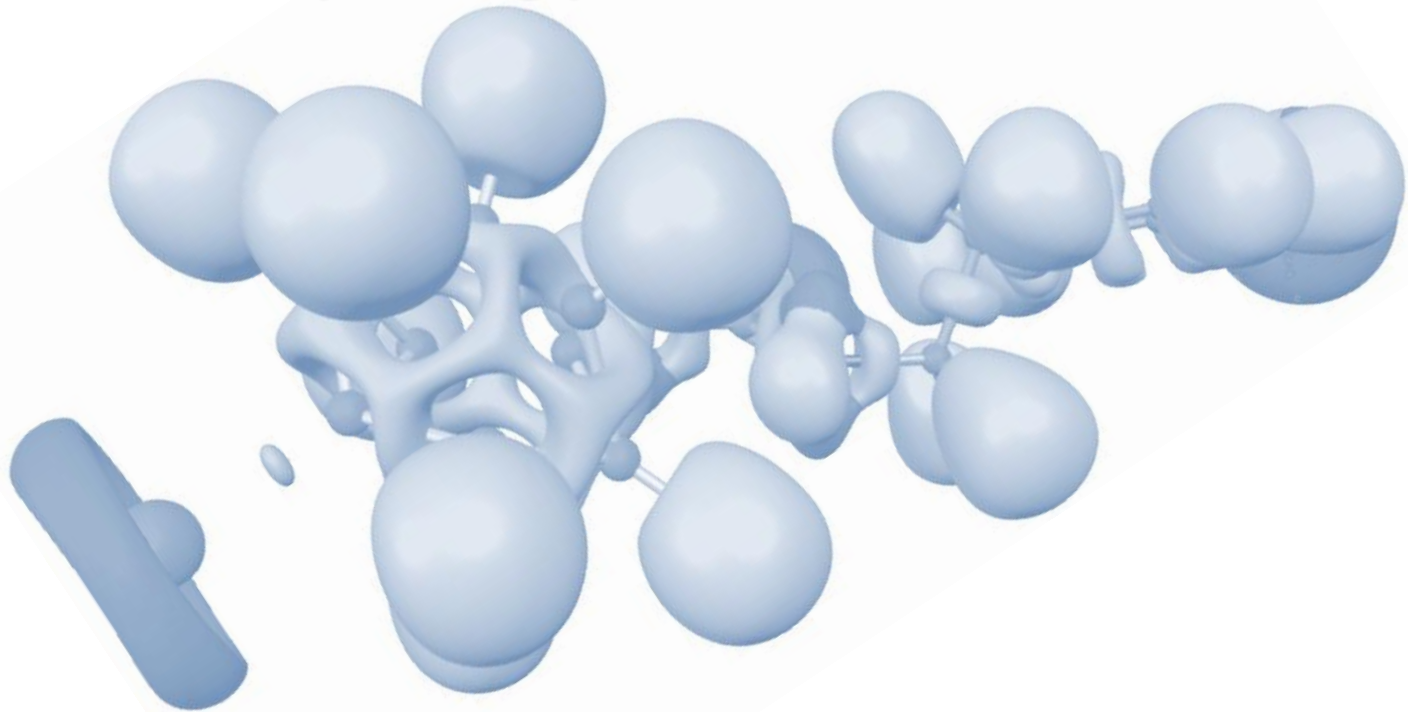


Beyond the QTAIM Partition

Julien Pilmé and Vanessa Labet

A. The Electron Localization Function (ELF) and its topology



A.J. Definitions

A simple measure of electron localization in atomic and molecular systems

A. D. Becke and K. E. Edgecombe
 Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6
 (Received 26 September 1989; accepted 24 January 1990)

We introduce in this work a new approach to the identification of localized electronic groups in atomic and molecular systems. Our approach is based on local behavior of the Hartree-Fock parallel-spin pair probability and is completely independent of unitary orbital transformations. We derive a simple "electron localization function" (ELF) which easily reveals atomic shell structure and core, binding, and lone electron pairs in simple molecular systems as well

I. INTRODUCTION

Of major importance in descriptive chemistry is the concept of localized groups of electrons, encompassing such notions as atomic shells, binding and lone electron pairs, pi-electron subsystems, etc. However, despite its undeniable utility, the concept of spatially localized electrons is theoretically and mathematically elusive. The canonical orbitals of Hartree-Fock theory are delocalized throughout the space of a molecule or crystal, and do not suggest localized electronic groups. On the other hand, it is well known that equivalent localized orbitals can be generated by unitary transformations of canonical orbitals, leaving Hartree-Fock total energy unchanged, according to various prescriptions. Unfortunately, such transformations are not unique and may even result in qualitatively different views of certain bonding situations. The dichotomy between "or" and "best" multiple bonds is a classic example. Ultimately, neither of such equivalent views can be given preference at the Hartree-Fock theoretical level. Hartree-Fock theory is defined entirely by its one-body density matrix (see Sec. II), which is completely invariant with respect to unitary orbital transformations. Theoretically meaningful definitions of electron localization must therefore be sought in the density matrix itself (or related functions) and not in the orbitals.

Alternative, orbital-independent descriptions of electron localization have received some attention in recent literature. Bader and co-workers¹ have noted that the total electronic density alone reveals atomic shell structure, electron pairs, etc., through the topography of its Laplacian $\nabla^2\rho$. This approach fully invokes the spirit of the so-called "density-functional" theory of multielectron systems, which re-

deration of the Hartree-Fock pair probability is developed. This work is a natural extension of previous investigations by one of the authors (A.D.B.) of the short-range behavior of the Fermi hole function in inhomogeneous systems² and is similar in some respects to the work of Lakshmi³ on localized orbitals and Fermi hole mobility.

In Sec. II of this paper, we introduce a new "electron localization function" (ELF) which depends on total electronic density, its gradient, and also the kinetic energy density. Application of this ELF to the noble gas atoms Ne through Ra in Sec. III easily and completely reveals their expected shell structure. In Sec. IV, ELF is applied to some classic freshman chemistry problems to illustrate its usefulness in identifying core, binding, and lone-pair regions in molecular systems, and, finally, concluding remarks are offered in Sec. V.

II. BASIC THEORY

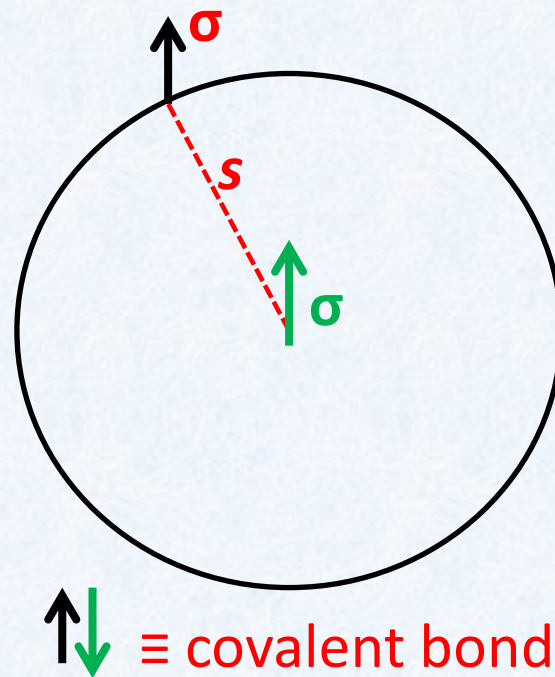
We assume in this section that the reader is familiar with the density matrix formulation of Hartree-Fock theory. An excellent account is provided in Ref. 7, though numerous other sources may also be consulted.

The Hartree-Fock probability of finding two particles of the same spin σ simultaneously at positions 1 and 2 in a multielectron system is given by the following expression:

$$P_{\sigma}^{\sigma}(1,2) = \rho_{\sigma}(1)\rho_{\sigma}(2) - \rho_{\sigma}^{\sigma}(1,2), \quad (1)$$

where $P_{\sigma}^{\sigma}(1,2)$ is the same-spin pair probability and $\rho_{\sigma}^{\sigma}(1,2)$ is the σ -spin one-body density matrix of the Hartree-Fock system.

The original formulation of ELF (Becke and Edgecombe) lies on the conditional pair probability $D^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{s})$, it's a measure of Pauli repulsion



$D^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{s})$ is the probability to find an electron of spin σ at a distance s from a reference electron of same spin σ , irrespective of direction.

$D^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{s}) \rightarrow 0 \equiv$ minimal Pauli repulsion $\equiv \uparrow\downarrow \equiv$ covalent bond

For the closed-shell case and a determinantal wave function (Hartree-Fock):

$$D^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{s}) \rightarrow \mathbf{D}(\mathbf{r}) = \underbrace{\sum_i |\nabla \varphi_i(\mathbf{r})|^2}_{\tau(\mathbf{r})} - \underbrace{\frac{1}{8} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})}}_{\tau^w(\mathbf{r})}$$

ELF corresponds to $D(\mathbf{r})$ scaled by the homogeneous electron gas kinetic energy $D_h(\mathbf{r})$

$0 \leq \text{ELF} \leq 1$, dimensionless

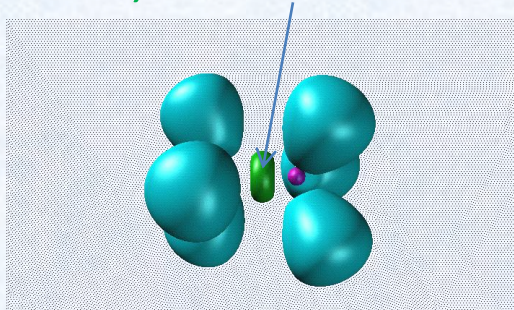
$$\text{ELF}(\mathbf{r}) = \frac{1}{1 + \left(\frac{\mathbf{D}(\mathbf{r})}{D_h(\mathbf{r})} \right)^2}$$

Within Kohn–Sham DFT, $D(\mathbf{r})$ is interpreted as an excess of *kinetic energy* $\tau(\mathbf{r}) - \tau^w(\mathbf{r})$ due to Pauli repulsion^(*)

* Savin, Jepsen, O.; Flad, J.; et al, H. G., *Angewandte* 31,187–188 (1992)

ELF physical limits

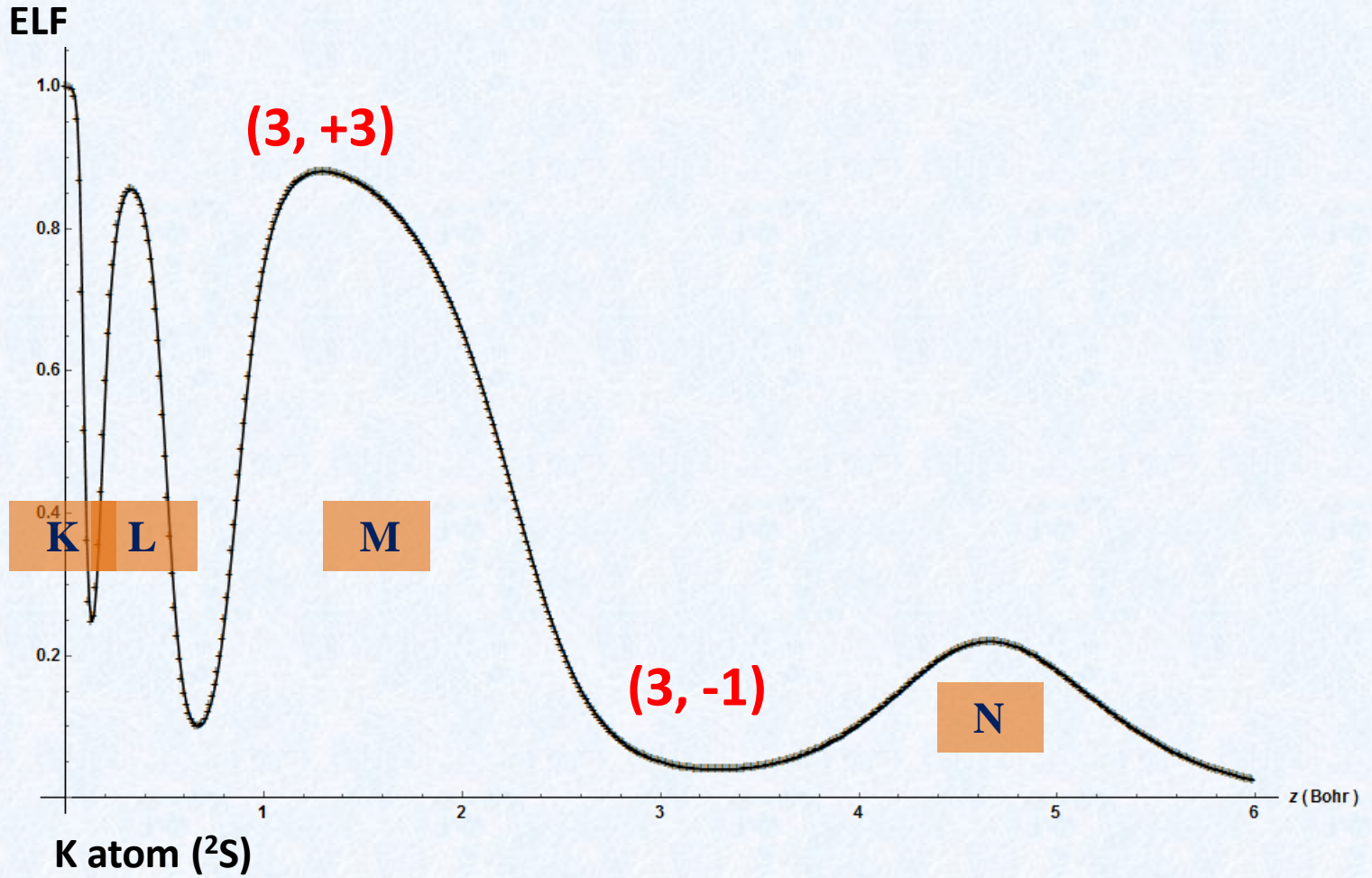
- ✓ $ELF \rightarrow 1$ $D(r) \rightarrow 0$, corresponds to a minimal Pauli repulsion cores, covalent bonds, lone pairs regions.



- ✓ $ELF = 1/2$ corresponds to same localization than the reference, i.e. the homogeneous electron gas

- ✓ $ELF \rightarrow 0$ less clear, related to intermolecular interactions.

Atomic shells



A.II. ELF Quantum Topology

B. Silvi, A. Savin, *Nature* 371, 683 (1994)



Classification of chemical bonds based on topological analysis of electron localization functions

B. Silvi & A. Savin

Laboratoire de Dynamique des Interactions Moléculaires, UPR271, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris cedex, France

The definitions currently used to classify chemical bonds (in terms of bond order, covalency versus ionicity and so forth) are derived from approximate theories¹⁻³ and are often imprecise. Here we outline a first step towards a more rigorous means of classification based on topological analysis of local quantum-mechanical functions related to the Pauli exclusion principle. The local maxima of these functions define 'localization attractors', of which there are only three basic types: bonding, non-bonding and core. Bonding attractors lie between the core attractors (which themselves surround the atomic nuclei) and characterize the shared-electron interactions. The number of bond attractors is related to the bond multiplicity. The spatial organization of localization attractors provides a basis for a well-defined classification of bonds, allowing an absolute characterization of covalency versus ionicity to be obtained from observable properties such as electron densities.

The valence theory of Lewis¹ remains the basis for most modern ideas on and classifications of the chemical bond^{2,3}. Most such classifications rely on molecular-orbital and valence-bond theories within schemes involving the linear combination of atomic orbitals (LCAO)^{4,5}.

The characterization of chemical bonds is a qualitative rather than a quantitative exercise, and the question is how one can distil the relevant information from experiment or from quantum-chemical calculations. The differential topology analysis of local scalar functions is a well-established mathematical approach that is well suited to handling this problem⁶. For a continuous, differentiable function $g(\mathbf{r})$ defined for any point in three-dimensional (R^3) space, the gradient \mathbf{X} defines a vector field. The theory of gradient vector fields has been successfully developed as a part of dynamical systems theory^{6,7} (see, for instance, Abraham and Marsden⁸ for a good introduction to the subject). Using this approach, one can identify trajectories of which the points corresponding to $t \rightarrow -\infty$ and $t \rightarrow \infty$ are respectively the α - and ω -limits. The set of ω -limits is the set of the attractors of the dynamical system. The basin of an attractor is the set of points for which this attractor is the ω -limit. This approach has been pioneered for chemical bonding by Bader⁹ who emphasized the role of the electron density $\rho(\mathbf{r})$. Definition of attractors allows one to define basins which are recognized as atoms in molecules. Further analysis allows one to identify objects associated with bonds. Alternatively, the topological type of density domains bounded by isosurfaces can be considered. When the threshold defining the bounding isosurface is varied, the shape of a given density domain may or may not change. A change of topological type that occurs at a critical value of the threshold is called a bifurcation. The characterization of these

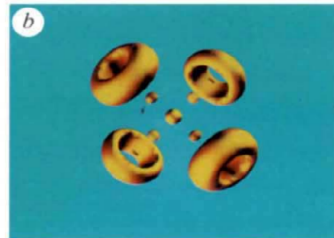
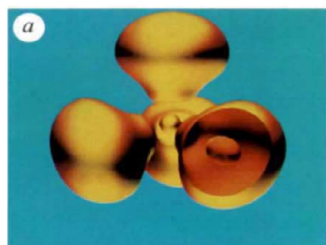
Cumberso¹⁰ and Becke and Edgecombe¹¹). An alternative interpretation of these so-called electron localization functions, $\eta(\mathbf{r})$, can be made by considering the excess local kinetic energy due to Pauli repulsion¹⁸. The local kinetic energy $K(\mathbf{r})$ is:

$$K(\mathbf{r}) = -\frac{1}{2} \sum_{i=1}^N \int \Psi^* \nabla_i^2 \Psi \, d\tau'$$

where Ψ is an N -particle wavefunction and the prime indicates that the integration is performed over the space and spin coordinates of all particles but one.

tion functions are calculated from approximate wavefunctions provided by quantum chemistry. However, it should be possible to derive procedures that will allow their determination from experimental densities^{20,21} or from the measurement of the Wigner function²².

For gradient-type dynamical systems, zero-dimensional attractors are generic⁷. In differential topology, generic means typical; a generic property holds for most systems, but it can be violated in exceptional cases. Nevertheless, for examples that are relevant to chemistry, the system could belong to a continuous symmetry group which in turn implies that the attractor could



Classification of basins

Definition: the synaptic order is the number of core basins with which they share a common boundary*

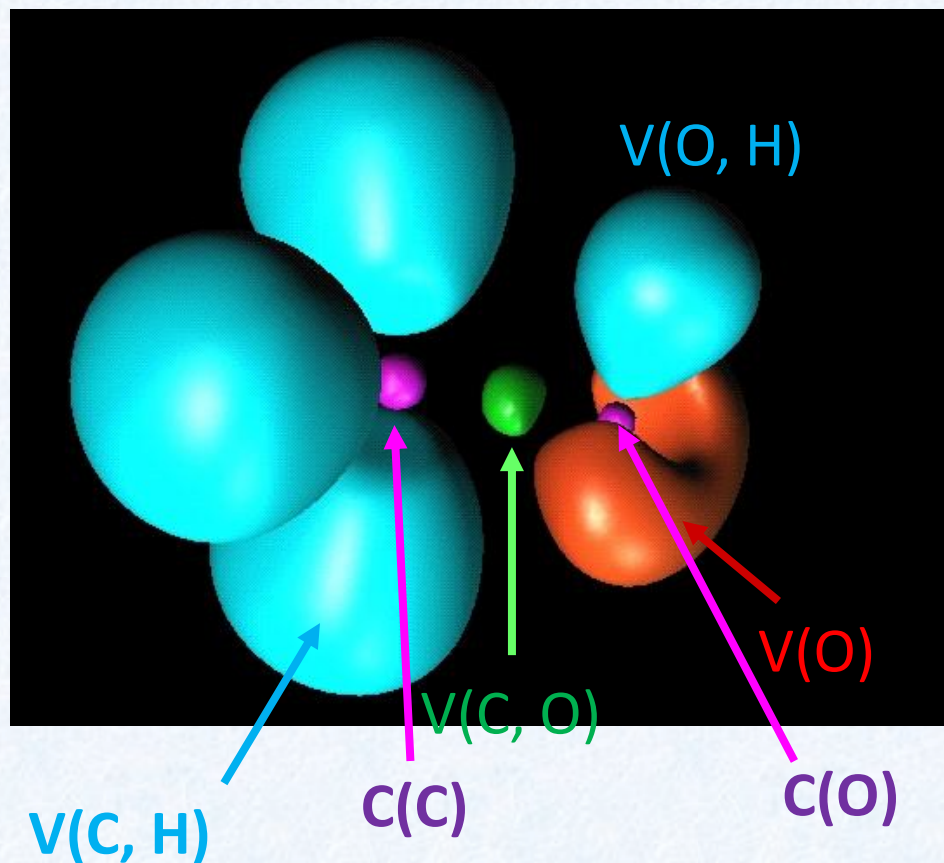
Core C(A)

Monosynaptic V(A) – lone pair

disynaptic V(A, B) – covalent bond

disynaptic protonated V(A, H)

ELF localization domains of CH₃-OH



* Silvi, B.: The synaptic order: a key concept to understand multicenter bonding
J. Molec. Struct. 614, 3 (2002)

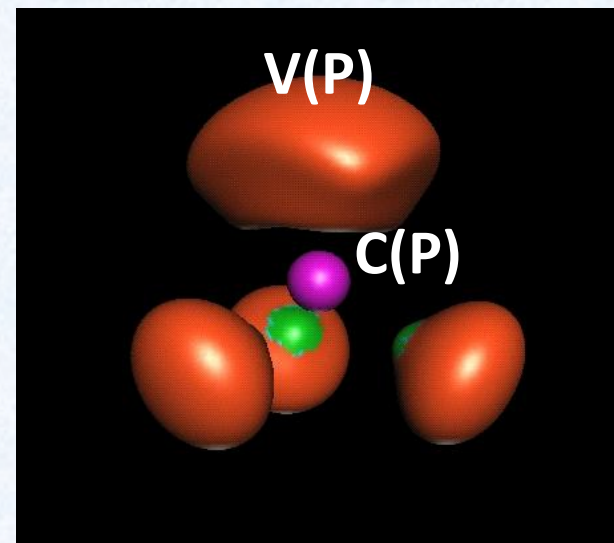
ELF Topology Connected with VSEPR

The geometrical patterns proposed in the VSEPR model are based on the properties of the **same spin pair density***



The distribution of the ELF localization domains provide a quantum mechanical confirmation of the VSEPR.

VSEPR-Type PCl_3 : trigonal pyramidal AX_3E



*J. Pilmé, E. A Robinson, R. J Gillespie *A topological study of the geometry of AF_6E molecules: weak and inactive lone pairs* *Inorg. Chem* 7:45 (2006)

Some Integrated Tools

$$\bar{N}[\Omega_i] = \int_{\Omega_i} \rho(\mathbf{r}) \, d\mathbf{r} \quad \text{basin } (\Omega) \text{ population}$$

$$\text{bpi}(A, B) = \frac{\bar{N}[V(A, B)|A] - \bar{N}[V(A, B)|B]}{\bar{N}[V(A, B)]} \quad \text{bond polarity index}^*$$

Gives the contributions of A and B QTAIM basins, respectively, to the total population of the $V(A, B)$ disynaptic basin. A strongly polarized bond $A \rightarrow B$ ($B \rightarrow A$) yields an index close to -1 (+1), respectively. By definition, the **bpi index is always restricted to [-1, 1]**

Chemical Reactivity : Bond Evolution Theory (BET)

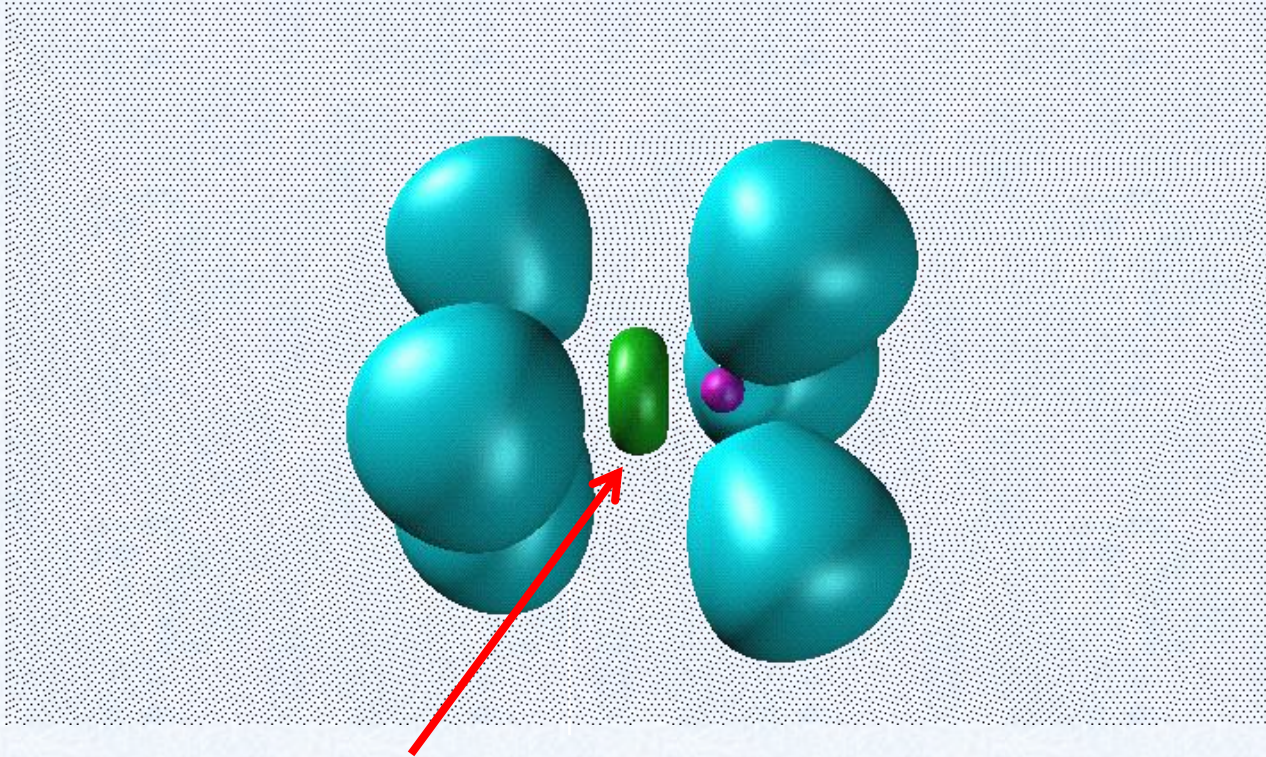
Using the ELF topological changes (modifications of critical points) and evaluating the basin populations along the reaction pathway, we can characterize these changes in the electronic structure. The methodology can provide a support to postulate 'curly arrows' schemes for the qualitative description of the mechanism. (*)

How can these rearrangements be related to chemical events such as the bond breaking/forming throughout the reaction progress ?

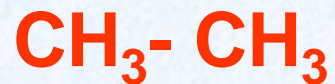
(*) Krokidis, X.; Noury, S.; Silvi, B. *Characterization of Elementary Chemical Processes by Catastrophe Theory*. *J. Phys. Chem. A*, 101, 7277–7782 (1997)

A.III. ELF elementary chemical processes: Prototype bonding schemes

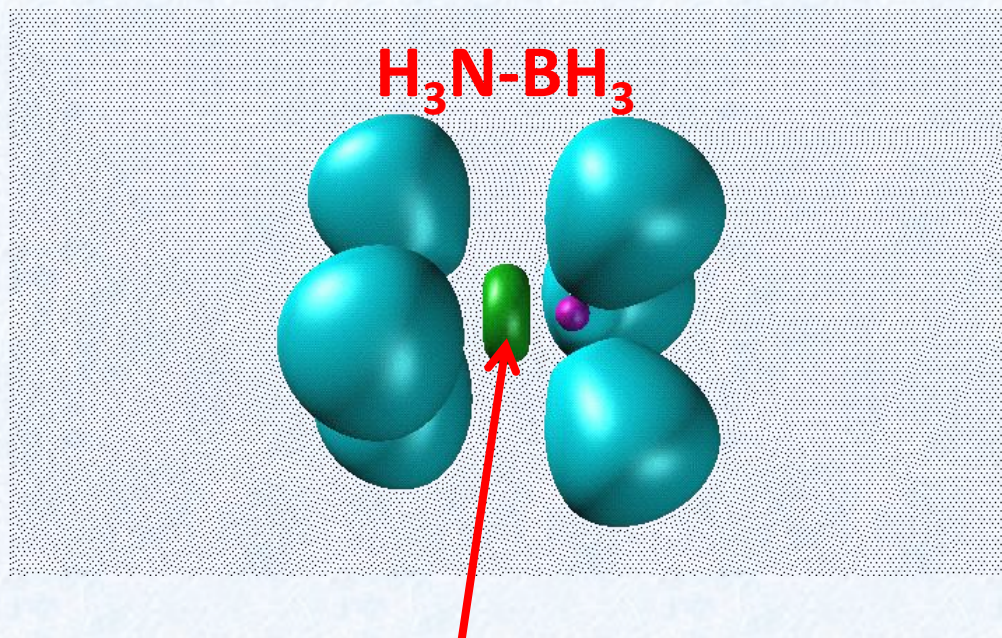
Covalent Bond



$N[V(C,C)] = 1.85 e \approx 2$ Formal Bond Order



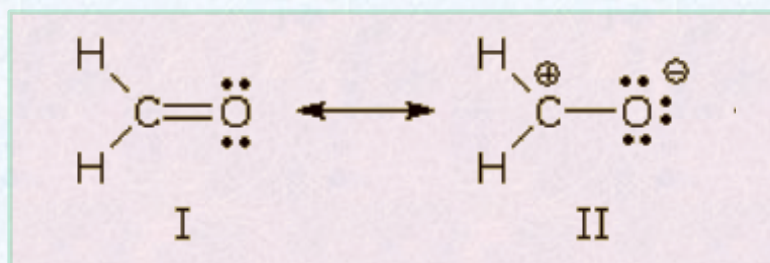
Donor-acceptor (dative) Bond



$$\bar{N}[V(B, N)] = 1.826 e$$

$$\begin{aligned} \text{bpi}(N, B) &= \frac{\bar{N}[V(B, N)|N] - \bar{N}[V(B, N)|B]}{\bar{N}[V(B, N)]} \\ &= \frac{1.752 - 0.074}{1.826} = 0.92 \end{aligned}$$

Weights of Lewis resonant structures



B3LYP/6-311+G(d,p) level of theory

populations $\rightarrow N[V(C, O)] = 2.43e$; $N[C(C)]=2.08e$; $N[C(O)]= 2.15e$

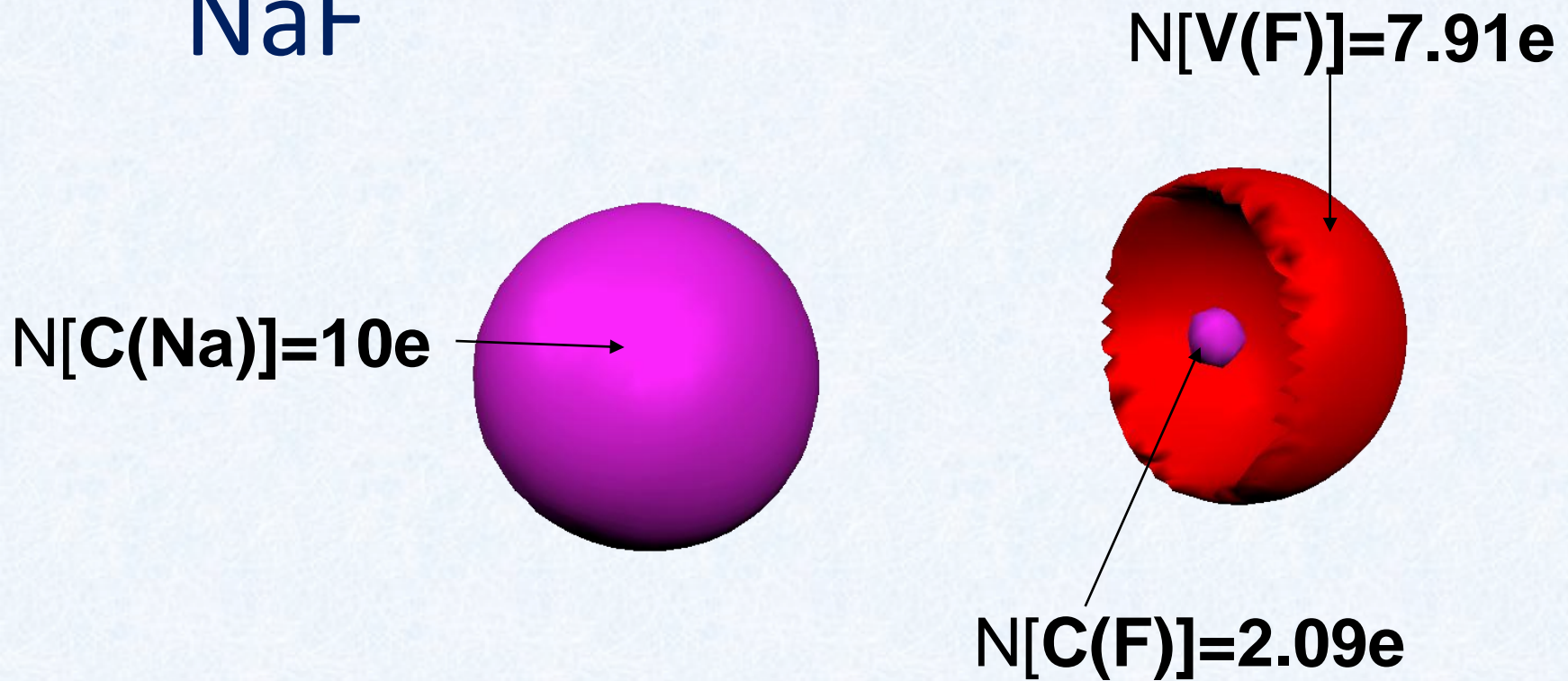
$$\text{C-O linear system} \rightarrow \begin{cases} 8 w_I + 6 w_{II} = 2.43 + 2.08 + 2.15 \\ w_I + w_{II} = 1 \end{cases}$$

Solution:

$$\begin{cases} w_I = 0.33 \\ w_{II} = 0.67 \end{cases} \rightarrow \text{strong contribution of the polarized structure } C^+ O^-$$

The ionic Bond : no disynaptic basin

NaF



The Charge-Shift Bond (CSB)*

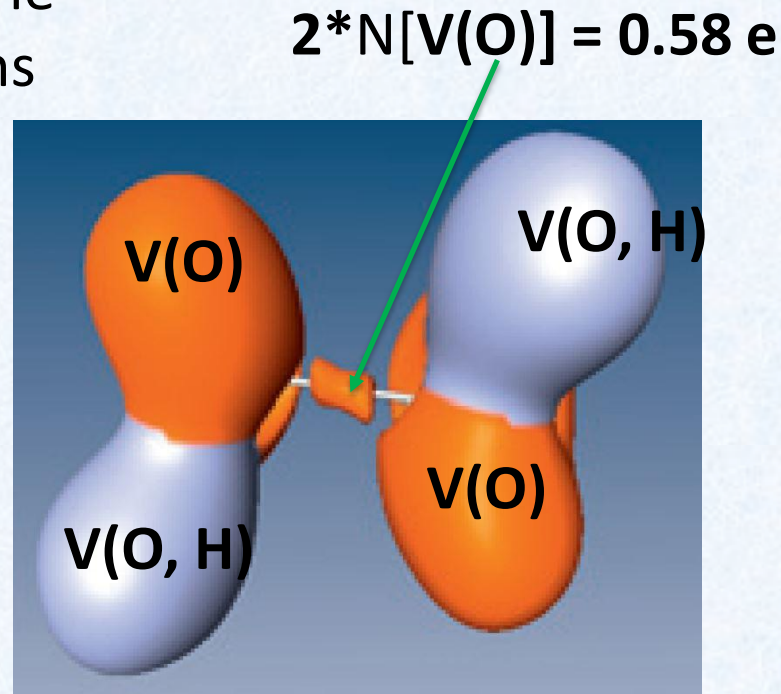
Charge-shift bonds* is an unusual bonding scheme alongside the familiar families covalent and ionic which arises from the resonance between ionic forms.

For example, the typical F-F interaction in F_2 is a resonance $[F^+ - F^- \leftrightarrow F^- - F^+]$

* Shaik, S. Danovich, D.; Wu, W.; Hiberty, P. C. Charge-shift bonding and its manifestations in chemistry. *Nature Chemistry*. **1** (6): 443–449. (2009)

ELF Signature for the CSB scheme*

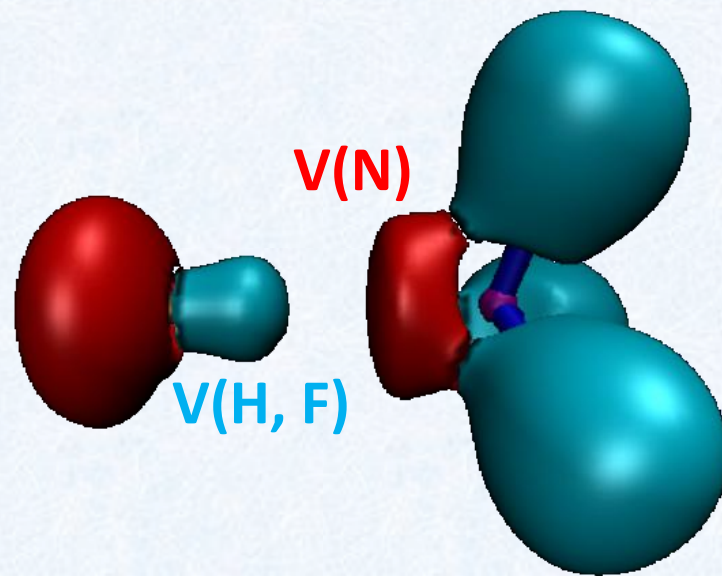
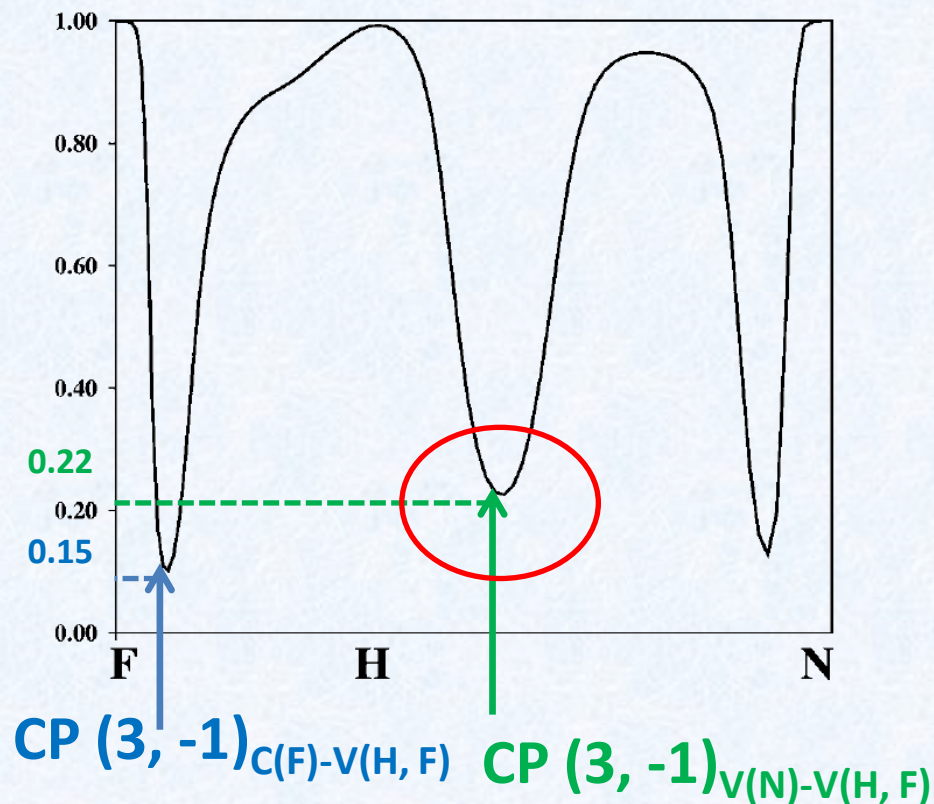
- ✓ homonuclear bond X-X or common case for X = F or Cl
- ✓ depleted bond population, **usually less than 1e**
- ✓ large delocalization between the populations of adjacent V(X) basins



* Shaik S., Danovich D., Silvi B., Lauvergnat D., Hiberty P. Charge-Shift Bonding—A Class of Electron-Pair Bonds That Emerges from Valence Bond Theory and Is Supported by the Electron Localization Function Approach *Chem. Eur. J.* 21, pp. 6358–6371 (2005)

ELF Core-Valence Bifurcation index (CVB) index *

The core-valence bifurcation index (CVB)* is designed to classify the A-H...B hydrogen bonds :



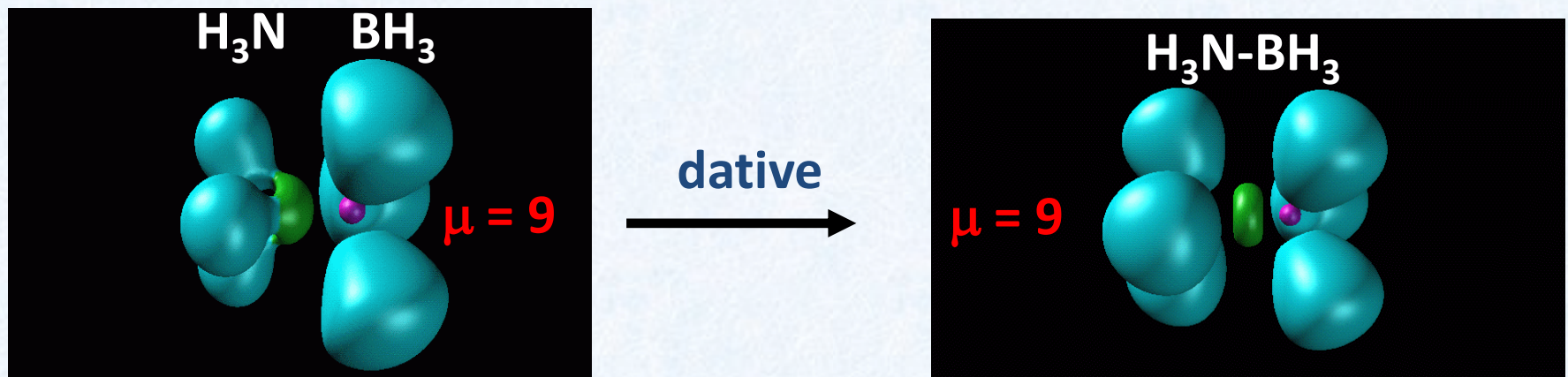
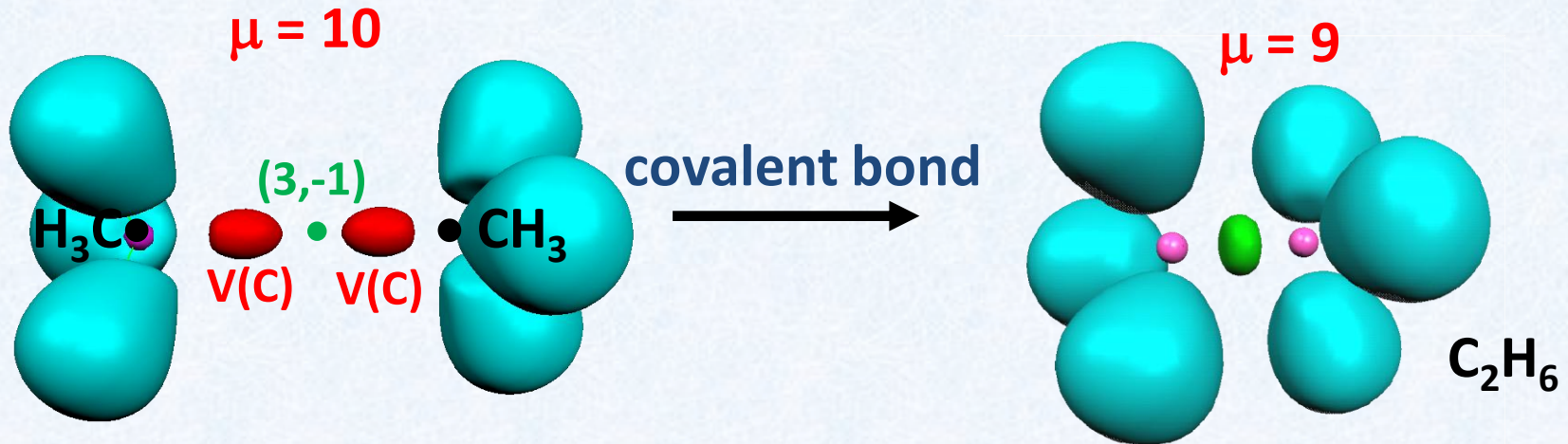
→ $CVB = 0.22 - 0.15 = 0.07 > 0$
Correlation with the
interaction energy FH-NH₃

* Fuster, F. and Silvi, B. Does the topological approach characterize the hydrogen bond ?
Th. Chem. Acc. 104, p 13–21 (2000)

Bond Evolution Theory: Covalent v.s. Dative

Topological changes occurring along the reaction path

$\mu \equiv$ number of basins

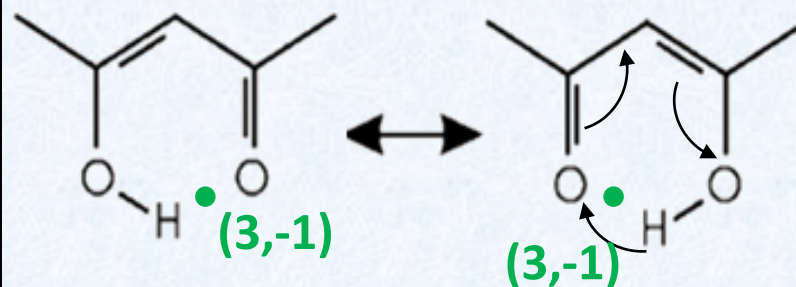


Chemical Reactivity: Bond Evolution Theory

Source: <https://www.lct.jussieu.fr/pagesperso/silvi/recherche.html>

Proton-transfer-assisted Hydrogen Bonds $\underline{\text{C}_3}\underline{\text{H}_4}\underline{\text{O}_2}$

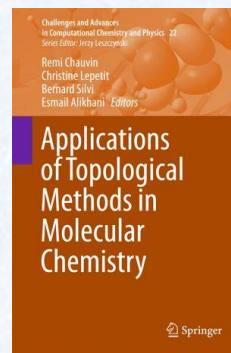
See exercise book



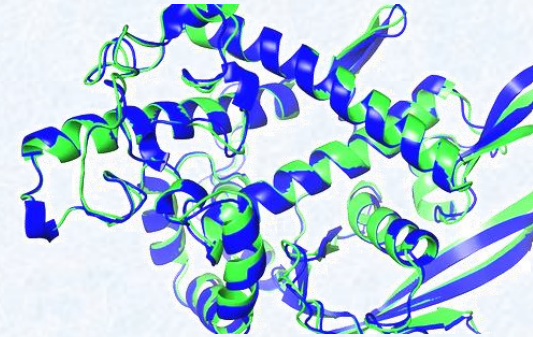
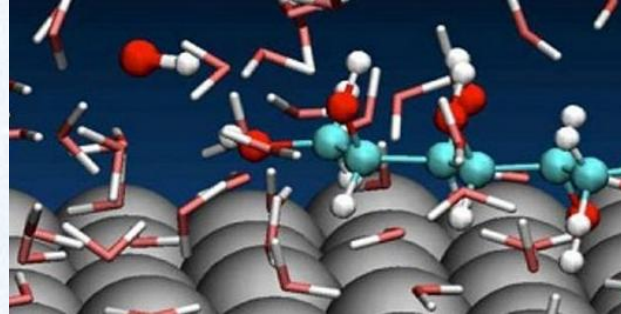
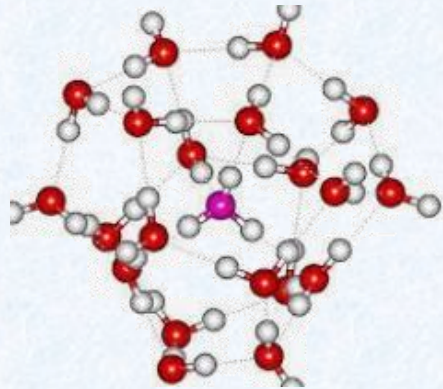
Books

B. Silvi, R.J. Gillespie and C. Gatti, 9.07 - *Electron Density Analysis, In Comprehensive Inorganic Chemistry II* (Second Edition), edited by Jan Reedijk and Kenneth Poeppelmeier, Elsevier, Amsterdam, **2013**, pp. 187-226

Applications of Topological Methods in Molecular Chemistry, Challenges and Advances in Computational Chemistry and Physics book series
Editors: R. Chauvin, C. Lepetit, B. Silvi, E. Alikhani



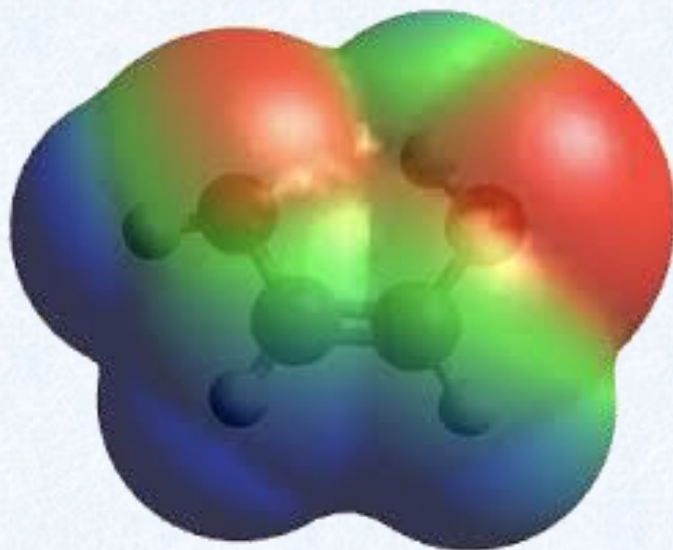
B. Non Covalent interactions



- water properties, solubility,
- surface chemistry,
- Biological chemistry, protein folding,
- Ligand-receptor binding,

....

B.I The Molecular Electrostatic Potential (MESP) and its topology



Molecular Electrostatic Potential

MESP (or MEP, $V(\mathbf{r})$) at \mathbf{r} , is the coulomb potential due to the electron density $\rho(\mathbf{r})$ and the nuclear charges is given by the equation:

$$V(\mathbf{r}) = \sum_A^N \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}') d^3 r'}{|\mathbf{r} - \mathbf{r}'|}$$

N is the total number of nuclei in the molecule and Z_A is the charge of the nucleus located at \mathbf{R}_A .

Molecular Electrostatic Potential

- It is rigorously defined and can be determined experimentally as well as computationally from the electron density and it is directly related to the electron density with the Poisson's equation:

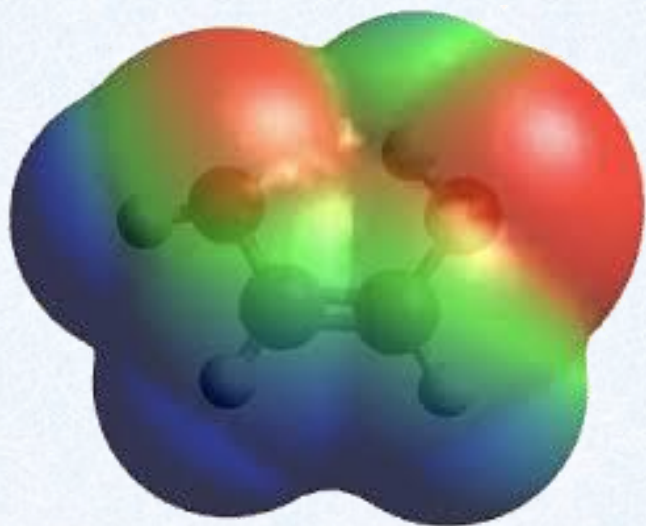
$$\nabla^2 V(\vec{r}) = 4\pi\rho(\vec{r})$$

- Depending on whether the effect of the nuclei or the electrons is dominant in any given region, $V(r)$ may be either positive or negative.

Chemical Reactivity:

- ✓ $MESP > 0$: electrophilic regions (nuclear is predominant)
- ✓ $MESP < 0$: nucleophilic regions (electronic is predominant)

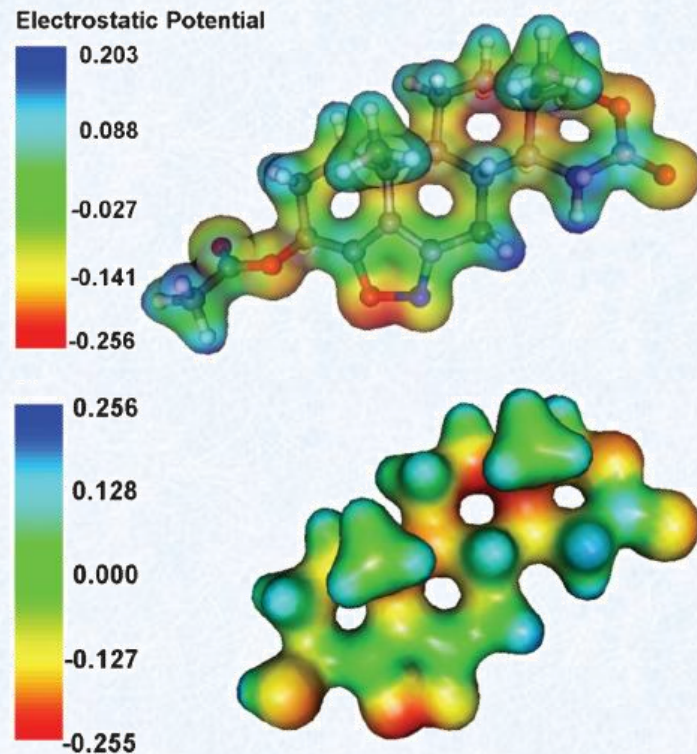
MESP projected on an electron density VdW isosurface ($\rho = 0.01$ a.u. ou $\rho = 0.001$ a.u.)



Code color:

✓ Blue: $MEP > 0$, electrophilic regions

✓ Red: $MEP < 0$, nucleophilic regions (lone pairs, π bonds)

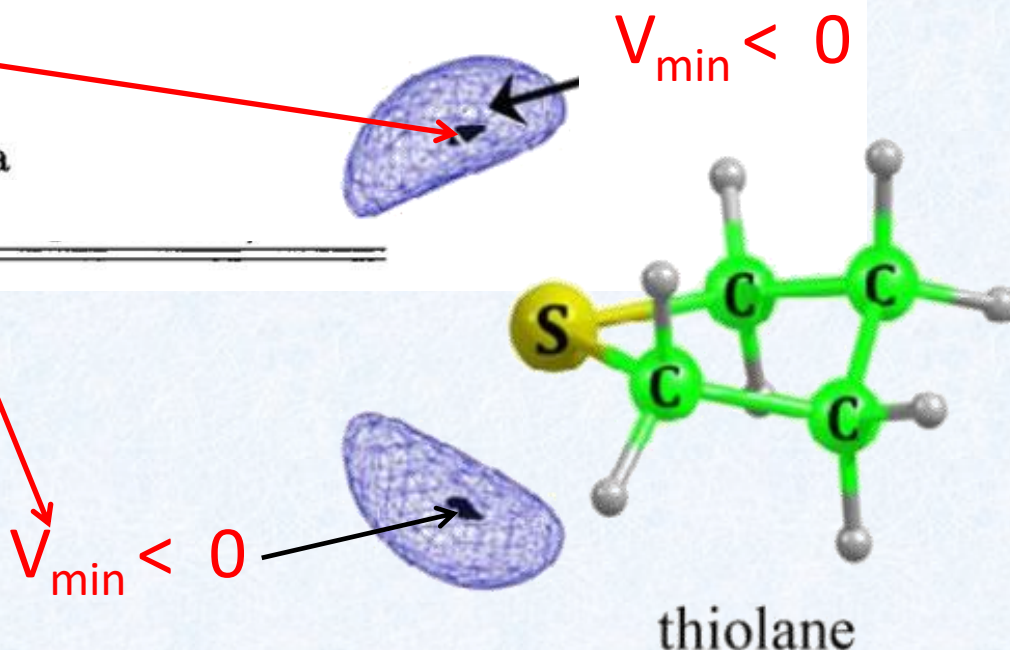


Source, DOI: 10.1039/c3ra41336e

MEP critical points

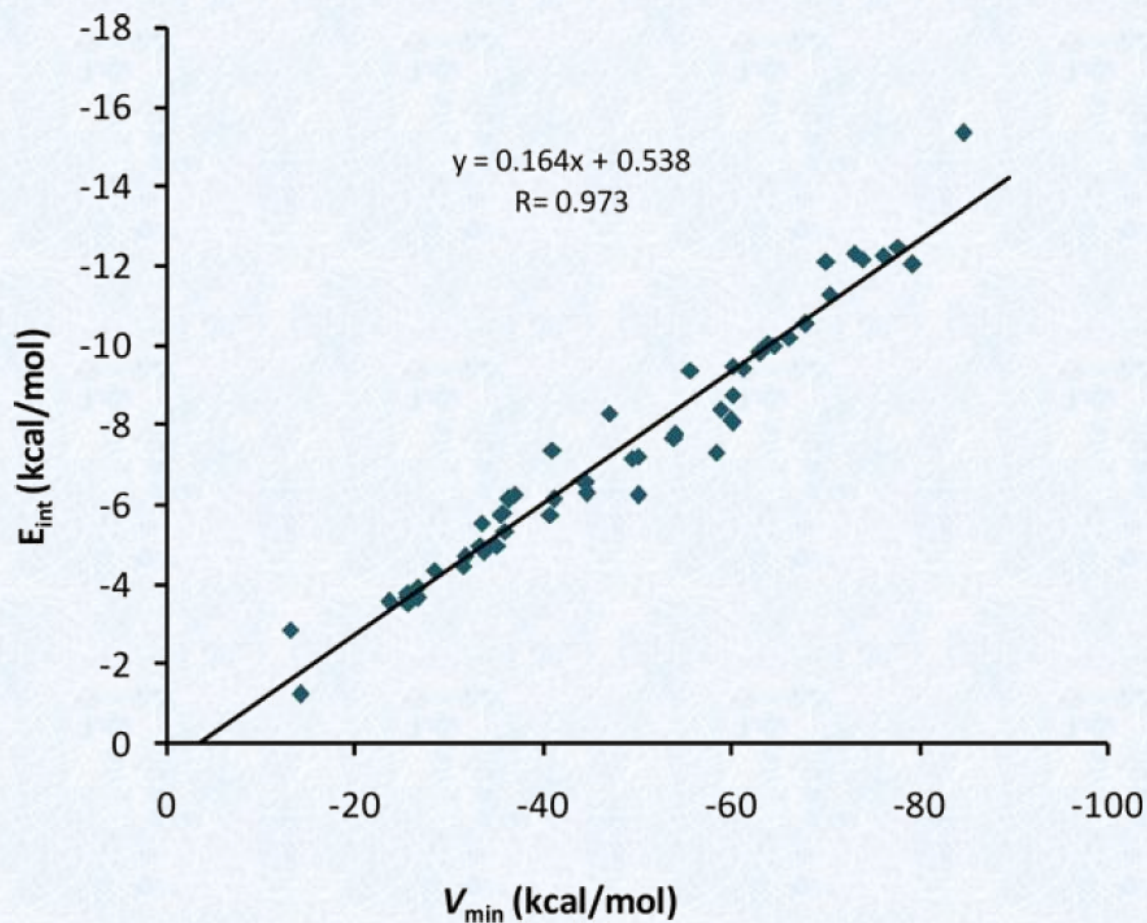
Table V: Type of CP and associated electronic structure characteristic.

Type of CP	Associated structural characteristic
$+(3, -1)$	σ bond
$+(3, +1)$	centre of ring
$-(3, +3)$	lone pair
$-(3, +3)$	π bond
$-(3, +1)$	inbetween minima



Correlation between V_{\min} and the interaction energy nucleophile/electrophile

See exercise book

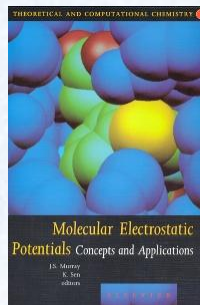


Some MESP references

Politzer P, Laurence PR, Jayasuriya K. *Molecular electrostatic potentials: an effective tool for the elucidation of biochemical phenomena*. *Environ Health Perspect*. 1985;61:191–202.

P. Politzer, D. G. Truhlar, *Chemical Applications of Atomic and Molecular Electrostatic Potentials: Reactivity, Structure, Scattering, and Energetics of Organic, Inorganic, and Biological Systems*; Springer: New York, 2013.

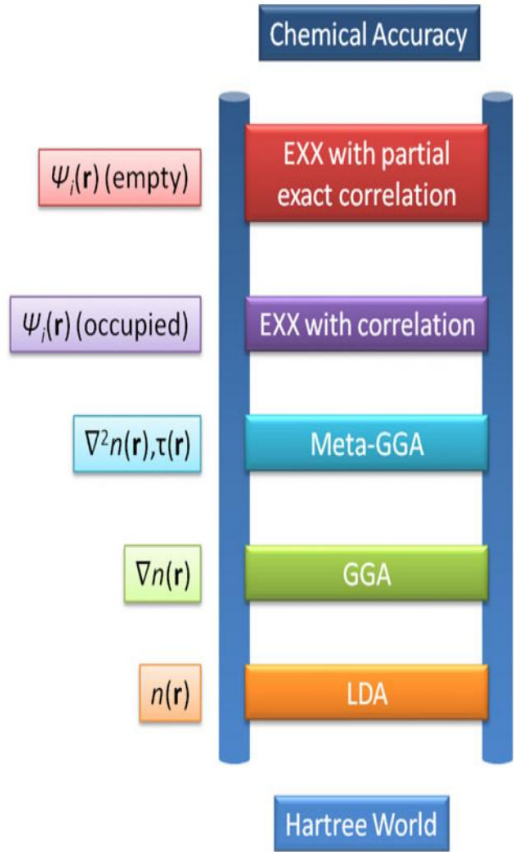
Book: *Molecular Electrostatic Potentials Concepts and Applications*. Jane S. Murray, Kalidas Sen, Volume 3, Pages 1-665 (1996)



Bijna et al *Electrostatics for probing lone pairs and their interactions*
J. Comput. Chem 2018 p, 488-499. DOI:10.1002/jcc.25082

B.II. The Non-Covalent interactions Index (NCI) and its topology

The function of interest



Jacob's ladder of DFT

Uniform Electron Gas
exchange energy density per volume

$$E_x^{GGA} = \sum_{\sigma} \int e_{x,\sigma}^{UEG} g_{x,\sigma}^{GGA} dr$$

Inhomogeneity correction factor

Reduced Density Gradient (RDG)

$$g_x^{GGA} = F(s)$$

$$s(r) \propto \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}}$$

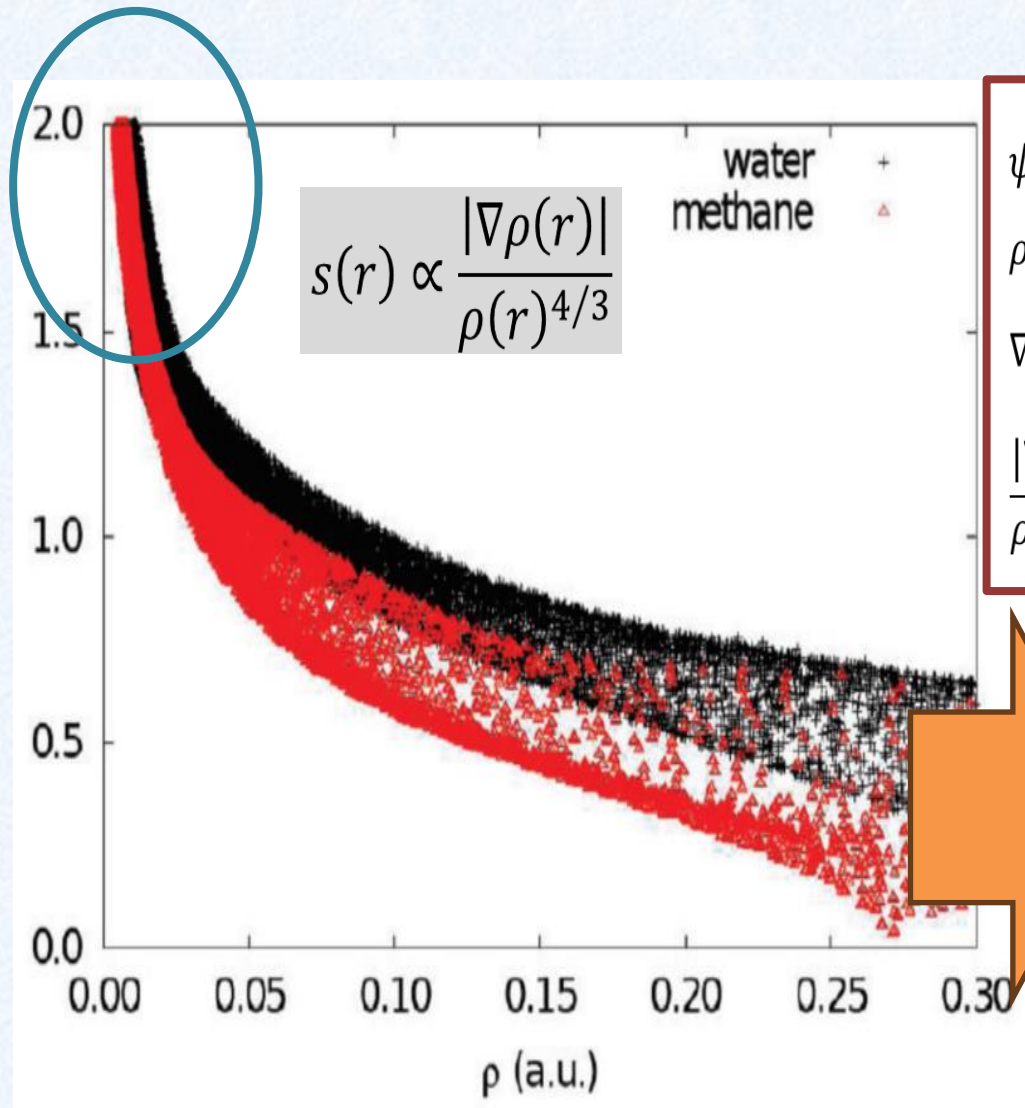
General behavior of s versus ρ

$$s \propto \rho^{-\frac{1}{3}}$$

Far from nuclei :

Large s , small ρ

($\rho \rightarrow 0$
more rapidly than
 $|\nabla\rho(r)| \rightarrow 0$)



$$\psi^{STO}(r) \propto e^{-\alpha r}$$

$$\rho^{STO}(r) \propto e^{-2\alpha r}$$

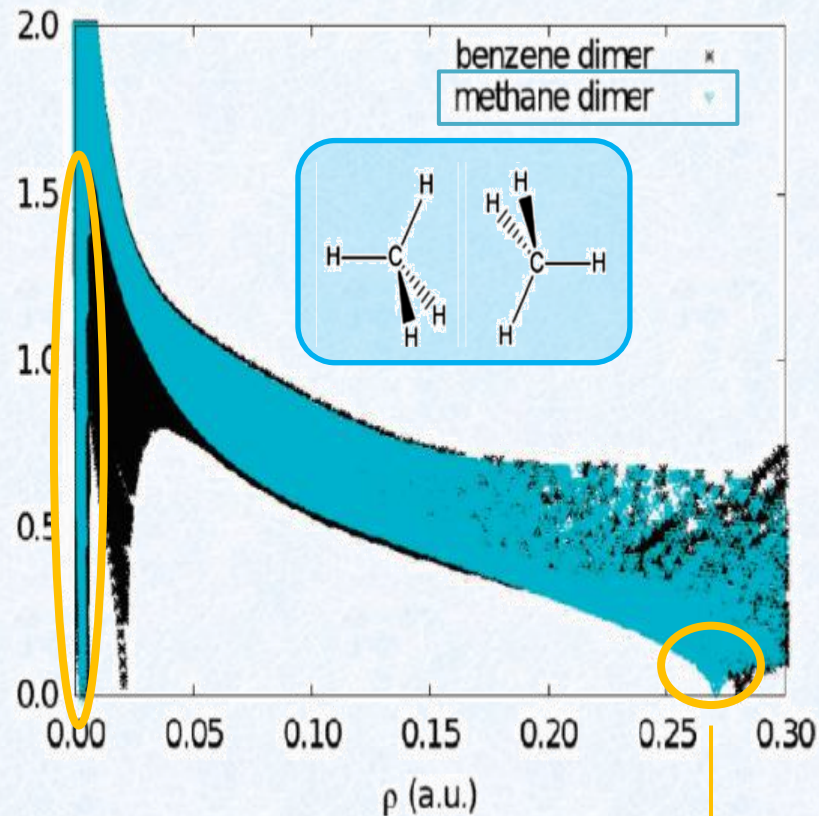
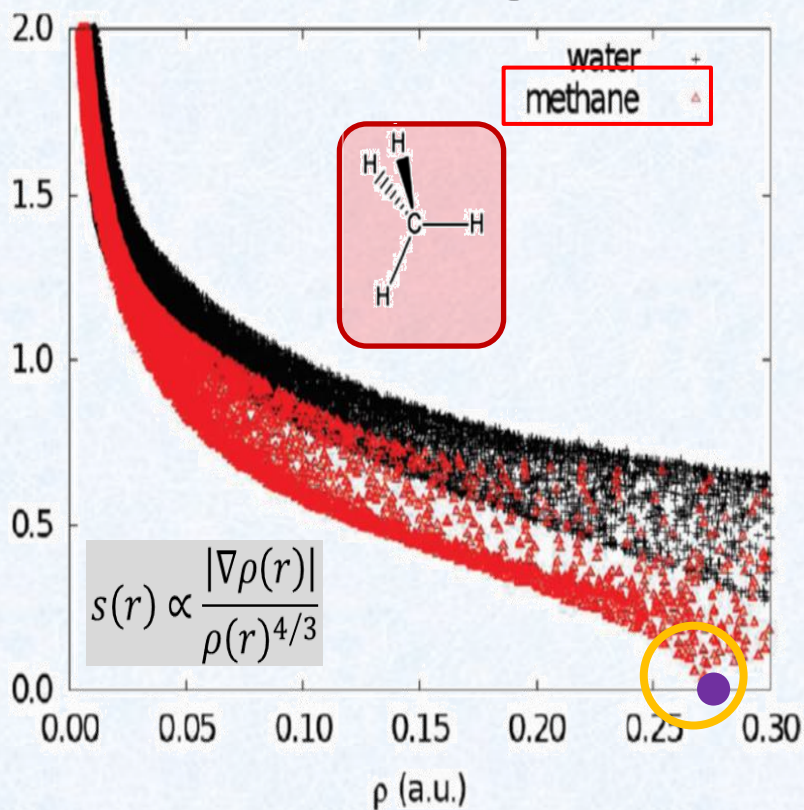
$$\nabla\rho^{STO}(r) \propto -2\alpha \times \rho^{STO}(r)$$

$$\frac{|\nabla\rho^{STO}(r)|}{\rho^{STO}(r)^{4/3}} \propto 2\alpha \times (\rho^{STO}(r))^{-\frac{1}{3}}$$

Close to nuclei :

Large ρ , small s

Which signature for interactions?



s spike/peak

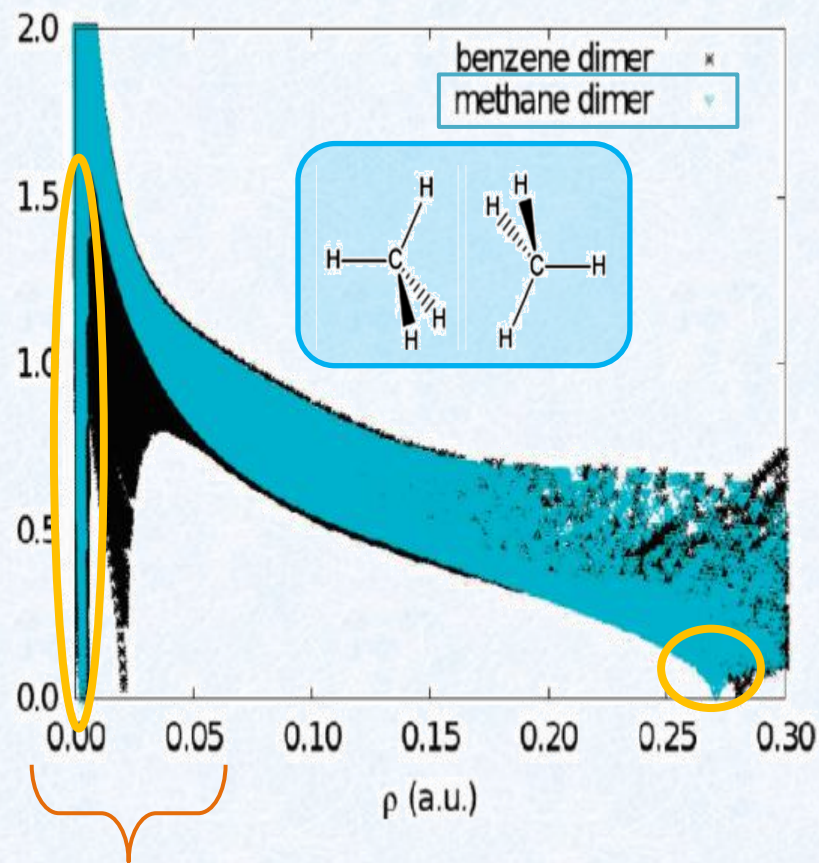
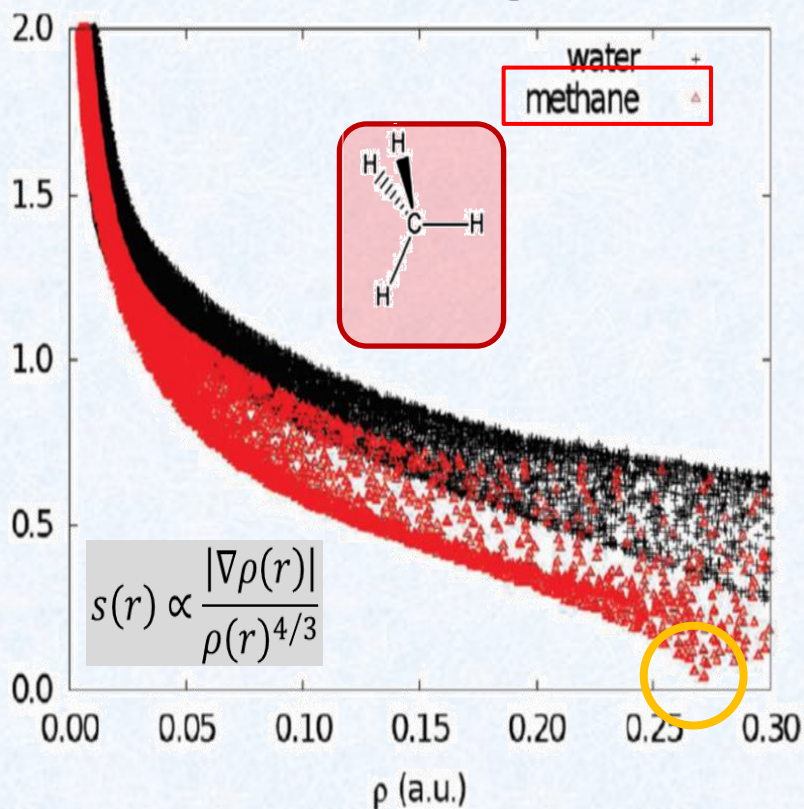
Additional s spike/peak
at much lower ρ

C-H bonds

$s = 0$

(QTAIM BCP of C-H bonds) vdW interaction

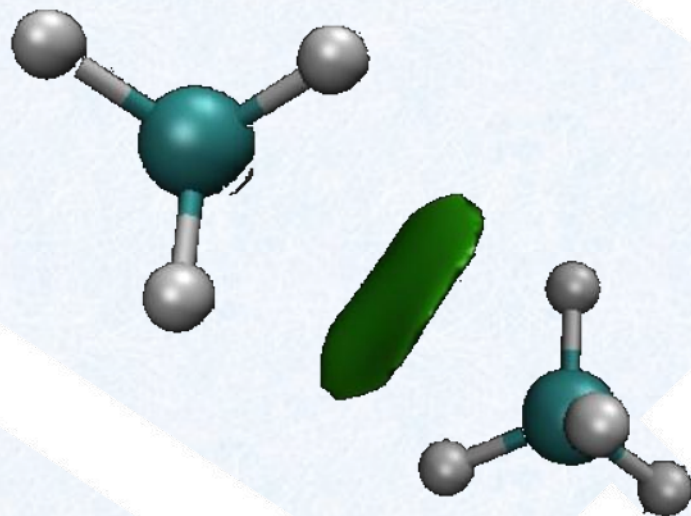
Which signature for interactions?



Range of interest for non-covalent interactions

s spike: signature of interaction (orbital overlap)

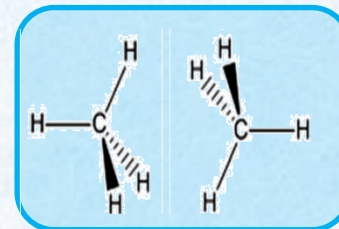
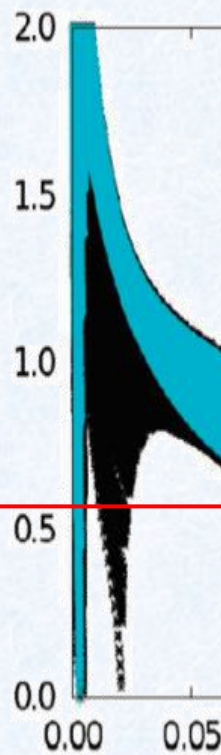
Visualising the NCI region in the real space



s isosurface
In the molecular space



Spatial localisation of the interaction

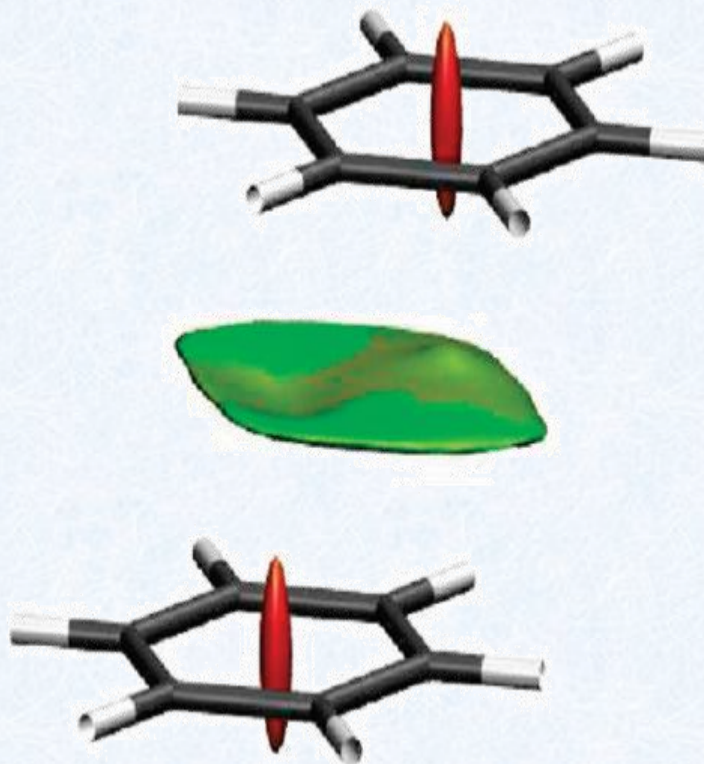


Several types of non covalent interactions



Steric clash

(2,2,3,3-tetramethylbutane)



π -stacking

(benzene dimer)



Hydrogen bond

(water dimer)

How to discriminate the different types of non covalent interactions?

QTAIM reminder :

$\nabla^2\rho < 0$ Local density concentration - Shared interaction (covalent)

$\nabla^2\rho > 0$ Local density depletion - Closed-shell interaction (ionic, vdW?)

$$\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3 \quad \text{with } \lambda_1 < \lambda_2 < \lambda_3$$

Nuclear attractors (NCP or ACP): $\lambda_1 < 0; \lambda_2 < 0; \lambda_3 < 0$

Center of cages (CCP): $\lambda_1 > 0; \lambda_2 > 0; \lambda_3 > 0$

Elsewhere

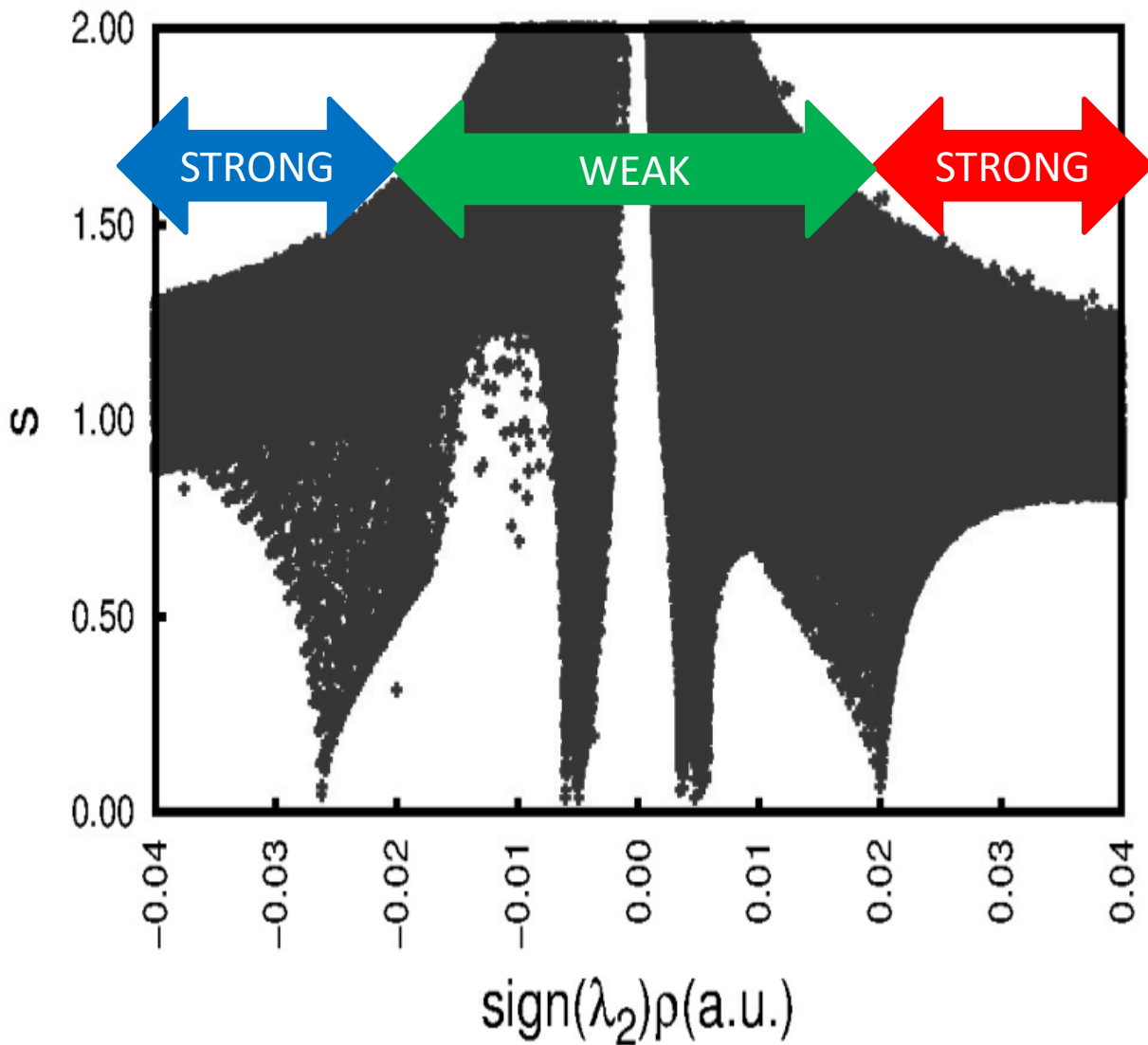
$\lambda_1 < 0; \lambda_3 > 0$ and $\lambda_2 < 0$ or $\lambda_2 > 0$

Sign(λ_2)

Attractive *Repulsive*
regions *regions*

Additional
information

Plotting s versus $\text{sign}(\lambda_2)\rho$



s spike

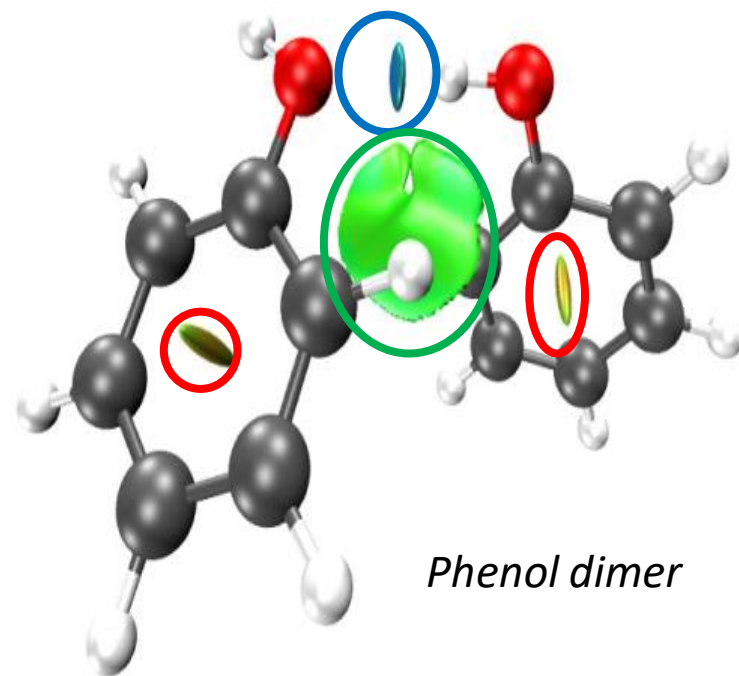
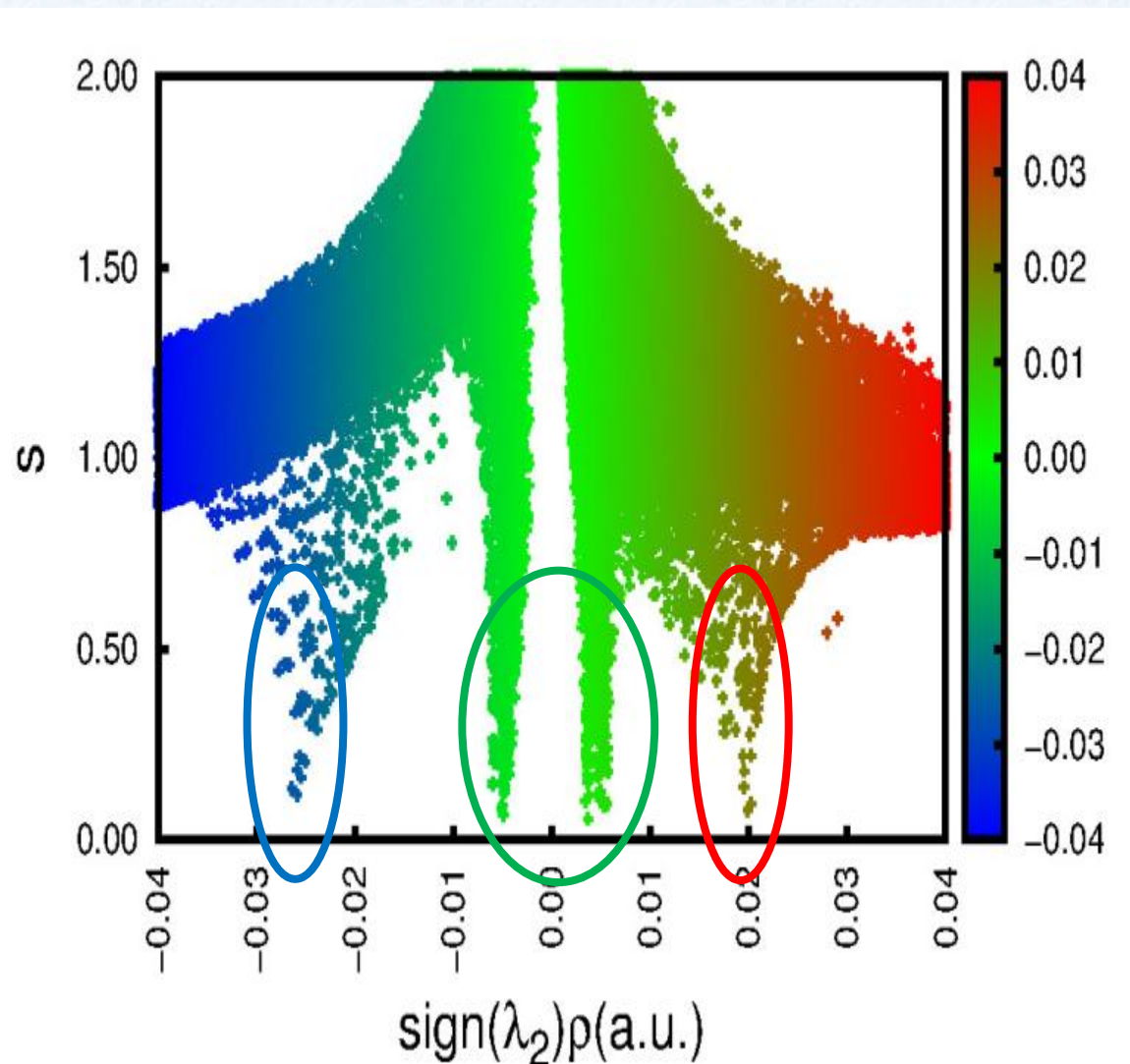
$\text{Sign}(\lambda_2)$:

attractive / repulsive character of the interaction

ρ : Strength of the interaction

← attractive → repulsive →

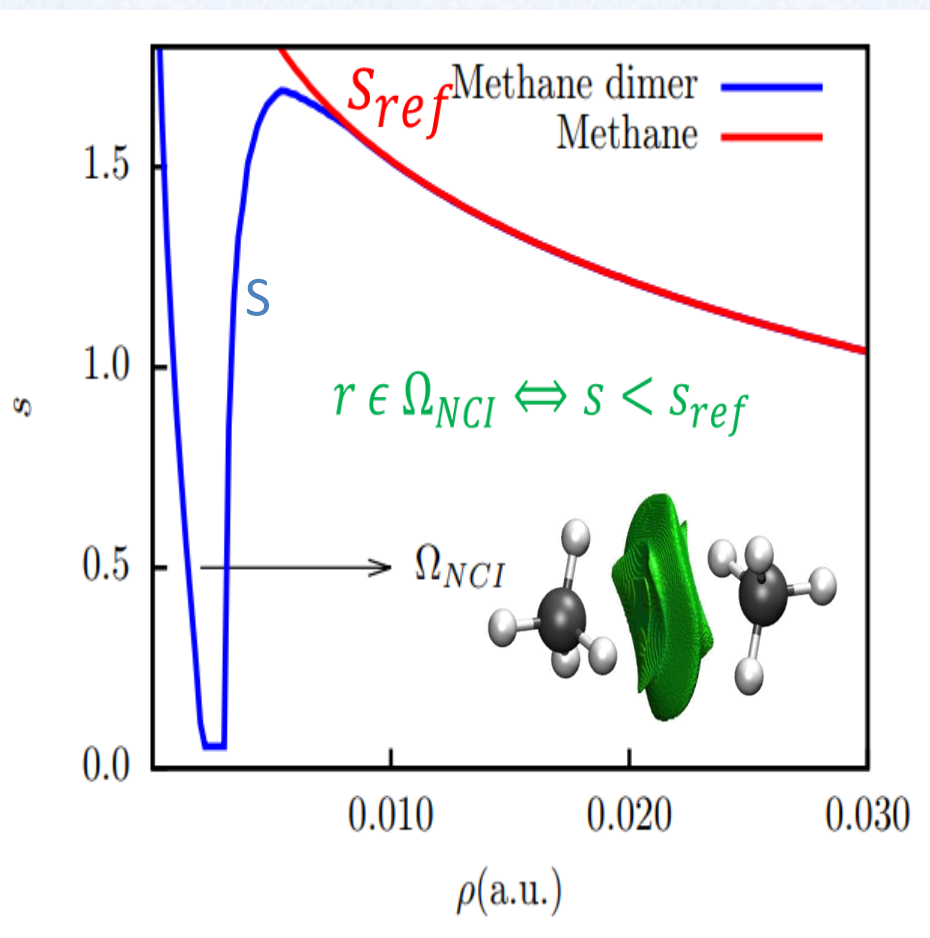
Plotting s versus $\text{sign}(\lambda_2)\rho$ with a color scale



Phenol dimer

Being more quantitative

Unambiguous definition of the interaction region



Possibility to integrate several quantities (volume, charge)

$$V_{NCI} = \int_{\Omega_{NCI}} \mathbf{dr},$$
$$N_{NCI} = \int_{\Omega_{NCI}} \rho(\mathbf{r}) \mathbf{dr},$$

implemented in NCIPLLOT4

Thank you for your attention !