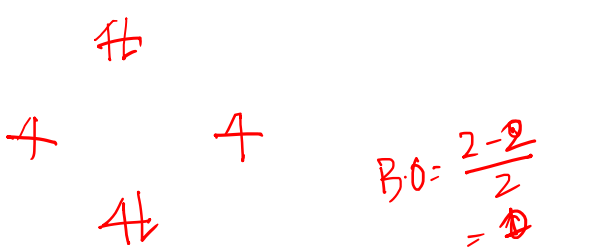
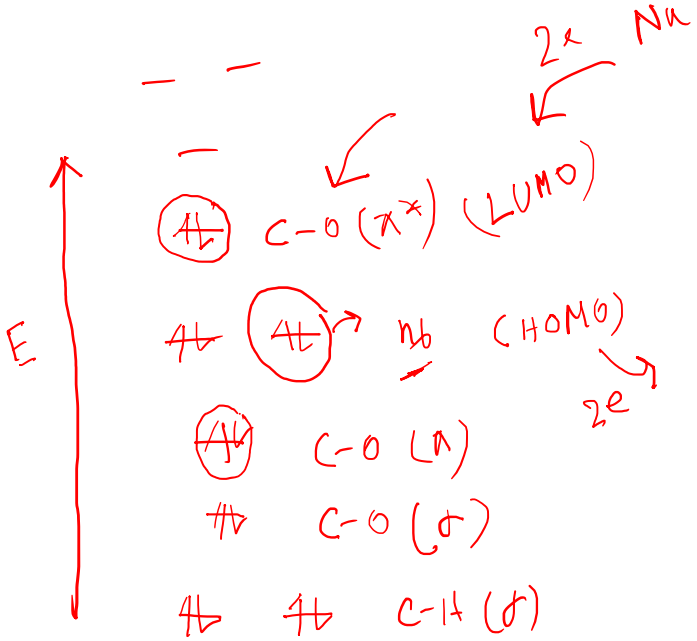
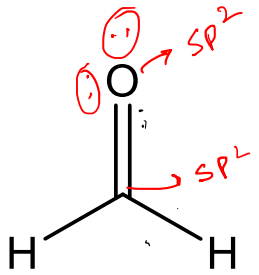
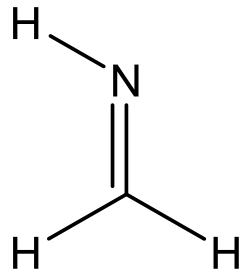
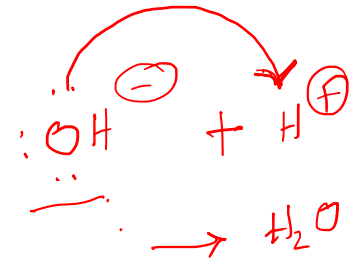
Aldehydes, Ketones and Imines

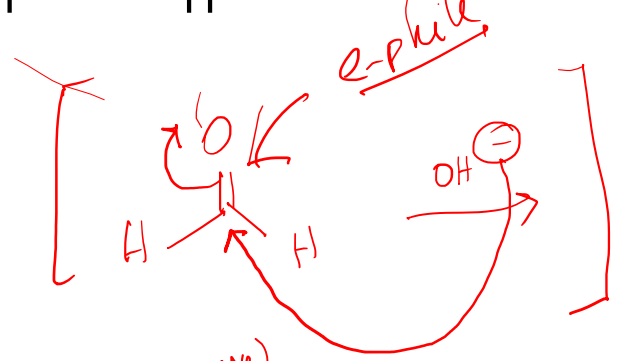


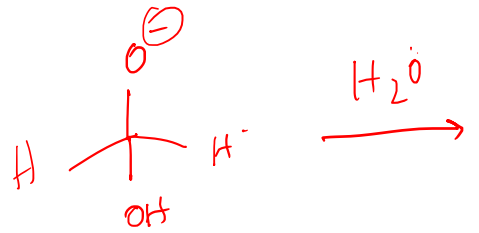


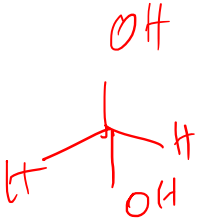


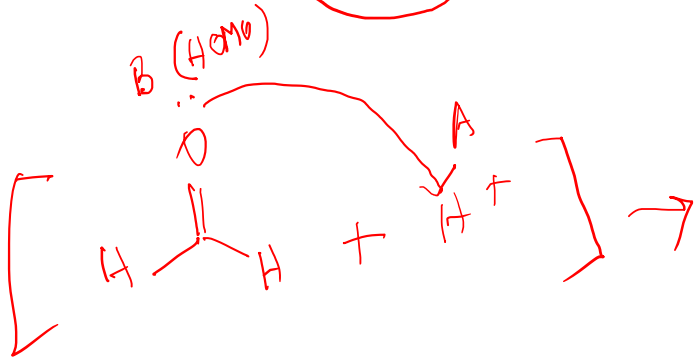


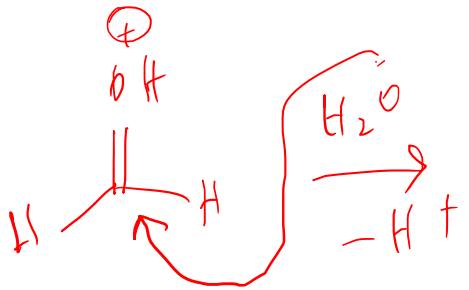


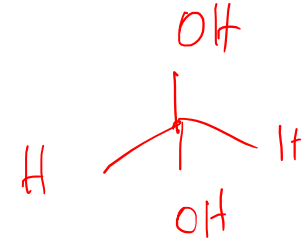








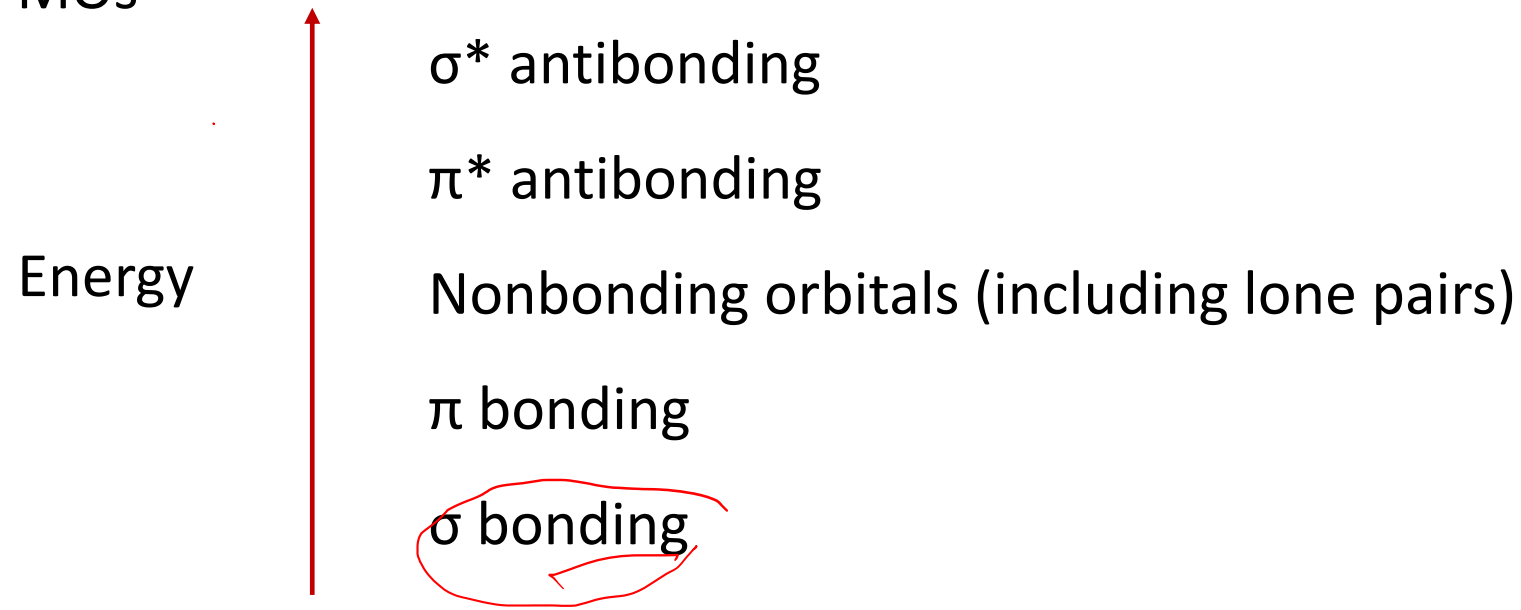




Chemistry is Dictated by HOMO-LUMO Interactions

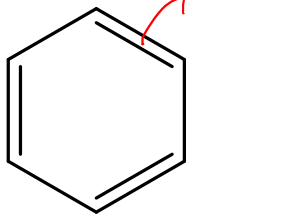
- ✓ It is important to identify the HOMO and LUMO of each of the reactants
- ✓ *HOMO and LUMO are termed as Frontier Molecular Orbitals*

- ✓ Energy Ordering of MOs

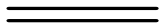


C-C: 1.54 Å
C=C: 1.34 Å

Conjugation and Delocalized Bonding

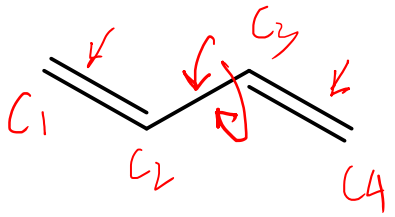


Benzene



Ethylene

$C_2 - C_3$: single

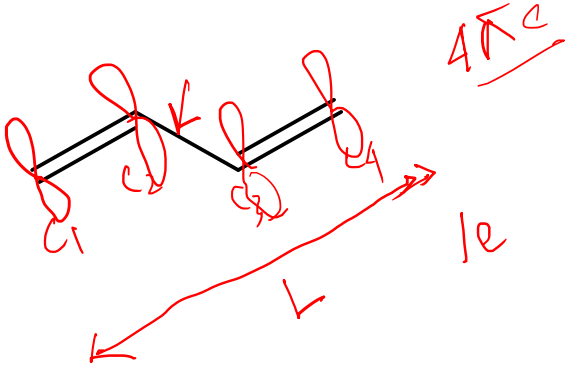


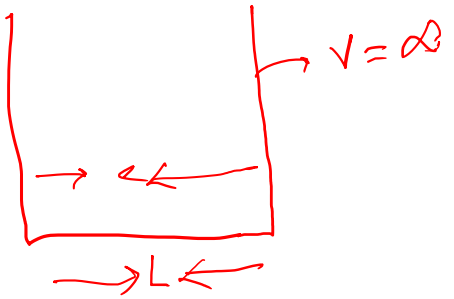
Butadiene

In butadiene:

- ✓ The barrier for rotation for the central C-C bond is 30 kJ/mol
- ✓ The value for a typical C-C bond is 15 kJ/mol
- ✓ Each carbon is sp^2 hybridized, these orbitals are used in σ-bonding (localized bonding)
- ✓ Single atomic 2p orbital is free on each carbon atom
- ✓ π-MOs are formed from these four 2p orbitals and they extend over the whole molecule (delocalized bonding)

π - Molecular Orbitals of Butadiene





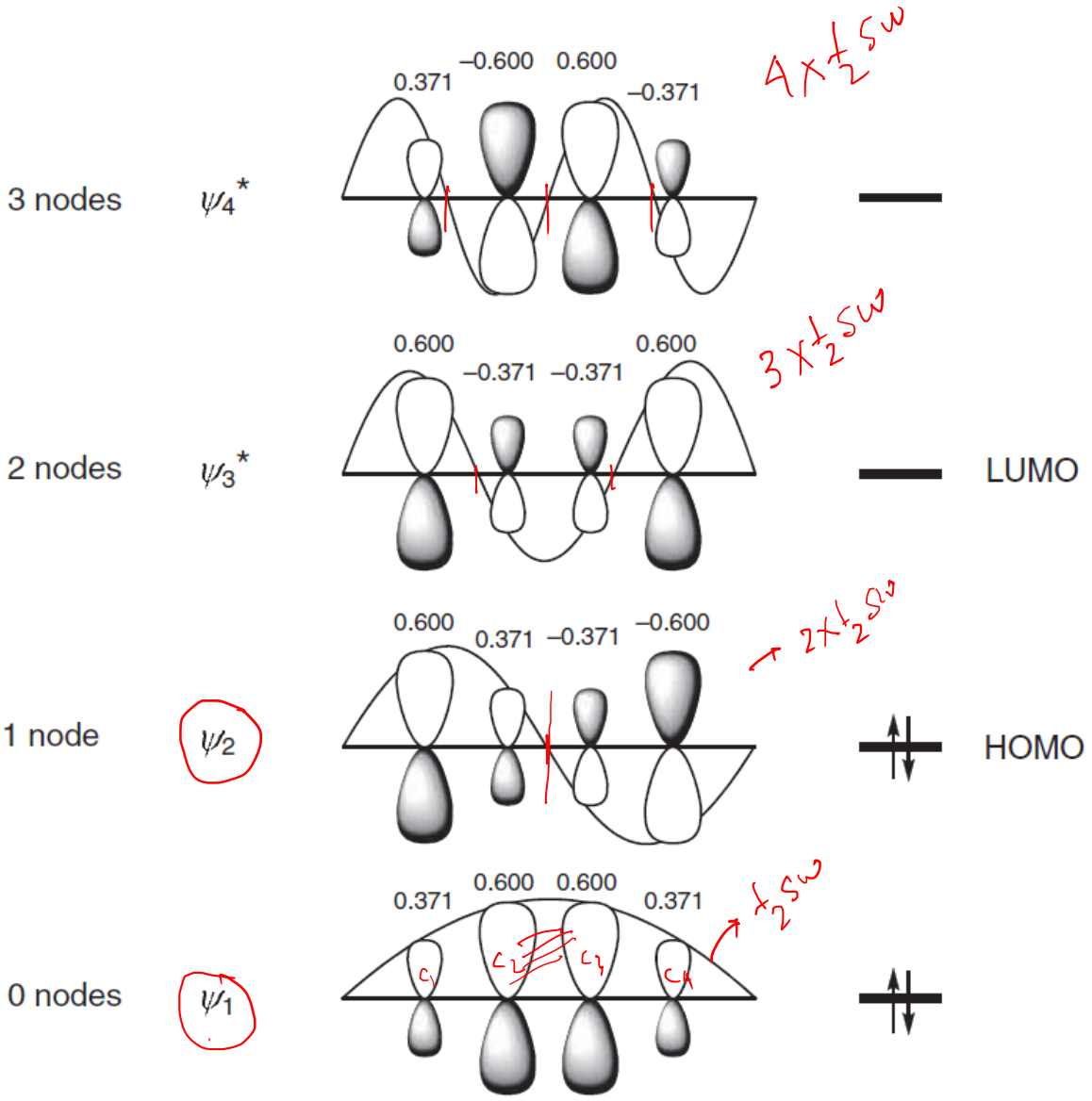
❑ Hückel theory

- ✓ Mixing of p orbitals leading to the formation of π MOs
- ✓ **Only π-electrons in conjugated systems (σ electrons are not considered)**

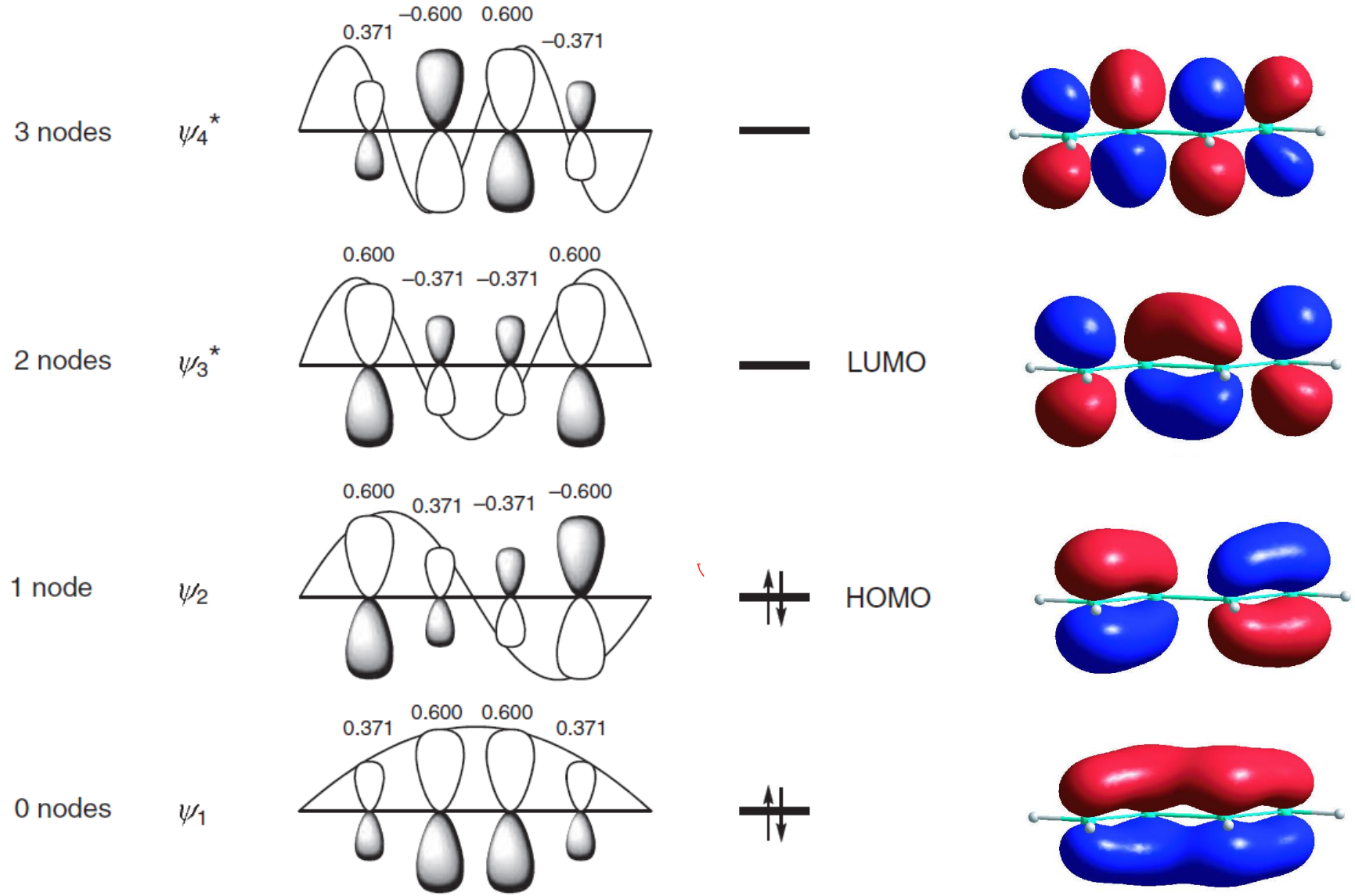
❑ LCAO: Linear Combination of Atomic Orbitals:

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$

π-Molecular Orbitals of Butadiene



- ✓ *The molecular orbitals (ψ) are one-electron wave functions (electron in a box)*
- ✓ *The coefficients (C) are the weights of the contributions of the atomic orbitals to the molecular orbitals*
- ✓ *4 MOs spread all over 4 carbon atoms*


3 nodes
ψ_4^*
0.371
−0.600
0.600
−0.371
2 nodes
ψ_3^*
0.600
−0.371
−0.371
0.600
LUMO
1 node
ψ_2
0.600
0.371
−0.371
−0.600
HOMO
0 nodes
ψ_1
0.371
0.600
0.600
0.371