

Density Functional Theory: Population Analysis

1 April 2020

Motivation

I have no idea how things I use are calculated.

Background

In my project I use DFT to extract:

- Charges
- Bond Orders
- Dipole Moment
- HOMO/LUMO
- NMR shifts

ORCA Population Analysis

MULLIKEN ATOMIC CHARGES

```

0 O : -0.440165
1 C : 0.333907
2 N : -0.216204
3 C : 0.227407
4 C : -0.355772
5 C : 0.151549
6 C : 0.380012
7 F : -0.147666
8 F : -0.147581
9 F : -0.146147
10 C : -0.355830
11 C : 0.170947
12 C : 0.385509
13 F : -0.148743
14 F : -0.148733
15 F : -0.144515
16 C : -0.331682
17 N : -0.199719
18 C : 0.183305
19 C : -0.331605
20 C : 0.192335
21 C : 0.378029
22 F : -0.143332
23 F : -0.148196
24 F : -0.149704
25 C : -0.379436
26 C : 0.174538
27 C : 0.379891
28 F : -0.146312
29 F : -0.148037
30 F : -0.147693
31 C : -0.334464
32 H : 0.269620
33 H : 0.160343
34 H : 0.149680
35 H : 0.143728
36 H : 0.271257
37 H : 0.144717
38 H : 0.155114
39 H : 0.143306
40 F : -0.683655

```

Sum of atomic charges: -1.0000000

LOEWDIN ATOMIC CHARGES

```

0 O : 0.023486
1 C : -0.511321
2 N : 0.174642
3 C : -0.196614
4 C : -0.076131
5 C : -0.139768
6 C : -0.639684
7 F : 0.185651
8 F : 0.197139
9 F : 0.199076
10 C : -0.082256
11 C : -0.139193
12 C : -0.639897
13 F : 0.187679
14 F : 0.191862
15 F : 0.204380
16 C : -0.064454
17 N : 0.176015
18 C : -0.196719
19 C : -0.063647
20 C : -0.138939
21 C : -0.640220
22 F : 0.204186
23 F : 0.187341
24 F : 0.192531
25 C : -0.082013
26 C : -0.139115
27 C : -0.639441
28 F : 0.196762
29 F : 0.198842
30 F : 0.186487
31 C : -0.073789
32 H : 0.178668
33 H : 0.163590
34 H : 0.167201
35 H : 0.164368
36 H : 0.181710
37 H : 0.164556
38 H : 0.166511
39 H : 0.162886
40 F : -0.592368

```

HIRSHFELD ANALYSIS

Total integrated alpha density = 124.999909590
Total integrated beta density = 124.999909590

ATOM	CHARGE	SPIN
0 O	-0.302938	0.000000
1 C	0.181923	0.000000
2 N	-0.111942	0.000000
3 C	0.056664	0.000000
4 C	-0.055976	0.000000
5 C	-0.037067	0.000000
6 C	0.250102	0.000000
7 F	-0.114626	0.000000
8 F	-0.100078	0.000000
9 F	-0.098572	0.000000
10 C	-0.056499	0.000000
11 C	-0.035181	0.000000
12 C	0.251415	0.000000
13 F	-0.112094	0.000000
14 F	-0.106987	0.000000
15 F	-0.092957	0.000000
16 C	-0.041584	0.000000
17 N	-0.109461	0.000000
18 C	0.056707	0.000000
19 C	-0.039671	0.000000
20 C	-0.035197	0.000000
21 C	0.252070	0.000000
22 F	-0.092862	0.000000
23 F	-0.111927	0.000000
24 F	-0.105820	0.000000
25 C	-0.055861	0.000000
26 C	-0.036126	0.000000
27 C	0.250815	0.000000
28 F	-0.102720	0.000000
29 F	-0.096946	0.000000
30 F	-0.114159	0.000000
31 C	-0.054813	0.000000
32 H	0.067615	0.000000
33 H	0.025233	0.000000
34 H	0.046191	0.000000
35 H	0.047266	0.000000
36 H	0.072046	0.000000
37 H	0.048896	0.000000
38 H	0.044943	0.000000
39 H	0.027590	0.000000
40 F	-0.457236	0.000000

TOTAL -0.999819 0.000000

%output
Print[P_Hirshfeld]
end

Methods to assign atomic charges

1. Partitioning the wave function in terms of the basis functions.
2. Derivation from electrostatic potential.
3. Partitioning the electron density into atomic domains (physical space partitioning).

1. Population analysis based on Basis Functions

The electron density ρ at a certain position \mathbf{r} from a single molecular orbital containing one electron is given as the square of the MO.

Assuming that the MO is expanded in a set of normalized, but non-orthogonal, basis functions χ , it can be written as:

$$\Phi^2_i = \sum_{\alpha\beta}^{Mbasis} c_{\alpha i} c_{\beta i} \chi_{\alpha} \chi_{\beta}$$

1. Population analysis based on Basis Functions

Total number of electrons (N_{elec}): Intergrading and summing over all occupied MOs.

$$N_{\text{elec}} = \sum_{\alpha\beta}^{M^{basis}} D_{\alpha\beta} S_{\alpha\beta}$$

D: The sum of the product of MO coefficients and the occupation numbers.
(Charge and bond order matrix)

S: The overlap matrices elements between the basis functions.

Mulliken Population Analysis

- Uses the $\mathbf{D} \cdot \mathbf{S}$ matrix for distributing the electrons into atomic contributions.
- The contributions from all AOs located on a given atom **A** may be summed up to give the number of electrons associated with atom **A**.
- It partitions the contribution equally between the atoms.

$$\rho_A = \sum_{\alpha \in A}^{\text{Mbasis}} \sum_{\beta}^{\text{Mbasis}} D_{\alpha\beta} S_{\alpha\beta}$$

- The gross charge on atom **A** is the sum of the nuclear and electronic contributions:

$$Q_A = Z_A - \rho_A$$

Lowdin Population Analysis

To partition the contributions between atoms:

$$N_{\text{elec}} = S^{1/2} \cdot D \cdot S^{1/2}$$

The Lowdin method is equivalent to a population analysis of the density matrix in the orthogonalized basis set formed by transforming the original set of functions by $S^{-1/2}$

Common problems

1. The diagonal elements may be larger than two. More than two electrons in an orbital, violating Pauli principle.
2. The off-diagonal elements may become negative. Negative number of electrons between two basis functions.
3. Why would you divide the off-diagonal contributions equally between the two orbitals?
4. A basis function centered on atom A may have a small exponent, describing the wave function far from atom A.
5. The dipole etc. moments are not conserved.

2. Population analysis based on Electrostatic Potential

The ESP at position \mathbf{r} is given as a sum of contributions from the nuclei and the electron density, where the latter is provided by the electronic wave function:

$$\Phi_{ESP}(\mathbf{r}) = \sum_A^{nuclei} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$\rho(\mathbf{r}') = |\Psi(\mathbf{r}')|^2$$

The electronic contribution is not available in FF methods. To model the ESP we assign partial charges to each atom.

Partial Atomic Charges in FF

Set of parameters that generates the best fit to the actual electrostatic potential as calculated from an electronic wave function and sampled in a number of points surrounding the molecule.

The computational problem can be formulated as minimization of an error function:

$$ErrF(Q) = N_{points}^{-1} \sum_i^{N_{points}} (\Phi_{ESP}(r_i) - \Phi_{Approx}(r_i))^2$$

$$\Phi_{Approx}(r_i) = \sum_A^{N_{atoms}} \frac{Q_A(R_A)}{|r_i - R_A|}$$

Common Problems

1. The different schemes for deriving the ESP atomic charges differ in the number and location of points used for sampling the ESP.
2. Every time different constraints can be employed (specific total charge, specific dipole moment, forcing subgroups to specific charge etc.)
3. The electrostatic potential depends on the total wave function and therefore converges as the size of the basis set and the amount of electron correlation is increased.
4. The fitting procedure becomes statistically underdetermined even for medium sized systems.

3. Population Analysis based on Electron Density

Base the population analysis on properties of the wave function or electron density itself. Not on the basis set chosen.

If we somehow divide the total molecular volume into subsections, each belonging to a specific nucleus.

$$N_A = \int_{\Omega_A} \rho(r) dr$$

$$Q_A = Z_A - N_A$$

Since the dividing surface is defined in terms of the electron density, the atomic charges will converge to specific values.

Hirshfeld Atomic Charges

Based on using atomic densities for partitioning the molecular electron density.

$$Q_A = Z_A - \int \frac{\rho_A^{\text{atomic density}}(r)}{\sum_A^{\text{Atoms}} \rho_A^{\text{atomic density}}(r)} dr$$

Ambiguity: The source of the atomic densities.

Usually, spherically averaged ground state densities are used for neutral atoms.

A fast Comparison

TABLE IV

H-charges based on MPA and HPA schemes are evaluated for selected chemical systems by employing the DFT-BLYP methods.

Molecules	Methods			
	MPA		HPA	
	BLYP/DND	BLYP/DNP	BLYP/DND	BLYP/DNP
CH₃Cl	0.2360	0.1160	0.0490	0.0497
CH₂Cl₂	0.2700	0.1615	0.0545	0.0545
CHCl₃	0.2950	0.1930	0.0541 ^a	0.0536 ^a
CH₃COOH	0.2407	0.1140	0.0529	0.0537
CH₂ClCOOH	0.2740	0.1565	0.0569	0.0574
CHCl₂COOH	0.3020	0.1900	0.0518 ^a	0.0518 ^a
CH₃COOH	0.4310	0.2680	0.1710	0.1685
CH₂ClCOOH	0.4390	0.2760	0.1803	0.1778
CHCl₂COOH	0.4450	0.2820	0.1850	0.1826
CCl₃COOH	0.4490	0.2850	0.1895	0.1870

Calculated H-charges are taken for the selected (shown in the bold) hydrogen atoms.

^a Trends are not as expected.

Saha, S., et al., Are the Hirshfeld and Mulliken population analysis schemes consistent with chemical intuition?
IJQC, 109(9), 1790-1806.

A fast Comparison

Hartree –Fock atomic populations

Molecule	Method	3-21G	6-31G	6-31G*
C ₂ H ₂	Mulliken	-0.33	-0.32	-0.28
	Hirshfeld	-0.10	-0.10	-0.10
CH ₄	Mulliken	-0.79	-0.62	-0.66
	Hirshfeld	-0.09	-0.11	-0.10
CO	Mulliken	0.43	0.33	0.27
	Hirshfeld	0.11	0.13	0.13

Further Reading

BOOKS

1. **Introduction to Computational Chemistry.** Jensen F. 2017 (3rd ed.)
2. **Essentials of Computational Chemistry: Theory and Models.** Cramer, C. J. 2004 (2nd ed.)

Journal Articles

1. Saha, Soumen, Ram Kinkar Roy, and Paul W. Ayers. "Are the Hirshfeld and Mulliken population analysis schemes consistent with chemical intuition?." *International Journal of Quantum Chemistry* 109.9 (2009): 1790-1806.
2. Contreras, Renato, Luis R. Domingo, and Bernard Silvi. "Electron Densities: Population Analysis and Beyond." *Encyclopedia of Physical Organic Chemistry* (2016): 1-114.
3. Carbó-Dorca, Ramon, and Patrick Bultinck. "Quantum mechanical basis for Mulliken population analysis." *Journal of mathematical chemistry* 36.3 (2004): 231-239.
4. Bultinck, Patrick, et al. "Critical analysis and extension of the Hirshfeld atoms in molecules." *The Journal of chemical physics* 126.14 (2007): 144111.
5. Hirshfeld, Fred L. "Bonded-atom fragments for describing molecular charge densities." *Theoretica chimica acta* 44.2 (1977): 129-138.
6. <http://www.q-chem.com/features40/F9htm.pdf>
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8. https://en.wikipedia.org/wiki/Mulliken_population_analysis
9. [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Quantum_States_of_Atoms_and_Molecules_\(Zielinski_et_al.\)/10%3A_Theories_of_Electronic_Molecular_Structure/10.07%3A_Mulliken_Populations](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Quantum_States_of_Atoms_and_Molecules_(Zielinski_et_al.)/10%3A_Theories_of_Electronic_Molecular_Structure/10.07%3A_Mulliken_Populations)

Thank you