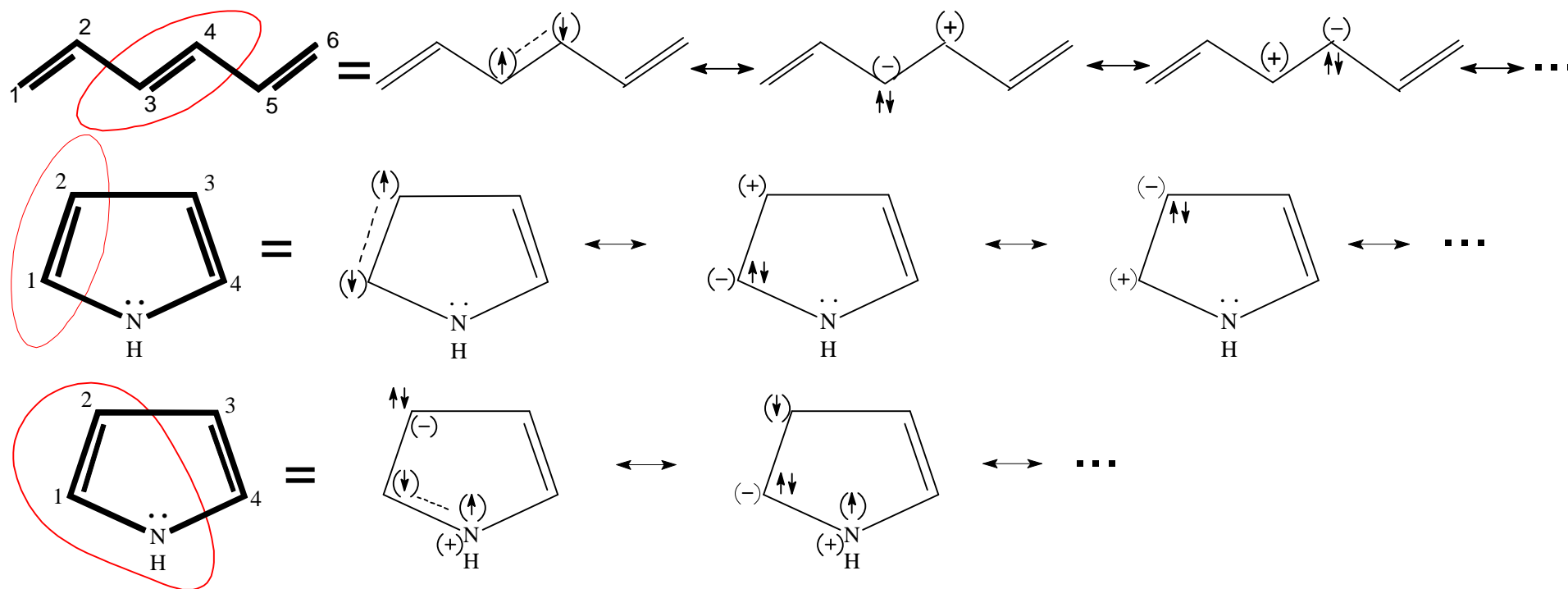# POLY-ELECTRON POPULATION ANALYSIS (PEPA) OF MO WAVEFUNCTIONS:

A '*theoretical Microscope*' to explore VB-type local structures.
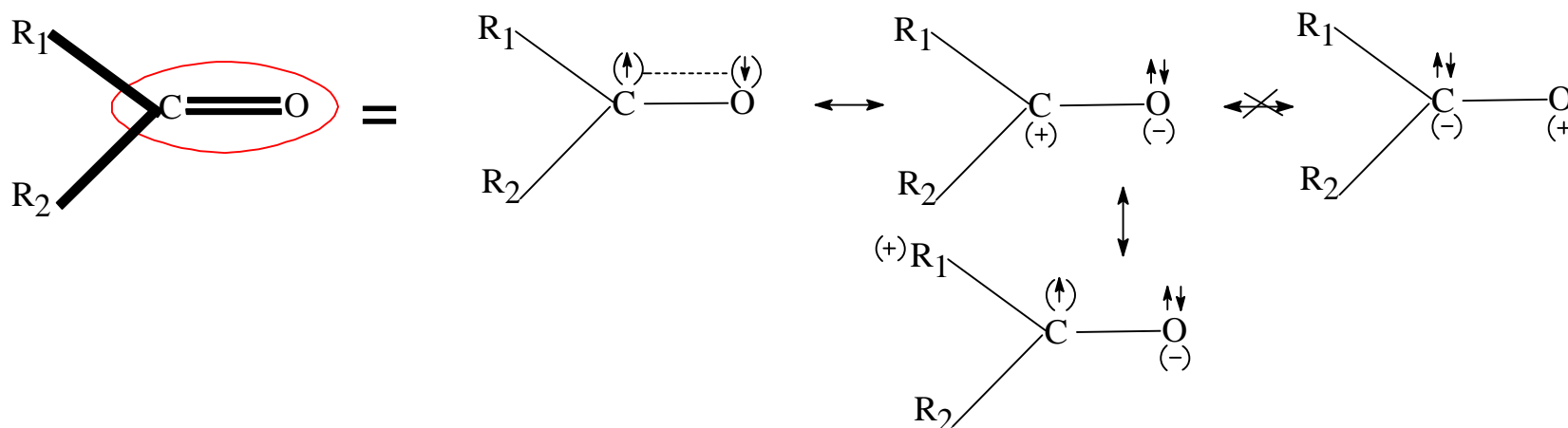
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ARISTOTLE   UNIVERSITY OF THESSALONIKI
GREECE

PEPA or (Natural) NPEPA:
Population analysis for both electrons and   electron-holes

(LOCAL) ELECTRONIC EVENTS (in the sense of *Loge Theory* [1])

Placing *functional groups* 'under the microscope'

[1] **R. Daudel**, in '*Localization and Delocalization in Quantum Chemistry*', Chalvet, O. *et al.*,(eds.), vol.I; Reidel, Dordrecht,1975, p. 3

METHOD

Extract a local information from a delocalized Ψ(MO) :

$$\langle \Psi(\mathbf{MO})^{1/2}\ \hat{\rho}\ ^{1/2}\Psi(\mathbf{MO})\rangle$$

$$\Downarrow$$

- Elaboration of **Ψ(MO)** within MOFFITT's theorem

$$(\ \Psi(MO)\ \rightarrow\ \Psi(TL)\ )$$

- Elaboration of $\hat{\rho}$ within SECOND QUANTIZATION

(include electron holes)

DELOCALIZED $\Psi(MO)$

$$\Psi(MO) = \sum_{I}^{CI} C_I \, |D_I|$$

$$|D_I| = \left\| \psi_{i_1^\alpha} \cdots \psi_{i_{n_\alpha}^\alpha} \; \overline{\psi}_{i_1^\beta} \cdots \overline{\psi}_{i_{n_\beta}^\beta} \right\|$$

$$(\text{MOs} \;\; \psi_{i_1} : \;\; \psi_{i_1} = \sum_k c_{k,i_1} \phi_k)$$

OR

One Slater Determinant, D_1 , involving the delocalized **Khon-Sham** orbitals, ψ_{i_1}

TOTALLY LOCAL $\Psi(TL)$

$$\Psi(TL) = \sum_K T_K \, |\Phi_K|$$

$$|\Phi_K| = \left\| \phi_{k_1^\alpha} \cdots \phi_{k_{n_\alpha}^\alpha} \; \overline{\phi}_{k_1^\beta} \cdots \overline{\phi}_{k_{n_\beta}^\beta} \right\|$$

MOFFITT's theorem

$$\overline{\Psi(MO) = \Psi(TL)}$$

Decomposition of MO-Slater determinants:

$$|D_I| = \sum_K T_K^I \, |\Phi_K| \qquad \text{(from identity relations)}$$

$$T_K^I = \begin{vmatrix} c_{k_1^\alpha \, i_1^\alpha} & \cdots & c_{k_1^\alpha \, i_{n_\alpha}^\alpha} \\ \vdots & & \vdots \\ c_{k_{n_\alpha}^\alpha \, i_1^\alpha} & \cdots & c_{k_{n_\alpha}^\alpha \, i_{n_\alpha}^\alpha} \end{vmatrix} \times \begin{vmatrix} c_{k_1^\beta \, i_1^\beta} & \cdots & c_{k_1^\beta \, i_{n_\beta}^\beta} \\ \vdots & & \vdots \\ c_{k_{n_\beta}^\beta \, i_1^\beta} & \cdots & c_{k_{n_\beta}^\beta \, i_{n_\beta}^\beta} \end{vmatrix}$$

$$T_K = \sum_I^s C_I \, T_K^I$$

DENSITY OPERATORS

Let **E** is the number of the target electrons, and **H** is the number of the target electron holes.
Placing 'under the microscope' **E** spin-orbitals:

$$\hat{\rho}_{E;0} \; (\; \varphi_{\lambda_1} \; \cdots \; \varphi_{\lambda_E} \; ; 0) \; = \; \varphi^+_{\lambda_1} \; \cdots \; \varphi^+_{\lambda_E} \; \varphi^-_{\lambda_E} \; \cdots \; \varphi^-_{\lambda_1}$$

or **E + H** spin-orbitals:

$$\hat{\rho}_{E;H} \; (\; \varphi_{\lambda_1} \varphi_{\lambda_E} \; ; \varphi_{\mu_1} \cdots \varphi_{\mu_H} \;) = \; \varphi^+_{\lambda_1} \; \cdots \; \varphi^+_{\lambda_E} \varphi^-_{\mu_1} \; \cdots \; \varphi^-_{\mu_H} \varphi^+_{\mu_H} \; \cdots \; \varphi^+_{\mu_1} \varphi^-_{\lambda_E} \; \cdots \; \varphi^-_{\lambda_1}$$

(for simplicity: creation φ^+ instead of a^+_φ , and annihilation φ^- instead of a_φ)

- Expectation values, $P_{E;H}$, of the generalized density operators:

$$P_{E;H}(\; \varphi_{\lambda_1} \; ... \; \varphi_{\lambda_E} \; ; \varphi_{\mu_1} \; ... \; \varphi_{\mu_H} \;) = \; <\Psi(TL)| \; \hat{\rho}_{E;H} \; (\; \varphi_{\lambda_1} \cdots \varphi_{\lambda_E} \; ; \varphi_{\mu_1} \; \cdots \; \varphi_{\mu_H} \;) \; | \Psi(TL)> \; =$$

$$= \; \sum_{K(\neq \varphi_{\mu_1} \cdots \varphi_{\mu_H})}^{(\varphi_{\lambda_1} \cdots \varphi_{\lambda_E})} \; W(\Phi_K)$$

Where $\displaystyle\sum_{K(\neq \varphi_{\mu_1} \cdots \varphi_{\mu_H})}^{(\varphi_{\lambda_1} \cdots \varphi_{\lambda_E})}$ represents a summation over Slater determinants, which involve

$\varphi_{\lambda_1} \cdots \varphi_{\lambda_E}$ and simultaneously SOs $\varphi_{\mu_1} \cdots \varphi_{\mu_H}$ are absent, and

$$W(\Phi_K)$$

is the **weight** of the local Slater determinant $|\Phi_K|$, depending on the (non-) orthogonality of orbitals.

Weights of the totally local Slater determinants, $\left|\Phi_K\right|$:

(i) orthogonal orbitals

$$W(\Phi_K) = T_K^2$$

Provides the **probability** of a given occupation scheme of (local) AO-positions

(ii) non-orthogonal orbitals (Mulliken partition for P.E.P.A)

The Coulson-Chirgwin definition for the weights of determinantal wave functions:

$$W(\Phi_K) = T_K^2 <\Phi_K|\Phi_K> + T_K \sum_{K'\neq K}^{\text{fullbasis}} T_{K'} <\Phi_K|\Phi_{K'}>$$

By adopting the Mulliken partition for P.E.P.A., the weights, $P_{E;H}$, of local electronic structures are <u>coherent with those of VB theory</u>. The principal difference is that VB weights are obtained from spin-eigenfunctions and <u>concern the whole electronic assembly</u>, while $P_{E;H}$ are obtained from the sums weights of single Slater determinants, and <u>concern local structures</u>.

Summary

The generalized Poly-Electron Population Analysis (PEPA)

requires <u>very simple</u> (formally) equation:

$$P_{E;H} \left(\varphi_{\lambda_1} \dots \varphi_{\lambda_E} \; ; \varphi_{\mu_1} \dots \varphi_{\mu_H} \right) = \sum_{K(\neq \varphi_{\mu_1}\dots\varphi_{\mu_H})}^{(\varphi_{\lambda_1}\dots\varphi_{\lambda_E})} W(\Phi_K)$$

[Note: The involved det $\{ \Phi_K \}$ have a fixed occupation in the target SOs $\{\varphi_\lambda , \varphi_\mu\}$, while the remaining SOs can have <u>anyone occupation</u>]

But, in medium size systems:
<u>Exponential scaling of computational difficulties</u> with the system size !

$$\Downarrow$$

<u>Efficient calculation of</u> $P_{E;H}$ <u>without approximations</u>:

(A) Mixed *local-non-local* Slater determinants

(B) The *hole-expansion* methodology

Efficient calculation of $P_{E;H}(\varphi_{\lambda_1} \cdots \varphi_{\lambda_E} ; \varphi_{\mu_1} \cdots \varphi_{\mu_H})$ (without approximations)

(A) Mixed local-non-local Slater determinants

The factorization of VB-type (Totally Local) Slater determinants
(i.e grouping the TL Slater determinants, having as 'common factor' the target electrons under the microscope)

The basic idea:

Any delocalized MO Slater determinant (of the initial wave function), $\left|D_I\right|$

$$\left|D_I\right| = \| \Psi_{i_1} \ldots \Psi_{i_N} \|$$

$$\leftarrow \text{ non-local } \rightarrow$$

is decomposed (i.e. expanded) in mixed local-non-local (LNL) Slater determinants, $\left| D_I^{LNL} \right|$

$$\left|D_I^{LNL}\right| = \| \varphi_{i_1} \ldots \varphi_{i_E} \psi_{i_{E+1}}^H \ldots \|$$

$$\leftarrow \text{local} \rightarrow \quad \leftarrow \text{ non-local } \rightarrow$$

A non-local ψ_i^H has the following form :

$$\psi_i^H = \sum_{k \neq \varphi_{i_1} .. \varphi_{i_E} \varphi_{\mu_1} .. \varphi_{\mu_H}} c_{k,i} \; \varphi_k$$

Generalizing the Moffitt's theorem we obtain:

$$\Psi(MO) = \sum_I^{LNL} C_I \left|D_I^{LNL}\right| + \Psi(\text{remaining})$$

Only this part is useful to calculate

$$< \Psi(MO) | \hat{\rho} | \Psi(MO)>$$

Efficient calculation of $P_{E;H}(\varphi_{\lambda_1} \cdots \varphi_{\lambda_E} ; \varphi_{\mu_1} \cdots \varphi_{\mu_H})$ (without approximations)

(B) The hole-expansion methodology [1]

The basic ideas:

(i) One can show [1] that a structure involving only electron holes can be calculated very efficiently (i.e. without generating and storing the extremely numerous TL Slater det.) :

$$P_{0;H}(0; \varphi_{\mu_1} \cdots \varphi_{\mu_H}) = \sum_I^{CI} C_I^* \sum_I^{CI} C_I < D_I | D_I^H >$$

where $\left| D_I \right|$ is a MO Slater determinant of the initial wave function:

$$\left| D_I \right| = \| \psi_{i_1} \cdots \psi_{i_N} \|$$

And D_I^H are Slater determinants involving (instead of MOs ψ_i) projected MO, ψ_i^H

$$\left| D_I^H \right| = \| \psi_{i_1}^H \cdots \psi_{i_N}^H \|$$

in which ψ_i^H is obtained from the corresponding ψ_i, in which the SOs involving holes, $\varphi_{\mu_1} \cdots \varphi_{\mu_H}$, are not excluded:

$$\psi_i^H = \sum_{k \neq \varphi_{\mu_1} \cdots \varphi_{\mu_H}} c_{k,i} \; \varphi_k$$

An overlap $< D_I | D_I^H >$ is a determinant involving as elements the overlaps $< \psi_i | \psi_i^H >$.

$$< D_I | D_I^H > = \begin{vmatrix} < \psi_{i_1} | \psi_{i_1}^H > & \cdots & < \psi_{i_1} | \psi_{i_N}^H > \\ & \cdot & \\ & \cdot & \\ & \cdot & \\ < \psi_{i_N} | \psi_{i_1}^H > & \cdots & < \psi_{i_N} | \psi_{i_N}^H > \end{vmatrix}$$

[1] P. Karafiloglou   *J. Chem. Phys.* **130** (2009) *164103*

(ii) One can show [1] that a structure involving only electrons can be expanded in terms involving only holes (**hole-expansion**), as for example:

$$P_{1;0}(\varphi_{\lambda_1};0) = 1 - P_{0;1}(0\varphi_{\lambda_1})$$

[a trivial example of a hole-expansion issued from the first order anticommutation relation]

$$P_{2;0}(\varphi_{\lambda_1}\varphi_{\lambda_2};0) = 1 - P_{0;1}(0;\varphi_{\lambda_1}) - P_{0;1}(0;\varphi_{\lambda_2}) + P_{0;2}(0;\varphi_{\lambda_1}\varphi_{\lambda_2})$$

$$P_{3;0}(\varphi_{\lambda_1}\varphi_{\lambda_2}\varphi_{\lambda_3};0) = 1 - P_{0;1}(0;\varphi_{\lambda_1}) - P_{0;1}(0;\varphi_{\lambda_2}) - P_{0;1}(0;\varphi_{\lambda_3}) + P_{0;2}(0;\varphi_{\lambda_1}\varphi_{\lambda_2}) +$$

$$P_{0;2}(0;\varphi_{\lambda_1}\varphi_{\lambda_3}) + P_{0;2}(0;\varphi_{\lambda_2}\varphi_{\lambda_3}) - P_{0;3}(0;\varphi_{\lambda_1}\varphi_{\lambda_2}\varphi_{\lambda_3})$$

etc

Generalizing these relations, one can show inductively the following general expansion:

$$P_{E;0}(\varphi_{\lambda_1} \ldots \varphi_{\lambda_E};0) = 1 + \sum_{q=1}^{E}(-1)^q \sum_{j_1<K}^{\lambda_E}\Lambda \sum_{<j_q}^{\lambda_E} P_{0;q}(0;\varphi_{j_1} \ldots \varphi_{j_q})$$

Similarly, for structures involving both electrons and holes:

$$P_{2;2}(\varphi_{\lambda_1}\varphi_{\lambda_2};\varphi_{\mu_1}\varphi_{\mu_2}) = P_{0;2}(0;\varphi_{\mu_1}\varphi_{\mu_2}) - P_{0;3}(0;\varphi_{\lambda_1}\varphi_{\mu_1}\varphi_{\mu_2}) -$$

$$- P_{0;3}(0;\varphi_{\lambda_2}\varphi_{\mu_1}\varphi_{\mu_2}) + P_{0;4}(0;\varphi_{\lambda_1}\varphi_{\lambda_2}\varphi_{\mu_1}\varphi_{\mu_2})$$

The general expression for any structure involving E electrons and H   holes is:

$$P_{E;H}(\varphi_{\lambda_1} \ldots \varphi_{\lambda_E};\varphi_{\mu_1} \ldots \varphi_{\mu_H}) = P_{0;H}(0;\varphi_{\mu_1} \ldots \varphi_{\mu_H}) +$$

$$+ \sum_{q=1}^{E}(-1)^q \sum_{j_1<K}^{\lambda_E}\Lambda \sum_{<j_q}^{\lambda_E} P_{0;q+H}(0;\varphi_{j_1} \ldots \varphi_{j_q}\varphi_{\mu_1} \ldots \varphi_{\mu_H})$$

ALGORTHM: Library of hole-structures

[1] P. Karafiloglou   *J. Chem. Phys.* **130** (2009) *164103*

A proposition for the VB workshop (Paris, July 2012)

$$\Psi(VB) \longrightarrow \Psi(TL)$$

From a V.B. wave function obtain the Coulson-Chirgwin weights, $W(\Phi_K)$, of single Slater determinants, Φ_K.

$$\Downarrow$$

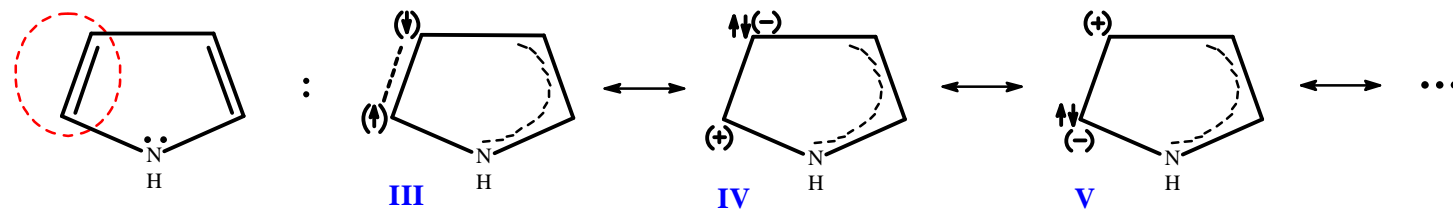**(An output file involving the weigths $W(\Phi_K)$ of single Slater determinants, Φ_K)**

$$\Downarrow$$

Poly-Electron Population Analysis of VB wave functions

Two-electron probability ($P_{2;0}$):
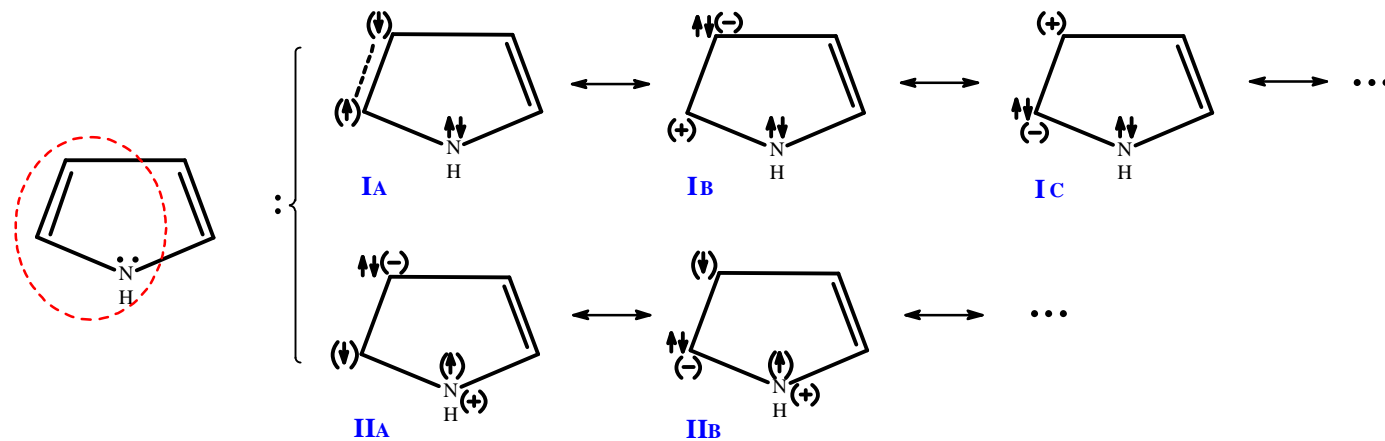
One-electron one-hole probability ($P_{1;1}$):

I   **II**

Two-electron two-hole probabilities ($P_{2;2}$):

III   **IV**   **V** $\cdots$

Three-electron one-hole probabilities ($P_{3;1}$):

I'   **II'** $\cdots$
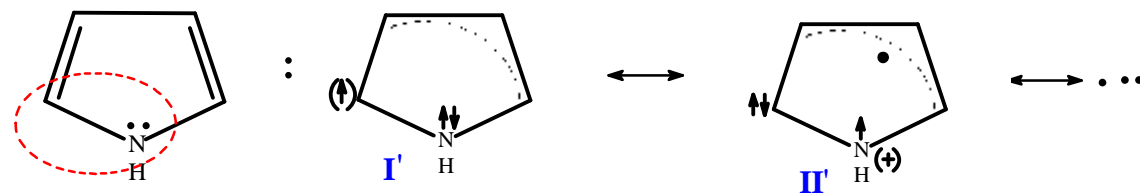
Four-electron two-hole probabilities ($P_{4;2}$):

I$_A$ **I$_B$**   **I$_C$** $\cdots$

II$_A$ **II$_B$** $\cdots$

Relationships between local structures
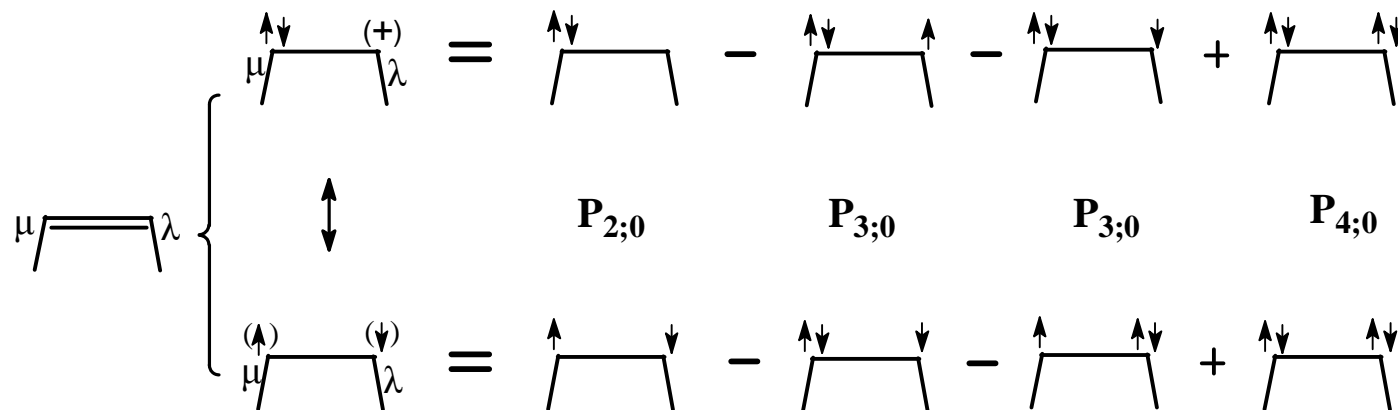
The *electron-expansion* methodology [1]

(Expand the holes in terms involving only electrons)

$$P_{2;2}(\mu, \bar{\mu} ; \nu, \bar{\nu}) = P_{2;0}(\mu, \bar{\mu}) - P_{3;0}(\mu, \bar{\mu}, \nu) - P_{3;0}(\mu, \bar{\mu}, \bar{\nu}) + P_{4;0}(\mu, \bar{\mu}, \nu, \bar{\nu})$$

$$P_{2;2}(\mu, \bar{\nu} ; \bar{\mu}, \nu) = P_{2;0}(\mu, \bar{\nu}) - P_{3;0}(\mu, \bar{\nu}, \bar{\mu}) - P_{3;0}(\mu, \bar{\nu}, \nu) + P_{4;0}(\mu, \bar{\nu}, \bar{\mu}, \nu), \text{etc} \ldots$$

where $P_{2;2}(\mu, \bar{\mu} ; \nu, \bar{\nu}) = \sum\limits_{K(\neq \nu, \bar{\nu})}^{(\mu\bar{\mu})} W(\Phi_K)$ and $P_{2;2}(\mu, \bar{\nu} ; \bar{\mu}, \nu) = \sum\limits_{K(\neq \bar{\mu}, \nu)}^{(\mu, \bar{\nu})} W(\Phi_K)$

… etc …

The $P_{3;0}$ contribute with a minus sign => The greater the contributions of the three-electron structures are, the less important are both covalent and ionic structures, and thus the more week is the bond: ***Déjà vu*** in the 'L.P.B.W.E. effect' of V.B. theory !

[1] P. Papanikolaou, P. Karafiloglou *J. Phys. Chem. A* **112** 8839, 2008

The 4th order anticommutation relation

$$\prod_{i=1}^{4} (a_i^+ a_i + a_i a_i^+) = 1$$

involves 16 terms :

$a_1^+ a_4^+ a_2 a_3 a_3^+ a_2^+ a_4 a_1 \;+\; a_2^+ a_3^+ a_1 a_4 a_4^+ a_1^+ a_3 a_1 \;+\; a_1^+ a_2^+ a_3 a_4 a_4^+ a_3^+ a_2 a_1 \;+$

$+\; a_3^+ a_4^+ a_1 a_2 a_2^+ a_1^+ a_4 a_3 \;+$

$+\; a_1^+ a_2 a_3 a_4 a_4^+ a_3^+ a_2^+ a_1 \;+\; a_3^+ a_1 a_2 a_4 a_4^+ a_2^+ a_1^+ a_3 \;+\; a_2^+ a_1 a_3 a_4 a_4^+ a_3^+ a_1^+ a_2 \;+$

$+\; a_4^+ a_1 a_2 a_3 a_3^+ a_2^+ a_1^+ a_4 \;+\; a_1 a_2 a_3 a_4 a_4^+ a_3^+ a_2^+ a_1^+ \;+$

$+\; a_1^+ a_3^+ a_4^+ a_2 a_2^+ a_4 a_3 a_1 \;+\; a_1^+ a_2^+ a_3^+ a_4 a_4^+ a_3 a_2 a_1 \;+\; a_2^+ a_3^+ a_4^+ a_1 a_1^+ a_4 a_3 a_2 \;+$

$+\; a_1^+ a_2^+ a_4^+ a_3 a_3^+ a_4 a_2 a_1 \;+\; a_1^+ a_2^+ a_3^+ a_4^+ a_4 a_3 a_2 a_1 \;+$

$+\; a_1^+ a_3^+ a_2 a_4 a_4^+ a_2^+ a_3 a_1^+ \;+\; a_2^+ a_4^+ a_1 a_3 a_3^+ a_1^+ a_4 a_2 \quad = \; 1$

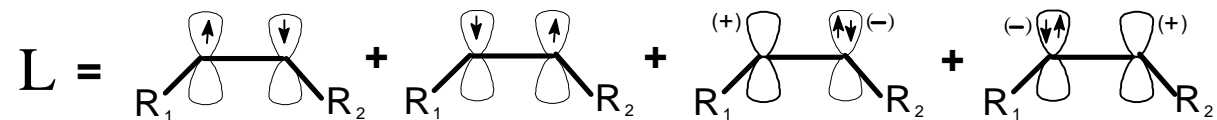By adopting the V.B. perspective for chemical bonding, and choosing the above spin-orbitals $(i = 1,2,3,4)$ such as

$i = 1 \rightarrow \varphi_\lambda$, $i = 2 \rightarrow \overline{\varphi}_\lambda$ and $i = 3 \rightarrow \varphi_\mu$, $i = 4 \rightarrow \overline{\varphi}_\mu$
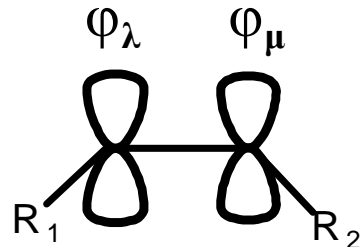
we obtain :
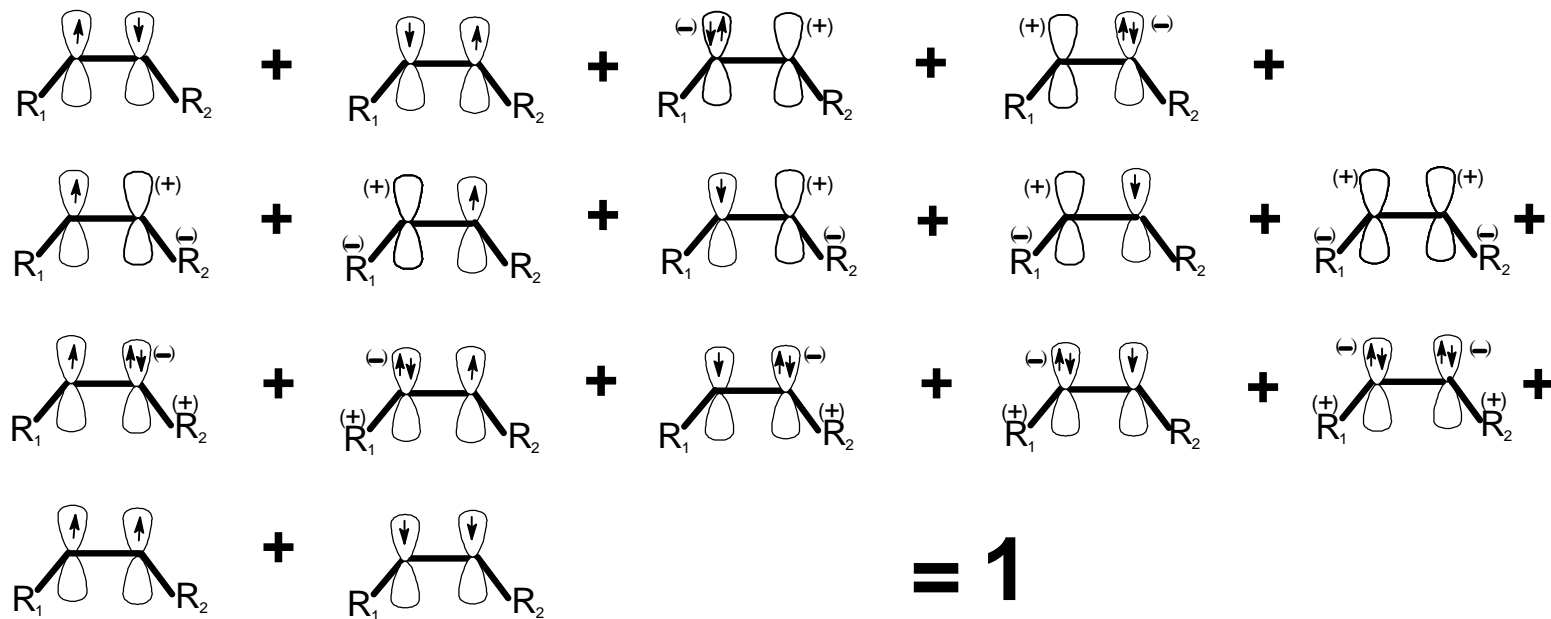
The *bond localization* (L) in **VB language**:

$$L = \quad + \quad + \quad +$$

or, the *bond delocalization* (D) :

$$D \; = \; 1 \; - \; L$$

Lionel Salem in '*The Molecular Orbital Theory of Conjugated Systems'*, p.86 (Benjam, N.York

*"Delocalization is a measure of the degree to which the electrons cannot
be assigned by **pairs** to individual bonds"*

Electron pairs in Chemical systems :

Coulomb and Fermi (or Exchange) correlations

Coulomb correlations in one orbital:

$$C(\lambda, \bar{\lambda}) = P_2(\lambda, \bar{\lambda}) - P_1(\lambda)\,P_1(\bar{\lambda})$$

Fermi correlations in one orbital:

$$C(\lambda, \lambda) = P_2(\lambda, \lambda)^{\nearrow 0} - P_1(\lambda)^2$$

$$C(\bar{\lambda}, \bar{\lambda}) = P_2(\bar{\lambda}, \bar{\lambda})^{\nearrow 0} - P_1(\bar{\lambda})^2$$

Coulomb correlations in two orbitals:

$$C(\lambda, \bar{\mu}) = P_2(\lambda, \bar{\mu}) - P_1(\lambda)\,P_1(\bar{\mu})$$
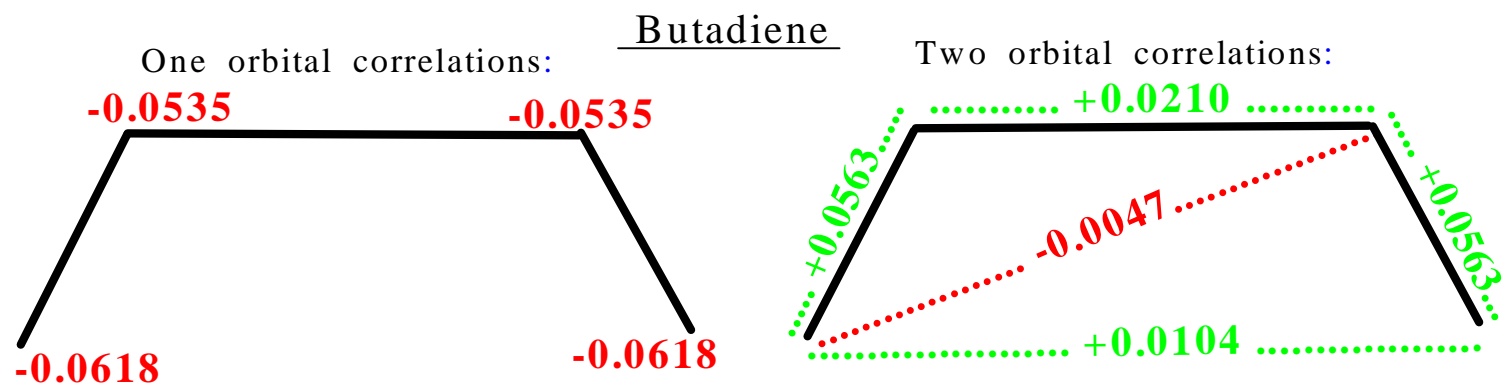
Fermi correlations in two orbitals:

$$C(\lambda, \mu) = P_2(\lambda, \mu) - P_1(\lambda)\,P_1(\mu)$$

$$C(\bar{\lambda}, \bar{\mu}) = P_2(\bar{\lambda}, \bar{\mu}) - P_1(\bar{\lambda})\,P_1(\bar{\mu})$$
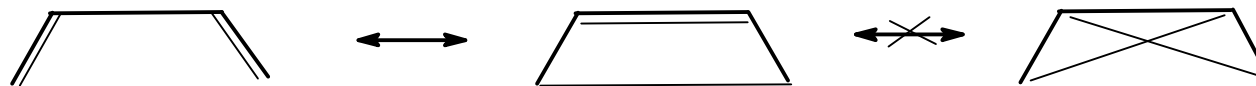
P. Karafiloglou, *J. Phys. Chem. A* 2001, *105, 4524*

From genuine chemical knowledge:

The chemical bond is a matter of an electron pair $(\uparrow \downarrow)$

$C(\lambda, \overline{\mu})$
- positive (> 0) => Favorable pairing $(\uparrow \downarrow)$ / Favorable bonding between φ_λ, φ_μ / "attractive" $\uparrow \cdots \downarrow$
- zero => no bonding (e.g. long range interactions)
- negative (< 0) => Unfavorable pairing $(\uparrow \downarrow)$ / Unfavorable bonding between φ_λ, φ_μ / "repulsive" $\uparrow \cdots \downarrow$

Butadiene

One orbital correlations:

-0.0535   -0.0535

-0.0618   -0.0618

Two orbital correlations:

+0.0210

+0.0563   -0.0047   +0.0563

+0.0104

This corroborates with the V.B. description of butadiene:

For a given φ_λ : $\sum_{\overline{\mu}} C(\lambda, \overline{\mu}) = 0$

Coulomb $(\uparrow\downarrow)$:

Fermi (or Exchange) $(\uparrow\uparrow)$:

+0.0210

+0.0563

−0.0047

+0.0563

+0.0104

−0.0317

−0.2250

+0.0074

−0.2250

−0.0306
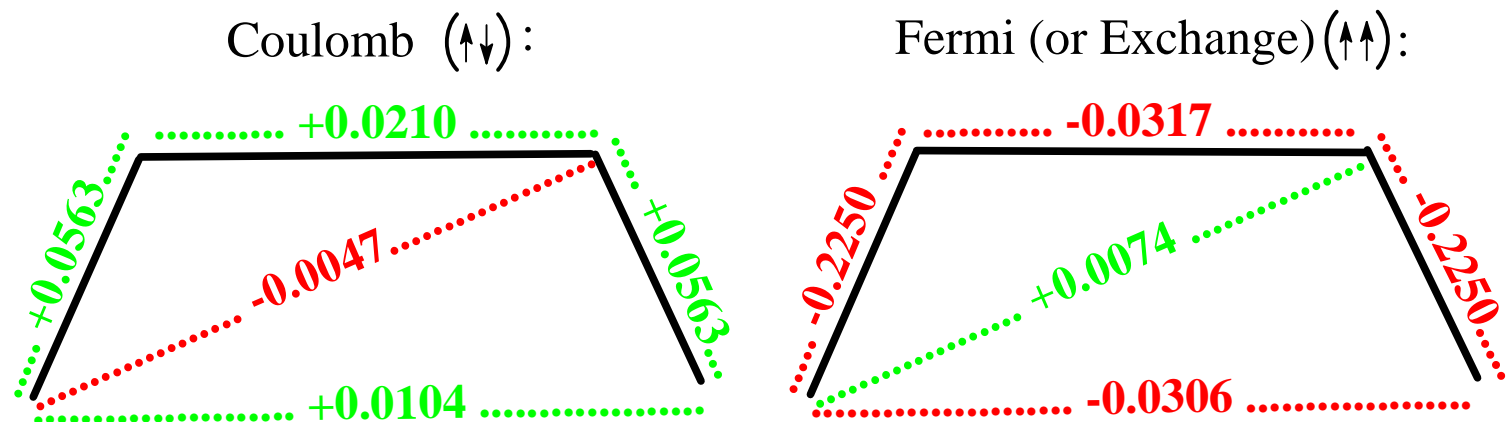
The absolutes values of Fermi are greater than the Coulomb correlations
(this holds without any exception)

<u>Note</u>: Methods based on the behaviour of parallel spins (c.f. to Pauli Principle)

(e.g. **Wiberg** indices, **E.L.F.**, **D.A.F.H.**), provide remarkably good results !

At least from etymological viewpoint 'Valence Bond' refers to a bond in Valence orbitals:

_____
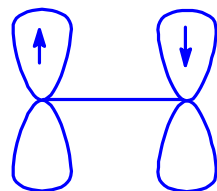
Conceptual problems can arise even in the simplest case of a double-zeta basis:
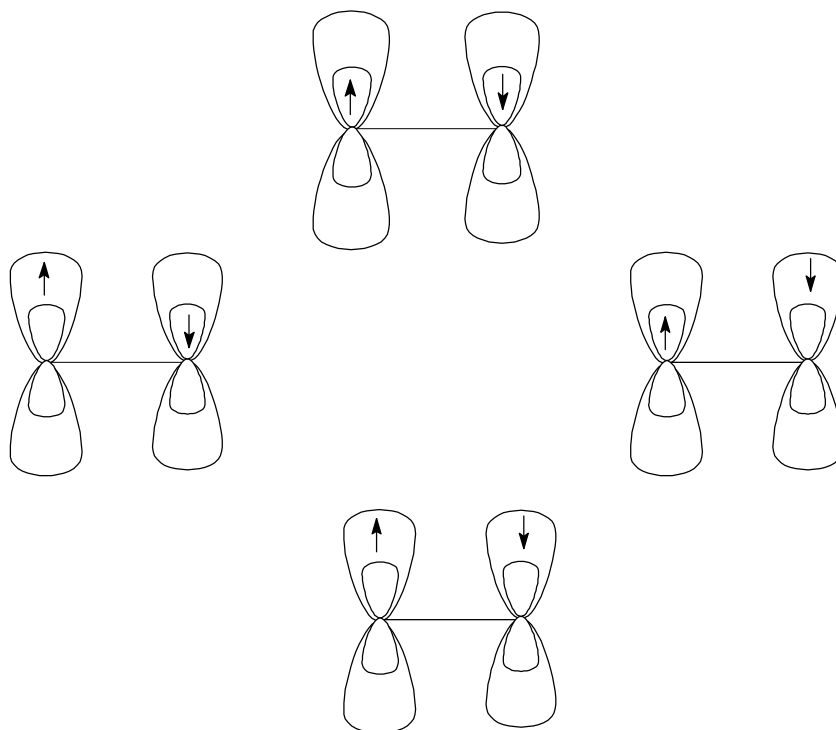
In which extent the outer orbital is Valence (and in which extent is Rydberg) orbital ?

CHOICE OF ORBITAL SPACES

Current calculations involve quite extended AO-basis sets:
Multiple zeta + polarization functions

$\Downarrow$

Conceptual problems to interpret 'accurate' calculations:
Which orbitals represent better the **valence** *orbitals and which the* **Rydberg** ?

For example, the C atom makes bonds by using the valence 2s, 2p,
although for quantum chem. investigations one must use :   s, s', s'',   p, p', p'', polarization

A very good solution:
Natural Orbitals (NAOs, NHOs, NBOs, …etc) [1]

¬ These orbitals are '*natural*' in the Löwdin sense and, thus, can be clearly
   distinguished in valence   and Rydberg.
¬ They show remarkable stability with the extension of the SCF AO- basis set.
¬ They span the complete SCF-AO basis set => The initial wavefunction can be transformed
   into the Natural basis without altering its approximation level; this holds even for
   correlated wavefunctions (linear combination of Slater determinants)
   => no approximations or additional assumptions for NPEPA.
¬ The bonding NBOs show a very good transferability.
¬ These Natural orbitals can be either orthogonal or non-orthogonal

[1] **F. Weinhold, C. R. Landis**, in '*Valency and Bonding: A Natural Bond Orbital
   Donor-Acceptor Perspective*'; **Cambridge U. Press,** 2005, and references cited therein

NON-ORTHOGONAL vs ORTHOGONAL ORBITALS

PNAOs $\xrightarrow{\text{O.W.S.O.}}$ NAOs

PNHOs $\xrightarrow{\text{O.W.S.O.}}$ NHOs (hybrid valence) etc ...
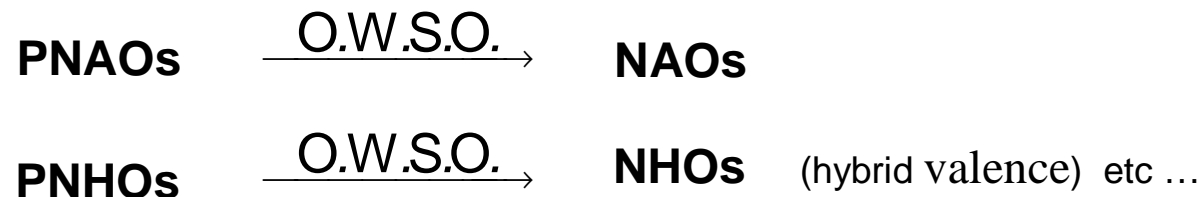
► π – Bonds : Both orthogonal and non-orthogonal orbitals are appropriate, providing the same conceptual pictures [1,2]

► σ – Bonds : For VB-type descriptions more appropriate are the (non-orthogonal) PNAOs, or, better, the PNHOs.

Note : The NBOs are appropriate for both π – Bonds and σ – Bonds.

[1] K. Hirao, H. Nakano, K. Nakayama J. Chem. Phys. 1997, 107, 9966
[2] P. Karafiloglou   J. Chem. Phys. 130 (2009) 164103
     P. Papanikolaou, P. Karafiloglou J. Phys. Chem. A 2008, 112 8839
     P. Karafiloglou, J. Phys. Chem. A 2001, 105, 4524

An intriguing Epistemological problem:

Although the chemical formula has been introduced before the development of Quantum Theory, remains (and will remain) a basic stone for Chemical Sciences !

Question: ***In which degree the traditional chemical formula describes correctly the physical (quantum) reality*** [1] ?

Quantum Probabilities for chemical formulae:
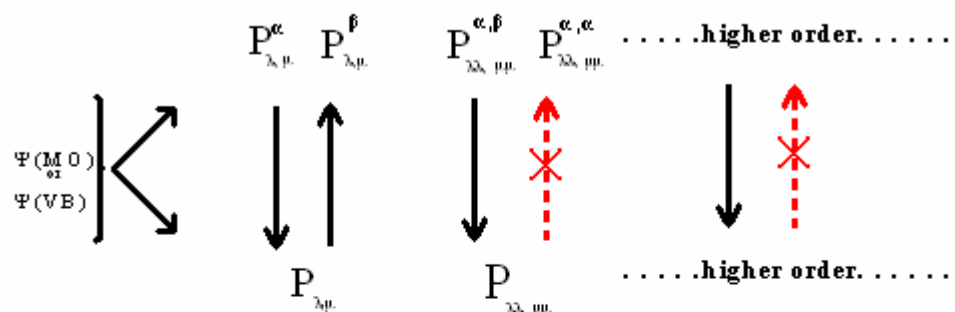
In each chemical formula we associate a Quantum Probability, $P_{N;0}$, i.e. a factor ranging to [0,1] :

$$P_{N;0} \quad \rightarrow \quad 1$$
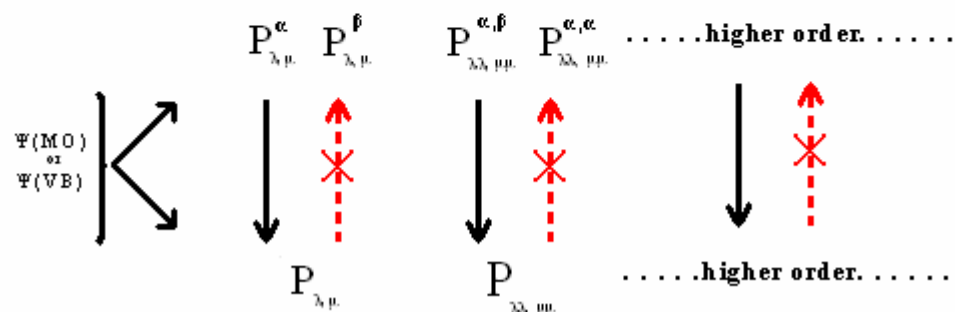$$\text{Chemical formula} \rightarrow \text{Physical Reality}$$

[1][A **NBO-based probability, $P_{N;0}$** , provides a quantitative measure of this degree]

Spin-dependent or spin-independent Population Analysis?

Closed shell systems:

$$P^{\alpha}_{\lambda,\mu} \quad P^{\beta}_{\lambda,\mu} \qquad P^{\alpha,\beta}_{\lambda\lambda,\mu\mu} \quad P^{\alpha,\alpha}_{\lambda\lambda,\mu\mu} \quad \ldots\ldots\text{higher order}\ldots\ldots$$

$\Psi(MO)$ or $\Psi(VB)$

$$P_{\lambda\mu} \qquad\qquad P_{\lambda\lambda,\mu\mu} \qquad \ldots\ldots\text{higher order}\ldots\ldots$$

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$\Psi(MO)$ or $\Psi(VB)$

$$P_{\lambda\mu} \qquad\qquad P_{\lambda\lambda,\mu\mu} \qquad \ldots\ldots\text{higher order}\ldots\ldots$$

Only for the 1-RDM (and for closed shell systems) one can use spin-free populations

For higher order RDM it is worthwhile to use spin-dependent populations