#### On the topology of the reduced density gradient

#### Roberto A. Boto, Julia Contreras García, Julien Tierny and Jean-Philip Piquemal

ICS-UPMC, Paris, France LCT, UMR 7616, UPMC Univ

July 10, 2015









Roberto A. Boto (ICS-LCT)



2 Local Quantum Theory

3 The topology of the reduced density gradient  $(s(\mathbf{r}))$ 



#### Introduction

- Quantum Chemical Topology focuses on any meaningful chemical or physical scalar field.
- Each scalar field leads to a different partition of real spaced into regions
- The physical meaning of depends on the seleced scalar field

$$\rho \Rightarrow Atoms$$

- $abla^2 \rho \Rightarrow \quad \text{Atomic Shells, Lone Pairs}$
- $\mathsf{ELF} \Rightarrow$  Atomic Shells, Electron Pairs

#### Introduction

- ${\mbox{\circle*{ \ or }}}$  The reduced density gradient  $s({\mbox{r}})$  has played a paramount role in the DFT development
- Closely connected to energetics
- It is able to reveal atomic structure
- $s(\mathbf{r})$  isosurfaces may reveal covalent and non-covalent interactions
- In this work we analyse some of the topological properties of  $s({f r})$

### The reduced density gradient $\mathbf{s}(\mathbf{r})$

• The origin of  $s(\mathbf{r})$  may be traced to the generalized gradient approximations (GGA) contributions to the exchange energy

$$E_x^{GGA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{\mathbf{x}}^{\mathbf{unif}} F_x(\mathbf{s}(\mathbf{r})) d\mathbf{r}$$

$$\epsilon_{\bf x}^{\rm unif} = -\frac{3{\bf p}_{\rm F}({\bf r})}{4\pi} \quad {\bf p}_{\rm F}({\bf r}) = (3\pi^2\rho({\bf r}))^{1/3}$$

$$\mathbf{s}(\mathbf{r}) = \frac{|\nabla \rho(\mathbf{r})|}{2\rho(\mathbf{r})\mathbf{p}_{\mathbf{F}}(\mathbf{r})}$$

 $\bullet~\mathbf{s}(\mathbf{r})$  accounts for local density inhomogeneity of the density

#### Local Quantum Theory

• Local Quantum Theory states that any physical observable represented by the operator  $\hat{A}$  may be decomposed in two local contributions

$$\hat{A} = \bar{A}(\mathbf{r}) + i\tilde{A}(\mathbf{r})$$

 $\bullet\,$  For a quantum system is the state  $\psi$ 

$$\bar{A}(\mathbf{r}) = \mathbf{Re}\left(\frac{\hat{A}\psi}{\psi}\right)(\mathbf{r})$$
 Local value  
 $\tilde{A}(\mathbf{r}) = \mathbf{Im}\left(\frac{\hat{A}\psi}{\psi}\right)(\mathbf{r})$  Local spread

• They obey the conditions

$$\langle \hat{A} \rangle_{\psi} = \langle \bar{A} \rangle_{\psi} \qquad \langle \tilde{A} \rangle_{\psi} = 0$$

•  $\bar{A}(\mathbf{r})$  is the classical estimate of the operator  $\hat{A}$  on  $\mathbb{R}^3$  (rather than  $L^2$ )

### Local kinetic energy theorem

Given a local representation of the kinetic energy operator  $\hat{\mathbf{K}}=-\frac{\nabla^2}{2}$  as

$$\mathbf{K}(\mathbf{r}) = \bar{\mathbf{K}}(\mathbf{r}) + i\tilde{\mathbf{K}}(\mathbf{r})$$

where the real part  $\bar{\mathbf{K}}(\mathbf{r})$  is given by

$$\bar{\mathbf{K}}(\mathbf{r}) = -\frac{1}{2} \left( \frac{\nabla^2 \rho(r)}{2\rho(r)} - \frac{\nabla \rho(r) \nabla \rho(r)}{4\rho(r)^2} \right)$$

The expectation value of the kinetic energy  $\langle \mathbf{K} \rangle$  is only given by its real part

$$\langle \hat{\mathbf{K}} \rangle = \langle \bar{\mathbf{K}}(\mathbf{r}) \rangle \quad \langle \tilde{\mathbf{K}}(\mathbf{r}) \rangle = 0$$

## Local kinetic energy theorem

The local kinetic energy theorem states that:

$$\langle \mathbf{K}(\mathbf{r}) \rangle = \frac{1}{8} \int \frac{\nabla \rho(r) \nabla \rho(r)}{\rho(r)} d\mathbf{r} = \langle \tau_{vw}(\mathbf{r}) \rangle$$

where  $\tau_{vw}(\mathbf{r})$  is the von Weizsäcker kinetic energy density

$$\frac{1}{2}[s(\mathbf{r})\mathbf{p}_{\mathbf{F}}(\mathbf{r})]^2 = \tau_{\mathbf{vw}}(\mathbf{r})$$

•  $s(\mathbf{r})$  is connected to the local value of the kinetic energy

# The topology of $s(\mathbf{r})$

$$s(\mathbf{r}) = C \frac{|\nabla \rho(\mathbf{r})|}{\rho(\mathbf{r})^{4/3}}, \qquad C = \frac{1}{(2(3\pi^2)^{1/3})}$$

•  $s(\mathbf{r}): \mathbb{R}^3 \to \mathbb{R}^+$ 

- $\lim_{\rho(\mathbf{r})\to 0} s(\mathbf{r}) = \infty$
- Two kinds of critical points
  - Kind 1:  $s(\mathbf{r}) = 0$ ,  $\nabla \rho(\mathbf{r}) = 0 \Rightarrow \mathsf{QTAIM}$

• Kind 2 : 
$$\nabla s(\mathbf{r}) = 0$$
,  $\nabla \rho(\mathbf{r}) \neq 0$ 

#### **One-electron Potential OEP(\mathbf{r})**

 $\bullet~ \mathbf{OEP}(\mathbf{r})$  is defined by

$$\mathbf{OEP}(\mathbf{r}) = -\bar{\mathbf{K}}(\mathbf{r}) = \frac{1}{2} \left( \frac{\nabla^2 \rho(r)}{2\rho(r)} - \frac{\nabla \rho(r) \nabla \rho(r)}{4\rho(r)^2} \right) = \mathbf{U} - \mathbf{E}$$
(1)

 $\bullet~ \mathbf{OEP}(\mathbf{r})$  splits the spaces into classically allowed and forbidden regions

- $\bullet~ {\bf OEP}({\bf r}) < 0$  Classically allowed regions: atomic shells and core, valence
- $\mathbf{OEP}(\mathbf{r}) > 0$  Classically forbidden regions: barriers between shells

# One-electron Potential OEP(r): O (<sup>3</sup>P)



#### Connection between OEP(r) and s(r)

• Let's define 
$$s'(\mathbf{r}) = \frac{\nabla \rho(\mathbf{r})}{2\rho(\mathbf{r})\mathbf{p_F}(\mathbf{r})}$$
,  $s(\mathbf{r}) = |s'(\mathbf{r})|$ 

•  $s'(\mathbf{r})$  is connected to  $\mathbf{OEP}(\mathbf{r})$  through its gradient

$$\nabla s'(\mathbf{r}) = \frac{1}{\mathbf{p}_{\mathbf{F}}(\mathbf{r})} \left[ 2\mathbf{OEP}(\mathbf{r}) - \frac{5}{6}\tau_{\mathbf{vw}}(\mathbf{r}) \right]$$

 $\bullet$  Critical points of  $s'({\bf r})$  are related to barriers between classically allowed-forbidden regions

# Example: $O(^{3}P)$



### Critical Points of $s(\mathbf{r})$

- Kind 1:  $s(\mathbf{r}) = 0$ ,  $\nabla \rho(\mathbf{r}) = 0$ 
  - They are always minima of  $s(\mathbf{r})$
  - They recover the Quantum Theory of Atoms in Molecules (QTAIM)
- Kind 2 :  $\nabla s'(\mathbf{r}) = 0$ 
  - They may be either maxima, minima or saddle points
  - Related with classically allowed-forbidden regions
  - It  $s(\mathbf{r})$  differentiates between Core-Valence regions

## Revealing atomic structure from $s(\mathbf{r})$ : O (<sup>3</sup>P)



Roberto A. Boto (ICS-LCT)

## Revealing atomic structure from $s(\mathbf{r})$ : O (<sup>3</sup>P)



Roberto A. Boto (ICS-LCT)

#### Revealing atomic structure from $s(\mathbf{r})$

Atom	$N_{\rm Core}$	$N_{\rm CV}$	$N_{\rm Valence}$
${}^4Be$	1.91	0.27	1.82
<sup>8</sup> 0	1.90	0.67	5.43
$^{10}Ne$	1.89	0.80	7.31
$^{12}Mg$	9.80	0.58	1.62
$^{18}Ar$	9.48	1.47	7.05

## $s(\mathbf{r})$ as functional of $\rho(\mathbf{r})$

• Let's consider  $s(\mathbf{r})$  as a functional of  $\rho(\mathbf{r})$ :  $s(\mathbf{r}) \rightarrow s[\rho]$ 



## $s(\mathbf{r})$ as functional of $\rho(\mathbf{r})$

• For a single STO density model,  $s(\mathbf{r})$  reduces to:

 $s(\mathbf{r}) \propto \rho^{-1/3}$ 

- Overlap between orbitals is revealed as a trough in  $s[\rho]$  diagram
- Troughs in  $s[\rho]$  diagrams matches with Core-Valence regions

The topology of the reduced density gradient ( $s(\mathbf{r})$ )

# $s(\mathbf{r})$ as functional of $\rho(\mathbf{r})$ : O (<sup>3</sup>P)



# $s(\mathbf{r})$ as functional of $\rho(\mathbf{r})$

- $s[\rho]$  diagrams may identified bonding situations
- $\bullet \ O_2 \ \text{case}$



• Mapping back  $s[\rho]$  to real space, interactions may be visualized



- $\bullet \ s(r)$  isosurfaces reveals covalent and non-covalent interaction simultaneously
- Adenine-Thymine complex



#### Conclusions

- Classical chemical concepts may be recovered by Quantum Chemical Topology
- $\bullet~s(\mathbf{r})$  applicability ranges from atomic structure to intermolecular interactions
- ${\ensuremath{\, \circ }}\xspace \ s({\ensuremath{\rm r}})$  critical points are closely connected to chemical concepts
- ${\ensuremath{\bullet}}$  Transition regions among shells are identified by  $s({\ensuremath{\mathbf{r}}})$

#### Acknowledge

#### This work undertaken (partially) in the framework of CALSIMLAB is supported by the public grant ANR-11-LABX-0037-01 overseen by the French National Research Agency(ANR) as part of the "*Investissements d'Avenir*" program (reference: ANR-11-IDEX-0004-02)



