Introduction to Computational Quantum Chemistry

Lesson 8: Population analysis

Importance

Pictures of orbitals are informative, however numerical values are much easier to quantified and compared. For example σ vs π bonding in organic 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

Mulliken Population Analysis

Advantages

- Most popular method
- Standard in program packages like Gaussian
- 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

Natural Bond Orbital Analysis

Natural Bond Orbital Analysis

Based on the theory of Natural Orbitals by Lowdin.

Two parts of the methods

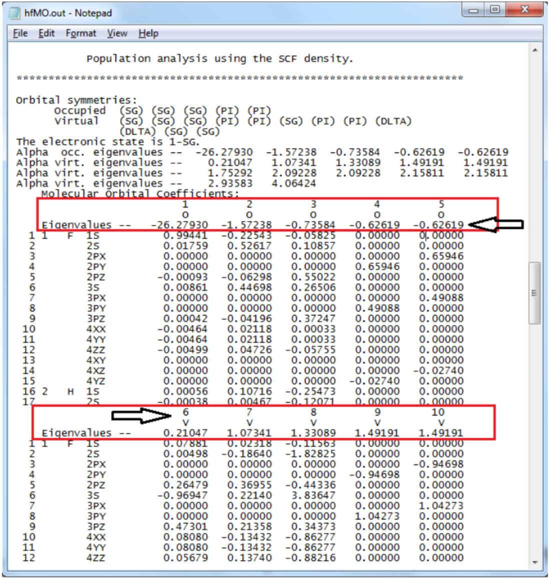
- NPA → Natural population analysis to identify the population numbers
- NBO → Analysis of the bond order based on the electron population obtained by NPA

Advantages

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

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



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            Population analysis using the SCF density.

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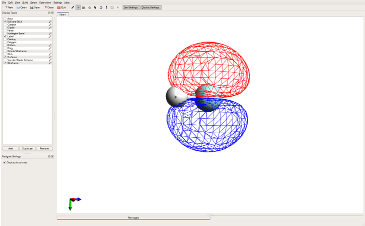
 Orbital symmetries:
       Occupied  (SG) (SG) (SG) (PI) (PI)
       Virtual   (SG) (SG) (SG) (PI) (PI) (SG) (PI) (PI) (DLTA)
                 (DLTA) (SG) (SG)
 The electronic state is 1-SG.
 Alpha  occ. eigenvalues --  -26.27930  -1.57238  -0.73584  -0.62619  -0.62619
 Alpha virt. eigenvalues --    0.21047   1.07341   1.33089   1.49191   1.49191
 Alpha virt. eigenvalues --    1.75292   2.09228   2.09228   2.15811   2.15811
 Alpha virt. eigenvalues --    2.93583   4.06424
     Molecular Orbital Coefficients:
                           1         2         3         4         5
                           O         O         O         O         O
     Eigenvalues --   -26.27930  -1.57238  -0.73584  -0.62619  -0.62619
   1 1   F  1S          0.99441  -0.22543  -0.05825   0.00000   0.00000
   2        2S          0.01759   0.52617   0.10857   0.00000   0.00000
   3        2PX         0.00000   0.00000   0.00000   0.00000   0.65946
   4        2PY         0.00000   0.00000   0.00000   0.65946   0.00000
   5        2PZ        -0.00093  -0.06298   0.55022   0.00000   0.00000
   6        3S          0.00861   0.44698   0.26506   0.00000   0.00000
   7        3PX         0.00000   0.00000   0.00000   0.00000   0.49088
   8        3PY         0.00000   0.00000   0.00000   0.49088   0.00000
   9        3PZ         0.00042  -0.04196   0.37247   0.00000   0.00000
  10        4XX        -0.00464   0.02118   0.00033   0.00000   0.00000
  11        4YY        -0.00464   0.02118   0.00033   0.00000   0.00000
  12        4ZZ        -0.00499   0.04726  -0.05755   0.00000   0.00000
  13        4XY         0.00000   0.00000   0.00000   0.00000   0.00000
  14        4XZ         0.00000   0.00000   0.00000   0.00000  -0.02740
  15        4YZ         0.00000   0.00000   0.00000  -0.02740   0.00000
  16 2   H  1S          0.00056   0.10716  -0.25473   0.00000   0.00000
  17        2S         -0.00038   0.00467  -0.12071   0.00000   0.00000
                           6         7         8         9        10
                           V         V         V         V         V
     Eigenvalues --     0.21047   1.07341   1.33089   1.49191   1.49191
   1 1   F  1S          0.07881   0.02318  -0.11563   0.00000   0.00000
   2        2S          0.00498  -0.18640  -1.82825   0.00000   0.00000
   3        2PX         0.00000   0.00000   0.00000   0.00000  -0.94698
   4        2PY         0.00000   0.00000   0.00000  -0.94698   0.00000
   5        2PZ         0.26479   0.36955  -0.44336   0.00000   0.00000
   6        3S         -0.96947   0.22140   3.83647   0.00000   0.00000
   7        3PX         0.00000   0.00000   0.00000   0.00000   1.04273
   8        3PY         0.00000   0.00000   0.00000   1.04273   0.00000
   9        3PZ         0.47301   0.21358   0.34373   0.00000   0.00000
  10        4XX         0.08080  -0.13432  -0.86277   0.00000   0.00000
  11        4YY         0.08080  -0.13432  -0.86277   0.00000   0.00000
  12        4ZZ         0.05679   0.13740  -0.88216   0.00000   0.00000
```

Visualizing the orbitals

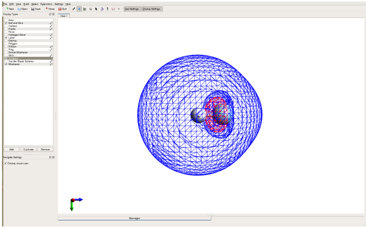
- Open the *FChk file in Avogadro
- Click on Extensions → Create Surface
- Select ”Molecular Orbital” as surface type
- Choose the MO you want to visualize and calculate

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



☐ Axes
☑ Ball and Stick
☐ Cartoon
☐ Dipole
☐ Force
☐ Hydrogen Bond
☑ Label
☐ Overlay
☐ Polygon
☐ Ribbon
☐ Ring
☐ Simple Wireframe
☐ Stick
☑ Surfaces
☐ Van der Waals Spheres
☑ Wireframe

☑ Display visual cues



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☑ Display visual cues

Lesson 8: Solvation models

Solvent effects

- The solvent environment influences structure, energies, spectra etc
- Short-range effects
    - Typically concentrated in the first solvation sphere
    - Examples: h-bonds, preferential orientation near an ion
- Long-range effects
    - Polarization

Imlicit vs. Explicit solvation

- Implicit solvation
  - Dielectric continuum
  - No water molecules *per se*
  - Wavefunction of solute affected by dielectric constant of solvent
  - At 20 ℃: Water - $\epsilon = 78.4$; benzene: $\epsilon = 2.3$ ...
- Explicit solvation
  - Solvent molecules included (i.e. with electronic & nuclear structure)
  - Used mainly in MM approaches
  - Microsolvation: only few solvent molecules placed around solute
  - Charge transfer with solvent can occur

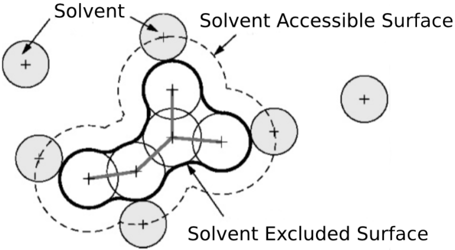
Implicit Models

Basic assumptions

- Solute characterized by QM wavefunction
- Born-Oppenheimer approximation
- Only interactions of electrostatic origin
- Isotropic solvent at equilibrium
- Static model

Cavity

- Solute is placed in a void of surrounding solvent called “cavity”
- Size of the cavity:
  - Computed using vdW radii of atoms (from UFF, for example)
  - Taken from the electronic isodensity level (typically ˜0.001 a.u.)
- The walls of cavity determine the interaction interface (Solvent Excluded Surface, SES)
- Size of the solvent molecule determines the Solvent Accessible Surface (SAS)



Visualizing cavity

- Geomview software (in the modules)
- SCRF=(read) in the route section of the job
- Use G03Defaults in SCRF command
- “geomview” in the SCRF specification
- Visualize the “tesserae.off” file

Electrostatic Interactions

- Self-consistent solution of solute-solvent mutual polarizations
- Solute induces polarization at the interface of cavity
- This polarization acts back on the solute changing its wavefunction
- Various solvation models use different schemes for evaluation of solvation effects
- Problems arise when electrostatics do not dominate solvent-solute interactions

Polarizable Continuum Model (PCM)

- Treats the solvent as polarizable dielectric continuum
- Induced surface charged represent solvent polarization
- Implemented in Gaussian, GAMESS

Solvation Model “Density” (SMD)

- Full solute density is used instead of partial charges
- Lower unsigned errors against experimental data than other models

COnductor-like Screening MOdel (COSMO)

- Solute in virtual conductor environment
- Charge q on molecular surface is lower by a factor $f(\epsilon)$:

$$q = f(\epsilon)q^* \tag{1}$$

- where $f(\epsilon) = (\epsilon - 1)/(\epsilon + x)$; x being usually set to 0.5 or 0
- Implemented in Turbomole, ADF

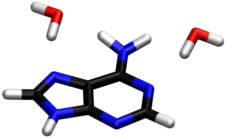
Beyond basic models

- Anisotropic liquids
- Concentrated solutions

Explicit Models

Two models:

- Microsolvation
  - Few solvent molecules (1 to 3) put at chemically reasonable place
  - Water close to exchangeable protons (OH, NH_2...)



- Macrosolvation
  - First (sometimes second) solvent layer around the whole molecule
  - Usually snapshots from MD

Pros & Cons

- +++ Modelling of real interactions with solvent (this can be crucial for exchangeable protons in protic solvents)
- \- Microsolvation lacks sampling
- \- Computationally more demanding
- \- For macrosolvation only single point calculations - the geometry is as good as forcefield

Practical task

Reaction

- Model the $Cl^- + CH_3Br \rightarrow CH_3Cl + Br^-$
- Find the energy barrier for the reaction
- Select any solvent from Gaussian library (be not concerned about solubility of species or chemical relevance)
- Assume S_{n1} and S_{n2} reaction pathways
- Use "SCRF=(solvent=XY)" in the route section of the calculation

Procedure

- Use B3LYP 6-31++g(d,p) method
- Usage of difuse functions when dealing with anions is crucial!
- Use ultrafine integration grid
- Use Frequency calculations to be sure where on PES you are
- For the scan use the distance between C and Cl as RC
- Negative value of step defines two atoms approaching

Module “qmutil”

- Extraction of values from gaussian runs:
    - *extract-gopt-ene* logfile
    - *extract-gopt-xyz* logfile
    - *extract-gdrv-ene* logfile
    - *extract-gdrv-xyz* logfile
    - *extract-xyz-str* xyzfile framenumber
    - *extract-xyz-numstr* xyzfile
- Values ready for plotting in your favorite software

Turbomole

- Prepare job using *define* module (see presentation 6 for help)
- Setup COSMO using *cosmoprep* module
- Set epsilon to 78.4 and rsolv to 1.93
- Leave all other values at their default
- Define radii of atoms using “r all o” for optimized values
- Optimize all geometries