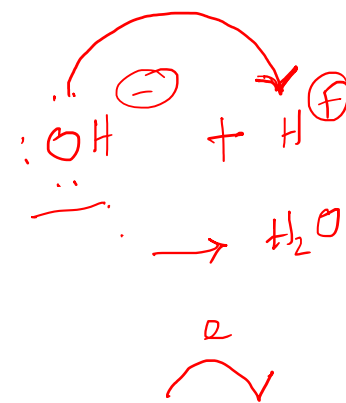
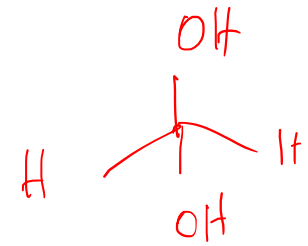
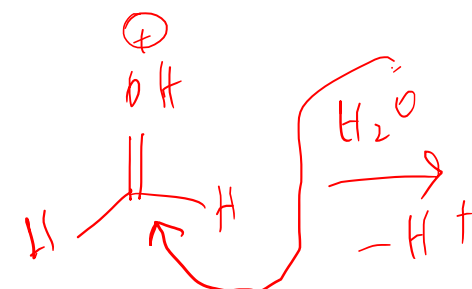
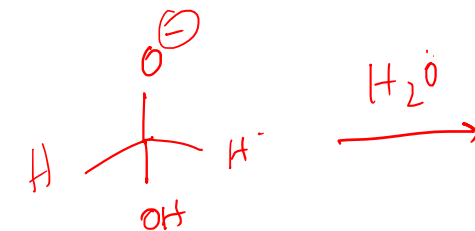
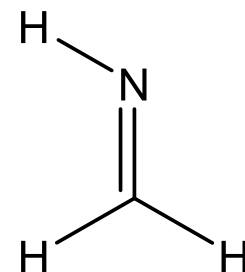
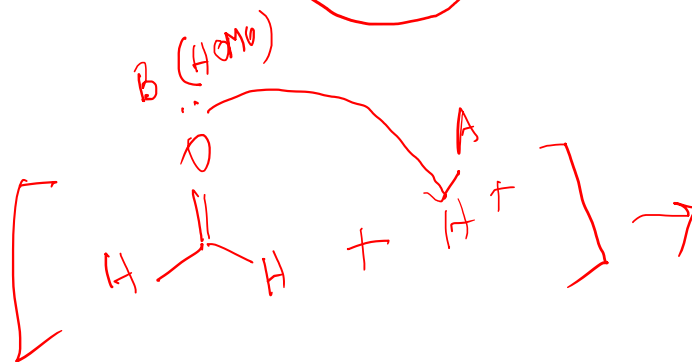
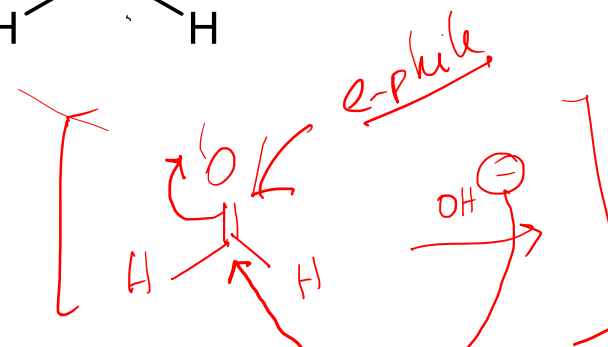
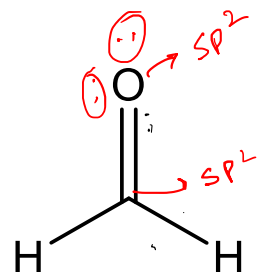
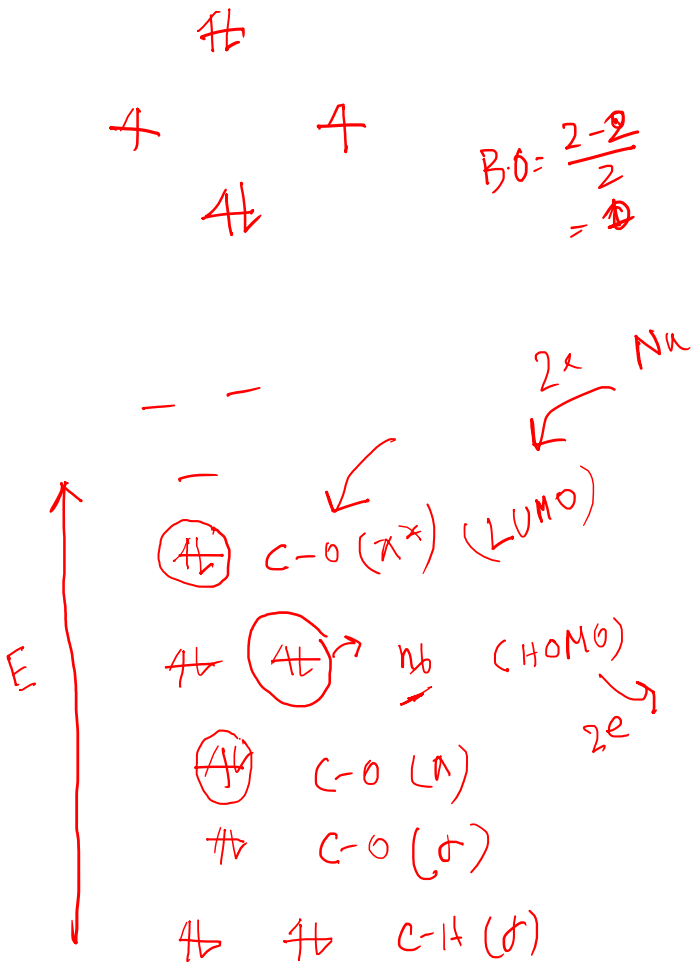


Aldehydes, Ketones and Imines



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

Energy

σ^* antibonding

π^* antibonding

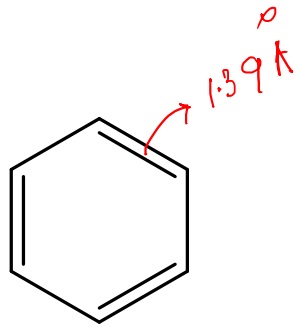
Nonbonding orbitals (including lone pairs)

π bonding

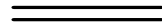
σ bonding

Conjugation and Delocalized Bonding

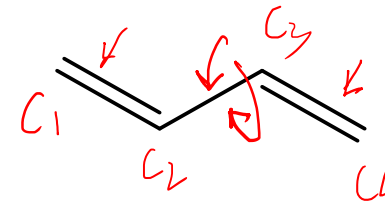
$C-C: 1.54 \text{ \AA}$
 $C=C: 1.34 \text{ \AA}$



Benzene



Ethylene



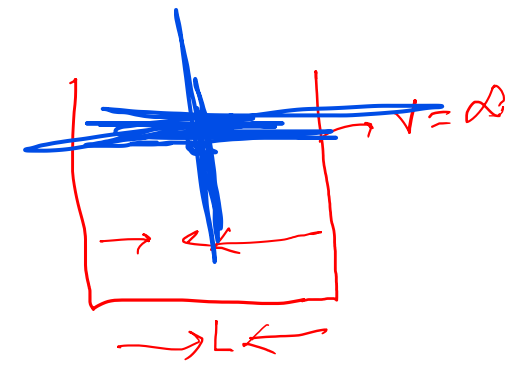
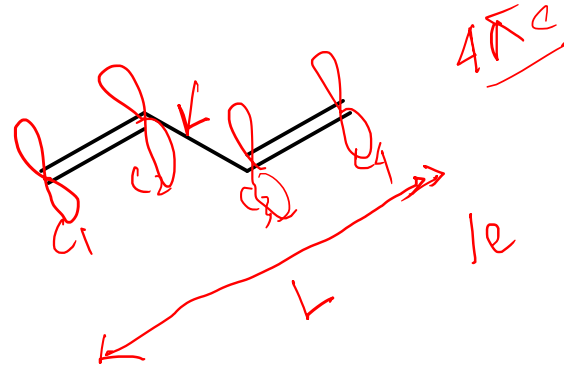
Butadiene

C_2-C_3 : single

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:

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

ψ_1
 ψ_2
 ψ_3
 ψ_4

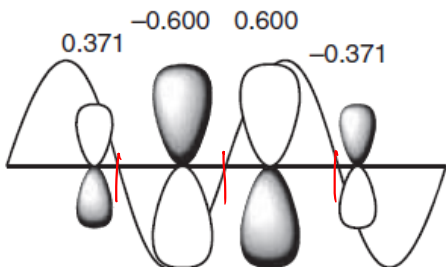
$$\sum C_i^2 = 1$$

π -Molecular Orbitals of Butadiene



3 nodes

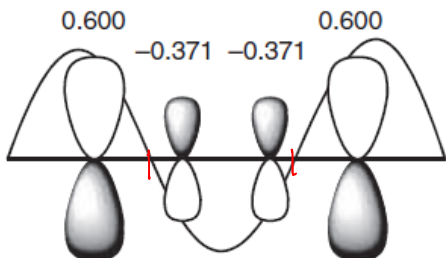
ψ_4^*



$4 \times \frac{1}{2} SW$

2 nodes

ψ_3^*

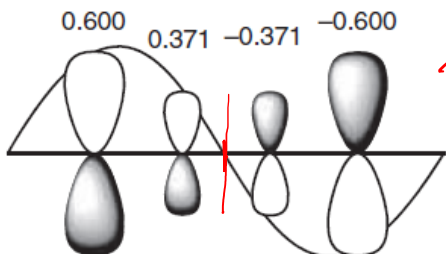


$3 \times \frac{1}{2} SW$

LUMO

1 node

ψ_2

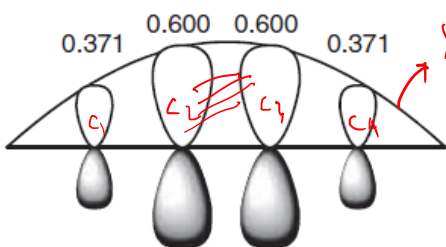


$2 \times \frac{1}{2} SW$

HOMO

0 nodes

ψ_1



$2 \times \frac{1}{2} SW$

- ✓ 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



