



Introduction to Chemical Bonding Analysis

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Need to Know

- ▶ This material is part of the course *New Tools for Chemical Bonding Analysis* given at the Univ. of Girona during 2014-2015 and 2015-2016 academic years as part of the MACMoM master.
<http://stark.udg.edu/macmom/>



- ▶ All these slides and other material in:
<http://iqc.udg.edu/~eduard/master.html>

Notation

- ▶ The coordinates of an electron: $\vec{r} \equiv \mathbf{r}$ and the spin ($\sigma = \alpha$ or β).
- ▶ $\mathbf{x}_1 \equiv \vec{\mathbf{x}}_1 = (\vec{r}, \sigma_1)$.
- ▶ We assume: $\mathbf{1} \equiv (\vec{r}_1, \sigma_1)$ and $d\mathbf{1} \equiv d\vec{r}_1 d\sigma_1$ for the derivatives.
- ▶ N denotes the number of electrons in the system.
- ▶ Wavefunction: $\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{N})$
- ▶ Atomic orbitals: $\phi_\mu(\mathbf{1})$
- ▶ Molecular orbitals: $\phi_i(\mathbf{1})$

The Wavefunction

The simplest (antisymmetric) wavefunction is the Slater determinant:

$$\psi_K(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_{k_1}(\mathbf{1}) & \phi_{k_1}(\mathbf{2}) & \dots & \phi_{k_1}(\mathbf{n}) \\ \phi_{k_2}(\mathbf{1}) & \phi_{k_2}(\mathbf{2}) & \dots & \phi_{k_2}(\mathbf{n}) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{k_N}(\mathbf{1}) & \phi_{k_N}(\mathbf{2}) & \dots & \phi_{k_N}(\mathbf{n}) \end{vmatrix}$$

A more accurate description includes a linear combination of n_C Slater determinants,

$$\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) = \sum_{K=1}^{n_C} c_K \psi_K(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) \quad \text{with} \quad \sum_{K=1}^{n_C} |c_K|^2 = 1$$

The HF and KS-DFT wavefunction are single-determinant wavefunctions.

The Density

From Born's rule we have

$$P(\mathbf{1})d_1 = \int d_2 \int d_3 \dots \int d_n |\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n})|^2 d_1$$

from which we can define the density

$$\rho(\mathbf{1}) = NP(\mathbf{1})$$

where $P(\mathbf{1})$ is the probability of finding one electron at position $\mathbf{1}$ (i.e., at position \vec{r}_1 with spin σ_1), regardless the position of the other ($N-1$) electrons. $\rho(\mathbf{1})$ integrated over Ω gives the *average number of electrons* in that region.

$$N_\Omega \equiv \langle N(\Omega) \rangle = \int_\Omega \rho(\mathbf{1})d_1 \quad (1)$$

This is the basis of electron population analysis.

The Density

For single-determinant (HF or KS-DFT) wavefunctions:

$$\rho(\mathbf{1}) = \sum_i^N \phi_i^*(\mathbf{1})\phi_i(\mathbf{1}) = \sum_i^N |\phi_i(\mathbf{1})|^2$$

for closed-shell single-determinant wavefunctions:

$$\rho(\mathbf{1}) = 2 \sum_i^{N/2} |\phi_i(\mathbf{1})|^2$$

In the case of correlated wavefunctions,

$$\rho(\mathbf{1}) = \sum_{ij}^M {}^1D_j^i \phi_i^*(\mathbf{1})\phi_j(\mathbf{1})$$

where ${}^1D_j^i$ will be called 1-density and it is a matrix representing the electron density in terms of molecular orbitals.

Natural Orbitals

NatOrb, $\eta_i(\mathbf{1})$, are the set of orbitals that *diagonalize* the 1-density

$$\rho(\mathbf{1}) = \sum_{ij}^M {}^1D_{ij}^i \phi_i^*(\mathbf{1}) \phi_j(\mathbf{1}) \quad \rightarrow \quad \rho(\mathbf{1}) = \sum_i n_i \eta_i^*(\mathbf{1}) \eta_i(\mathbf{1})$$

where n_i are the associated occupancies (or occupations) and

$${}^1D\mathbf{L} = \mathbf{L}\mathbf{n} \quad \mathbf{n} = \text{Diag}(n_1, \dots, n_M)$$

$$\eta = \mathbf{L}\phi \quad \eta_i(\mathbf{1}) = \sum_j L_{ij} \phi_j(\mathbf{1})$$

and

$$\phi^\dagger = (\phi_1(\mathbf{1}), \dots, \phi_M(\mathbf{1})) \quad \eta^\dagger = (\eta_1(\mathbf{1}), \dots, \eta_M(\mathbf{1}))$$

Natural orbitals do not have an associated energy, only an occupancy, that is associated to the probability that an electron occupies this orbital.

The first-order reduced density matrix

The formula for the first-order reduced density matrix (1-RDM) reads:

$$\rho_1(\mathbf{1}; \mathbf{1}') = N \int d_2 d_3 \dots \int d_n \Psi^*(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) \Psi(\mathbf{1}', \mathbf{2}, \dots, \mathbf{n})$$

The density function (or simply the density), is actually the diagonal part of the 1-RDM, *i.e.*, $\rho(\mathbf{1}) = \rho_1(\mathbf{1}; \mathbf{1})$. In terms of natural orbitals and occupancies the 1-RDM can be written as

$$\rho_1(\mathbf{1}; \mathbf{1}') = \sum_i n_i \eta_i^*(\mathbf{1}) \eta_i(\mathbf{1}')$$

The pair density

Born's interpretation can be further extended to include the pair density,

$$\rho_2(\mathbf{1}, \mathbf{2}) = N(N - 1)P(\mathbf{1}, \mathbf{2})$$

where

$$P(\mathbf{1}, \mathbf{2})d_1d_2 = \int d_3 \dots \int d_n \Psi^*(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n})\Psi(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n})d_1d_2$$

$P(\mathbf{1}, \mathbf{2})$ is the probability of finding two electrons, one at $\mathbf{1}$ and the other at $\mathbf{2}$, regardless of the position of the other $N - 2$ electrons. The expected number of electron pairs in Ω read:

$$N_{\Omega\Omega} \equiv \langle N^2(\Omega) \rangle = \int_{\Omega} \int_{\Omega} \rho_2(\mathbf{1}, \mathbf{2})d_1d_2 + N_{\Omega}$$

$$N_{\Omega_1\Omega_2} \equiv \langle N_{\Omega_1} N_{\Omega_2} \rangle = \int_{\Omega_1} \int_{\Omega_2} \rho_2(\mathbf{1}, \mathbf{2})d_1d_2 + N_{\Omega_1 \cap \Omega_2}$$

The exchange-correlation density

The exchange-correlation density (XCD)

$$\rho_{xc}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) - \rho_2(\mathbf{1}, \mathbf{2})$$

is the difference between the pair density and a *fictitious* pair density of independent electrons that do not respect the Pauli principle,

$$\rho_2^{\text{IE}}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2})$$

$$\rho_{xc}^{\text{SD}}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) - \rho_2^{\text{SD}}(\mathbf{1}, \mathbf{2}) = \rho_1(\mathbf{1}; \mathbf{2})\rho_1(\mathbf{2}; \mathbf{1}) = |\rho_1(\mathbf{1}; \mathbf{2})|^2 \geq 0$$

because

$$\rho_2^{\text{SD}}(\mathbf{1}, \mathbf{2}) = \begin{vmatrix} \rho(\mathbf{1}) & \rho_1(\mathbf{1}; \mathbf{2}) \\ \rho_1(\mathbf{2}; \mathbf{1}) & \rho(\mathbf{2}) \end{vmatrix}$$

where the superscript SD is used to identify a SD-wfn.

Covariances and Variance

The variance of the number of electron in Ω

$$\sigma^2 [N_\Omega] = N_{\Omega\Omega} - N_\Omega^2$$

and the covariance of electrons populations

$$\text{cov} (N_{\Omega_1}, N_{\Omega_2}) = N_{\Omega_1\Omega_2} - N_{\Omega_1} N_{\Omega_2} = N_{\Omega_1 \cap \Omega_2} - \int_{\Omega_1} \int_{\Omega_2} \rho_{xc}(\mathbf{1}, \mathbf{2}) d_1 d_2$$

which gives the measure of how much the number of electrons in Ω_1 and Ω_2 change together. The XCD is the workhorse for the methods that account for electron localization. XCD reduces to the density,

$$\int \rho_{xc}(\mathbf{1}, \mathbf{2}) d_2 = \rho(\mathbf{1}), \quad \rightarrow \quad \int \int \rho_{xc}(\mathbf{1}, \mathbf{2}) d_1 d_2 = N.$$

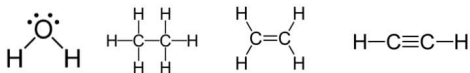
The XCD has been used to define many popular tools in bonding analysis, such as the electron-sharing indices (or bond-orders).

The atom

- ▶ The first idea of an atom is due to Democritus (390 BC).
- ▶ In 1807 Dalton provided the modern atomic theory (father of chemistry).
- ▶ In 1891 Stoney coined the term *electron*.
- ▶ In 1913 Bohr formulated his atomic model including orbits and quanta.
- ▶ In 1924 Pauli provided the forth quantum number: the spin.
- ▶ The advent of quantum mechanics brought the concept of wavefunction.

The Lewis Model

- ▶ The **chemical bond** is one of the most fundamental concepts in chemistry.
- ▶ The **Lewis model** describes the electronic structure of a molecule in terms of electron pairs (**2c-2e bonds**).
- ▶ These electron pairs can be classified as **lone pairs** (electrons which are localized in one atom), **bonding pairs** (electrons that are shared between two atoms), **core electrons**.

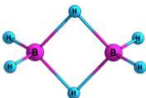


- ▶ However, this intuitive picture of electron distribution does not take into account the **quantum nature of electrons**.

Non-standard Chemical Bonds

MULTICENTER BONDING

B_2H_6 3-center bonding



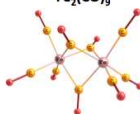
HYPERVALENCE

SF_6

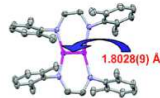


METAL-METAL BONDING

$Fe_2(CO)_9$

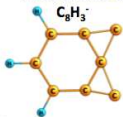


ULTRASHORT Cr-Cr BOND



TETRACOORDINATED PLANAR CARBON

$C_6H_3^-$



PENTACOORDINATED CARBON

$CaI_3Be_2^-$

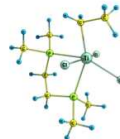


BORON WHEEL

B_{19}^-



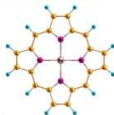
AGOSTIC BONDS



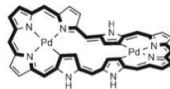
ALL-METAL AROMATIC CLUSTERS



METALLOPORPHYRINS



EXPANDED PORPHYRINS



An atom in a molecule

- ▶ Need to characterize an atom inside a molecule \rightarrow *atomic partition*.
- ▶ From an atomic partition we can define atomic properties.
- ▶ There is not a unique atomic partition, there have been many suggestions.
- ▶ Two main groups:
 - (i) Hilbert-space based.
 - (ii) Real space partitioning.

Some Atomic Partitions:

- 1.- **Mulliken**: Hilbert space partitioning.^a
 - AIM → set of orbitals.
 - Cheap, exact (analytic). **Issue**: Basis set dependence (BSD).
- 2.- **QTAIM**: 3D-space, based on the density.^b
 - AIM → an attractor surrounded by *zero flux surface* or by *infinity*.
 - Non-overlapping regions. No BSD. **Issue**: Expensive
- 3.- **FUZZY**: 3D-space, based on Becke Multicenter scheme.^c
 - AIM → a sum weights through the space.
 - Uses weight functions. No BSD. Cheap. **Issue**: Bond-orders.
- 4.- **TFVC**: 3D-space, mixed Bader-Becke scheme.^d
 - AIM → boundaries determined by BCPs.
 - Gives QTAIM-like results at fuzzy expense.

^aMulliken, *JCP* **23**, 1833 (1955); ^bBader, *ACR* **18**, 9 (1985)

^cMayer, Salvador, *CPL* **383** 638 (2004)

^dSalvador, Ramos-Cordoba, *JCP* **139**, 071103 (2013)

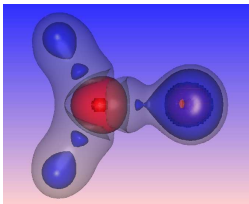
An atom in a molecule: Hilbert-space partition

- ▶ Schrödinger Eq. solved by a finite basis set \rightarrow atomic orbitals.
- ▶ This partition uses the assignment of orbitals to atomic centers.
- ▶ Mulliken was the first to use it to compute populations.¹
- ▶ Advantage: low cost; analytical
- ▶ Drawback: basis set dependence, not clear assignment (diffuse, polarization).

¹Mulliken, *JCP* **23**, 1833 (1955)

Quantum Theory of Atoms-in-Molecules

- ▶ Due to Richard F.W. Bader (1931-2012), McMaster University (Ontario).
- ▶ It consists on the topological analysis of the **electron density**.
- ▶ The density defines the distribution of electrons, and electrons determine the chemistry.
- ▶ Behind the electron density hides the concepts of atoms, bonds, chemical structure and structural stability.



Bader RFW, ACR 18, 9-15 (1985)

QTAIM: Premises

- ▶ Atoms that have the electron distribution make the same contribution to the total energy of the system.
- ▶ Quantum subsystems are open systems defined in real space, their boundaries being determined by a particular property of the electronic charge density.
- ▶ QTAIM defines the atom through a partitioning of the real space as determined by the topological analysis of a molecular charge distribution.

Bader RFW, Beddall PM, JCP 56, 3320-3329 (1972)

QAIM: The Topology of Electron Density

- ▶ The density is the central quantity of DFT and QAIM.
- ▶ Simple object compared to wavefunction (3 coordinates vs. $3N$).
- ▶ Observable (X-ray) and very intuitive.
- ▶ The density is a continuous function.
- ▶ Defined at every point in the space.
- ▶ The **critical points** fulfill $\nabla\rho(\mathbf{r}_c) = 0$.
- ▶ The three curvatures (x,y,z) define the nature of the CP.

$$\mathbf{H}[\rho(\mathbf{r})] = \begin{pmatrix} \frac{\partial^2 \rho(\mathbf{r})}{\partial x^2} & \frac{\partial^2 \rho(\mathbf{r})}{\partial x \partial y} & \frac{\partial^2 \rho(\mathbf{r})}{\partial x \partial z} \\ \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial x} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y^2} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial z} \\ \frac{\partial^2 \rho(\mathbf{r})}{\partial z \partial x} & \frac{\partial^2 \rho(\mathbf{r})}{\partial y \partial z} & \frac{\partial^2 \rho(\mathbf{r})}{\partial z^2} \end{pmatrix} \rightarrow \begin{pmatrix} \frac{\partial^2 \rho(\mathbf{r})}{\partial x_1^2} & 0 & 0 \\ 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial y_1^2} & 0 \\ 0 & 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial z_1^2} \end{pmatrix}$$

Critical points of a 3D function

There are four types of critical points (CP):

$$\mathbf{H}[\rho(\mathbf{r})] \rightarrow \begin{pmatrix} \frac{\partial^2 \rho(\mathbf{r})}{\partial x_1^2} & 0 & 0 \\ 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial y_1^2} & 0 \\ 0 & 0 & \frac{\partial^2 \rho(\mathbf{r})}{\partial z_1^2} \end{pmatrix} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}$$

(3,-3): Attractors (ACP) all the curvatures at \mathbf{r}_c are negative.

(3,-1): Bond CP (**BCP**) 2 curvatures are negative and 1 positive.

(3,+1): Ring CP (**RCP**) 1 curvatures are negative and 2 positive.

(3,+3): Cage CP (**CCP**) 3 curvatures are positive.

Poncairé-Hopf relationship:

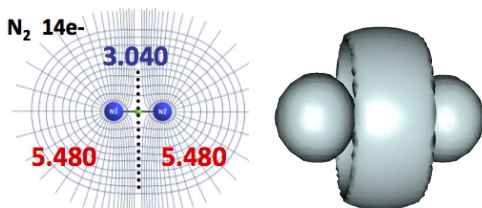
$$n_{ACP} - n_{BCP} + n_{RCP} - n_{CCP} = 1$$

The Laplacian of the electron density

- ▶ The Laplacian of the density accounts for electron localization.

$$\nabla^2 \rho(\mathbf{r}) = \frac{\partial^2 \rho(\mathbf{r})}{\partial x^2} + \frac{\partial^2 \rho(\mathbf{r})}{\partial y^2} + \frac{\partial^2 \rho(\mathbf{r})}{\partial z^2}$$

- ▶ $\nabla^2 \rho(\mathbf{r}) < 0$ electron accumulation \rightarrow localization.
- ▶ $\nabla^2 \rho(\mathbf{r}) > 0$ electron depletion \rightarrow delocalization.



Population analysis

Assuming M number of basis functions an MO can be expanded:

$$\phi_i(\mathbf{1}) \equiv \phi_i^{\text{MO}}(\mathbf{1}) = \sum_{\mu}^M c_{\mu i} \phi_{\mu}^{\text{AO}}(\mathbf{1})$$

$$|\phi_i(\mathbf{1})|^2 = \sum_{\mu\nu}^M c_{\mu i} c_{\nu i} \phi_{\mu}^*(\mathbf{1}) \phi_{\nu}(\mathbf{1})$$

and

$$\begin{aligned} N &= \int \rho(\mathbf{1}) d\mathbf{1} = \sum_i^N n_i \int |\phi_i(\mathbf{1})|^2 d\mathbf{1} = \sum_i^N \sum_{\mu\nu}^M c_{\mu i} c_{\nu i} n_i \int \phi_{\mu}^*(\mathbf{1}) \phi_{\nu}(\mathbf{1}) d\mathbf{1} \\ &= \sum_{\mu\nu}^M \left(\sum_i^N c_{\mu i} c_{\nu i} n_i \right) \int \phi_{\mu}^*(\mathbf{1}) \phi_{\nu}(\mathbf{1}) d\mathbf{1} = \sum_{\mu\nu}^M P_{\mu\nu} S_{\mu\nu} = \text{Tr}(\mathbf{P} \cdot \mathbf{S}) \end{aligned}$$

where \mathbf{P} and \mathbf{S} are the density matrix (in AO) and the overlap matrix, respectively.

Population analysis: Mulliken

By taking the functions of each atom separately

$$N = \int \rho(\mathbf{1}) d\mathbf{1} = \sum_A \sum_{\mu \in A} \sum_{\nu}^M P_{\mu\nu} S_{\mu\nu} = \text{Tr}(\mathbf{P} \cdot \mathbf{S})$$

we can define the Mulliken electron population and gross charge of A :

$$N_A = \sum_{\mu \in A} \sum_{\nu}^M P_{\mu\nu} S_{\mu\nu}$$

$$Q_A = Z_A - N_A$$

where Z_A is atomic number of A .

The gaussian keyword **pop=full** perform an analysis of the electron population.

Population analysis: real space

In the real space we need to perform a **numerical integration** over the atomic domain of A :

$$N_A = \int_A \rho(\mathbf{1}) d\mathbf{1} = \sum_i n_i \int_A |\phi_i(\mathbf{1})|^2 d\mathbf{1}$$

$$Q_A = Z_A - N_A$$

where we need the diagonal part of the **atomic overlap matrix** (AOM):

$$S_{ij}(A) = \int_A \phi_i^*(\mathbf{1}) \phi_j(\mathbf{1}) d\mathbf{1}$$

- ▶ These analysis are done with the appropriate software
- ▶ One should check the accuracy of the integration performed.
- ▶ The computational cost can be beyond our possibilities.

The Pair and the Exchange-Correlation Densities

Probabilistic interpretation of the wavefunction [assume $\mathbf{1} \equiv (\vec{r}, s)$]:

$$P(\mathbf{1} \in r_1) \rightarrow \rho(\mathbf{1}) = N \int |\Psi(\mathbf{1}, \dots, \mathbf{N})|^2 d\mathbf{2} \dots d\mathbf{N}$$

$$P(\mathbf{1} \in r_1, \mathbf{2} \in r_2) \rightarrow \rho(\mathbf{1}, \mathbf{2}) = N(N-1) \int |\Psi(\mathbf{1}, \dots, \mathbf{N})|^2 d\mathbf{3} \dots d\mathbf{N}$$

We can construct a *fictitious* pair density of non-correlated pairs, and compare it with the real pair density:

$$\rho_{xc}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1})\rho(\mathbf{2}) - \rho_2(\mathbf{1}, \mathbf{2})$$

The exchange-correlation density (XCD) integrates to N and accounts for electron localizability: ¹

$$\int \int \rho_{xc}(\mathbf{1}, \mathbf{2}) d\mathbf{1} d\mathbf{2} = N$$

¹Bader, Stephens *JACS* **94**, 7391 (1975), Bader, Stephens *CPL* **26**, 445 (1974)

The Electron Sharing Indices

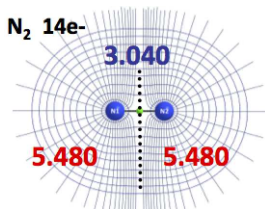
The XCD gives rise to the Electron Sharing Indices (ESI).

The delocalization index (DI):

$$\delta(A, B) = \int_A \int_B d\mathbf{1} d\mathbf{2} \rho_{xc}(\mathbf{1}, \mathbf{2})$$

The localization index (LI):

$$\lambda(A) = \int_A \int_A d\mathbf{1} d\mathbf{2} \rho_{xc}(\mathbf{1}, \mathbf{2})$$

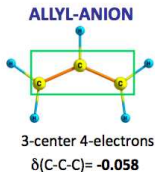
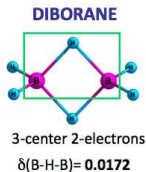


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- Bader, Stephens *JACS* **94**, 7391 (1975), Bader, Stephens *CPL* **26**, 445 (1974)
 Fulton *JPC* **97**, 7516 (1993); Ángyán, Mayer, Loos, *JPC* **98**, 5244 (1994)
 Fradera, Austen, Bader *JPCA* **103**, 304 (1999)
 Matito, Solà, Salvador, Duran *Faraday Discuss.* **135**, 325 (2007)

Multicenter Bonding

Accounts for electron-sharing between n centers (atoms).
It is related to the n -order central moment of the electron population.

$$D(A_1, \dots, A_n) \sim \left\langle \left(\hat{N} - \overline{N} \right)^n \right\rangle_{A_1, \dots, A_n}$$

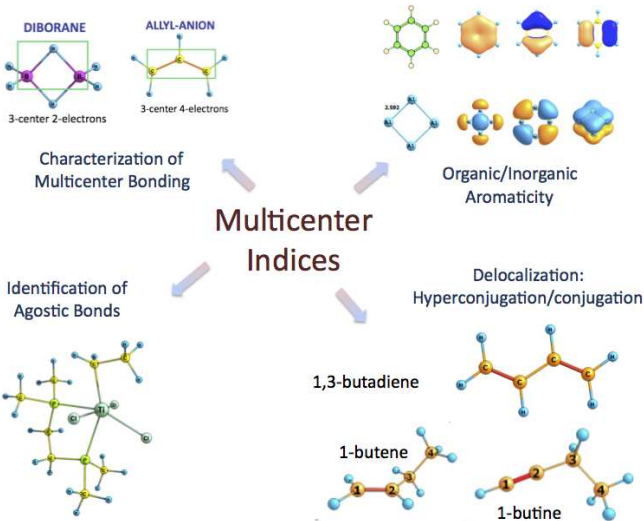


Giambiagi, de Giambiagi, Mundim, *Struc. Chem.* **1**, 423 (1990)

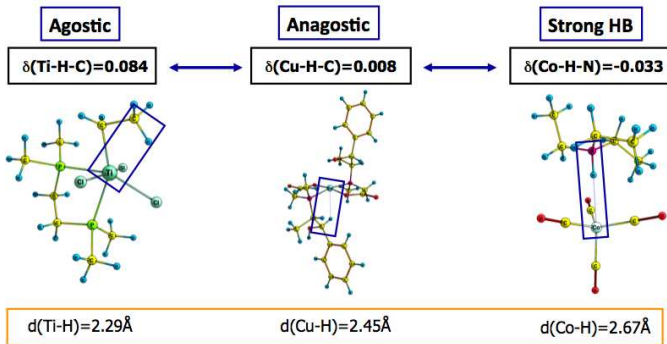
Ponec, Mayer, *JPCA* **101**, 1738 (1997)

Bochicchio, Ponec, Torre, Lain, *TCA* **105**, 292 (2001)

nc-ESI: What is it good for?






Agostic Bonds

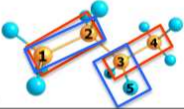
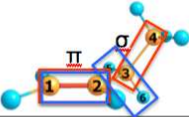
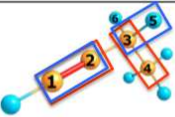


Interaction	3-center ESI
Agostic Bond (3c-2e)	3c-ESI > 0
Anagostic Interaction	3c-ESI \approx 0
Hydrogen Bond (3c-4e)	3c-ESI < 0

Feixas, Matito, Maseras, Poater, Solà, *in preparation*

Conjugation and Hyperconjugation effects

Conjugation	butane		1,3-butadiene		1,3-butadiyne	
						
4c-DI	B3LYP	CCSD	B3LYP	CCSD	B3LYP	CCSD
$\delta(C_1-C_2-C_3-C_4)$	-0.0045	-0.0034	-0.0798	-0.0452	-0.1678	-0.0929
$\delta_\pi(C_1-C_2-C_3-C_4)$			-0.0775		-0.1675	

Hyperconjugation	butane		1-butene		1-butine	
						
4c-DI	B3LYP	CCSD	B3LYP	CCSD	B3LYP	CCSD
$\delta(C_1-C_2-C_3-C_4)$	-0.0045	-0.0034	-0.0133	-0.0085	-0.0182	-0.0114
$\delta(C_1-C_2-C_3-H_5)$	-0.0005	-0.0003	-0.0013	-0.0009	-0.0191	-0.0121
$\delta(C_1-C_2-C_3-H_6)$	-0.0005	-0.0003	-0.0142	-0.0092	-0.0191	-0.0121

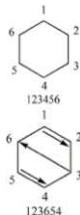
Aromaticity

Let $\mathcal{A} = \{A_1, A_2, \dots, A_n\}$ represent a ring.

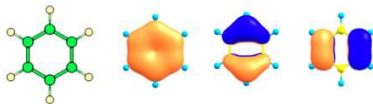
$$I_{ring}(\mathcal{A}) = \sum_{i_1, i_2, \dots, i_n} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \dots S_{i_n i_1}(A_n)$$

$$MCI(\mathcal{A}) = \sum_{\mathcal{P}(\mathcal{A})} I_{ring}(\mathcal{A})$$

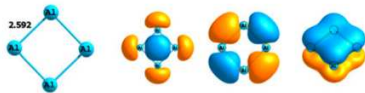
The n^{th} root of these quantities correlates with the TREPE.



C₆H₆
MCI = 0.071
MCI_σ = 0.000
MCI_π = 0.071



Al₄²⁻
MCI = 0.356
MCI_σ = 0.169
MCI_π = 0.187



Giambiagi, *et al.*, *PCCP* **2**, 3381 (2000); Bultinck, *et al.* *JPOC* **18**, 706 (2005)

Multicenter Indices: Formulae

$$\delta(A, B) = -2 \int_A \int_B d\mathbf{1}d\mathbf{2} \gamma(\mathbf{1}, \mathbf{2}) = \text{Cov}(N(A), N(B))$$

$$\delta(A, B, C) = 2 \int_A \int_B \int_C d\mathbf{1}d\mathbf{2}d\mathbf{3} \gamma(\mathbf{1}, \mathbf{2}, \mathbf{3})$$

$$\delta(A_1, A_2, \dots, A_n) = \frac{(-2)^{n-1}}{(n-1)!} \int_{A_1} \int_{A_2} \dots \int_{A_n} d\mathbf{1}d\mathbf{2} \dots d\mathbf{n} \gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n})$$

Functions that upon integration give the above ESIs:

$$\gamma(\mathbf{1}, \mathbf{2}) = \rho_{xc}(\mathbf{1}, \mathbf{2}) = \rho(\mathbf{1}, \mathbf{2}) - \rho(\mathbf{1})\rho(\mathbf{2})$$

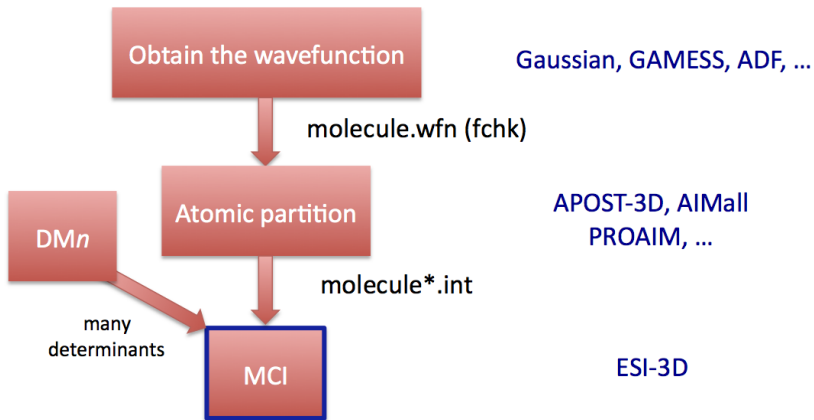
$$\gamma(\mathbf{1}, \mathbf{2}, \mathbf{3}) = \rho(\mathbf{1}, \mathbf{2}, \mathbf{3}) - \rho(\mathbf{1})\rho(\mathbf{2})\rho(\mathbf{3}) - \hat{P}_{1,2,3}(\rho_{xc}(\mathbf{1}, \mathbf{2})\rho(\mathbf{3}))$$

$$\gamma(\mathbf{1}, \mathbf{2}, \dots, \mathbf{n}) = \langle (\hat{\rho}_1 - \bar{\rho}_1)(\hat{\rho}_2 - \bar{\rho}_2) \dots (\hat{\rho}_n - \bar{\rho}_n) \rangle$$

they depend on the ***n*-order density (*n*-density)**.

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Computational Details



ESI-3D: <http://ematito.webs.com>

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