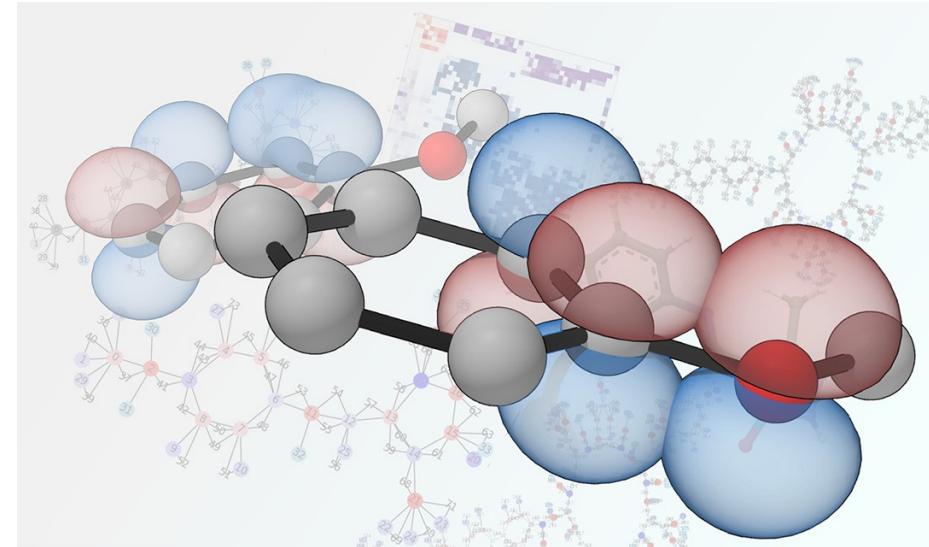


Aula 10 – Análise de Cargas

Ref: Cap 10 - Jensen

Prof. Elvis Soares
elvis@peq.coppe.ufrj.br

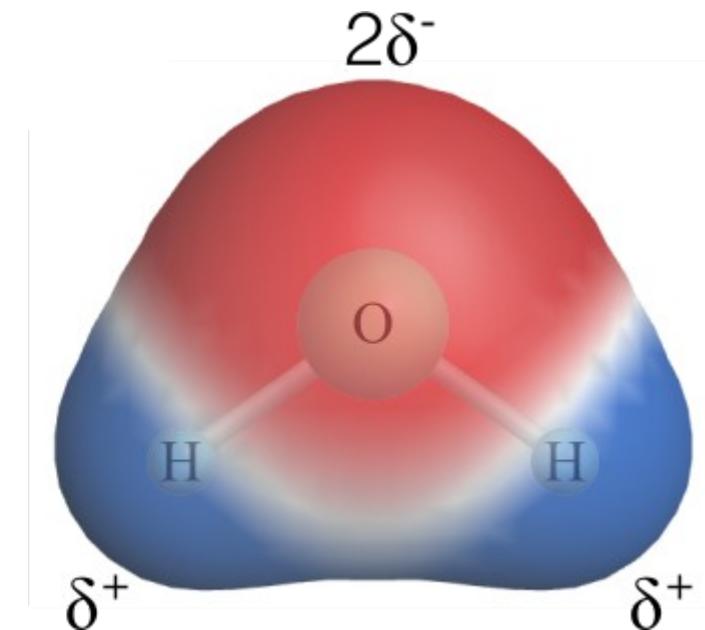


$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$

$$|\Psi\rangle = |\psi\rangle e^{-iEt/\hbar}$$
$$\hat{H} |\psi\rangle = E |\psi\rangle$$

Tipos de análise de populacional ou de cargas

- Baseada em Função de Onda
 - Mulliken / Lowdin
- Baseada em Densidade eletrônica
 - Bader
 - Hirshfeld / CM5
- Baseada em Potencial Eletrostático (ESP)
 - ChelpG (Charges from Electrostatic Potentials using a Grid-based method)
 - RESP (Restrained ElectroStatic Potential)



Análise de Cargas por Função de Onda

Orbitais Moleculares

$$|\psi_i\rangle = \sum_{\mu} c_{\mu i} |\phi_{\mu}\rangle$$



$$\begin{aligned}\rho(\mathbf{r}) &= 2 \sum_{i=1}^{N/2} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \\ &= \sum_{\mu\nu} P_{\mu\nu} \phi_{\mu}^*(\mathbf{r}) \phi_{\nu}(\mathbf{r})\end{aligned}$$



Número de Elétrons

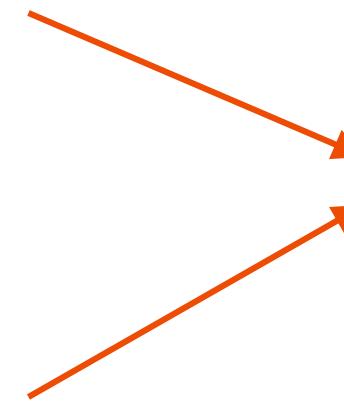
$$N = \int \rho(\mathbf{r}) \, d\mathbf{r}$$

Matriz de Densidade

$$P_{\mu\nu} = \sum_{i=1}^{N/2} c_{\mu i}^* c_{\nu i}$$

Matriz de Overlap

$$S_{\mu\nu} = \langle \phi_{\mu} | \phi_{\nu} \rangle$$



Cargas de Mulliken

$$Q_A = Z_A - \sum_{\substack{\mu \in A \\ \mu\nu}} P_{\mu\nu} S_{\mu\nu}$$

Análise de Cargas por Densidade Eletrônica

Cargas de Hirshfeld

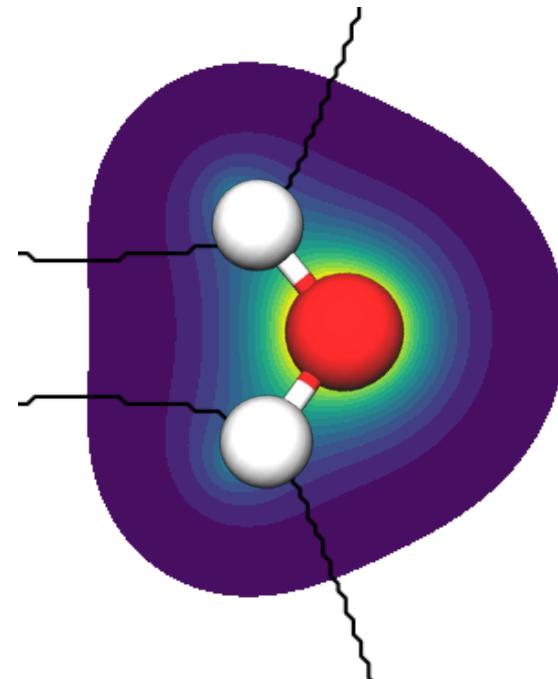
$$Q_A = Z_A - \int \left[\frac{\rho_A^{(0)}(\mathbf{r})}{\sum_B \rho_B^{(0)}(\mathbf{r})} \right] \rho(\mathbf{r}) \, d\mathbf{r}$$

$\rho_A^{(0)}(\mathbf{r})$: densidade eletrônica de A
como um átomo isolado

Cargas de Bader

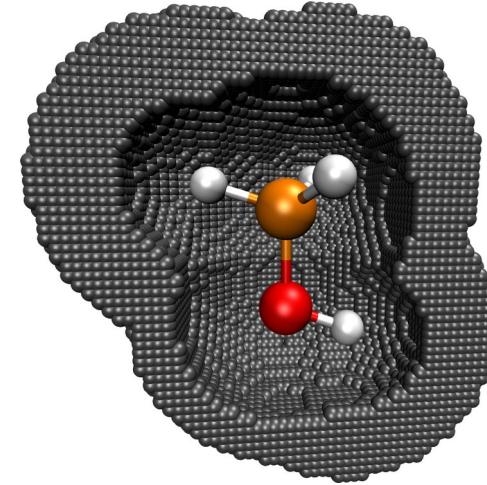
$$Q_A = Z_A - \int_{V \subset S_A^{(\min)}} \rho(\mathbf{r}) \, d\mathbf{r}$$

$S_A^{(\min)}$: superfície de densidade
mínima ao redor de A



Análise de cargas por ESP

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

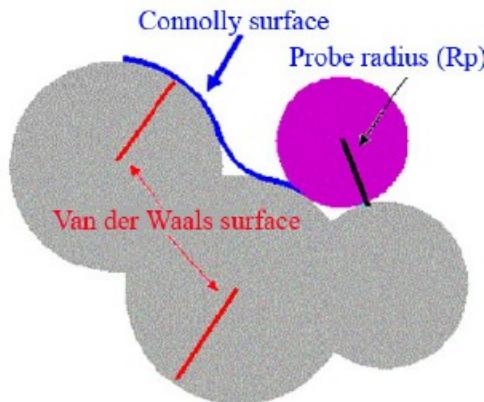


Potencial de cargas pontuais

$$\phi_{\text{approx}}(\mathbf{r}) = \sum_A^{\text{nucleos}} \frac{Q_A}{|\mathbf{r} - \mathbf{R}_A|}$$

$$\varepsilon(\{Q_A\}) = \frac{1}{n} \sum_k^n [\phi_{\text{ESP}}(\mathbf{r}_i) - \phi_{\text{approx}}(\mathbf{r}_i)]^2$$

n : n° de pontos numa grid

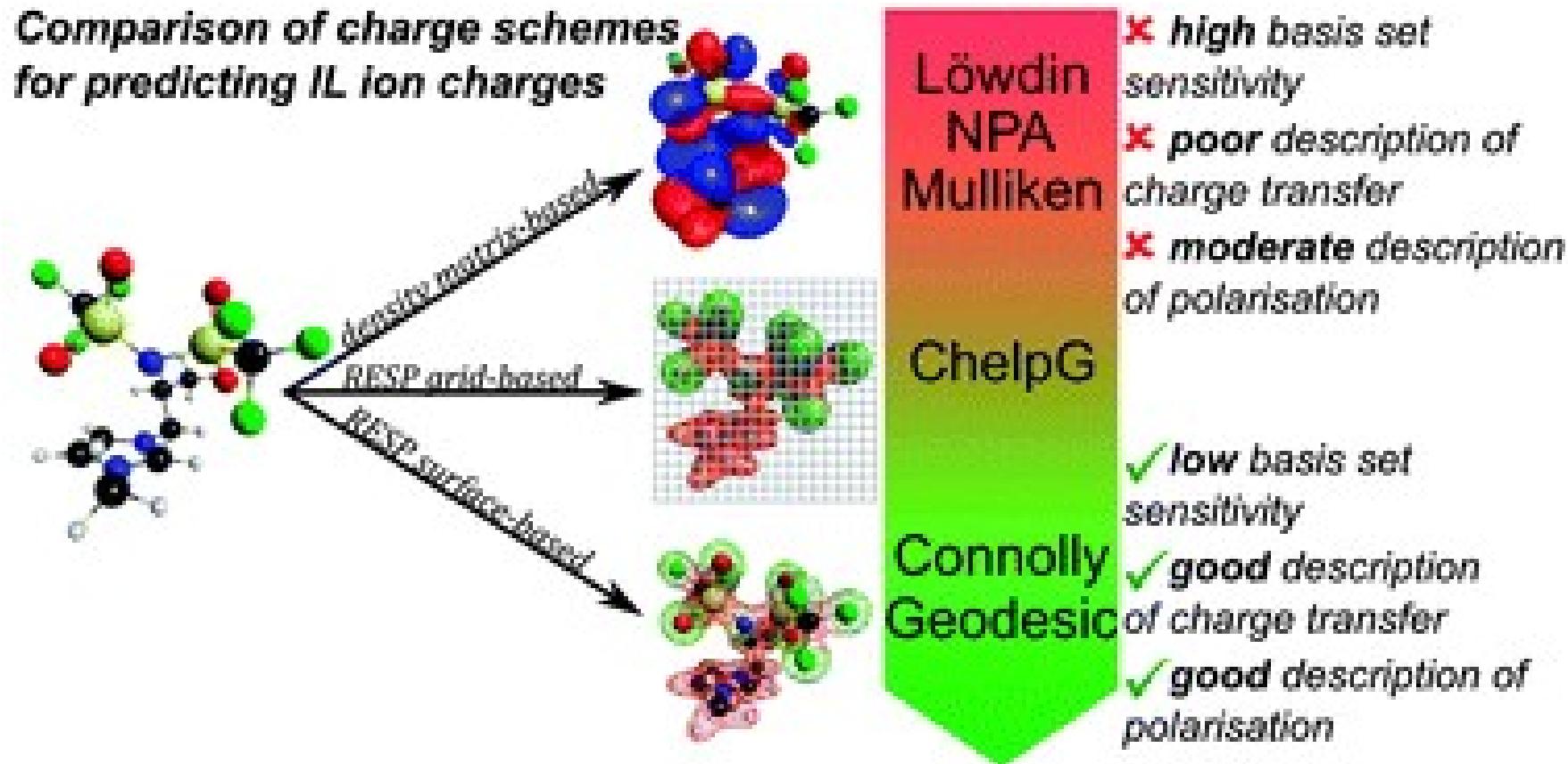


Discretização numa grid

CHELPG → grid cúbica regular

RESP → grid na superfície de Connolly

Prós e Contras



Rigby, J., & Izgorodina, E. I. (2013). Physical Chemistry Chemical Physics, 15(5), 1632-1646.

Análise de Bader

HenkelmanGroup



group members teaching research code funding publications

forum

CODE: BADER CHARGE ANALYSIS

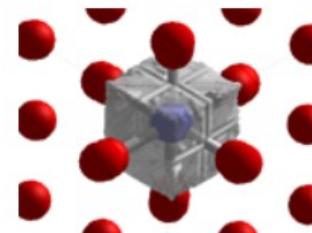
NEWS

08/19/23 - Version 1.05 Released

Proper reading of negative direct coordinates. Thanks to Yuri Mastrikov for identifying this issue.

INTRODUCTION

Richard Bader, from McMaster University, developed an intuitive way of dividing molecules into atoms. His definition of an atom is based purely on the electronic charge density. Bader uses what are called zero flux surfaces to divide atoms. A zero flux surface is a 2-D surface on which the charge density is a minimum perpendicular to the surface. Typically in molecular systems, the charge density reaches a minimum between atoms and this is a natural place to separate atoms from each other.



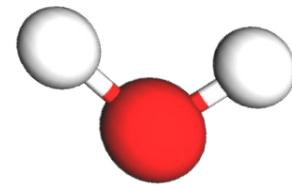
<https://theory.cm.utexas.edu/henkelman/code/bader/>

bader chargefile

chargefile is a VASP CHGCAR file or a Gaussian CUBE file.

Análise de Bader

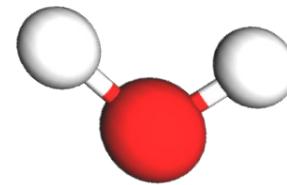
$$Z = 1$$



$$Z = 1$$

$$N = 0.344$$

$$N = 0.344$$



$$Z = 8$$

$$N = 9.249$$

Cargas Parciais de Bader

$$Q_A = Z_A - N_A$$

Vide
[notebook_Aula10.ipynb](#)

Momento de Dipolo da Água

