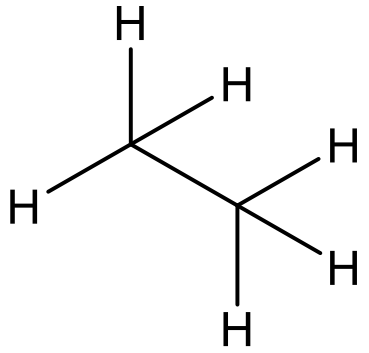
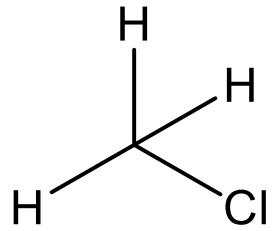
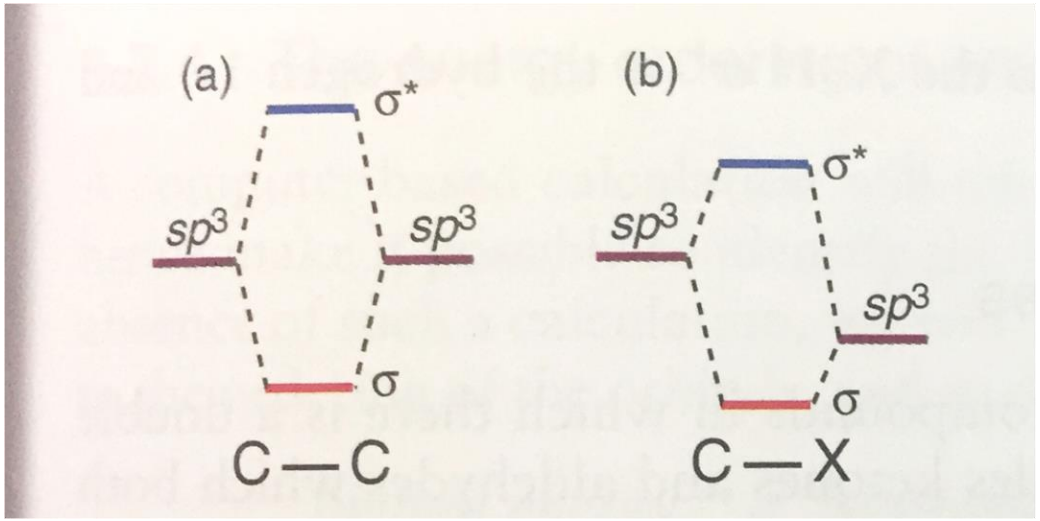


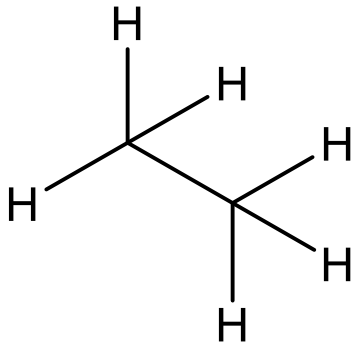


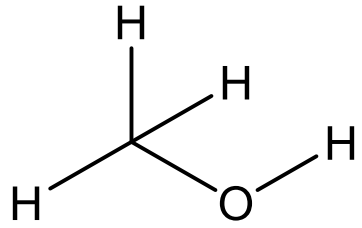


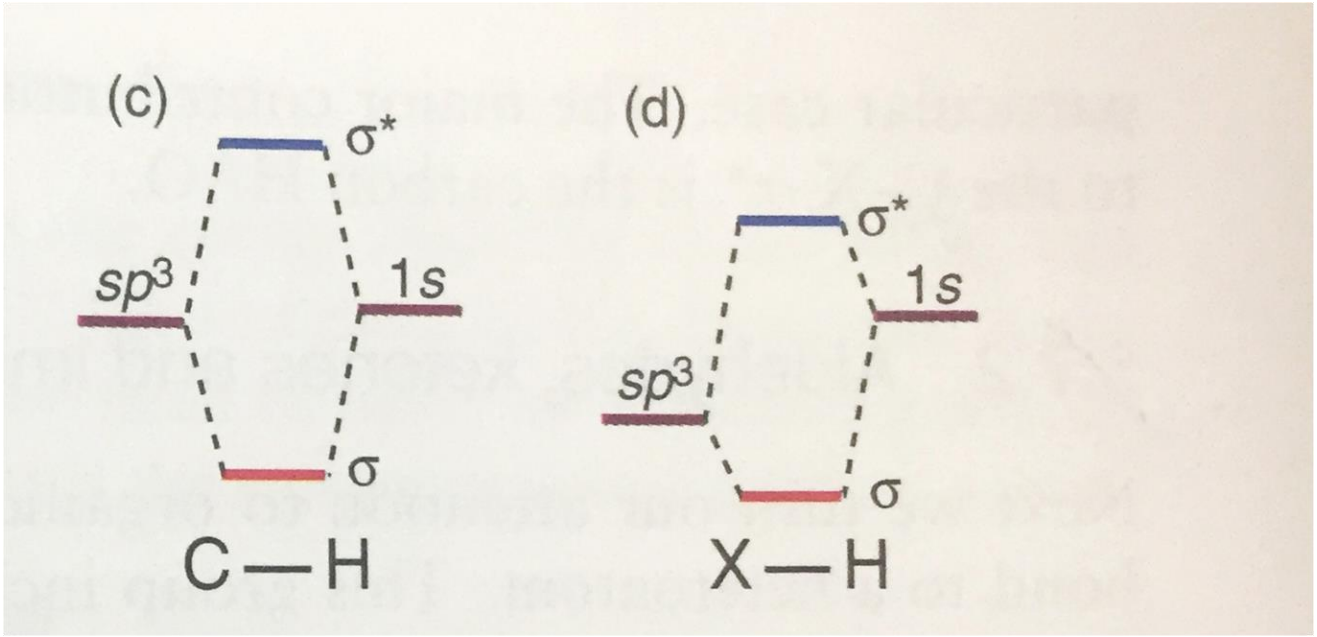
✓ σ* (C-X) is lower in energy than the σ* (C-C)

✓ In case of the attack of a nucleophile, the electrons will be initially donated to the σ* orbital

✓ Between C-C and C-X bond, a nucleophile would prefer to react with C-X bond since it has a lower energy σ*



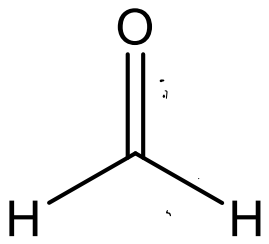


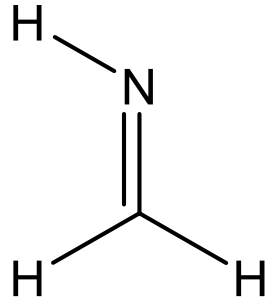


✓ σ* (X-H) is lower in energy than the σ* (C-H)

✓ X-H is more acidic than C-H

Aldehydes, Ketones and Imines



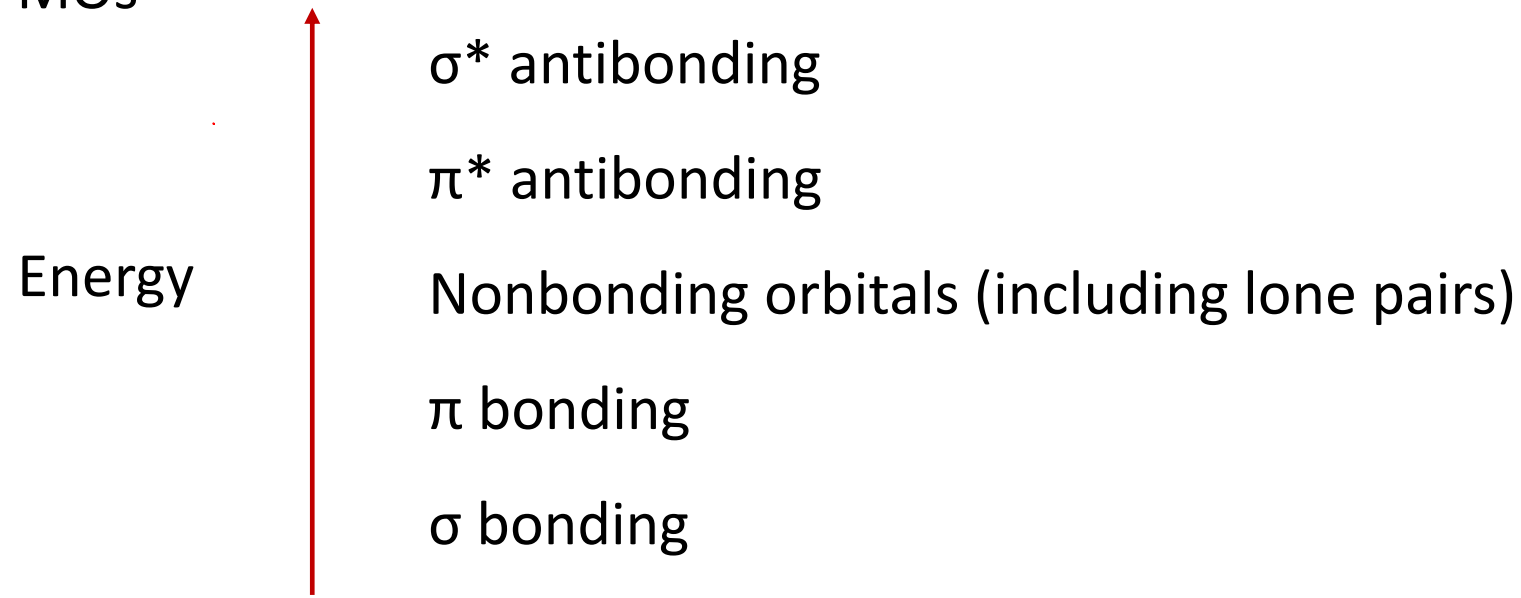


- ✓ What is the energy level ordering of different MOs in formaldehyde and imine?
- ✓ Aldehydes and ketones undergo acid/base catalysed hydration in water. Which orbitals are involved and how they are connected to the mechanism to the reactions?

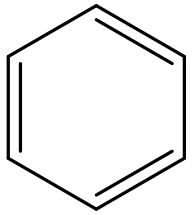
Chemistry is Dictated by HOMO-LUMO Interactions

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

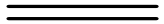
- ✓ Energy Ordering of MOs



Conjugation and Delocalized Bonding



Benzene



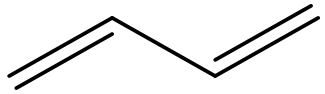
Ethylene

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

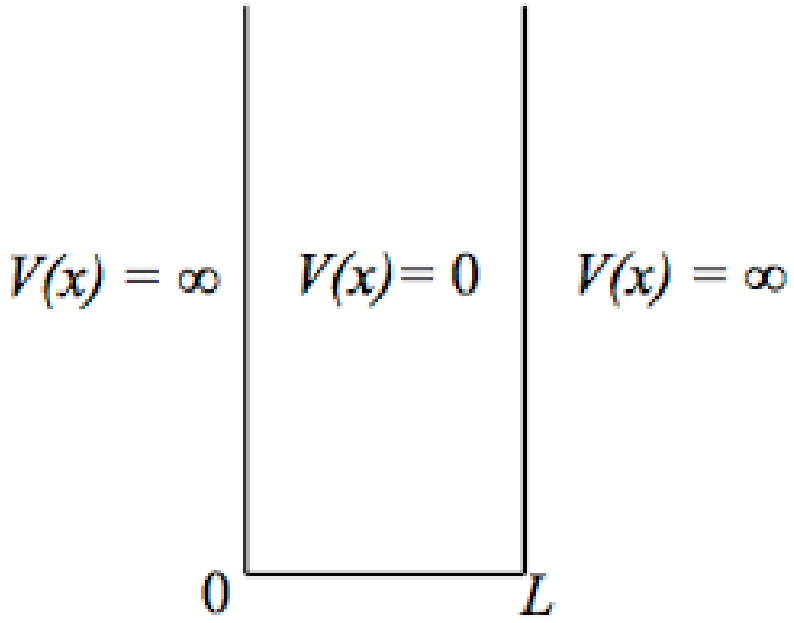
✓ **Only π-electrons in conjugated systems (σ electrons are not considered)**

❑ LCAO: Linear Combination of Atomic Orbitals:

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

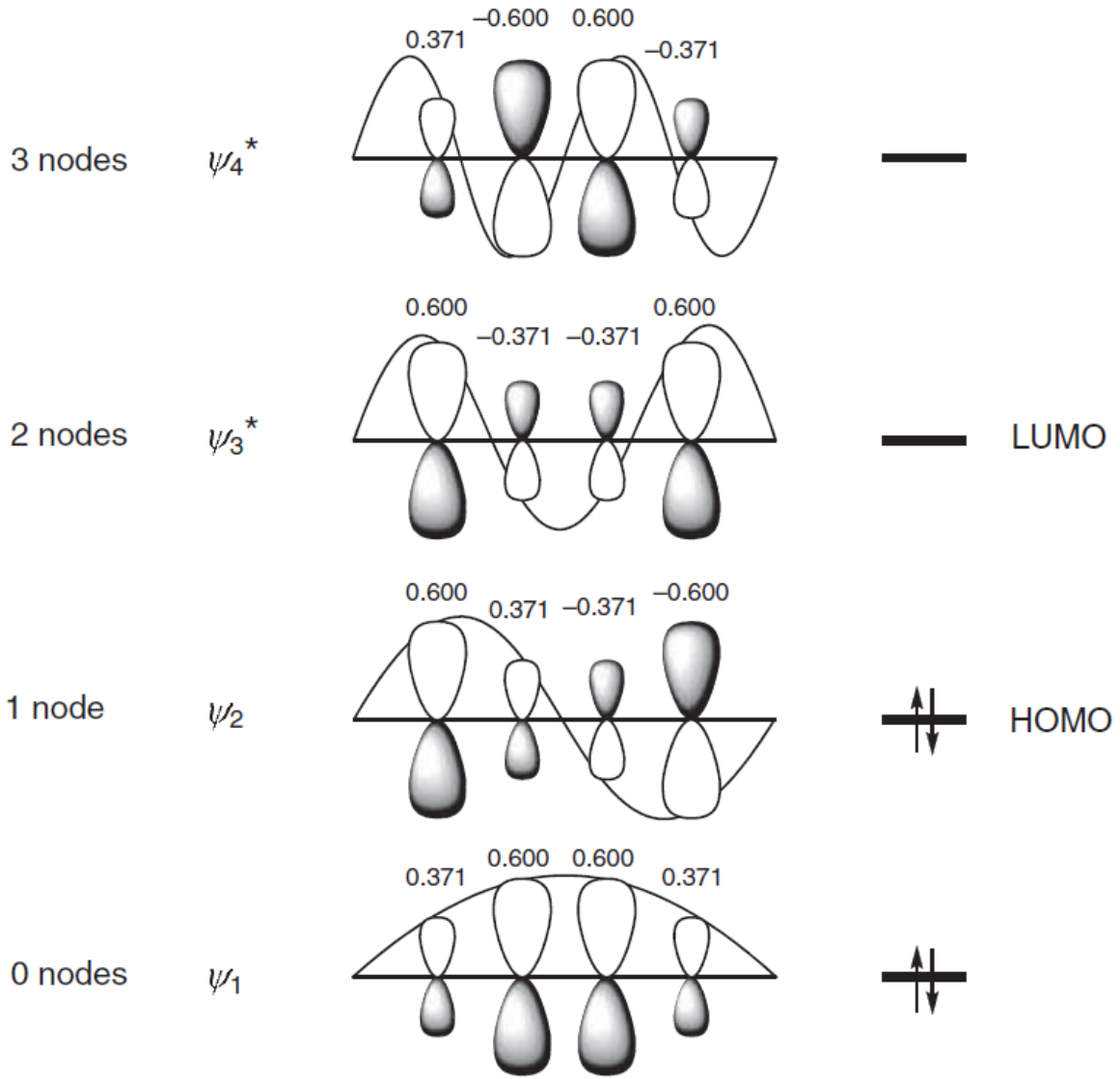
❑ Particle in a box

Particle is confined in a 1D box:



✓ The dimension of box can be compared to the length of a molecule

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*
- ✓ *Bonding electrons reside on ψ_1 and ψ_2*