Multicenter Bond Index: a versatile tool to characterize electron delocalization and aromaticity.

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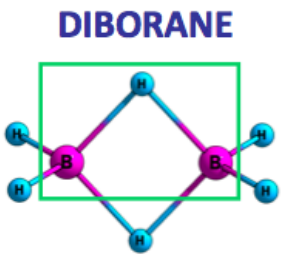
Contents

Multicenter Bonding

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

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

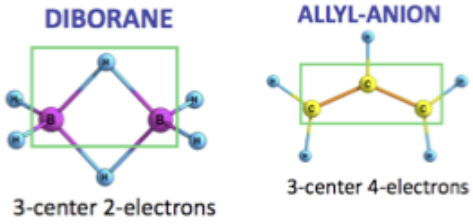


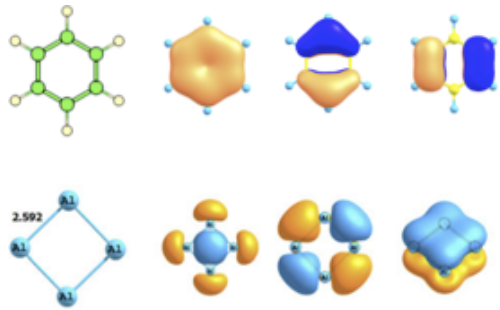
Giambiagi, de Giambiagi, Mundim, Struc. Chem. 1, 423 (1990)

Ponec, Mayer, JPCA 101, 1738 (1997)

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

nc-ESI: What is it good for?



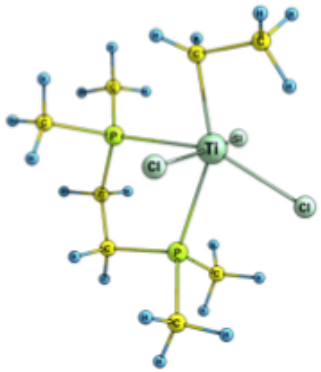


Characterization of Multicenter Bonding

Organic/Inorganic Aromaticity

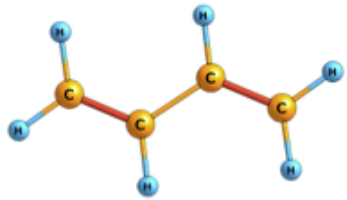
Multicenter Indices

Identification of Agostic Bonds

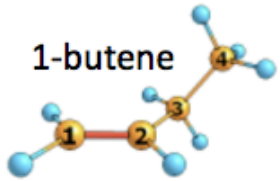


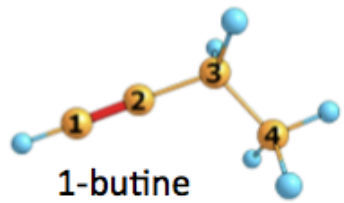
Delocalization: Hyperconjugation/conjugation

1,3-butadiene

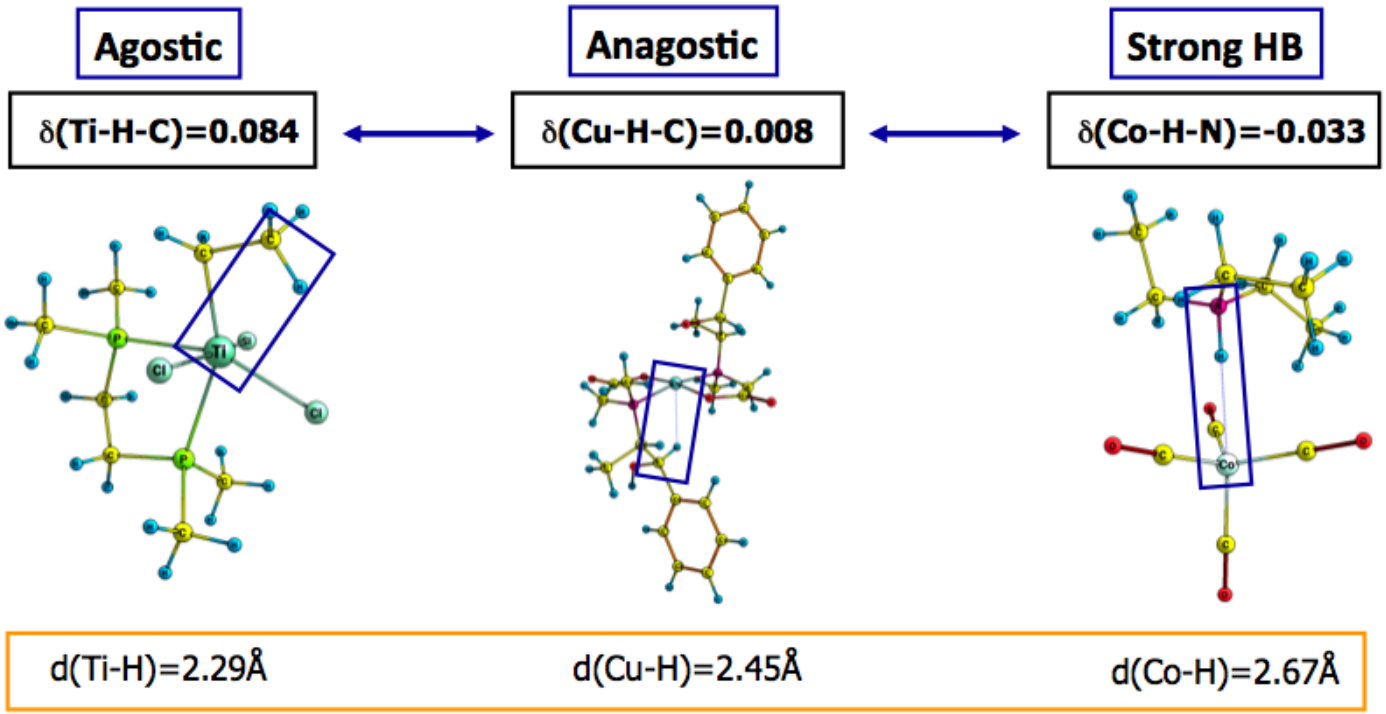


1-butene





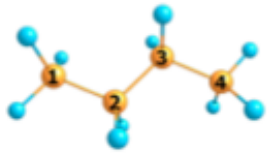
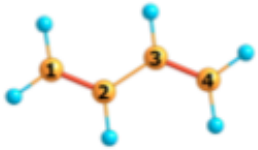
Agostic Bonds

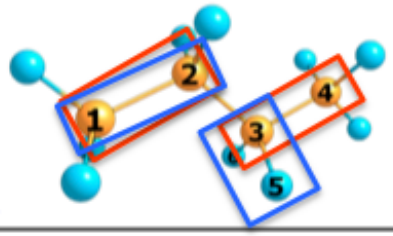
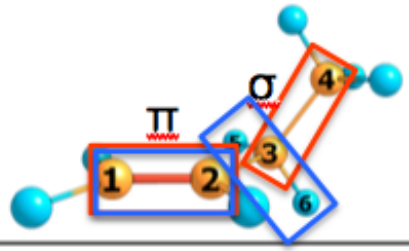
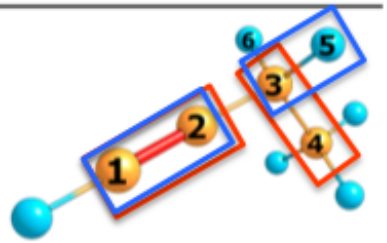


Interaction	3-center ESI
Agostic Bond (3c-2e)	3c-ESI > 0
Anagostic Interaction	3c-ESI ≃ 0
Hydrogen Bond (3c-4e)	3c-ESI < 0

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
$\delta(C_1\text{-}C_2\text{-}C_3\text{-}C_4)$	-0.0045	-0.0034	-0.0798	-0.0452	-0.1678	-0.0929
$\delta_\pi(C_1\text{-}C_2\text{-}C_3\text{-}C_4)$			-0.0775		-0.1675	

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

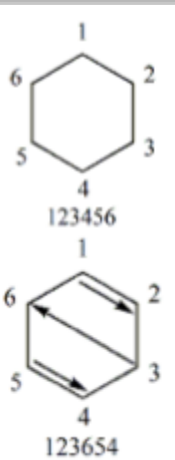
Feixas, Matito, Poater, Solà, JPCA 115, 13104 (2011)

Aromaticity

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

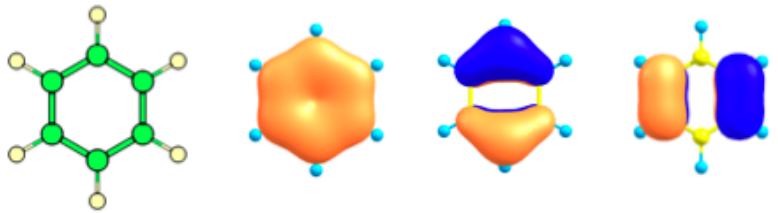
$$I_{ring}(\mathcal{A}) = \sum_{i_1,i_2,\ldots,i_n} S_{i_1 i_2}(A_1)S_{i_2 i_3}(A_2)\ldots S_{i_n i_1}(A_n)$$

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

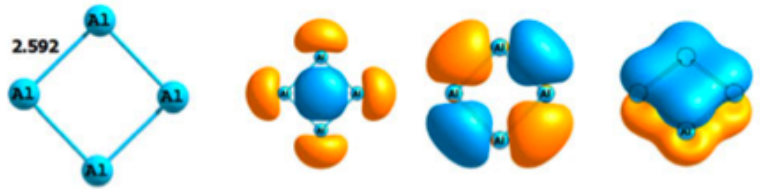


The nth root of these quantities correlates with the TREPE.

C_6H_6 **MCI = 0.071**
MCI_σ = 0.000
MCI_π = 0.071

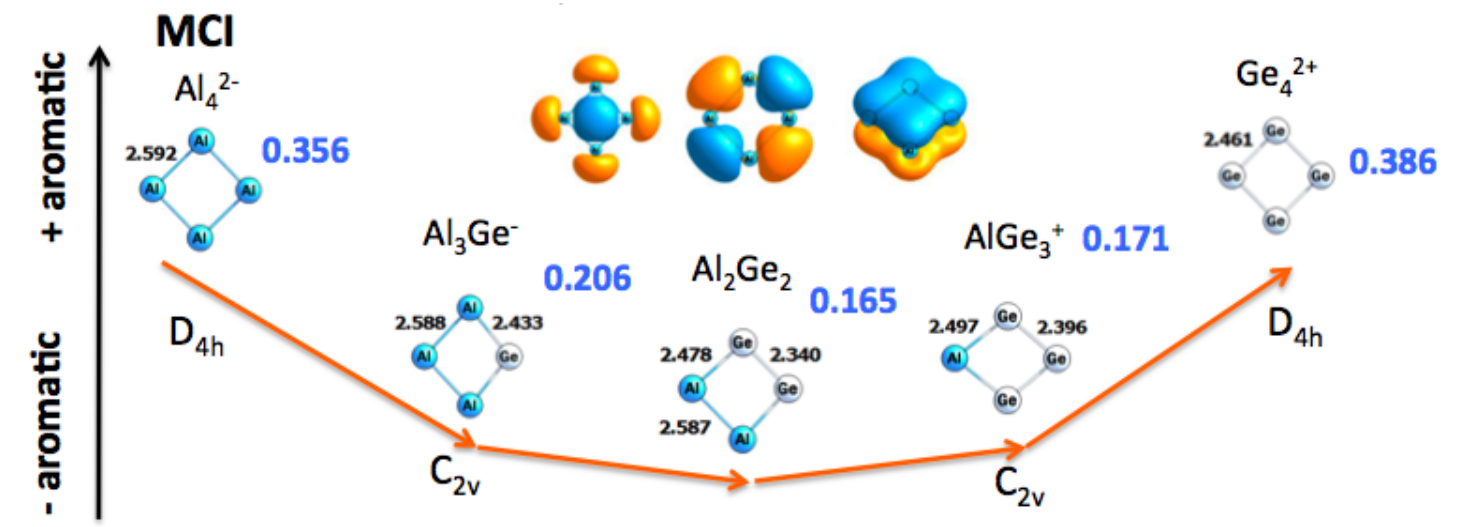


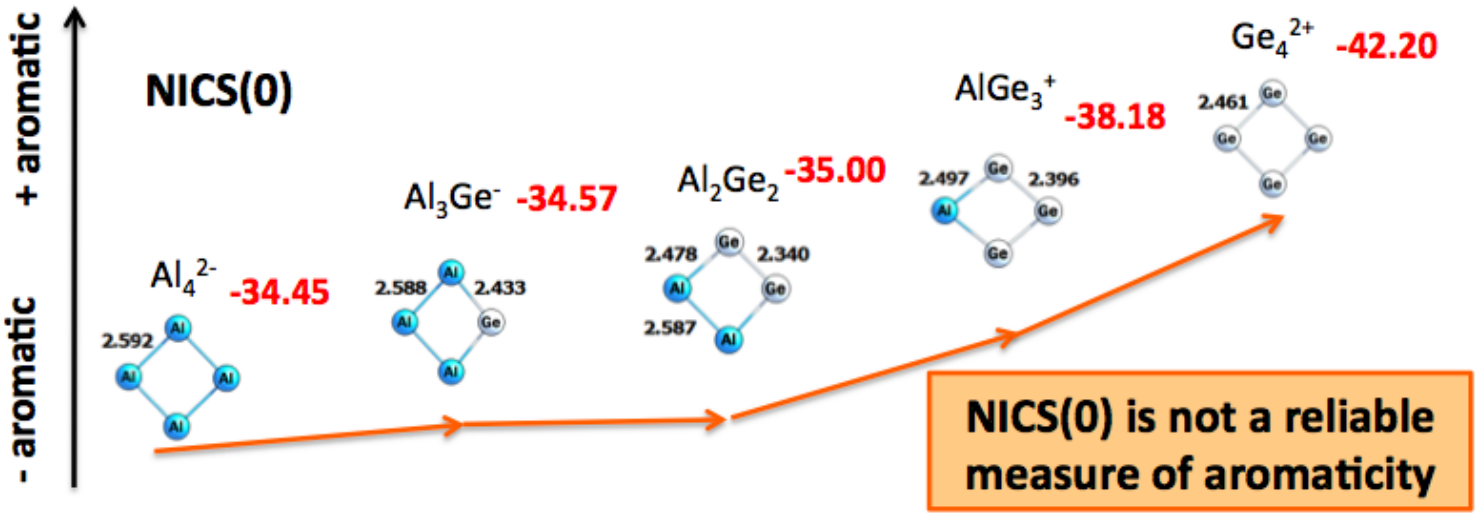
Al_4^{2-} **MCI = 0.356**
MCI_σ = 0.169
MCI_π = 0.187



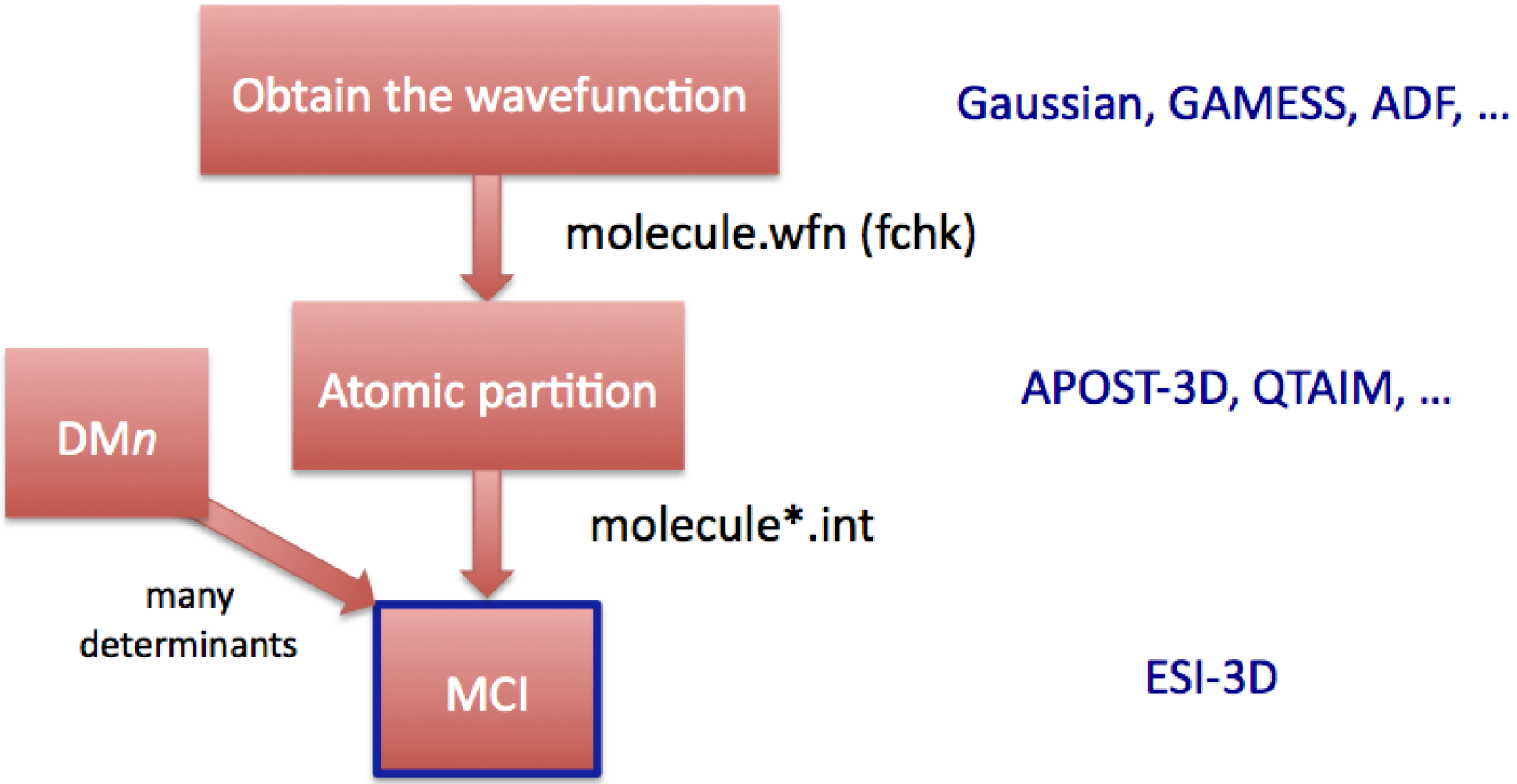
Giambiagi, de Giambiagi, Figuereido, PCCP 2, 3381 (2000)

Aromaticity





Computational Details



Multicenter Indices: Formulae

Functions that upon integration give the ESIs [assume $1 \equiv (\vec{r}, s)$]:

$$\begin{aligned}
\delta(A,B) &= -2\int_A\int_B d1d2\,\gamma(1,2) = Cov\left(N(A),N(B)\right) \\
\delta(A,B,C) &= 2\int_A\int_B\int_C d1d2d3\,\gamma(1,2,3) \\
\delta(A_1,A_2,...,A_n) &= \frac{(-2)^{n-1}}{(n-1)!}\int_{A_1}\int_{A_2}\cdots\int_{A_n} d1d2...dn\,\gamma(1,2,...,n)
\end{aligned}$$

which are

$$\begin{aligned}
\gamma(1,2) &= \rho^{xc}(1,2) = \rho(1,2) - \rho(1)\rho(2) \\
\gamma(1,2,3) &= \rho(1,2,3) - \rho(1)\rho(2)\rho(3) - \hat{\mathcal{P}}_{1,2,3}\left(\rho^{xc}(1,2)\rho(3)\right) \\
\gamma(1,2,\ldots,n) &= \langle(\hat{\rho}_1 - \bar{\rho}_1)(\hat{\rho}_2 - \bar{\rho}_2)\cdots(\hat{\rho}_n - \bar{\rho}_n)\rangle
\end{aligned}$$

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

Martín Pendás, Francisco, Blanco JCP **127** 144103 (2007)

Multicenter Indices: Bottleneck

The function that gives the *n*c-ESI is *symmetric* to the exchange $1, 2, \ldots$

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

and so it is the *n*c-ESI calculated. Thus, we cannot calculate I_{ring}-like expressions with this formulation; only MCI.

Unfortunately,

$$\gamma(1, 2, \ldots, n) = \gamma(1, 2, \ldots, n)[\rho(1, 2, \ldots, n)]$$

i.e., the cost of these indices grows with the size of the *n*-RDMs (M^{2n}).

Shall we approximate them?

Martín Pendás, Francisco, Blanco JCP **127** 144103 (2007)

Approximation for the 3-RDM

The HF expression for the three-body density (3-RDM):

$$\rho^{\mathrm{HF}}(1,2,3) = \begin{vmatrix} \rho(1) & \rho(1|2) & \rho(1|3) \\ \rho(2|1) & \rho(2) & \rho(2|3) \\ \rho(3|1) & \rho(3|2) & \rho(3) \end{vmatrix}$$

leads to a very simple expression

$$\tilde{\gamma}^{\mathrm{HF}}(1,2,3) = 2\sum_{ijk} \eta_i\eta_j\eta_k \phi_j(1)\phi_i^*(1)\phi_k(2)\phi_j^*(2)\phi_i(3)\phi_k^*(3) \rightarrow \tilde{\delta}(A,B,C)$$

In the spirit of Müller approach we suggest:

$$\tilde{\gamma}(1,2,3) = 2\sum_{ijk} (\eta_i\eta_j\eta_k)^{1/2} \phi_j^*(1)\phi_i^*(1)\phi_k(2)\phi_j^*(2)\phi_i(3)\phi_k^*(3) \rightarrow \tilde{\delta}(A,B,C)$$

and

$$\tilde{\gamma}(1,2,3) = 2\sum_{ijk} (\eta_i\eta_j\eta_k)^{1/3} \phi_j(1)\phi_i^*(1)\phi_k(2)\phi_j^*(2)\phi_i(3)\phi_k^*(3) \rightarrow \tilde{\delta}(A,B,C)$$

Approximations for the 3c-ESI

In the spirit of Müller approach, let us take the simplest natural orbital formulation that integrates to the number of electrons:

$$\tilde{\delta}(A_1, A_2, A_3) = 2 \sum_{i_1, i_2, i_3} n_1^{1/3} n_2^{1/3} n_3^{1/3} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) S_{i_3 i_1}(A_3)$$

We will also include the previous ones:

$$\tilde{\delta}(A_1, A_2, A_3) = 2 \sum_{i_1, i_2, i_3} n_1 n_2 n_3 S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) S_{i_3 i_1}(A_3)$$

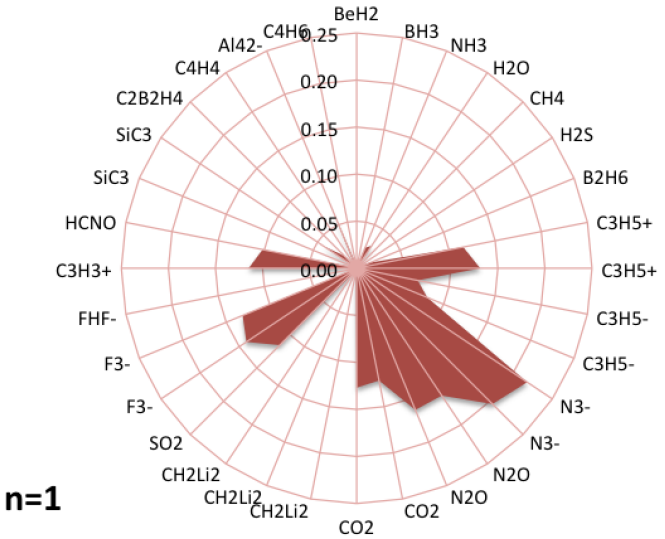
$$\tilde{\delta}(A_1, A_2, A_3) = 2 \sum_{i_1, i_2, i_3} n_1^{1/2} n_2^{1/2} n_3^{1/2} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) S_{i_3 i_1}(A_3)$$

$${}^3D^{Val} = {}^1D^3 + 3({}^2D - {}^1D^2) \wedge {}^1D = 3^2D \wedge {}^1D - 2^1D^3$$

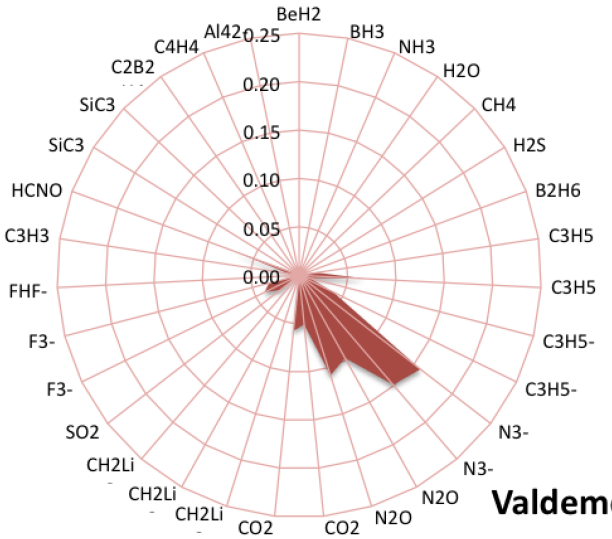
Similar idea was used in six-member rings, that needs the prohibitive 6-RDM:

Olmechenko, Shishkin, Gorb, Leszcynski, Fias, Bultinck, PCCP **13** 20536 (2011)

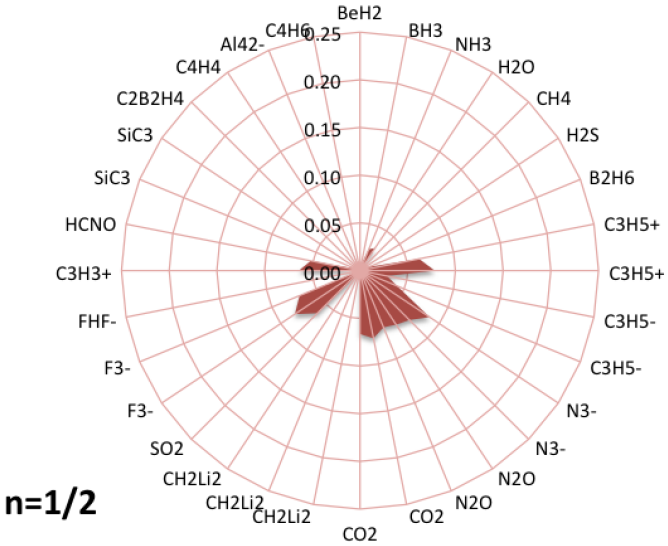
Performance of DM3 approximations



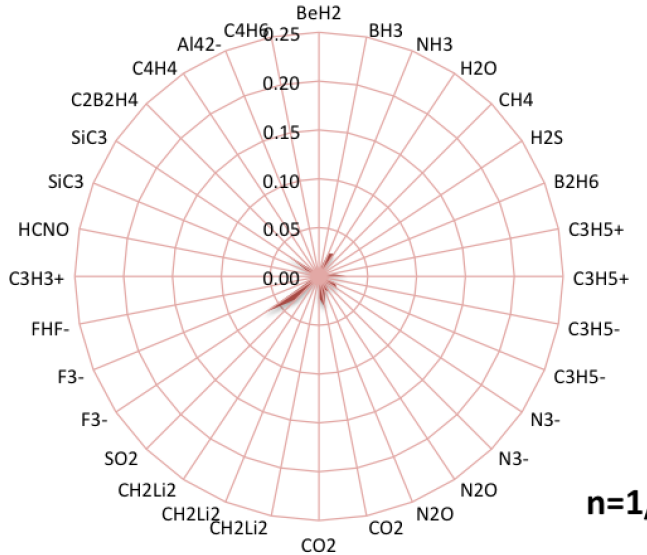
n=1



Valdemoro



n=1/2



n=1/3

We suggest a new formula for the 3-RDM:

$$\tilde{\rho}(1,2,3) = \tilde{\gamma}(1,2,3) + \rho(1)\rho(2)\rho(3) + \hat{\mathcal{P}}_{1,2,3}\left(\rho^{xc}(1,2)\rho(3)\right)$$

where

$$\tilde{\gamma}(1,2,3) = \sum_{ijk} \eta_i^{1/3}\eta_j^{1/3}\eta_k^{1/3}\phi_i(1)\phi_j(1)\phi_k(2)\phi_j(2)\phi_i(3)\phi_k(3)$$

- Fulfills the sum rule.
- Contains the exact 2-RDM but...
- ...it does not bring the 2-RDM upon integration of one coordinate.
- The three-body part is approximated as an expression of NOs.

Conclusions and prospective work

- Multicenter indices are connected to several important chemical noumenons such as agostic bonds, conjugation and aromaticity.
- The interpretation is clear but expression depends on huge n-RDMs.
- Noone goes beyond 3-RDM, and $n = 1$ (HF-like) approx. is poor.
- Two new approxs. based on NOs ($n = 1/2, n = 1/3$) have been put forward, these and Valdemoro's (uses 2-RDM!) perform much better than $n = 1$ (HF-like).

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