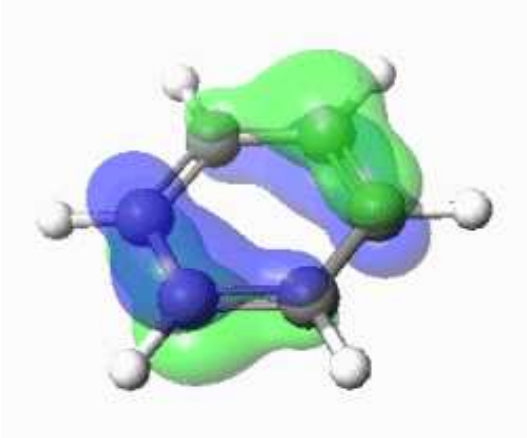
Orbital coefficients in organic reactions



Gerrit Jürjens

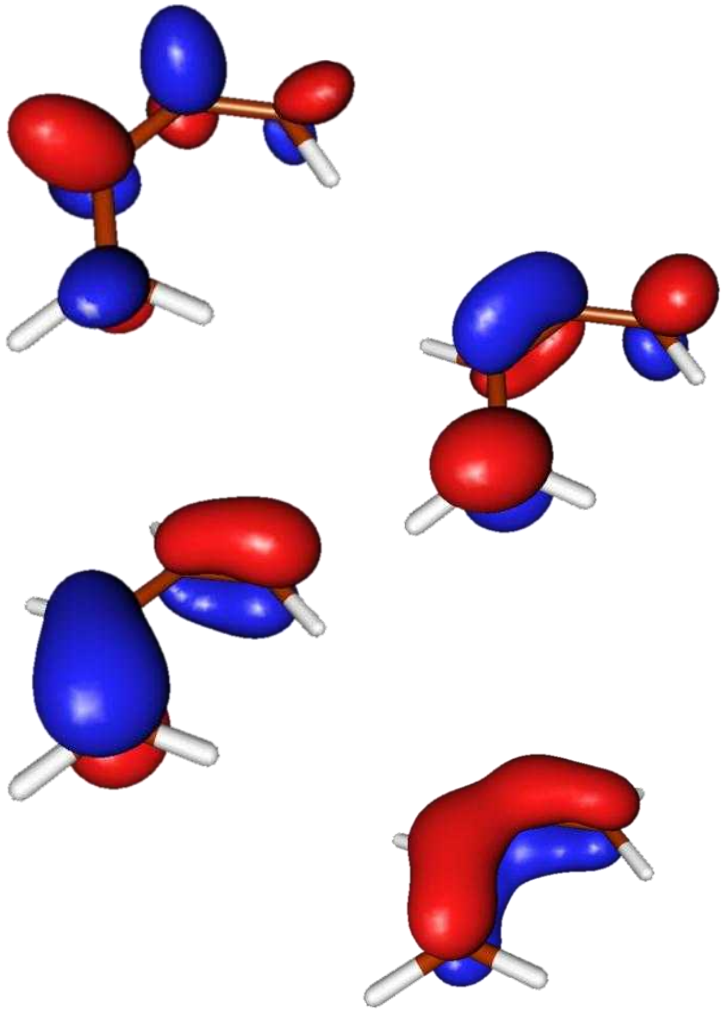
8.10.2012

Based on

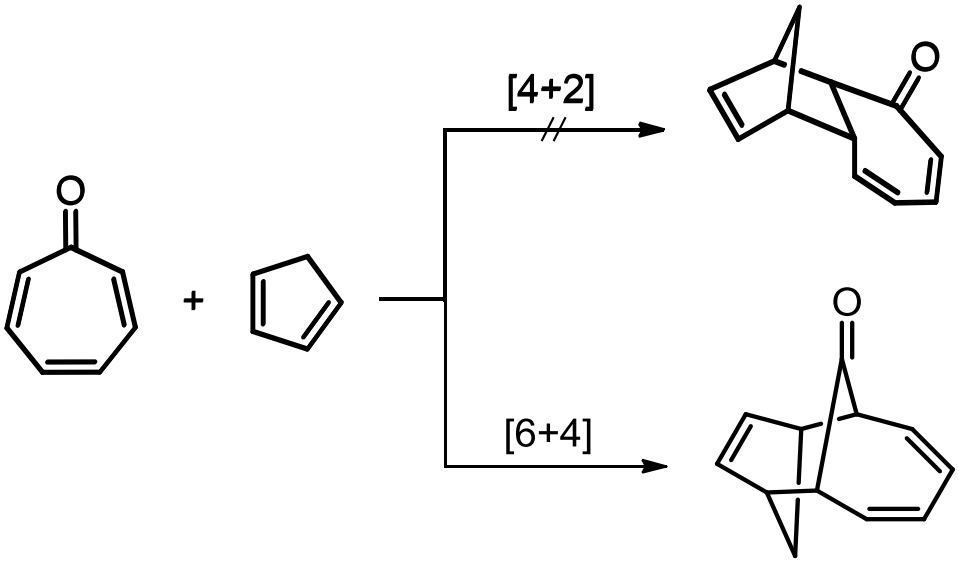
I. Fleming, *Molecular Orbitals and Organic Chemical Reactions*, 2009, John Wiley & Sons Ltd.

Overview

- Introduction
- Molecular orbitals
- Orbital coefficients
  - Linear systems
  - Aromatic systems
- Coefficients in organic reactions
  - Orbital vs. charged controlled reactions
  - Conjugated additions
  - Periselectivity
- Conclusion



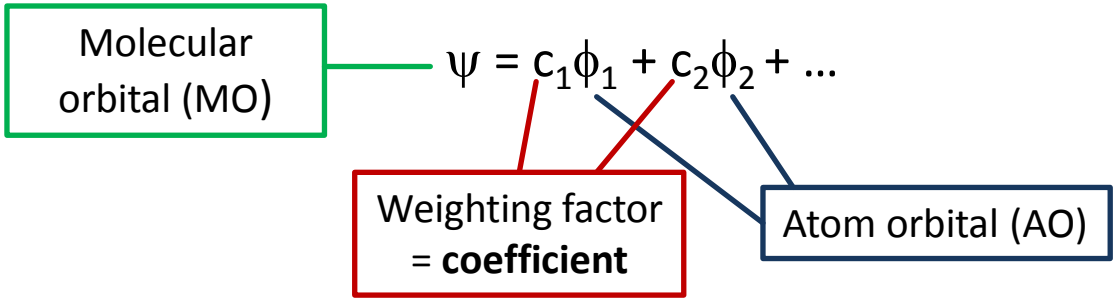
Why look at orbital coefficients?



- When several pericyclic reactions are possible it ist not always clear which one occurs
- Sometimes partial charges are not sufficient to determine/explain regiochemistry

Molecular orbitals

- Linear combination of atom orbitals in general:

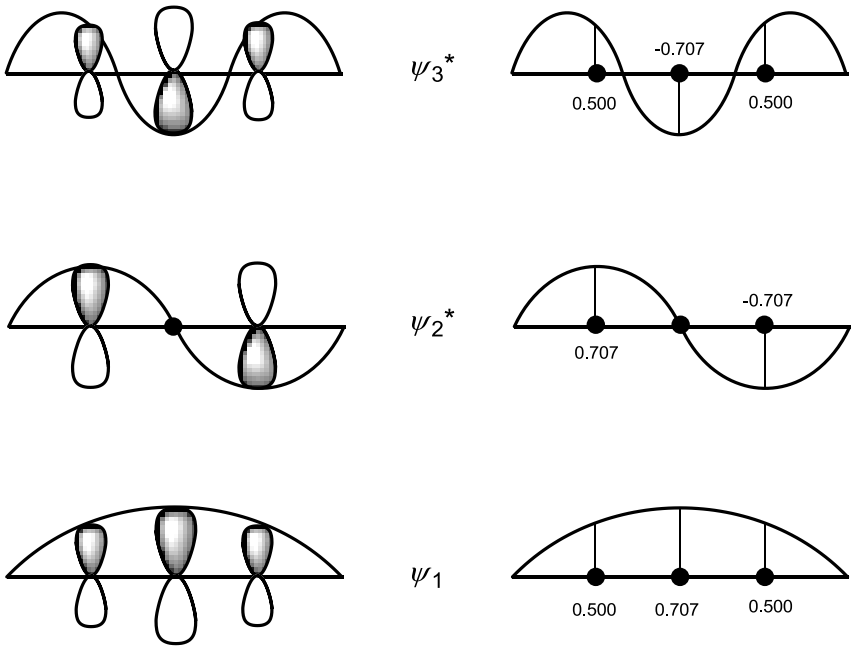


- Energies of the electrons in MOs:

$$E_{bonding} = \frac{\alpha + \beta}{1 + S} \qquad E_{antibonding} = \frac{\alpha - \beta}{1 - S}$$

- α = Coulomb integral; i.e. the energy of an electron in an **isolated** orbital
- β = Resonance integral; i.e. energy of an electron in the field of two nuclei
- S = Overlap integral of the orbitals

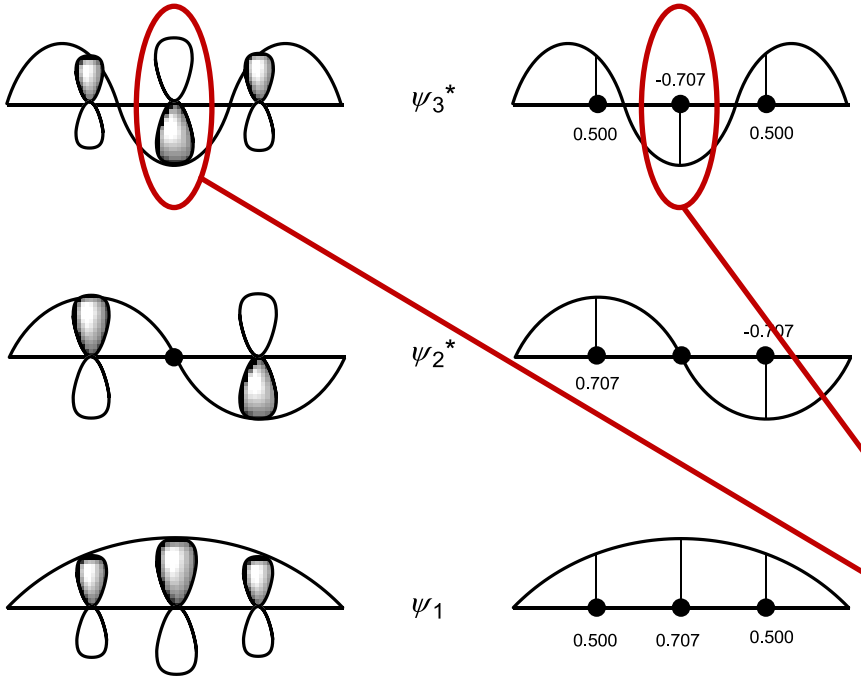
What is an orbital coefficient?



$$c_{jr} = \sqrt{\frac{2}{n+1}} \sin \frac{rj\pi}{n+1}$$

- Describes the **electron population** with respect to the wave function in a particular atom of a molecular orbital as a numerical value
- Sum of all squares within a single MO or of a single atom in all MOs equals 1
- Overall electron population in a molecule can be obtained by summing the squares of the coefficients of all bonding molecular orbitals
- In **linear systems** the coefficient is defined by position in the sine curve and therefore proportional to the sine angle

What is an orbital coefficient?



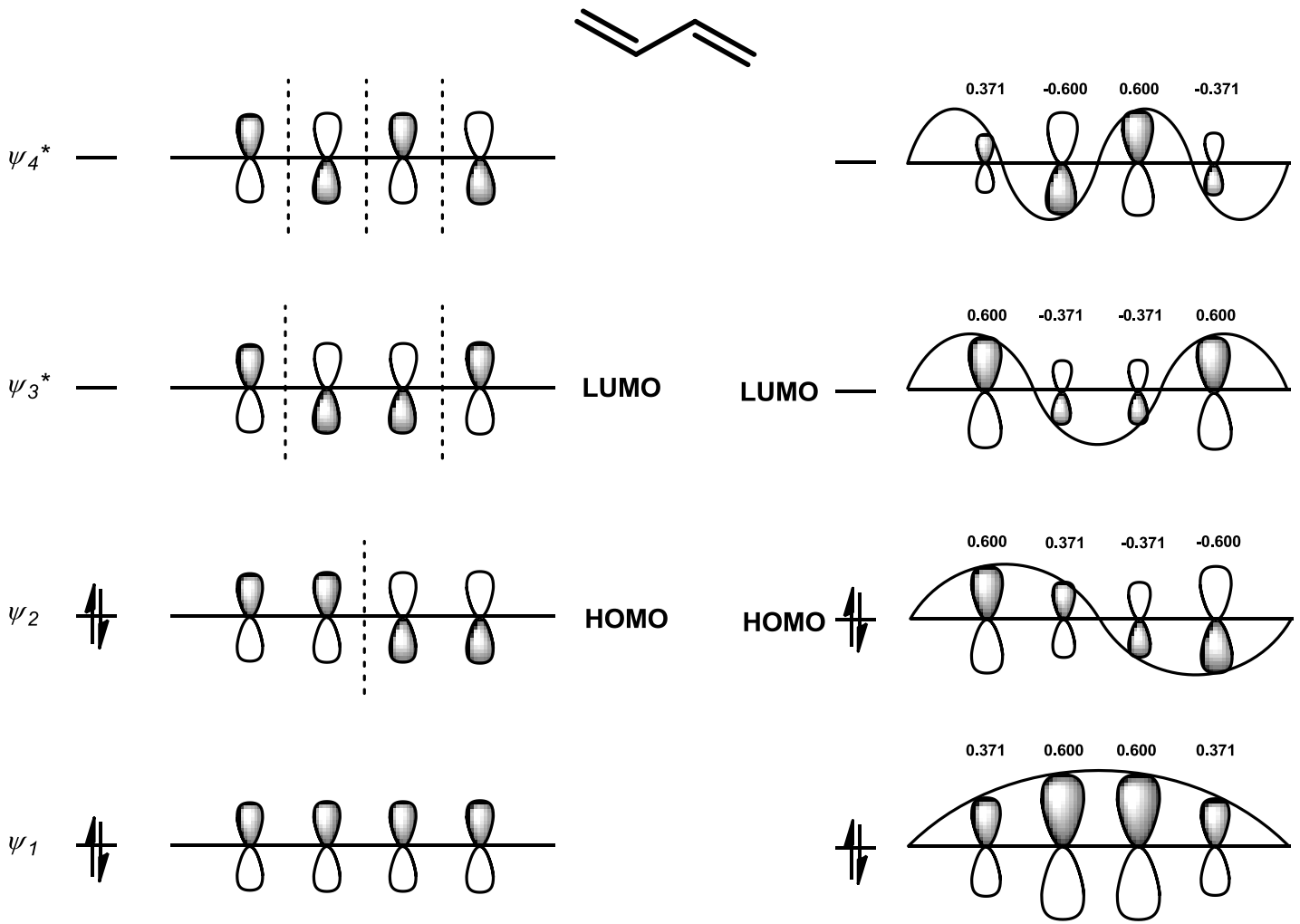
$$c_{jr} = \sqrt{\frac{2}{n+1}} \sin\frac{rj\pi}{n+1}$$

$$c_{23} = \sqrt{\frac{2}{3+1}} \sin\frac{3*2*\pi}{3+1}$$

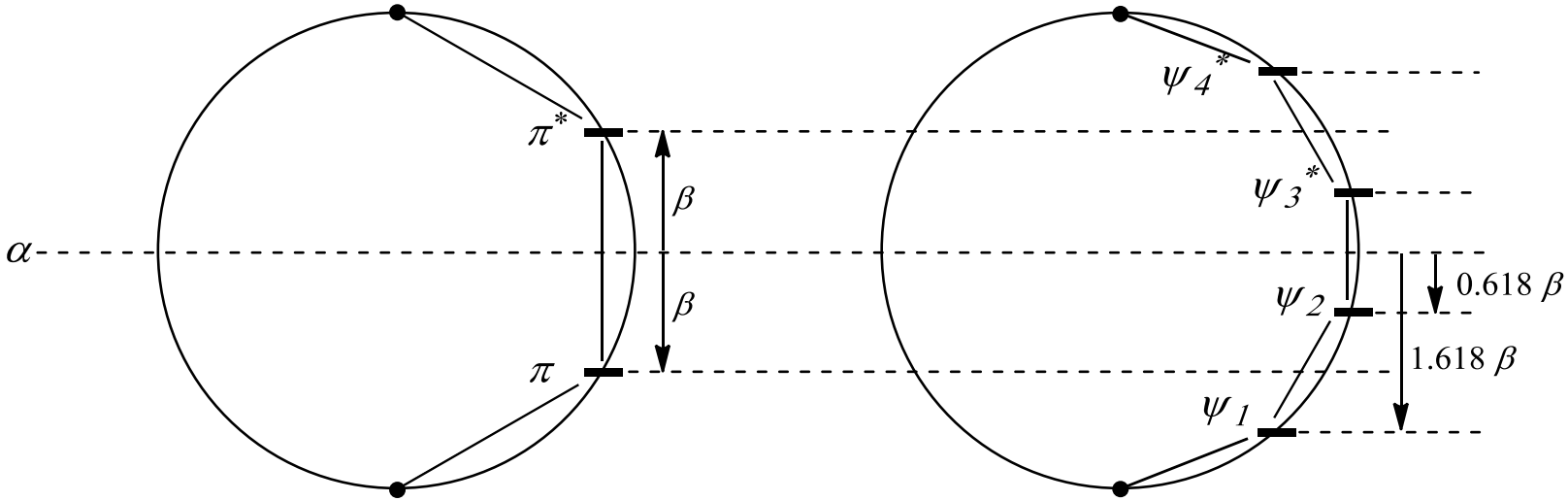
$$= -0.70710678$$

- c = coefficient
- j = atom
- r = molecular orbital ψ_r
- n = number of atoms in the conjugated system

Butadiene

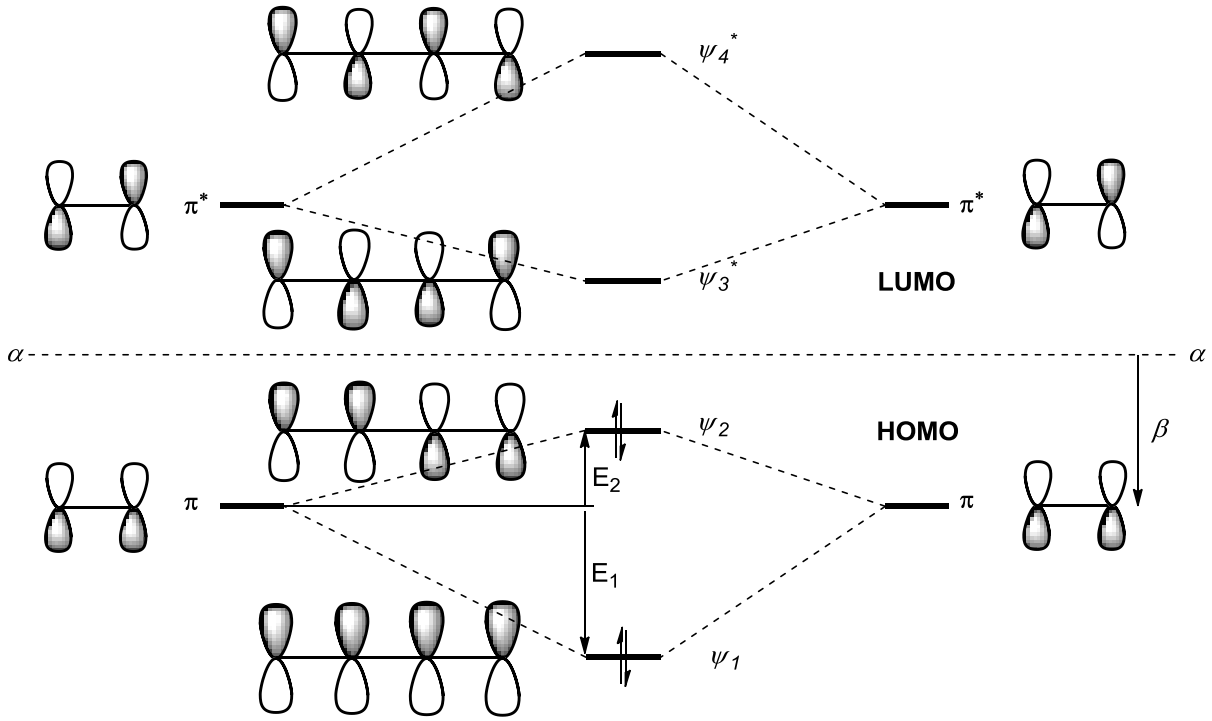

ψ4*
ψ3*
LUMO
ψ2
HOMO
ψ1
0.371 -0.600 0.600 -0.371
LUMO
0.600 -0.371 -0.371 0.600
HOMO
0.600 0.371 -0.371 -0.600
0.371 0.600 0.600 0.371

Coefficients and energy



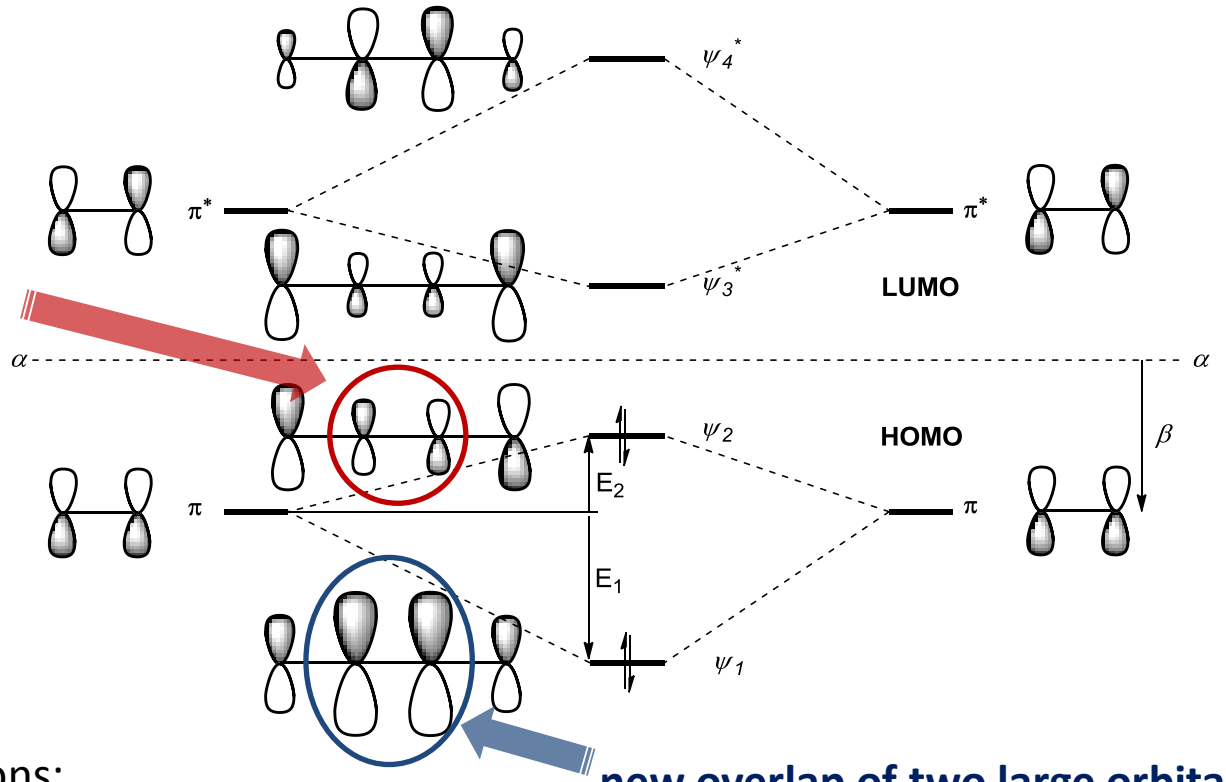
- α = energy level of a lone p orbital of carbon; β = energetical difference from α when combining two carbon p orbitals
- Orbital energy levels of the molecular orbitals can be estimated with a simplified Frost-Musulin circle which shows the energy gain when conjugating two π bonds
- The geometrical depiction gives no electronical explaination why the overall energy is more favorable

Coefficients and energy



- Recombination of both p orbitals results in ψ_1 and ψ_2 with different energy values E1 and E2
- ψ_2 is raised lower in energy while ψ_1 is lowered in more energy, making conjugation in this case favorable

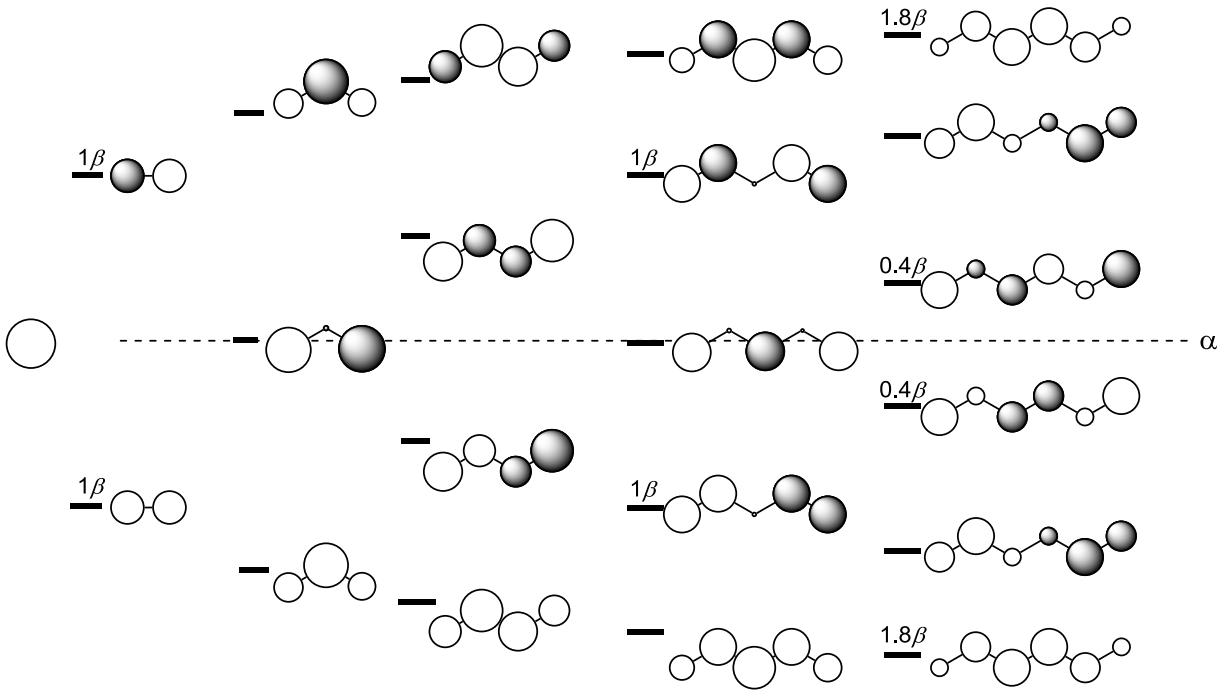
Coefficients and energy



New interactions:

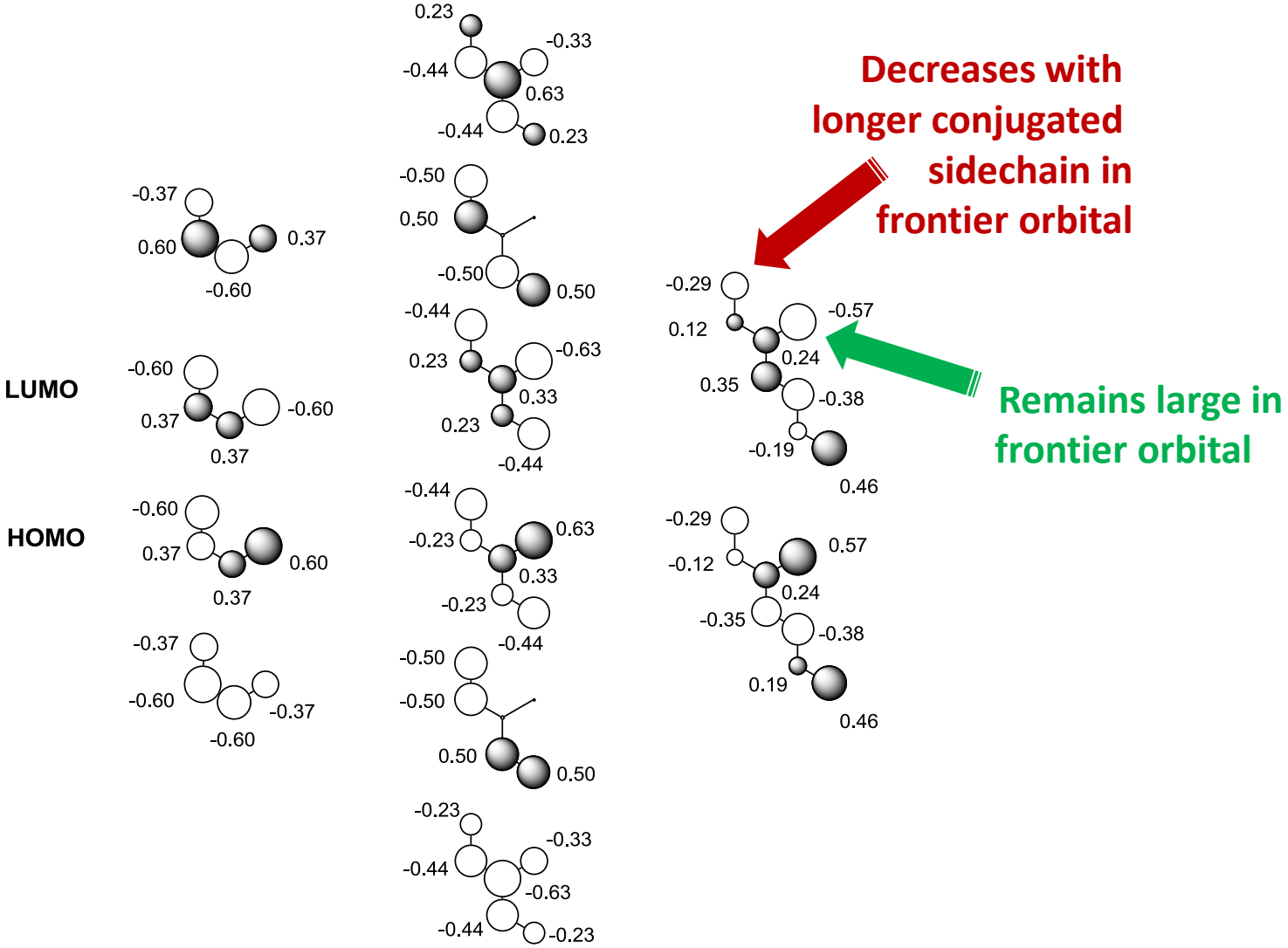
- Energy lost by recombination of large orbitals in ψ_1 is increased by overlap of the two orbitals
- Repulsion of the small orbitals not in the same phase is decreased, so less energy is needed to form ψ_2

Conjugation: C-substituents



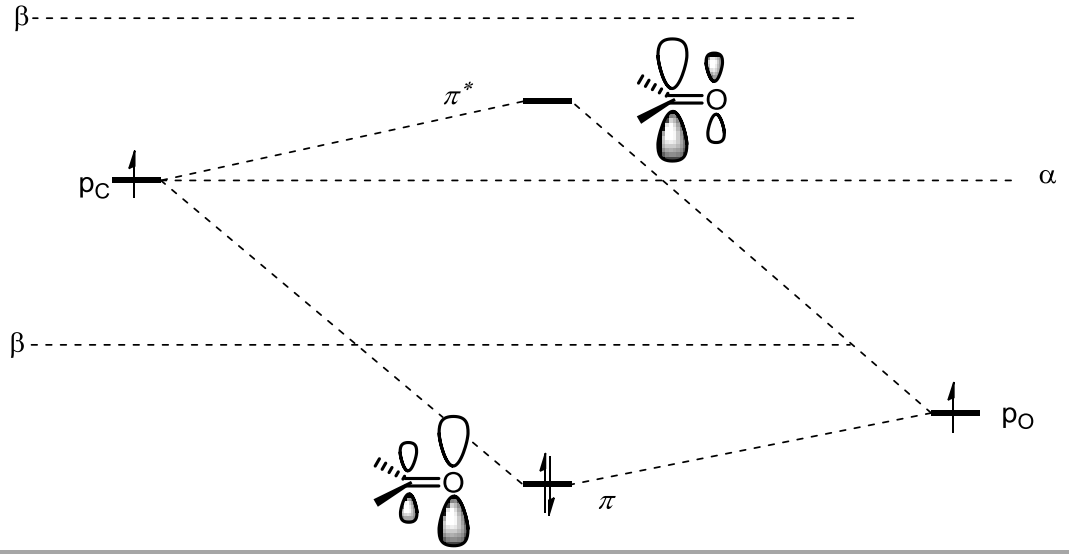
- For linear systems the coefficients can be calculated using the aforementioned formula
- In general: terminal coefficients in frontier orbitals are large, internal coefficients smaller

Conjugation: C-substituents

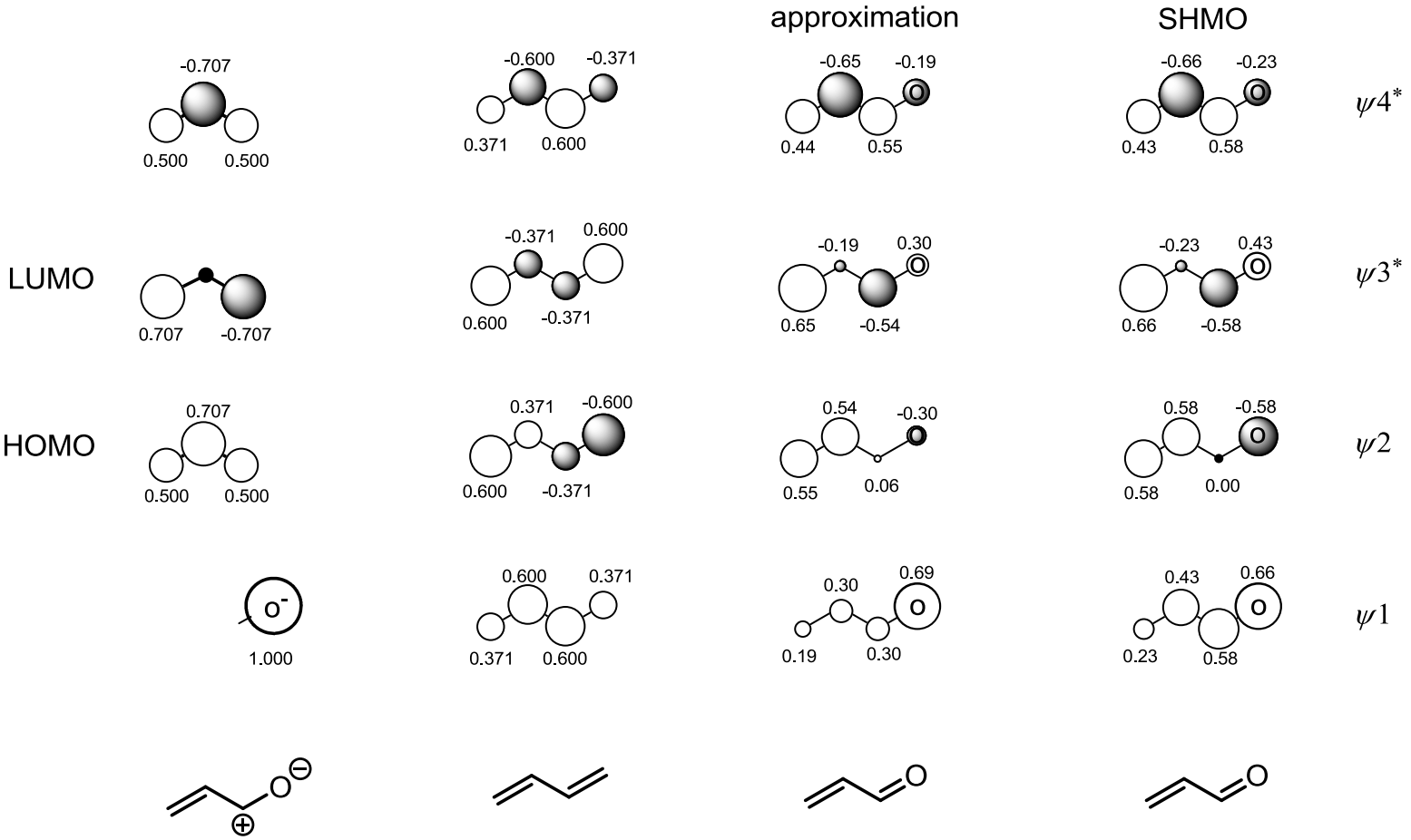


C-heteroatom bonds

- Interactions of orbitals with unequal energy results in a decreased energy lowering compared to interaction of orbitals with equal energy
- Coefficients describe the electron density
  - The coefficient of the more electron negative atom is larger in the binding orbitals
  - Since the sum of squares of all coefficients must equal one, the situation is reversed in the antibonding orbitals

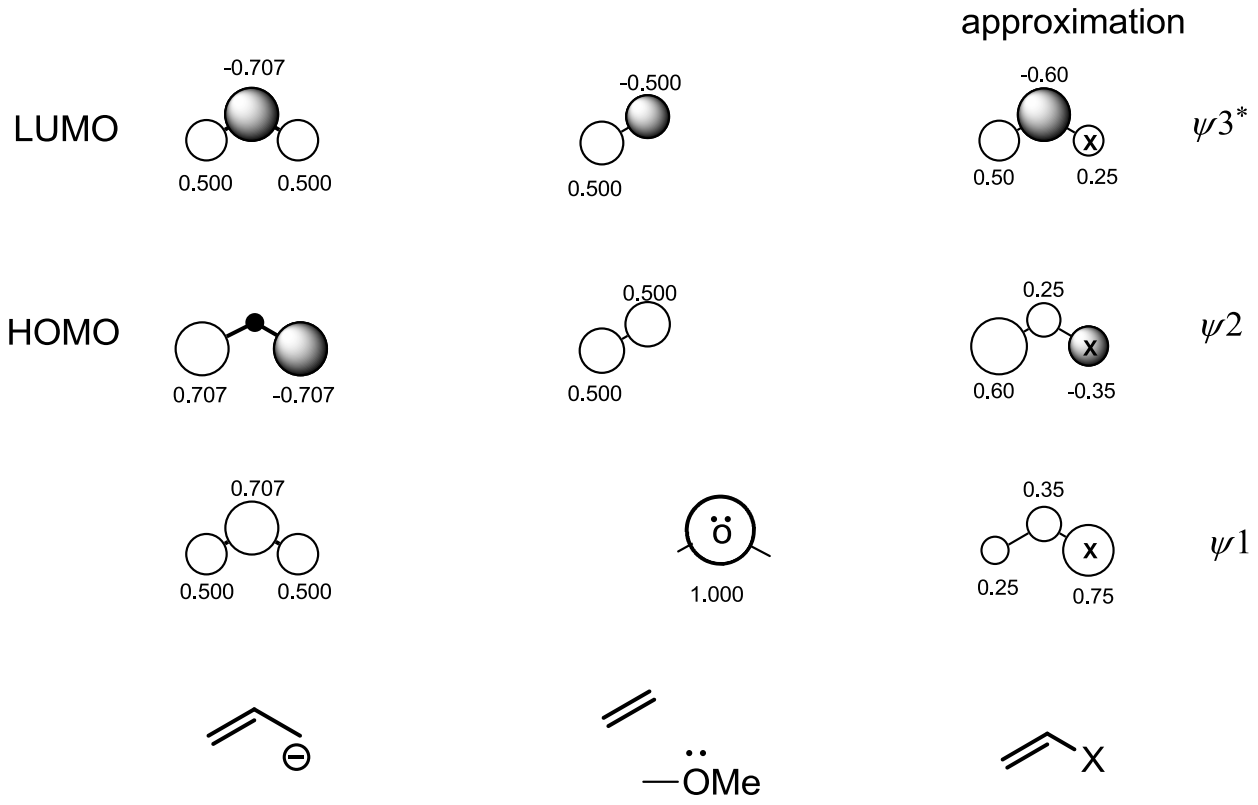


Conjugation: Z-substituents



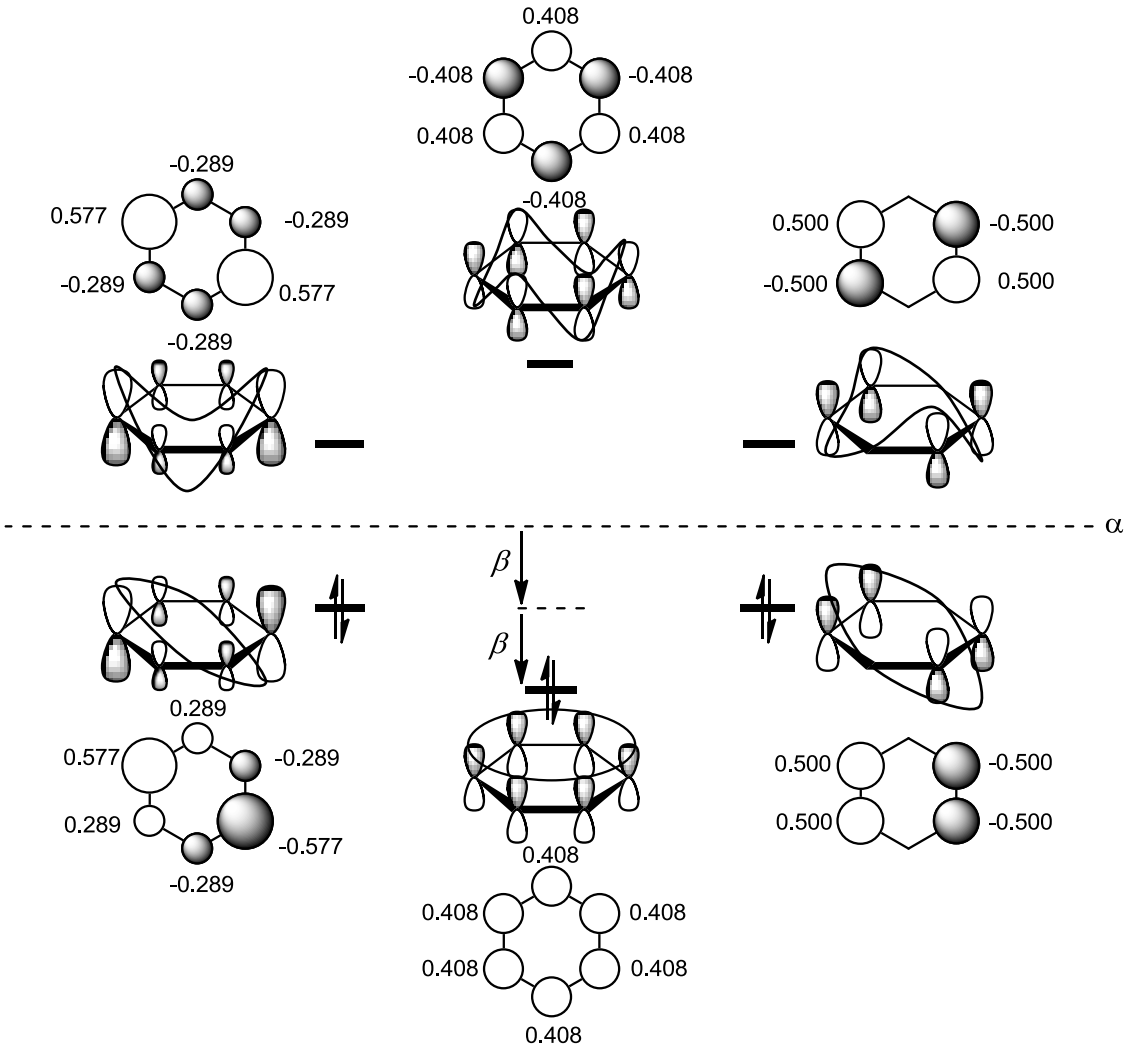
- An approximation of the Z system can be done by combining the coefficients of the allyl cation system with the butadiene
- Coefficient pattern is similar to other Z-groups

Conjugation: X-substituents

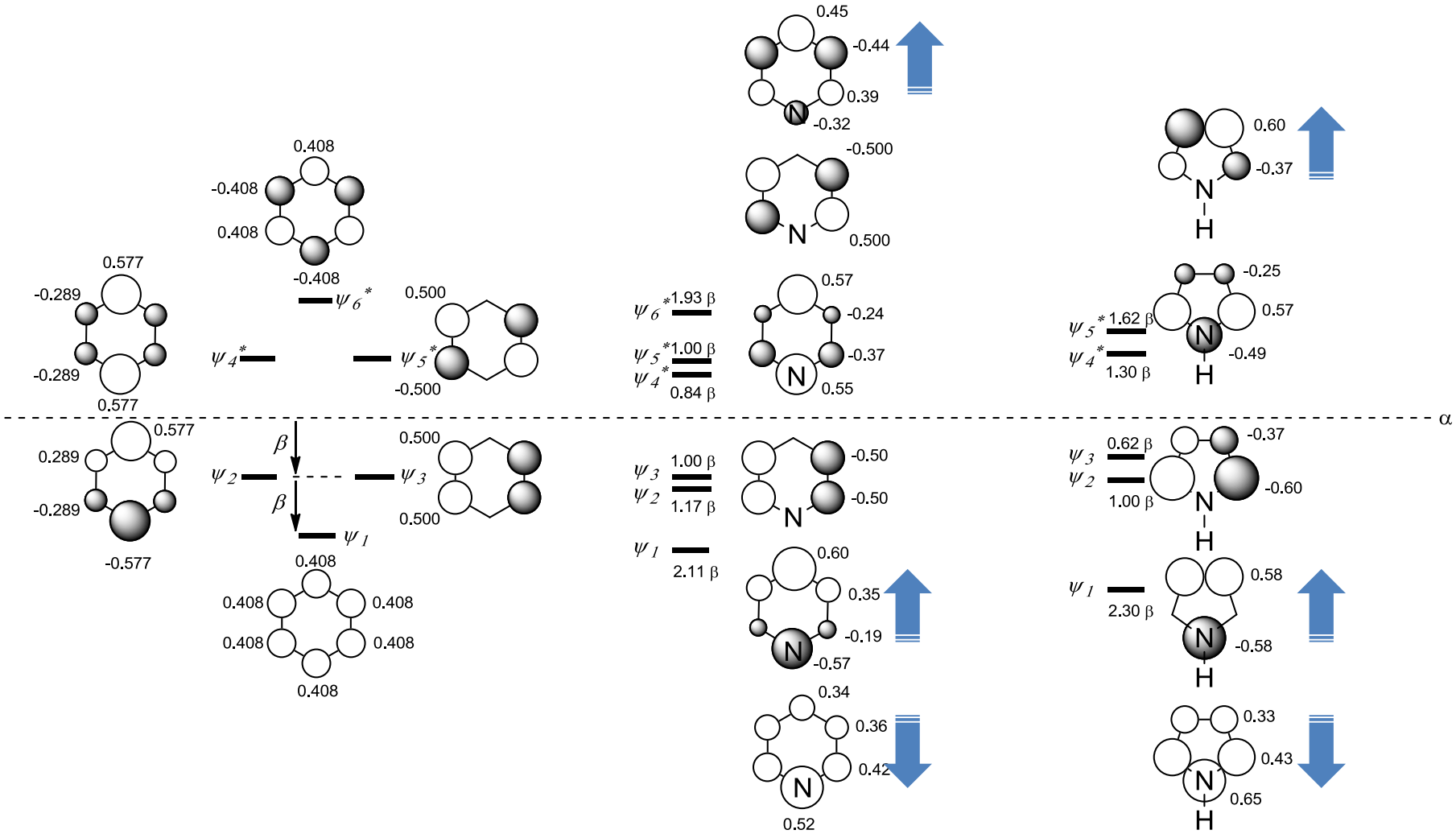


- An approximation of the Z system can be done by combining the coefficients of the allyl cation system with the butadiene

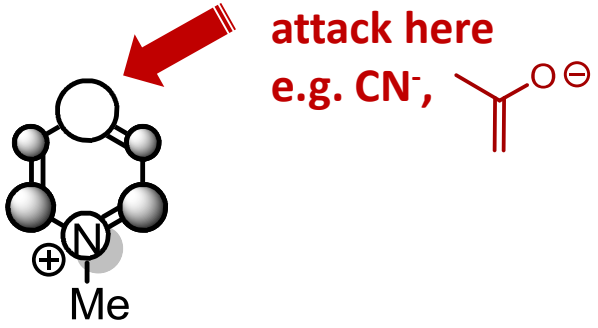
Aromatic systems

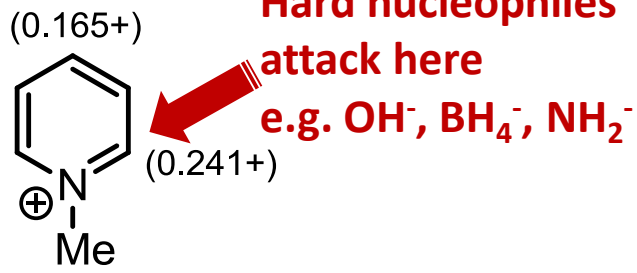


Heteroaromatic systems



Orbital controlled vs. charge controlled reactions



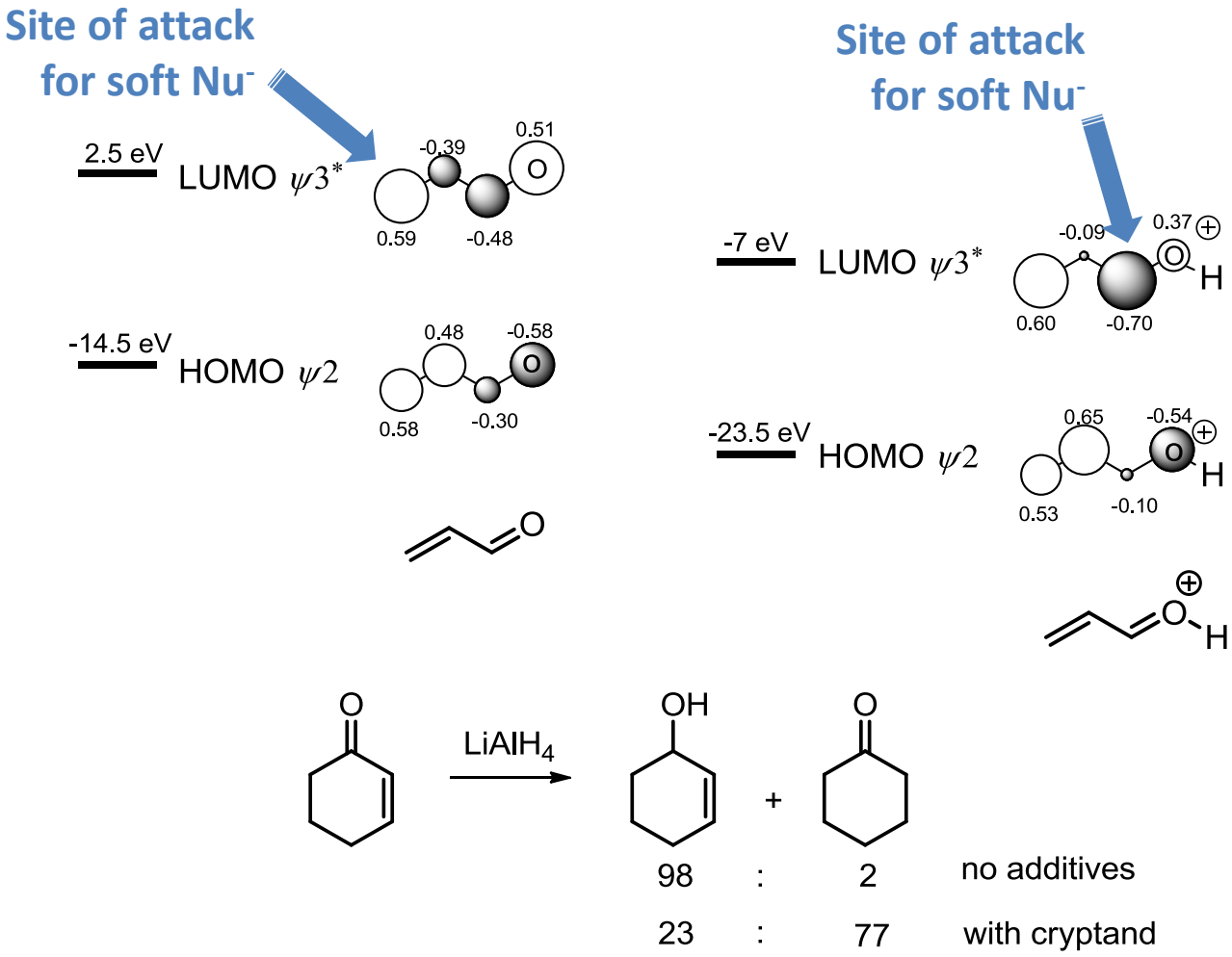


- Can be predicted by comparing orbital coefficients and π-electron charge/deficiency
- π-electron charge:

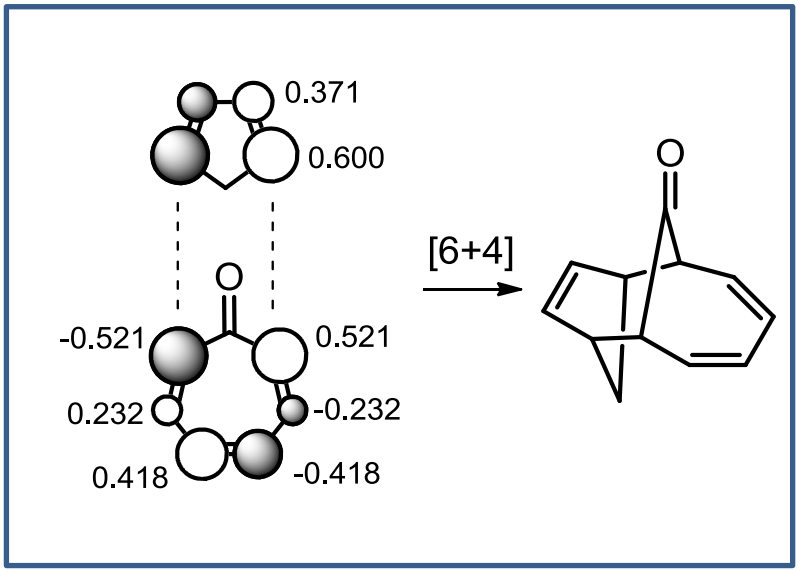
  $\sum c^2$ of an atom in all binding molecular orbitals
- π-electron deficiency:

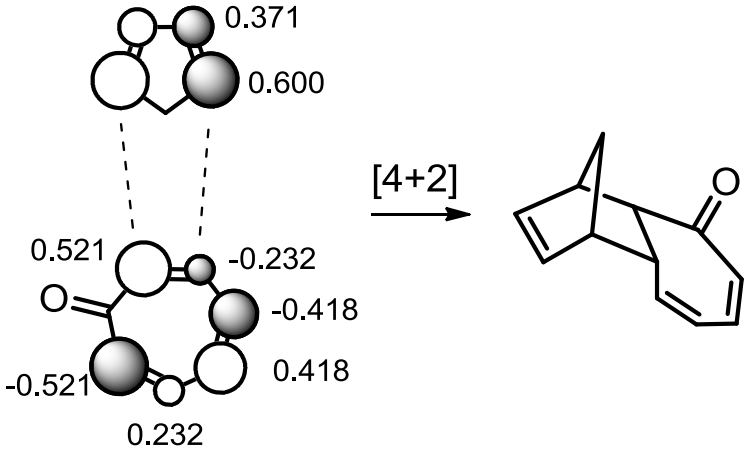
  $\sum c^2$ of an atom in all binding molecular orbitals in relation to the highest π-electron charge

Conjugated addition

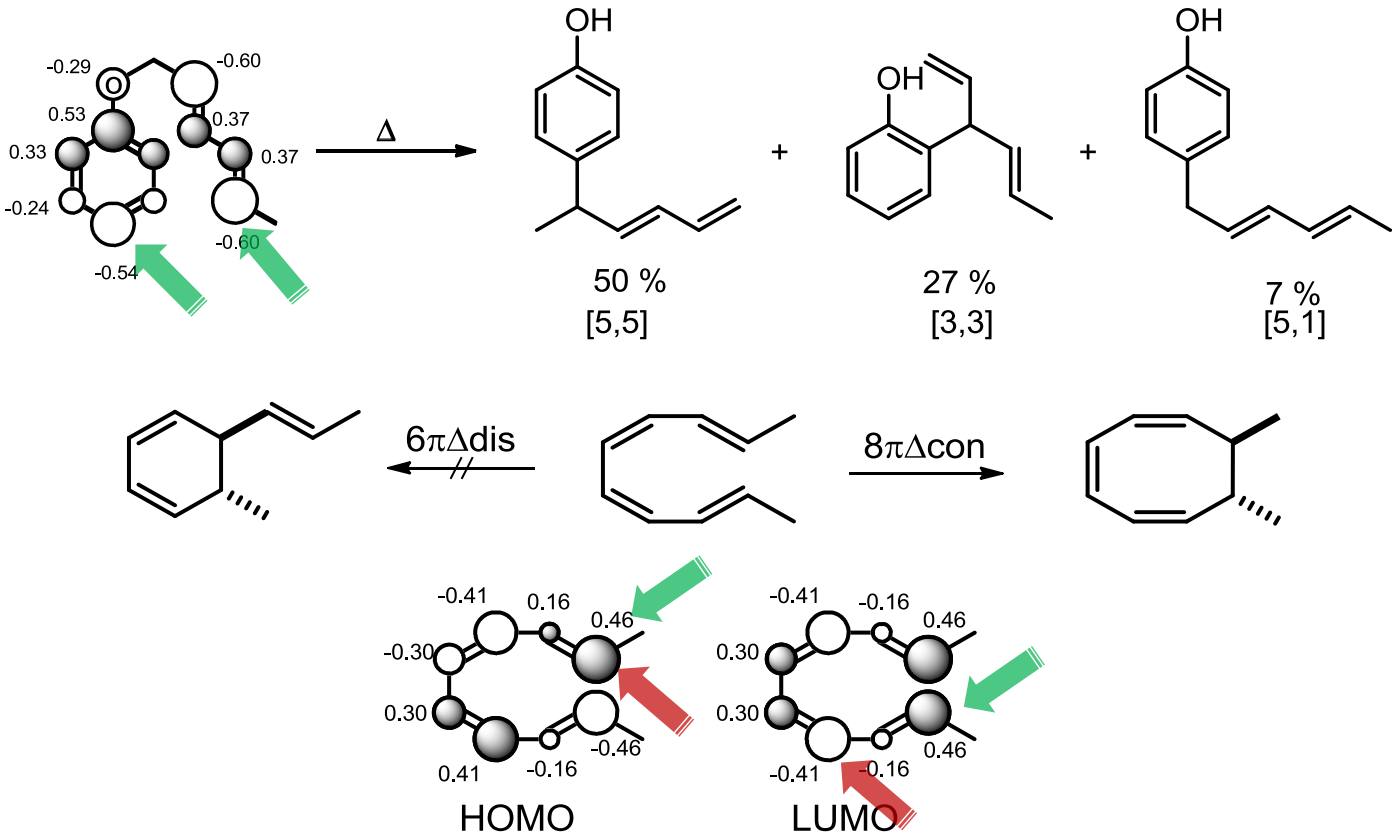


Periselectivity





Periselectivity



- *General rule:* allowed pericyclic reactions which mobilize the most π-electrons are preferred over allowed pericyclic reactions mobilizing less π-electrons
- *Exceptions:* carbenes and ketenes

Conclusion

- Useful beyond Diels-Alder reactions and 1,3-dipolar cycloadditions
- Orbital coefficients can often be used to explain reaction preferrences
- Can be used to identify soft or hard reaction types
- Hückel calculations make determination of coefficients fast and easy accessible (e.g. http://www.chem.ucalgary.ca/SHMO/)

Thank you for your attention