Lesson 8: Population analysis

Importance

Population analysis is the study of charge distribution within molecules.

What does a population analysis deliver?

- Determination of the distribution of electrons in a molecule
- Creating orbital shape
- Derivation of atomic charges and dipole (multiple) moments

Methods of calculation

- Based on the wave function (Mulliken, NBO)
- Based on the electron density (Atoms in Molecules)
- Fitted to the electrostatic potential (CHELPG, MK)

Mulliken Population Analysis

Advantages

- Most popular method
- Available in nearly every software program for molecular modeling.
- Fast and simple method for determination of electron distribution and atomic charged

Disadvantage

- Strong dependance of the results from the level of theory (basis set or kind of calculation)

Example: Li-charge in LiF

Population	basis set	q(Li,RHF)	q(Li,B3LYP)
Mulliken	STO-3G	+0.227	+0.078
	6-31G	+0.743	+0.593
	6-311G(d)	+0.691	+0.558

Löwdin population analysis

Advantages

- Sought to improve upon the Mulliken method
- More stable than Mulliken with changes in basis set.

Disadvantage

- More computationally expensive

Natural Bond Orbital Analysis

Natural Bond Orbital Analysis

NBO classifies atomic orbitals into two distinct groups: NAOs, NBOs. NAOs are made up of basis sets of single atoms (core, valence and Rydberg) and the NBOs are a combination of basis set atomic orbitals of two atoms.

Two parts of the methods

- NPA $\rightarrow$ Natural population analysis to identify the population numbers
- NBO $\rightarrow$ Analysis of the bond order based on the electron population obtained by NPA

Advantages

- Smaller dependence on the basis set
- better reproducibility for different molecules
- Orientates itself at the formalism for Lewis formulas

Disadvantages

- More computationally expensive.
- tends to predict larger charged.
- best used for comparing differences rather than absolute atomic charges.

The population analysis using Atoms in Molecules theory is requested by keyword AIM in a Gaussian input file. Atoms in Molecules theory bases its calculations on the calculated electron density. The existence of critical points defines the existence of a bond between two nuclei in AIM.

Advantage:

- Almost no dependence on the level of basis sets.

Disadvantage:

- For a low level of theory mostly inappropriate
- Unstability during calculation runs
- relatively computationally expensive.

Practical task

- Draw HF molecule, optimize the geometry and generate G09 input.
- Use pop=(nbo,savenbo) for NBO or Pop=Full for Mulliken
- After Pop command, add a space and type ”FormCheck”
- Run the calculation

Visualizing the orbitals

- Open the *FChk file in Avogadro
- Click on Extensions $\rightarrow$ Create Surface
- Select ”Molecular Orbital” as surface type
- Choose the MO you want to visualize and calculate

You should be able to see something like these that shows the HOMO and LUMO of HF molecules