

# Localization and delocalization in quantum chemistry: chemical bond and entanglement

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- 1 The standard VB approach
- 2 The orthogonal VB approach
- 3 Entanglement in quantum chemistry
- 4 Entanglement for  $H_2$  in the minimal basis set
- 5 Entanglement in other molecules

## The VB structures

The standard VB approach starts from the consideration that for two non interacting H atoms (A and B) the exact ground state wave function is the antisymmetrized product of the two  $1s_A$  and  $1s_B$  orbitals. Following the spin coupling of the two unpaired electrons, two possibilities can be considered:

$$\begin{aligned}
 {}^1\Psi &= \frac{1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)}{\sqrt{2}} \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \\
 {}^3\Psi &= \frac{1s_A(1)1s_B(2) - 1s_B(1)1s_A(2)}{\sqrt{2}} \left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \\ \beta(1)\beta(2) \end{array} \right\}
 \end{aligned}$$

These wave functions are degenerate at  $R \rightarrow \infty$  and are “neutral” (each atom bears one of the two electrons).

## The VB structures

The simplest version of VB is based on the use of these wave functions also for the  $H_2$  molecule:

$$\begin{aligned}
 {}^1\Psi_{N,g}^n &= \frac{1s_A 1s_B + 1s_B 1s_A}{\sqrt{2(1+S^2)}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \\
 {}^3\Psi_{N,u}^n &= \frac{1s_A 1s_B - 1s_B 1s_A}{\sqrt{2(1-S^2)}} \left\{ \begin{array}{c} \alpha\alpha \\ \frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \\ \beta\beta \end{array} \right\}
 \end{aligned}$$

$S = \langle 1s_A | 1s_B \rangle$  is the overlap between the two  $1s$  orbitals.

The two wave functions are orthogonal (different space and spin symmetries).

## The VB structures

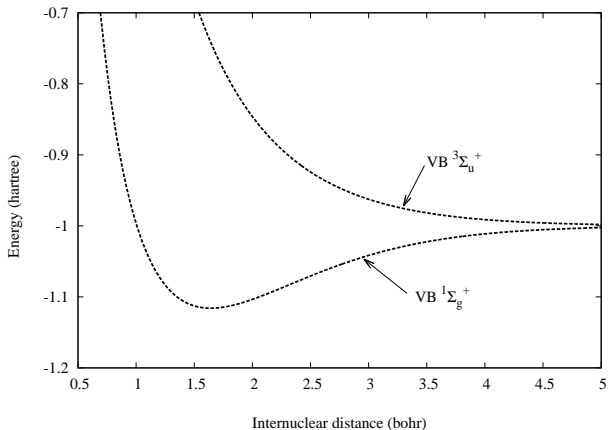
The energy associated to these wave functions can be computed analytically as a function of the internuclear distance  $R$

$$\begin{aligned}\langle {}^1\Psi_{N,g}^n | \hat{\mathcal{H}} | {}^1\Psi_{N,g}^n \rangle &= -1 + \frac{1}{R} + \frac{2KS + 2J + J' + K'}{1 + S^2} \\ \langle {}^3\Psi_{N,u}^n | \hat{\mathcal{H}} | {}^3\Psi_{N,u}^n \rangle &= -1 + \frac{1}{R} + \frac{-2KS + 2J + J' - K'}{1 - S^2}\end{aligned}$$

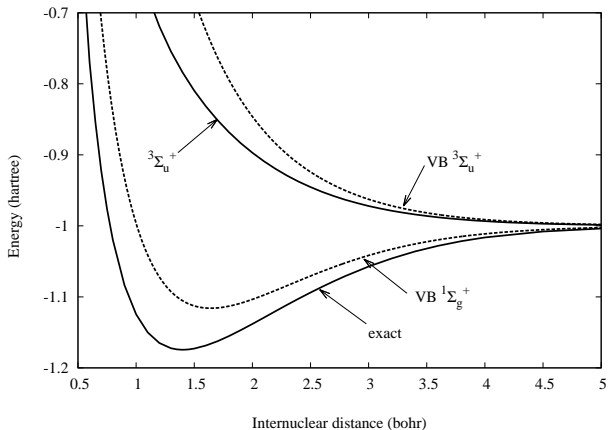
where

$$\begin{aligned}S &= \langle 1s_A | 1s_B \rangle = e^{-R} \left( 1 + R + \frac{R^2}{3} \right) \\ J &= \left\langle 1s_A \left| -\frac{1}{r_{b1}} \right| 1s_A \right\rangle = -\frac{1}{R} + e^{-2R} \left( 1 + \frac{1}{R} \right) \\ K &= \left\langle 1s_A \left| -\frac{1}{r_{b1}} \right| 1s_B \right\rangle = -e^{-R} (1 + R)\end{aligned}$$

Energy of the  ${}^1\Psi_{N,g}^n$  and  ${}^3\Psi_{I,u}^n$  structures and of the GS and  ${}^3\Sigma_u^+$  states.



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# Energy of the ${}^1\Psi_{N,g}^n$ and ${}^3\Psi_{I,u}^n$ structures and of the GS and ${}^3\Sigma_u^+$ states.

The energy of both states are pretty well described by the two VB structures.

The triplet is dissociative, while the singlet describes the chemical bond between the two H atoms.

The stabilization of  $H_2$  with respect to two H atoms is ascribed to the “exchange” interaction between the two electrons.

The didactic presentation of VB normally stops here!



## The ionic (polar) structures.

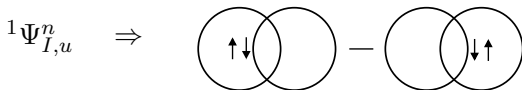
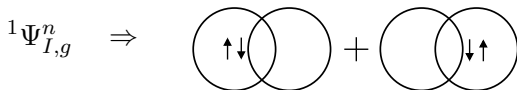
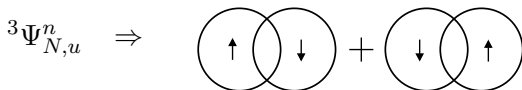
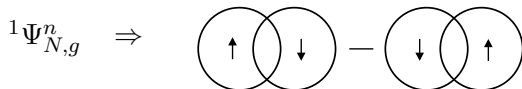
Actually, other structures can be considered. They have been firstly introduced by Majorana in 1931 (he was 25 years old!!) in a paper published in Italian and then used by Weinbaum in 1933 (J. Chem. Phys.)

$$\begin{aligned} {}^1\Psi_{I,g}^n &= \frac{1s_A 1s_A + 1s_B 1s_B}{\sqrt{2(1+S^2)}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \\ {}^1\Psi_{I,u}^n &= \frac{1s_A 1s_A - 1s_B 1s_B}{\sqrt{2(1+S^2)}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \end{aligned}$$

The two wave functions are orthogonal (different space symmetries).

# The ionic (polar) structures.

In total, we have four structures



## The ionic (polar) structures.

Among the 4 VB structures, the two  $g$  singlets interact and are used to describe two  ${}^1\Sigma_g^+$  states,

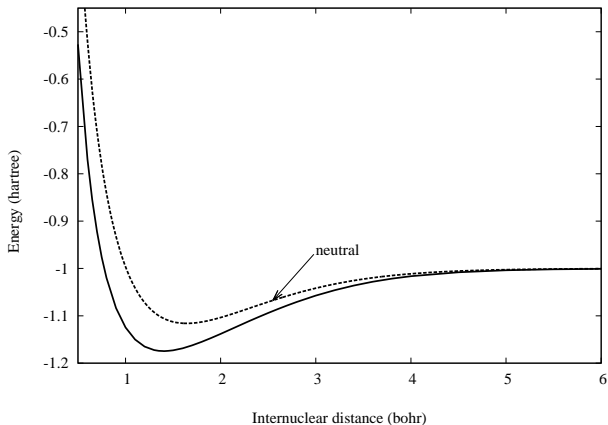
$$\Psi_1 ({}^1\Sigma_g^+) = C_N {}^1\Psi_{N,g}^n + C_I {}^1\Psi_{I,g}^n$$

$$\Psi_2 ({}^1\Sigma_g^+) = C'_N {}^1\Psi_{N,g}^n + C'_I {}^1\Psi_{I,g}^n$$

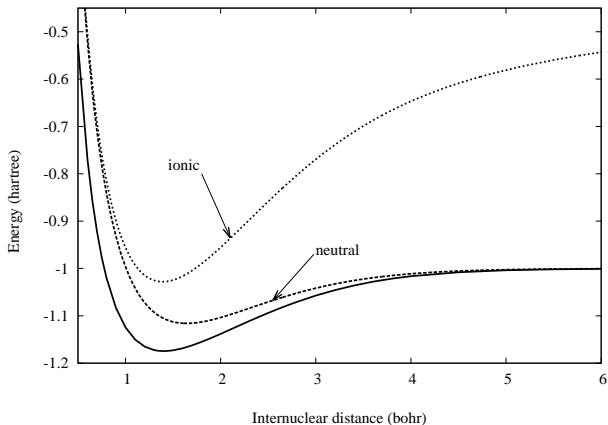
while the other two structures describe the  ${}^3\Sigma_u^+$  and  ${}^1\Sigma_u^+$  states:

$$\Psi_1 ({}^3\Sigma_u^+) = {}^3\Psi_{N,u}^n \qquad \Psi_1 ({}^1\Sigma_u^+) = {}^1\Psi_{N,u}^n$$

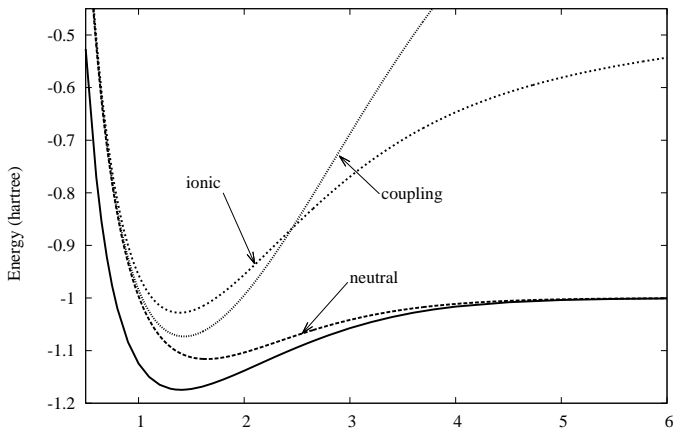
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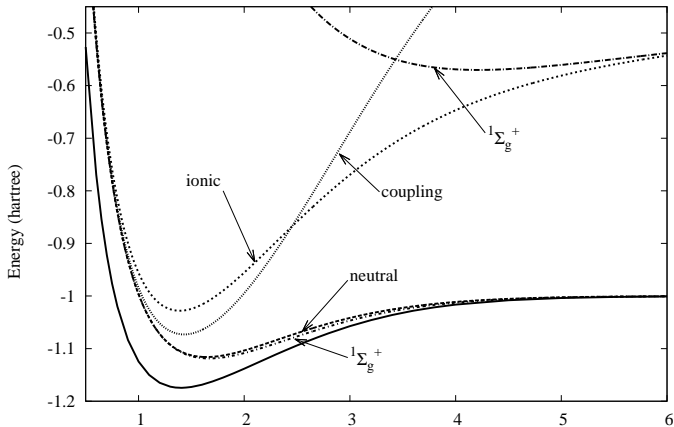
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## Nature of the chemical bond in $H_2$ : the VB description.

- The GS is fairly well described by the neutral VB configuration (Coulomb and exchange integrals).
- The bond formation is ascribed to the exchange integral.
- The ionic structure gives a modest improvement of  $D_e$  (marginal for the chemical bond).

### Considerations:

- In the HF wf the neutral and ionic structures have the same weight and HF gives a correct description near  $R_e$ .
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## Origin of the interpretative problems: non-orthogonality

Due to the non orthogonality of the  $1s_A$  and  $1s_B$  orbitals, the two  $g$  singlet structures are non orthogonal:

$$\langle {}^1\Psi_{I,g}^n | {}^1\Psi_{N,g}^n \rangle = \frac{2S}{1+S^2} \quad S = \langle 1s_A | 1s_B \rangle$$

Non-orthogonality consequences

- Practical: the working equation for the diagonalization of the Hamiltonian matrix is

$$\mathbf{Hc} = E\mathbf{M}\mathbf{c} \quad \mathbf{M} = \begin{pmatrix} 1 & \frac{2S}{1+S^2} \\ \frac{2S}{1+S^2} & 1 \end{pmatrix}$$

- Philosophical: the overlap indicates that one cannot describe H<sub>2</sub> with either structure in an exclusive manner (the neutral form is partially ionic and *vice versa*).

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## A paradoxical example of the non-orthogonality problem.

In a rather old article published by J. M. Norbek and G.A Gallup (*Ab Initio Valence Bond Calculation of Benzene*, J. Am. Chem. Soc., 95, 4460, 1973) an inconsistency of the classic VB description of Benzene has been reported.

The energy obtained from the resonance of the covalent (Kekulé and Dewar) structures is higher than the energy obtained from the resonance of the ionic structures.



The neutral and ionic wave functions have a very large overlap (they are substantially the same wave function)!!

## The orthogonal VB approach.

In OVB the structures are built using orthogonal atomic orbitals (OAOs). The OAOs are obtained by the Löwdin (symmetric or “democratic”) orthogonalization of the  $1s_A$  and  $1s_B$  atomic orbitals:

$$a = \frac{1}{2} \left( \frac{1}{\sqrt{1+S}} + \frac{1}{\sqrt{1-S}} \right) 1s_A + \frac{1}{2} \left( \frac{1}{\sqrt{1+S}} - \frac{1}{\sqrt{1-S}} \right) 1s_B$$
$$b = \frac{1}{2} \left( \frac{1}{\sqrt{1+S}} - \frac{1}{\sqrt{1-S}} \right) 1s_A + \frac{1}{2} \left( \frac{1}{\sqrt{1+S}} + \frac{1}{\sqrt{1-S}} \right) 1s_B$$



# The orthogonal VB approach.

$${}^1\Psi_{N,g}^o = \frac{ab + ba}{\sqrt{2}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}}$$

$${}^3\Psi_{N,u}^o = \frac{ab - ba}{\sqrt{2}} \left\{ \begin{array}{c} \alpha\alpha \\ \frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \\ \beta\beta \end{array} \right\}$$

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## The relation between OVB and VB.

$${}^1\Psi_{N,g}^o = \frac{\sqrt{1+S^2}}{1-S^2} \left( -S {}^1\Psi_{I,g}^n + {}^1\Psi_{N,g}^n \right)$$

$${}^1\Psi_{I,g}^o = \frac{\sqrt{1+S^2}}{1-S^2} \left( {}^1\Psi_{I,g}^n - S {}^1\Psi_{N,g}^n \right)$$

$$\langle {}^1\Psi_{N,g}^o | {}^1\Psi_{I,g}^o \rangle = 0 !$$

$${}^3\Psi_{N,u}^o = {}^3\Psi_{N,u}^n$$

$${}^1\Psi_{I,u}^o = {}^1\Psi_{I,u}^n$$

# The valence states in OVB.

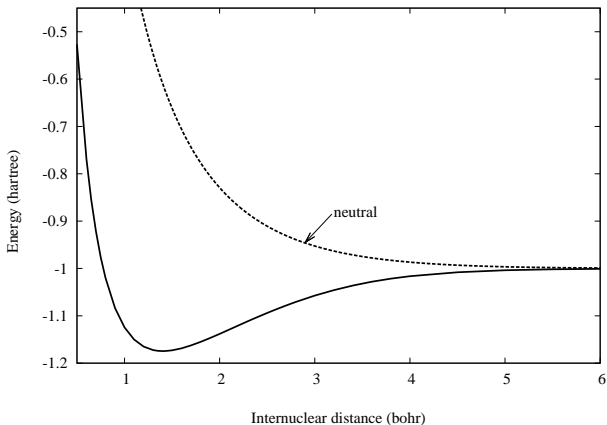
$$\Psi_1 \left( {}^1\Sigma_g^+ \right) = C_N {}^1\Psi_{N,g}^o + C_I {}^1\Psi_{I,g}^o$$

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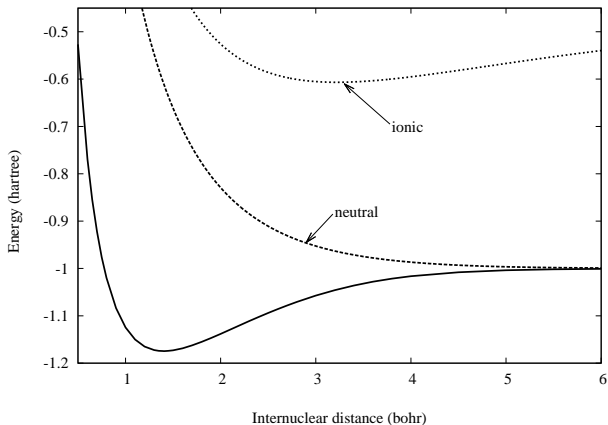
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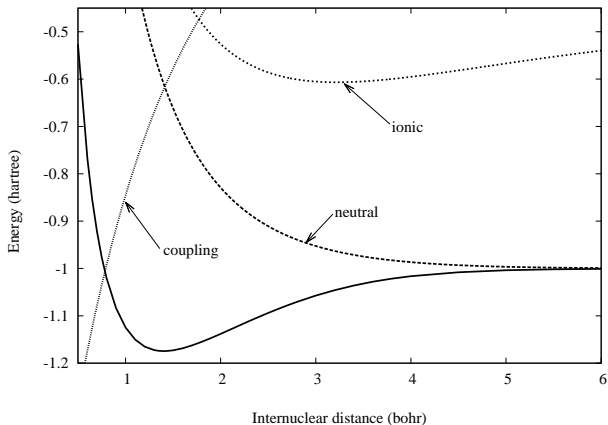
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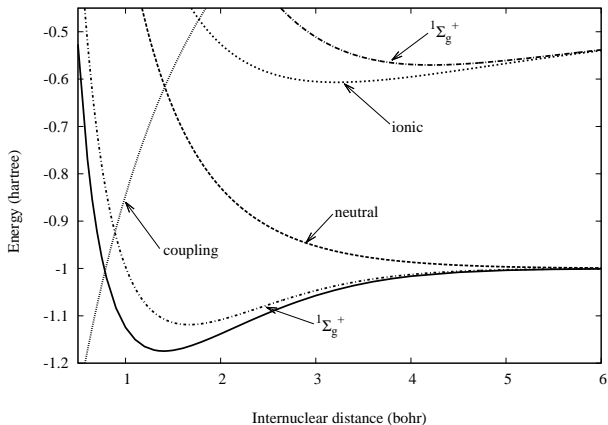
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## Nature of the chemical bond in $H_2$ : the OVB description.

- The neutral structure gives a dissociative curve (no bond!).
- The energy stabilization with respect to the atoms comes from the ionic structure (electron delocalization) which has a large effect on the energy and on the wave function  $\Rightarrow$  this structure has to be included in the calculation.

### **A clear interpretation (no overlap) but:**

The OAOs have a large weight on one atom and a tail on the other atom  $\rightarrow$  are the neutral and ionic structures really neutral and ionic?



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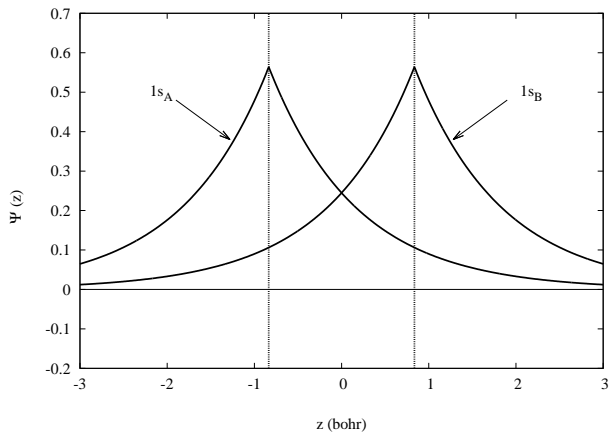
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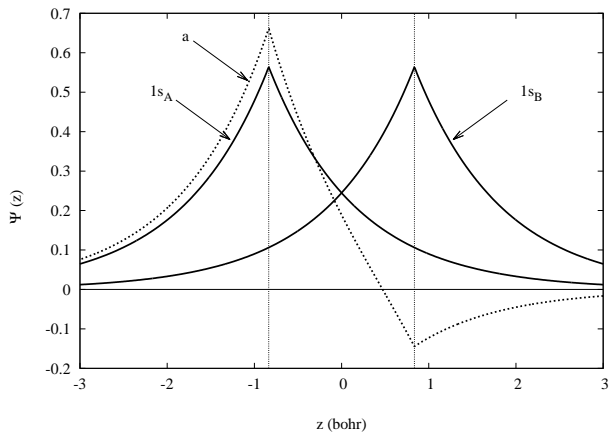
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# The “tail” problem



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## The “tail” problem

The overlap integral between a generic orbital  $\varphi$  and  $1s_B$  can be considered as a measure of the occupation of  $\varphi$  of the space around B.

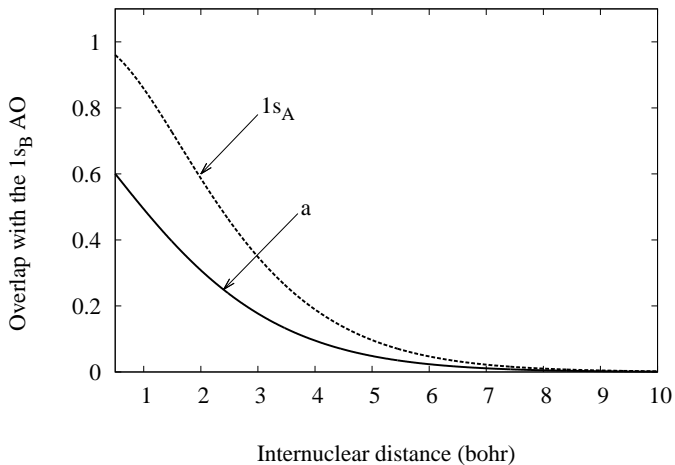
In the AO basis one has

$$\langle 1s_A | 1s_B \rangle = S$$

while in the OAO basis

$$\langle a | 1s_B \rangle = \frac{\sqrt{1+S} - \sqrt{1-S}}{2}$$

# The “tail” problem



## OVB and VB: the diabatic point of view

The key questions are:

Which structure is actually “neutral”?

$$\frac{1s_A 1s_B + 1s_B 1s_A}{\sqrt{2(1+S^2)}} \quad (\text{VB}) \quad \text{or} \quad \frac{ab + ba}{\sqrt{2}} \quad (\text{OVB})$$

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## OVB and VB: the diabatic point of view

In the Born-Oppenheimer approximation, the possibility to “decouple” the nuclear motion from the electronic one is based on the assumption that terms like

$$\left\langle \Psi_1 \left| \frac{\partial}{\partial R} \right| \Psi_2 \right\rangle \quad \Psi_i = \text{electronic wavefunction}$$

can be considered vanishing.

These terms are called nonadiabatic couplings: they are usually small, but they play a key role in many dynamic processes (e.g. photochemistry) where they control the possibility to jump from one electronic surface to another (surface hopping). These processes are considered in the “nonadiabatic molecular dynamics” field.

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## Diabatic states

The eigenfunctions of the electronic Hamiltonian ( $\Psi_i$  and  $\Psi_j$  above) are called “adiabatic” states.

One can consider a set of electronic states for which the nonadiabatic couplings are zero (they do not diagonalize the electronic Hamiltonian!!): these states are called “diabatic” states.

In the definition of strictly diabatic states in polyatomic molecules one actually faces problems (they do not exist!), and only “almost” diabatic (quasi-diabatic) states can be computed.

Nevertheless, the concept of diabatic states is important: they play a key role in the interpretation of the electronic wfs in chemical terms, because they are supposed to keep a well defined nature at all nuclear geometries.

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## Diabatic states

At  $R \rightarrow \infty$  the VB and OVB structures become identical and have a clear nature (neutral and ionic) and they are diabatic.

What happens at finite values of  $R$ ?

For the VB structures the nonadiabatic couplings are

$$\left\langle {}^1\Psi_{I,g}^n \left| \frac{\partial}{\partial R} \right| {}^1\Psi_{N,g}^n \right\rangle = \left\langle {}^1\Psi_{N,g}^n \left| \frac{\partial}{\partial R} \right| {}^1\Psi_{I,g}^n \right\rangle = \frac{1 - S^2}{(1 + S^2)^2} \frac{\partial S}{\partial R}$$

$\Rightarrow$  they are not diabatic

$\Rightarrow$  they change in nature along  $R$ .

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$$\left\langle {}^1\Psi_{I,g}^n \left| \frac{\partial}{\partial R} \right| {}^1\Psi_{N,g}^n \right\rangle = \left\langle {}^1\Psi_{N,g}^n \left| \frac{\partial}{\partial R} \right| {}^1\Psi_{I,g}^n \right\rangle = \frac{1 - S^2}{(1 + S^2)^2} \frac{\partial S}{\partial R}$$

⇒ they are not diabatic

⇒ they change in nature along  $R$ .



## Diabatic states

At  $R \rightarrow \infty$  the VB and OVB structures become identical and have a clear nature (neutral and ionic) and they are diabatic.

What happens at finite values of  $R$ ?

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$\Rightarrow$  they are not diabatic

$\Rightarrow$  they change in nature along  $R$ .

## Diabatic states

On the contrary, for the OVB structures one has

$$\left\langle {}^1\Psi_{I,g}^o \left| \frac{\partial}{\partial R} \right| {}^1\Psi_{N,g}^o \right\rangle = \left\langle {}^1\Psi_{N,g}^o \left| \frac{\partial}{\partial R} \right| {}^1\Psi_{I,g}^o \right\rangle = 0$$

⇒ the OVB structures are diabatic

⇒ they keep their nature as  $R$  changes

⇒ they are the “actual” neutral and ionic structures.

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$\Rightarrow$  they are the “actual” neutral and ionic structures.

## Conclusions: comparison of VB and OVB

The VB approach gives good energies with a wave function more compact than the OVB one. The non orthogonality of the structures brings some problem (practical and interpretative).

OVB gives a coherent (diabatic) description of the neutral and ionic configurations but it requires the explicit inclusion of the ionic structures to describe the bond formation.

Moreover, it can be directly linked to MO methods: by a simple localization (unitary transformation) of the active MOs one can have an OVB reading of the CASSCF wave function.

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## The molecular orbital description

The MO approach starts from a completely different point of view. The first step is the identification of the molecular “boxes” where the electrons are accommodated

$$\sigma_g = \frac{1s_A + 1s_B}{\sqrt{2(1+S)}} = \frac{a+b}{\sqrt{2}}$$

$$\sigma_u = \frac{1s_A - 1s_B}{\sqrt{2(1-S)}} = \frac{a-b}{\sqrt{2}}$$



## The molecular orbital description

The  $g$  many-electron wave functions are

$$\|\sigma_g\bar{\sigma}_g\| = \frac{{}^1\Psi_{I,g}^o + {}^1\Psi_{N,g}^o}{\sqrt{2}} = \frac{1}{\sqrt{2}} \frac{\sqrt{1+S^2}}{1+S} \left( {}^1\Psi_{I,g}^n + {}^1\Psi_{N,g}^n \right)$$

$$\|\sigma_u\bar{\sigma}_u\| = \frac{{}^1\Psi_{I,g}^o - {}^1\Psi_{N,g}^o}{\sqrt{2}} = \frac{1}{\sqrt{2}} \frac{\sqrt{1+S^2}}{1-S} \left( {}^1\Psi_{I,g}^n - {}^1\Psi_{N,g}^n \right)$$

Both determinants, with a closed shell nature in MO, are a superposition with equal weight of the ionic (closed shell) and neutral (open shell) VB or OVB structures.

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Both determinants, with a closed shell nature in MO, are a superposition with equal weight of the ionic (closed shell) and neutral (open shell) VB or OVB structures.

## The molecular orbital description

The ground state wave function,  $\Psi_{GS}$  is

$$\begin{aligned}\Psi_{GS} &= \lambda \|\sigma_g \bar{\sigma}_g\| - \mu \|\sigma_u \bar{\sigma}_u\| && \lambda, \mu > 0 \\ &= \frac{(\lambda + \mu)}{\sqrt{2}} {}^1\Psi_{N,g}^o + \frac{(\lambda - \mu)}{\sqrt{2}} {}^1\Psi_{I,g}^o \\ &= \frac{\sqrt{1+S^2}}{\sqrt{2}} \left[ \left( \frac{\lambda}{1+S} + \frac{\mu}{1-S} \right) {}^1\Psi_{N,g}^n + \right. \\ &\quad \left. + \left( \frac{\lambda}{1+S} - \frac{\mu}{1-S} \right) {}^1\Psi_{I,g}^n \right]\end{aligned}$$

One obtains strictly the same wave function in the three formalisms.

## The molecular orbital description

For the  $u$  functions one has the noteworthy relations

$${}^3\Psi_u = \frac{\|\sigma_g\bar{\sigma}_u\| - \|\sigma_u\bar{\sigma}_g\|}{\sqrt{2}} = {}^3\Psi_{N,u}^o = {}^3\Psi_{N,u}^n$$

$${}^1\Psi_u = \frac{\|\sigma_g\bar{\sigma}_u\| + \|\sigma_u\bar{\sigma}_g\|}{\sqrt{2}} = {}^1\Psi_{I,u}^o = {}^3\Psi_{I,u}^n$$

Both  $u$  states are combination of open shell determinants in MO, but in VB and OVB one is open shell (triplet) and one closed shell (singlet).

Warning: be careful to identify a state as “close” or “open” shell!!  
An orbital transformation can completely change the description!!

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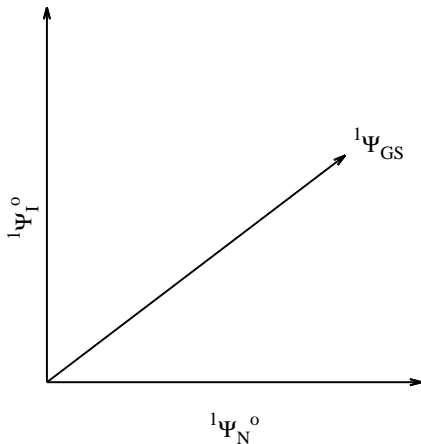
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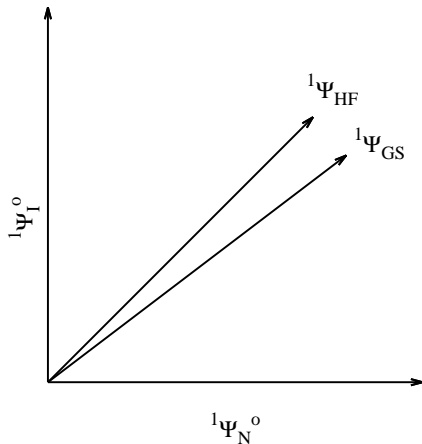
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# Graphical representation of the wave function composition: $R = 1.64 \text{ au.}$

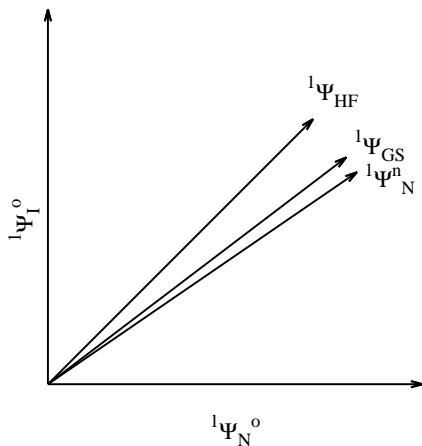


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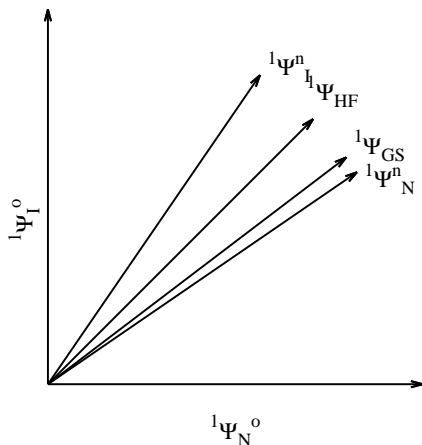




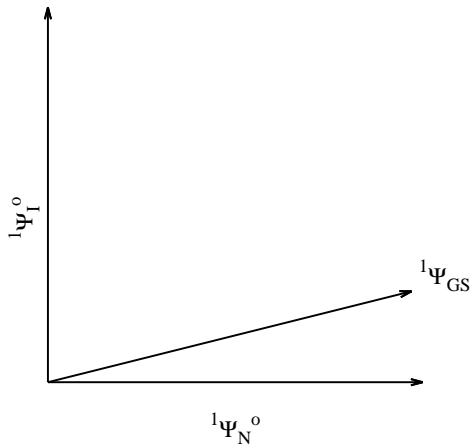
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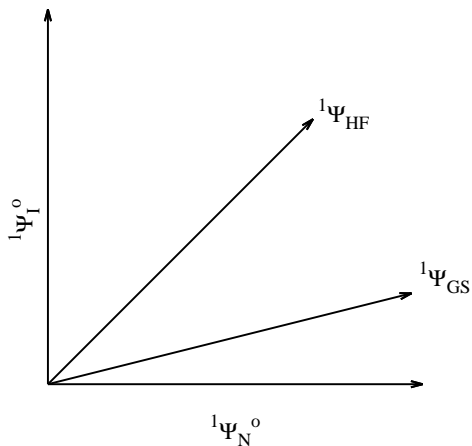
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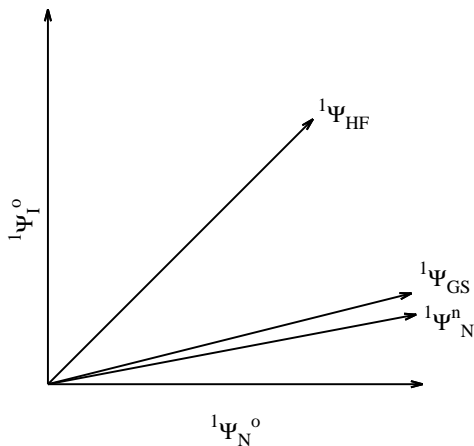
# Graphical representation of the wave function composition: $R = 4.00 \text{ au.}$



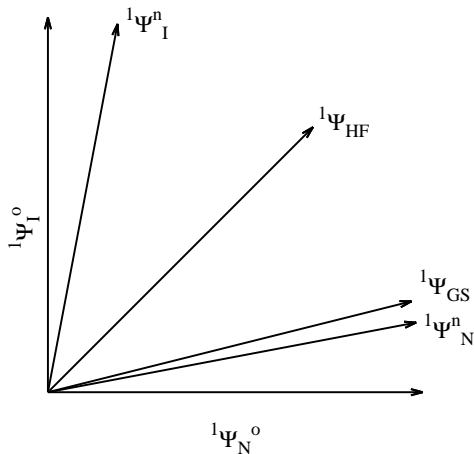
# Graphical representation of the wave function composition: $R = 4.00 \text{ au.}$



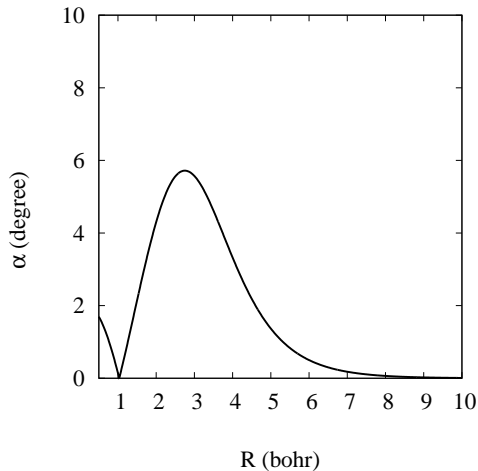
# Graphical representation of the wave function composition: $R = 4.00 \text{ au.}$



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# Dependence on $R$ of the angle $\alpha$ between $\Psi_{GS}$ and ${}^1\Psi_{N,g}^n$ .



## A possible definition of entanglement

Entanglement has recently been introduced in quantum chemistry (adopted from the DMRG approach in solid-state physics) through the von Neumann entropy  $s$ .

One introduces the one-orbital von Neumann entropy:

$$s(1)_i = - \sum_{\alpha=1}^4 \omega_{\alpha,i} \ln \omega_{\alpha,i}$$

- $i \Rightarrow$  one-electron functions (DMOs, LMOs, OAOs)
- $\omega_{\alpha,i} \Rightarrow$  eigenvalues of the one-orbital Reduced Density Matrix (not to be confused with the occupation numbers!)
- $\alpha \Rightarrow |-\rangle, |\uparrow\rangle, |\downarrow\rangle, \text{ and } |\updownarrow\rangle,$



## A possible definition of entanglement

Then, the two-orbital von Neumann entropy is:

$$s(2)_{i,j} = - \sum_{\alpha=1}^{16} \omega_{\alpha,i,j} \ln \omega_{\alpha,i,j}$$

- $i, j \Rightarrow$  one-electron functions (DMOs, LMOs, OAOs)
- $\omega_{\alpha,i,j} \Rightarrow$  eigenvalues of the two-orbital Reduced Density Matrix
- $\alpha \Rightarrow |--\rangle, |\uparrow-\rangle, |\downarrow-\rangle, |\uparrow\uparrow-\rangle, \dots, |\uparrow\uparrow\uparrow\uparrow\rangle$ .

## A possible definition of entanglement

If the one-electron functions (sites?)  $i$  and  $j$  are not entangled with each others,  $s(1)_i + s(1)_j = s(2)_{i,j}$ .

The entanglement between  $i$  and  $j$ ,  $I_{i,j}$  (*mutual information*), can be defined as:

$$I_{i,j} = \frac{1}{2} [s(1)_i + s(1)_j - s(2)_{i,j}] (1 - \delta_{ij})$$

A simple interpretation:

- $s(1)_i$  and  $s(1)_j$  describe the entanglement of  $i$  and  $j$  with the rest of the system
- $s(2)_{i,j}$  describe the entanglement of the pair of  $i, j$  with the rest of the system
- the entanglement between  $i$  and  $j$  reduces  $s(2)_{i,j}$  with respect to the sum of  $s(1)_i$  and  $s(1)_j$

## Entanglement in $H_2$ : the MO approach

The MO approach:

$$\Psi_{GS}^{MO} = \lambda \|\sigma_g \bar{\sigma}_g\| - \sqrt{1 - \lambda^2} \|\sigma_u \bar{\sigma}_u\|$$

- $\lambda^2 \Rightarrow$  probability to find two electrons in  $\sigma_g$  and zero in  $\sigma_u$
- $1 - \lambda^2 \Rightarrow$  probability to find two electrons in  $\sigma_u$  and zero in  $\sigma_g$

Diagonal elements (eigenvalues) of the one-orbital Reduced Density Matrix

	$\sigma_g$	$\sigma_u$
$ -\rangle$	$1 - \lambda^2$	$\lambda^2$
$ \uparrow\rangle$	0	0
$ \downarrow\rangle$	0	0
$ \uparrow\downarrow\rangle$	$\lambda^2$	$1 - \lambda^2$

## Entanglement in $H_2$ : the MO approach

The one-orbital entropy is

$$s(1)_{\sigma_g} = s(1)_{\sigma_u} = -\lambda^2 \ln(\lambda^2) - (1 - \lambda^2) \ln(1 - \lambda^2)$$

In the two-orbital RDM, among the  $16^2$  elements only 4 are not vanishing:

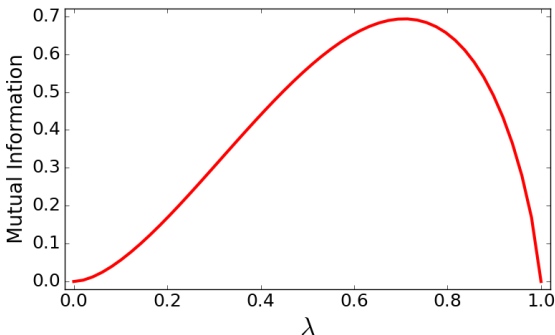
$$RDM(2) = \begin{bmatrix} \begin{matrix} |-\uparrow\downarrow\rangle \\ 1 - \lambda^2 \\ -\lambda\sqrt{1 - \lambda^2} \end{matrix} & \begin{matrix} |\uparrow\downarrow-\rangle \\ -\lambda\sqrt{1 - \lambda^2} \\ \lambda^2 \end{matrix} \end{bmatrix} \begin{matrix} |-\uparrow\downarrow\rangle \\ |\uparrow\downarrow-\rangle \end{matrix}$$

For any value of  $\lambda$  the eigenvalues are  $\omega_{1,\sigma_g,\sigma_u} = 0$  and  $\omega_{2,\sigma_g,\sigma_u} = 1$ , therefore  $s(2)_{\sigma_g,\sigma_u} = 0$

## Entanglement in $H_2$ : the MO approach

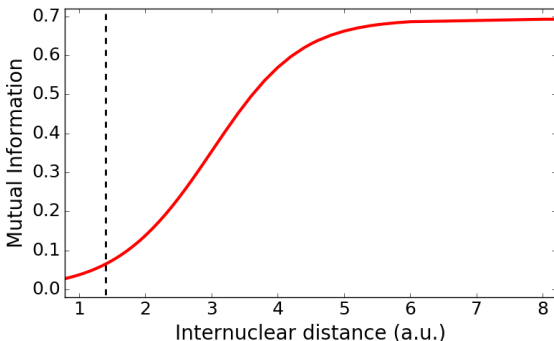
The mutual information,  $I_{\sigma_g, \sigma_u}$ , is therefore:

$$I_{\sigma_g, \sigma_u} = - \left[ \lambda^2 \ln(\lambda^2) + (1 - \lambda^2) \ln(1 - \lambda^2) \right]$$



## Entanglement in $H_2$ : the MO approach

Dependence of the mutual information on the internuclear distance using MOs. The black dashed line indicates the equilibrium geometry.



## Entanglement in H<sub>2</sub>: the OVB approach

In the OVB approach  $\Psi_{GS}^{OVB} = \lambda \frac{\|a\bar{b}\| + \|b\bar{a}\|}{\sqrt{2}} + \sqrt{1 - \lambda^2} \frac{\|a\bar{a}\| + \|b\bar{b}\|}{\sqrt{2}}$

Diagonal elements (eigenvalues) of the one-orbital Reduced Density Matrix using OAOs

	<i>a</i>	<i>b</i>
$ \bar{-}\rangle$	$(1 - \lambda^2)/2$	$(1 - \lambda^2)/2$
$ \uparrow\rangle$	$\lambda^2/2$	$\lambda^2/2$
$ \downarrow\rangle$	$\lambda^2/2$	$\lambda^2/2$
$ \uparrow\downarrow\rangle$	$(1 - \lambda^2)/2$	$(1 - \lambda^2)/2$

$$s(1)_a = s(1)_b = -\lambda^2 \ln\left(\frac{\lambda^2}{2}\right) - (1 - \lambda^2) \ln\left(\frac{1 - \lambda^2}{2}\right)$$

## Entanglement in $H_2$ : the OVB approach

The two-orbital RDM in OVB is:

$$RDM(2) = \frac{1}{2} \begin{bmatrix} |-\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\uparrow\downarrow\rangle \\ 1 - \lambda^2 & \lambda\sqrt{1 - \lambda^2} & -\lambda\sqrt{1 - \lambda^2} & 1 - \lambda^2 \\ \lambda\sqrt{1 - \lambda^2} & \lambda^2 & -\lambda^2 & \lambda\sqrt{1 - \lambda^2} \\ -\lambda\sqrt{1 - \lambda^2} & -\lambda^2 & \lambda^2 & -\lambda\sqrt{1 - \lambda^2} \\ 1 - \lambda^2 & \lambda\sqrt{1 - \lambda^2} & -\lambda\sqrt{1 - \lambda^2} & 1 - \lambda^2 \end{bmatrix}$$

$$\omega_{1,a,b} = \omega_{1,a,b} = \omega_{3,a,b} = 0 \text{ and } \omega_{4,a,b} = 1$$

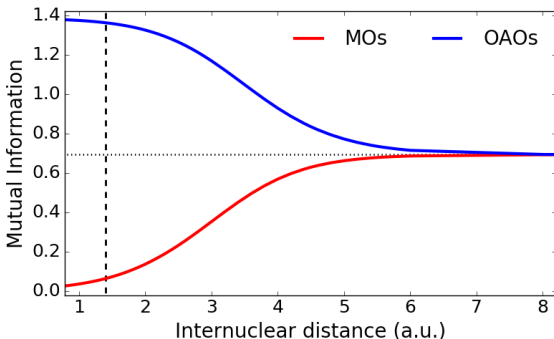
$$s(2)_{a,b} = 0$$

$$I_{a,b} = -[\lambda^2 \ln(\lambda^2) + (1 - \lambda^2) \ln(1 - \lambda^2)] + \ln(2)$$



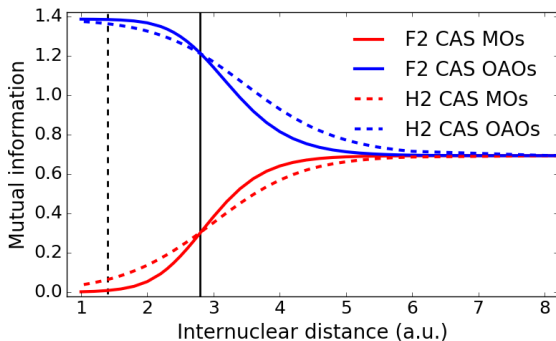
## Entanglement in $H_2$ : the OVB approach

Dependence of the mutual information on the internuclear distance using MOs and OAOS. The black pointed horizontal line indicates the limit  $\ln(2)$ .



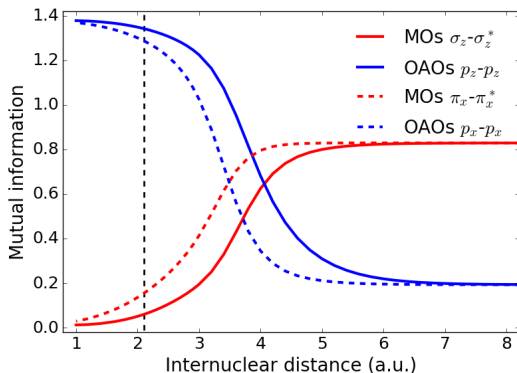
## Entanglement in other diatomic molecules: $F_2$

Mutual information as a function of the internuclear distance with MOs and OAOs for  $F_2$  and  $H_2$  dimers. The black solid and dashed vertical lines indicate  $R_e$  for  $F_2$  and  $H_2$ , respectively.



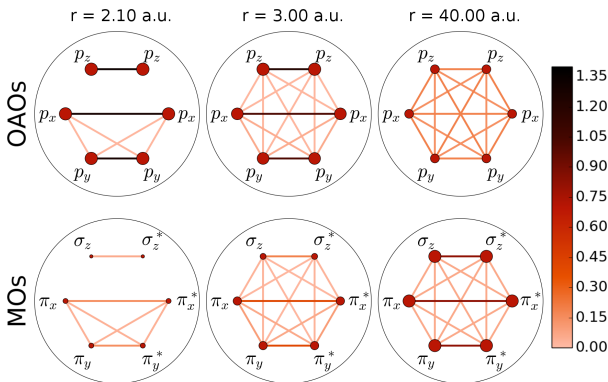
## Entanglement in other diatomic molecules: $N_2$

Dependence of the mutual information on the internuclear distance using MOs and OAOs for  $N_2$ . The black dashed horizontal line indicates the equilibrium geometry.



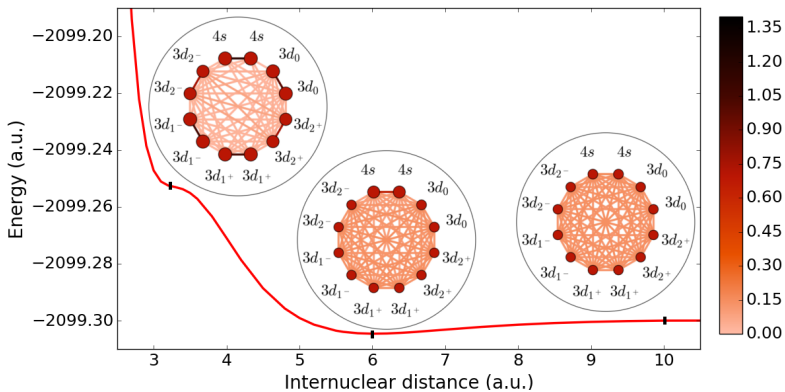
## Entanglement maps: $N_2$

Entanglement maps for  $N_2$  for MOs and OAOs. The color of the lines indicates the amplitude of the mutual information, the size of the red circles is proportional to the one-orbital entropy.



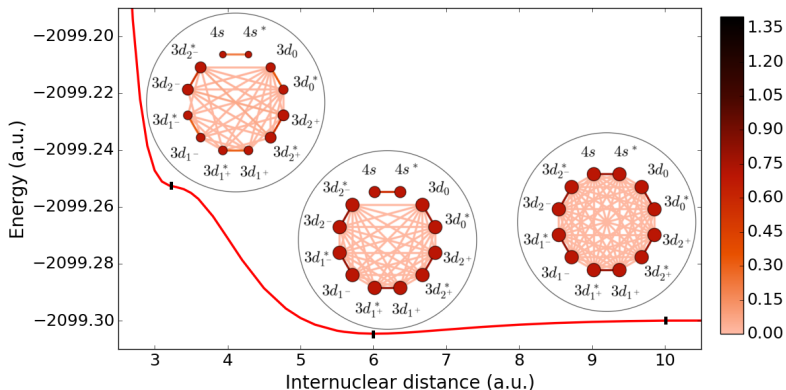
## Entanglement maps: $Cr_2$ in OAOs

Entanglement maps for  $Cr_2$  using orthogonal atomic orbitals at different internuclear distances.

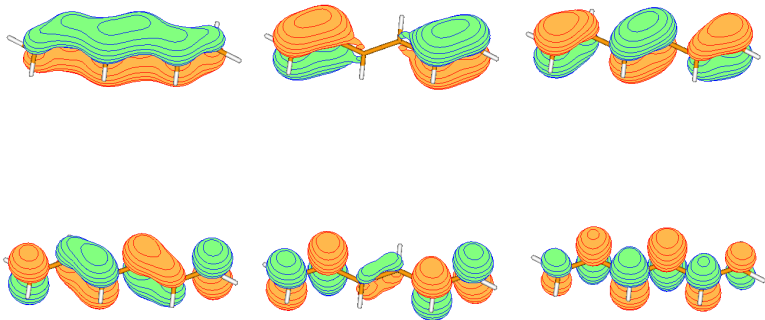


## Entanglement maps: $Cr_2$ in MOs

Entanglement maps for  $Cr_2$  using delocalized orbitals at different internuclear distances.

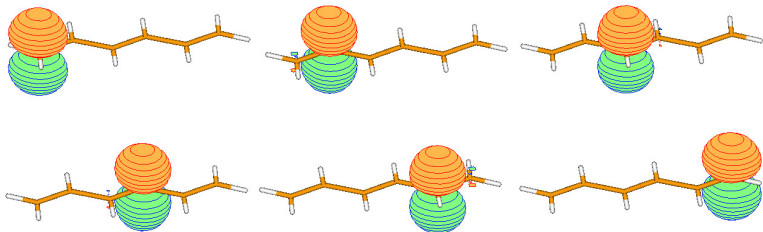


## One-electron basis in hexatriene: delocalized MOs



CASSCF delocalized molecular orbitals of hexatriene.

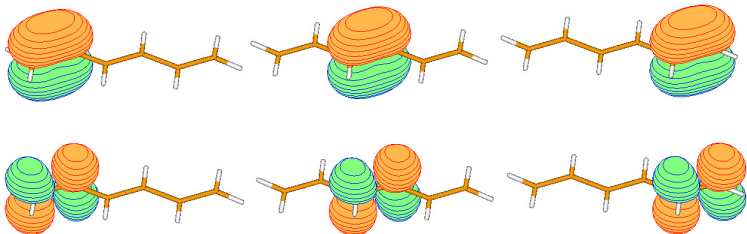
## One-electron basis in hexatriene: OAOs



CASSCF localized orthogonal atomic orbitals of hexatriene.

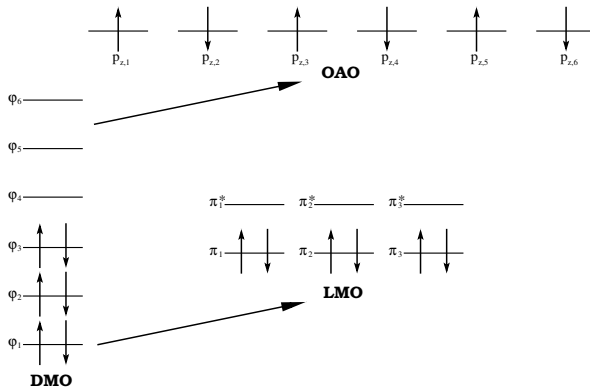


## One-electron basis in hexatriene: localized MOs



CASSCF localized molecular (bond) orbitals of hexatriene.

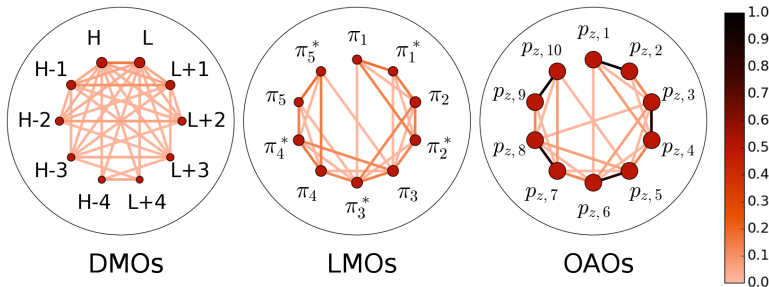
# CASSCF determinants



Determinants written in different orbital bases.

## Entanglement in other molecules: decapentaene

Entanglement maps for Decapentaene using three different orbital sets:  
CASSCF(10, 10).



# Entanglement in magnetic systems

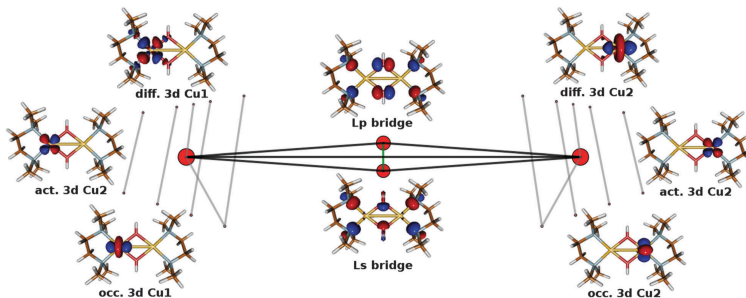
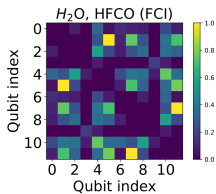
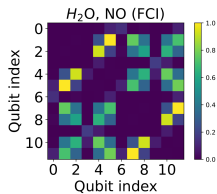


Fig. 9 Entanglement measures for  $Cu_2(OH)_2$ . Triplet wavefunction, CAS(6,4) + DDC2.

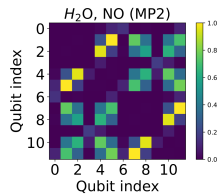
# Entanglement and quantum computing



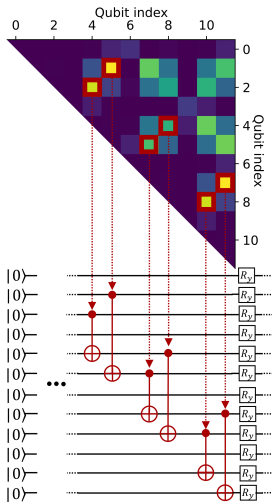
i)



j)



# Entanglement and quantum computing



The mutual information maps (for simple wfs, like MP2) can be used to build a circuit for a quantum computer.

Entangled qubits (spinorbitals) are mapped on CNOT two-qubit quantum gates  $\rightarrow$  heuristic ansatz for the wf. Various problems (order, cross-entanglement, etc.).

A more compact mutual information map reduces the “depth” of the quantum circuit.

## Entanglement and quantum computing

Comparison of quantum information (entanglement) obtained using the von Neumann (quantum) or the Shannon (classic) definition of the one-site and two-site entropies.

## Entanglement in H<sub>2</sub>: the OVB approach. von Neumann vs Shannon entropies

$$\text{RDM}(2) = \frac{1}{2} \begin{bmatrix} |-\uparrow\uparrow\rangle & |\uparrow\downarrow\rangle & |\downarrow\uparrow\rangle & |\uparrow\downarrow\rangle \\ 1 - \lambda^2 & \lambda\sqrt{1 - \lambda^2} & -\lambda\sqrt{1 - \lambda^2} & 1 - \lambda^2 \\ \lambda\sqrt{1 - \lambda^2} & \lambda^2 & -\lambda^2 & \lambda\sqrt{1 - \lambda^2} \\ -\lambda\sqrt{1 - \lambda^2} & -\lambda^2 & \lambda^2 & -\lambda\sqrt{1 - \lambda^2} \\ 1 - \lambda^2 & \lambda\sqrt{1 - \lambda^2} & -\lambda\sqrt{1 - \lambda^2} & 1 - \lambda^2 \end{bmatrix}$$

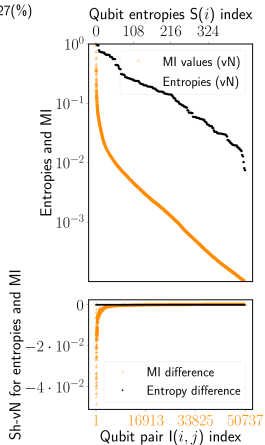
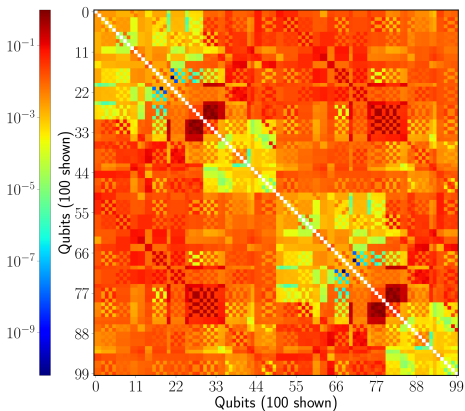
von Neuman (quantum)  $s(2)_{i,j} = -\sum_{\alpha=1}^{16} \omega_{\alpha,i,j} \ln \omega_{\alpha,i,j}$   
 $\omega_{\alpha,i,j}$  eigenvalues of RDM(2)

Shannon (classic)  $s(2)_{i,j} = -\sum_{\alpha=1}^{16} \text{RDM}(2)_{\alpha,i,j} \ln \text{RDM}(2)_{\alpha,i,j}$   
 $\text{RDM}(2)_{\alpha,i,j}$  diagonal elements of RDM(2)



# Entanglement and quantum computing

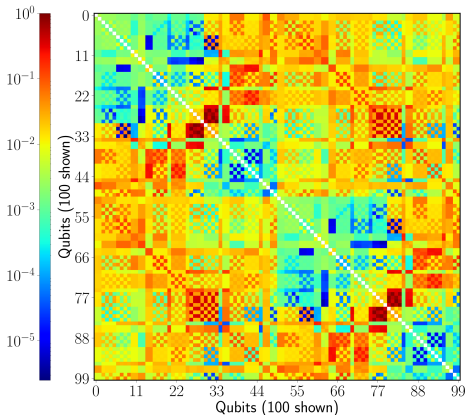
Benzene dimer, HF Canonical Orbitals CISC,  $L1=7.827(\%)$



# Entanglement and quantum computing

Benzene dimer, Natural Orbitals

CISD, L1=0.105(%)



Qubit entropies  $S(i)$  index  
 0 114 228 342

