The VB reading of MO-based wave functions

Paris VB workshop

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Targets and content

- How to define a Valence space?
- Which basis to the valence space? The orthogonality problem
- Localized MOs, Bond MOs, Atom-centered Orbitals

  -e.g. the aromatic contribution to the energy
- The physical analysis of the non-dynamical correlation energy: reading the CASSCF functions

  -single bond

  -multiple bond

- Beyond the valence space: the content of dynamical correlation

  -the dynamical polarization effect and the impact of the dynamical correlation on the valence wave function

. Diabatization of chemical reactions

General considerations about the relations between VB and MO-based approaches

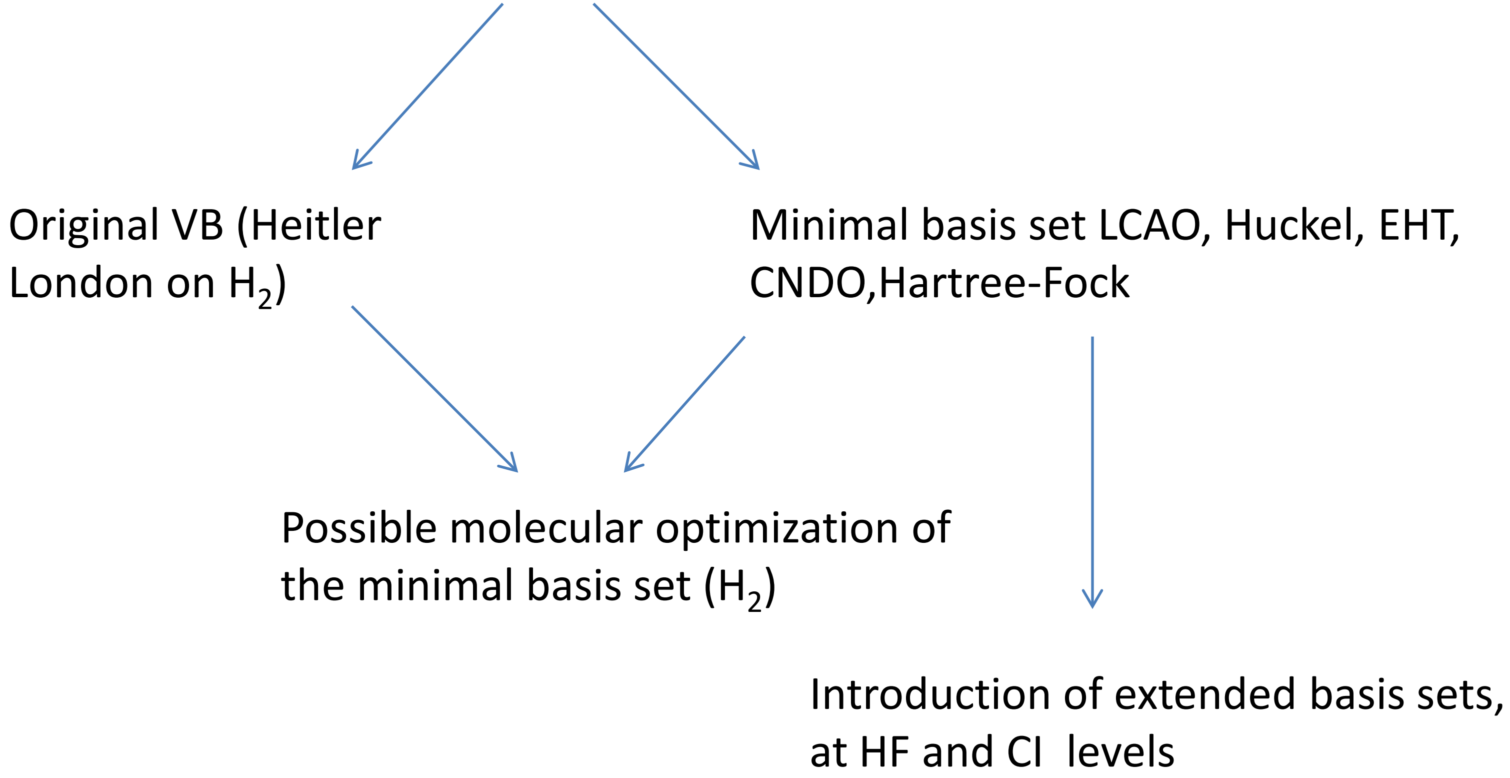
We consider that quantum chemistry has two tasks:

-reach accurate precisions (numbers), but also

-furnish pictorial interpretations.

The notion of Valence MOs and Valence configurations

History: molecules from atoms, hence a leading role of the outermost (valence) atomic orbitals of the atoms → minimal basis set descriptions



Original VB (Heitler London on H_2)

Minimal basis set LCAO, Huckel, EHT, CNDO,Hartree-Fock

Possible molecular optimization of the minimal basis set (H_2)

Introduction of extended basis sets, at HF and CI levels

Question: is the valence basis set a meaningless concept?

A posteriori justification of the concept of valence monoelectronic orbitals

Whatever the level of correlation, one may calculate a density matrix of the ground state, $$R = \sum_{k,l} a_k^+ a_k$$ $$R_0 = \langle \Psi_0 | R | \Psi_0 \rangle$$

diagonalize R_0 → naturals MOs (NOs). $R_0 \varphi_k = n_k \varphi_k$

If the molecule has M bonds and N core and lone pairs,

- M+N NOs have occupation numbers close to 2, they look like the canonical HF MOs
- M other have occupation numbers of an order of magnitude close to 0.1, they are essentially on valence AOs, have the same phases as the virtual MOs in a minimal basis set,
- others have smaller occupation numbers, and are essentially supported by non-valence AOs

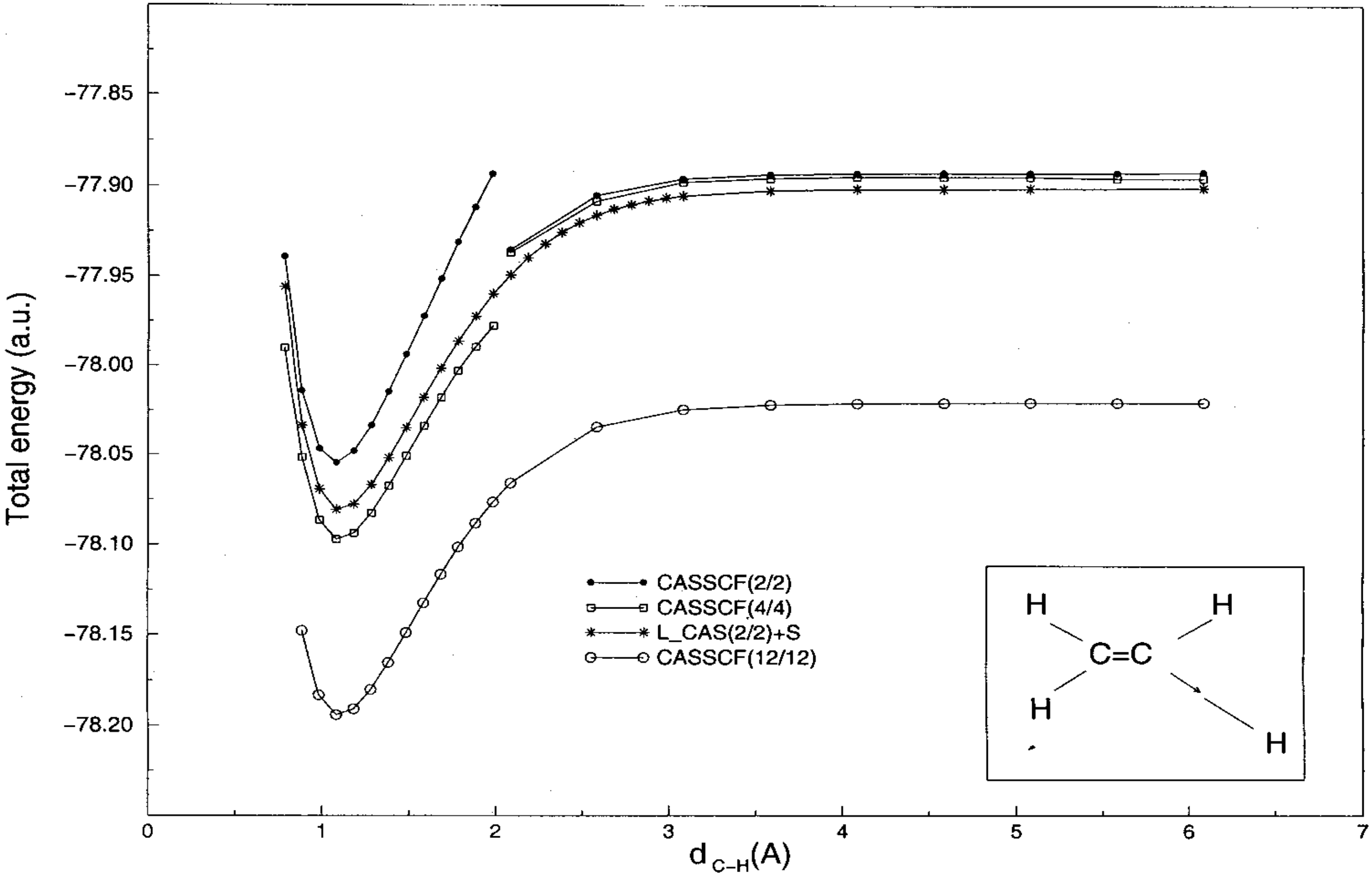
Constructivist justification : the valence CASSCF step

- The valence CASSCF defines an « optimal » valence only wave function
- optimal core
- optimal bonding, non-bonding and anti-bonding MOs
- optimal linear combination of valence configurations (i.e. a full CI of the valence electrons in valence bonding and anti-bonding MOs)

- Warrants a correct dissociation into atoms or fragments

- Truncated CAS: in practice the valence CAS may be too large to be performed but one may always get local CASSCF for one or a few bonds:

  entering a CASSCFcalculation from guess bonding and antibonding active MOs on a given chemical bond, one obtains a CASSCF solution for this bond, even when other bonds are more correlated (Evangelisti et al). One finds a CASSCF(2e-/2OM) solution for each bond. Which confirms the legitimacy of the Lewis' bond e- pair beyond HF.



Maynau et al, J. Chem. Phys. 116, 10060 (2002)

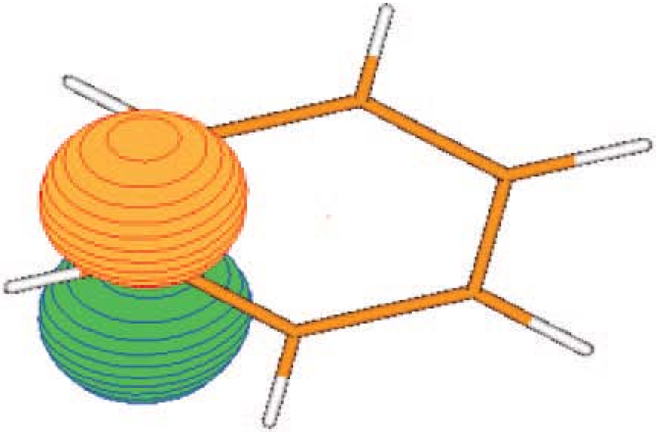
From symmetry-adapted to local orbitals

Natural MOs are symmetry-adapted

Unitary localizing transformation of the M+N most occupied NOs→core, bond and lone pair Orbitals
Unitary transformation of the 2M+N most occupied NOs→atom-centered core and valence Orbitals

CASSCF MOs define a space of valence monoelectronic wave functions φ_i
The canonical MOs are symmetry-adapted but one define many other basis of this space of projector $P_0 = \sum_i |\varphi_i\rangle\langle\varphi_i|$

Direct localization techniques of the active MOs:
-Rotations maximizing a localization criterion: Boys, Pipek-Mezey
→ Orthogonal Atom-centered Orbitals
Then on may express the active space in terms of anti-symmetrized products of these OAOs: Orthogonal VB determinants
The CASSCF wave function may be re-expressed in this basis set
→ OVB reading of the CASSCF function



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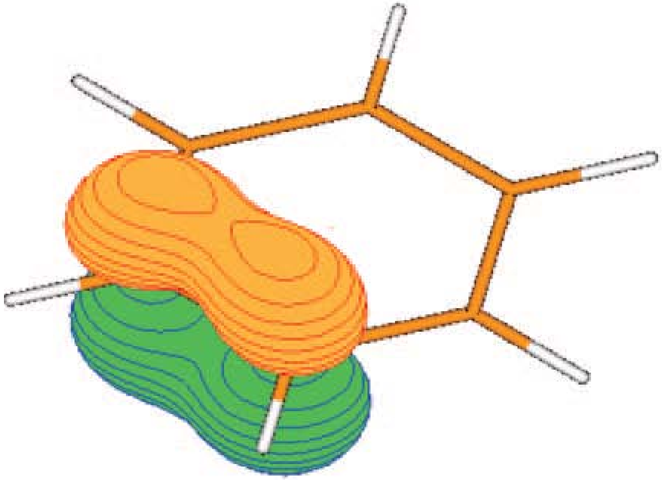

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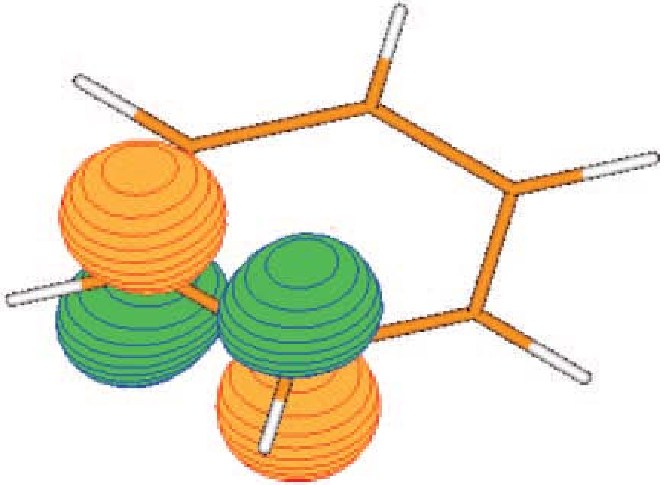

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Projection techniques

-Project guess MOs (fragment MOs, Bond MOs, AOs) in the valence space
e.g.: start from a valence orbital of an atom, χ_p, then

$$\left|\chi'_p\right\rangle = P_0\left|\chi_p\right\rangle = \sum_i \left|\varphi_i\right\rangle\left\langle\varphi_i\right|\chi_p\rangle$$

is an atom-centered CASSCF MO, they are not orthogonal, but have tails on adjacent atoms

One may build determinants products of these orbitals,
→VB-CASSCF determinants which span the CASSCF space,
and express the CASSCF function in this basis
→VB reading of the CASSCF wave function.

Other approach: diagonalize the restriction of the density matrix to the orbitals of the atom P, gives molecularly-adapted atomic orbitals: the most occupied, $\tilde{\chi}_p$ may be used in place of the isolated atom AOs

Eventually orthogonalize the set $\chi'_p \rightarrow \chi''_p$ through $S^{-1/2}$ or hierarchically, gives a basis of orthogonal atom-centered CASSCF MOs,
again → OVB reading of the CASSCF function

Trivial problems: homonuclear diatomic molecules

Single bonds:

H_2, 2 e^- in 2 MOs CASSCF, g and u and $\Psi = \lambda|g\bar{g}| - \mu|u\bar{u}|$ with $\lambda\mu>0$

g and u define 2 OAO, centered on atoms A and B respectively,

$$a = (g + u)/\sqrt{2},$$
$$b = (g - u)/\sqrt{2},$$

$$\Psi = (a\bar{b} + b\bar{a})(\lambda + \mu)/2 + (a\bar{a} + b\bar{b})(\lambda - \mu)/2$$

with an s/p/d optimal hybridization, and optimal ionic/valence ratio…

F_2, same CAS, same localizing rotation for the lone pairs

Multiple bonds:

N_2: 6 e- in 6 MOs CAS, rotation of σ_g and σ_u → σ_A , σ_B
π_u^x and π_u^x → π_A^x , π_B^x

Status of valence CASSCF versus VBSCF wave-functions

A unique set of valence orbitals, like in HSW (Hiberty Shaik Wu) VB but without constraint of strict locality , hence

$E_{CASSCF} < E_{HSW\text{-}VB}$

Less flexibility than in BO-VB which uses different orbitals for different VB determinants, hence one may expect (despite a locality constraint)

$E_{BO\text{-}VB} < E_{CASSCF}$

What about GVB Perfect–Pairing? No locality constraint of mono-electronic functions but if one only takes “neutral” VB structures, it will depend on the problem (identical for single bonds)

The orthogonality/non-orthogonality problem

General remark: to establish the respective role of two categories, better to have an exclusive definition of these categories: either/ or. What is the respective role of neutral (covalent) versus ionic components if they overlap?

The 2 e- in 2 orbital problem
Non-orthogonal AOs a’ and b’, with <a’|b’>=S
Orthogonal, a and b

$$a = (a'(\sqrt{1+S} + \sqrt{1-S}) - b'(\sqrt{1+S} - \sqrt{1-S}))/(2(1-S^2))$$

↓

Orthogonalization tail of a on b’

↓

a and b are not local?

But what is neutral and what is ionic? $\left\langle a'\overline{b}' \middle| a'\overline{a}' \right\rangle = S$

The triplet state is neutral in both basis

$$|gu| = |ab| = |a'b'|/(1-S^2)$$

The singlet state of u symmetry is ionic in both basis

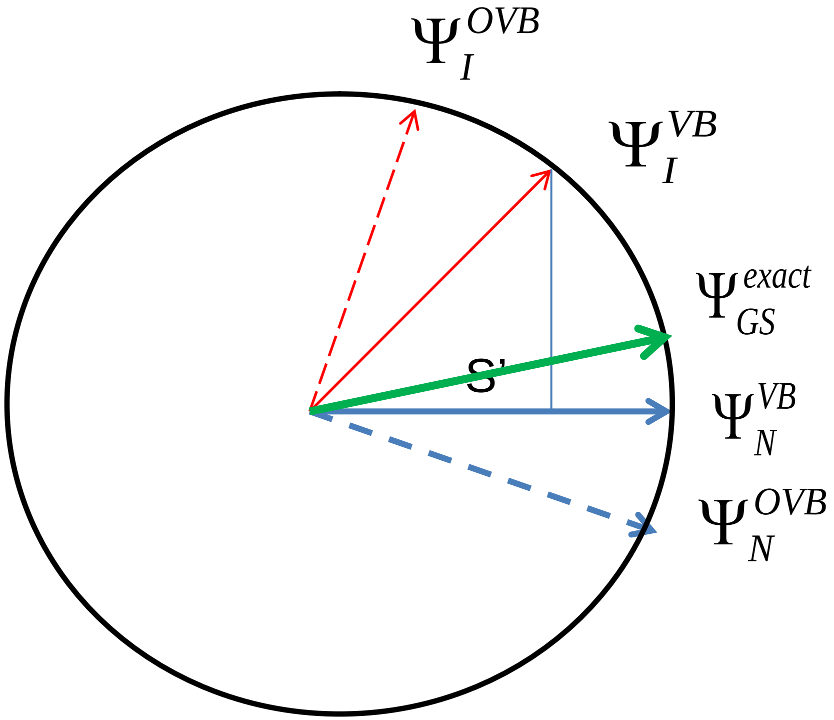
$$(|g\bar{u}| + |u\bar{g}|)/\sqrt{2} = (|a\bar{a}| - |b\bar{b}|)/\sqrt{2} = (|a'\bar{a}'| - |b'\bar{b}'|)/(\sqrt{2}(1-S^2))$$

The energy of the neutral OVB function $\Psi_N = (|a\bar{b}| + |a\bar{b}|)/\sqrt{2}$

only differs from that of the triplet by small exchange integral $2K_{ab}$

The energy of the ionic OVB function $\Psi_I = (|a\bar{a}| + |b\bar{b}|)/\sqrt{2}$

only differs from that of the ionic state of u symmetry by $2K_{ab}$



$$\left\langle \Psi_N^{OVB} \middle| \Psi_I^{OVB} \right\rangle = \frac{2S}{1+S^2} = S'$$

Minimal basis set descriptions

In general

- Larger contribution of the ionic VB structures in OVB (CASSCF) decomposition
- Never been performed: a non-orthogonal VB reading of the CASSCF functions

- Electronic order (correlation) between two bonds

The double bond, one σ and one π, with the corresponding antibonding MOs

HF = $|\sigma\underline{\sigma}\pi\underline{\pi}|$

CASSCF, 4 e- in 4 MOs, also provides one σ* and one π* antibondond Mos, hence 4 OAOs

a and b in σ, a’ and b’ in π , from which one builds a basis of 16 OVB determinants

one may express the HF and CASSCF wave functions in this OVB basis

5 types of determinants in HF wf

of increasing energy

with the same coeff. 1/ 4

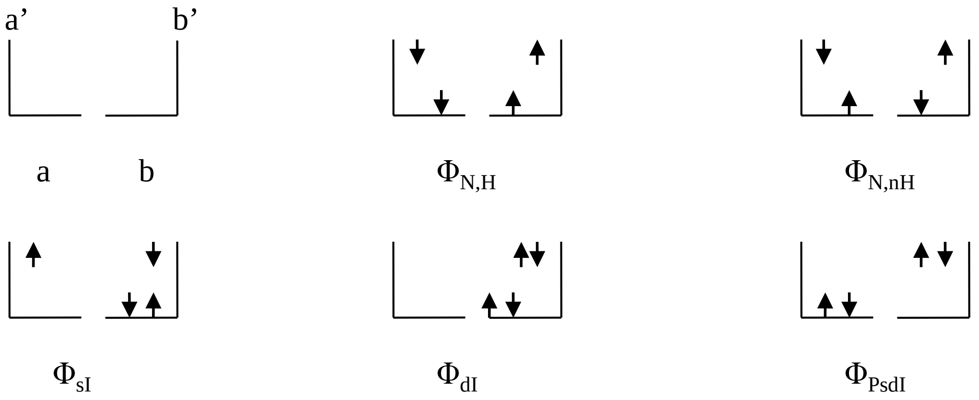
. neutral with single orbitalar occup. respecting Hund, $\Phi_{N,H}$

″ ″ ″ violating Hund, $\Phi_{N,nH}$

″ with double orbitalar occup., Φ_{PsdI}

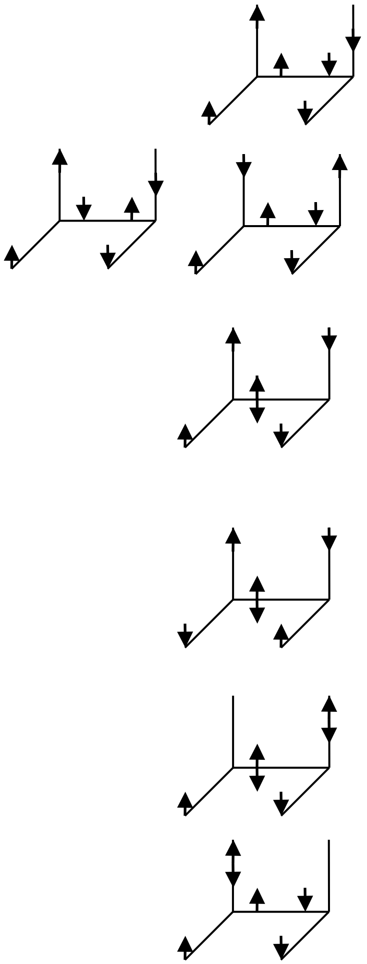
. singly ionic, either in σ or in π, Φ_{sI}

. doubly ioinic, Φ_{dI}

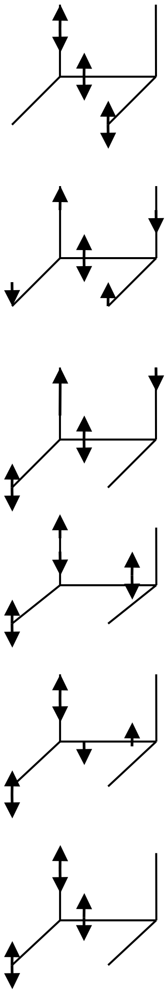


The multiple bonds: the N_2 molecule at equilibrium

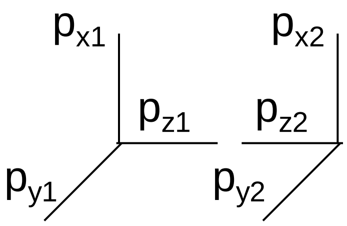
$|N_1 \equiv N_2|$



	CAS	CASSD
Neutral Hund	.1786	*.1760*
Neutral non-Hund	.1637 .1564	*.1650* *.1555*
Mono ion. in σ, Hund	.1535	*.1546*
Mono ion. in σ, non-H	.1404	*.1408*
Neutral , 2 transfert	.1352	*.1326*
Mono ion. in π, Hund	.1244	*.1 266*



	CAS	CASSD
Mono ion., 2 transferts	.1196	*.1203*
Mono ion. in π, n-H	.1192	*.1196*
Di ion., in πσ	.0888	*.0896*
Mono ion., in π	.0864	*.0850*
Di ion., in π	.0633	*.0617*
Tri ionic	.0378	*.0359*



Coefficients of the OVB determinants in the GS CASSCF and *CAS.SD* wf

J. Comp. Chem, **28**, 35 (2007)

At HF level all coefficients of 64 OVB determinants are equal to 0.125

Diminution of the fluctuation of the atomic charge
Increase of the fluctuation of the atomic spin momentum

This illustrates the electronic disorder of the independant particle model,

- . priority to the delocalization,
- . neglect of the preferences of the atoms for neutrality, e- spread in degenerate orbitals and for the highest spin multiplicity

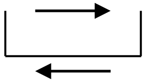
The non-dynamical correlation partly satisfies these preferences of the atoms

Four types of double excitations

1) intra-bond double excitations $(\sigma\sigma\rightarrow\sigma^*\sigma^*)$ or $(\pi\pi\rightarrow\pi^*\pi^*)$ diminish the weight of ionic components in each bond, but independantly, leaving an equal weight to doubly ionic et pseudo-dionic.

Interaction $\langle\Phi_0|H|\Phi^*\rangle = K_{\sigma\sigma^*} = (J_{aa}-J_{ab})/2$

2) inter-bond double excitation $^1(\sigma\rightarrow\sigma^*).^1(\pi\rightarrow\pi^*)$, product of 2 singlet single excitations in σ and in π, diminishes the doubly ionic, increases the pseudo-dionic components.



Interaction $\langle\Phi_0|H|\Phi^*\rangle = (\sigma\sigma^*, \pi\pi^*) = (J_{aa'} - J_{ab'})/2$,

when a distribution A^-B^+ appears in σ, a distribution A^+B^- tends to appear in π.

3) inter-bond double excitation $^1(^3(\sigma\rightarrow\sigma^*).^3(\pi\rightarrow\pi^*))$, singlet product of 2 triplet single excitations in σ and in π, increases the weight of neutral Hund-compatible components.

This Singlet is $(T^+_{\sigma\sigma^*}.T^-_{\pi\pi^*} + T^-_{\sigma\sigma^*}.T^+_{\pi\pi^*} - 2\,T^0_{\sigma\sigma^*}.T^0_{\pi\pi^*})/\sqrt{6}$

Interaction $\langle\Phi_0|H|\Phi^*\rangle = \sqrt{3}(\sigma\pi^*, \pi\sigma^*) = (K_{aa'} - (ba',ab'))\sqrt{3}/2$

The 2nd integral is negligible. The working factor is the mono-centric exchange integral, dynamical spin polarization, phenomenon existing in closed-shell systems!

4) Double excitations $(\sigma\sigma\rightarrow\pi^*\pi^*)$ or $(\pi\pi\rightarrow\sigma^*\sigma^*)$, putting 4 e- in one bond, zero in the other one, of negligible weight

Beyond the CAS description: role of the dynamical correlation

- Effect of the charge fluctuation of the active e- on the inactive e- : the dynamical polarization

Ex: the F_2 diatom, single bond, 2e- in 2MOs, surrounded by 3 lone pairs on each atom, $2s^2$ $2p_x^2$ $2p_y^2$ the bond being essentially formed by the $2p_z$ orbitals.

- In the ionic OVB determinants (A^- B^+),

the lone pairs on the negative centre

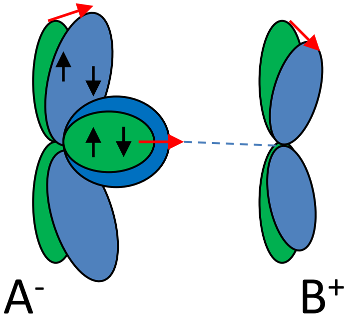
expand spacially (breathing, excitations to OAOs of same l),

lean towards the positive centre (dynamical hybridization through excitations to OAOs of (l+/-1) value)

the lone pairs on the positive centre

contract (respiration, (breathing, excitations to OAOs of same l),

lean off the negative centre (dynamical hybridization, same type of excitations)



- (Hypo-)Thesis: the main effect of the dynamical correlation on the binding energy is due to the dynamical polarization, i.e. to the single excitations on the various determinants of the CAS (1hole 1particle excitations on the CAS) =CAS+S=BOVB

Examples:

F_2, De at HF -1.32 eV, at CASSCF 0.40 eV, at CAS+Singles 1.40 eV (exp: 1.40 eV)

Cr_2, De at CASSCF 12 e- in 12 OM, -1.6eV, CAS+Singles in NEVPT2 1.49 eV (exp. 1.47 eV) despite the fact that single excitations only bring 10% of the dynamical correlation.

Thesis developed by Hiberty and Shaik who proposed a BO-VB calculation with optimal relaxation of the valence AOs of each VB determinant .

Other dynamical correlation effect: radial and angular correlation in the doubly occupied orbitals in ionic VB components (double excitations, not in BOVB)

Physical effect : lowering of the effective energy of the VB ionic components / their value when described with the mean-field OAOs, hence, as a side effect, a small re-increase of the weight of these components due to the dynamical correlation: too large at the HF step, slightly too weak at the CASSCF level (cf. N_2 , cf. slide 17)

Evaluation of the cyclic delocalization energy in aromatic or anti-aromatic rings

Recipe: illustrated on a 6-membered ring

1) Start from a full π CASSCF→ valence MOs
2) Localize them to get valence atom-centered orbitals $\chi_1, \chi_2, \dots, \chi_6$
3) Build fully localized bonding and antibonding MOs

$$\begin{aligned} \varphi_1 &= (\chi_1 + \chi_2)/\sqrt{2}, \\ \varphi_1^* &= (\chi_1 - \chi_2)/\sqrt{2} \\ \varphi_2 &= (\chi_3 + \chi_4)/\sqrt{2}, \\ &etc\dots \end{aligned}$$

4) Define a Kékulé type strongly localized determinant

$$\Phi_0 = \left|\varphi_1 \overline{\varphi}_1 \varphi_2 \overline{\varphi}_2 \varphi_3 \overline{\varphi}_3\right|$$

5) Perturb it by the effect of single excitations from a bonding MO to antibonding MOs of adjacent bond

   2nd order: back and forth delocalization $\left\langle \Phi_0 \middle| H \middle| a_{j^*}^{+} a_i \Phi_0 \right\rangle = F_{ij^*}$

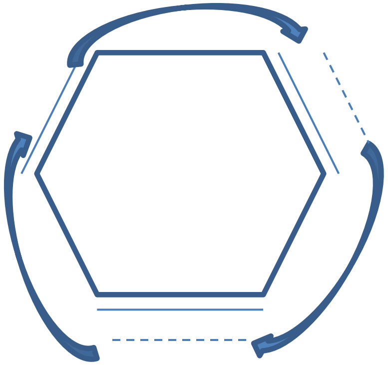
$$\varepsilon^{(2)} = \sum_{i,j^*} \frac{F_{ij^*} F_{j^*i}}{F_{ii} - F_{jj^*}}$$

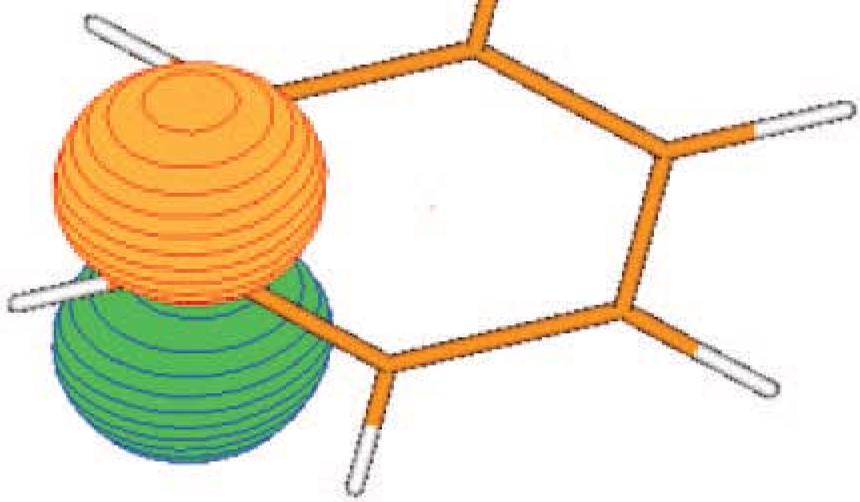
3rd order : cyclic movements along the ring

$$\varepsilon^{(3)} = \sum_{i,j^*,k^*} \frac{F_{ij^*}F_{j^*k^*}F_{k^*i}}{(F_{ii}-F_{j^*j^*})(F_{ii}-F_{k^*k^*})} - \sum_{i,j^*,k^*} \frac{F_{ij^*}F_{ik}F_{j^*k}}{(F_{ii}-F_{j^*j^*})(F_{kk}-F_{j^*j^*})}$$

A direct estimate of the cyclic contribution to the energy: 20 kcal/mole

One may show that this cyclic contribution fights against the bond alternation, maximum for equal bond lengths





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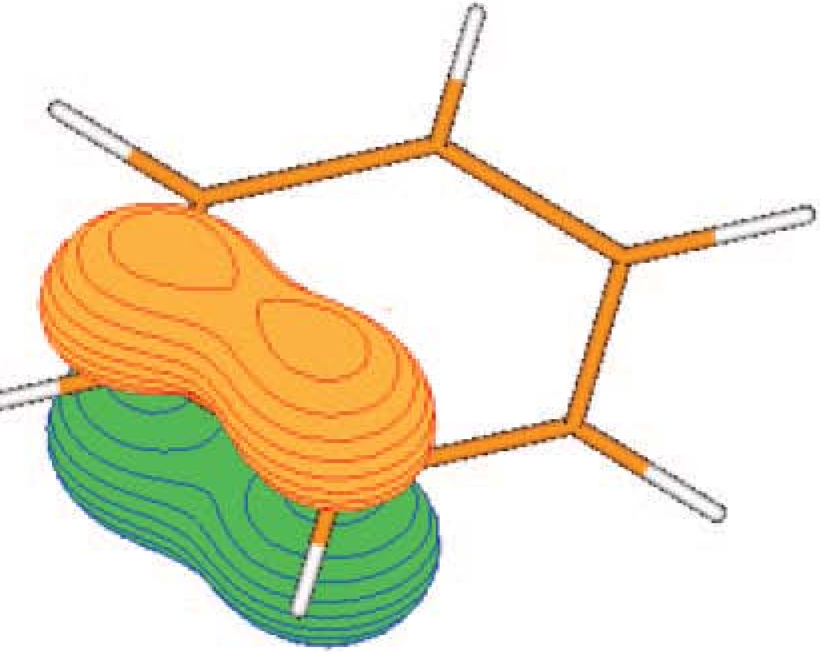

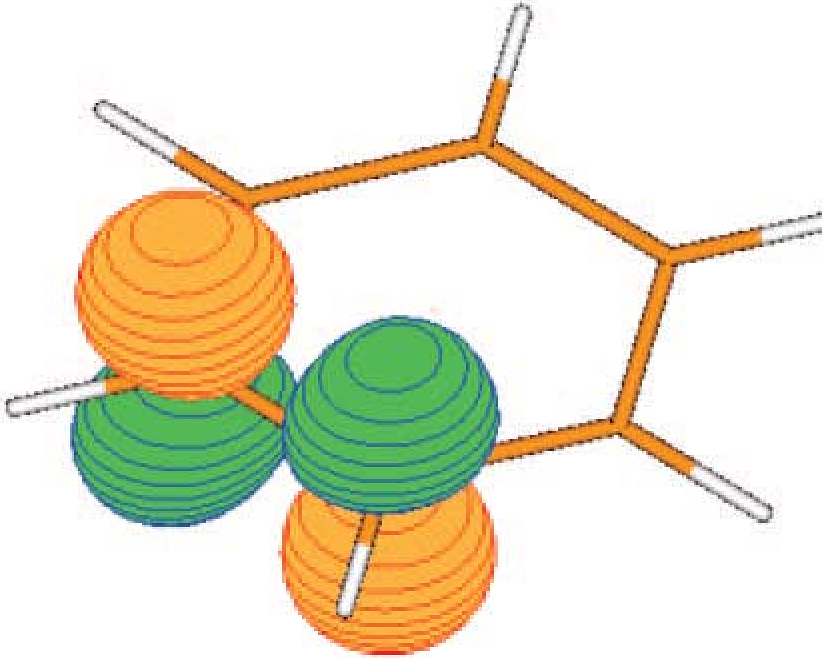

Evolutions of the π-delocalization energy (right side scale, × symbols, dashed line) and of the cyclic π-delocalization energy (left side scale, + symbols, full line). δ is the displacement from the equilibrium geometry (regular hexagon): for the short bond rCC = 1.396 − δ, for the long bond rCC = 1.396 + δ.

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Effective valence Hamiltonians from extended (post-CAS) CI wave functions

If you have calculated M valence eigenstates $\Psi_k \quad H\Psi_k = E_k\Psi_k$
and have defined M VB leading configurations Φ_I
which constitute a model space of projector

$$P_{OVB} = \sum_I |\Phi_I\rangle\langle\Phi_I| \qquad P_{VB} = \sum_I |\Phi_I\rangle(S^{-1})_{IJ}\langle\Phi_J|$$

Project the eigenstates in the VB model space

$$\overline{\Psi}_k = P_{(O)VB}\Psi_k$$

Orthogonalize the projections through S$^{-1/2}$ $\rightarrow \overline{\Psi}'_k$

Define an effective hamiltonian in the model space by the conditions

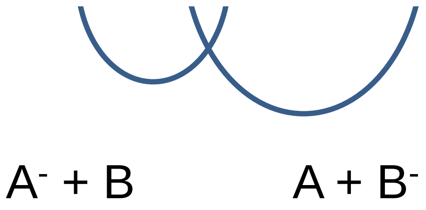
$$H^{eff}\left|\overline{\Psi}'_k\right\rangle = E_k\left|\overline{\Psi}'_k\right\rangle$$

Exact energies, projections of the exact eigenvectors in the VB space. Then

$$\langle\Phi_I|H^{eff}|\Phi_J\rangle = \sum_k E_k\langle\Phi_I|\overline{\Psi}'_k\rangle\langle\overline{\Psi}'_k|\Phi_J\rangle$$

Example: Possible modelization of chemical reactions in terms of a few interacting configurations from CAS or post-CAS CI wave functions

Example 1: mixed valence compounds and charge exchange $A^- + B \rightarrow A + B^-$.



Modelization through an effective Hamiltonian

$$\begin{array}{c|cc|} \overline{\Psi}_{A^-B} & H^{eff}_{AA} & H^{eff}_{AB} \\ \overline{\Psi}_{AB^-} & H^{eff}_{BA} & H^{eff}_{BB} \end{array}$$

Strategy:

- start from a state average CASSCF 1-electron in 2 LUMO (or 5 electrons in 2 HOMO and 2 LUMO) ,
- localize the active MOs on A and B,
- define localized reference functions Ψ_{A^-B} and $\Psi_{A\ B^-}$
- project the 2 lowest eigenfunctions (CAS or post-CAS) on the model space,
- apply effective Hamiltonian Theory of Bloch and get the desired 2x2 matrix

Adiabatic eigenstates Ψ_1, Ψ_2 , of energies E_1, E_2

Express the vectors as $\Psi_1 = \lambda\Psi_{A^-B} + \mu\Psi_{AB^-} + ... \rightarrow \overline{\Psi}_1 = \lambda\Psi_{A^-B} + \mu\Psi_{AB^-}$

$$\Psi_2 = -\mu\Psi_{A^-B} + \lambda\Psi_{AB^-} + ... \rightarrow \overline{\Psi}_2 = -\mu\Psi_{A^-B} + \lambda\Psi_{AB^-}$$

By definition $H^{eff} = E_1\left|\overline{\Psi}_1\right\rangle\left\langle\overline{\Psi}_1\right| + E_2\left|\overline{\Psi}_2\right\rangle\left\langle\overline{\Psi}_2\right|$

$$\left\langle\Psi_{A^-B}\middle|H^{eff}\middle|\Psi_{A^-B}\right\rangle = E_1\lambda^2 + E_2\mu^2$$

$$\left\langle\Psi_{A^-B}\middle|H^{eff}\middle|\Psi_{AB^-}\right\rangle = (E_1 - E_2)\lambda\mu$$

$$\left\langle\Psi_{AB^-}\middle|H^{eff}\middle|\Psi_{AB^-}\right\rangle = E_1\mu^2 + E_2\lambda^2$$

The most rigorous reduction of information, exact energies projections of the exact eigenvectors in the model space

CONCLUSIONS

VB is a crucial way of analyzing the wavefunctions and physics

One may always provide a VB analysis from CAS (or MR belonging to a CAS) (+dynam. correl.)

Possible construction of an OVB or VB effective Hamiltonian by projection techniques from any MO-CI wave functions

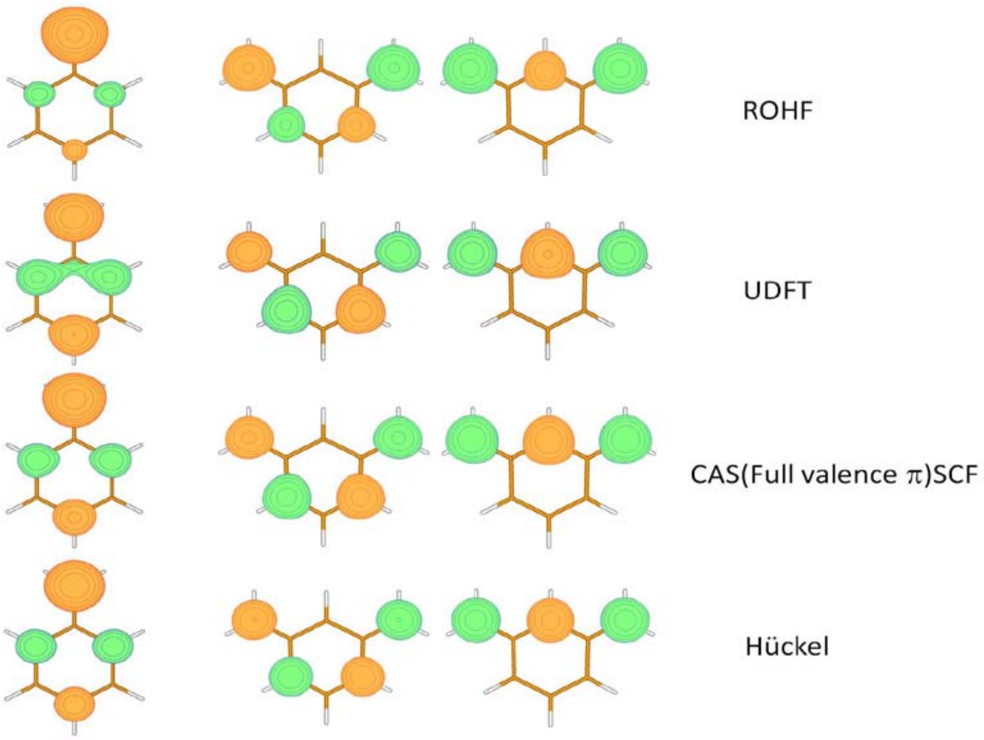
Advantages:
- efficient standard MRCI or MRPT techniques,
- no locality restriction on the active MOs,
- the projection of the eigenvectors on the model space is easier when the eigenvectors and the model space vectors are expressed in the same MO basis,
- the active MOs may be delocalized, for instance in organic systems (e.g. in the electron transfer problem, A= naphtalene , B=anthracene, or magnetic orbitals in conjugated diradicalar hydrocarbons)

Drawbacks:

-need for more configurations than in non orthogonal VB? To be studied.

-the CASSCF active MOs may present defects: the magnetic MOs given by CASSCF calculations are more localized than the Natural magnetic MOs

Caveat: the minimal CASSCF functions may be biased



The two communities, VB and MO ones, should get closer!

In this spirit, thanks for the invitation and thanks for your attention!

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