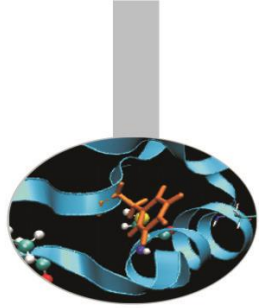
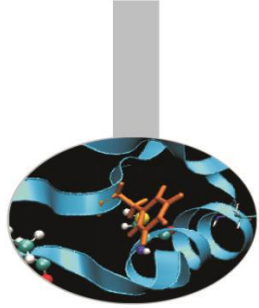
CINECA SCAI
SuperComputing Applications and Innovation



Visualization in Chemistry

Giovanni Morelli

PRACE CINECA

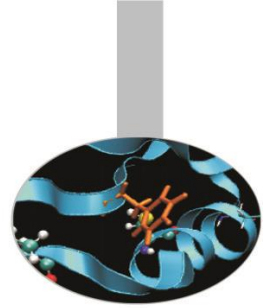


What is Chemistry ?

If we provide a good answer to this question
maybe we can understand what graphics
can do for chemistry … and chemists

What is Chemistry ?

A possible answer



boiling point, electrical conductivity, specific heat, reactivity, color….

Properties of matter

Chemistry

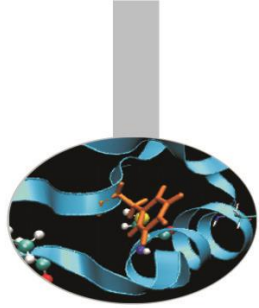
Is one of the possibilities to understand this link

Molecular geometry, **Electron Density**, **Electrostatic Potential , Molecular orbital**,…

Structure of matter

Jmol module

Topics covered



Structure of matter

Molecular geometry
Electron Density
Electrostatic Potential
Molecular orbital,…

By….

Jmol

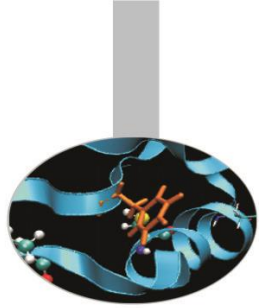
- **Introduction** to basic nomenclature of the Molecular Modelling
- **Explanation** of “some” chemical concept (we need a common vocabulary)
- **Discussion** of some examples of “chemistry by image”

Today

- **Introduction** of a specific tool for the molecular visualization : Jmol
- **Exploring** chemical proprierty on real molecules by Jmol

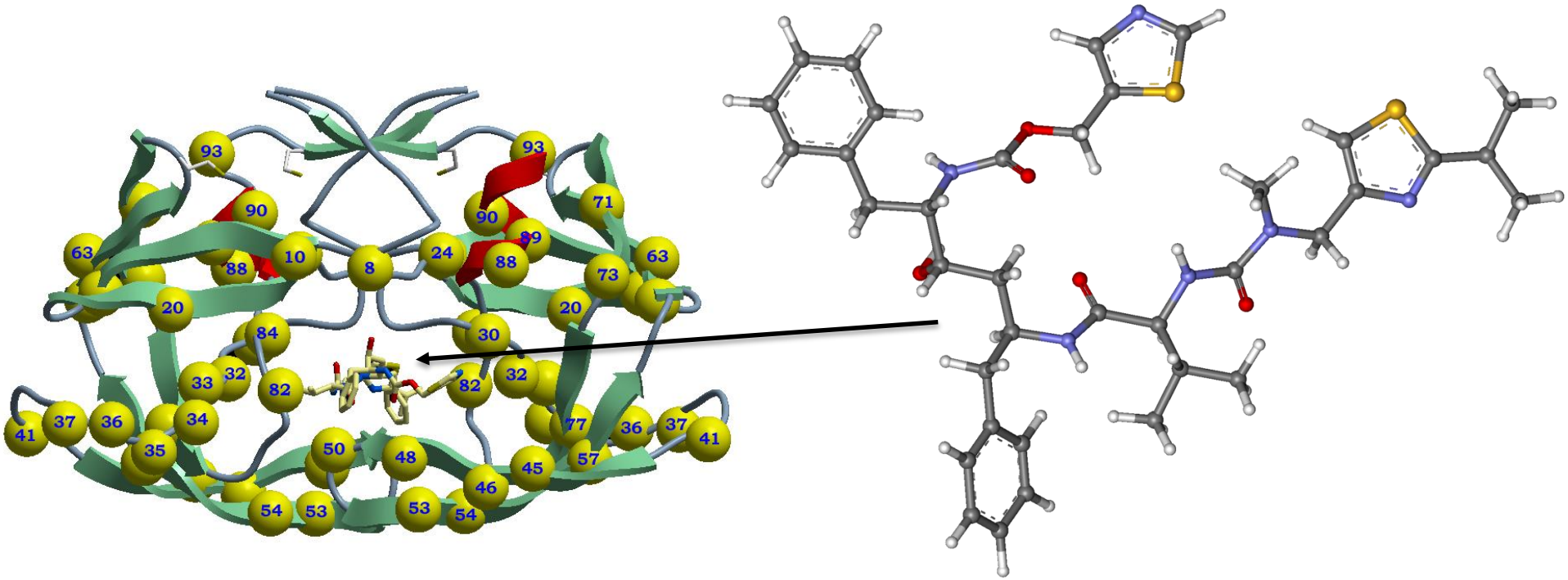
Thursday

Molecular Modelling



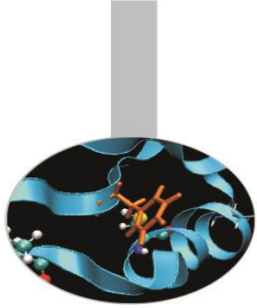
From Wikipidia

Molecular modelling encompasses all methods, theoretical and computational, used to model or mimic the behaviour of molecules.

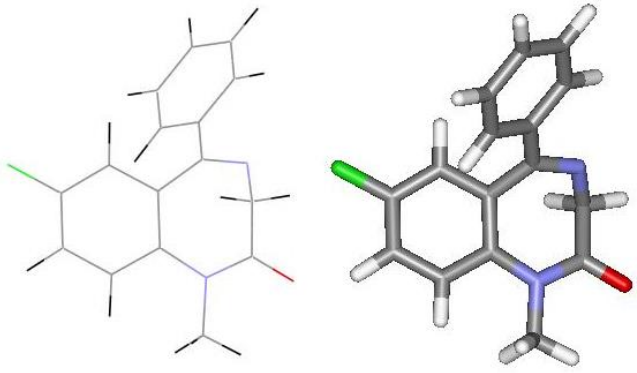


The action of Ritonavir, a drug against HIV. Adapting within the protease (**band structure**), an enzyme essential for the spread of HIV, the Ritonavir (**ball and stick**) prevents the enzyme to perform its normal function in HIV propagation.

Three-dimensional structures

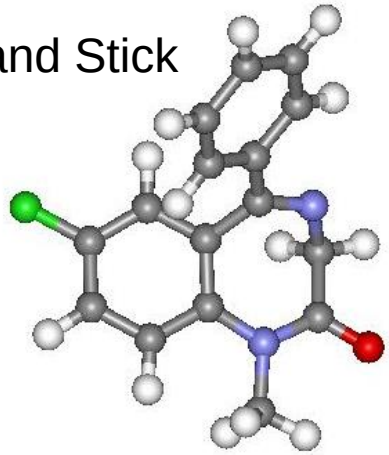


Stick Models



Focus on the geometrical structure

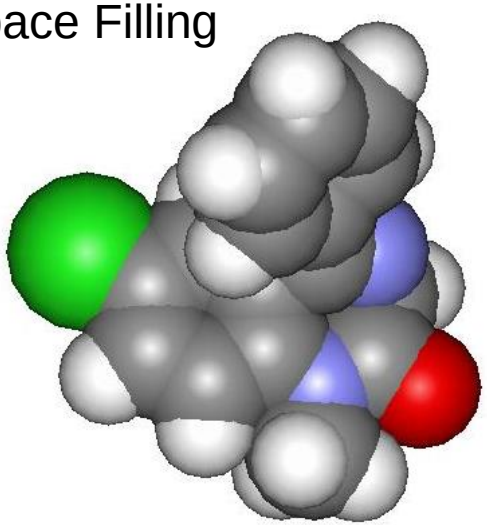
Ball and Stick



Shows three-dimensional arrangement of atoms and bonds.

Identification of atoms requires a key of color representations.

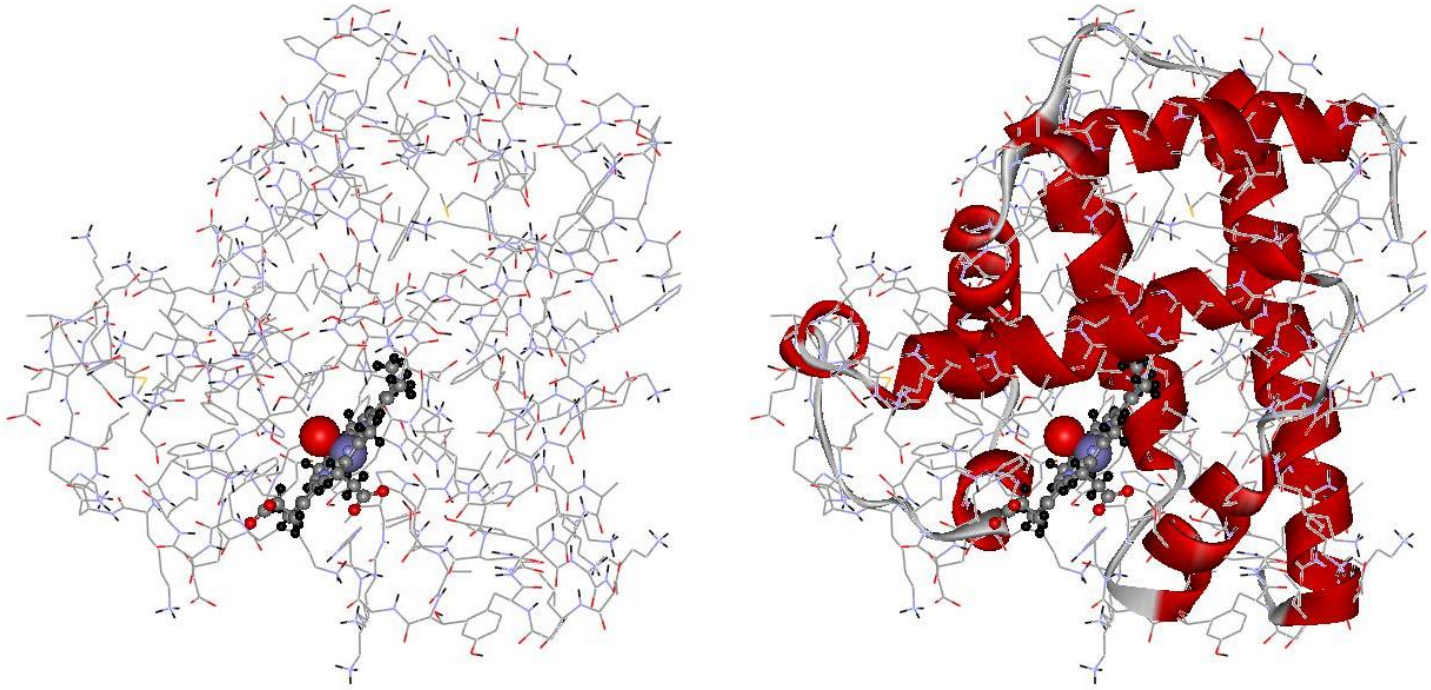
Space Filling



Shows three-dimensional arrangement as well as size relationships between atoms.

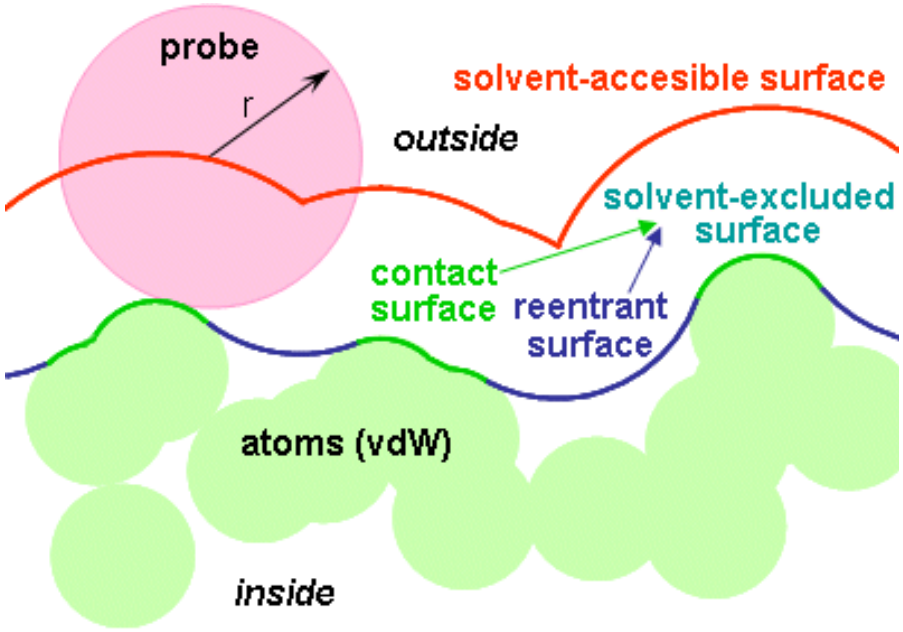
Bonding between atoms can sometimes be difficult to distinguish.

Three-dimensional structures

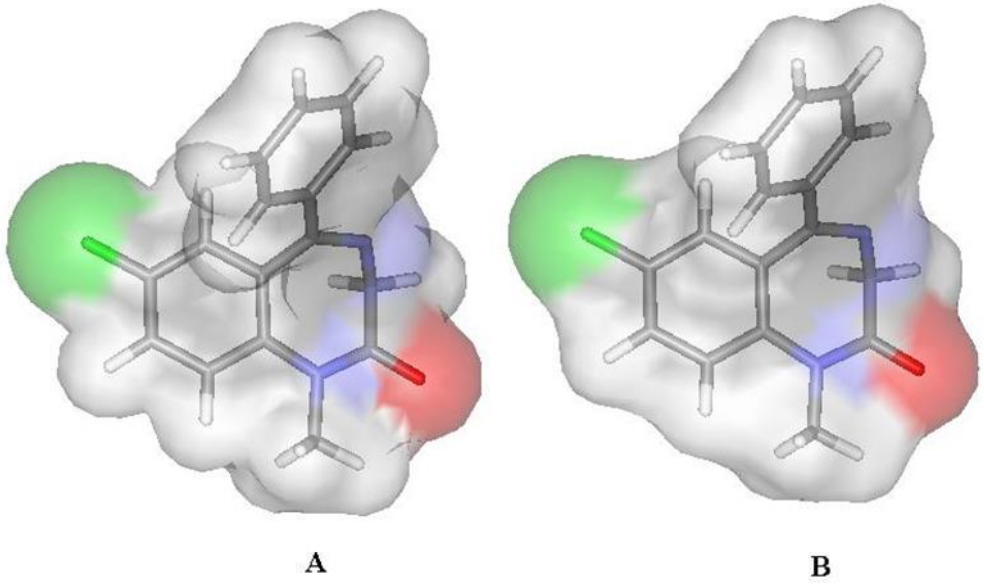


Ribbon Models

Three-dimensional Surface



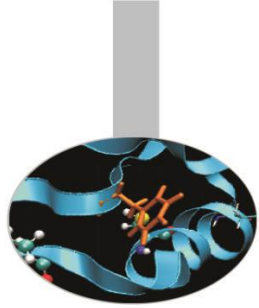
Based on http://geometry.molmovdb.org/3v/
and http://www.netsci.org/Science/Compchem/feature14e.html



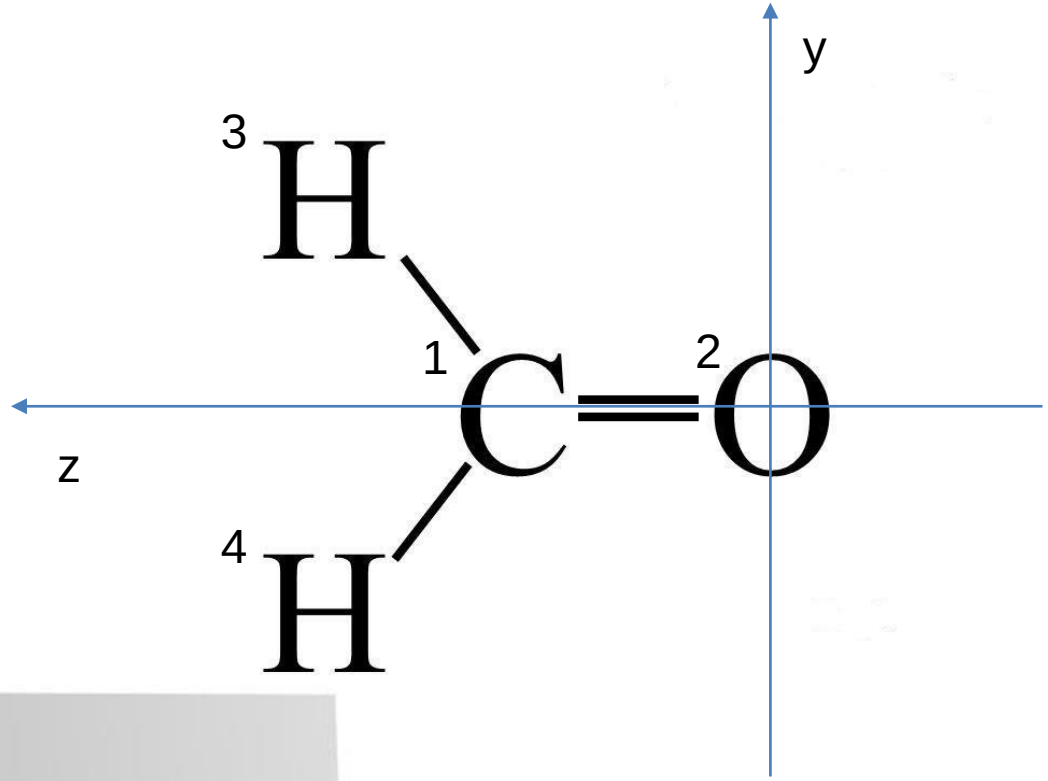
A) Van der Waals surface
B) Solvent accessible Surface (r=1.4 Angstrom)

Molecular Geometry

Coordinate system



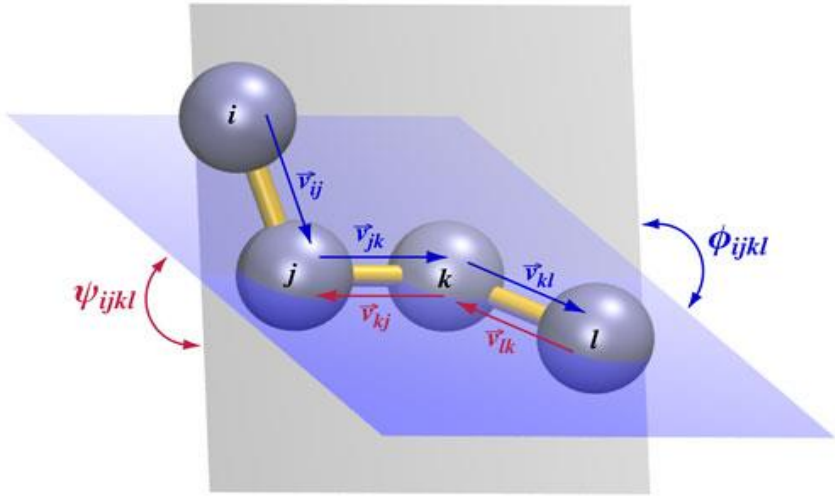
Cartesian			3N
O	0.0	0.0	0.0
C	0.0	0.0	-1.213013
H	0.0	0.937662	-1.797273
H	0.0	-0.937662	-1.797273



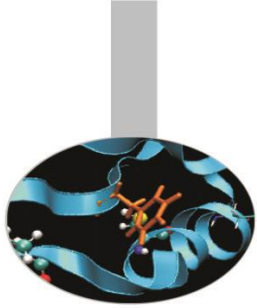
Internal 3N - 6

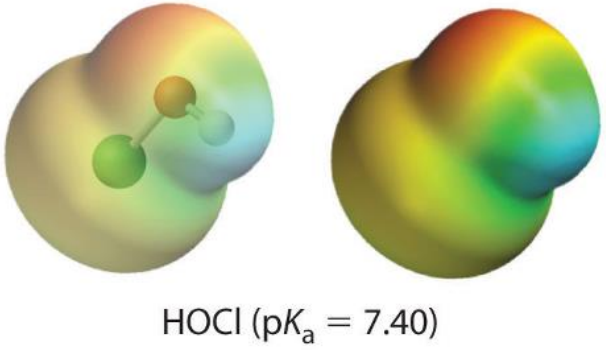
```
0 1
C1
O2  1  r2
H3  1  r3  2  a3
H4  1  r4  2  a4  3  d4

r2=1.20
r3=1.0
r4=1.0
a3=120.
a4=120.
d4=180.
```

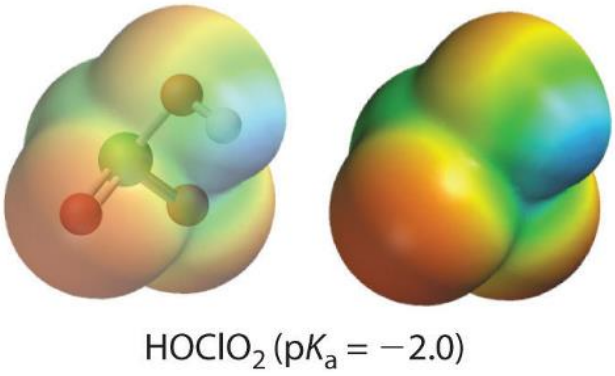


Electron Density
(Electrostatic Potential)

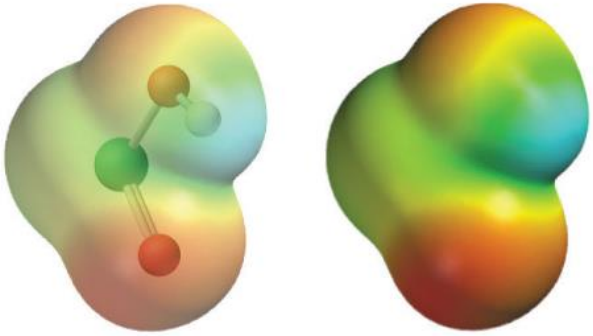




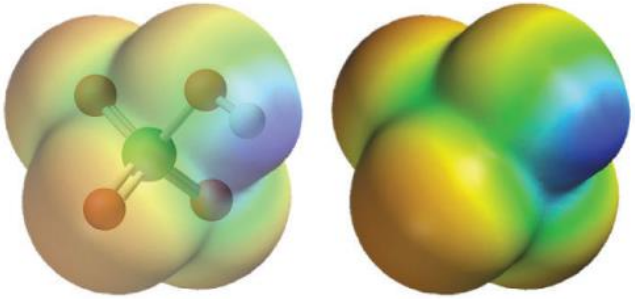
HOCl ($pK_a = 7.40$)



$HOClO_2$ ($pK_a = -2.0$)



HOClO ($pK_a = 1.96$)



$HOClO_3$ ($pK_a = -7.3$ to -8)

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\Psi_i(\mathbf{r})|^2$$

$$V_{nuclei}(\mathbf{r}) = \sum_{A}^{nuclei} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$$

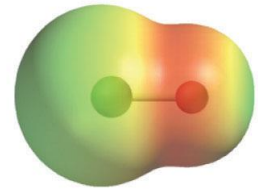
$$V_{elettroni}(\mathbf{r}) = -\int \frac{\rho(\mathbf{r})\, d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}$$

Formal charge on i-atom

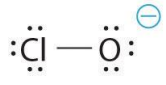
$$V(\mathbf{r}) = \sum_{i}^{atomi} \frac{q_i}{|\mathbf{r} - \mathbf{R}_i|}$$

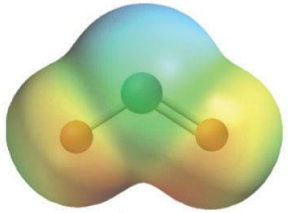
Source: Chlorine oxoacids pK_a values from J. R. Bowser, *Inorganic Chemistry* (Pacific Grove, CA: Brooks-Cole,1993).

Electron Density
(structure/properties)

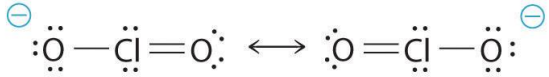


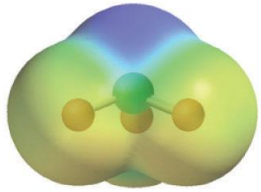
ClO^-



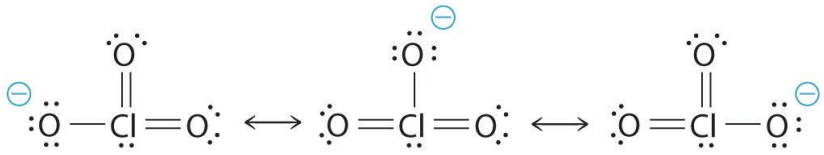


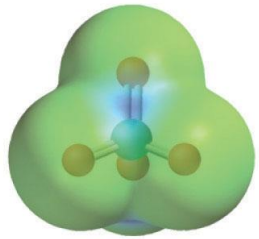
ClO_2^-



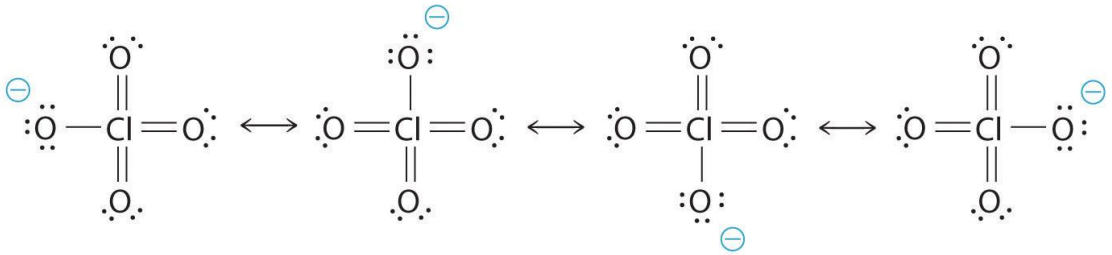


ClO_3^-





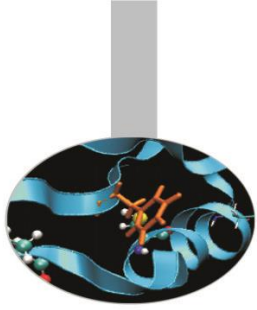
ClO_4^-

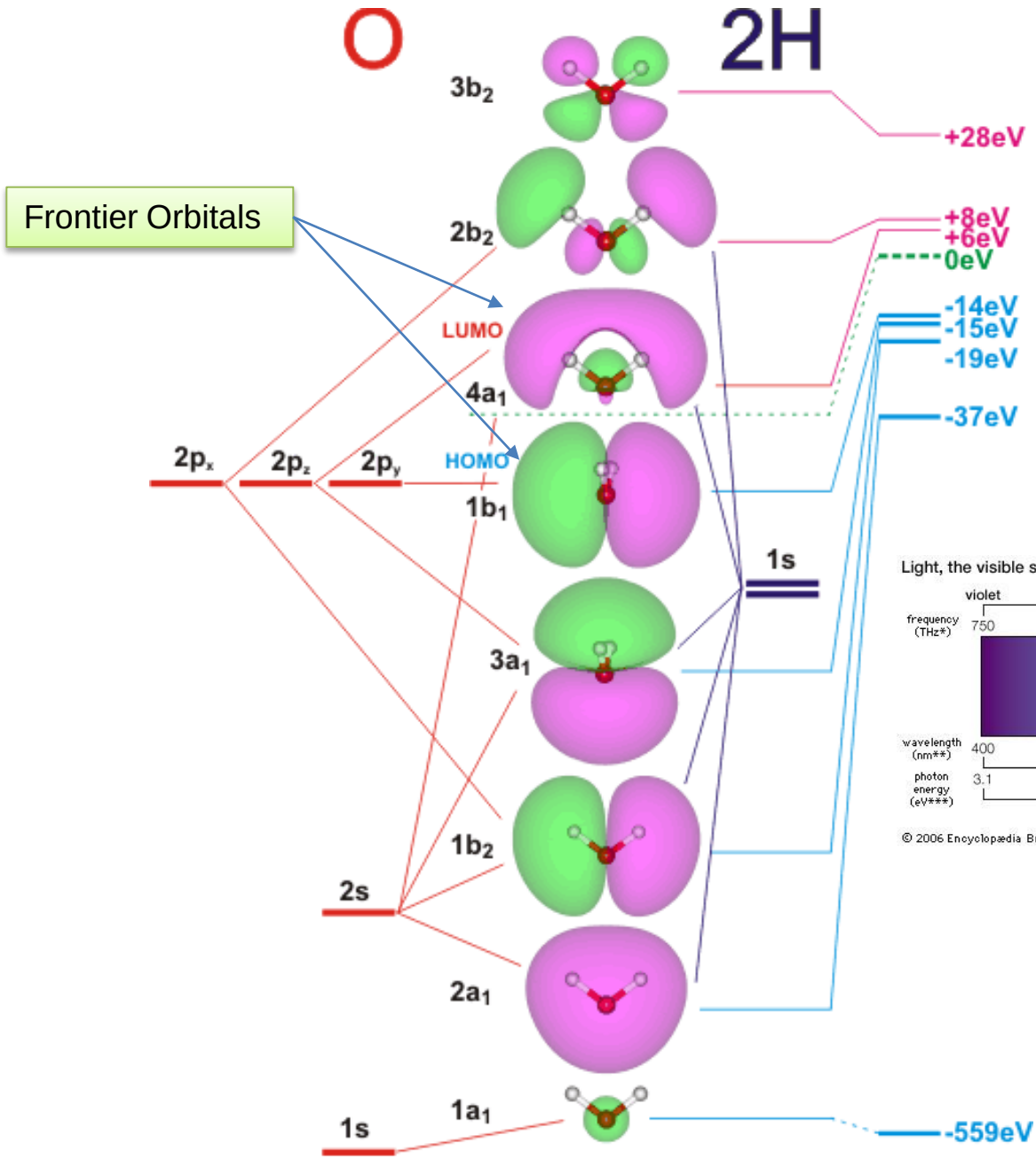


The Relationship between Delocalization of the Negative Charge in the Oxoanions of Chlorine and the Number of Terminal Oxygen Atoms

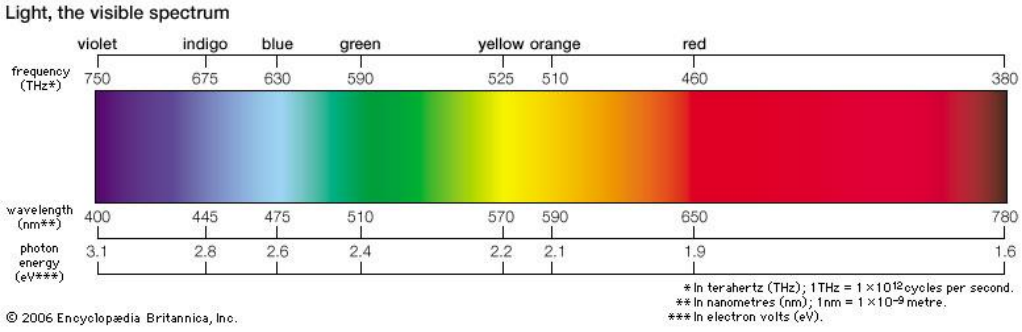
https://saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/s20-03-molecular-structure-and-acid-b.html

Molecular Obital



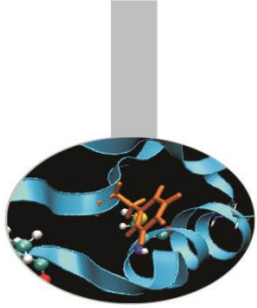


E_{LUMO}-E_{HOMO} = 20 eV !!!



Molecular Obital

HOMO/LUMO: Frontier Orbitals



The Nobel Prize in Chemistry 1981
Kenichi Fukui, Roald Hoffmann

Share this: 2

Kenichi Fukui - Facts

Kenichi Fukui

Born: 4 October 1918, Nara, Japan

Died: 9 January 1998, Kyoto, Japan

Affiliation at the time of the award: Kyoto University, Kyoto, Japan

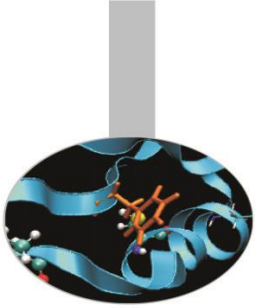
Prize motivation: "for their theories, developed independently, concerning the course of chemical reactions"

Field: theoretical chemistry

Prize share: 1/2

Molecular Obital

HOMO/LUMO: The Nobel Lecture



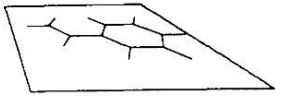
THE ROLE OF FRONTIER ORBITALS IN CHEMICAL REACTIONS

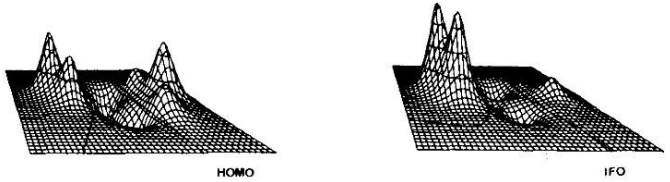
Nobel lecture, 8 December, 1981

by

KENICHI FUKUI

Department of Hydrocarbon Chemistry, Kyoto University, Sakyo-ku, Kyoto 606, Japan





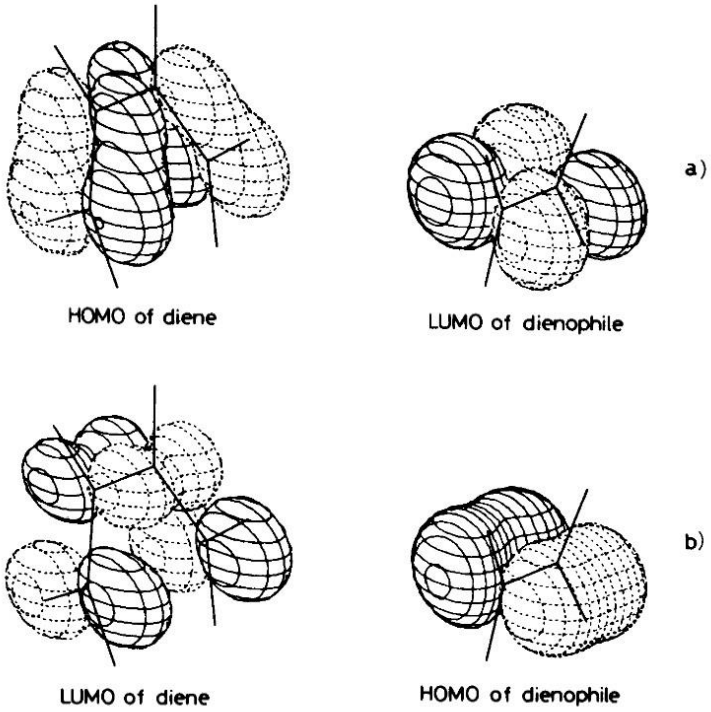


Fig. 2. The significance of orbital symmetry in the HOMO-LUMO overlapping in Diels-Alder reactions.

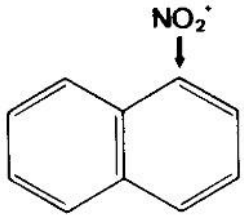
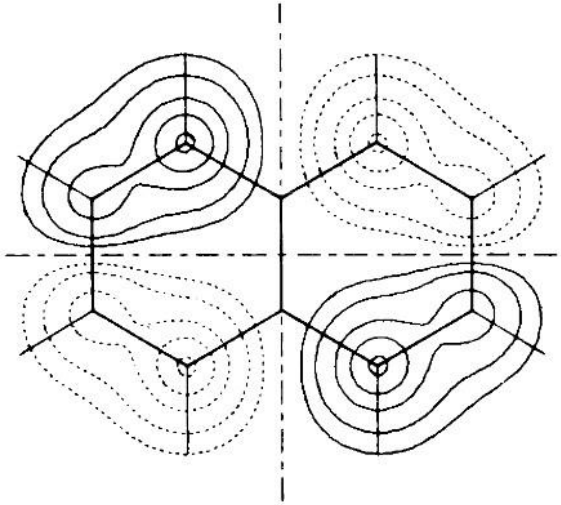
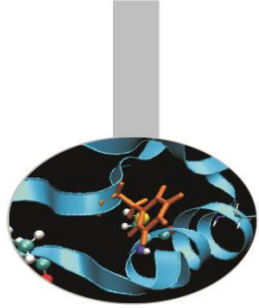


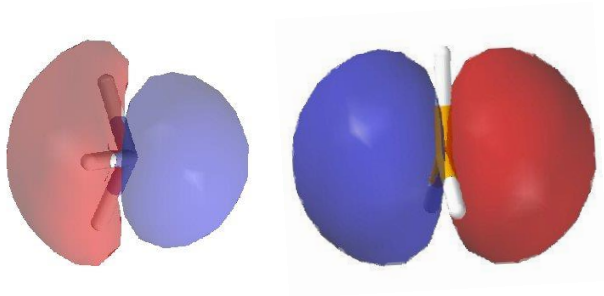
Fig. 1. Nitration of naphthalene.



Molecular Obital

HOMO/LUMO: examples

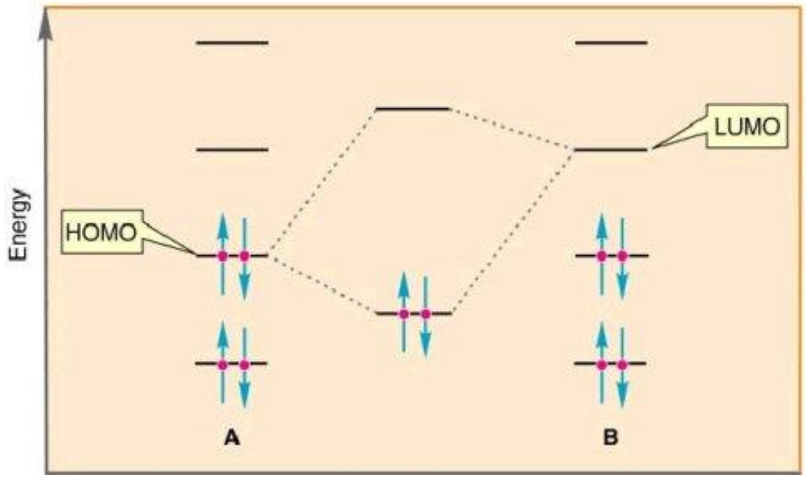




NH_3 HOMO BH_3 LUMO

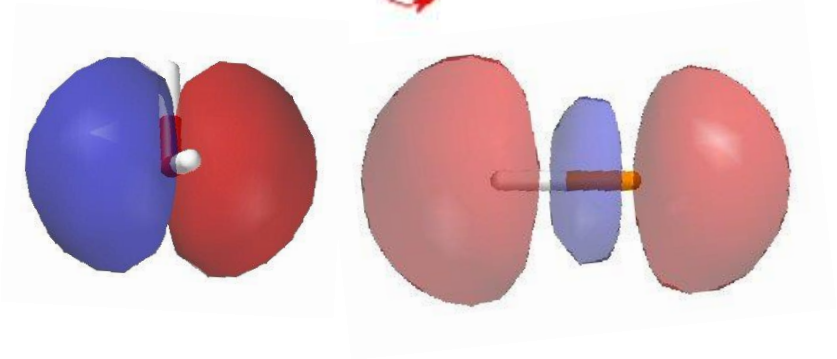
Lewis base
nucleophilic

Lewis acid → Acid/Basic reaction
electrophile → Nucleophilic substitution (S_{N1}/S_{N2})

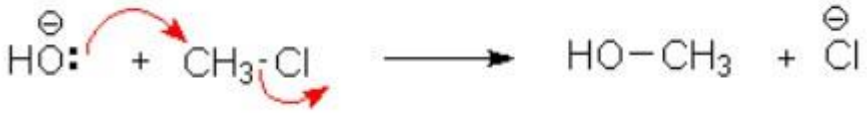


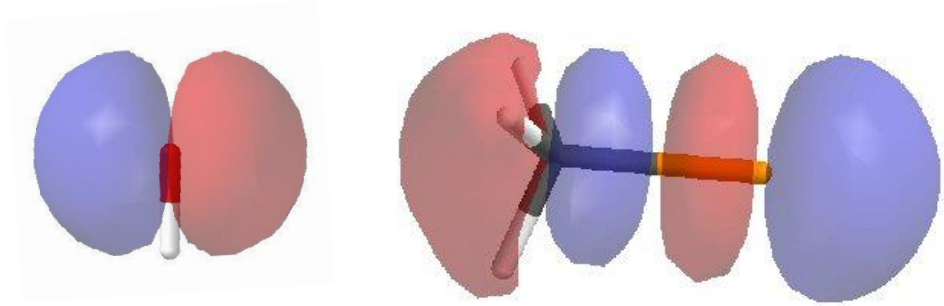
Molecular Obital

HOMO/LUMO: examples



The interaction stabilizes the unshared pair of the oxygen, while simultaneously breaking the H-Cl bond because the interaction is with the antibonding orbital.

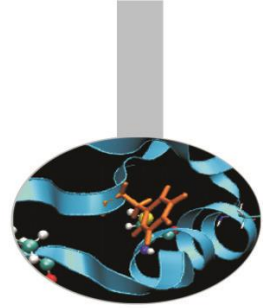




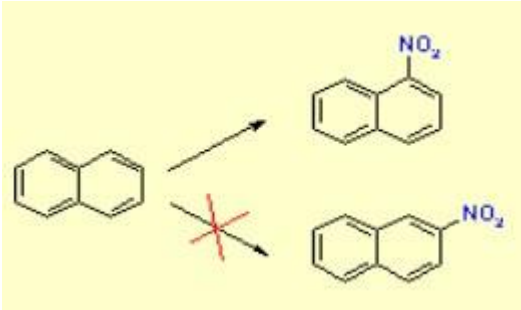
The interaction stabilizes the unshared pair of the oxygen, while simultaneously breaking the CH3-Cl bond because the interaction is with the antibonding orbital.

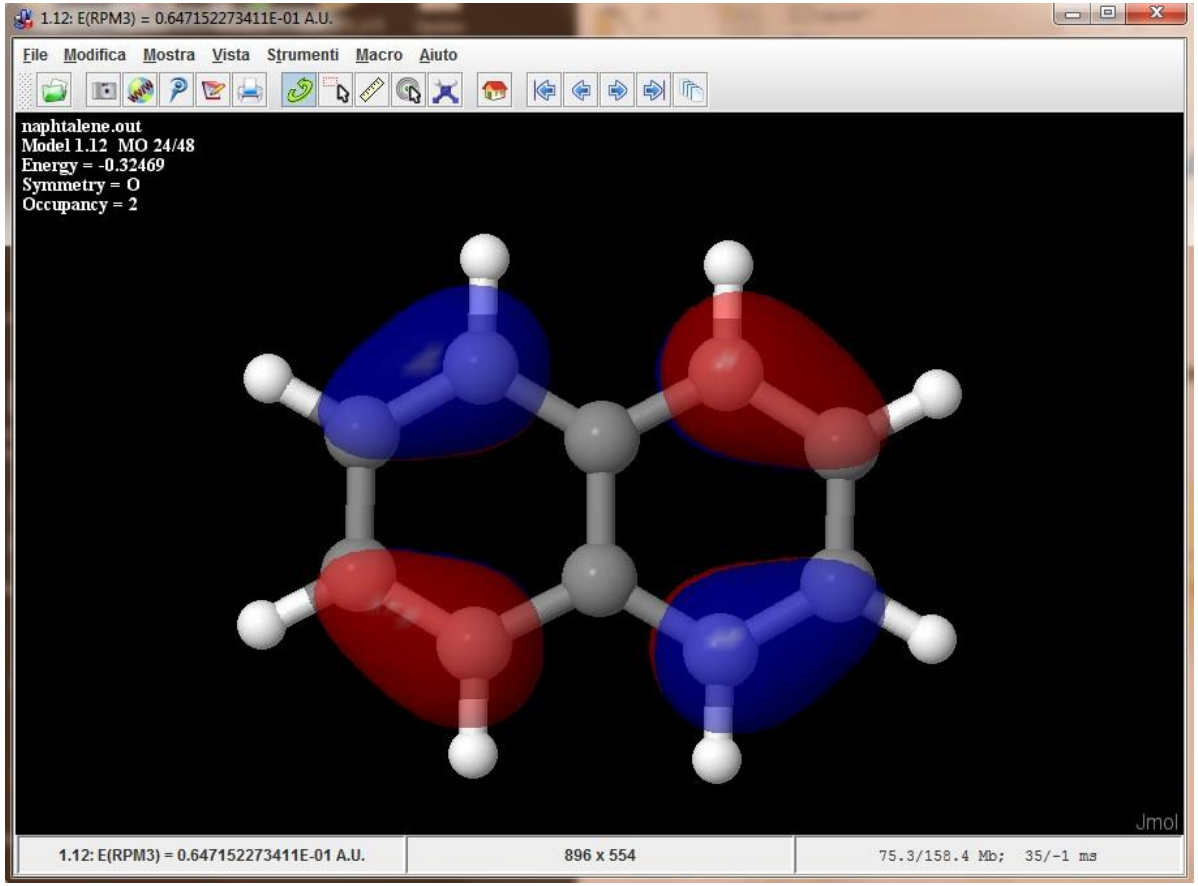
Molecular Obital

HOMO/LUMO: examples



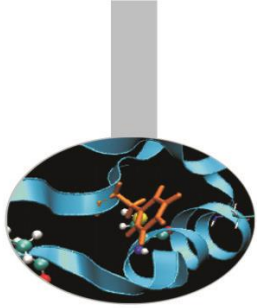
Predicted reactivity from the shape of HOMO Molecular Orbital

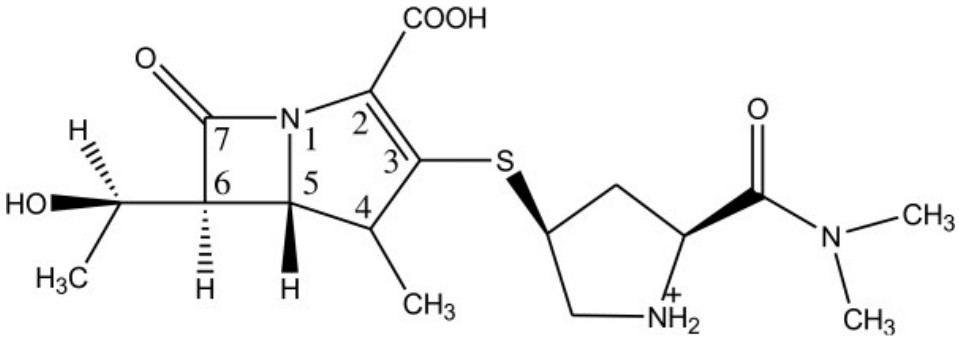


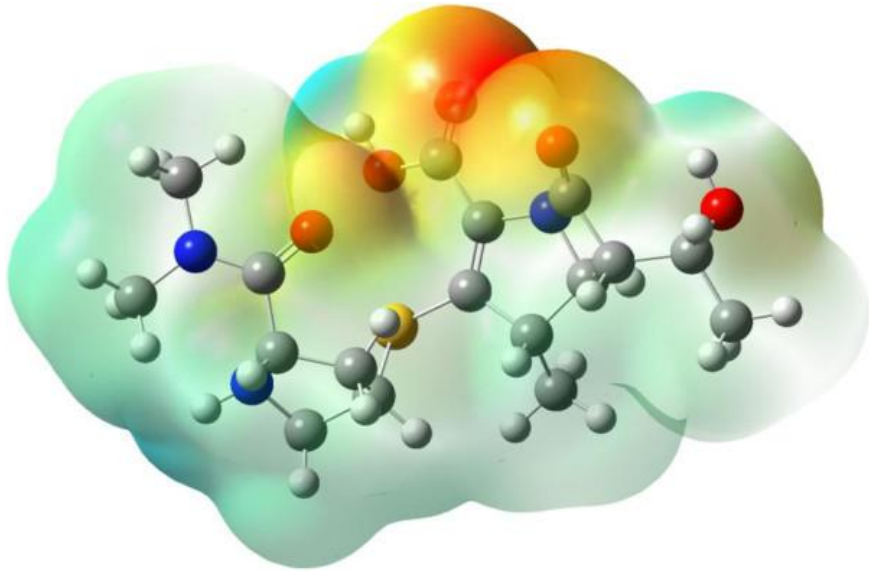


Molecular Obital

HOMO/LUMO: examples







In order to predict reactive sites for electrophilic and nucleophilic attack in **meropenem**, the MEP was also established. The different values of electrostatic potential on the surface are represented by colors. The **positive** (**blue**) regions of MEP show **electrophilic** while the **negative** (**red**) areas **nucleophilic** reactivity. In meropenem, the most pronounced are the negative regions, localized on the carboxylic and carbonyl groups, that indicate possible sites for nucleophilic activity.

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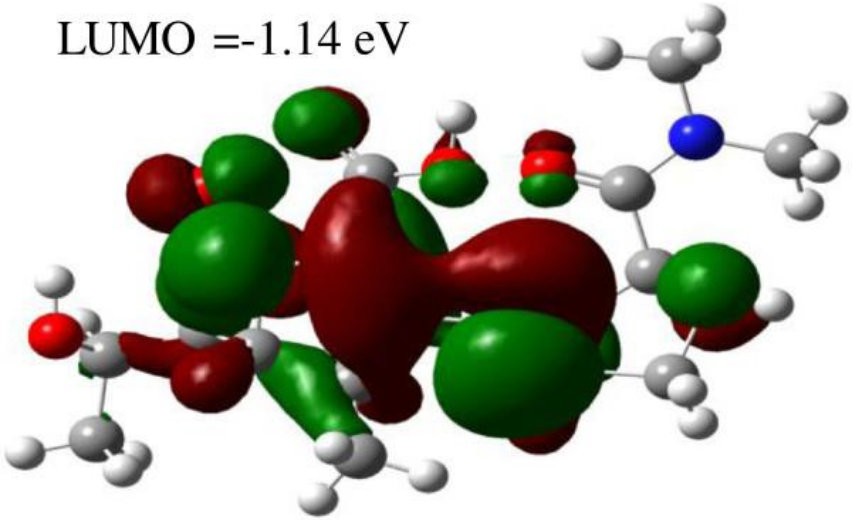
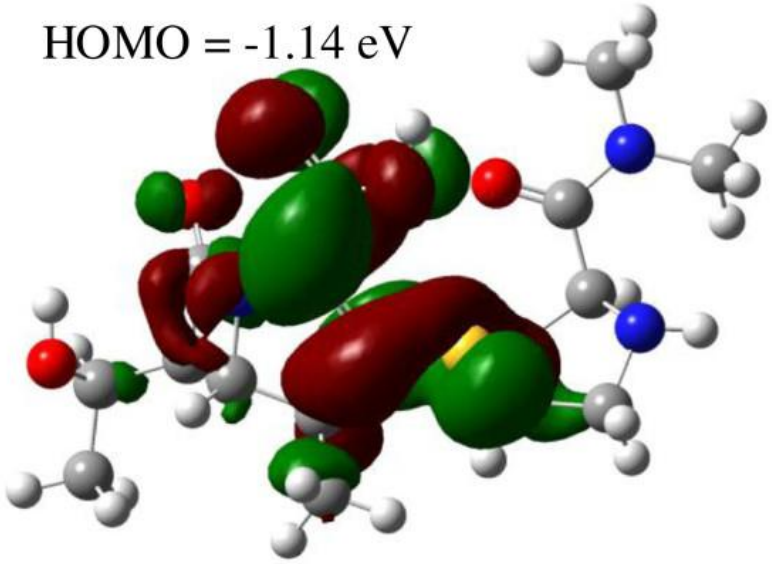
Molecular Obital

HOMO/LUMO: examples





The localization of charge density on the frontier molecular orbitals demonstrates a ***similar localization for the lowest unoccupied molecular orbital and the highest occupied molecular orbital.***

For both the HOMO and LUMO, the charge density was localized on the β-lactam and pyrrolidine 4:5 bicyclic fused rings and the carboxylic and carbonyl groups.

Since the FMOs are the main orbitals involved in reactivity, the 4:5 bicyclic fused rings of meropenem may be proposed as the main areas where acceptor-donor electron reactions occur.

The low value of HOMO-LUMO gap energy for meropenem confirms its significant susceptibility to degradation

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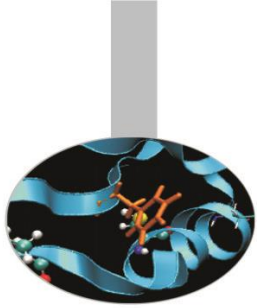
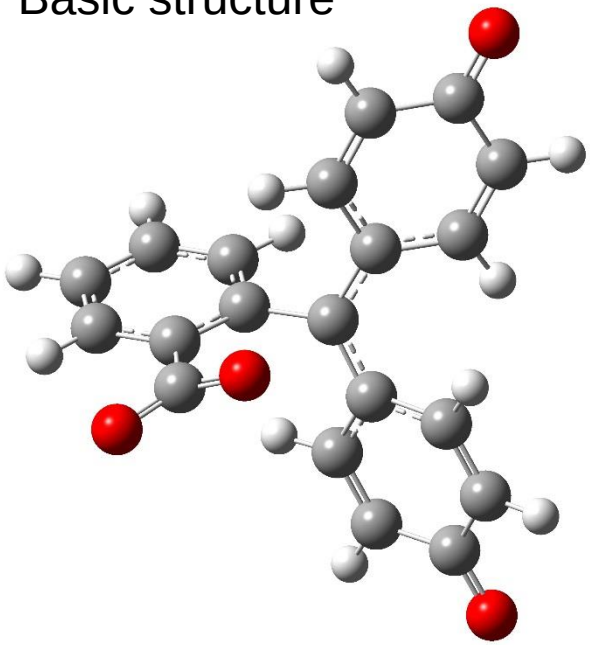
Molecular Obital

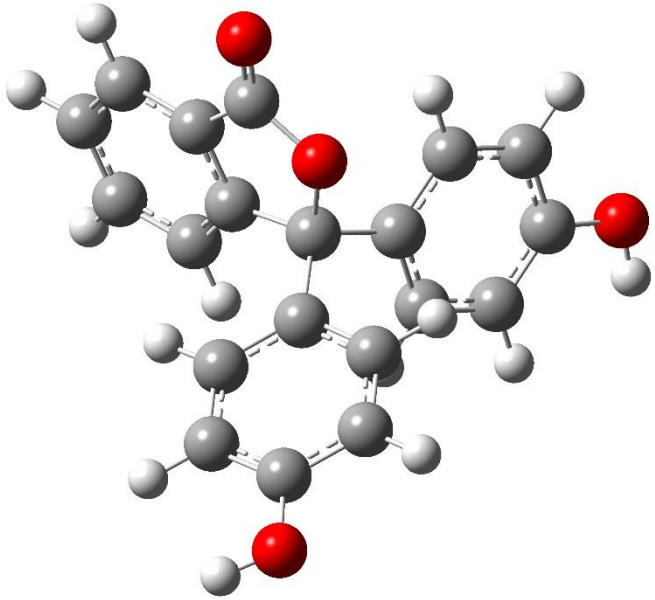
Phenolphthalein colors

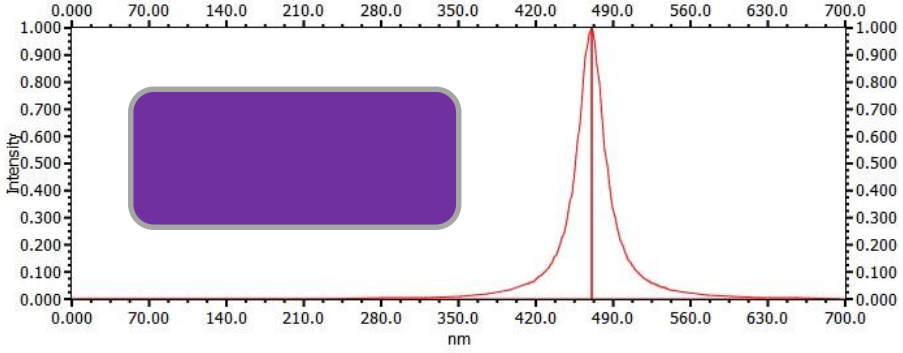


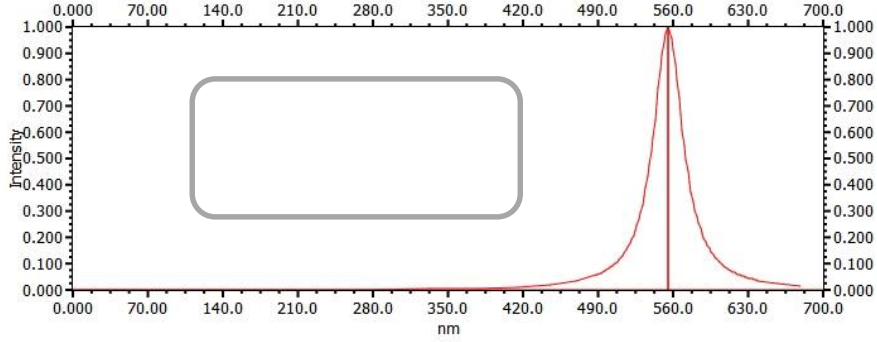
Basic structure



Acid structure







We will analyze FMO by Jmol in the Lab….