New Insights in Bader's Theory

Christian Tantardini
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Brief Introduction to Bader’s Theory

The molecules are: (a)-(f) the normal alkanes from methane to hexane

$$\nabla \rho(r) \cdot n(r) = 0 \ \forall r \in S_{\Omega}$$
Brief Introduction to Bader’s Theory

Ethene molecule in the plane containing the nuclei. Values of $\rho(r)$ above an arbitrarily chosen value are not shown

$\rho(r) = \text{charge density}$
Brief Introduction to Bader’s Theory

Definition of curvature as the limiting difference ($\Delta x \to 0$) in the tangent lines which bracket a given point; at $x_1$ where $f(r)$ is a minimum and the curvature is positive and at $x_2$ where $f(x)$ is a maximum and the curvature is negative.

- ($3, -3$) all curvatures are negative - maximum
- ($3, -1$) two curvatures are negative – maximum; one curvature positive – minimum
- ($3, +1$) two curvatures are positive – minimum; one curvature negative - maximum
- ($3, +3$) all curvatures are positive - minimum

Bader, Atoms in Molecule: A Quantum Theory 1990
Brief Introduction to Bader’s Theory

Molecular graphs for some molecules in their equilibrium geometries. A bond critical point (BCP) is denoted by a black dot.

Bader, Atoms in Molecule: A Quantum Theory 1990
Introduction to the Source Function \((SF')\)

\[
\rho(r) = \int_{all \ space} LS(r, r') \cdot dr' = \sum_\Omega \int LS(r, r') \cdot dr' \equiv \sum_\Omega SF(r, \Omega)
\]

Local Source

\[
LS(r, r') = -\frac{(1/4\pi)}{|r - r'|} \nabla^2 \rho(r')
\]

Green Function determines the weight of the cause \(\nabla^2 \rho(r') dr'\) to contribute to the effect, \(\rho(r)\)

\(\nabla \rho(r) \cdot n(r) = 0 \ \forall r \in S_\Omega\)

Zero Flux Surface

Source Function of Spin Density

\[ s(r) = \rho_\alpha(r) - \rho_\beta(r) \]

**SPIN DENSITY**

\[ s(r) = \int_{all\ space} LS_s(r, r') \cdot dr' = \sum_\Omega \int LS_s(r, r') \cdot dr' \equiv \sum_\Omega SF_s(r, \Omega) \]

- **Local Source for the Spin density**
  \[ LS_s(r, r') = - \left( 4\pi \cdot \left| r - r' \right| \right)^{-1} \cdot \nabla^2 s(r') \]

- **Local cause:** \[ \nabla^2 s(r') \cdot dr' = \nabla^2 [\rho_\alpha(r') - \rho_\beta(r')] \cdot dr' \]

- **Global Effect:** \[ s(r) \]

- **Effectiveness:** the same as for \( \rho \), being a purely geometrical factor

\[ \nabla \rho(r) \cdot n(r) = 0 \ \forall \ r \in S_\Omega \]

Zero Flux Surface

Gatti, Orlando, Lo Presti Chem. Sci. 2015, 6, 3845-3852
\[ \rho(r') \quad \nabla^2 \rho(r') \quad \text{LS}(r') \quad \text{Effects on } \rho(r) \]

<table>
<thead>
<tr>
<th>( \rho(r') )</th>
<th>( \nabla^2 \rho(r') )</th>
<th>( \text{LS}(r') )</th>
<th>( \text{Effects on } \rho(r) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 0</td>
<td>&gt; 0</td>
<td>&lt; 0</td>
<td>decrease ( \rho )</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>&lt; 0</td>
<td>&gt; 0</td>
<td>increase ( \rho )</td>
</tr>
</tbody>
</table>

\[ \nabla^2 \rho(r') \mathrm{d}r' \]

\[ \text{LS}(r,r') \]

\[ \nabla^2 s(r') \mathrm{d}r' \]

\[ \text{LS}_s(r,r') \]

\[ s(r) \]

\[ \nabla^2 s(r') \]

\[ \nabla^2 \rho(r') \mathrm{d}r' \]

\[ \nabla^2 s(r') \mathrm{d}r' \]

\[ \text{LS}_s(r,r') \]

\[ s(r) \]

\[ \nabla^2 s(r') \mathrm{d}r' \]

\[ \text{LS}_s(r,r') \]

\[ s(r) \]
SF applied to plane wave charge density

- For a periodic system:
  - The plane waves that appear in this expansion can be represented as a grid in k-space.
  - Only true for periodic system but the grid used it is discrete.
  - In principle, still need infinite number of plane waves.

\[ \varphi_k(\vec{r}) = \frac{1}{\Omega} \sum_G c_{k,G} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \]

- In practice, the contribution from higher Fourier components (large \(|\vec{k}+\vec{G}|\)) is small.
- So truncate the expansion at some value of \(|\vec{k}+\vec{G}|\).
- Traditional to express this cut off in energy unit:

\[ \frac{\hbar^2 |\vec{k} + \vec{G}|}{2m_e} \leq E_{\text{cut}} \]
**SF applied to plane wave charge density**

**Pseudopotential**

In the chemical bond the core electrons don't interact, thus in the first approximation it is possible to consider the core electrons frozen.

PAW, NC, US

DFT functionals: PBE, PW91, BLYP, B3LYP
Different Approximation of $E_{xc}$

$E_{xc}^{LDA}[n] = \int \epsilon_{xc}(n)n(\vec{r})d^3r$

$E_{xc}^{LSDA}[n \downarrow n \uparrow] = \int \epsilon_{xc}(n \downarrow, n \uparrow)n(\vec{r})d^3r$

$E_{xc}^{GGA}[n \downarrow n \uparrow] = \int \epsilon_{xc}(n \downarrow, n \uparrow, \vec{\nabla}\rho \downarrow, \vec{\nabla}\rho \uparrow)n(\vec{r})d^3r$

$E_{xc}^{MGGA}[n \downarrow n \uparrow] = \int \epsilon_{xc}(n \downarrow, n \uparrow, \vec{\nabla}\rho \downarrow, \vec{\nabla}\rho \uparrow, \vec{\nabla}^2\rho \downarrow, \vec{\nabla}^2\rho \uparrow)n(\vec{r})d^3r$

$E_{xc}^{hyb} = E_{xc}^{LDA} + a(E_{x}^{HF} - E_{x}^{LDA}) + b(E_{x}^{GGA/MGGA} - E_{x}^{LDA}) + E_{c}^{LDA} + c(E_{c}^{GGA/MGGA} - E_{c}^{LDA})$
$SF$ applied to plane wave charge density

Input:
- file *.out & file *.cube

Process:
1. CRITIC2
2. Laplacian of Charge Density
3. Check condition $|r - r'|^2 \leq 10^{-8}$
   - If NO, discard $r'$
   - If YES, accept $r'$

Decision:
- Discarded
- Accepted

Integration:
Integrated with YT or BADER

Output:
$SF$ for each $\Omega$
SF applied to plane wave charge density

SF% hydrogen atomic average values obtained with YT and BADER integration methods with all permutations of DFT functional + pseudo-potential, values are compared to LBS values as reference (red line), for ethane molecule.
Average atomic SF% values for ethane carbon atoms. Values have been obtained with both the YT and BADER integration methods with all available DFT functional + pseudo-potential permutations. Values are compared to LBS based values as reference (red), for ethane molecule.
$SF$ applied to plane wave charge density

PBE-PAW vs PBE/6-311G(d,p)
Pseudopotential

The pseudo-orbitals are the variational parameters of the calculation


The pseudo-orbitals are the variational parameters of the calculation

Core region

\[ |\tilde{\psi}_i\rangle \approx \sum_i |\tilde{\phi}_i\rangle \langle \beta_i |\tilde{\psi}_i\rangle \]
$SF$ applied to plane wave charge density

- Cyclohexene
- 1,3-cyclohexadiene
- Benzene
- Cyclopentadienyl
- Tropylium
- $\text{B}_2\text{H}_6$

Aromaticity

3-center-2-electron
SF applied to plane wave charge density

(Left) SF% average value of ortho carbon vs Ry of kinetic energy, in red the reference obtained with LBS. (right) Difference in absolute value between ortho carbon SF% average value and reference, for cyclohexene molecule.
SF applied to plane wave charge density

(Left) SF% average value of metha carbon vs Ry of kinetic energy, in red the reference obtained with LBS. (right) Difference in absolute value between metha carbon SF% average value and reference, for cyclohexene molecule.
SF applied to plane wave charge density

(Left) SF% average value of para carbon vs Ry of kinetic energy, in red the reference obtained with LBS. (right) Difference in absolute value between para carbon SF% average value and reference, for cyclohexene molecule.
SF applied to plane wave charge density

Comparison in diborane at the BCP of 3 center 2 electron bonding between SF% atomic values calculated at AE PBE/6-311G(d,p) and PBEPAW. The dotted line indicates SF(PW)/SF(AE)=1.
SF applied to plane wave charge density

Comparison in diborane at the BCP of 2 centre 2 electron bonding between SF% atomic values calculated at AE PBE/6-311G(d,p) and PBE-PAW. The dotted line indicates SF(PW)/SF(AE)=1.
Source Function and Plane Waves: Toward Complete Bader Analysis

Christian Tantardini, Davide Ceresoli, and Enrico Benassi

The source function (SF) is a topological descriptor that was introduced and developed by C. Cattel and R.W. Bader in 1998. The SF describes the contribution of each atom to the total electron density at a given point. To date, this descriptor has only been calculable from electron densities generated by all-electron (AE) methods for the investigation of single molecules or periodic systems. This study broadens the accessibility of the SF, offering its calculation from electron densities generated by plane wave (PW) methods. The new algorithm has been implemented in the open source code CRITIC2. Our novel approach has been validated on a series of test systems, comparing the results obtained at PW level with those previously obtained through AE methods. © 2016 Wiley Periodicals, Inc.

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CRITIC2

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Dr. Enrico Benassi
SNS Pisa
\[ SF(r, \Omega) = -\frac{1}{4\pi} \oint_{\Omega} \frac{V^2 \rho(r')}{|r-r'|} \, dr' \]
Failure

\[ \nabla \rho(r) \cdot n(r) = 0 \quad \forall r \in S_\Omega \]

- Vanishing of atomic domains at the vibrational nodes
- Two ZFS for isolated hydrogen atom

Virial Theorem

\[ E = \langle \hat{T} \rangle = \langle \hat{V} \rangle / 2 \]

\[ \gamma = \langle \hat{V} \rangle / \langle \hat{T} \rangle = 2 \]

\[ \langle \hat{V} \rangle *(1 + g) \]

\[ \langle \hat{T} \rangle *(1 + 1/g) \]

The estimation of kinetic energy was demonstrated to be less than 0.4 kJ/mol.

Bader, Atoms in Molecule: A Quantum Theory 1990
Engineering of unsubstituted quinoid-like frameworks enabling 2 V vs. Li⁺/Li redox voltage tunability and related derivatives†

D. Tomerini, C. Gatti and C. Frayret*†

A criterion for redox voltage tuning (0.96–3.96 V vs. Li⁺/Li) was derived from DFT calculations on quinoneazine and analogues (C/O replacing N). As rationalized through spin–charge distributions and energetic criteria, high–low voltage implying a bridge with delocalized–localized bond nature mainly originates from ring stabilization. Established guidelines serve to propose optimal derivatives.

These investigations highlight the interest of looking at frontier orbitals or electron delocalization to account for electrochemical properties or to guide the direction of electron transport. Their impact is expected to significantly grow in the near future. Screening new molecules through computational modelling should prevent very expensive and time consuming trial and error experimental tests. The role played by theoretical studies is thus
\[ \mathbf{P}_{\text{BADER}} \]

\[ \mathbf{P}_{\text{BADER}}(\Omega) = \frac{E(\Omega)}{V(\Omega)} \]

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Domain averaged Fermi Hole

Bader like calculated values of 3-centre bond indexes for X_{ax}–P–X_{ax} and 2-centre bond indexes for P–X_{ax} in PX5

<table>
<thead>
<tr>
<th>Bond</th>
<th>6-31G**</th>
<th>6-311G**</th>
<th>cc-pVTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{ax}–P–H_{ax}</td>
<td>-0.013</td>
<td>-0.013</td>
<td>-0.011</td>
</tr>
<tr>
<td>F_{ax}–P–F_{ax}</td>
<td>0.010</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P–H_{ax}</td>
<td>0.654</td>
<td>0.643</td>
<td>0.636</td>
</tr>
<tr>
<td>P–F_{ax}</td>
<td>0.341</td>
<td>0.434</td>
<td>0.323</td>
</tr>
</tbody>
</table>
$P_{BADER}$  \[ PX_5 \rightarrow PX_3 + X_2 \]

$\Delta P_{BADER}(\Omega)$

- $\Delta P_{BADER}(F_{eq}) = \text{-0.0133 a.u. per Bohr}^3$
- $\Delta P_{BADER}(H_{eq}) = 0.0006 \text{ a.u. per Bohr}^3$
- $\Delta P_{BADER}(F_{ax}) = 0.0610 \text{ a.u. per Bohr}^3$
- $\Delta P_{BADER}(H_{ax}) = 0.0006 \text{ a.u. per Bohr}^3$
Topography vs. thermodynamics in chemical reactions: the instability of $\text{PH}_5^+$

Christian Tantardini and Enrico Benassi

The topological approach, based on Bader theory, is compared to the common thermodynamical methodology to study chemical reactivity. It is shown how the former indeed has numerous advantages and provides a more detailed description with respect to the latter about the course of the reaction. The comparison between the two approaches is performed by considering a classical reaction, i.e., the decomposition of $\text{PX}_4$ ($X = H, F$). The topological investigation was supported by using different state-of-the-art topological tools, such as the source function, Espinosa indexes, delocalization indexes, and domain-averaged Fermi hole analysis. Furthermore, in this work a new topological descriptor, the Bader energy density, $\rho_{\text{Bader}}$, is introduced and applied to the study case. For the first time since Bader theory was introduced, the distribution of atomic energies in the atomic basins was analysed in detail and used to explain the chemical reactivity a priori.

Introduction

The last decades have seen the development of modern theories to study charge density. Various theories, including the quantum theory of atoms in molecules (QTAIM), have found important applications in the understanding of chemical, physical and biological phenomena. The description of existing correlations between electronic structure and chemical reactivity is a research field of particular interest and relevance. In this field the main objective is to predict and to describe the reaction path of an arbitrary process a priori, simply through analysis of the charge density. In some reactions involving "heavy" elements (e.g., P, S, etc.), they may change their valence shell violating the so-called "octet rule:" an expansion of the atom’s valence shell is the cause of filling empty d-orbitals with energy close to those of valence orbitals. This description - introduced by there is no expansion of the valence shell with violation of the octet rule as previously proposed by Pauling. Nevertheless the "hypervalency" theory is still widely evoked in many different chemistry textbooks, being the easiest way to give an apparently convincing description of chemical bonding, which does not require any knowledge about the quantum mechanics and electronic structure, as for Bader’s theory. For example in 2015, Durrant took into account different Pauling- and Musher-like models to examine the “hypervalency” of “heavy” elements in some compounds. These findings were compared with theoretical and experimental atomic charge maps in the framework of Bader’s theory showing no fundamental differences in chemical bonding for hypervalent and non-hypervalent species. Nevertheless, hypervalency is associated with chemical instability, as well as a high degree of covalent rather than ionic bonding.

In this work we consider as a working example a model...
Спасибо за внимание