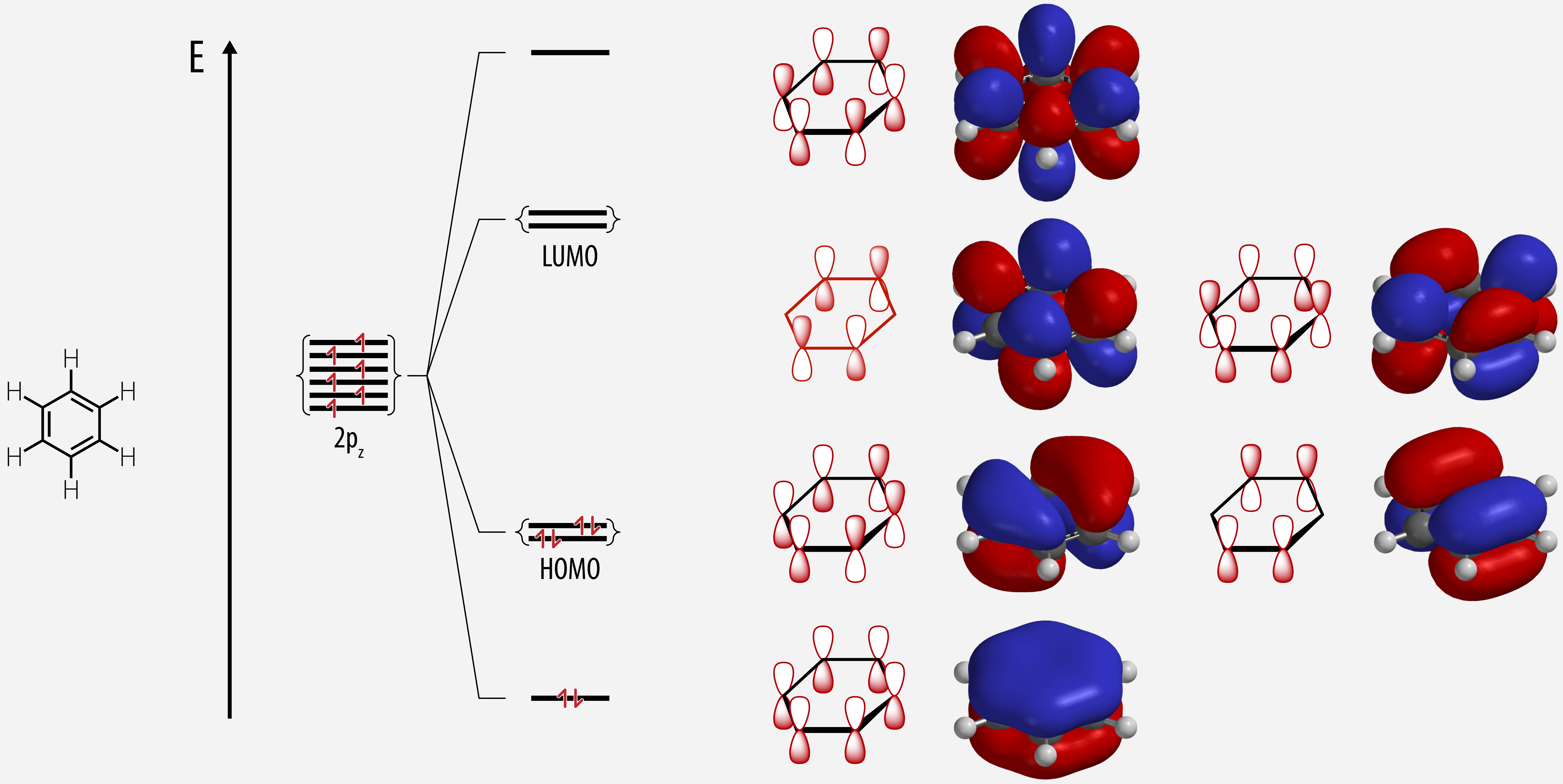






- **all π-orbitals extend over all six carbons, “do not look like” double bond MO**
- **lowest MO is a constant, all others come in pairs of two (sin, cos), othogonal, degenerate in energy**
- **two degenerate HOMO better stabilized than π* in ethene; aromatic π-system more stable**

Electron in a Box” Model for Cyclic π-Conjugated Systems



- **two degenerate HOMO better stabilized than π* in ethene; aromatic π-system very stable**

Hückel Theory of Cyclic π-Conjugated Systems

- Hückel theory can also be applied to cyclic π-conjugated systems with *N* carbons
- interactions between “first” and “last” carbons of the cycle result in additional off-diagonal elements

Hückel, *N* = 6, linear

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

Hückel, *N* = 6, cyclic

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

- eigenvalues for Schrödinger equation for Hückel model of cyclic system with *N* carbons:

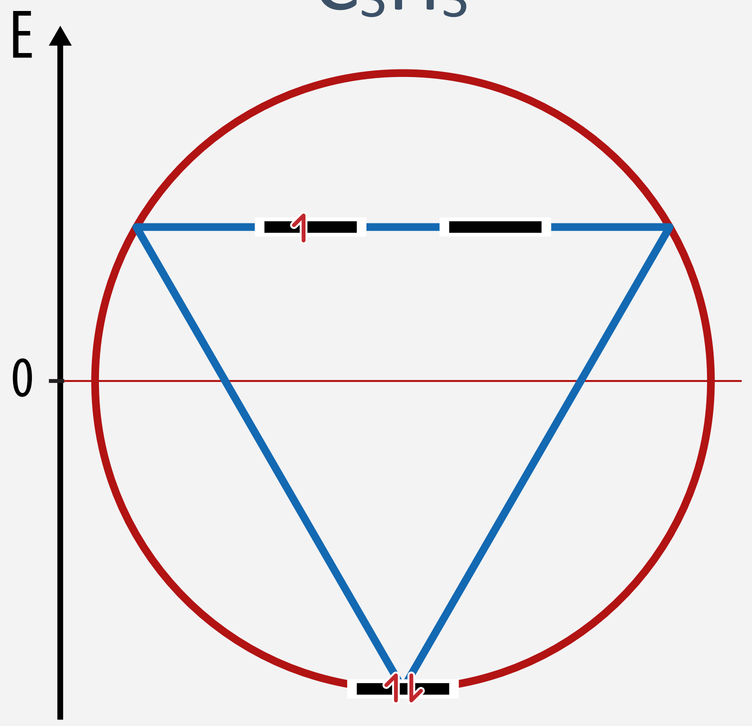
$$E_n = \alpha + 2\beta cos(\frac{2n\pi}{N})$$

- **energy level differences for cyclic systems from Hückel theory scale with** $\Delta E \sim 1/N$

C.A. Coulson, Proc. Poy. Soc. 1938, A164, 383; 1939, A169, 413; 1947, A192, 16.

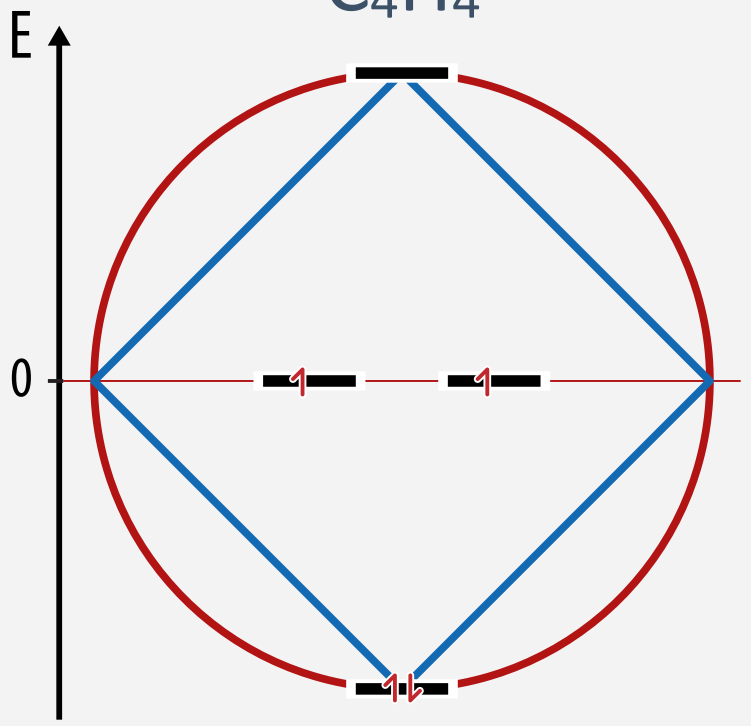
Approximation for the MO Energy Diagrams of Cyclic π-Conjugated Systems

$C_3H_3^{\bullet}$



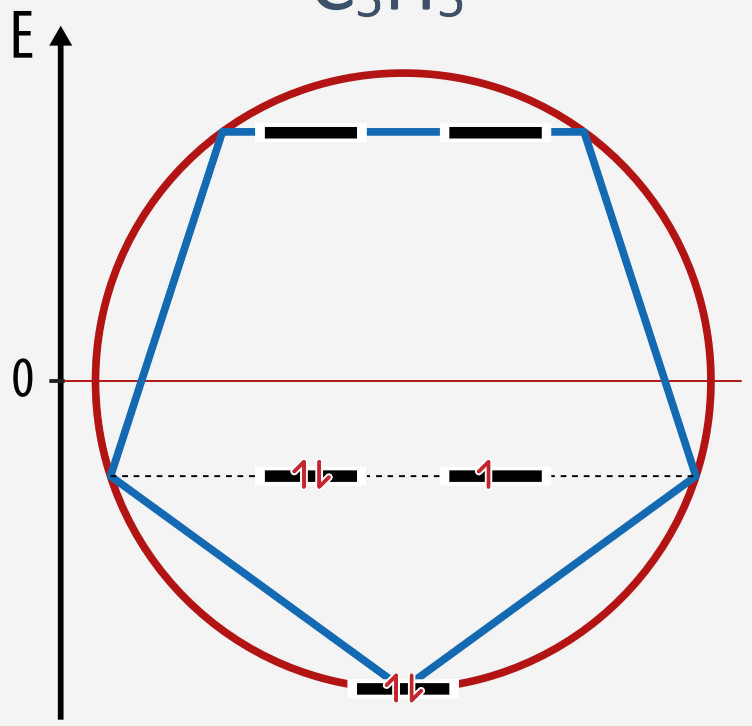
very unstable
open shell, destabilized

C_4H_4



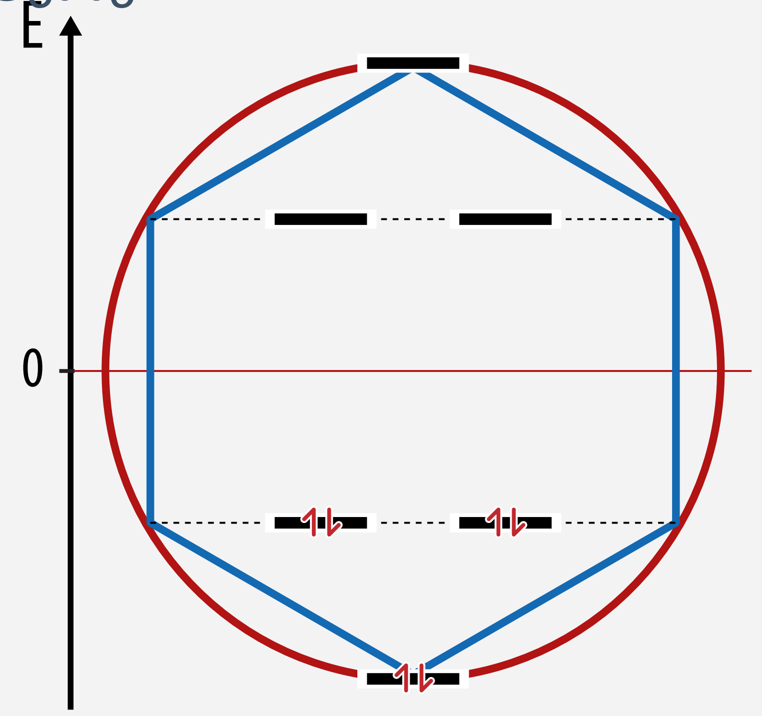
very unstable
open shell, destabilized

$C_5H_5^{\bullet}$



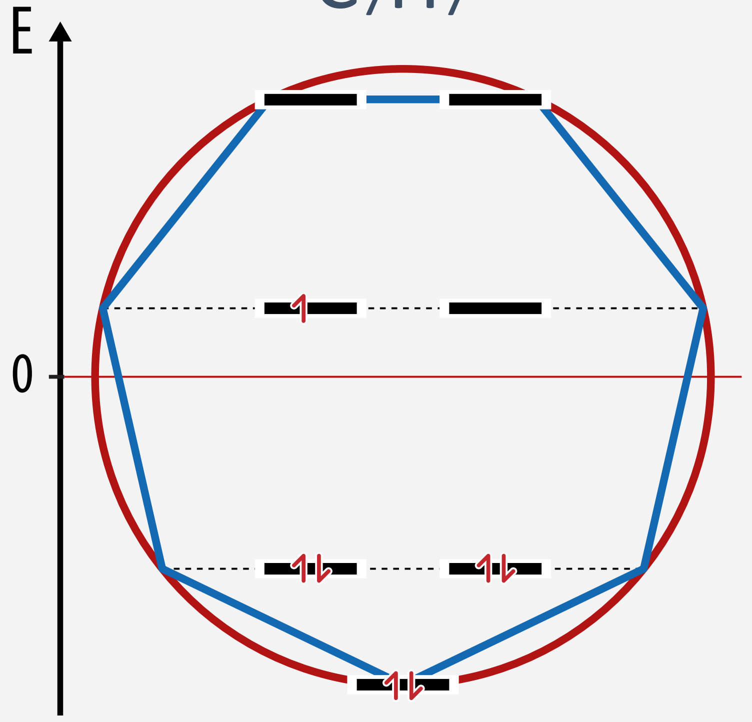
unstable
open shell, stabilized

C_6H_6



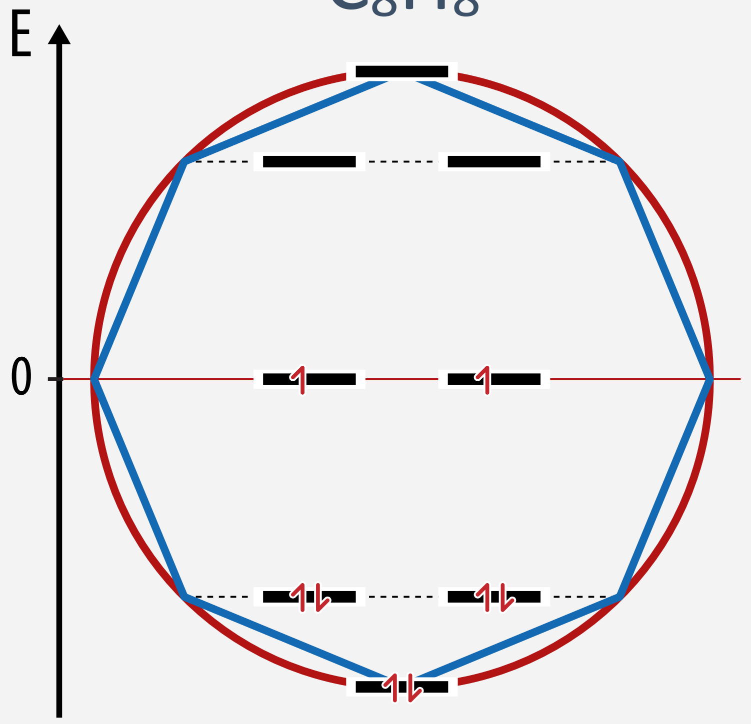
very stable
closed shell, stabilized

$C_7H_7^{\bullet}$



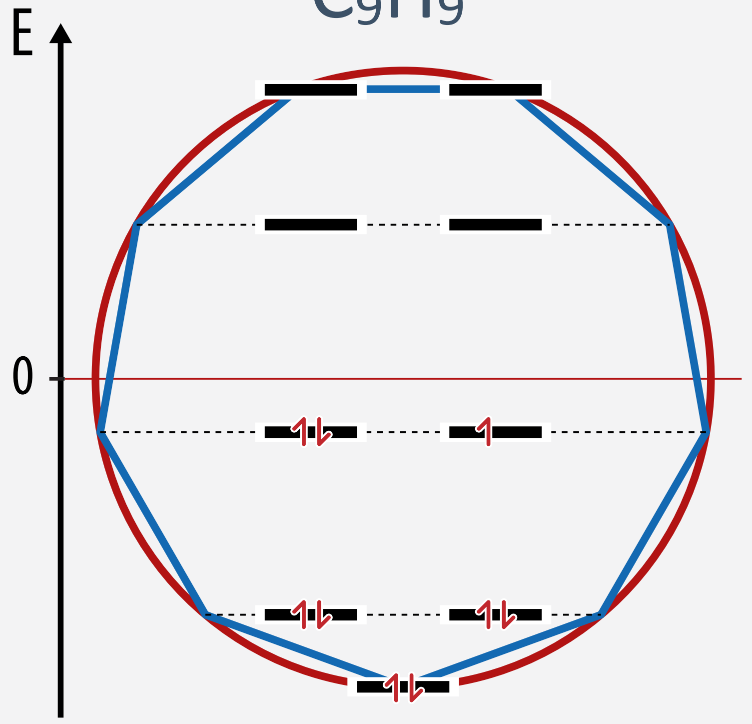
very unstable
open shell, destabilized

C_8H_8



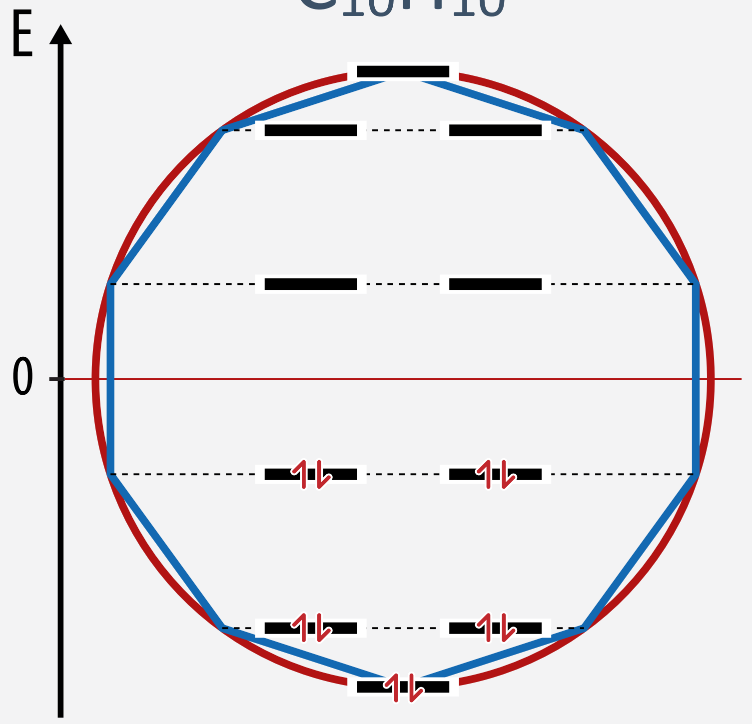
very unstable
open shell, destabilized

$C_9H_9^{\bullet}$



unstable
open shell, stabilized

$C_{10}H_{10}$

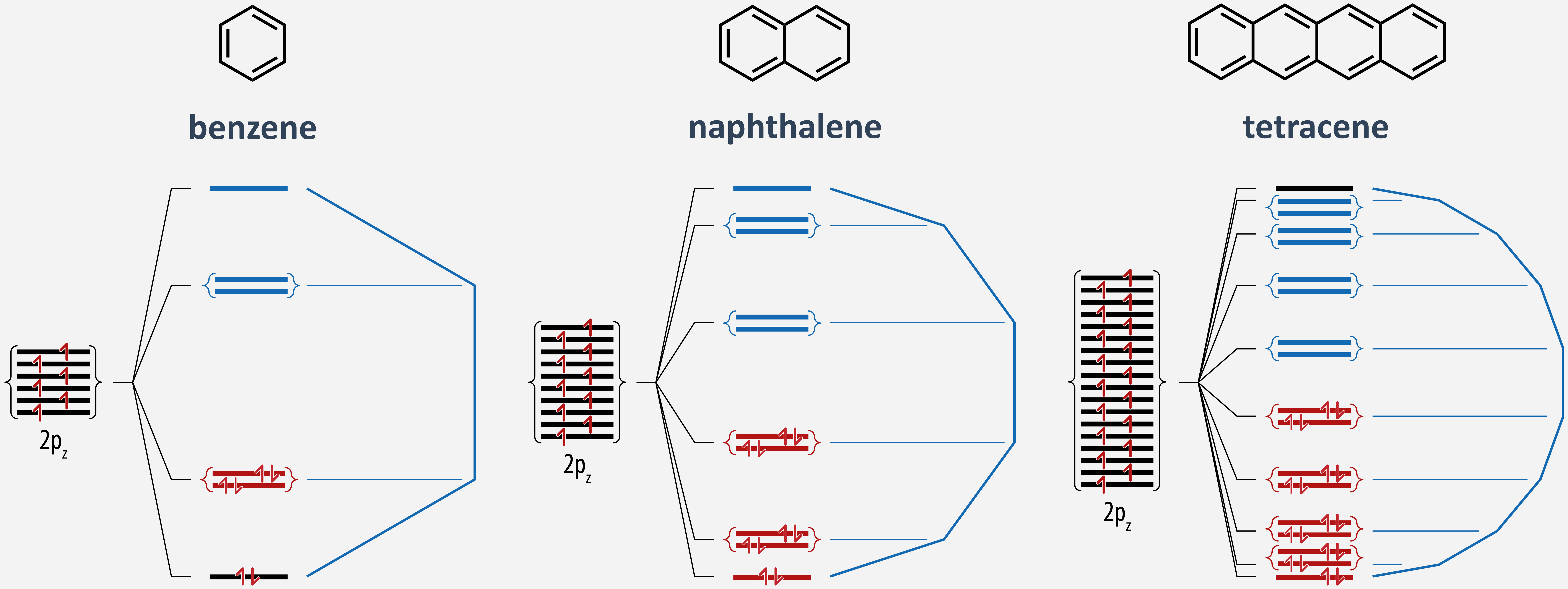


very stable
closed shell, stabilized

- **Hückel rule for aromaticity: monocyclic conjugated systems, 4*n*+2 electrons, highly stable**

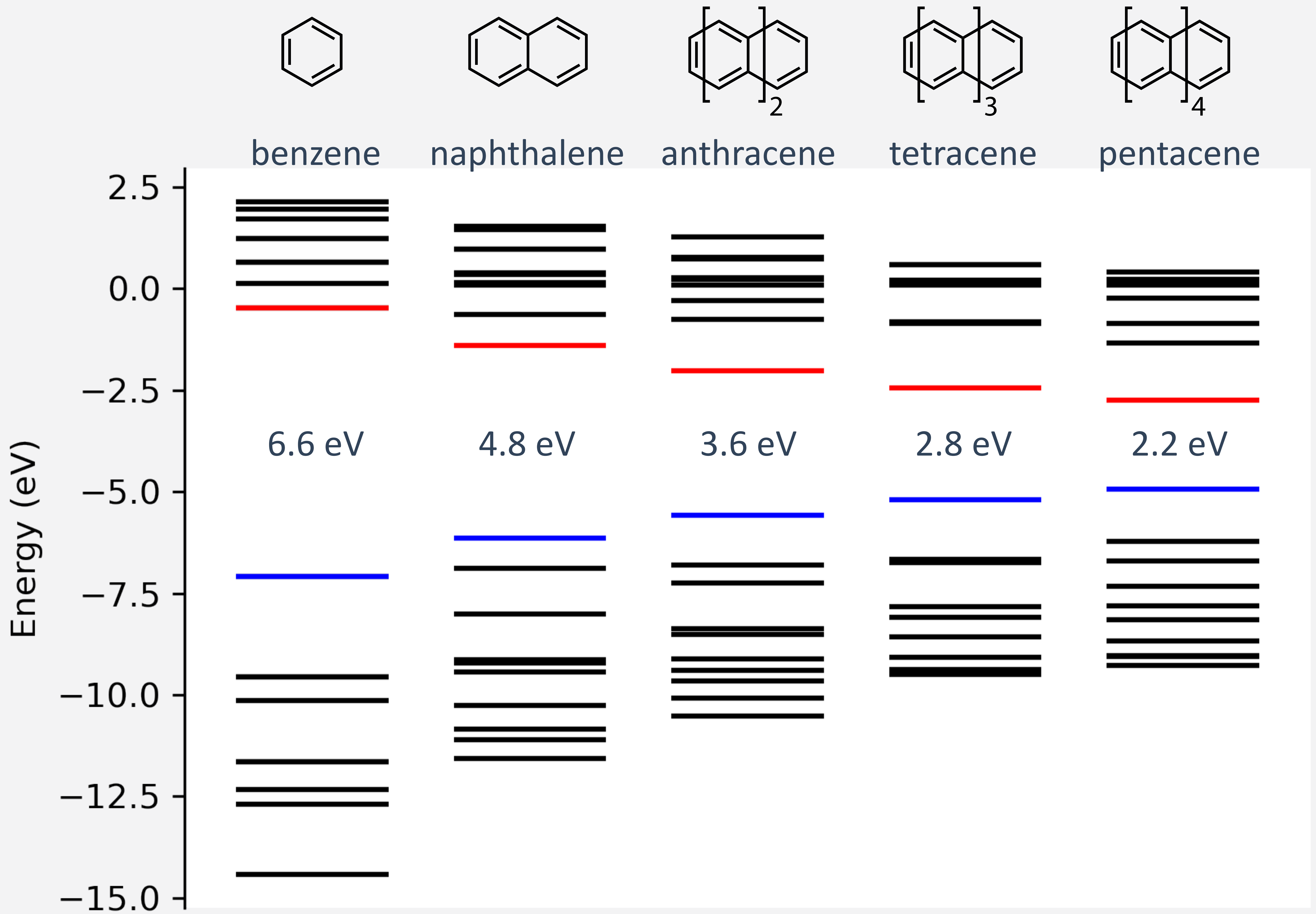
Energy Levels in Hückel Theory of Linear π-Conjugated Systems

- the same graphical method can also be used as a coarse approximation for the acene series
- a more exact treatment would require additional matrix elements (for cross-ring bonds)



- **due to S = 0, symmetric energy splitting centred around pz orbital level**
- **isolated, not evenly spaced MO levels, but energy differences scale with** $\Delta E \sim 1/N$

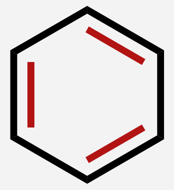
Electronic Structure of Polycyclic Aromatic Hydrocarbons



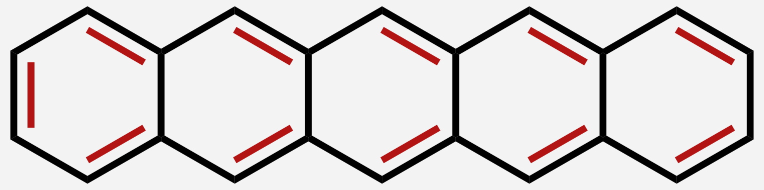
- **HOMO-LUMO gap narrows, MO levels get closer, but still located MO, no bands**
- **high MW acenes would be metallic conductors but become too reactive to be handled**

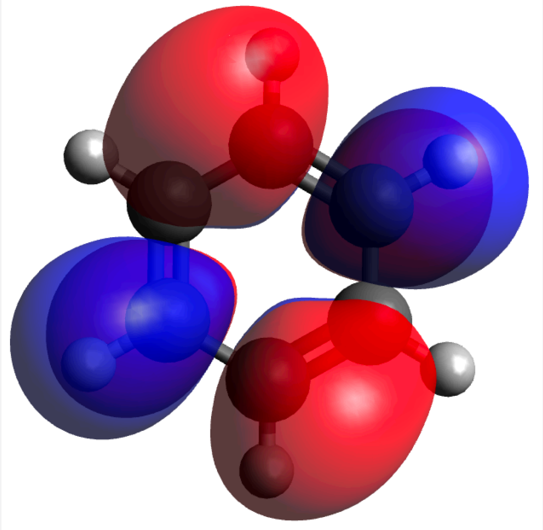
Frontier Orbitals of Benzene and Pentacene

benzene

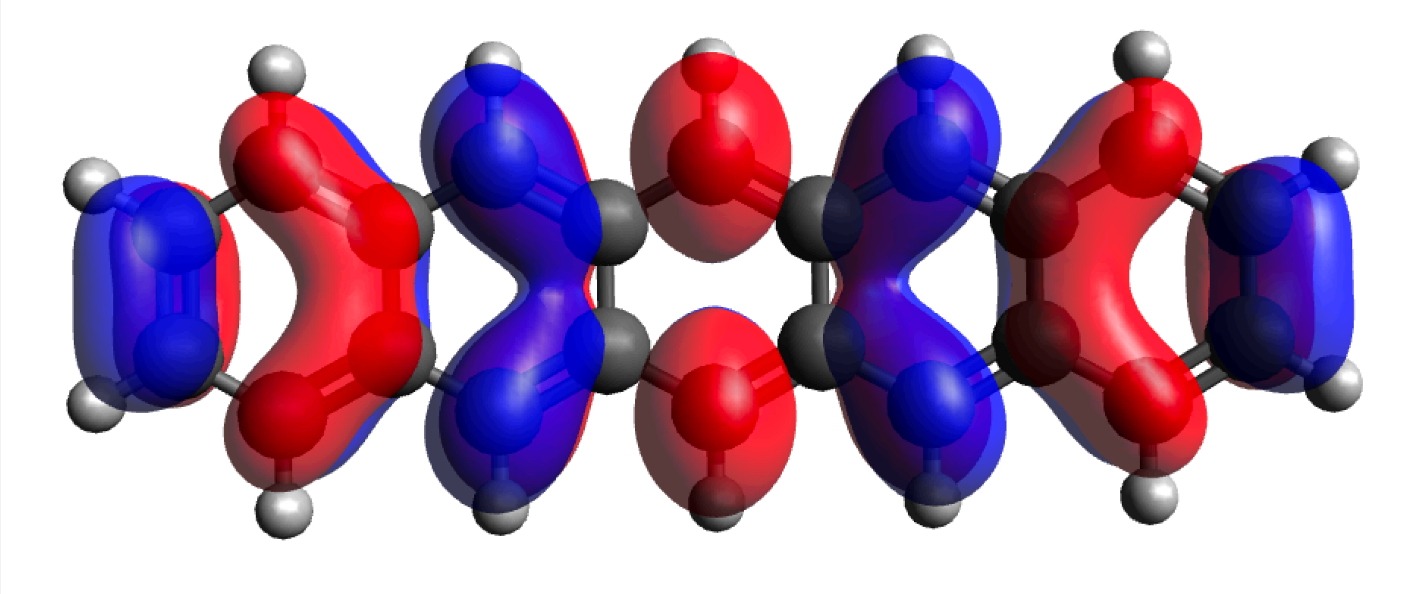


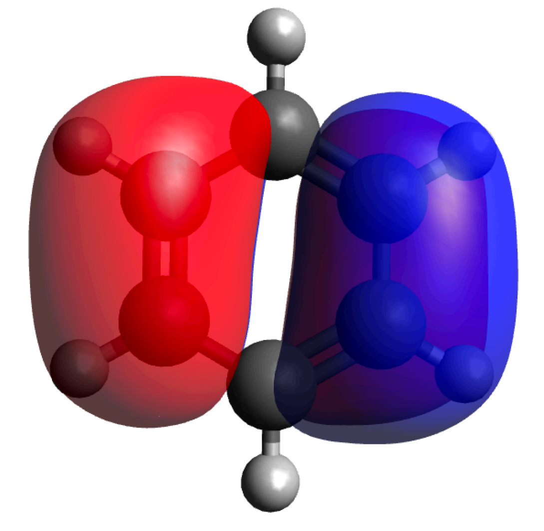
pentacene



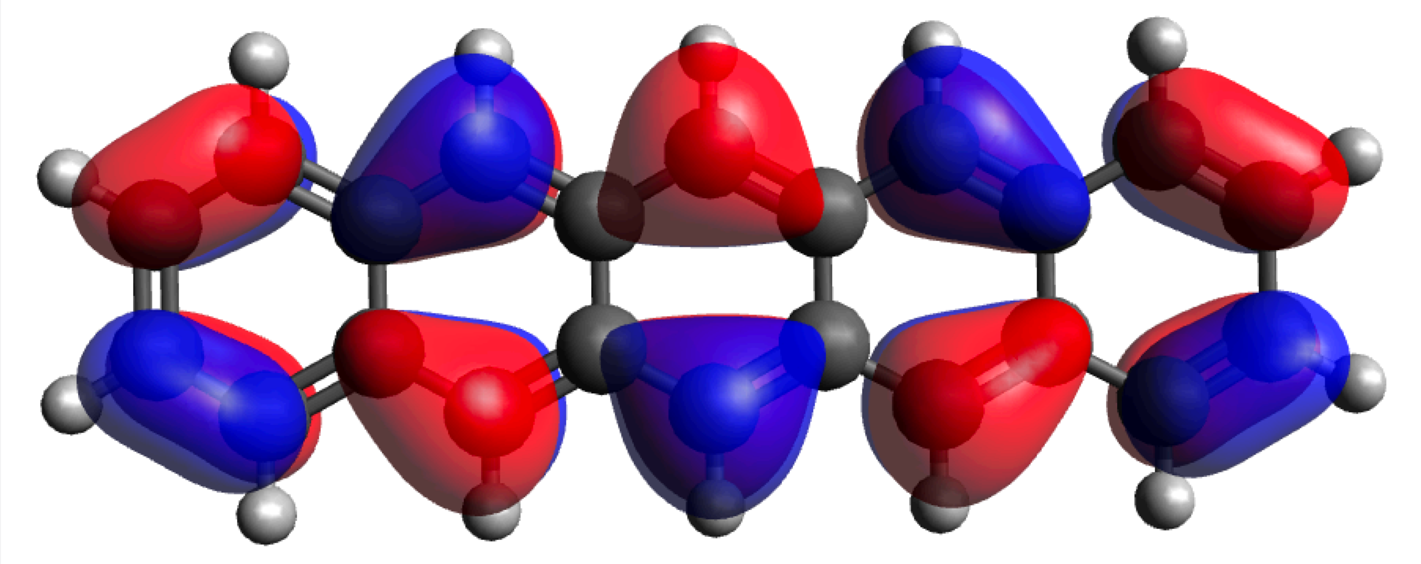


LUMO





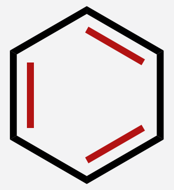
HOMO



Examples of Aromaticity and Aromatic Compounds

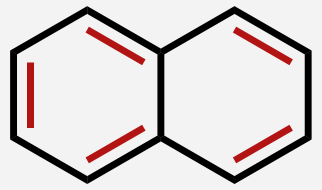
- “aromaticity” is a historically derived concept to describe “unusual” chemical stability

benzene



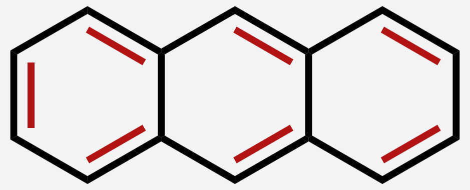
6π

naphthalene



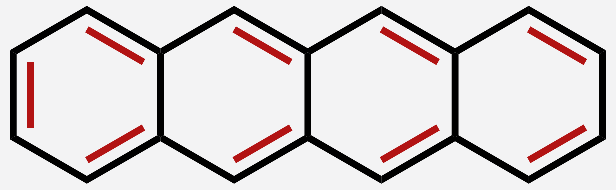
10π

anthracene



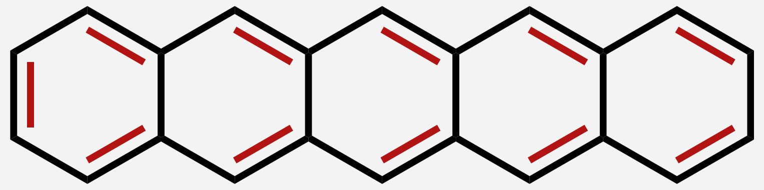
14π

tetracene



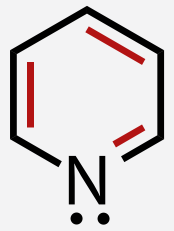
18π

pentacene



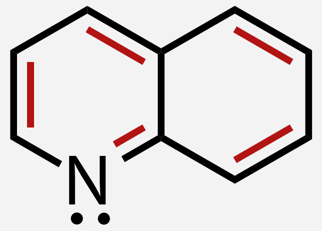
22π

pyridine



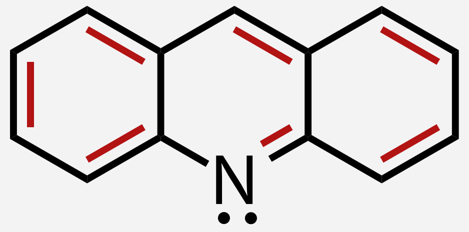
6π

quinoline



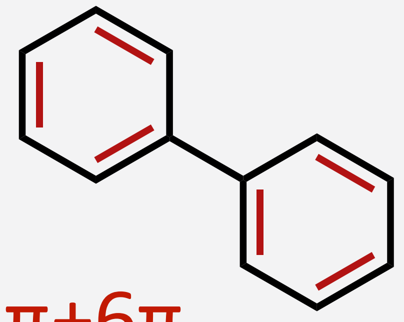
10π

acridine



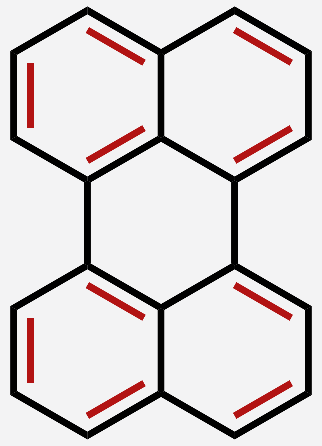
14π

biphenyl



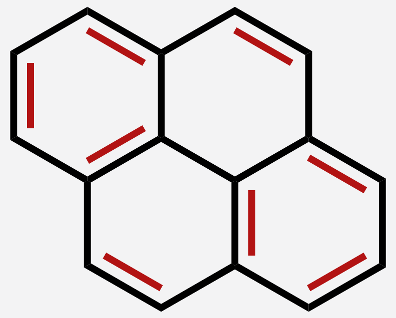
6π+6π

perylene



10π+10π

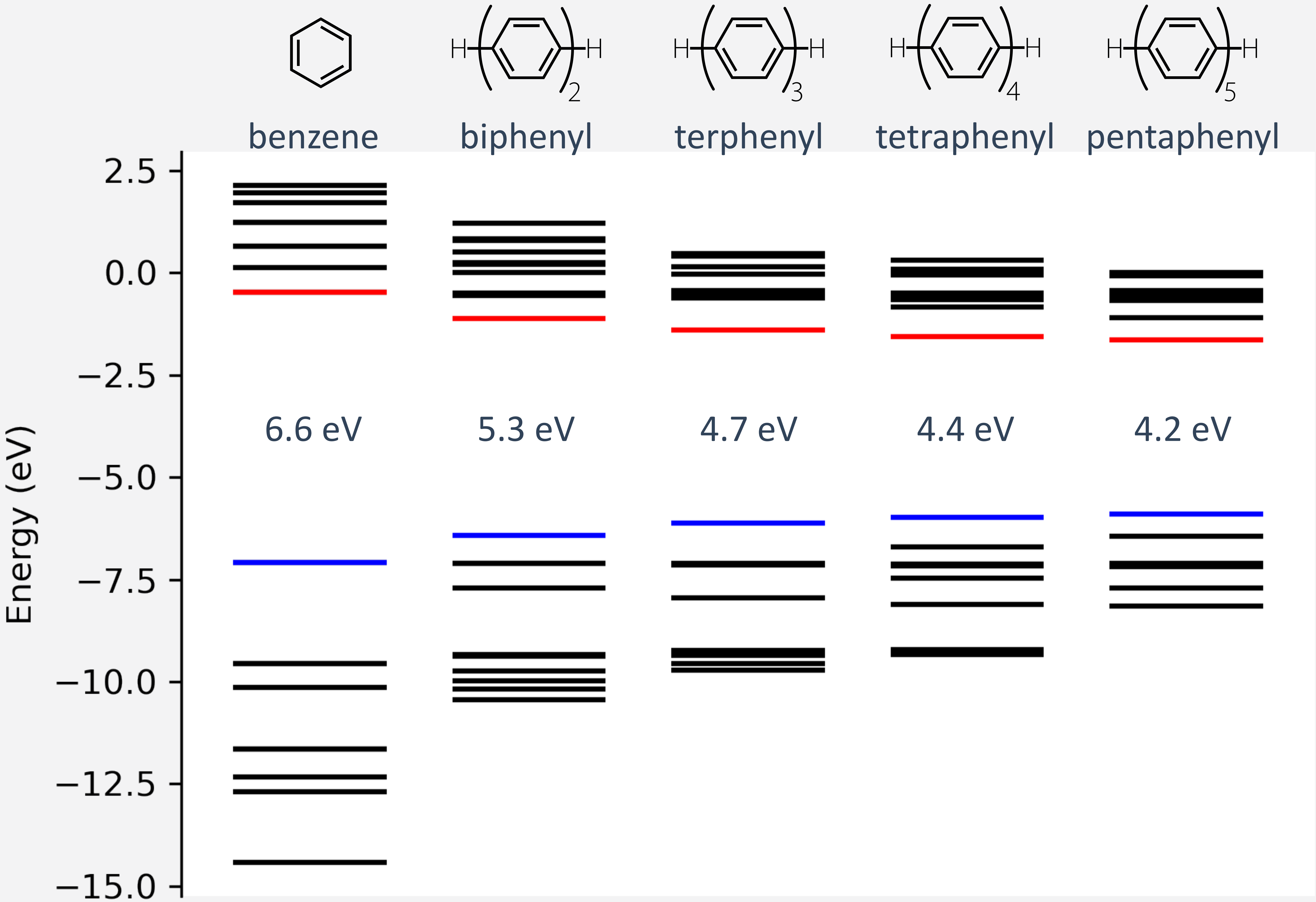
pyrene



16π

- **only benzene strictly fulfills Hückel definition of aromaticity (monocyclic, 4n+2 π electrons)**
- **in a broader sense, all compounds with cyclic conjugated π-systems are called “aromatic”**
- **including compounds with heteroatoms, or systems with 4n π electrons (less stable)**

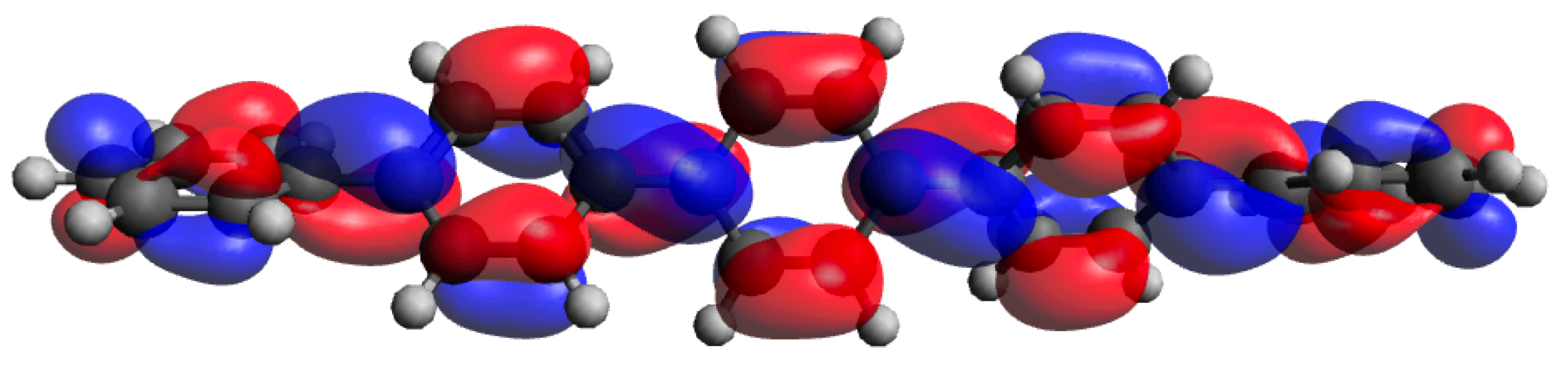
Electronic Structure of Polycyclic Aromatic Hydrocarbons



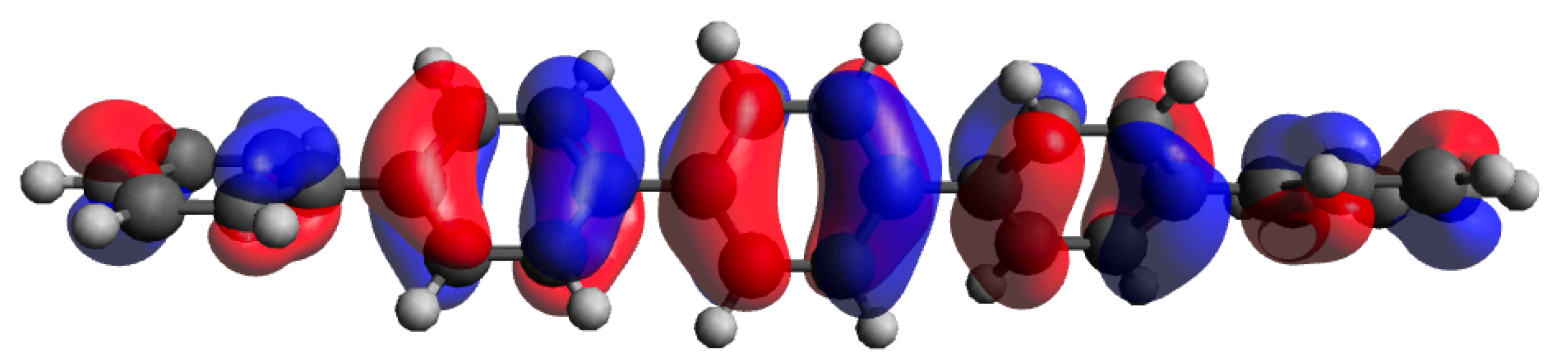
- **upon increasing the size of the conjugated system, the HOMO-LUMO gap narrows**
- **MO levels get closer, start to interact with one another, but still located MO, no bands**

Frontier Orbitals of Pentaphenyl

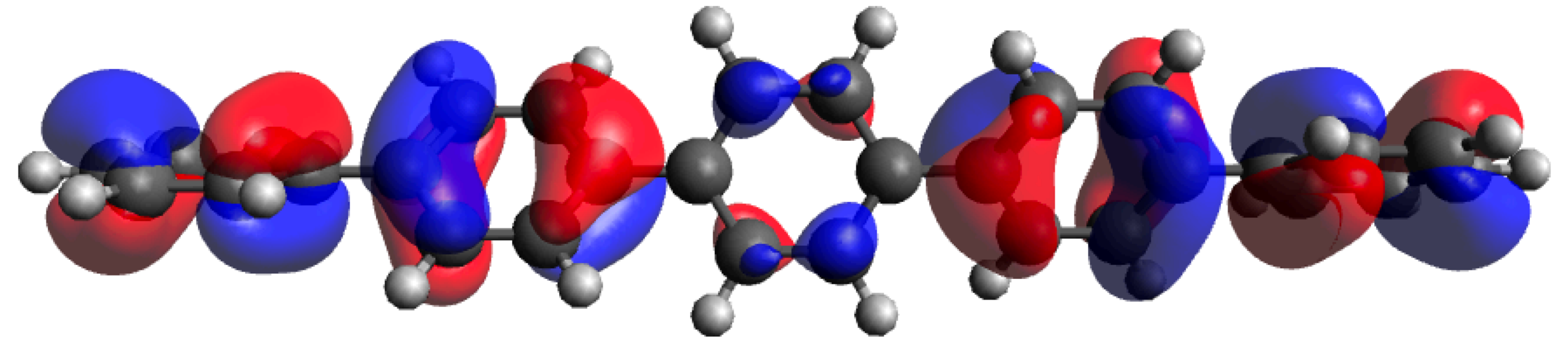
LUMO



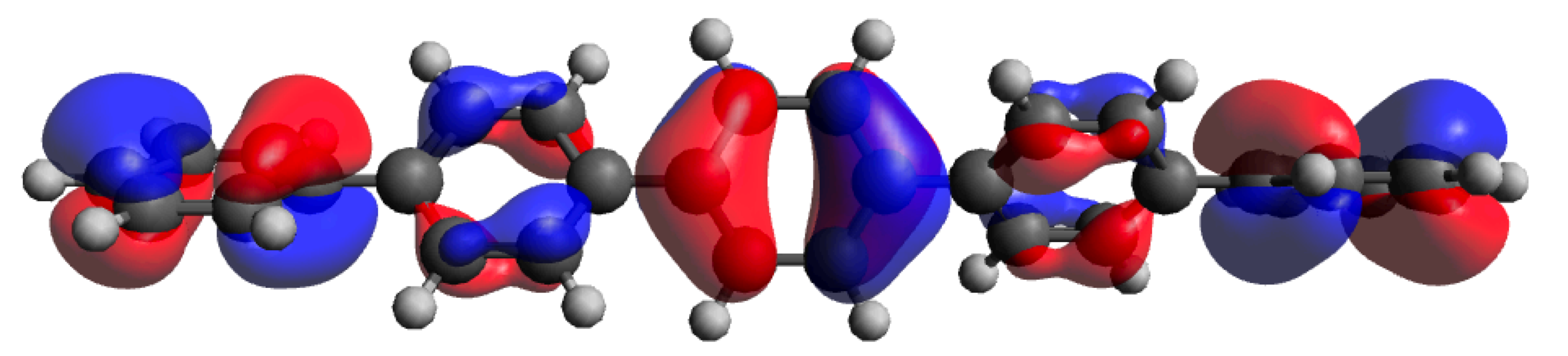
HOMO



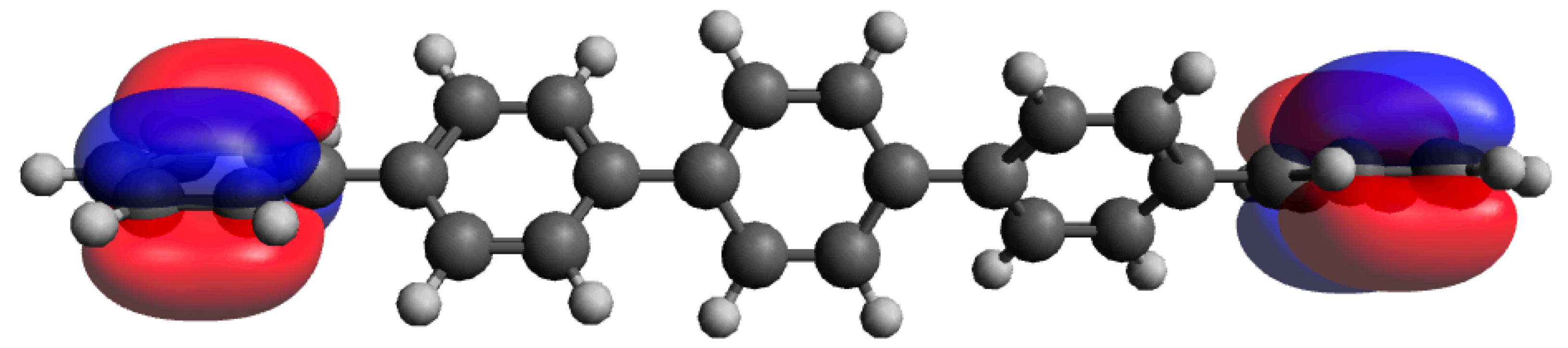
HOMO-1



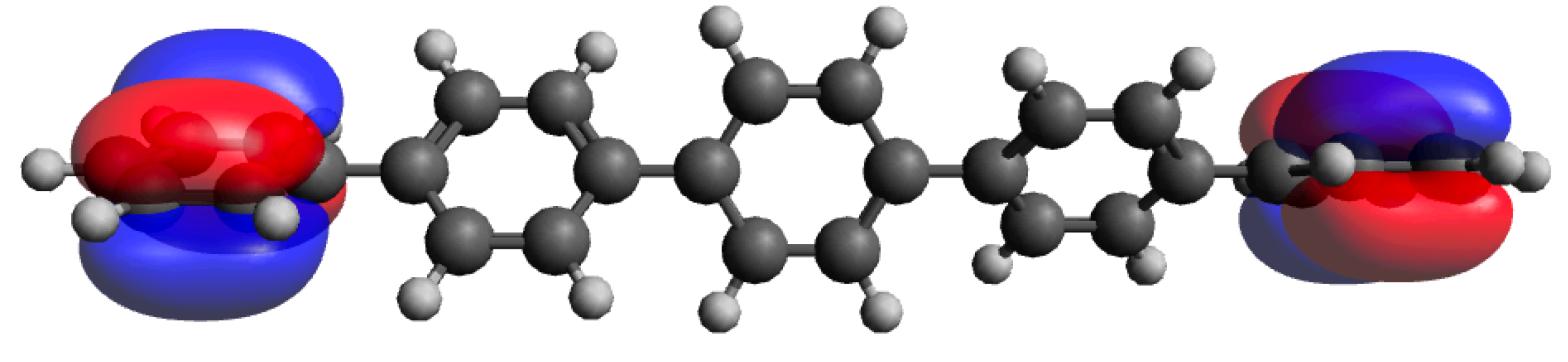
HOMO-2



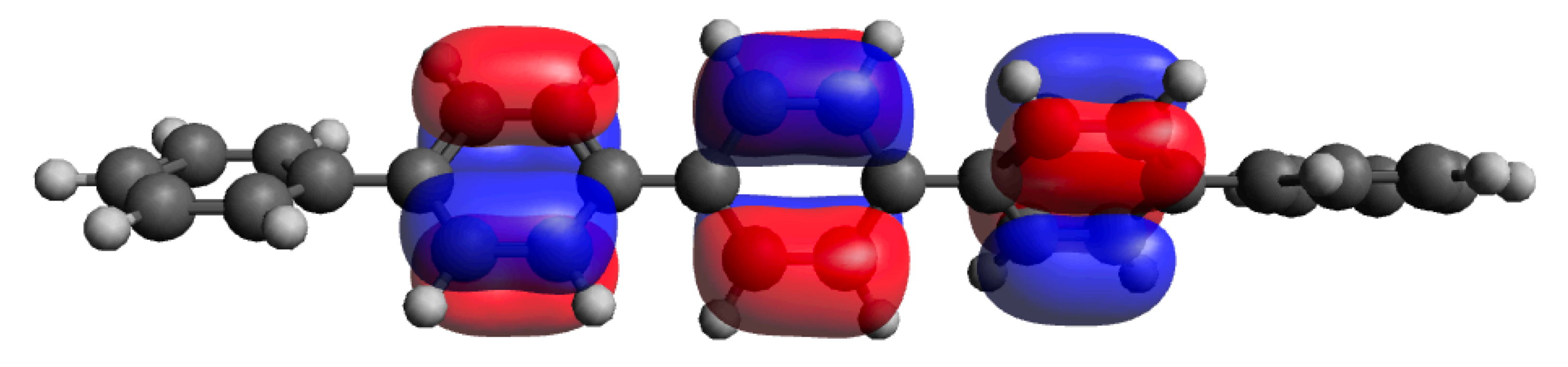
HOMO-3



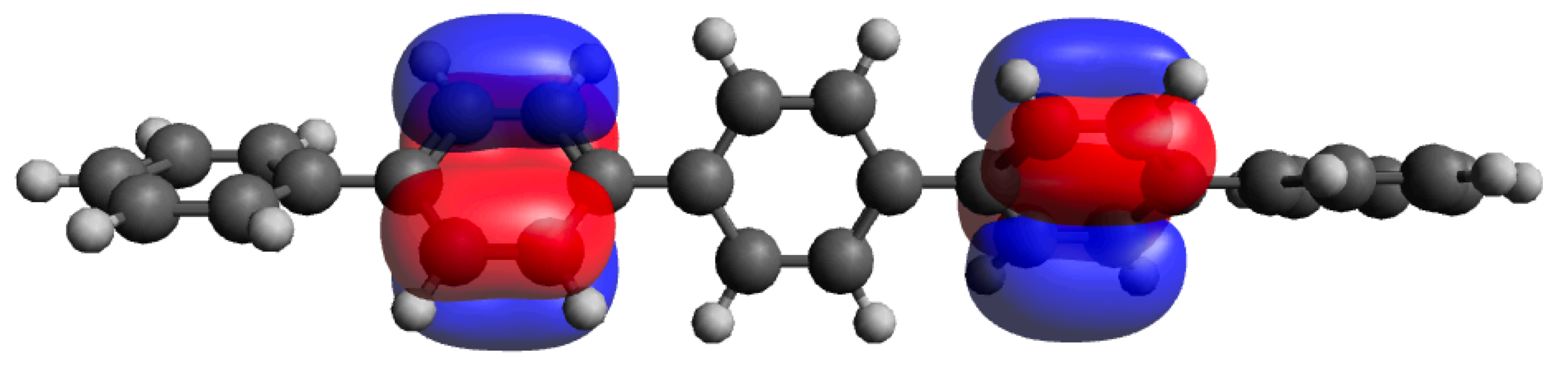
HOMO-4



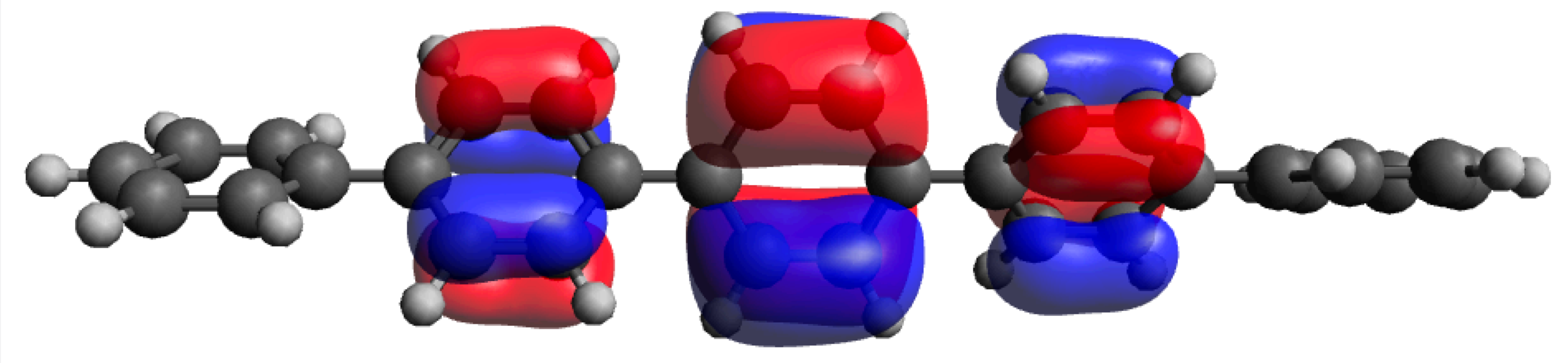
HOMO-5



HOMO-6

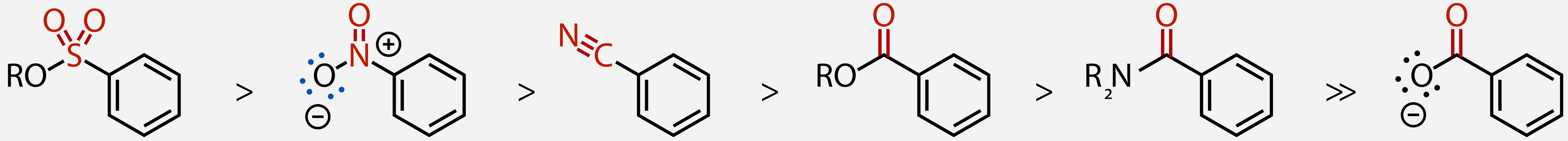


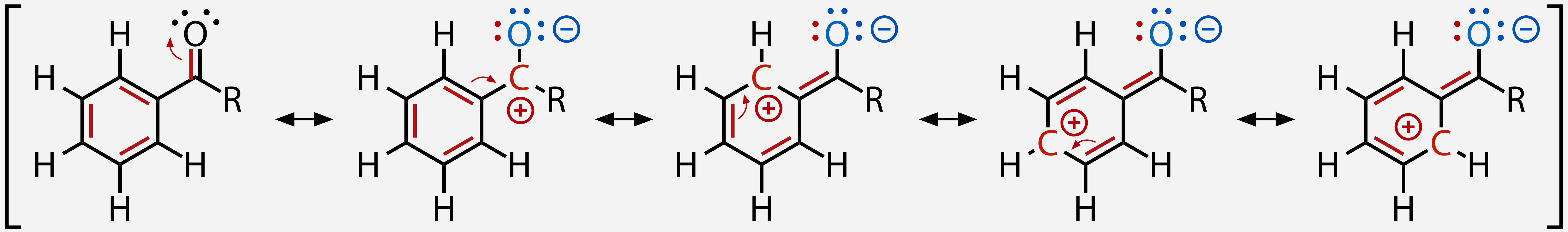
HOMO-7

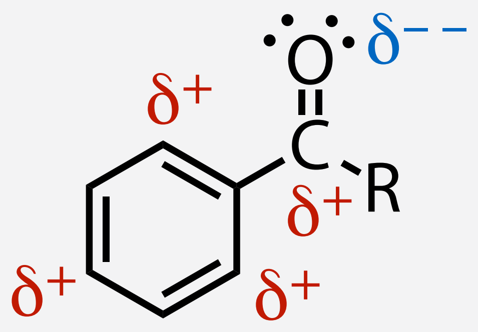


Resonance Structures Involving Electron-Withdrawing Groups

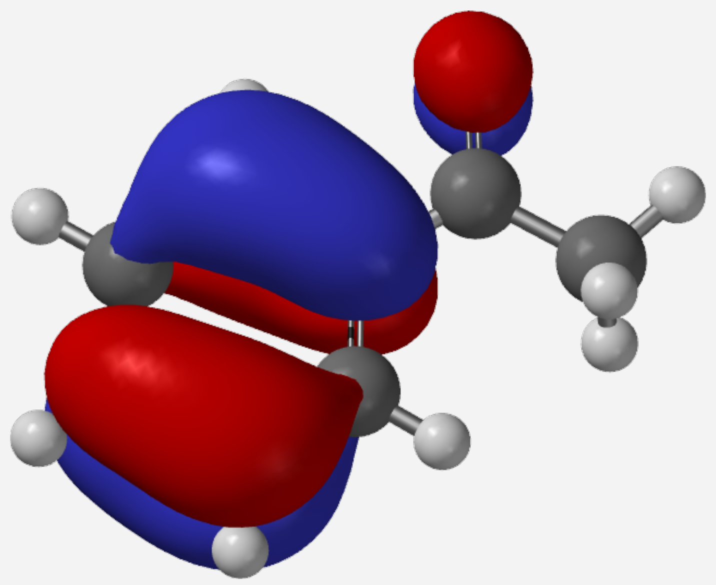
- –M substituents determine electron density and reactivity patterns in π-conjugated systems



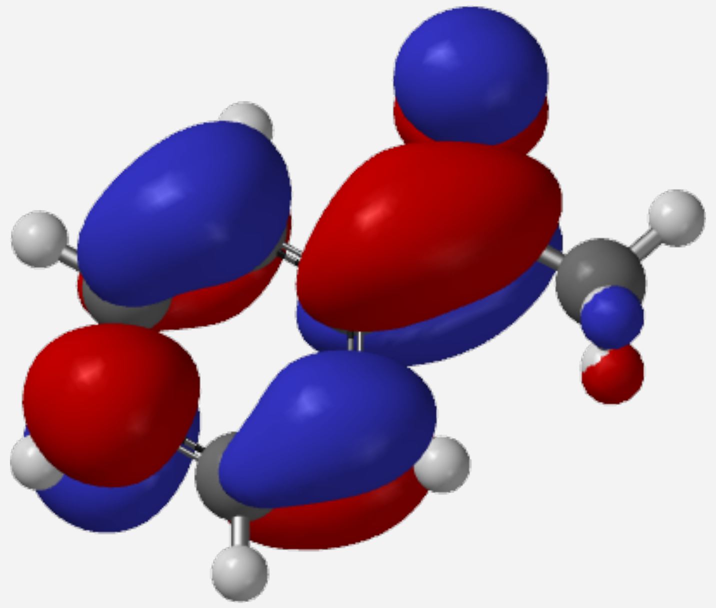




charge distribution



HOMO

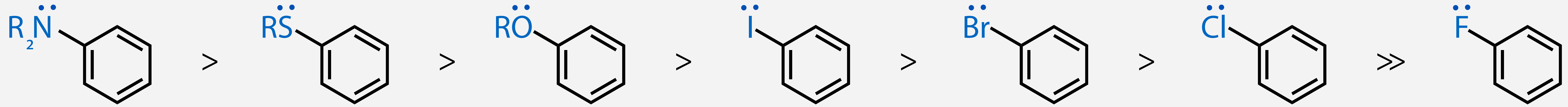


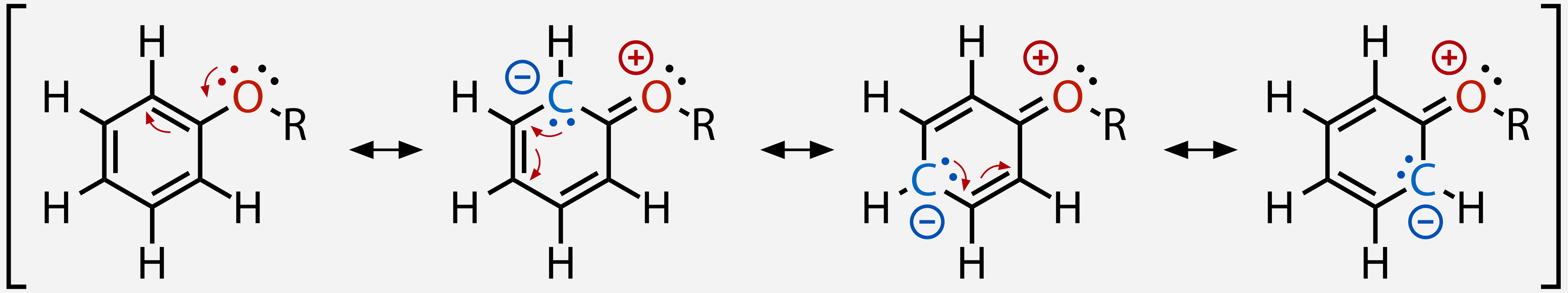
LUMO

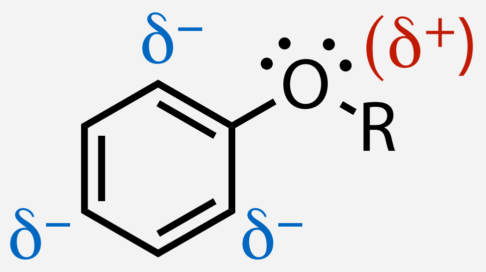
- **overall electron density in the π-system decreased (compared to benzene)**
- **every second carbon in delocalized π system is electron-poor (positive partial charge δ+)**

Resonance Structures Involving Electron-Donating Groups

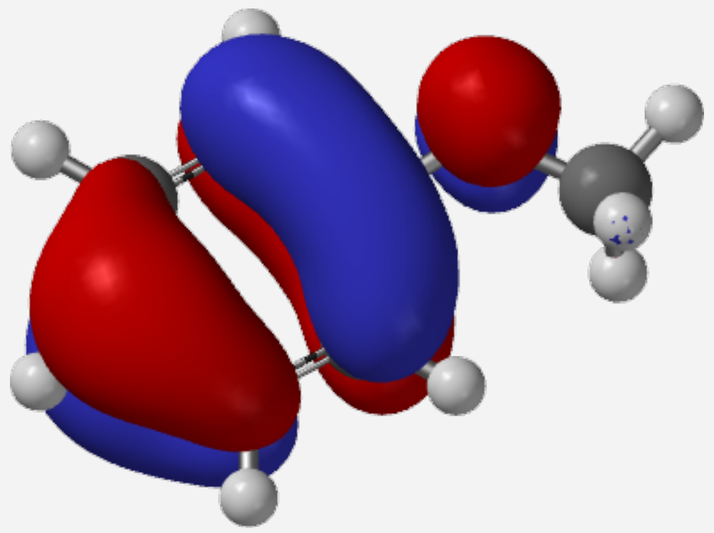
- +M substituents determine electron density and reactivity patterns in π-conjugated systems



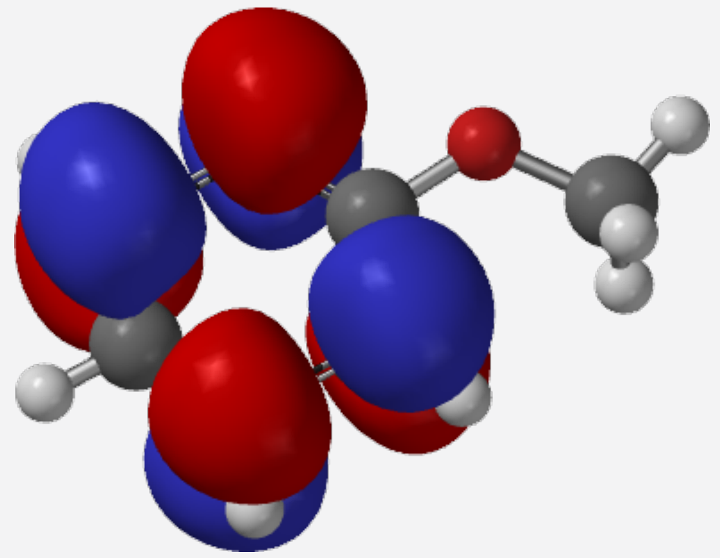




charge distribution



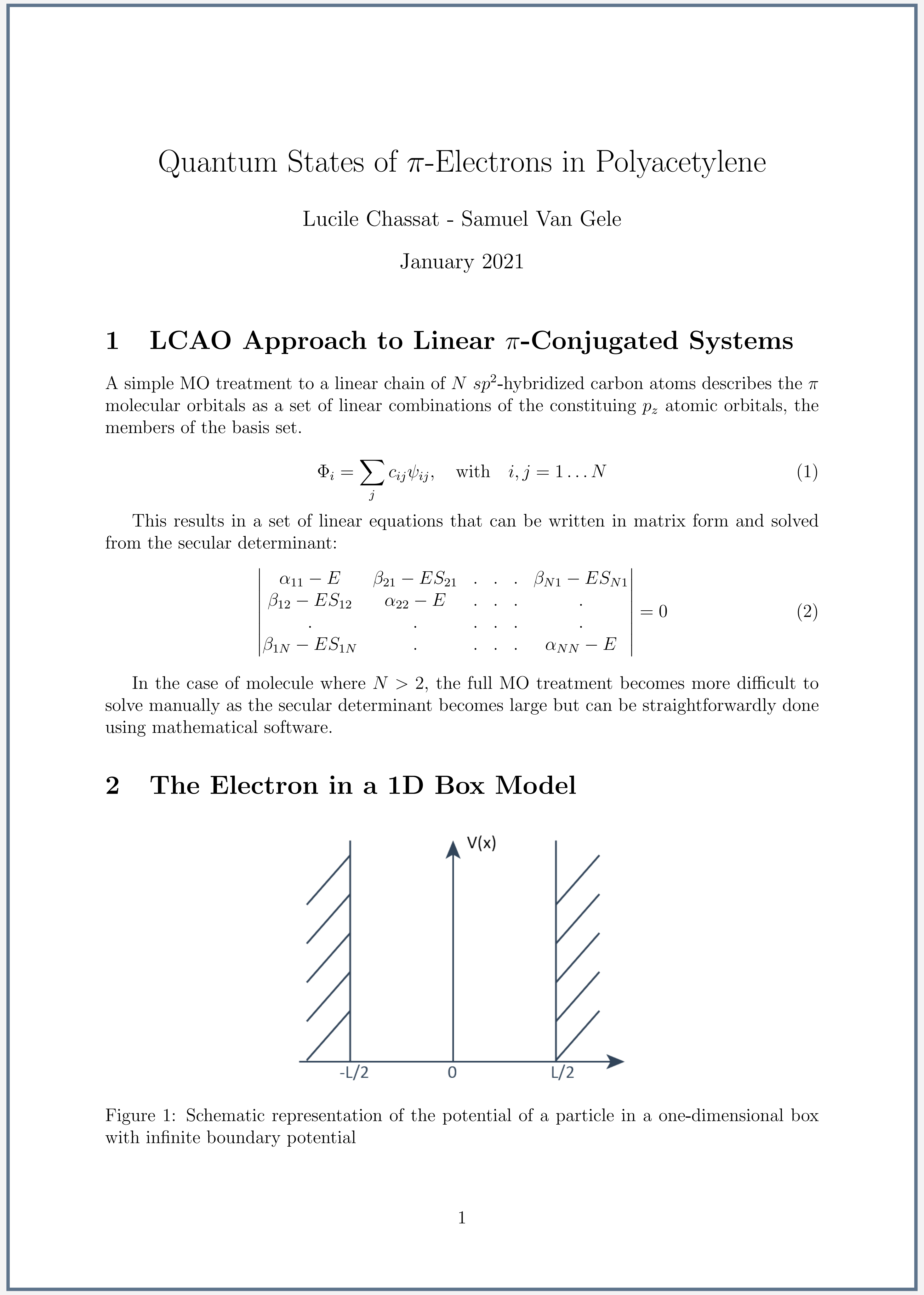
HOMO



LUMO

- **overall electron density in the π-system increased (compared to benzene)**
- **every other carbon in delocalized π system is electron-rich (negative partial charge δ⁻)**

Homework and Reading Assignments



Quantum States of π-Electrons in Polyacetylene

Lucile Chassat - Samuel Van Gele

January 2021

1 LCAO Approach to Linear π-Conjugated Systems

A simple MO treatment to a linear chain of N sp^2-hybridized carbon atoms describes the π molecular orbitals as a set of linear combinations of the constituing p_z atomic orbitals, the members of the basis set.

$$\Phi_i = \sum_j c_{ij}\psi_{ij}, \quad \text{with} \quad i,j = 1\dots N \tag{1}$$

This results in a set of linear equations that can be written in matrix form and solved from the secular determinant:

$$\begin{vmatrix} \alpha_{11}-E & \beta_{21}-ES_{21} & \cdot\;\cdot\;\cdot & \beta_{N1}-ES_{N1} \\ \beta_{12}-ES_{12} & \alpha_{22}-E & \cdot\;\cdot\;\cdot & \cdot \\ \cdot & \cdot & \cdot\;\cdot\;\cdot & \cdot \\ \beta_{1N}-ES_{1N} & \cdot & \cdot\;\cdot\;\cdot & \alpha_{NN}-E \end{vmatrix} = 0 \tag{2}$$

In the case of molecule where $N > 2$, the full MO treatment becomes more difficult to solve manually as the secular determinant becomes large but can be straightforwardly done using mathematical software.

2 The Electron in a 1D Box Model

Figure 1: Schematic representation of the potential of a particle in a one-dimensional box with infinite boundary potential

1

P. W. Atkins, *Physical Chemistry*, Chapter 10, 11th edition, Oxford University Press, **2017**.

Learning Outcome

- **conjugated multiple bonds interact, and electrons are delocalized**
- **all π-orbitals extend over all carbons and “do not look like” double bond MO**
- **electron delocalization particularly pronounced for (poly)cyclic systems**
- **delocalization can be represented by resonance structures**
- **delocalization in extended π-systems results in smaller bandgap**
  - large systems (polymers) theoretically have a band-like continuum of states
  - Peierl’s distortion prohibits complete delocalization, opens bandgap