

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

A ‘theoretical Microscope’ to explore VB-type local structures.

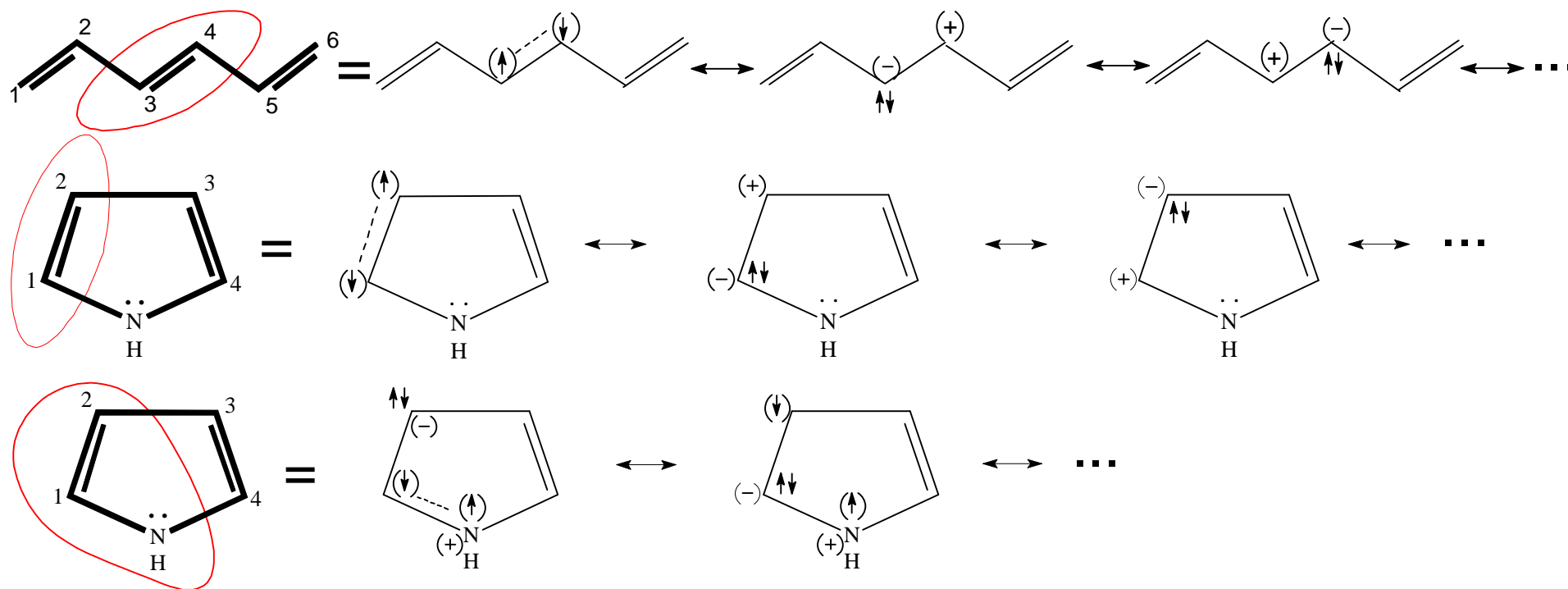
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PEPA or (Natural) NPEPA:
Population analysis for both electrons and electron-holes

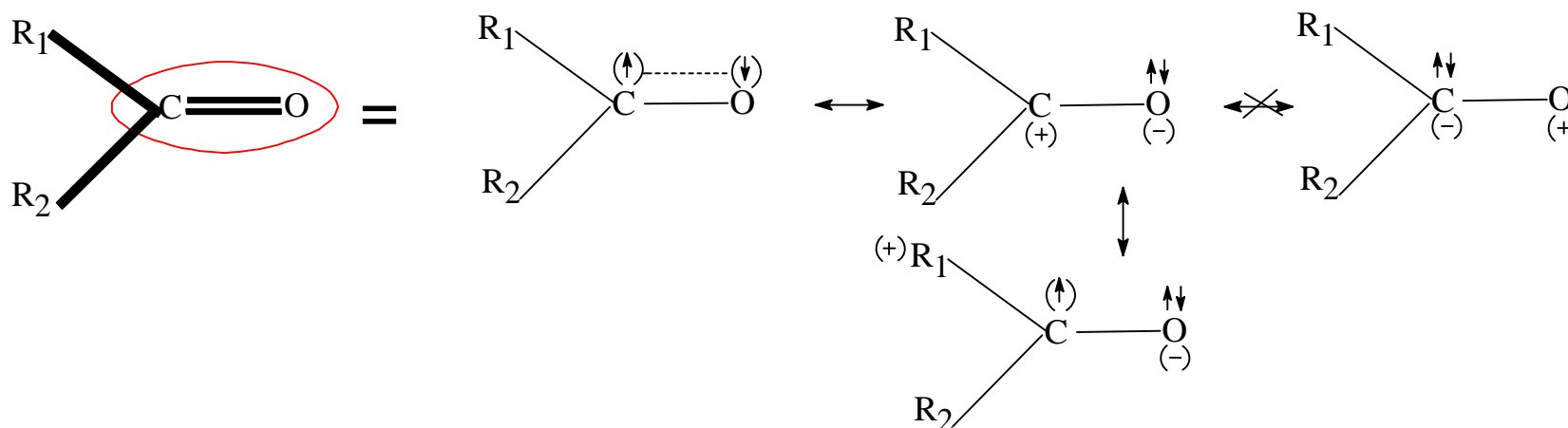
P. Karafiloglou *J. Chem. Phys.* [130](#) (2009) 164103

P. Papanikolaou, P. Karafiloglou *J. Phys. Chem. A* [112](#) (2008) 8839

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



Placing *functional groups* 'under the microscope'



METHOD

Extract a local information from a delocalized $\Psi(\text{MO})$:

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



- Elaboration of $\Psi(\text{MO})$ within MOFFITT's theorem

($\Psi(\text{MO}) \rightarrow \Psi(\text{TL})$)

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

(include electron holes)

DELOCALIZED $\Psi(\text{MO})$

$$\Psi(\text{MO}) = \sum_I^{\text{CI}} C_I |D_I|$$

$$|D_I| = \left\| \psi_{i_1} \dots \psi_{i_n} \bar{\psi}_{i_1} \dots \bar{\psi}_{i_n} \right\|$$

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

OR

One Slater Determinant, D_I , involving

the delocalized **Kohn-Sham** orbitals, ψ_{i_1}

TOTALLY LOCAL $\Psi(\text{TL})$

$$\Psi(\text{TL}) = \sum_K T_K |\Phi_K|$$

$$|\Phi_K| = \left\| \Phi_{k_1^\alpha} \dots \Phi_{k_{i_\alpha}^\alpha} \bar{\Phi}_{k_1^\beta} \dots \bar{\Phi}_{k_{i_\beta}^\beta} \right\|$$

MOFFITT's theorem

$$\underline{\underline{\Psi(\text{MO}) = \Psi(\text{TL})}}$$

Decomposition of MO-Slater determinants:

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

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

$$T_K = \sum_I^S C_I T_K^I$$

DENSITY OPERATORS

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

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

or $\mathbf{E} + \mathbf{H}$ spin-orbitals:

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

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

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

$$\begin{aligned} P_{\mathbf{E};\mathbf{H}}(\varphi_{\lambda_1} \cdots \varphi_{\lambda_E} ; \varphi_{\mu_1} \cdots \varphi_{\mu_H}) &= \langle \Psi(\text{TL}) | \hat{\rho}_{\mathbf{E};\mathbf{H}} (\varphi_{\lambda_1} \cdots \varphi_{\lambda_E} ; \varphi_{\mu_1} \cdots \varphi_{\mu_H}) | \Psi(\text{TL}) \rangle = \\ &= \sum_{\mathbf{K}(\neq \varphi_{\mu_1} \cdots \varphi_{\mu_H})}^{(\varphi_{\lambda_1} \cdots \varphi_{\lambda_E})} W(\Phi_{\mathbf{K}}) \end{aligned}$$

Where $\sum_{\mathbf{K}(\neq \varphi_{\mu_1} \cdots \varphi_{\mu_H})}^{(\varphi_{\lambda_1} \cdots \varphi_{\lambda_E})}$ 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

$$W(\Phi_{\mathbf{K}})$$

is the **weight** of the local Slater determinant $|\Phi_{\mathbf{K}}|$, depending on the (non-) orthogonality of orbitals.

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

(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:

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

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

Summary

The generalized Poly-Electron Population Analysis (PEPA)

requires very simple (formally) equation:

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

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

In medium size systems:

Exponential scaling of computational difficulties with the system size !



Efficient calculation of $P_{E;H}$ without approximations:

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

(B) The *hole-expansion* methodology

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

(A) Mixed local-non-local Slater determinants [1]

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), $|D_I|$

$$|D_I| = \|\psi_{i_1} \dots \psi_{i_N}\|$$

← non-local →

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

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

← local → ← non-local →

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

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

Generalizing the Moffitt’s theorem we obtain:

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

Only this part is useful to calculate
 $\langle \Psi(\text{MO}) | \hat{\rho} | \Psi(\text{MO}) \rangle$

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

Efficient calculation of $P_{E;H}(\varphi_{\lambda_1} \dots \varphi_{\lambda_E}; \varphi_{\mu_1} \dots \varphi_{\mu_H})$ (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.):

$$P_{0;H}(0; \varphi_{\mu_1} \dots \varphi_{\mu_H}) = \sum_I^{CI} C_I^* \sum_I^{CI} C_I \langle D_I | D_I^H \rangle$$

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

$$|D_I\rangle = \|\psi_{i_1} \dots \psi_{i_N}\|$$

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

$$|D_I^H\rangle = \|\psi_{i_1}^H \dots \psi_{i_N}^H\|$$

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

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

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

$$\langle D_I | D_I^H \rangle = \begin{vmatrix} \langle \psi_{i_1} | \psi_{i_1}^H \rangle & \dots & \langle \psi_{i_1} | \psi_{i_N}^H \rangle \\ \vdots & & \vdots \\ \langle \psi_{i_N} | \psi_{i_1}^H \rangle & \dots & \langle \psi_{i_N} | \psi_{i_N}^H \rangle \end{vmatrix}$$

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

$$P_{1;0}(\varphi_{\lambda_1};0) = 1 - P_{0;1}(0\varphi_{\lambda_1}) \quad \text{[a trivial example of a hole-expansion issued from the first order anticommutation relation]}$$

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

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

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

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

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

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:

$$P_{E;H}(\varphi_{\lambda_1} \dots \varphi_{\lambda_E};\varphi_{\mu_1} \dots \varphi_{\mu_H}) = P_{0;H}(0;\varphi_{\mu_1} \dots \varphi_{\mu_H}) + \\ + \sum_{q=1}^E (-1)^q \sum_{j_1 < \dots < j_q}^{\Lambda} P_{0;q+H}(0;\varphi_{j_1} \dots \varphi_{j_q} \varphi_{\mu_1} \dots \varphi_{\mu_H})$$

ALGORITHM: Library of hole-structures

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

$$\Psi(\text{VB}) \longrightarrow \Psi(\text{TL})$$

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



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

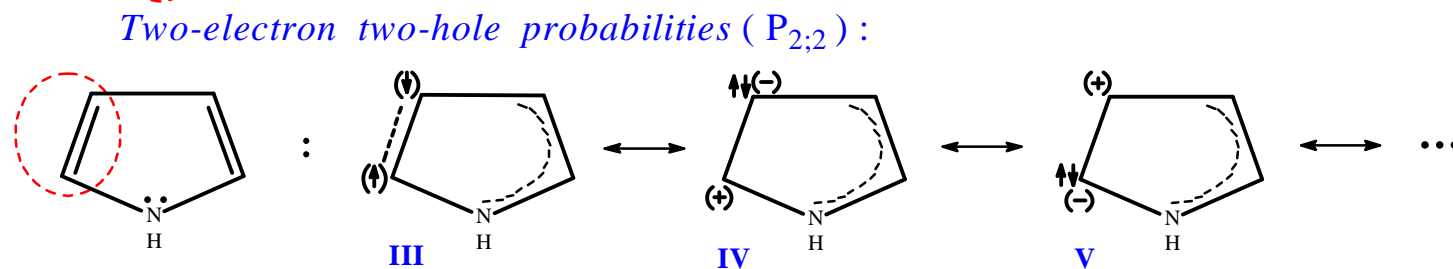


Poly-Electron Population Analysis of VB wave functions

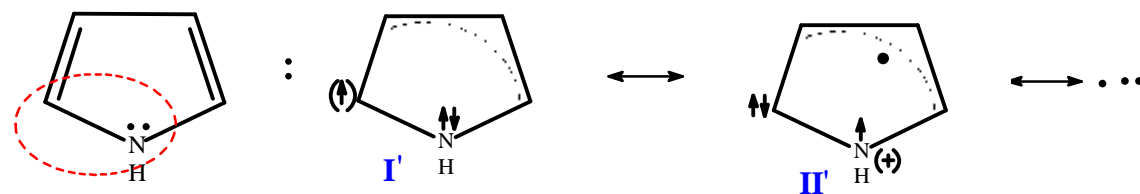
Two-electron
probability ($P_{2;0}$):



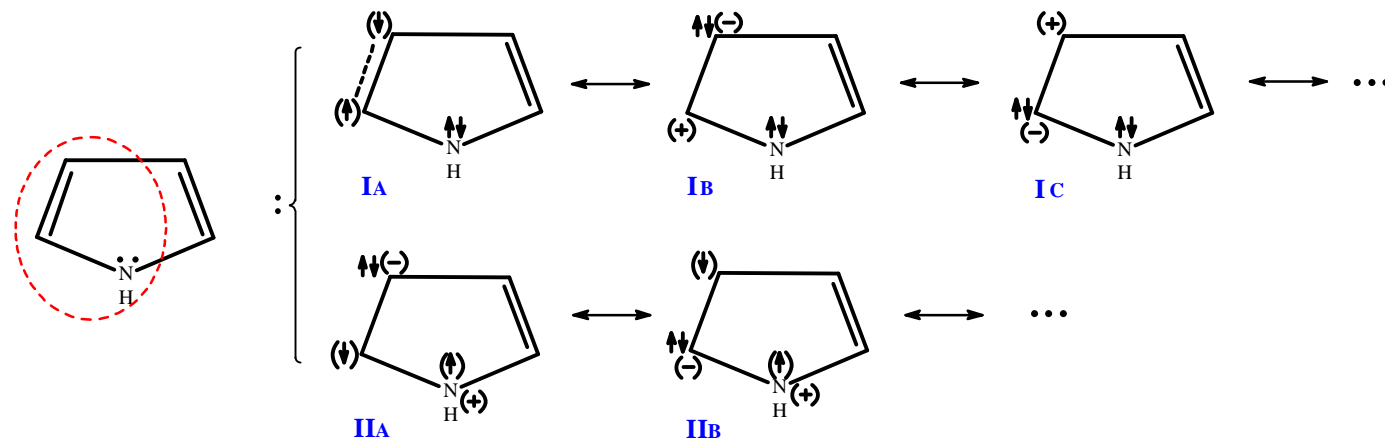
One-electron one-hole
probability ($P_{1;1}$):



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



Four-electron two-hole probabilities ($P_{4;2}$):



Relationships between local structures

The *electron-expansion* methodology [1]

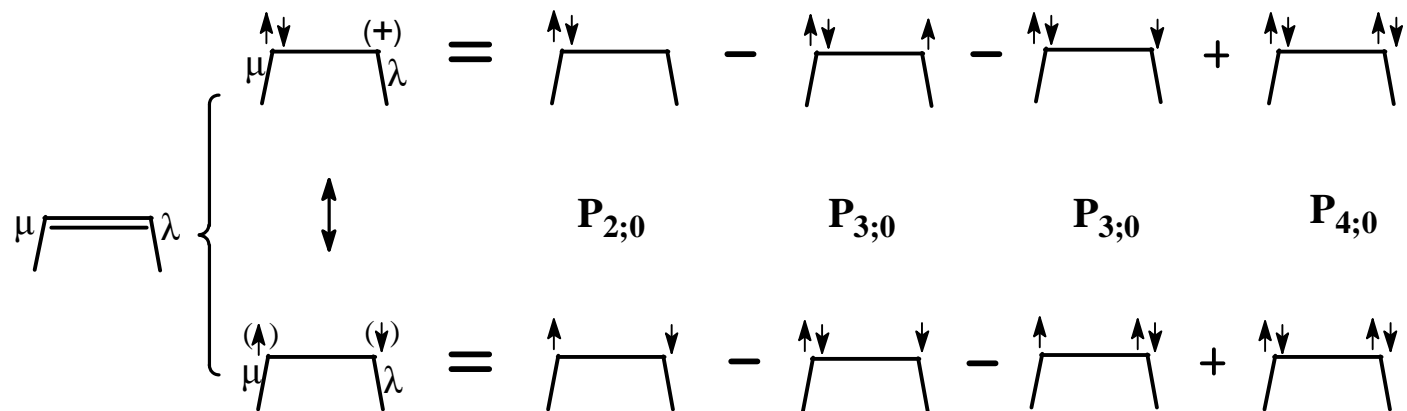
(Expand the holes in terms involving only electrons)

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

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

$$\text{where } P_{2,2}(\mu, \bar{\mu}; \nu, \bar{\nu}) = \sum_{\mathbb{K}(\neq \nu, \bar{\nu})}^{(\mu, \bar{\mu})} W(\Phi_{\mathbb{K}}) \quad \text{and} \quad P_{2,2}(\mu, \bar{\nu}; \bar{\mu}, \nu) = \sum_{\mathbb{K}(\neq \bar{\mu}, \nu)}^{(\mu, \bar{\nu})} W(\Phi_{\mathbb{K}})$$

... etc ...



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

The 4th order anticommutation relation

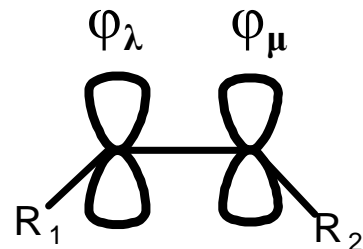
$$\prod_{i=1}^4 (a_i^+ a_i + a_i a_i^+) = 1$$

involves 16 terms :

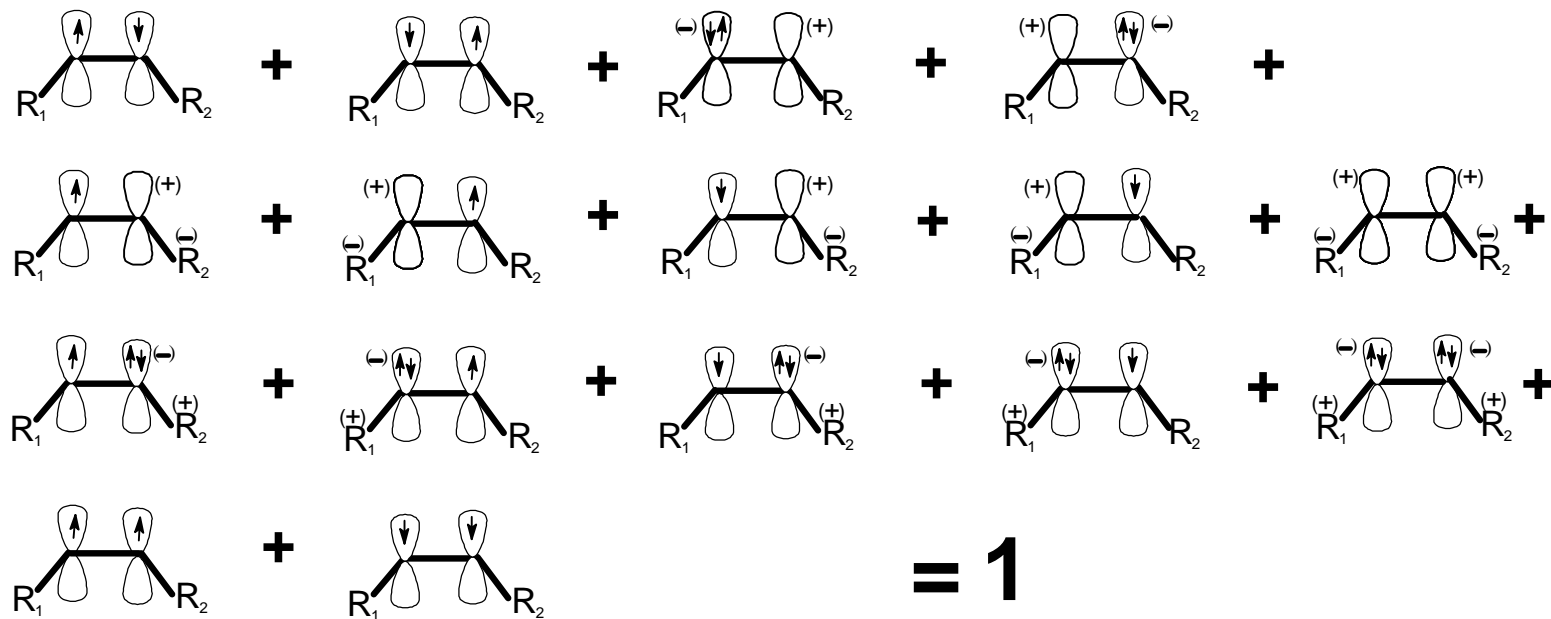
$$\begin{aligned} & a_1^+ a_4^+ a_2 a_3 a_3^+ a_2^+ a_4 a_1 + a_2^+ a_3^+ a_1 a_4 a_4^+ a_1^+ a_3 a_1 + a_1^+ a_2^+ a_3 a_4 a_4^+ a_3^+ a_2 a_1 + \\ & + a_3^+ a_4^+ a_1 a_2 a_2^+ a_1^+ a_4 a_3 + \\ & + a_1^+ a_2 a_3 a_4 a_4^+ a_3^+ a_2^+ a_1 + a_3^+ a_1 a_2 a_4 a_4^+ a_2^+ a_1^+ a_3 + a_2^+ a_1 a_3 a_4 a_4^+ a_3^+ a_1^+ a_2 + \\ & + a_4^+ a_1 a_2 a_3 a_3^+ a_2^+ a_1^+ a_4 + a_1 a_2 a_3 a_4 a_4^+ a_3^+ a_2^+ a_1^+ + \\ & + a_1^+ a_3^+ a_4 a_2 a_2^+ a_4 a_3 a_1 + a_1^+ a_2^+ a_3^+ a_4 a_4^+ a_3 a_2 a_1 + a_2^+ a_3^+ a_4 a_1 a_1^+ a_4 a_3 a_2 + \\ & + a_1^+ a_2^+ a_4 a_3 a_3^+ a_4 a_2 a_1 + a_1^+ a_2^+ a_3^+ a_4 a_4^+ a_3 a_2 a_1 + \\ & + a_1^+ a_3^+ a_2 a_4 a_4^+ a_2^+ a_3 a_1 + a_2^+ a_4 a_1 a_3 a_3^+ a_1^+ a_4 a_2 = 1 \end{aligned}$$

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

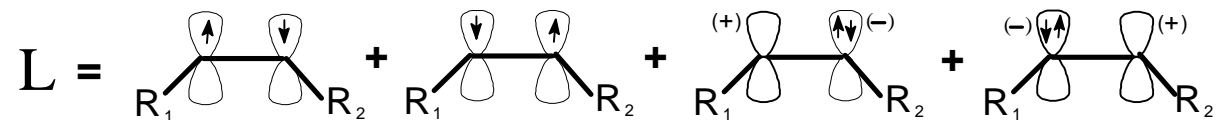
$$i = 1 \rightarrow \varphi_\lambda, \quad i = 2 \rightarrow \bar{\varphi}_\lambda \quad \text{and} \quad i = 3 \rightarrow \varphi_\mu, \quad i = 4 \rightarrow \bar{\varphi}_\mu$$



we obtain :



The *bond localization* (L) in VB language:



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:

$$C(\lambda, \lambda) = P_2(\lambda, \lambda) - P_1(\lambda)^2$$

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



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:

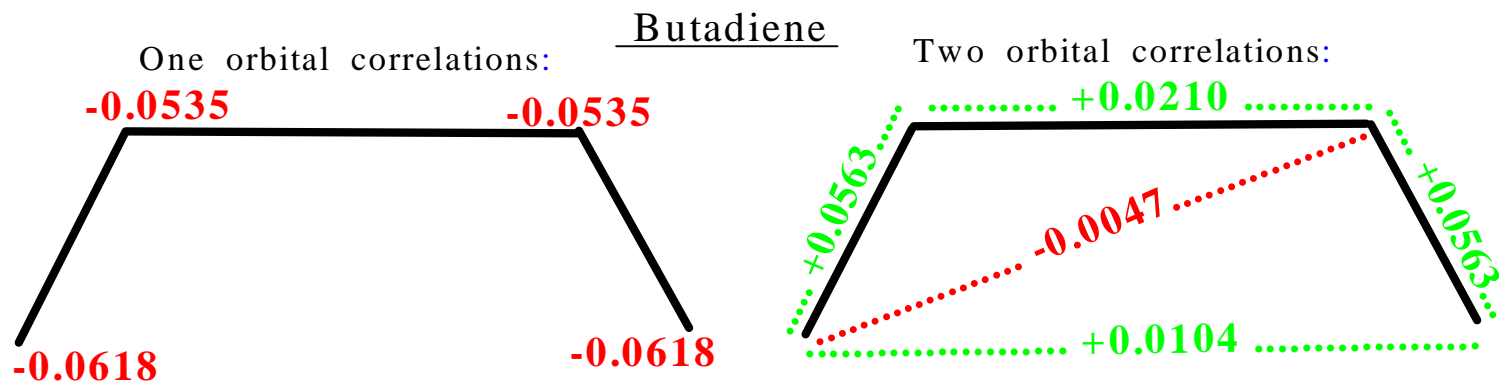
$$C(\lambda, \mu) = P_2(\lambda, \mu) - P_1(\lambda) P_1(\mu)$$

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

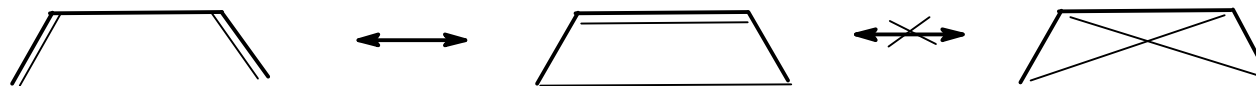
From genuine chemical knowledge:
The chemical bond is a matter of an *electron pair* ($\uparrow\downarrow$)

$C(\lambda, \bar{\mu})$

- positive (> 0) \Rightarrow Favorable pairing ($\uparrow\downarrow$) / Favorable bonding between $\varphi_\lambda, \varphi_\mu$ / "attractive"
 $\uparrow \dots \downarrow$
- zero** \Rightarrow no bonding (e.g. long range interactions)
- negative (< 0) \Rightarrow Unfavorable pairing ($\uparrow\downarrow$) / Unfavorable bonding between $\varphi_\lambda, \varphi_\mu$ / "repulsive"
 $\uparrow \dots \downarrow$



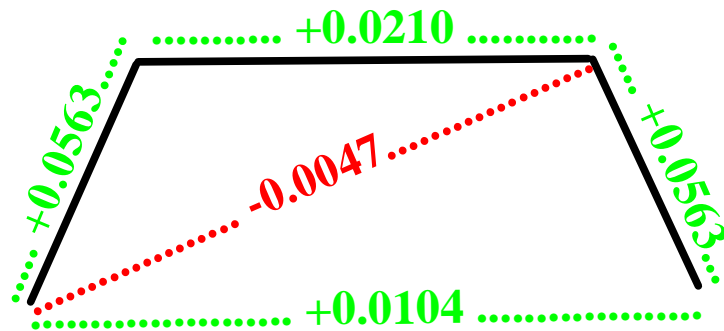
This corroborates with the V.B. description of butadiene:



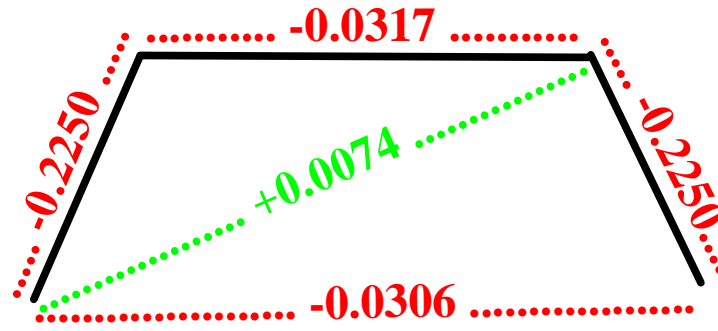
For a given φ_λ :

$$\sum_{\bar{\mu}} C(\lambda, \bar{\mu}) = 0$$

Coulomb ($\uparrow\downarrow$):



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

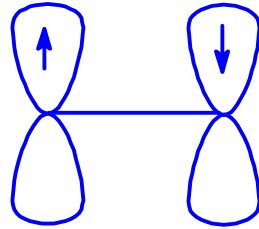


The absolute values of Fermi are greater than the Coulomb correlations
(this holds without any exception)

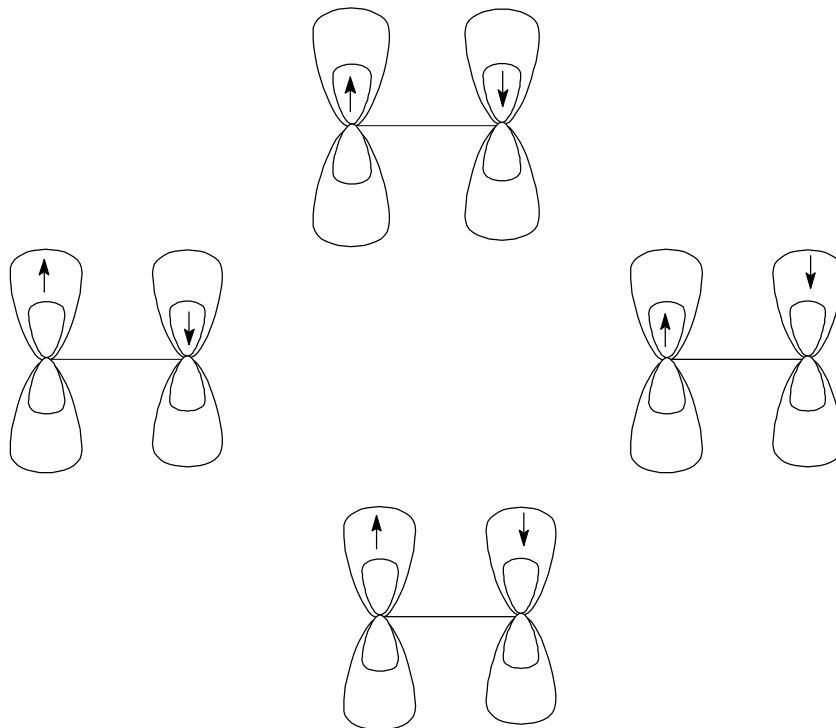
Note: Methods based on the behaviour of parallel spins (c.f. to Pauli Principle)

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

The covalent bonding is between 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



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

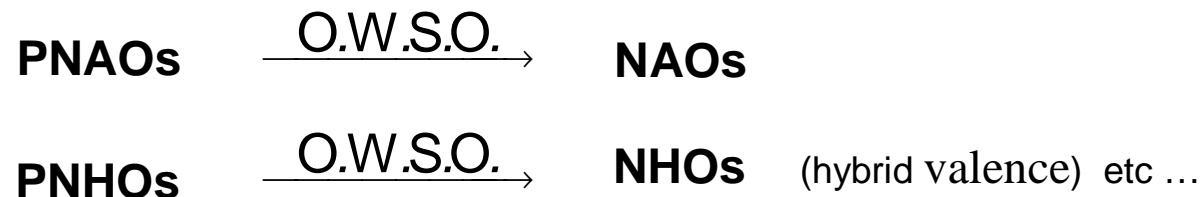
A very good solution:

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



- ▶ π – Bonds : Both orthogonal and non-orthogonal orbitals are appropriate, providing the same conceptual pictures [1,2]
- ▶ σ – Bonds : For VB-type description 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. Papanikolaou, P. Karafiloglou *J. Phys. Chem. A* 2008, 112, 8839

P. Karafiloglou, J. P. Launay *J. Phys. Chem. A* 1998, 102, 8004

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 $[0,1]$:

$$\begin{array}{ccc} P_{N;0} & \rightarrow & 1 \\ \text{Chemical formula} & \rightarrow & \text{Physical Reality} \end{array}$$

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

A reminder:

The Coulomb correlations included in valence NAO or (PNAO) is **negative**

The Coulomb correlations between two valence in valence NAO or (PNAO) of a bond is **positive**

⇒ The Coulomb correlations, $C(\omega^\alpha \omega^\beta)$, included in bonding NBO, ω , is **small**.

(A) For a totally localized (isolated) bond, $C(\omega^\alpha \omega^\beta) = 0$

(the more localized is the bonding orbital, ω , the closer to zero is Coulomb correlation included in ω .)

(B) Since a NBO is Natural in the Lowdin sense ⇒ it has the maximum occupation that a bonding orbital can have inside a given molecular environment.

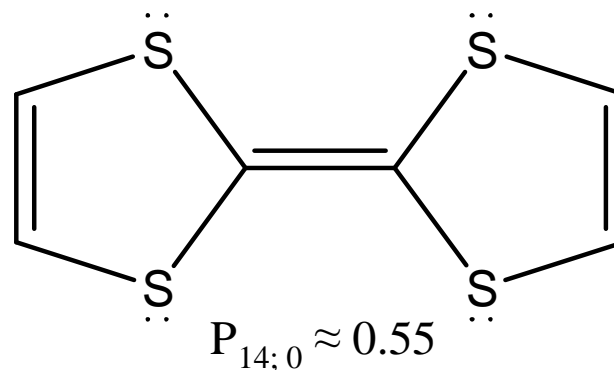
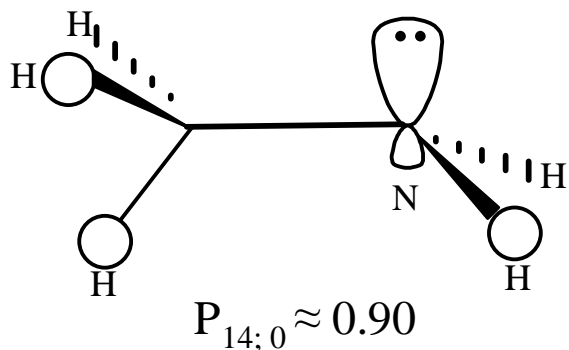
(A) and (B) ⇒ The Coulomb correlation included in a NBO is maximum ⇒

The NBO Lewis structure is a quantum description which is the closest possible to the chemical formula

The probability of finding an electron pair in NBO ω_1 simultaneously an electron pair in ω_2 ... an electron pair in $\omega_{N/2}$, is obtained from NPEPA:

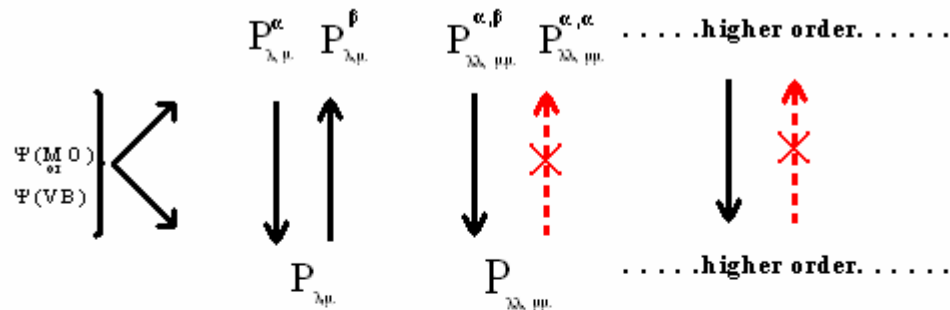
$$P_{N;0}(\omega_1 \omega_1 \omega_1 \omega_1 \dots \omega_{N/2} \omega_{N/2}) = \langle \Psi | \hat{\rho}_{\text{NBO}} | \Psi \rangle$$

Example: 14 electrons, 7 pairs:

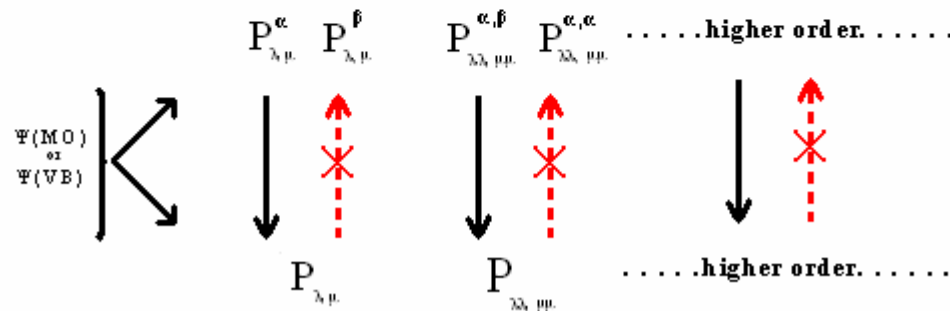


Spin-dependent or spin-independent Population Analysis?

Closed shell systems:



Open shell systems:



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

Information provided by PEPA and VB methods

1. **VB** : Spin-independent structures (\Leftarrow spin-eigenfunctions)

PEPA: Spin-dependent structures (\Leftarrow single Slater determinants)

2. **VB** : Provides a weight of a N-electron structure (N= total number
of electrons)

PEPA: Provides a sum of weights of N-electron structures

$$P_{2;0}(\mu, \bar{\mu}; 0) = \sum_K^{(\mu, \bar{\mu})} W(\Phi_K)$$

	Orthogonal orbitals	Non-orthogonal orbitals
1	Probability of finding simultaneous two α, β electrons	X
2	Number of electron pairs (among the $N^\alpha N^\beta$)	
3	Sum of VB weights = The weight of a local structure (while the remaining electrons can reside anywhere else)	