Physics of electron correlation

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Introduction

Aims of this lecture :

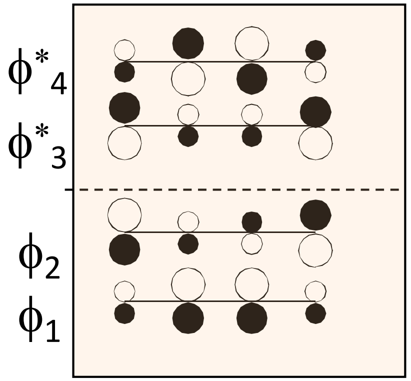
- Provide an understanding of the physical content of electron correlation separating various types of effects as they appear in a wave function based approach
- Discuss briefly the levels of theoretical description required to treat these effects
- Show the benefit of playing with the schizophrenia (or bilingualism) of quantum chemists, i.e. using both localized MOs (Valence Bond) and delocalized (Sym. Adapted MOs) orbitals

Outline

Preliminary. The various languages of chemists: localized versus delocalized orbitals

1. The role of antisymmetrization (Fermi hole)
2. The Coulomb hole : a utopia?
3. Atomic correlation. Two electrons in an atomic orbital : radial and angular dynamic correlation
4. Molecular correlation in two-active-electron problems.
    - i) Two electrons in a bond orbital : left-right non-dynamic correlation (H_2 catastroph)
    - ii) Beyond the CAS : dynamic effects
        - a)Dynamic polarization effect in H_2. Role of the 1p and 2p excitations
        - b) Dynamic polarization effect in F_2. Role of the 1h1p excitations.
        - c) Charge and spin polarizations in magnetic systems (Cu_2 complex): Role of the 1h1p excitations.
        - d) Role of other excitations (2h, 2p, 2h1p, 1h2p) in magnetic systems.
        - e) Role of inactive double excitations (2h2p).
5. Molecular correlations in multiple bonds.
    - i) Physical content of non-dynamic correlation in N_2: charge and spin orders.
    - ii) Dynamic correlation effects in N_2: Revision of the CAS components.
    - iii) Extension to magnetic systems.
6. Molecular correlations between adjacent and remote bonds
7. Molecular correlations between adjacent and remote bonds and origin of dispersion
8. Extended systems

Preliminary : the various languages of chemists

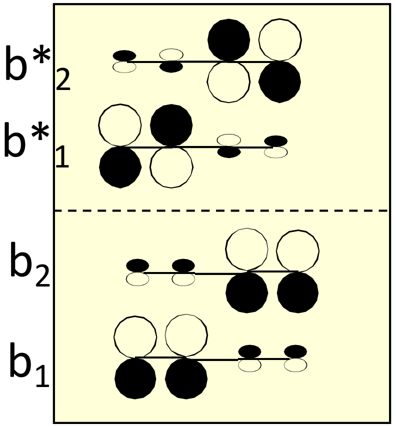


SA-MO

A) Delocalized MOs :

Often the language of theoreticians. The MO solutions of the Fock operator (canonical MOs) are symmetry adapted (SA-MO): they account for the symmetry of the compounds. Owing to the Koopmans theorem (and compensation errors), they give a good approximation of the ionization potential.

$$\Psi_0 = \left|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\right|$$

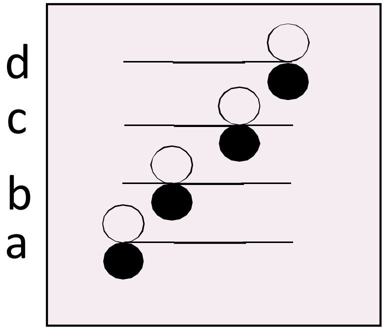


Bond MOs

B) Bond molecular orbitals and lone pairs: Lewis

Often the language of experimentalists. These MOs are obtained by rotations of the occupied SA-MOs. The Slater determinant is unchanged. All observables calculated on this determinant have the same values.

$$\Psi_0 = \left|b_1\bar{b}_1b_2\bar{b}_2\right|$$

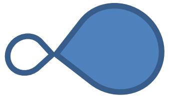


AO

C) Atomic orbitals (orthogonalized OAOs or not AOs)

Used in Valence Bond (VB) (orthogonalized or not).

The orthogonal atomic orbitals (OAO) are obtained by rotations of the SA-MOs (occupied and virtual). Due to the mixing between occupied and virtual orbitals, the function Ψ_0 becomes a linear combination of VB determinants expressed using these orbitals.



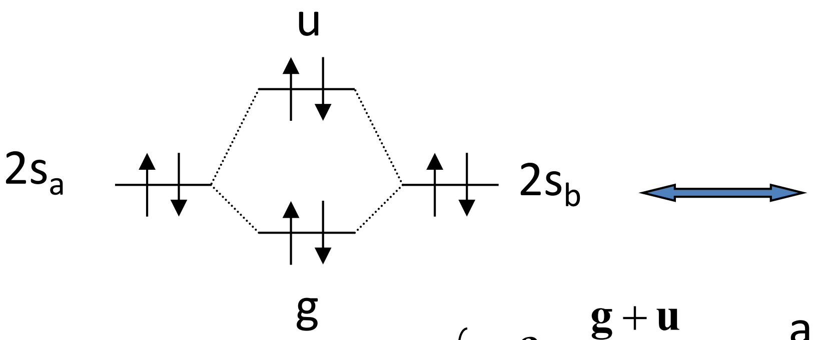
D) And others (orthogonalized hybrid orbitals)

The analysis of the physical content of a wave function often requires to use localized orbitals: definition of the magnetic orbitals

The wave functions (orbitals) of the Fock operator are symmetry adapted, they are delocalized if the molecule is symmetric.

However Ψ_0 is invariant under rotation between occupied MOs.

Ex : Be$_2$

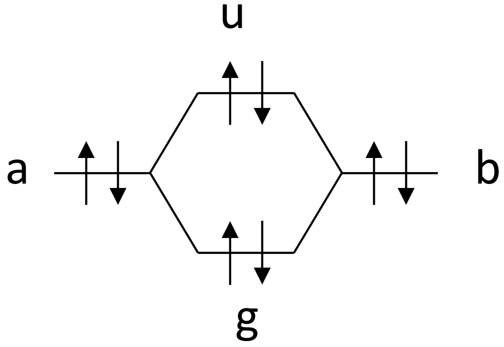


Compatibility with Lewis

|Be Be|

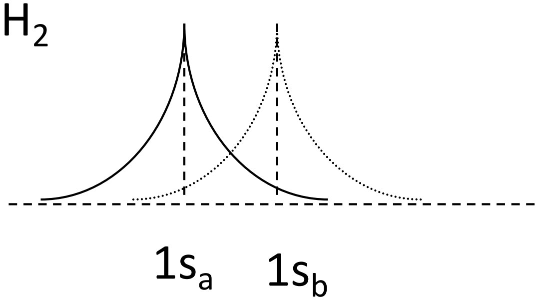
$$\Psi_0 = |g\bar{g}u\bar{u}| = |a\bar{a}b\bar{b}| \quad \text{where} \quad \begin{cases} \mathbf{a} = \dfrac{\mathbf{g}+\mathbf{u}}{\sqrt{2}} \\ \mathbf{b} = \dfrac{\mathbf{g}-\mathbf{u}}{\sqrt{2}} \end{cases}$$

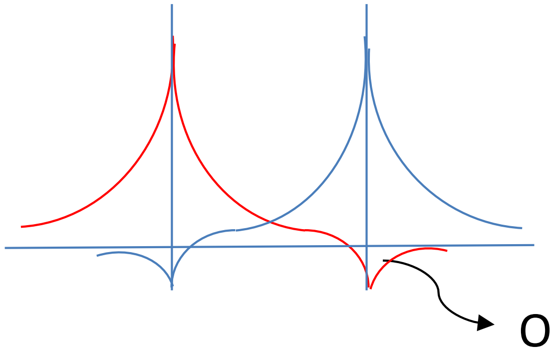
a and b have
a higher energy
than
2s$_a$ and 2s$_b$



a and b are called the magnetic orbitals : they are localized and orthonormalized.

Ex : H$_2$





1) The preliminary work of antisymmetrization

Electron correlation energy is defined as the energy difference between the Hartree Fock solution and the exact one.

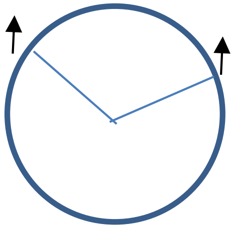
As we will see, electron correlation introduces charge order and spin fluctuation.

In this respect, the antisymmetrization which restores the antisymmetric nature of the wavefunction (Pauli principle) and the undiscernability of the electron already introduces some order.

The local Fermi hole ($P(\mathbf{r}_1,\mathbf{r}_2)= 0$ when $\mathbf{r}1=\mathbf{r}2$ for electrons of same spin), but not only.

i) Example : In the triplet 2s3s of beryllium : the function is zero (node) when $r_1=r_2$

$$ {}^3S_{Ms=1} = \frac{1}{\sqrt{2}}\left(2s(\mathbf{r}_1)3s(\mathbf{r}_2) - 2s(\mathbf{r}_2)3s(\mathbf{r}_1)\right) $$



and this is also true for the Ms=0 component.

Interlude : let us have a look to the physics of the beryllium excited states…

Spatial nature of both excited singlet and triplet S states of beryllium

$$^{1}\Psi_{Ms=0} = \frac{1}{\sqrt{2}}\left|2s(\mathbf{r}_1)3\bar{s}(\mathbf{r}_2) + 3s(\mathbf{r}_1)2\bar{s}(\mathbf{r}_2)\right|$$

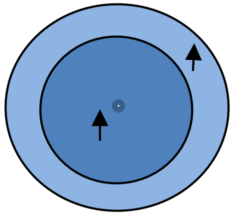
Introducing the more diffuse s’ and more concentrated s” orbitals:

$$s' = \frac{1}{\sqrt{2}}(2s + 3s) \quad and \quad s'' = \frac{1}{\sqrt{2}}(2s - 3s)$$

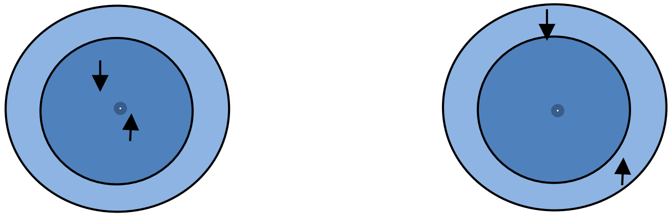
One gets :

$$^{3}S_{Ms=1} = \frac{1}{\sqrt{2}}\left(s'(\boldsymbol{r}_1)s''(\boldsymbol{r}_2) - s'(\boldsymbol{r}_2)s''(\boldsymbol{r}_1)\right)$$

$$^{1}S_{Ms=0} = \frac{1}{\sqrt{2}}\left|s'(\boldsymbol{r}_1)\bar{s}'(\boldsymbol{r}_2) - s''(\boldsymbol{r}_1)\bar{s}''(\boldsymbol{r}_2)\right|$$



The electrons are far apart in the triplet

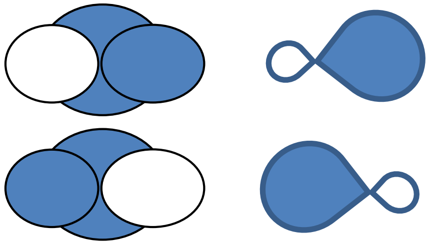


The electrons alternate between close positions and far positions in the singlet

Spatial nature of both excited singlet and triplet P states of beryllium

$$^3P_{Ms=1} = \frac{1}{\sqrt{2}}\left(2s(\mathbf{r}_1)2p(\mathbf{r}_2) - 2s(\mathbf{r}_2)2p(\mathbf{r}_1)\right) \qquad ^1P_{Ms=0} = \frac{1}{\sqrt{2}}\left|2s(\mathbf{r}_1)2p(\mathbf{r}_2) + 2s(\mathbf{r}_2)2p(\mathbf{r}_1)\right|$$

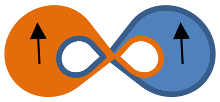
Introducing the left h_l and right h_r hybrid orbitals:



$$h_l = \frac{1}{\sqrt{2}}(2s + 2p) \quad and \quad h_r = \frac{1}{\sqrt{2}}(2s - 2p)$$

One gets :

$$^3P_{Ms=1} = \frac{1}{\sqrt{2}}\left(h_l(\mathbf{r}_1)h_r(\mathbf{r}_2) - h_l(\mathbf{r}_2)h_r(\mathbf{r}_1)\right) \qquad ^1P_{Ms=0} = \frac{1}{\sqrt{2}}\left|h_l(\mathbf{r}_1)\bar{h}_l(\mathbf{r}_2) - h_r(\mathbf{r}_1)\bar{h}_r(\mathbf{r}_2)\right|$$



Energy difference between the two states: $\Delta E_{ST} = 2K_{sp} = J_{h_l h_l} - J_{h_l h_r}$

NB1: the Exchange in one basis becomes a Coulomb interaction in another basis!

NB2: electron correlation and more particularly the Coulomb hole will play differently in the singlet and the triplet (where there is already a Fermi hole).

Localized versus delocalized MOs: a different language provides a different reading...

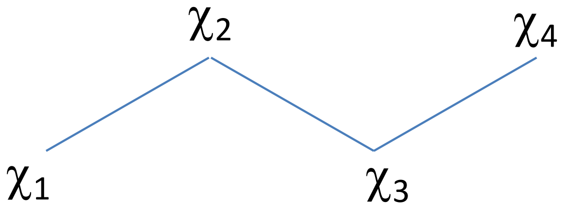
ii) Introducing antsymmetrization on the uncorrelated Hückel model

Chain 1 electron / AO : α and β electrons are independent = 1e$^-$ α for 2 sites

- One diagonalizes the Hückel Hamiltonian matrix in the basis of Valence Bond determinants keeping only the α spins

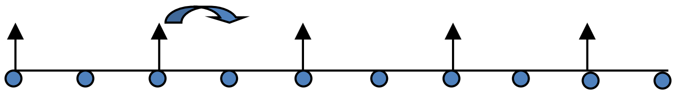
t=β of Hückel:
« hopping» integrals

$$\begin{array}{c} |\chi_1\chi_2| \\ |\chi_1\chi_3| \\ |\chi_1\chi_4| \\ |\chi_2\chi_3| \\ |\chi_2\chi_4| \\ |\chi_3\chi_4| \end{array} \begin{pmatrix} \Delta & t & 0 & 0 & 0 & 0 \\ t & \Delta & t & t & 0 & 0 \\ 0 & t & \Delta & 0 & t & 0 \\ 0 & t & 0 & \Delta & t & 0 \\ 0 & 0 & t & t & \Delta & t \\ 0 & 0 & 0 & 0 & t & \Delta \end{pmatrix}$$



- Which VB determinant has the largest coefficient?

Those having the largest number of interactions (t) with the others: alternation of e$^-$ 1 site over 2.

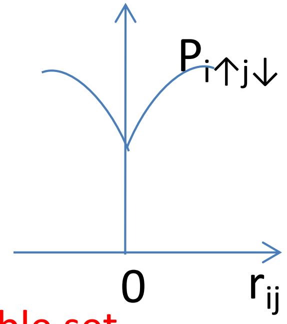


But when introducing the beta spins, one has the same weight of the spin and charge waves:

The antisymmetrization introduces a global « antiferromagnetic » order, but since the α and β spins are independent, there is still a charge disorder.

Electron correlation will restore the correct charge order.

2) The Coulomb hole: a utopia?



The probability to find 2 e- having different M_s in $\mathbf{r}_1$ and $\mathbf{r}_2$, $\rho(\mathbf{r}_1,\mathbf{r}_2)$ shows a cusp in $\mathbf{r}_1=\mathbf{r}_2$
The slope of the hole near the cusp is universal : $+1/R_{12}$.

Impossible to realize if one does not have an orbital with a node at each point of R^3

→ Impossible to realize even with an inifinite basis set as it is an infinite countable set

In practice, one introduces additional orbitals :

- more diffuse orbitals (with higher n values), double, triple ζ (but less diffuse than the spectroscopic ones)
- orbitals with higher l values, said polarization orbitals.

Kutzelnigg: "if one increases the basis set with orbitals of increasing n and l values ($l_{max} = n$) the residual error to the exact correlation energy behaves as $(l_{max})^{-3}$".

One may introduce prefactors in the wavefunction for instance $(1+r_{ij}/2)\Psi_0$, such methods are called explicitly correlated methods.

A broad variety of methods , neither necessarily with the proper cusp nor the proper slope, avoid the electrons to approach too much in the whole space

→ Speeds considerably the convergence of the results as a function of the basis set size.

F. Neese: "The prefactor saves two values of n: Double Zeta with prefactor ≈ Quadruple Zeta"

Hopefully, realizing the Coulomb hole is not crucial for most of the chemical and spectroscopic properties when sufficiently flexible basis sets are used, but to which extent?

Note : Ambiguity in the definition of dynamic correlation

Historically, the term ”dynamic correlation” was dedicated to non valence excitations. Still valid for atoms : dynamic correlation is brought by excitations to non valence virtual orbitals (extended basis set).

“dynamic” comes from the fact that these orbitals have a larger kinetic energy (Sinanoglu early sixties).

Over time “dynamic correlation” has been extended to valence excitations for molecules (out of active space) : dynamic correlation is brought by non reference determinants (charge polarization, spin polarization, etc.)

Nevertheless, while part of dynamic correlation is brought by the use of extended basis set, another contribution comes from valence excitations.

3) Some examples of the role of dynamic correlation in atoms

Radial and angular correlation in atoms

Additional virtual orbitals should stay close to the occupied orbitals to interact with them. They are less diffuse than the spectroscopic orbitals.

Ex: Be : 2 e- in 2s $\Psi_0 = |\mathrm{core}\ 2s2\bar{s}|$

3s concentrated enough for a large effect (K_{2s3s} large)

i) Radial correlation :

di-excitation from $2s\overline{2s}$ to $3s\overline{3s}$

$$\left\langle \Psi_0 \middle| H \middle| \left| core\ 3s\overline{3s} \right| \right\rangle = K_{2s3s} > 0$$

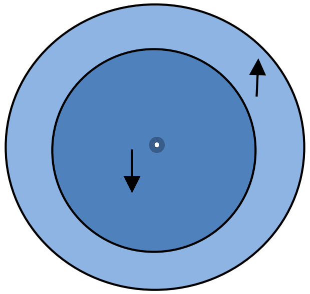
$$\left\langle \Psi_0 \middle| H \middle| \Psi_0 \right\rangle - \left\langle 3s\overline{3s} \middle| H \middle| 3s\overline{3s} \right\rangle < 0$$

$$\Phi = \lambda^2 \Psi_0 - \mu^2 \left| core\ 3s\overline{3s} \right|$$

If one introduces *s'= λ2s +μ3s* (more diffuse) and *s'' = λ2s -μ3s* (less diffuse)

$$\Phi = \left| core.\frac{s'\,\bar{s}'' + s''\,\bar{s}'}{\sqrt{N}} \right|$$

one electron is closer, the other is farer



The role of dynamic correlation is to allow the electrons to avoid each other, as if they were less repulsive than in the Hartree Fock MOs.

ii) Angular correlation :

di-excitation from $2s\overline{2s}$ to $2p_z\overline{2p_z}$

$$\Phi = \gamma^2\Psi_0 - \delta^2\left|core\ 2p_z\overline{2p_z}\right| \longleftarrow$$

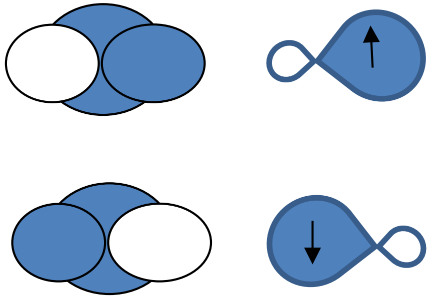
$$\left\langle\Psi_0\middle|H\middle|\left|core\ 2p_z\overline{2p_z}\right|\right\rangle = K_{2s2p_z} > 0$$

$$\langle\Psi_0|H|\Psi_0\rangle - \left\langle 2p_z\overline{2p_z}\middle|H\middle|2p_z\overline{2p_z}\right\rangle < 0$$

Let us introduce : *h=γ2s +δ2p*$_z$, hybrid towards positive z values and

h'= γ2s - δ2p$_z$, hybrid towards negative z values

$$\Phi = \left|core.\frac{h\overline{h}'+h'\overline{h}}{\sqrt{N}}\right|$$



one electron is more in the right region of the nucleus, the other one is more on the left

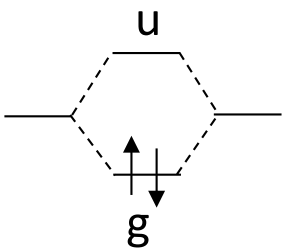
By increasing the basis set one diminishes the repulsion between the electrons and progressively approaches the Coulomb hole

4) Molecular correlation: illustration on the H_2 « desaster »

i. Role of non-dynamic correlations

The treatment of bond breakings crucial in chemical reactivity (bonds break or form).

Dissociation of H_2 in a minimal basis set



Single determinantal description : Slater determinant Ψ_0 built on the sigma MO

$$\Psi_0 = |g\bar{g}| = g(1)g(2)\underbrace{\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\text{Singlet function}}/\sqrt{2}$$

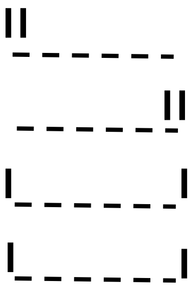
What is the physical content of the Slater determinant Ψ_0 ?

Let us express Ψ_0 in the basis of the localized orbitals a and b :

$$\mathrm{a} = \frac{1}{\sqrt{2}}(\mathrm{g}+\mathrm{u})$$

$$\mathrm{b} = \frac{1}{\sqrt{2}}(\mathrm{g}-\mathrm{u})$$

$$\boxed{|g\bar{g}| = \frac{1}{2}\left(|a\bar{a}| + |b\bar{b}| + |a\bar{b}| + |b\bar{a}|\right)}$$



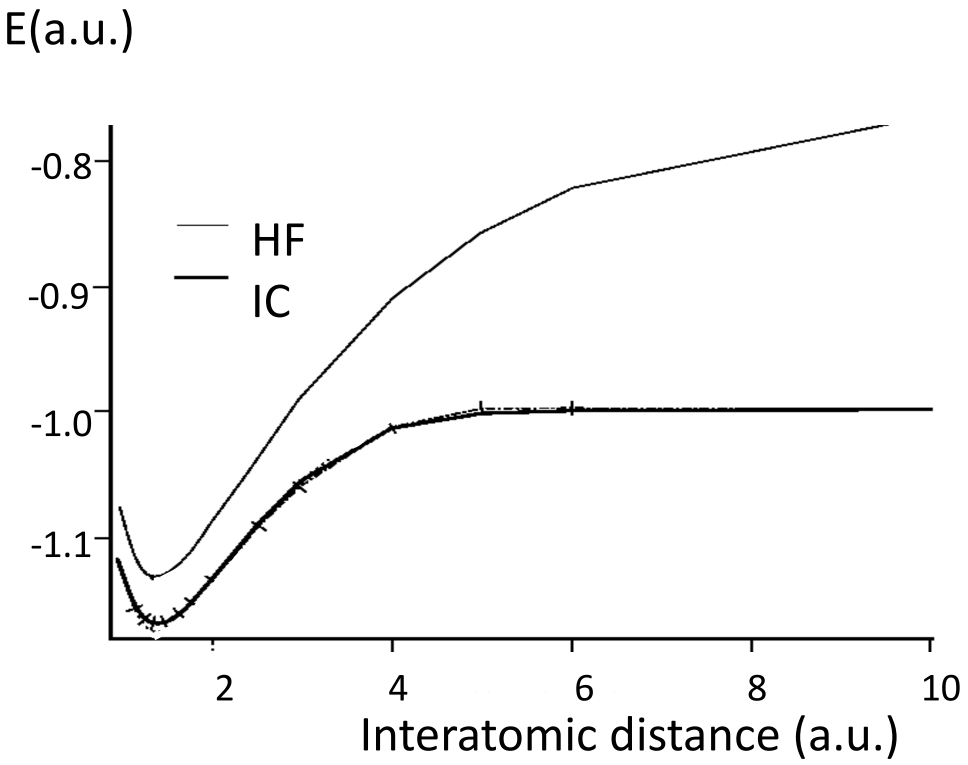
$$\left.\begin{array}{l}|a\bar{a}|\\ |b\bar{b}|\end{array}\right\}\ \text{Ionic forms } H^-\,H^+$$

$$\left.\begin{array}{l}|a\bar{b}|\\ |b\bar{a}|\end{array}\right\}\ \text{Neutral forms } H^\bullet\,H^\bullet$$

The determinant $|g\bar{g}|$ contains the same amount of neutral and ionic forms!

At short distances : the electrons move in a bond and a wavefunction which possesses the same amount of neutral and ionic forms provides reasonable results.

At long distances : when the H_2 bond breaks, each atom recuperates its electron and the ground state wavefunction is dominated by neutral forms.



$(H^{\bullet}+H^{\bullet}+H^{+}+H^{-})/2$

$H^{\bullet}+H^{\bullet}$

M. Grüning, O.V. Gritsenko, and E.J. Baerends.
J. Chem. Phys., 118(16):7183-7192, 2003.

The HFSCF determinant does not have the correct physics at long distances.

Magnetic systems : magnetic centers are far from each other, they interact but do not form a covalent bond (as H_2) :

$Cu^{\bullet}$ -------$Cu^{\bullet}$

The function must have more neutral forms than ionic forms in magnetic systems.

Multideterminantal description : role of non-dynamic correlation (CAS(2,2) for instance)

Restores qualitatively the physics of the problem

The 2e- in 2 MOs CASSCF enables the system to dissociate correctly.
The optimized MOs g and u define “an optimal” valence set.

$$\Phi_0^{CAS} = \lambda|g\bar{g}| - \mu|u\bar{u}|, \quad \lambda > \mu > 0$$

λ/μ decreases and -->1 when the bond is stretched

The CASSCF function may be expressed in an Orthogonal Valence Bond reading.

$$a = \frac{1}{\sqrt{2}}(g+u) \qquad \mathrm{b} = \frac{1}{\sqrt{2}}(\mathrm{g}-\mathrm{u})$$

$$\Phi_0^{CAS} = (\lambda+\mu)(|a\bar{b}| + |b\bar{a}|)/2 + (\lambda-\mu)(|a\bar{a}| + |b\bar{b}|)/2$$

The reading in OAO provides a deeper insight in the physics of electron correlation.

ii. Beyond the CASSCF, “dynamic effects inside and outside the valence”

The CASSCF is supposed to contain the so called static (or non-dynamic) correlation effects.

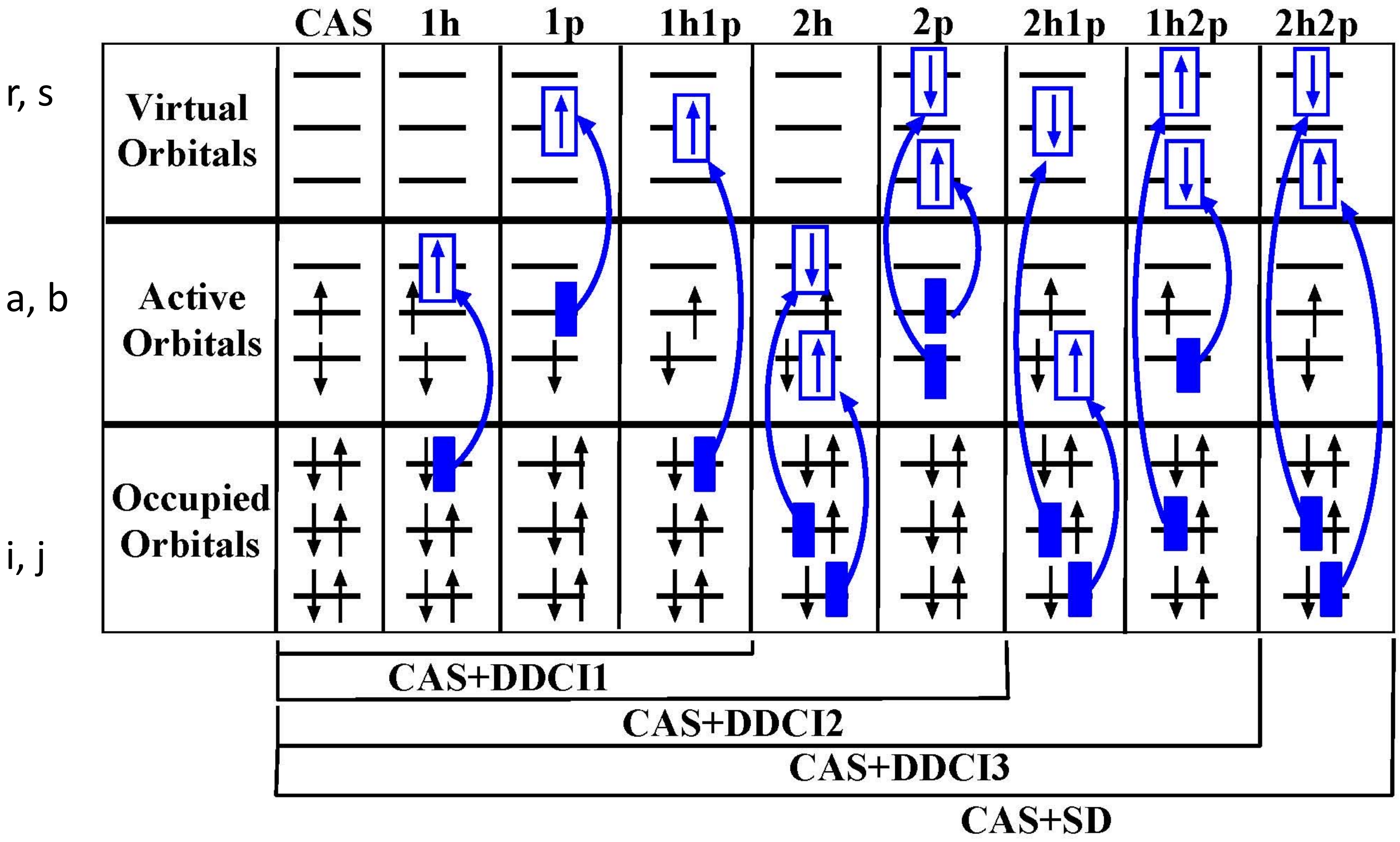
One frequently hears that beyond that, the remaining effects (the so-called dynamic correlations) are short-range correlation effects and essentially the carving of the Coulomb hole.

This vision is misleading: a complex physics takes place at intermediate-range or even long-range, as illustrated in next slides

The leading effects come from double excitations on the top of CAS determinants, necessarily involve inactive occupied (holes) or virtual (particles) MOs: 8 classes, playing different roles

2h-2p
2h-1p and 1h-2p
2h
2p
1h-1p
1h and 1p

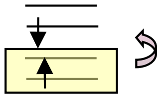
Classes of excitations



DDCI : Difference Dedicated Configuration Interactions

a) Dynamic effects on the active orbitals : illustration in H_2

Dynamic repolarization : effect of the 1p

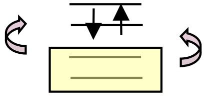


The neutral and ionic components would prefer to have different orbitals, in $|a\bar{a}|$, i.e. A^-B^+, the orbital *a* would be more diffuse and hybridized with $2p_z$ orbital toward the atom B.

Methods:

-“breathing orbitals” (BOVB) in VB approaches (different orbitals for different VB components)

- In OVB-CI, brought by excitations from the active to virtual non-valence MOs, determinant, “1-particle” class (also in MO-CI)

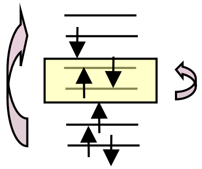


Dynamic correlation : effect of the 2p

In $|a\bar{a}|$ the electrons are close, the 2p diminish their repulsion through double excitations to $|a'\bar{a}'|$, where a’ are 2s-type (radial correlation), or 2p-type (angular correlation) virtual orbitals, “2-particle” class (also in MO-CI)

As in beryllium!!!

b) Dynamic polarization of inactive MOs: illustration in F_2



Single bond σ ($2p_z$), + 6 lone pairs 2s, $2p_x$ and $2p_y$ ⇒ CAS(2,2) 2 e- in 2 MOs : σ_g and σ_u

Bond energy : Experiment=38Kcal/mol

HF =-36Kcal/mol !!

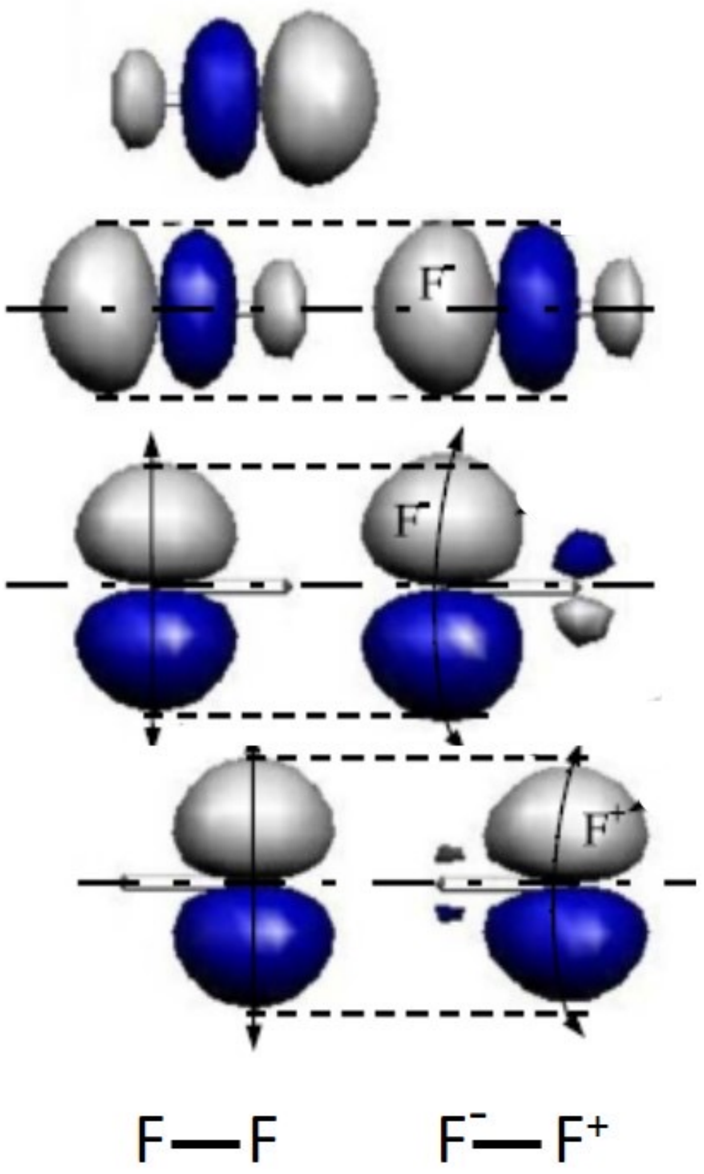
CASSCF 2e- in 2 MO (or 10e- in 6MOs) =11Kcal/mol !

Enlarging the CAS to the lone-pair electrons is useless.

CAS+S=38 Kcal/mol (partly cancellation of errors?)

Dynamic polarization : effect of the 1h1p

(CAS+S) is crucial : specific adaptation of the orbitals to each VB form



The orbital of F$^-$ expands to diminish the repulsion which is increased by the additional electron

The lone pairs of F$^-$ lean in the direction of F$^+$

AOs of F$^+$ lean towards the external side to avoid the F$^-$ center

- ’’Breathing’’ and ’’dynamic distortion’’ of all the valence orbitals

What is required to incorporate such an effect in calculations?

- In Valence Bond: Breathing Orbitals Valence Bond (BOVB) : optimization of the orbitals in the ionic form
- In CI: the 1hole-1particle class of excitations:

1. if one works with equivalent OAOs this effect is brought by the 1h-1p.
For the ionic $\left|core.a\bar{a}\right|$ determinants the field is different from the mean field $\left|core.a\bar{b}\right|$

The electrons of the surrounding electron pairs react to the fluctuation of the field created by the active electrons in the bond, act as supporters

2. if one works with symmetry-adapted MOs this effect is brought by double excitations:

a single excitation $\sigma_g \rightarrow \sigma_u$ in the actives
a single excitation from occupied inactive to virtual inactive 2p→3p and 3d

Feed-back effect of dynamic correlation on the CAS components of the wave-function:

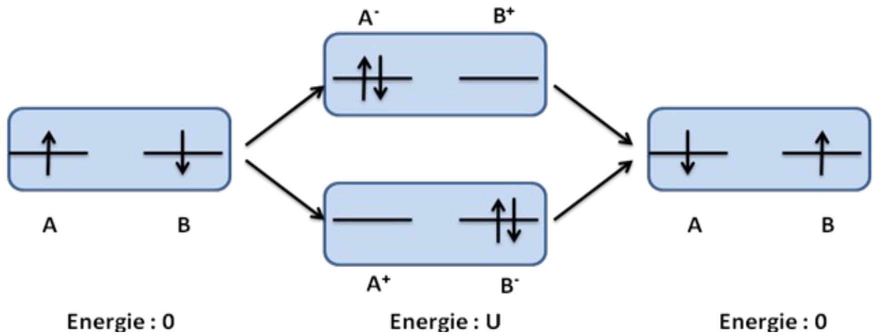
Dynamic polarization increases the weight of ionic components : CASSCF is biased!

	R(Angstrom)	1.4119	2.0	3.0
CAS-CI	C_I/C_N	0.5717	0.2178	0.0256
CAS-SDCI	C_I/C_N	0.6279	0.2507	0.0340
MR-CC	C_I/C_N	0.6373	0.2553	0.0354
Full CI	C_I/C_N	0.6420	0.2560	0.03614

↑

Magnetic regime

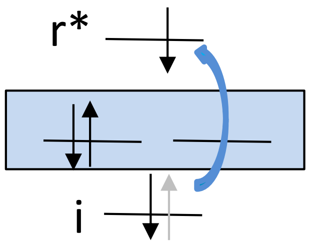
c) Polarization effects on the singlet triplet gap in magnetic systems 1h-1p

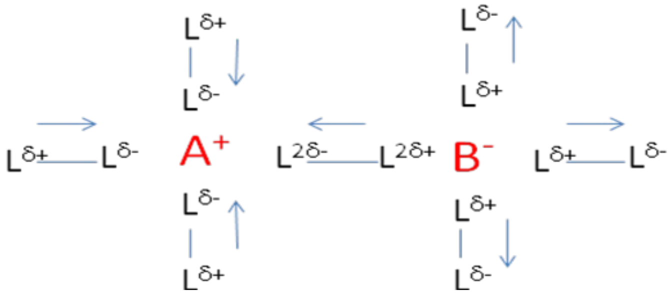


Charge polarization (1h-1p) impacts U: screening of U in solid state physics

$\Phi = \left| \frac{(\lambda+\mu)}{2} i\bar{i}\left(a\bar{b} + b\bar{a}\right) + \frac{(\lambda-\mu)}{2} i\bar{i}\left(a\bar{a} + b\bar{b}\right) \right|$ interacts with $\Psi^{Pert} = \frac{\left|g\bar{u} + u\bar{g}\right|}{\sqrt{2}} = \frac{\left|a\bar{a} - b\bar{b}\right|}{\sqrt{2}}$ Perturbator at energy U

Throught 1h1p excitations





$$U^{eff} = U - \sum_{i,r} \frac{\langle i | J_a - J_b | r \rangle \langle r | J_a - J_b | i \rangle}{U + E_r - E_i}$$

2nd order

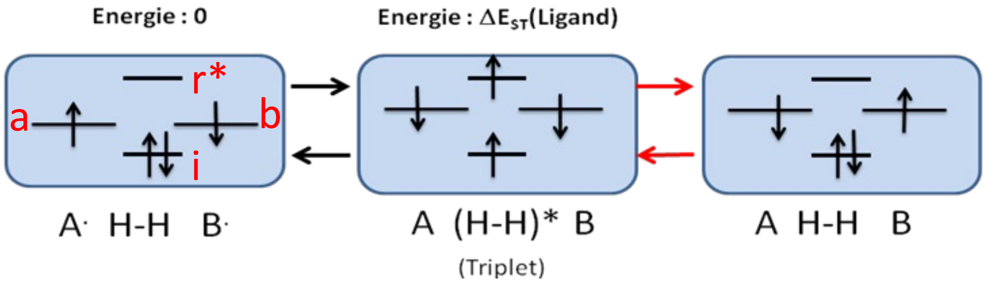
Spin polarization contribution (1h-1p) impacts the effective K (of Hubbard)

As well as the charge polarization that stabilizes the ionic forms, some excitations affect differentially the singlet and the triplet states: at the CAS+S level

$$\begin{array}{c|cc} & \left|\left|i\bar{i}a\bar{b}\right|\right\rangle & \left|\left|i\bar{i}\bar{a}b\right|\right\rangle \\ \hline \left\langle\left|i\bar{i}a\bar{b}\right|\right| & E_{PS} & -K_{ab}-\Delta K \\ \left\langle\left|i\bar{i}\bar{a}b\right|\right| & -K_{ab}-\Delta K & E_{PS} \end{array} \qquad \text{with} \qquad |E_{PS}| > |\Delta K|$$

But only ΔK plays a role in the energy difference between the magnetic states.

Most important contributions at the second order of perturbation: Double-spin polarization

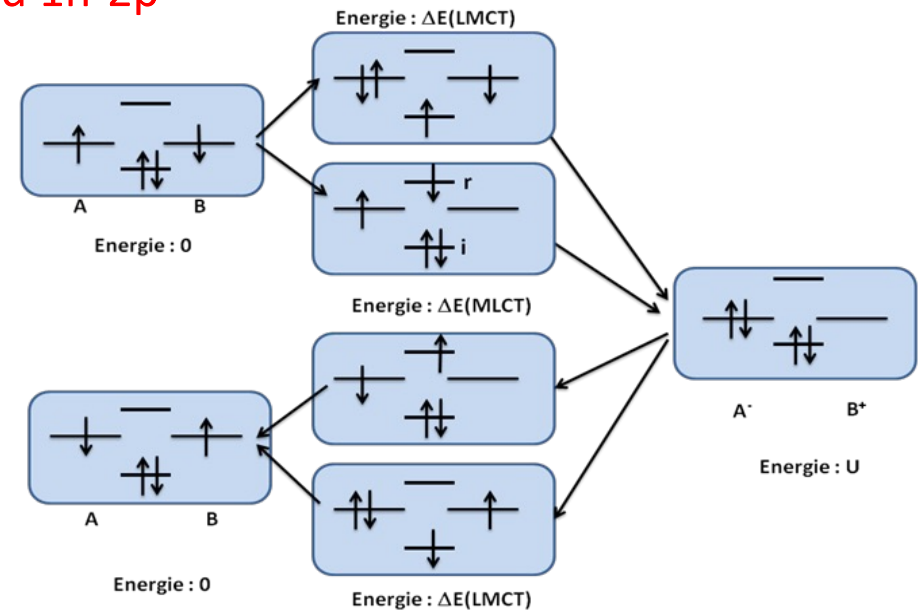


$$E_{PS} = -2\sum_{i,r}\frac{\left\langle\left|i\bar{i}a\bar{b}\right|\right|\hat{H}\left|\left|i\bar{r}a\bar{b}\right|\right\rangle\left\langle\left|i\bar{r}a\bar{b}\right|\right|\hat{H}\left|\left|i\bar{i}a\bar{b}\right|\right\rangle}{\varepsilon_r-\varepsilon_i}$$

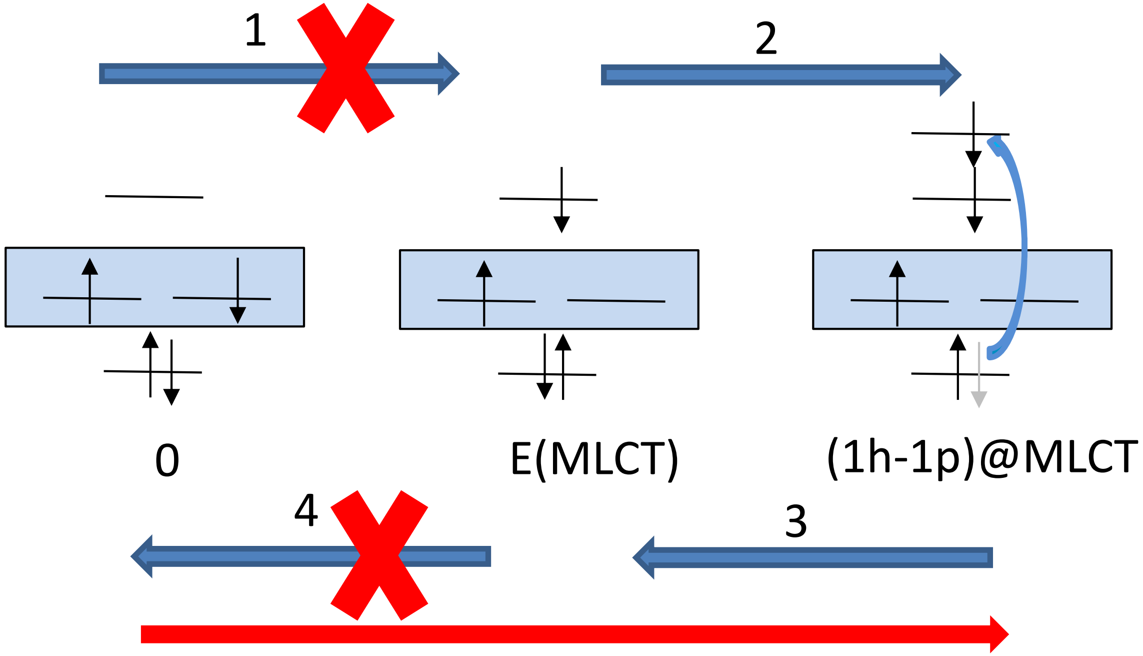
$$\Delta K = 2\sum_{i,r}\frac{\left\langle\left|i\bar{i}a\bar{b}\right|\right|\hat{H}\left|\left|i\bar{r}a\bar{b}\right|\right\rangle\left\langle\left|i\bar{r}a\bar{b}\right|\right|\hat{H}\left|\left|i\bar{i}\bar{a}b\right|\right\rangle}{\varepsilon_r-\varepsilon_i} = 2\sum_{i,r}\frac{\langle i|K_a|r\rangle\langle r|K_b|i\rangle}{\varepsilon_r-\varepsilon_i}$$

d) Polarization of the MLCT/LMCT states 2h-1p and 1h-2p

Metal to ligand charge transfer (MLCT)
Ligand to metal charge transfer (LMCT)



Also impacts the magnetic couplings



$$\langle \Psi_0|\hat{H}|Di\rangle\langle Di|\hat{H}|MLCT\rangle\langle MLCT|\hat{H}|Di'\rangle\langle Di'|\hat{H}|\Psi_0\rangle$$

4th order effect

Brillouin : coef. of the MLCT (singles) ≈0

Interactions through doubles

- increase the coef. of the MLCT
- Increase the extent of the magnetic orbitals over the ligand

Inactive double excitations : 2h-2p

ij→ *rs* excitations: no differential effect on vertical energy differences of the CAS states at 2nd-order for a single set of orbitals (State Average)

$$\varepsilon^{(2)}_{ij\to rs} = \frac{\langle ij \| rs \rangle^2}{F_{ii} + F_{jj} - F_{rr} - F_{ss}}$$

(normal if these MOs are far from the active orbitals)

Logical foundation of Difference Dedicated Configuration Interaction (DDCI)

But:

- The 2h-2p double excitation effects may be different for states with strongly different active orbitals (example : spin-crossover systems S=0 vs S=2), they must be included in vertical energy differences in such cases using state specific orbitals optimizations.
- The 2h-2p double excitations vary from one geometry to another, must be included in non-vertical energy differences
- They play a role in vertical energy differences from 3rd order

They can be accounted for perturbatively

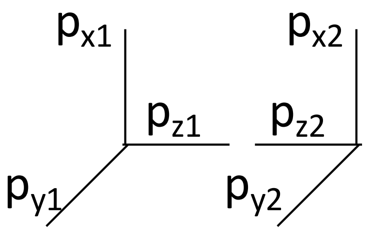
5) The correlation in multiple bonds : illustration on N_2

$|N_1 \equiv N_2|$

i) Non dynamic correlation:

The triple bond in N_2: 6 e- in 6 MOs CAS gives σ, σ^*, π_1, π_1^* and π_2, π_2^*

In OAO, all OVB forms (64) have the same coefficient: .125

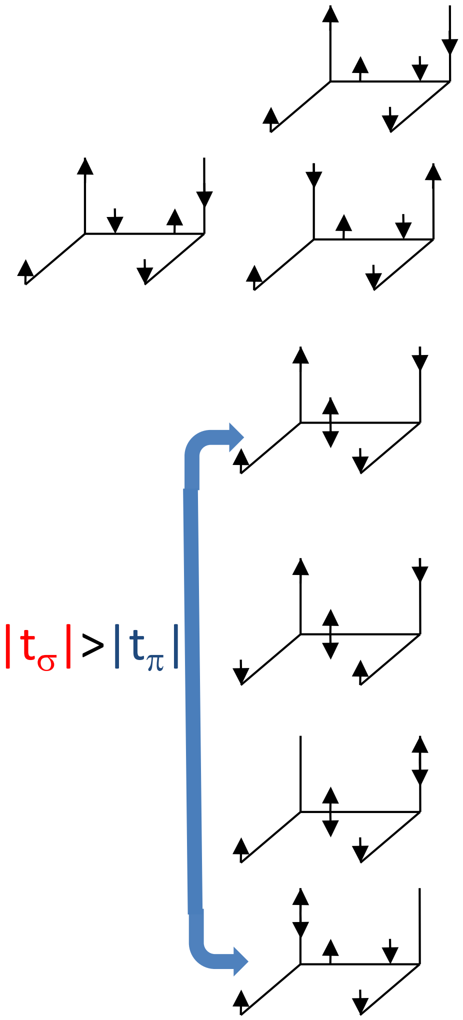


Big disorder of the Hartree Fock solution:

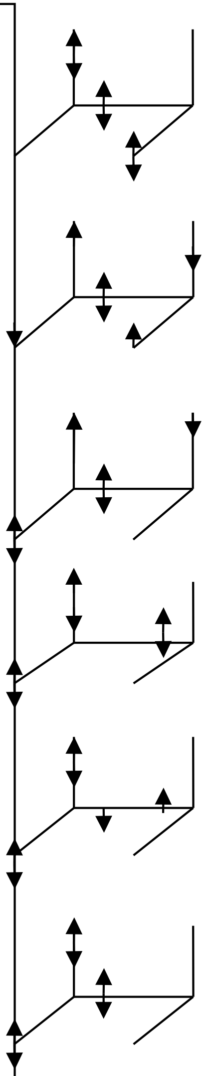
- no spin fluctuation (same weight for Hund and non-Hund functions)
- huge charge fluctuation (same weight for N (neutral) – N(neutral) and for N^{3+} – N^{3-}

Illustration of non dynamic correlations : multiple bond of N_2

$|N_1 \equiv N_2|$



	OVB coef.	Energy
Neutral Hund	.1786	0
Neutral non-Hund	.1637	$2K_{\sigma\pi}+2K_{\pi\pi}$
	.1564	$4K_{\sigma\pi}$
Singly ionic in σ, Hund	.1535	$2K_{\sigma\pi}+U_\sigma$
Singly ionic in σ, non-H	.1404	$2K_{\sigma\pi}+2K_{\pi\pi}+U_\sigma+R$
Neutral , 2 charge transfers	.1352	$\Delta J_\sigma+\Delta J_\pi+$ $3K_{\sigma\pi}+K_{\sigma\pi}$
Singly ionic in π, Hund	.1244	$U_\pi+\Delta J_\pi+K_{\sigma\pi}+R$

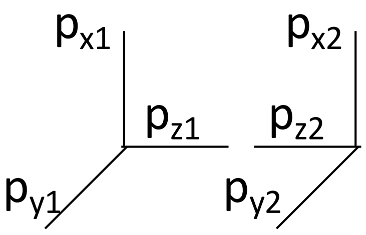


	OVB coef. In GS	Energy
Singly ionic, 2 e- transfers	.1196	$U_\sigma+\Delta J_\sigma+2\Delta J_\pi$ $2K_{\sigma\pi}+2K_{\pi\pi}+R$
Singly ionic in π non-Hund	.1192	$U_\sigma+2K_{\sigma\pi}+2K_{\pi\pi}+R$
Di ionic in πσ	.0888	$U_\sigma+U_\pi+$ $K_{\sigma\pi}+K_{\pi\pi}+2R$
Singly ionic in π	.0864	$2U_\pi+2R+2K_{\sigma\pi}$
Di ionic in π	.0633	$2U_\pi+2R+2K_{\sigma\pi}$
Tri ionic	.0378	$U_\sigma+2U_\pi+3R$

At the HF level, all coefficients are equal to .125

Decrease of the atomic charge fluctuation

Increase of the atomic spin fluctuation



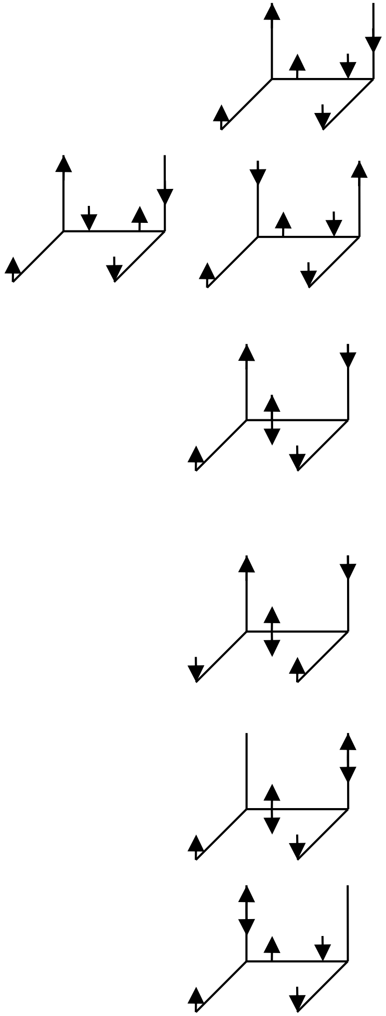
ii) Effects of dynamic correlation in multiple bonds

The electrons are closer in ionic VB components
All the effects analyzed in F_2 are present

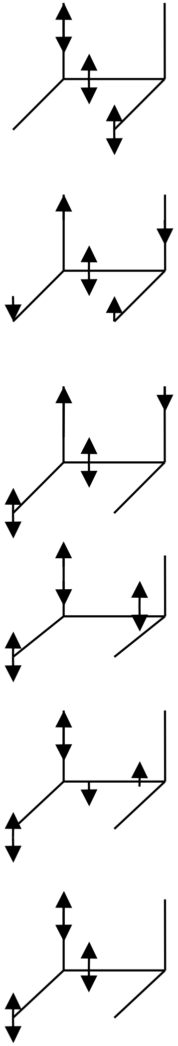
-breathing of the active orbitals
-dynamic polarization of the inactive electron pairs (lone pairs and adjacent bonds)
-radial and angular correlation of the intra-atomic electron pairs in ionic components
-revisions of the active MOs to natural MOs through 2h-1p and 1h-2p excitations

Overall effect: the coefficients of the ionic VB components are slightly increased with respect to the CASSCF values

Distinct effects of dynamic and non dynamic correlations : multiple bonds of N_2

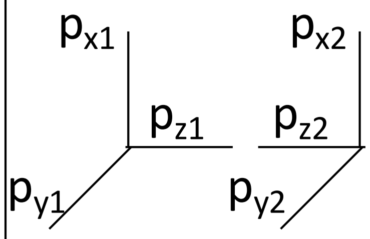


	CAS	CASSD
Neutral Hund	.1786	.1760
Neutral non-Hund	.1637	.1650
	.1564	.1555
Singly ionic in σ, Hund	.1535	.1546
Singly ionic in σ, non-H	.1404	.1408
Neutral , 2 charge transfers	.1352	.1326
Singly ionic in π, Hund	.1244	.1266



	CAS	CASSD
Singly ionic, 2 e- transfers	.1196	.1203
Singly ionic in π, non-Hund	.1192	.1196
Di ionic in $\pi\sigma$	.0888	.0896
Singly ionic in π	.0864	.0850
Di ionic in π	.0633	.0617
Tri ionic	.0378	.0359

$|N_1 \equiv N_2|$



Coefficients at the CASSCF and CASSD levels for the determinants in the ground state

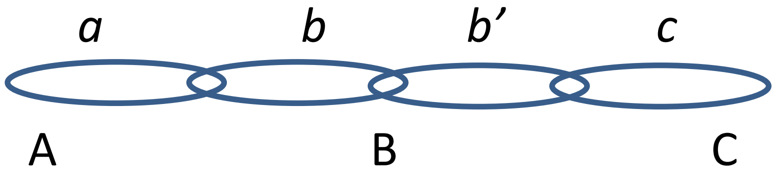
After dynamic correlation, penalties brought by the CAS are reduced

J.P. Malrieu, N. Guihéry, C.J. Calzado, C. Angeli Bond electron pair: Its relevance and analysis from the quantum chemistry point of view, J. COMP. CHEM. 28 (2007) 35

6) Correlation between (single) bonds

A) Adjacent single bonds

Two localized Bond MOs on an A—B—C molecule (OH_2 for instance)
4 e- in 4 MOs CAS→ 4 localized OAO, a, b, b' and c

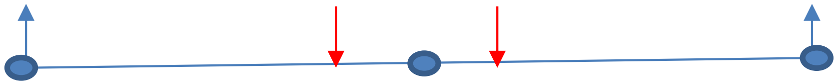


H-Be-H

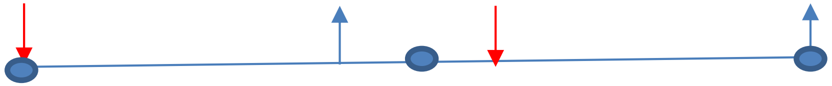
CASSCF 4e-/4MO, localize the two "occupied" MOs σ_{AB} and σ_{BC},
the two virtual MOs σ^*_{AB} and σ^*_{BC}.
From σ_{AB} and σ^*_{AB} one obtains OAOs *a* and *b* magnetic orbitals

OVB components with different ionicities, from neutral to di-ionic have equal weights in the single determinant:

$$\Phi_0 = \left| \sigma_{AB} \overline{\sigma_{AB}} \sigma_{BC} \overline{\sigma_{BC}} \right|$$

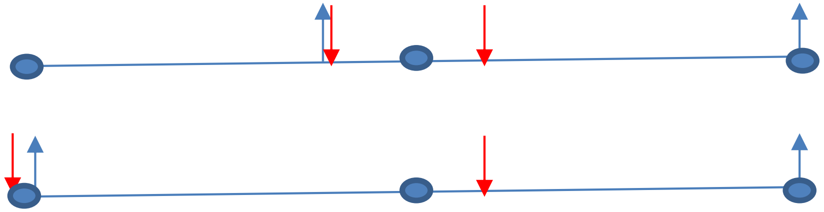


Neutral Hund on B



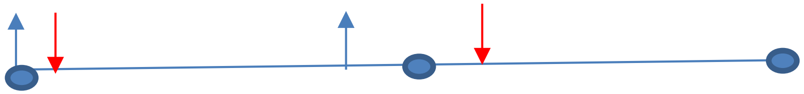
Neutral non Hund

Singly ionic short distance



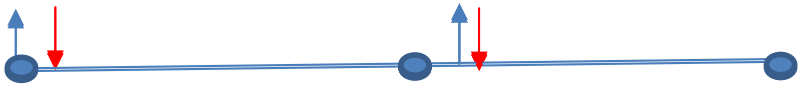
$A^+ B^- \; C$

Singly ionic long distance

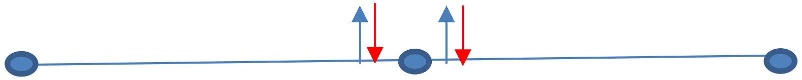


$A^- B \; C^+$

Singly ionic long distance with double occupancy of 2 OAOs



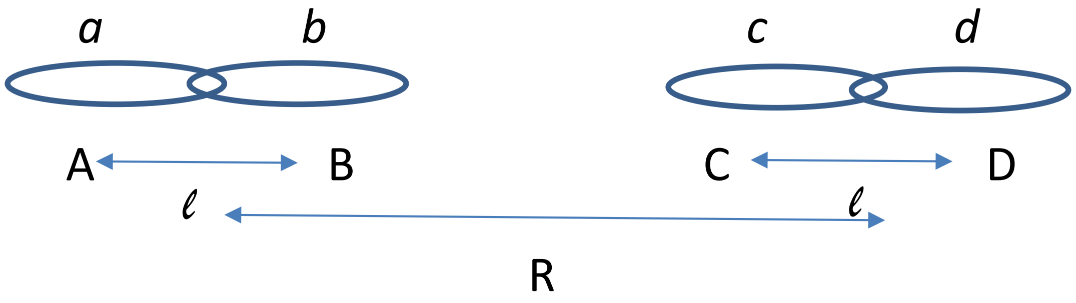
Doubly ionic



$A^+ B^{2-} C^+$ or $A^- B^{2+} C^-$

Same effects of non dynamic and dynamic correlations as in N_2. Note that these effects cannot be seen in delocalized MOs

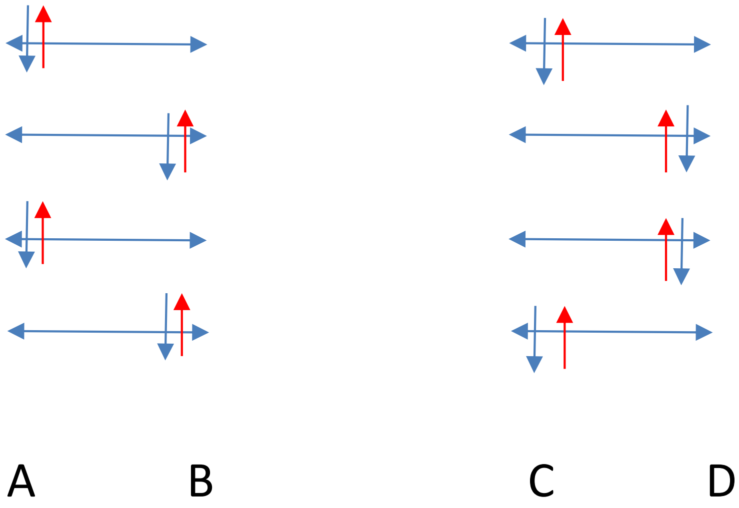
7) Correlation between remote (single) bonds and dispersion energies



Significant double excitations from $\Phi_0 = \left|\sigma_{AB}\overline{\sigma}_{AB}\sigma_{CD}\overline{\sigma}_{CD}\right|$

- intra-bond excitations, diminish the weight of intra-bond ionic components

- inter-bond excitation ${}^1(\sigma_{AB} \rightarrow \sigma^*_{AB}).{}^1(\sigma_{CD} \rightarrow \sigma^*_{CD}) = (a\overline{a} - b\overline{b})(c\overline{c} - d\overline{d})/2$



$a\overline{a}c\overline{c}$ 1/R

$b\overline{b}d\overline{d}$ 1/R

$a\overline{a}d\overline{d}$ 1/(R+l)

$b\overline{b}c\overline{c}$ 1(R-l)

Origin of the valence part of the dispersion energy

$$\left\langle \Phi_0 \left| H \right| {}^1(\sigma_{AB} \to \sigma^*_{AB}).{}^1(\sigma_{CD} \to \sigma^*_{CD}) \right\rangle = (J_{ac} + J_{bd} - J_{ad} - J_{bc})/2$$

$$= (\frac{2}{R} - \frac{1}{R+l} - \frac{1}{R-l})/2 \cong \frac{l^2}{2R^3}$$

Energy contribution

$$-\frac{\left\langle \Phi_0 \left| H \right| {}^1(\sigma_{AB} \to \sigma^*_{AB}).{}^1(\sigma_{CD} \to \sigma^*_{CD}) \right\rangle^2}{\Delta E_{\sigma_{AB} \to \sigma^*_{AB}} + \Delta E_{\sigma_{CD} \to \sigma^*_{CD}}} \cong -\frac{l^4}{8R^6 \Delta E}$$

Relation with the bond transition dipole and the bond polarizability

NB: double excitations to non-valence virtual MOs situated around AB and CD contribute also to the dispersion, but it is erroneous to classify the dispersion energy as an essentially dynamic correlation effect.

Note : In He….He the dispersion is a dynamic correlation effect

di-excitations from $2s_a 2s_b$ to $2p_a 2p_b$ introduce the following interactions

$$\left\langle \Psi_0 \middle| \hat{\mathrm{H}} \middle| \Psi^* \right\rangle = \left\langle \mathrm{s}_a(1)\mathrm{s}_b(2) \middle| \mathrm{r}_{12}^{-1} \middle| \mathrm{p}_a(1)\mathrm{p}_b(2) \right\rangle = \left(\mathrm{s}_a(1)\mathrm{p}_a(1), \mathrm{s}_b(2)\mathrm{p}_b(2)\right)$$

2 transition moments

$$\varepsilon^{(2)} = \frac{\left\langle \Psi_0 \middle| \hat{H} \middle| \Psi^* \right\rangle^2}{2(F_{ss} - F_{pp})} = 4\frac{\left(s_a(1)p_a(1), s_b(2)p_b(2)\right)^2}{2(F_{ss} - F_{pp})}$$

interaction $\boldsymbol{\mu}_a \boldsymbol{\mu}_b / R_{ab}^{-3}$ Correction of 2nd order in R_{ab}^{-6}

(Other multipole distributions→ other powers R^{-n})

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Thank you for your kind attention !