



# New Insights in Bader's Theory

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Christian Tantardini

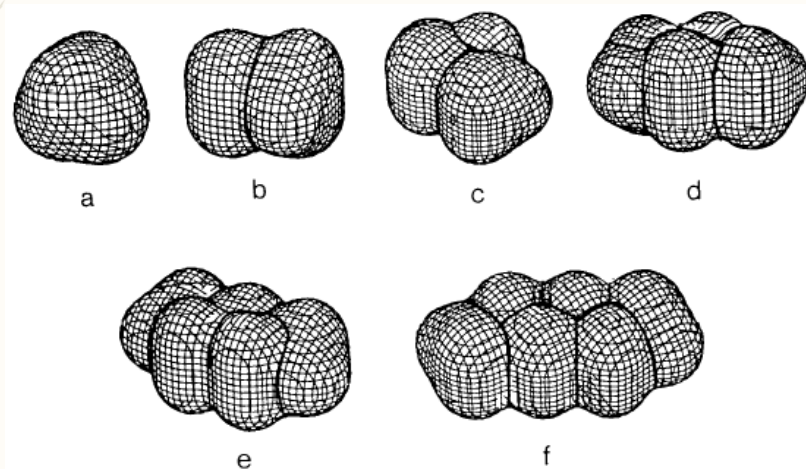


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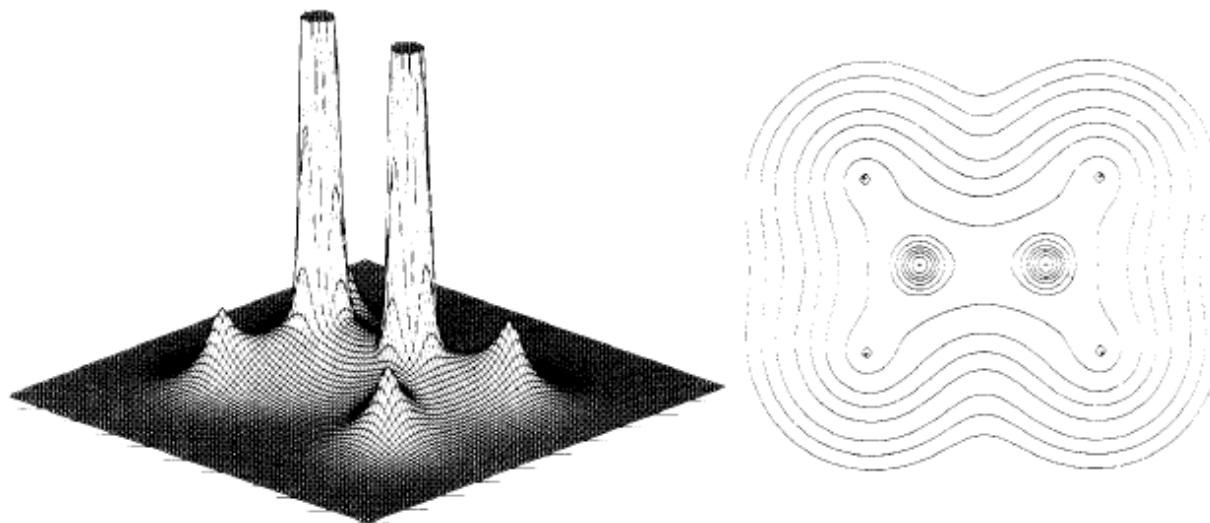
# Brief Introduction to Bader's Theory



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

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in S_{\Omega}$$

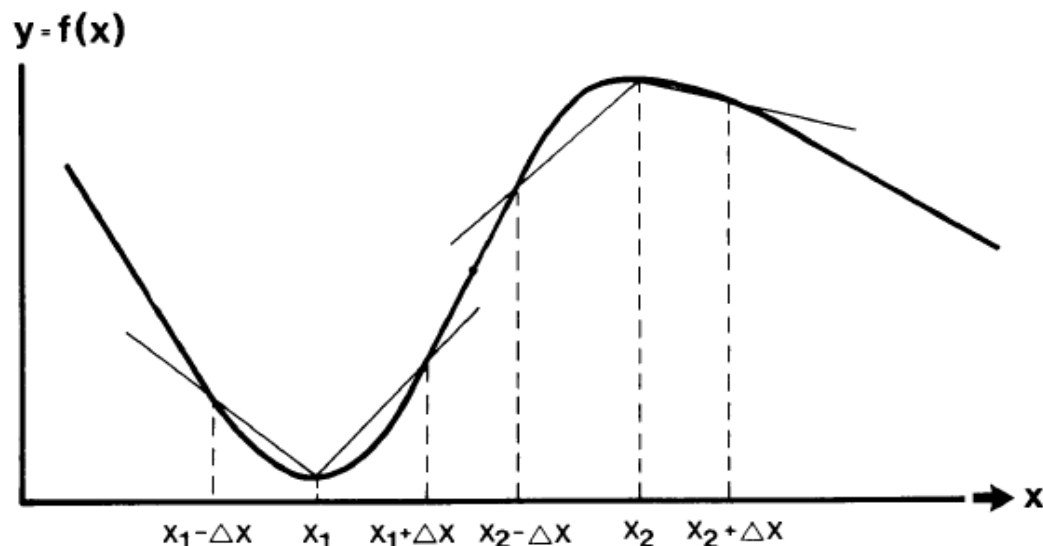
# Brief Introduction to Bader's Theory



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

$\rho(\mathbf{r})$  = charge density

# Brief Introduction to Bader's Theory



Definition of curvature as the limiting difference ( $\Delta x \rightarrow 0$ ) 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

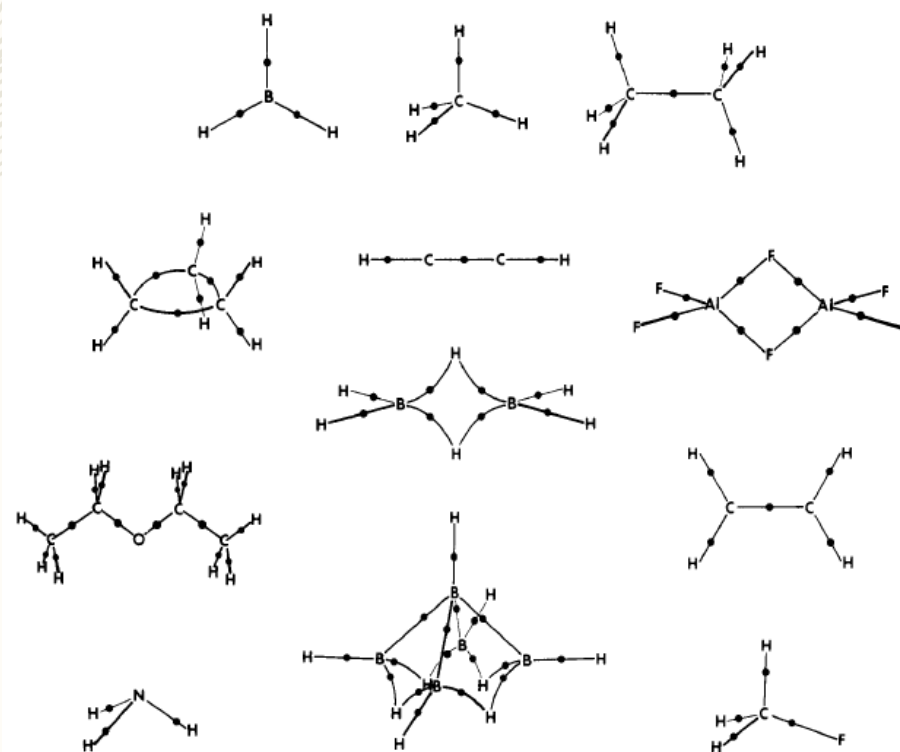
(3, -3) all curvatures are **negative** - maximum

(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

# 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.



# Introduction to the Source Function ( $SF$ )

$$\rho(\mathbf{r}) = \int_{all\ space} LS(\mathbf{r}, \mathbf{r}') \cdot d\mathbf{r}' = \sum_{\Omega} \int_{\Omega} LS(\mathbf{r}, \mathbf{r}') \cdot d\mathbf{r}' \equiv \sum_{\Omega} SF(\mathbf{r}, \Omega)$$

Local Source

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

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in S_{\Omega}$$

Zero Flux Surface

$-\frac{(1/4\pi)}{|\mathbf{r} - \mathbf{r}'|}$  **Green Function** determines the **weight** of the **cause**  $\nabla^2 \rho(\mathbf{r}') d\mathbf{r}'$  to contribute to the **effect**,  $\rho(\mathbf{r})$

# Source Function of Spin Density

$$s(\mathbf{r}) = \rho_{\alpha}(\mathbf{r}) - \rho_{\beta}(\mathbf{r}) \quad \text{SPIN DENSITY}$$

$$s(\mathbf{r}) = \int_{all\ space} \textcircled{\text{LS}_s(\mathbf{r}, \mathbf{r}') \cdot d\mathbf{r}'} = \sum_{\Omega} \int_{\Omega} \text{LS}_s(\mathbf{r}, \mathbf{r}') \cdot d\mathbf{r}' \equiv \sum_{\Omega} SF_s(\mathbf{r}, \Omega)$$

$$\nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in S_{\Omega}$$

Zero Flux Surface

$$\text{LS}_s(\mathbf{r}, \mathbf{r}') = - (4\pi \cdot |\mathbf{r} - \mathbf{r}'|)^{-1} \cdot \nabla^2 s(\mathbf{r}') \quad \text{Local Source for the Spin density}$$

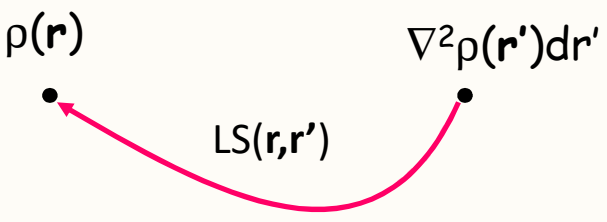
Local cause:  $\nabla^2 s(\mathbf{r}') d\mathbf{r}' = \nabla^2 [\rho_{\alpha}(\mathbf{r}') - \rho_{\beta}(\mathbf{r}')] d\mathbf{r}'$

Global Effect:  $s(\mathbf{r})$

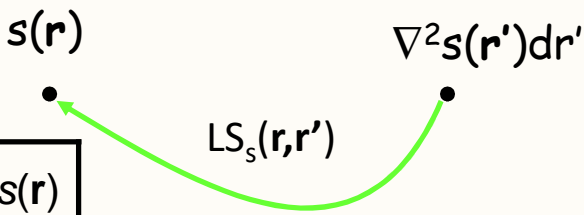
Effectiveness: the same as for  $\rho$ , being a purely geometrical factor



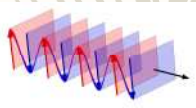
$\rho(\mathbf{r}')$	$\nabla^2 \rho(\mathbf{r}')$	$LS(\mathbf{r}')$	Effects on $\rho(\mathbf{r})$
$> 0$	$> 0$	$< 0$	decrease $\rho$
$> 0$	$< 0$	$> 0$	increase $\rho$



$s(\mathbf{r}')$	$\nabla^2 \rho_\alpha(\mathbf{r}')$	$\nabla^2 \rho_\beta(\mathbf{r}')$	$\nabla^2 s(\mathbf{r}')$	$LS_s(\mathbf{r}')$	Effects on $s(\mathbf{r})$
$\pm$	$> 0$	$> 0$	$\nabla^2 \rho_\alpha > \nabla^2 \rho_\beta \quad > 0$ $\nabla^2 \rho_\alpha < \nabla^2 \rho_\beta \quad < 0$	$< 0$ $> 0$	$\rightarrow \beta$ $\rightarrow \alpha$
$\pm$	$> 0$	$< 0$	$> 0$	$< 0$	$\rightarrow \beta$
$\pm$	$< 0$	$> 0$	$< 0$	$> 0$	$\rightarrow \alpha$
$\pm$	$< 0$	$< 0$	$ \nabla^2 \rho_\alpha  >  \nabla^2 \rho_\beta  \quad < 0$ $ \nabla^2 \rho_\alpha  <  \nabla^2 \rho_\beta  \quad > 0$	$> 0$ $< 0$	$\rightarrow \alpha$ $\rightarrow \beta$



# SF applied to plane wave charge density

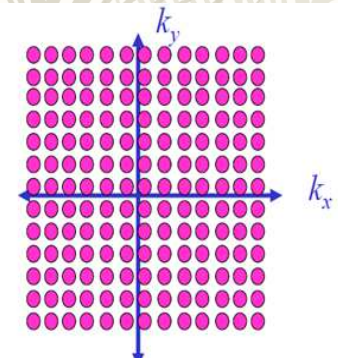


- ▶ For a periodic system

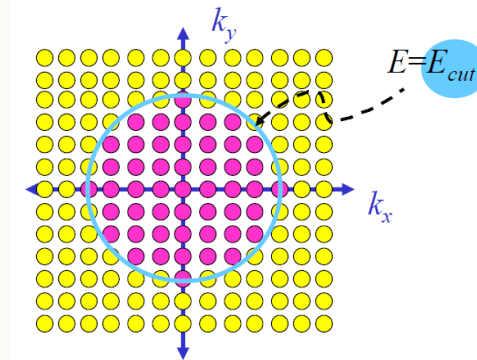
$$\varphi_k(\vec{r}) = \frac{1}{\Omega} \sum_G c_{k,G} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}$$

reciprocal lattice vector

- 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**

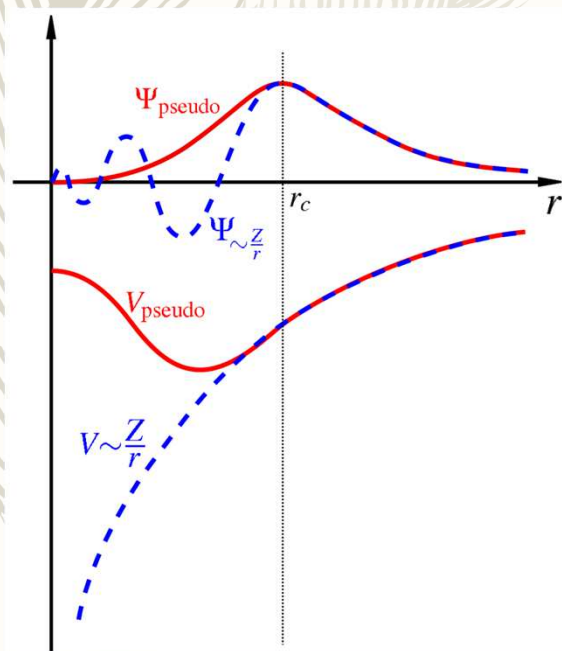


- ▶ In practice, the contribution from higher Fourier components (large  $|\mathbf{k} + \mathbf{G}|$ ) is small
- ▶ So **truncate** the expansion at some value of  $|\mathbf{k} + \mathbf{G}|$
- ▶ Traditional to express this cut off in **energy unit**

$$\frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m_e} \leq E_{cut}$$

# *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 $E_{xc}$

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

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

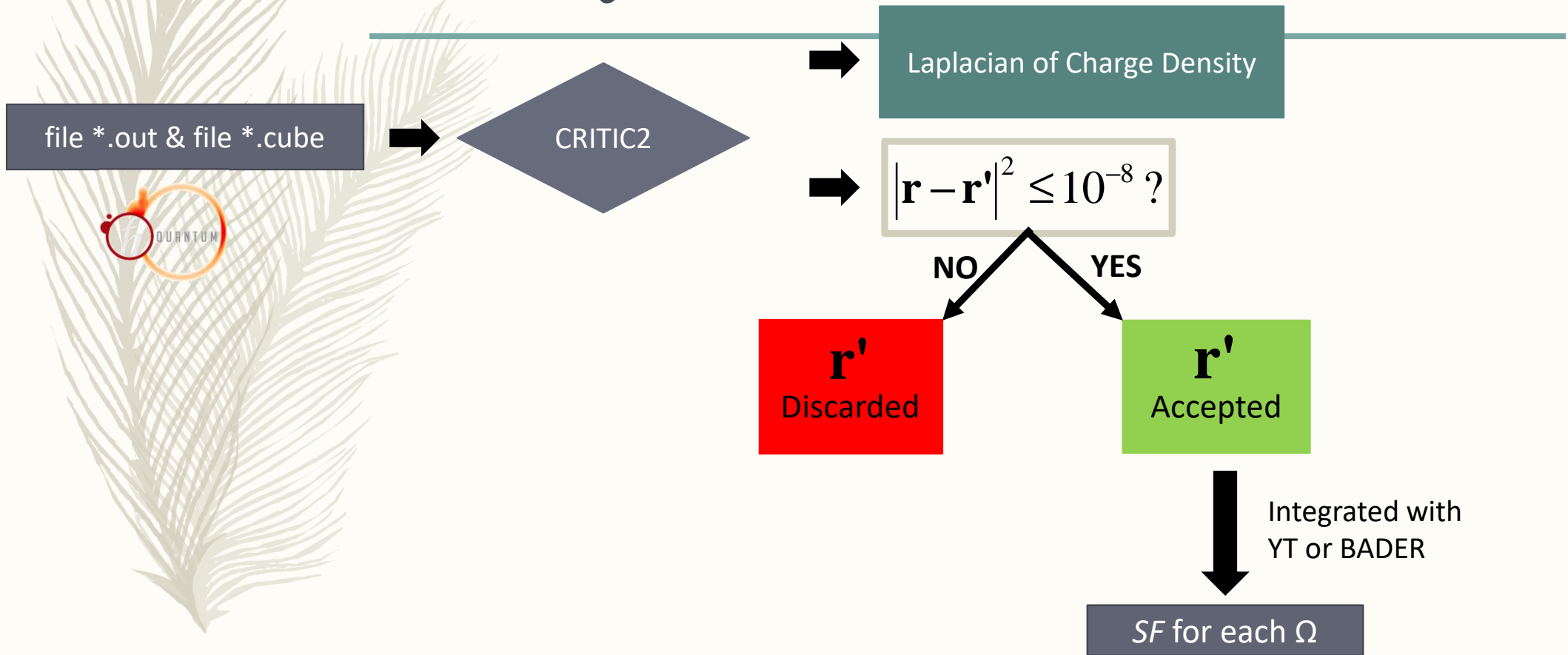
$$E_{xc}^{GGA}[n \downarrow n \uparrow] = \int \epsilon_{xc}(n \downarrow, n \uparrow, \vec{\nabla} \rho \downarrow, \vec{\nabla} \rho \uparrow) n(\vec{r}) d^3r$$

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

$$E_{xc}^{hyb} = E_x^{LDA} + a(E_x^{HF} - E_x^{LDA}) + b(E_x^{GGA/MGGA} - E_x^{LDA}) + E_c^{LDA} + c(E_c^{GGA/MGGA} - E_c^{LDA})$$

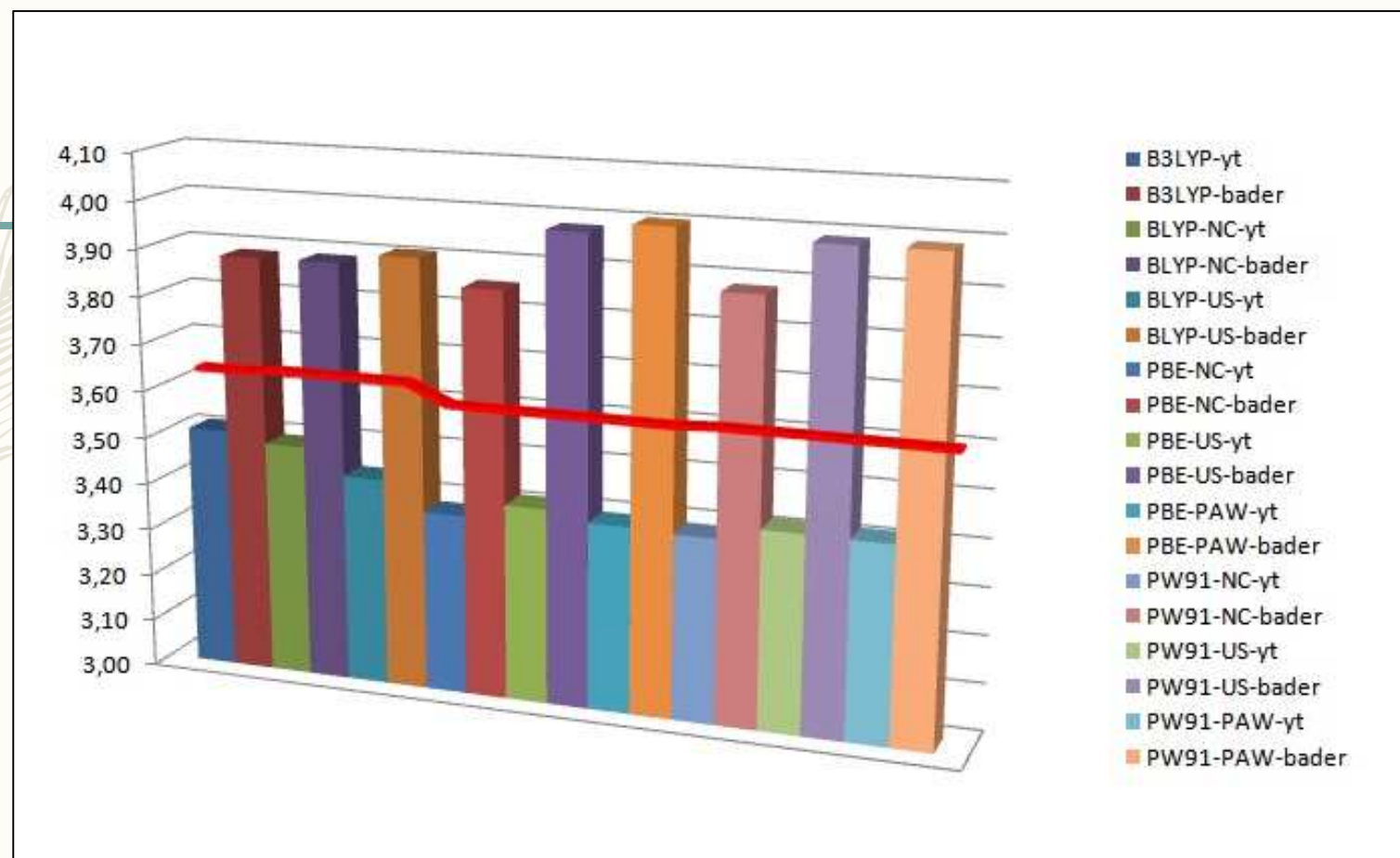
Perdew, Phys. Rev. Let. 77, 18, 3865 (1996)  
Carter, J. Chem.Theory Comput. 10, 3423 (2014)

# *SF* applied to plane wave charge density





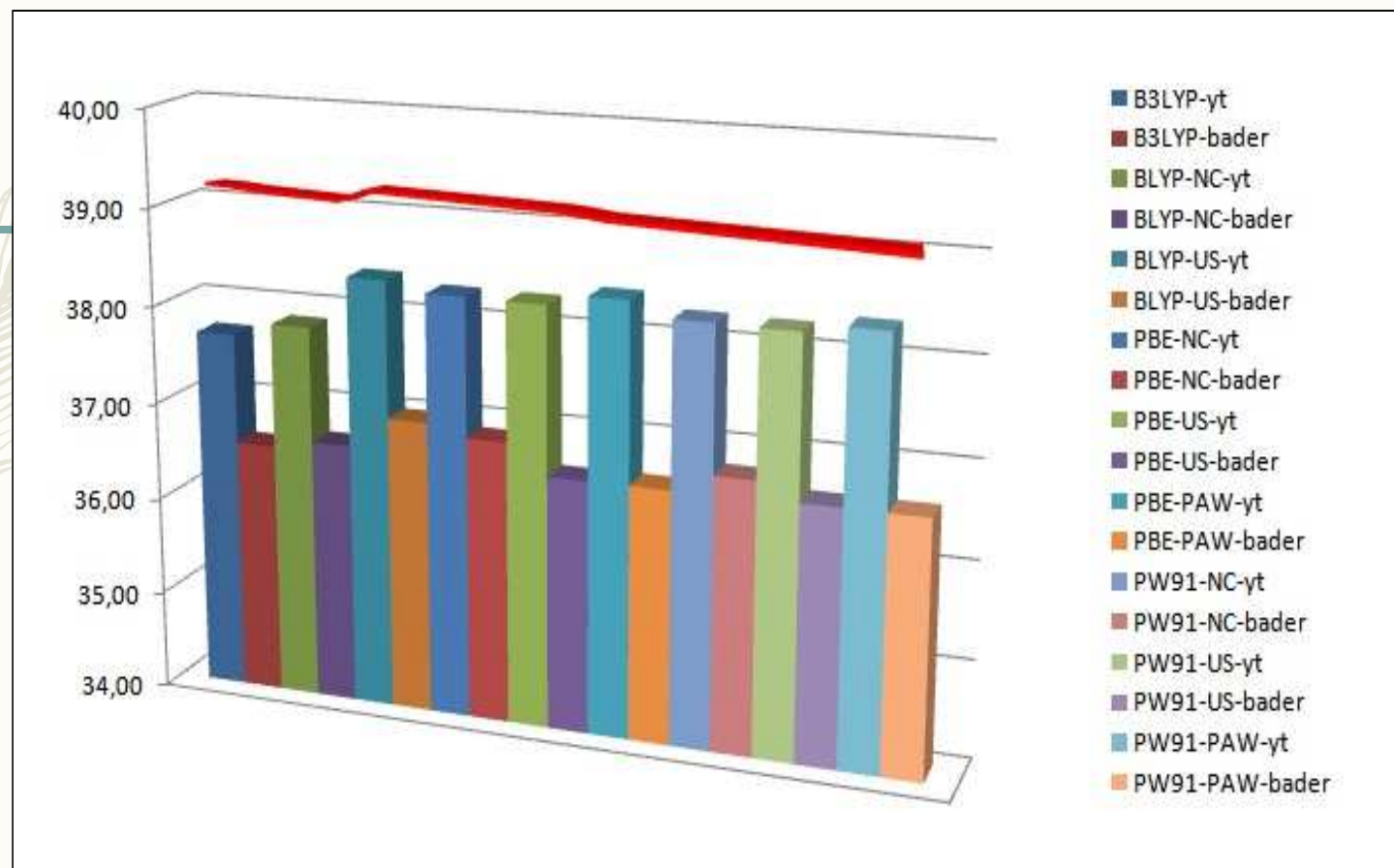
# $SF$ applied to plane wave charge density



**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.

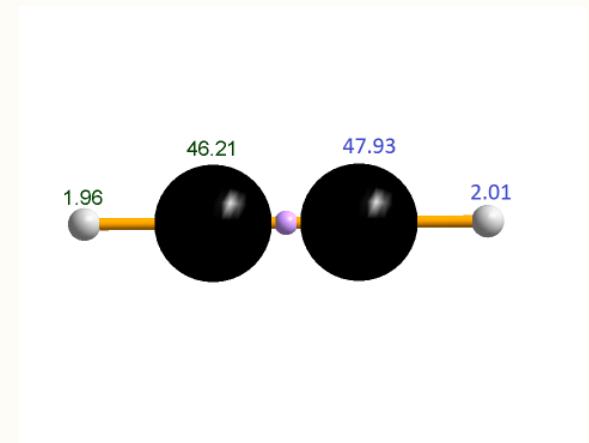
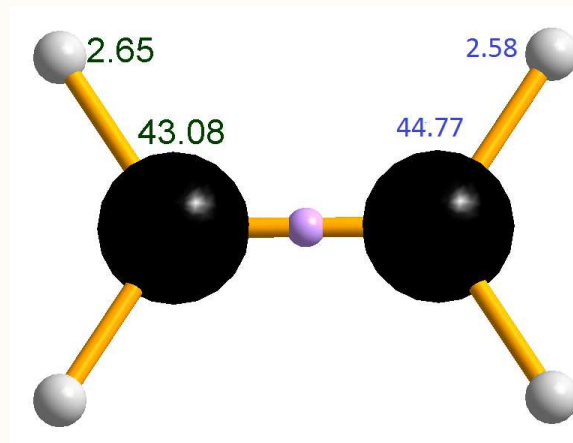
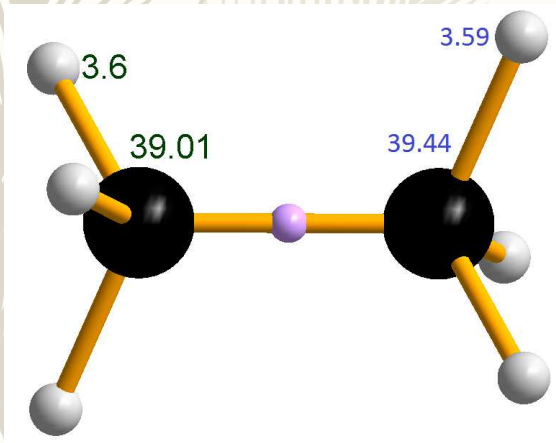


# $SF$ applied to plane wave charge density



**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

**P**rojector **A**ugmented **W**aves

“Pseudo”  
orbitals

$$|\psi_l\rangle = \hat{T}|\tilde{\psi}_l\rangle = |\tilde{\psi}_l\rangle + \sum_i (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle)\langle\beta_i|\tilde{\psi}_l\rangle$$

“True”  
orbitals

Linear  
transformation

$$\langle\beta_i|\tilde{\varphi}_m\rangle = \delta_{im} \Rightarrow \hat{T}|\tilde{\varphi}_i\rangle = |\varphi_i\rangle$$

Pseudo  
waves

“True” atomic  
state

- The pseudo-orbitals are the variational parameters of the calculation

Core region

$$|\tilde{\psi}_l\rangle \approx \sum_i |\tilde{\varphi}_i\rangle\langle\beta_i|\tilde{\psi}_l\rangle$$



# *SF* applied to plane wave charge density

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- Cyclohexene
- 1,3-cyclohexadiene
- Benzene
- Cyclopentadienyl
- Tropylium
- B<sub>2</sub>H<sub>6</sub>

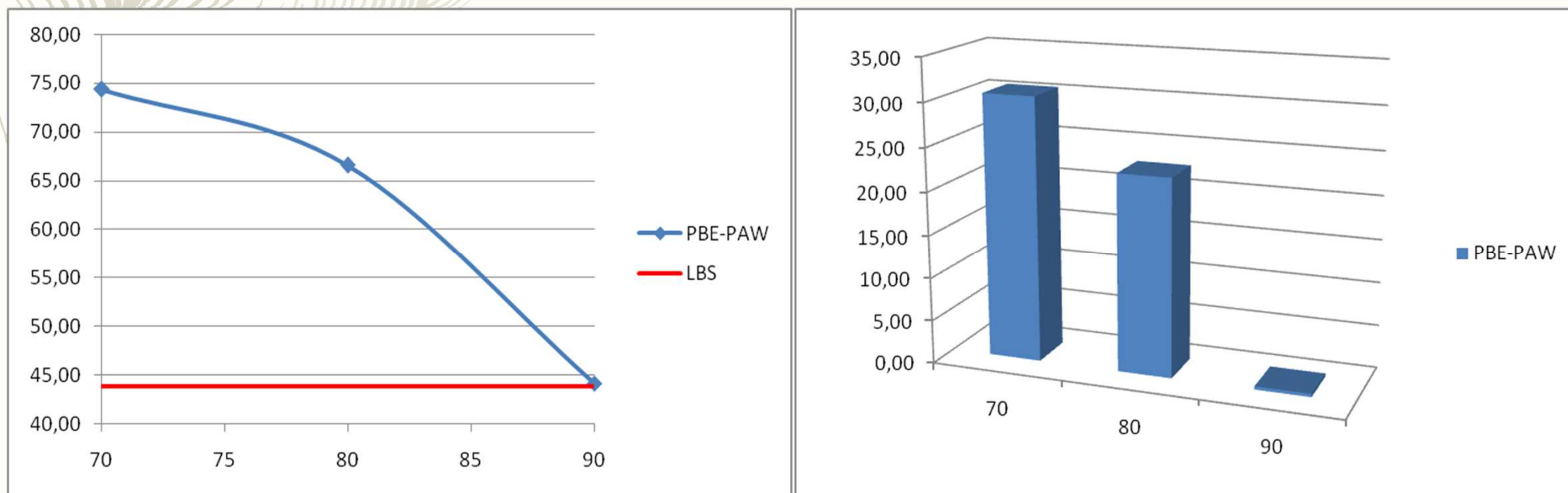


Aromaticity



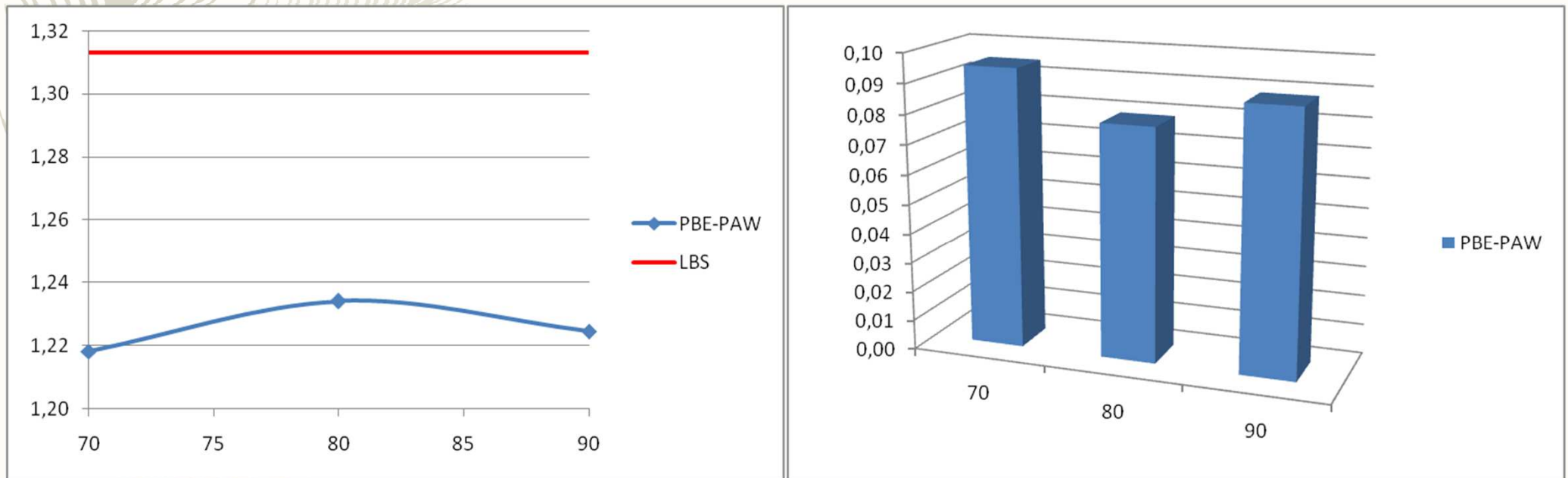
3-center-2-electron

# *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.**

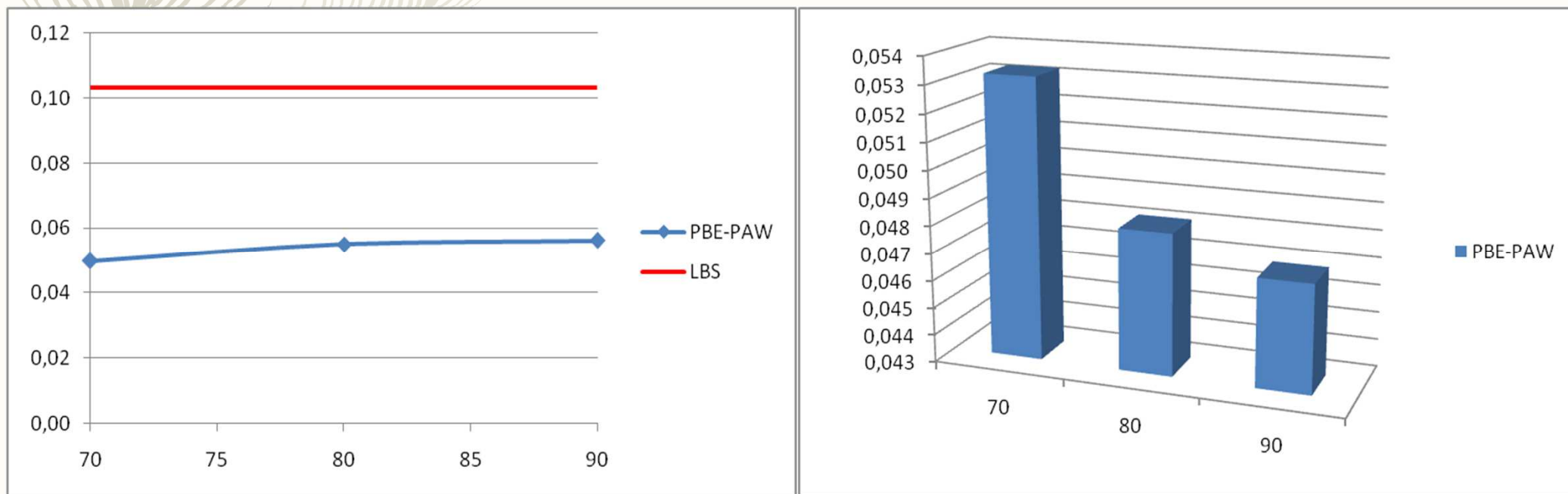
# $SF$ applied to plane wave charge density



(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.**

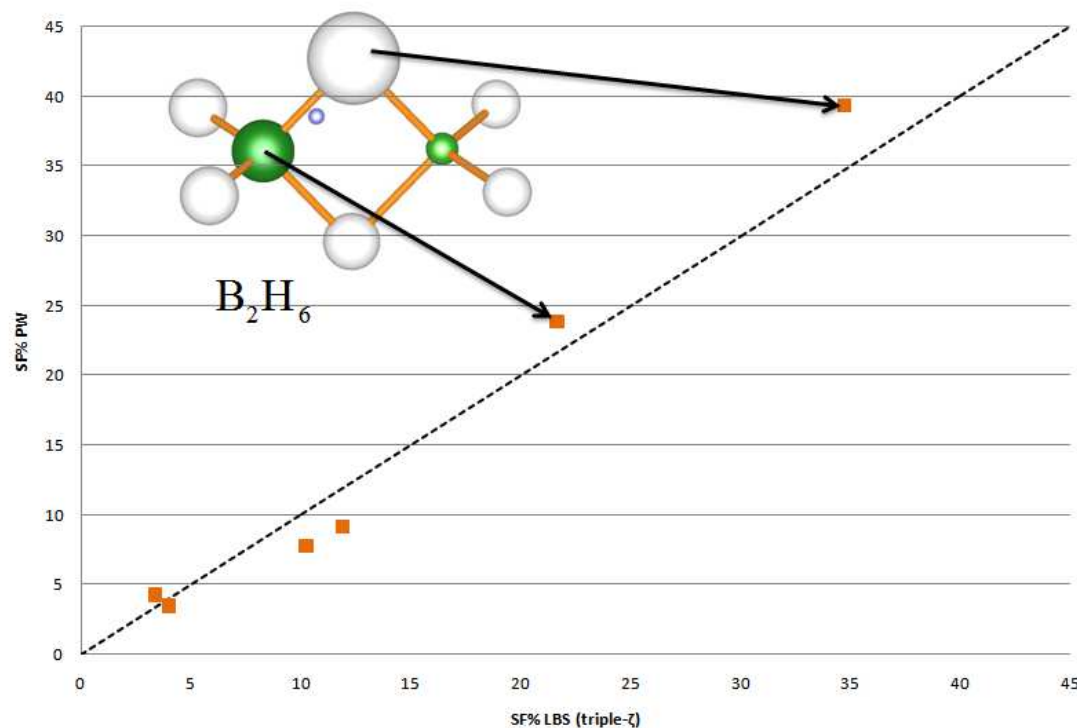


# $SF$ applied to plane wave charge density



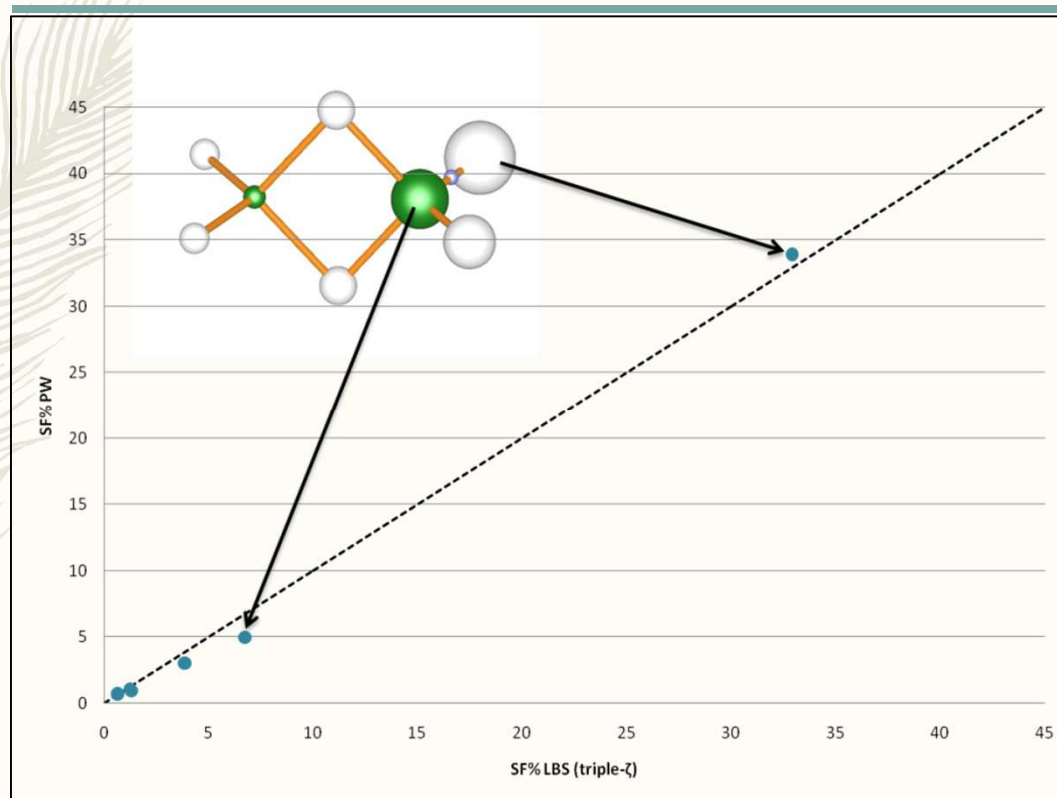
(Left) **SF% average value of para carbon** vs Ry of kinetic energy, in **red** the reference obtained with **LBS**. (right) **Difference in absolute value between para carbon SF% average value and reference, for cyclohexene molecule.**

# *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,<sup>\*,[a]</sup> Davide Ceresoli,<sup>[b,c,d]</sup> and Enrico Benassi<sup>[a,e]</sup>

The source function (SF) is a topological descriptor that was introduced and developed by C. Gatti 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 gener-

ated 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.

DOI: 10.1002/jcc.24433

# CRITIC2



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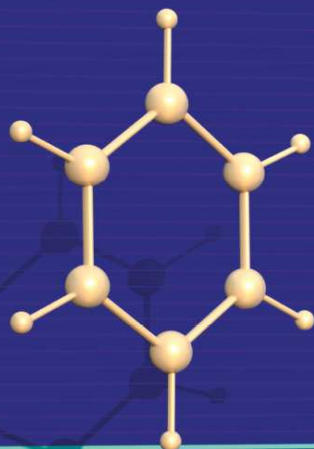
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Volume 37 | Issues 23–24 | 2016  
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$$SF(\mathbf{r}, \Omega) = -\frac{1}{4\pi} \int_{\Omega} d\mathbf{r}' \frac{\nabla^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



Editors:  
Charles L. Brooks III • Masahiro Ehara • Gernot Frenking • Peter R. Schreiner

WILEY





P<sub>BADER</sub>

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## Failure

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0 \quad \forall \mathbf{r} \in S_{\Omega}$$

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





P<sub>BADER</sub>

# 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.**

PCCP

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Cite this: *Phys. Chem. Chem. Phys.*,  
2015, 17, 8604

Received 21st December 2014,  
Accepted 23rd February 2015

DOI: 10.1039/c4cp05998k

[www.rsc.org/pccp](http://www.rsc.org/pccp)

## Engineering of unsubstituted quinoid-like frameworks enabling 2 V vs. $\text{Li}^+/\text{Li}$ redox voltage tunability and related derivatives†

D. Tomerini,<sup>ab</sup> C. Gatti<sup>c</sup> and C. Frayret<sup>\*ab</sup>

**A criterion for redox voltage tuning (0.96–2.96 V vs.  $\text{Li}^+/\text{Li}$ ) 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.**

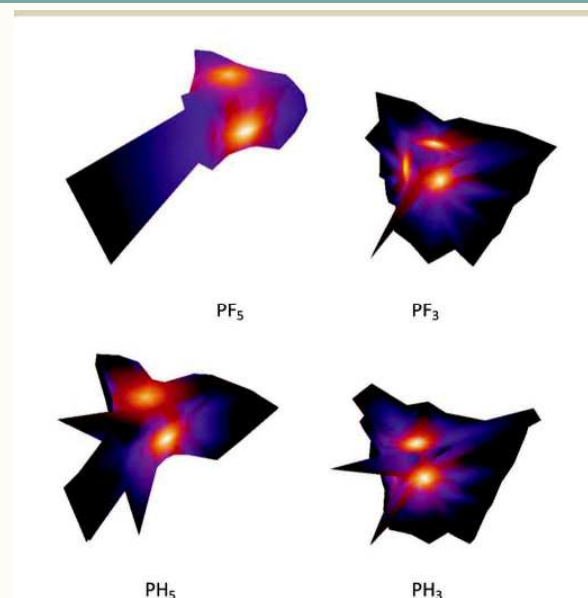
These investigations highlight the interest of looking at frontier orbitals or electron delocalization<sup>1f,5a,b</sup> to account for electrochemical properties or to guess the direction of electron transport. Their impact is expected to significantly grow in the near future. Screening new molecules through computational modelling should prevent very expensive and time consuming trial and error experimental tests. The role played by theoretical studies is thus

# P<sub>BADER</sub>



$$P_{\text{BADER}}(\Omega) = E(\Omega)/V(\Omega)$$

Table Volume (V), electronic energy (E) and Bader's energy density (P <sub>BADER</sub> ) of atomic basins							
Atom	V (Bohr <sup>3</sup> )	E (a.u.)	P <sub>BADER</sub> (a.u. per Bohr <sup>3</sup> )	Atom	V (Bohr <sup>3</sup> )	E (a.u.)	P <sub>BADER</sub> (a.u. per Bohr <sup>3</sup> )
PX <sub>5</sub>							
P	45.73	-339.47	-7.4239	P	14.15	-338.37	-23.9126
H <sub>eq</sub>	75.24	-0.86	-0.0114	F <sub>eq</sub>	106.95	-100.28	-0.9376
H <sub>ax</sub>	83.40	-0.88	-0.0106	F <sub>ax</sub>	106.95	-100.28	-0.9498
PX <sub>3</sub>							
P	149.82	-340.23	-2.2710	P	108.67	-339.59	-3.1251
H	76.26	-0.82	-0.0108	F	114.31	-100.21	-0.8766
X <sub>2</sub>							
H	59.02	-0.59	-0.0099	F	103.47	-99.65	-0.9630



Plot of atomic basins of P with charge density depicted from highest concentration (white) to lowest concentration (black; 10<sup>-3</sup> e/Bohr<sup>3</sup>).



$P_{\text{BADER}}$

---

## Domain averaged Fermi Hole

Bader like calculated values of 3-centre bond indexes for  $X_{\text{ax}}\text{--P--}X_{\text{ax}}$  and 2-centre bond indexes for  $\text{P--}X_{\text{ax}}$  in  $\text{PX}_5$

	6-31G**	6-311G**	cc-pVTZ
$\text{H}_{\text{ax}}\text{--P--H}_{\text{ax}}$	-0.013	-0.013	-0.011
$\text{F}_{\text{ax}}\text{--P--F}_{\text{ax}}$	0.010	-	-
$\text{P--H}_{\text{ax}}$	0.654	0.643	0.636
$\text{P--F}_{\text{ax}}$	0.341	0.434	0.323



$P_{\text{BADER}}$



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

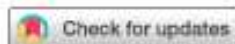
$\Delta P_{\text{BADER}}(F_{\text{eq}}) = -0.0133 \text{ a.u. per Bohr}^3$

$\Delta P_{\text{BADER}}(H_{\text{eq}}) = 0.0006 \text{ a.u. per Bohr}^3$

$\Delta P_{\text{BADER}}(F_{\text{ax}}) = 0.0610 \text{ a.u. per Bohr}^3$

$\Delta P_{\text{BADER}}(H_{\text{ax}}) = 0.0006 \text{ a.u. per Bohr}^3$





Cite this: *Phys. Chem. Chem. Phys.*,  
2017, 19, 27779

Received 8th September 2017,  
Accepted 25th September 2017

DOI: 10.1039/c7cp06130g

rsc.li/pccp

## Topology vs. thermodynamics in chemical reactions: the instability of $\text{PH}_5^\dagger$

Christian Tantardini<sup>a</sup> and Enrico Berassi<sup>ab</sup>

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  $\text{PX}_5$  ( $X = \text{H}, \text{F}$ ). The topological investigation was supported by using different state-of-the-art topological tools, such as the source function, Espinosa indexes, delocalisation indexes, and domain-averaged Fermi hole analysis. Furthermore, in this work a new topological descriptor, the Bader energy density,  $P_{\text{Bader}}$ , 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.<sup>1</sup> Various theories, including the quantum theory of atoms in molecules (QTAIM),<sup>2</sup> 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.<sup>3–9</sup> 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”;<sup>10</sup> 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.<sup>1,11</sup> Nevertheless the “hypervalency” theory is still widely evoked in many different chemistry text books, 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,<sup>15</sup> Durrant took into account different Pauling- and Musher<sup>16</sup>-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

