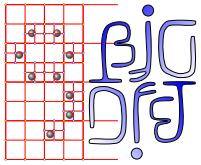


Daubechies Wavelets in Electronic Structure Calculation: BigDFT Code Tutorial

CECAM - GRENOBLE

Charge Analysis: Atoms in Molecules

Ali Sadeghi

Basel University

21 November 2011

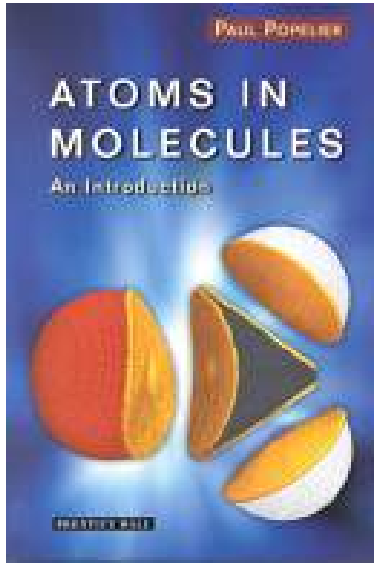
Charge Analysis

An output of electronic structure calculations like DFT is the electronic density $n(\mathbf{r}) = |\psi(\mathbf{r})|^2$ which is a continuous quantity.

Charge partitioning between atoms

- Q: where are atoms in molecules/bulks?
- Main-product:
  charge exchange between bonded atoms
  - ideal ionic bond: 1e transfered ($q_\alpha = \pm 1$)
  - ideal covalent bond: 2e shared ($q_\alpha = 0$)
  - otherwise **?**
- Side-product: decomposed quantities

$$A = \sum_{\alpha}^{atoms} A_\alpha$$



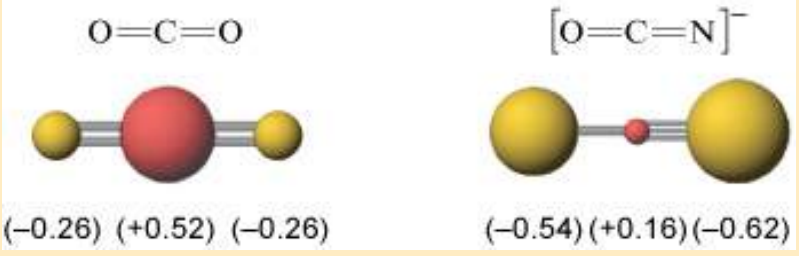
Atomic Domains

Atomic domains?

- No real & clear boundaries between atoms!
- Many possible definitions & methods

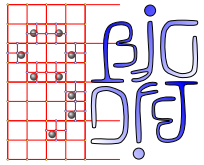
Still a useful tool for:

- bonding analysis
- partial charges
- partial multipoles
- atomic DOS
- ...



s-owl.cengage.com

Methods



Methods

- No quantum-mechanical considerations
- Not using electronic structure
- Using atomic wave-functions $\psi_\alpha(\mathbf{r})$
- Using the real-space electronic density $n(\mathbf{r})$

Approaches

- Partitioning the space

$$q_\alpha = Z_\alpha - \int_{V_\alpha} n(\mathbf{r}) d^3 r$$

- Partitioning the charge density

$$q_\alpha = Z_\alpha - \int n_\alpha(\mathbf{r}) d^3 r$$

Methods

Non QM-based methods:

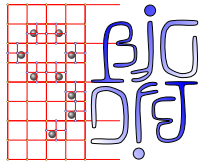
Using experimental data

- charges, dipoles, ...

Voronoi polyhedra

- assign nearest atom to each point
- $q_\alpha = Z_\alpha - \int_{V_\alpha} n(\mathbf{r}) d^3 r$
- solely mathematical!
- atomic types not considered
- possible unreasonable results!

Methods



Non electronic structure based methods

ESP fitting method

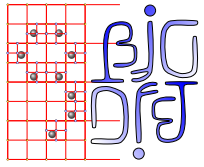
- Point charges as effective atomic charges q_α
- Fitting q_α to reproduce electrostatic potential (ESP)
- Least-squares minimization with constraints
  - total charge
  - total dipole
  - ...

$$\sum_{i}^{M_{sampling}} \left(\sum_{\alpha}^{N_{atom}} V^{q_\alpha}(\vec{r}_i) - V^{o}(\vec{r}_i) \right)^2 + \lambda \left(\sum_{\alpha}^{N_{atom}} q_\alpha - q_{tot} \right)^2 + \dots$$

- Sampling points $\vec{r}_i$ only out of atomic regions e.g. r^{α}_{vdW}
- Small RMS is not guaranteed!

D. Chen et al JPC. A, 114, 37 (2010)

Methods



Electronic structure based methods

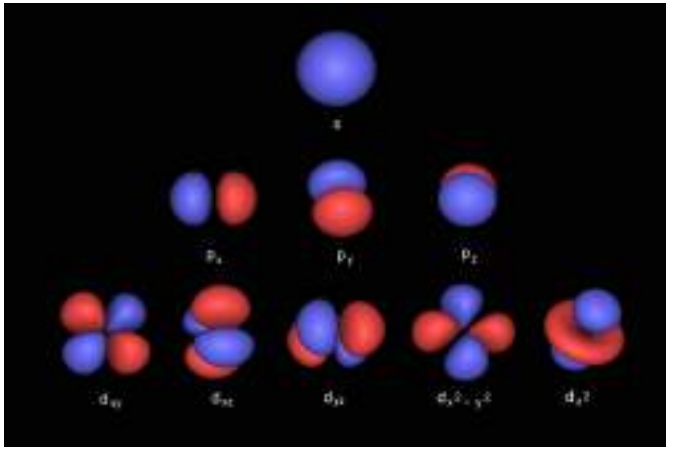
Using atomic wave-functions $\psi_\alpha(\mathbf{r})$

- easy for LCAO basis :)
- dependency on basis set :(
- unreasonable q_α without orthogonal basis (**Lowdin**)

The most common method:

Mulliken population analysis

- projecting $\psi(\mathbf{r})$ on atomic basis
- $n_\alpha(\mathbf{r}) = |\Psi_\alpha|^2$
- $q_\alpha = Z_\alpha - \int n_\alpha(\mathbf{r}) d^3r$
- orbitals population analysis
- old and simple



Methods

Electronic structure based methods

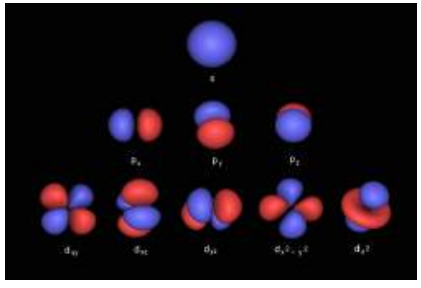
Voronoi Deformation Density

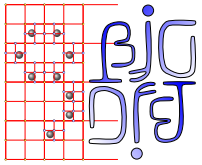
- Space is partitioned by Voronoi polyhedra
- Use
  - electronic density $n(\mathbf{r})$
  - WRT density of non-interacting atoms n^o_α
  - i.e. the deformation density $\Delta n = n - \sum_\alpha n^o_\alpha$
- $q_\alpha = \int_{V_\alpha} \Delta n d^3 r$

In addition to n, it uses both:

geometry

atomic orbitals





Electronic structure based methods

Weighted distributing

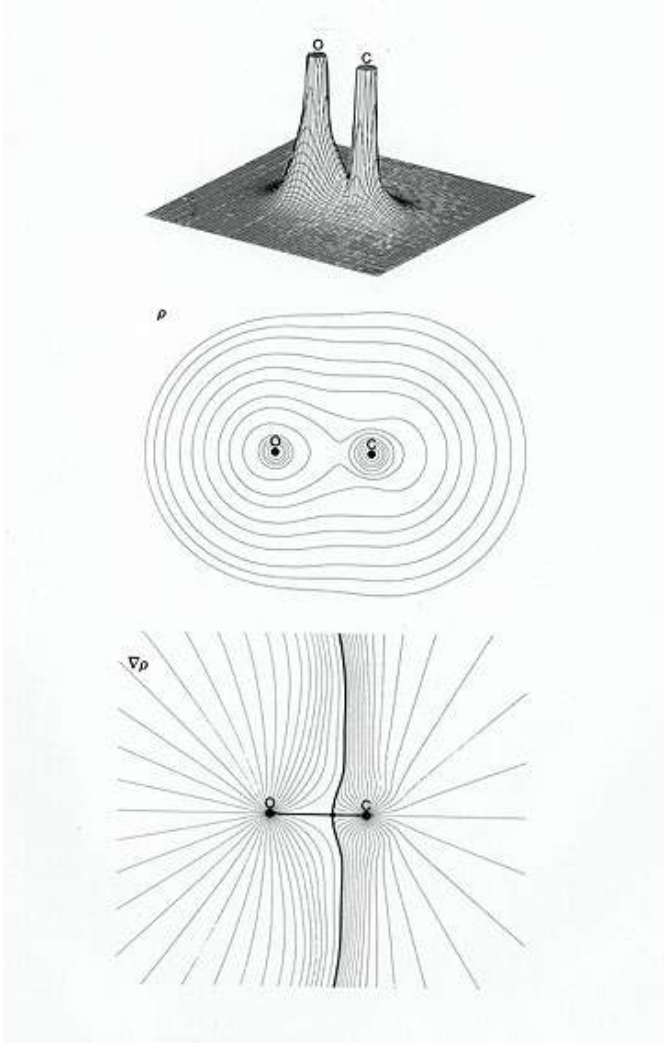
- Distribute $n(\mathbf{r})$ according to atomic weights $w_\alpha(\mathbf{r})$
  - $n_\alpha(\mathbf{r}) = w_\alpha(\mathbf{r})n(\mathbf{r})$
  - weights are normalized: $\sum_\alpha w_\alpha(\mathbf{r}) = 1$
  - fuzzy boundaries (if w_α are not truncated)
  - $q_\alpha = Z_\alpha - \int w_\alpha(\mathbf{r})n(\mathbf{r})d^3r$
- Simple Gaussian $w_\alpha(\mathbf{r}) \propto e^{-|\mathbf{r}-\mathbf{r}_\alpha|^2/r_{\alpha,o}^2}$
  - $r_{\alpha,o}$ = covalence, ionic, vdW, ... radius
- Hirshfeld $w_\alpha(\mathbf{r}) \propto n_\alpha^o(\mathbf{r})$
  - $q_\alpha = \int (n_\alpha^o - w_\alpha n)d^3r = \int n_\alpha^o(1 - \frac{n(\mathbf{r})}{\sum n_\alpha^o})d^3r$
- Non-interacting atoms are important:
  - either atomic radius or electronic density

Methods

Electronic structure based methods

Bader (AIM)

- Only use real-space density $n(\mathbf{r})$
- sharp boundaries!
- $q_\alpha = Z_\alpha - \int_{V_\alpha} n d^3 r$
- Use n-topology to find V_α:
  - n is maximized on nuclei
  - curvatures=eigenvalues of $\nabla^2 n$
  - critical points: $\vec{\nabla} n = 0$
  - zero-flux surfaces are boundaries: $\vec{\nabla} n \cdot \vec{u} = 0$

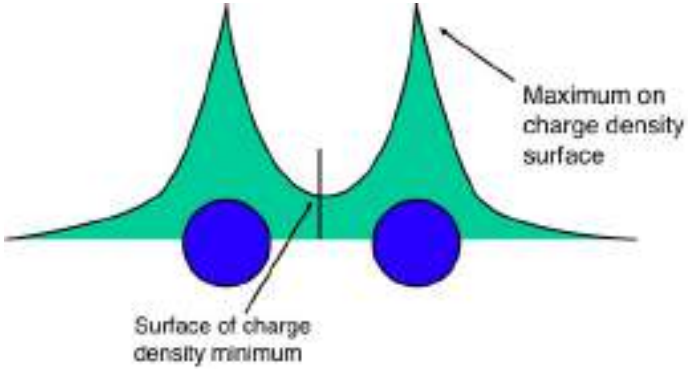


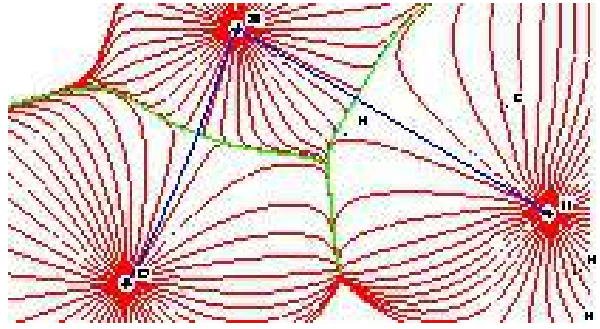
Bader Method

Topology of electronic density $n(\mathbf{r})$ helps:

Tracking Gradient of n

- $\vec{\nabla} n$ shows the steepest ascent direction at any point
- maxima in n coincide with nuclei positions
- the space is partitioned to some basins:
  - ideally, one Bader volume for each atom



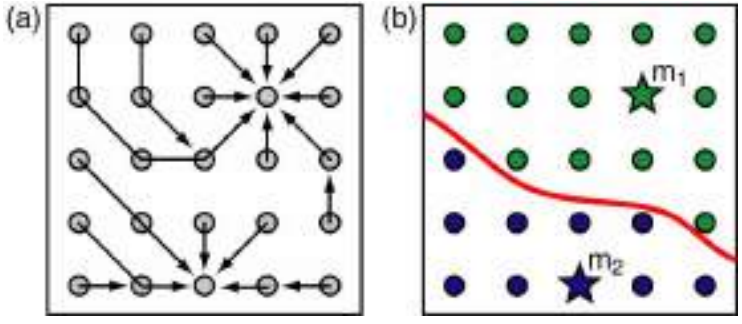


http://theory.cm.utexas.edu/henkelman/research/bader

Bader Method

Grid-based tracking of $\vec{\nabla} n$

- A fast, robust and linear scaled numerical algorithm:
  - Follow steepest ascent path along $\vec{\nabla} n$ to next grid point
  - repeat until an n maximum is reached (a nuclei is found)
  - assign all points in the path to this maximum
  - repeat for any unassigned grid point
  - if previously assigned points are reached, terminate the path and group them together (linearity)
- refinement needed at boundaries
- might fail for smooth pseudopotential (shallow maxima)



http://theory.cm.utexas.edu/henkelman/research/bader

Bader Method

The Henkelman's group implementation

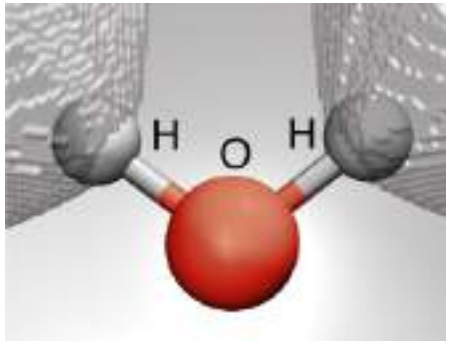
- is already used as a post-processing tool in different packages including BigDFT
- can be used for periodic or molecular systems:

B atoms in Si crystal:

$q_{B_1} = -0.9e$

$q_{B_3} = -1.5e$

Water molecule:



$q_H = +0.59$

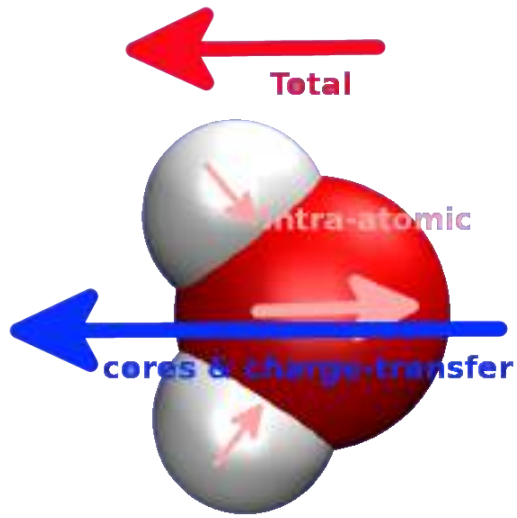
$q_O = -1.18$

http://theory.cm.utexas.edu/henkelman/research/bader

Multipole Moments

- charge: $q = \sum_\alpha q_\alpha = \sum_\alpha (Z_\alpha - \int_{V_\alpha} n d^3 r)$
- dipole: $\vec{P} = \sum_\alpha (\vec{P}_\alpha^{chg} + \vec{P}_\alpha) = \sum_\alpha (Z_\alpha \vec{r}_\alpha - \int_{V_\alpha} \vec{r} n d^3 r)$
- quadrupoles : $Q^{i,j} = \sum_\alpha Q_\alpha^{i,j}$

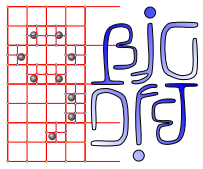
- $q = 0 \Rightarrow \vec{P}$ is origin-independent.
- If $\vec{P} \neq 0 \Rightarrow Q^{i,j}$ are origin-dependent!
- $q_\alpha \neq 0 \Rightarrow \vec{P}_\alpha$ depends on origin!
- $\vec{P}_\alpha + \vec{P}_\alpha^{chg}$ is origin-independent
  - $\vec{P}_\alpha$: from intra-atomic polarization
  - $\vec{P}_\alpha^{chg}$: from cores & charge-transfer



Could atomic contributions be defined? $A = \sum_\alpha^{N_{atoms}} A_\alpha$

Yes, but with special care!

Charge Analysis with BigDFT



Charge analysis with BigDFT is possible in two ways:

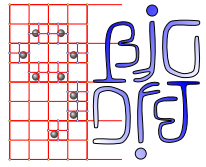
1. On-the-fly: Mulliken population analysis
   - set `InputPsiId=10` in `input.dft`

```
------------------------------------------------- Mulliken Charge Population Analysis
 Center No. |    Shell    | Rad (AU) | Chg (up) | Chg (down) | Net Pol  | Gross Chg
      1     |  s          |    0.88  |  0.28516 |  0.28516   |  0.00000 |  0.42969
                Center Quantities :  |  0.28516 |  0.28516   |  0.00000 |  0.42969
 ------------------------------------------------------------------------------------
      2     |  s          |    0.46  |  0.91603 |  0.91603   |  0.00000 |  0.16793
      2     |  px         |    0.31  |  0.98456 |  0.98456   |  0.00000 | -0.63578
      2     |  py         |    0.31  |  0.81913 |  0.81913   |  0.00000 | -0.30492
      2     |  pz         |    0.31  |  0.67762 |  0.67762   |  0.00000 | -0.02191
                Center Quantities :  |  3.39734 |  3.39734   |  0.00000 | -0.79468
```

2. Post-processing: Bader or Veronoi charge analysis
   - set `Output_Grid=1` in `input.dft` to get charge density
   - use `bader` tool with the charge density
     - `bader [-c voronoi] [electronic_density.cube]`

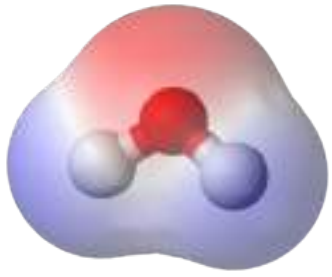
```
 atom#      CHARGE:  core      electronic     net
-------------------------------------------------
   1                +1.00000    -0.40727    +0.59273
   2                +6.00000    -7.18542    -1.18542
   3                +1.00000    -0.40731    +0.59269
-------------------------------------------------
```

Comparison



BigDFT-tools

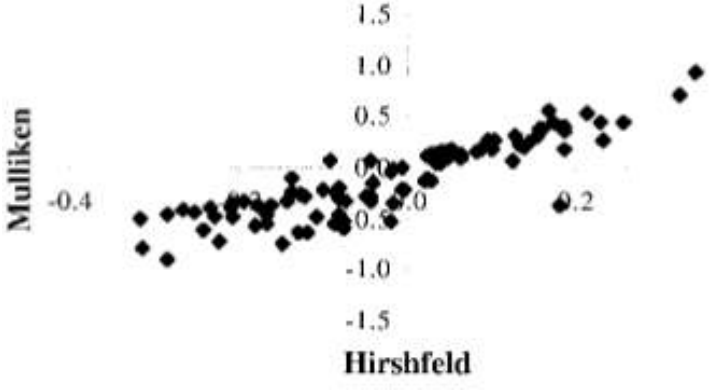
Water molecule with BigDFT:
Comparing to Bader's method (AIM),

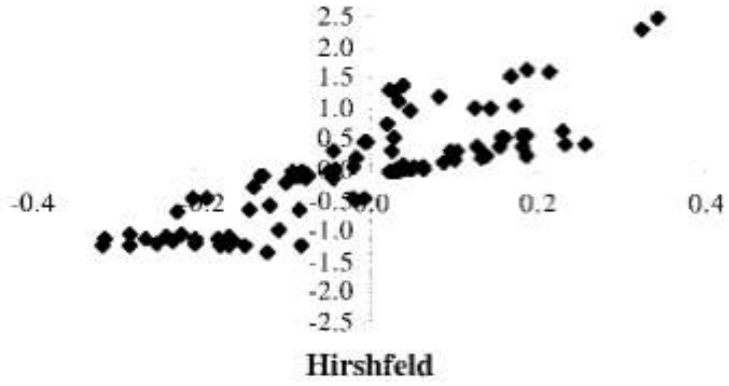


- Mulliken underestimates
- Gaussian overestimates
- Voronoi is not trustable!

	Bader	Mulliken	Gaussian	Voronoi
O	-1.2	-0.8	-1.3	+0.7
H	+.0.6	+0.4	+0.65	-0.35

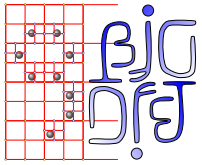
For a series of organic molecules: $|q_{Hirshfeld}| < |q_{Mullekin}| < |q_{Bader}|$





(D. Proft et al. J. Comp. Chem. 23, 12 (2002))

Summary



- Several existing definitions/methods:
  - either partition space or charge between atoms
  - use molecule geometry, electrostatic potential, atomic orbitals/radii, electronic density (n), ...
  - are not completely consistent
- Atoms in a molecule can not (always) be clearly defined!
- Bader's method, based on n-topology, seems more reliable
- Grid method, a computational method, is efficient, robust, and linearly scaled with grid size; the code is freely available
- Care should be taken in defining atomic contributions to an observable $A = \sum_{\alpha}^{N} A_{\alpha}$
- With BigDFT one can do Mulliken, Bader, Voronoi and Gaussian charge analysis

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Thank you for your attention!