



# **VB reading of CASSCF wavefunctions: a few examples for ground and excited states**

Celestino Angeli

Department of Chemistry,  
University of Ferrara, Italy

## VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

---

A different approach  
to benzene

---

Polyenes

---

Singlet-Triplet  
splitting in Ullman's  
diradical

---

# The non-orthogonal VB and the orthogonal VB approaches: a comparison for the H<sub>2</sub> molecule.

**C. Angeli, R. Cimiraglia, J.-P. Malrieu, “On the  
relative merits of non-orthogonal and  
orthogonal Valence Bond methods illustrated on the  
hydrogen molecule**

*J. Chem. Ed.*, **85(1)**, 150-158, (2008).

# The standard VB approach.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

In the standard VB approach the valence states of H<sub>2</sub> are described using 4 structures (2 neutral and 2 ionic):

$${}^1\Psi_{N,g}^n = \frac{1s_A 1s_B + 1s_B 1s_A}{\sqrt{2(1+S^2)}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}}$$

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

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

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

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

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

The 4 VB structures are used to describe two  ${}^1\Sigma_g^+$  states,

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

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

and one  ${}^3\Sigma_u^+$  and one  ${}^1\Sigma_u^+$  states:

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

# Energy of the two ${}^1\Psi_{N,g}^n$ and ${}^1\Psi_{I,g}^n$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

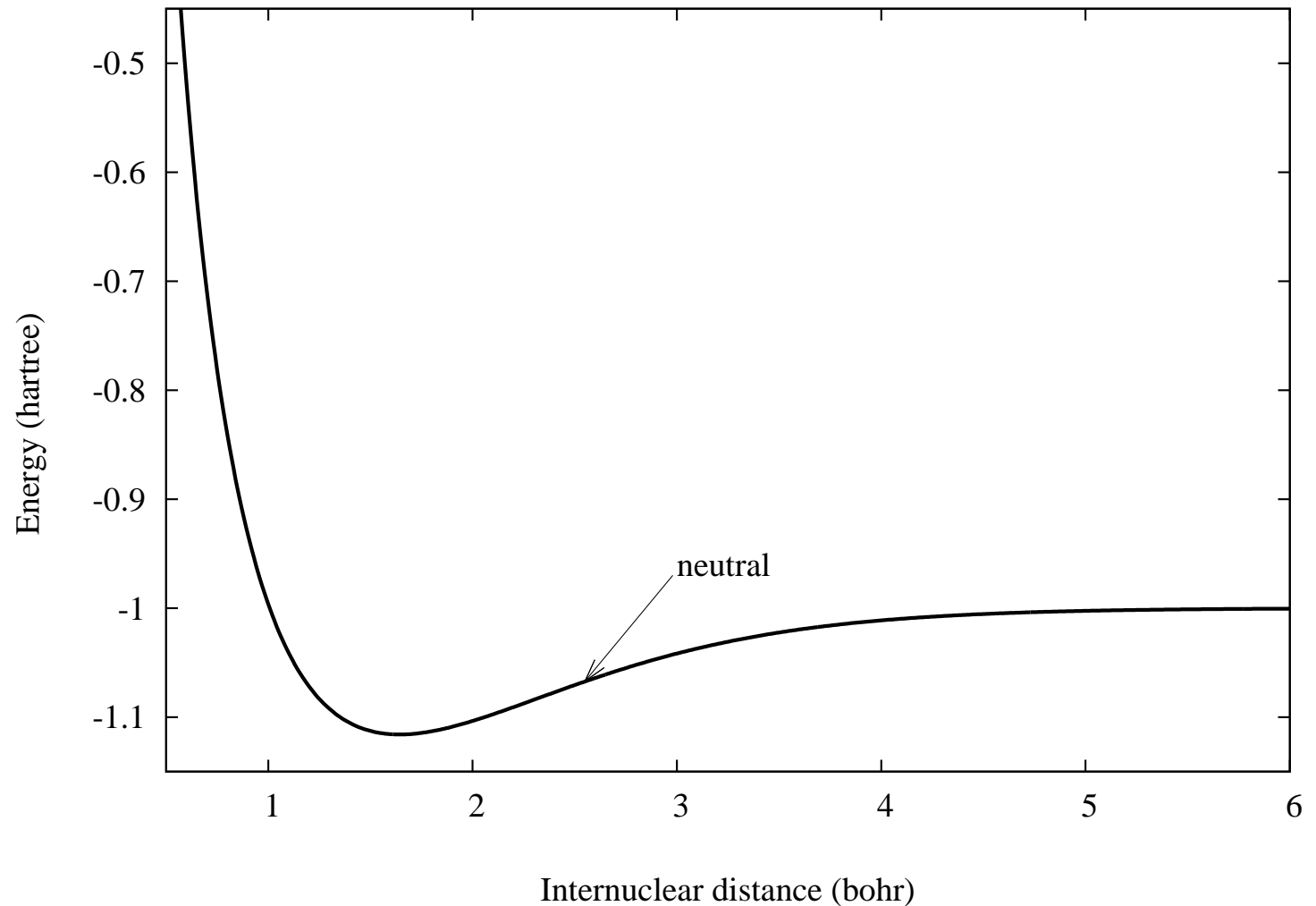
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



# Energy of the two ${}^1\Psi_{N,g}^n$ and ${}^1\Psi_{I,g}^n$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

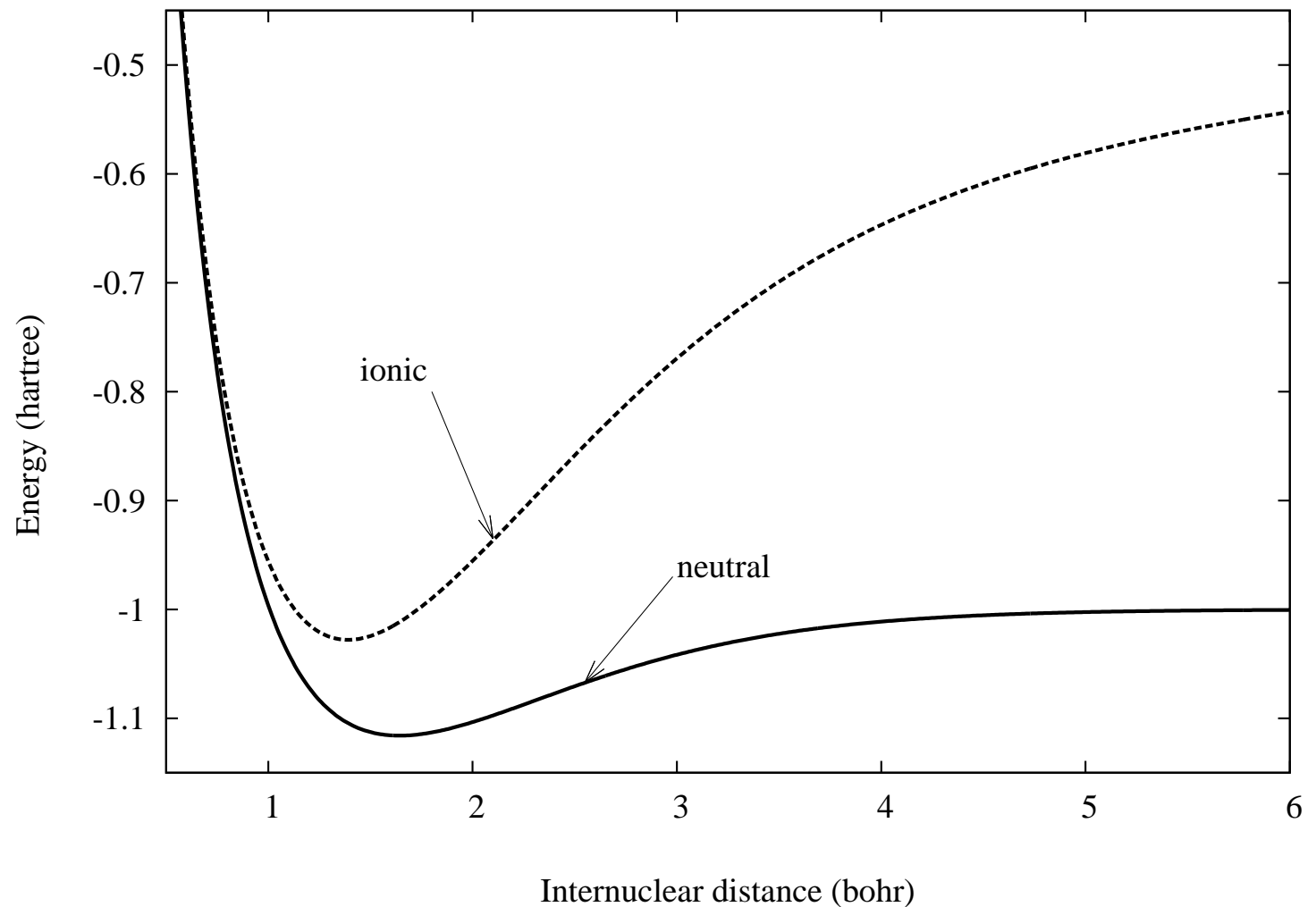
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



# Energy of the two ${}^1\Psi_{N,g}^n$ and ${}^1\Psi_{I,g}^n$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

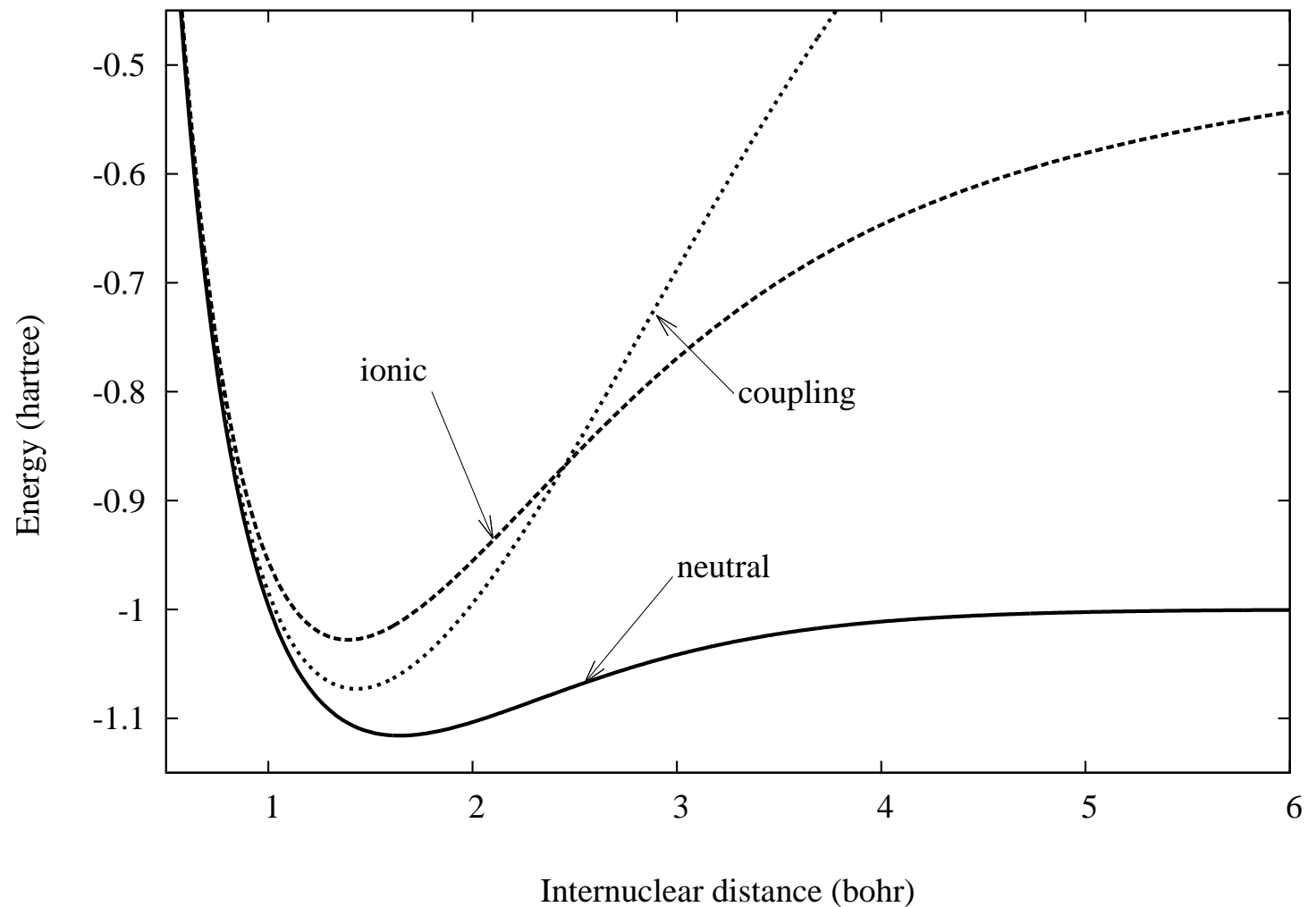
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical





# Energy of the two ${}^1\Psi_{N,g}^n$ and ${}^1\Psi_{I,g}^n$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

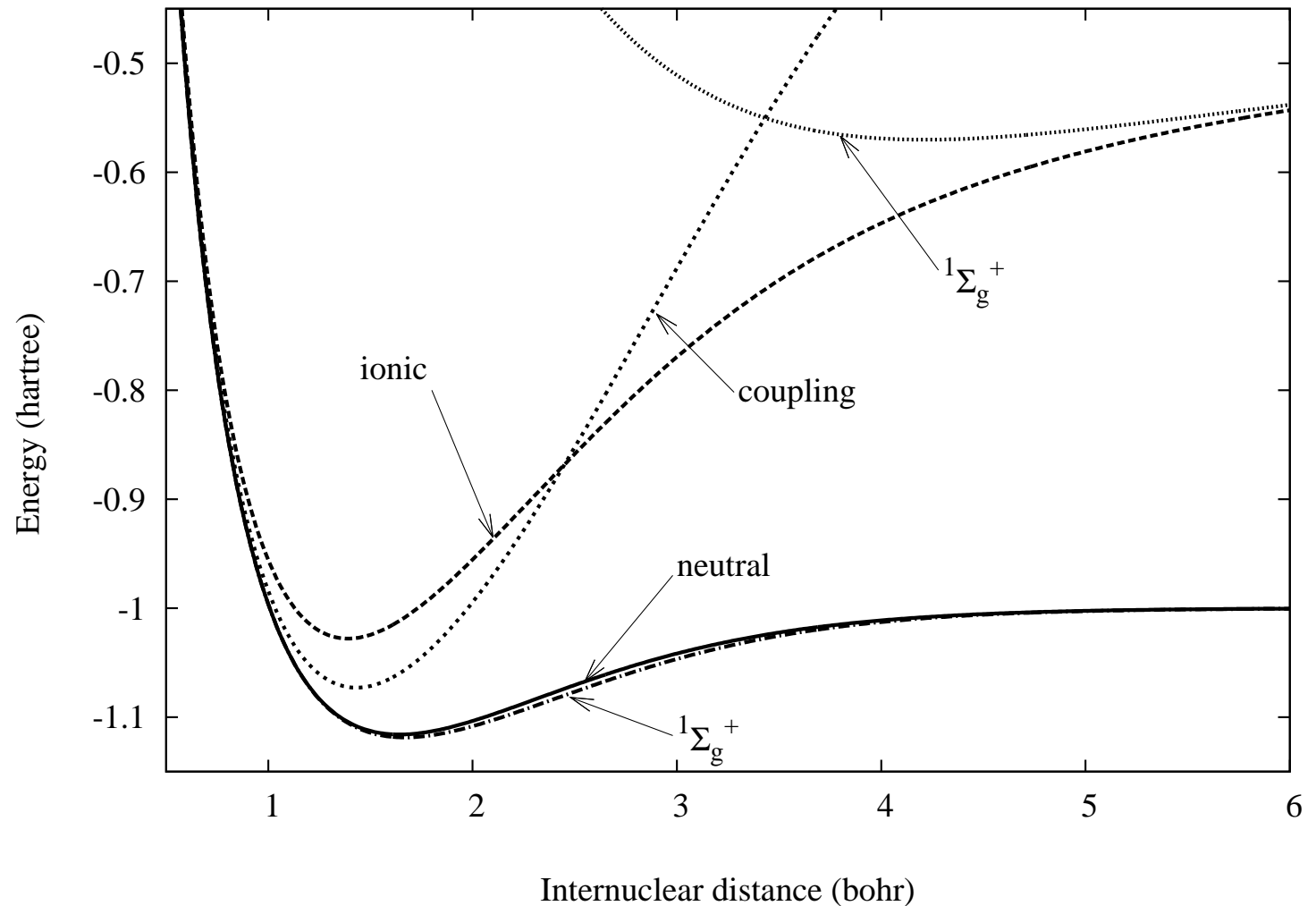
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



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

VB and OVB:  $H_2$

Standard VB

Orthogonal VB  
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

- The GS is fairly well described by the neutral VB configuration (Coulomb and exchange integrals).

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

VB and OVB:  $H_2$

Standard VB

Orthogonal VB  
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

- The GS is fairly well described by the neutral VB configuration (Coulomb and exchange integrals).
- The bond formation is ascribed to the exchange integral.

# Nature of the chemical bond in H<sub>2</sub>: the VB description.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB  
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

- 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).

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

VB and OVB:  $H_2$

Standard VB

Orthogonal VB  
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

- 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  $R_e$ .
- ✓ The ionic structure gives a modest energy modification, but has a large weight in the wf (ionic and neutral are close in energy with a large interaction).

# Origin of the interpretative problems: non-orthogonality

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

## Non-orthogonality consequences

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

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

- ✓ Philosophical: the overlap between the two forms indicates that one cannot describe the system with either structure in an exclusive manner (the neutral form has partially ionic nature and *vice versa*).

# Energy of the two ${}^3\Psi_{N,u}^n$ ( ${}^3\Sigma_u^+$ ) and ${}^1\Psi_{I,u}^n$ ( ${}^1\Sigma_u^+$ ) structures.

VB and OVB: H<sub>2</sub>

Standard VB

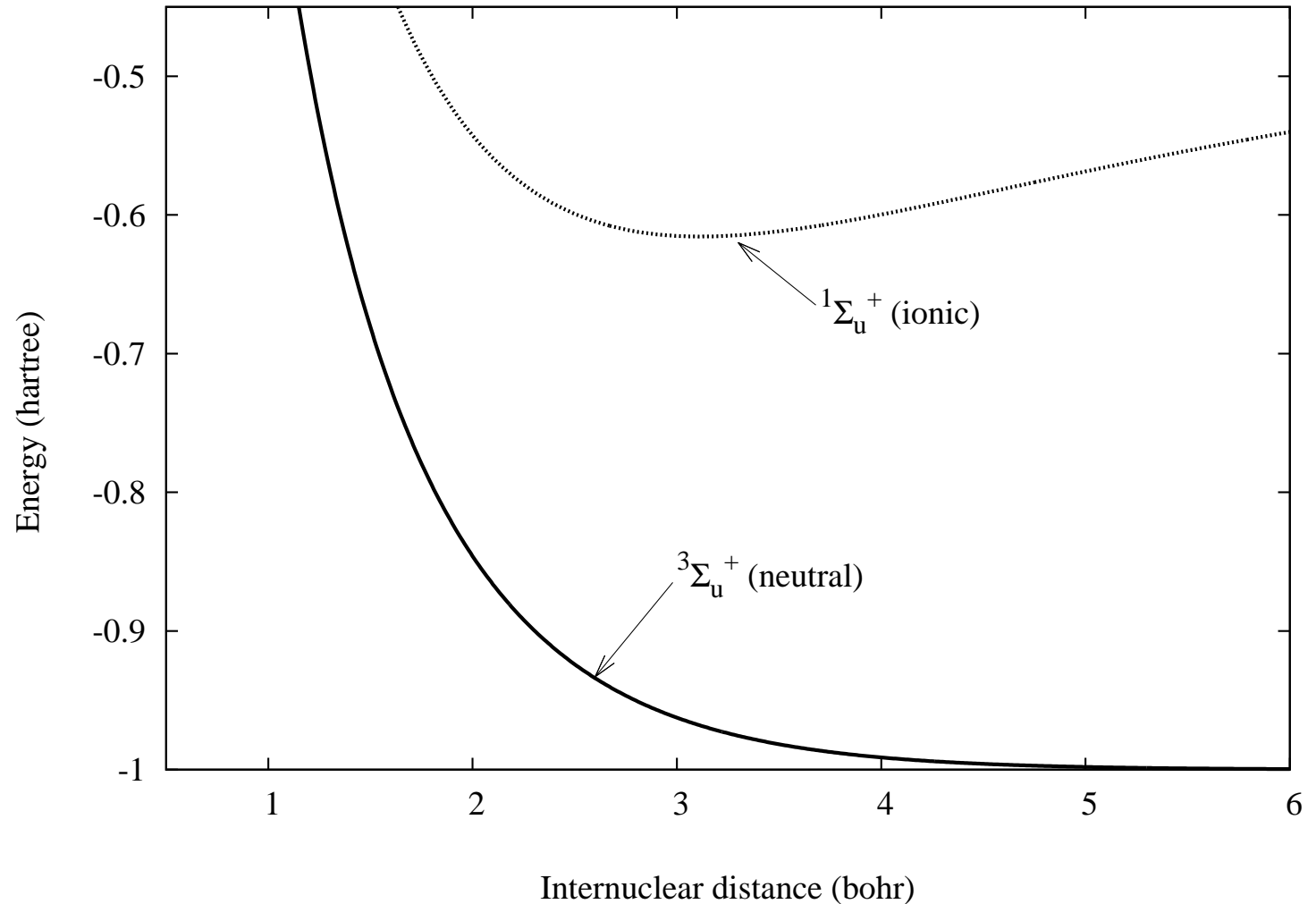
Orthogonal VB  
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# The orthogonal VB approach.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

In OVB the structures are built using orthogonal atomic orbitals (OAOs). The OAOs are obtained by 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 OVB structures.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

$$\begin{aligned} {}^1\Psi_{N,g}^o &= \frac{ab + ba}{\sqrt{2}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \\ {}^3\Psi_{N,u}^o &= \frac{ab - ba}{\sqrt{2}} \left\{ \begin{array}{c} \alpha\alpha \\ \frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \\ \beta\beta \end{array} \right\} \\ {}^1\Psi_{I,g}^o &= \frac{aa + bb}{\sqrt{2}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \\ {}^1\Psi_{I,u}^o &= \frac{aa - bb}{\sqrt{2}} \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \end{aligned}$$

# The relation between OVB and VB.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

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

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

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

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

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

# The valence states in OVB.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

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

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

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

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

# Energy of the two ${}^1\Psi_{N,g}^o$ and ${}^1\Psi_{I,g}^o$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

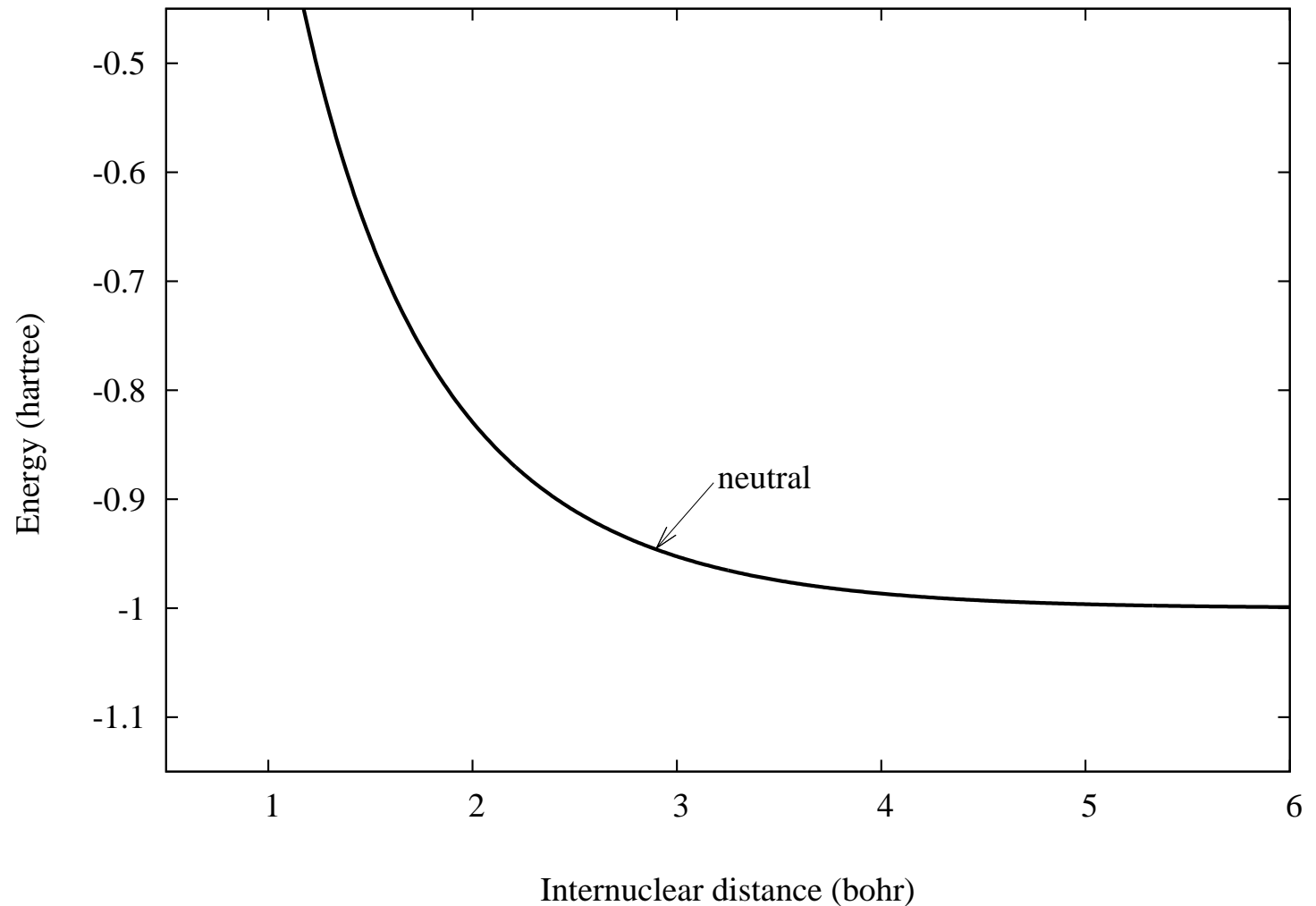
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



# Energy of the two ${}^1\Psi_{N,g}^o$ and ${}^1\Psi_{I,g}^o$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

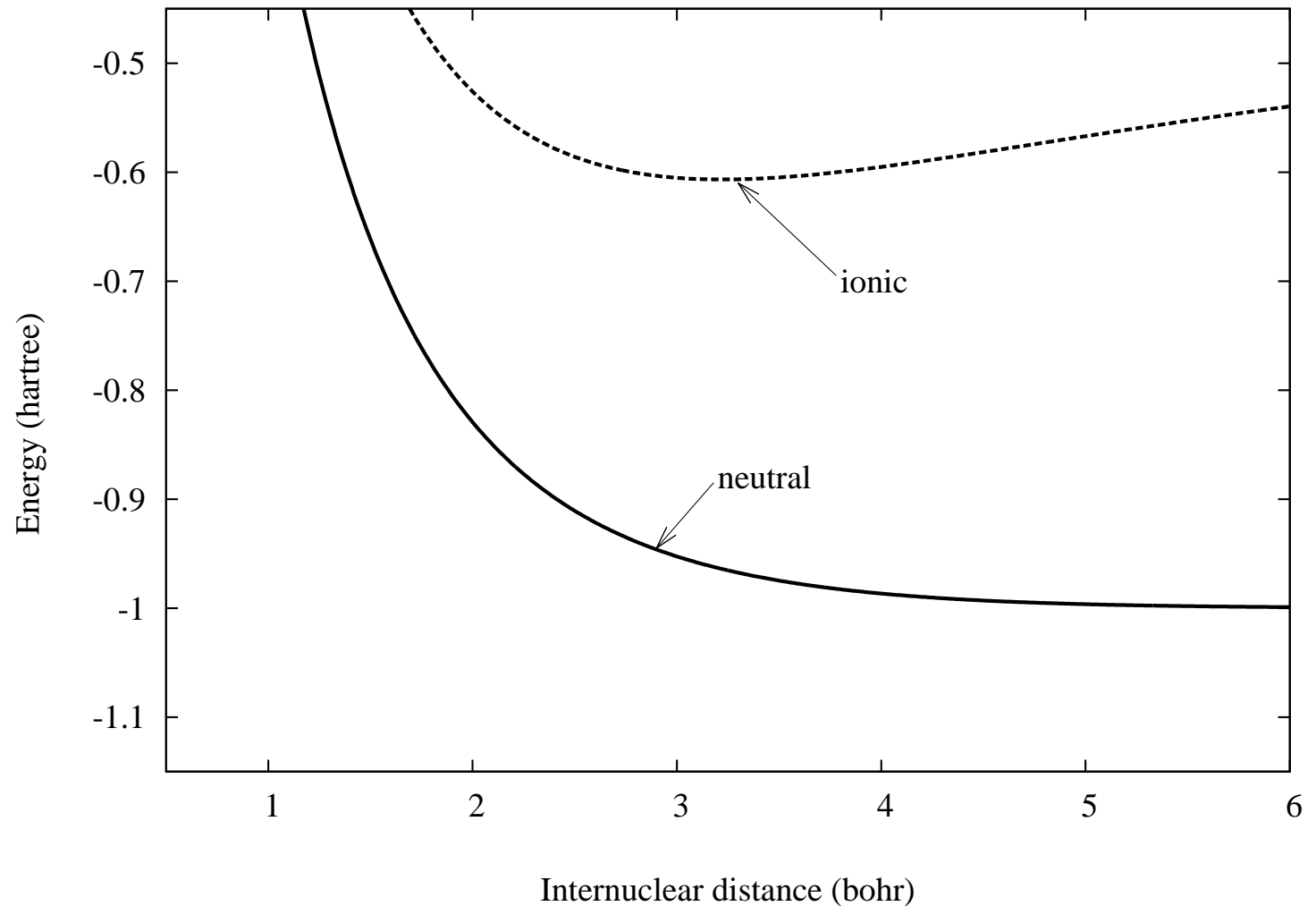
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



# Energy of the two ${}^1\Psi_{N,g}^o$ and ${}^1\Psi_{I,g}^o$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

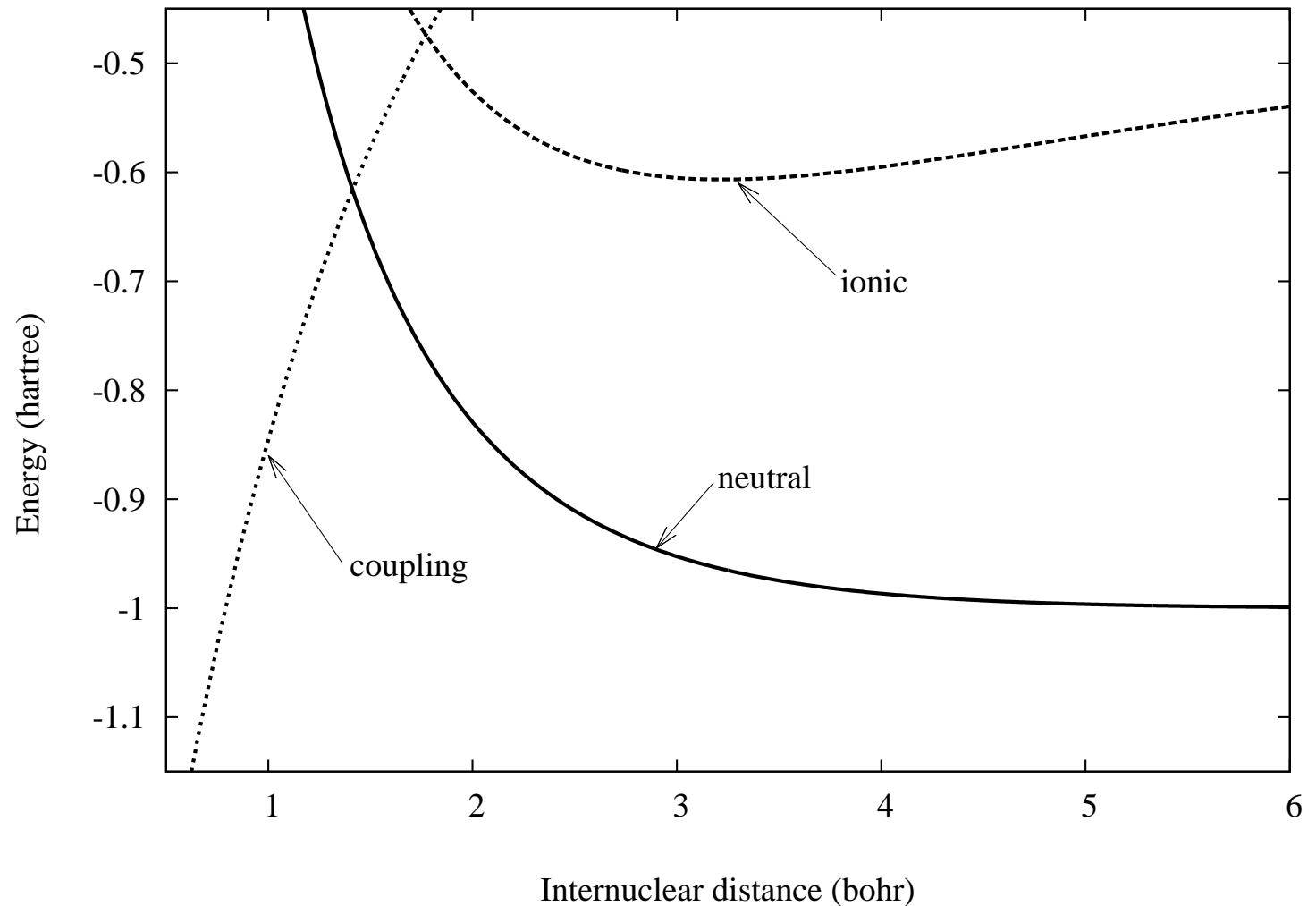
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



# Energy of the two ${}^1\Psi_{N,g}^o$ and ${}^1\Psi_{I,g}^o$ structures, and of the two ${}^1\Sigma_g^+$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

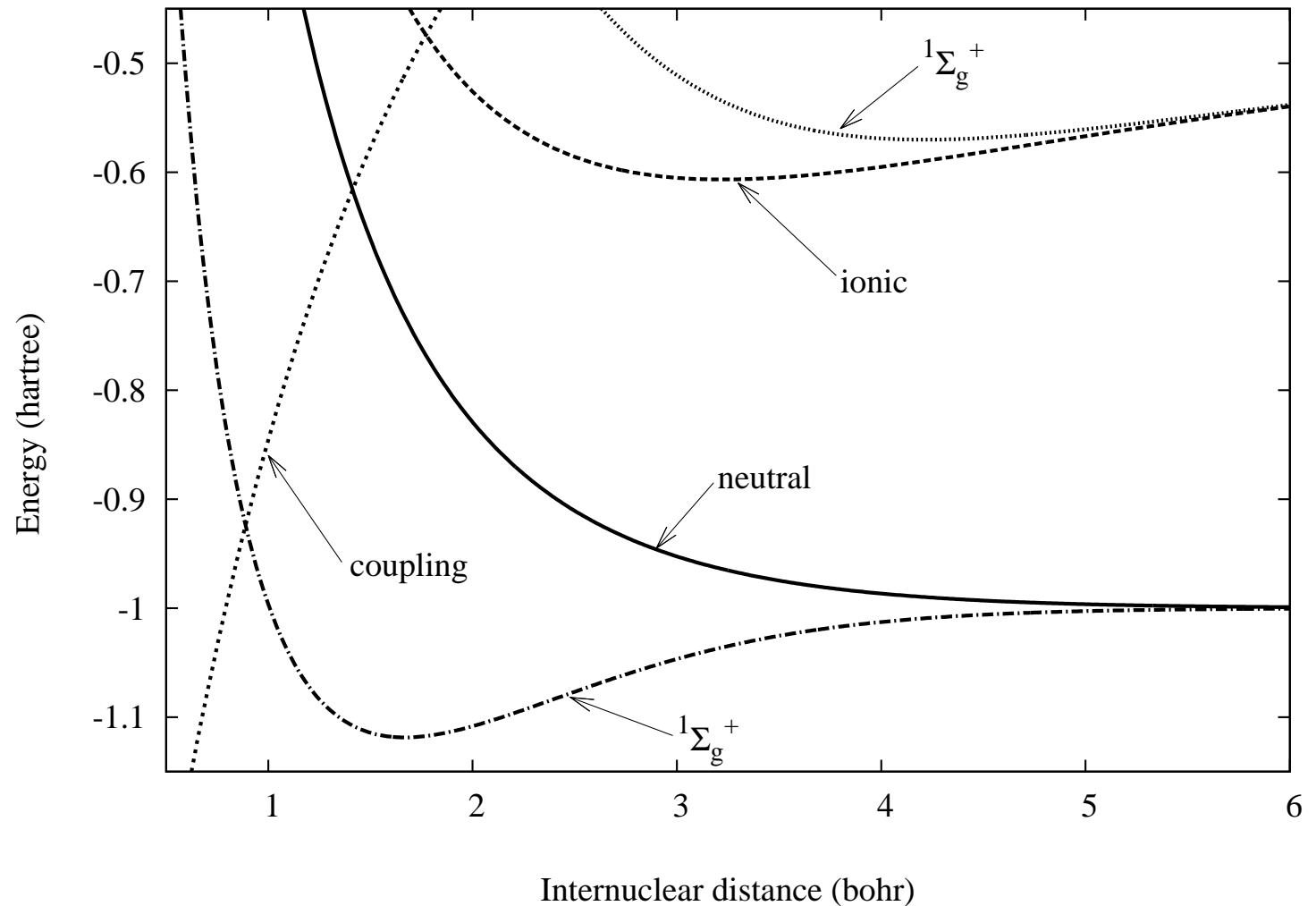
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



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

VB and OVB:  $H_2$

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

---

A different approach  
to benzene

---

Polyenes

---

Singlet-Triplet  
splitting in Ullman's  
diradical

---

- The neutral structure gives a dissociative curve (no bond!).



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

VB and OVB:  $H_2$

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

- 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 have a large effect on the energy and on the wavefunction  $\Rightarrow$  this structure has to be included in the calculation.

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

VB and OVB:  $H_2$

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

- 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 have a large effect on the energy and on the wavefunction  $\Rightarrow$  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?

# A comparison of VB and OVB: OVB and the $\Sigma_u$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

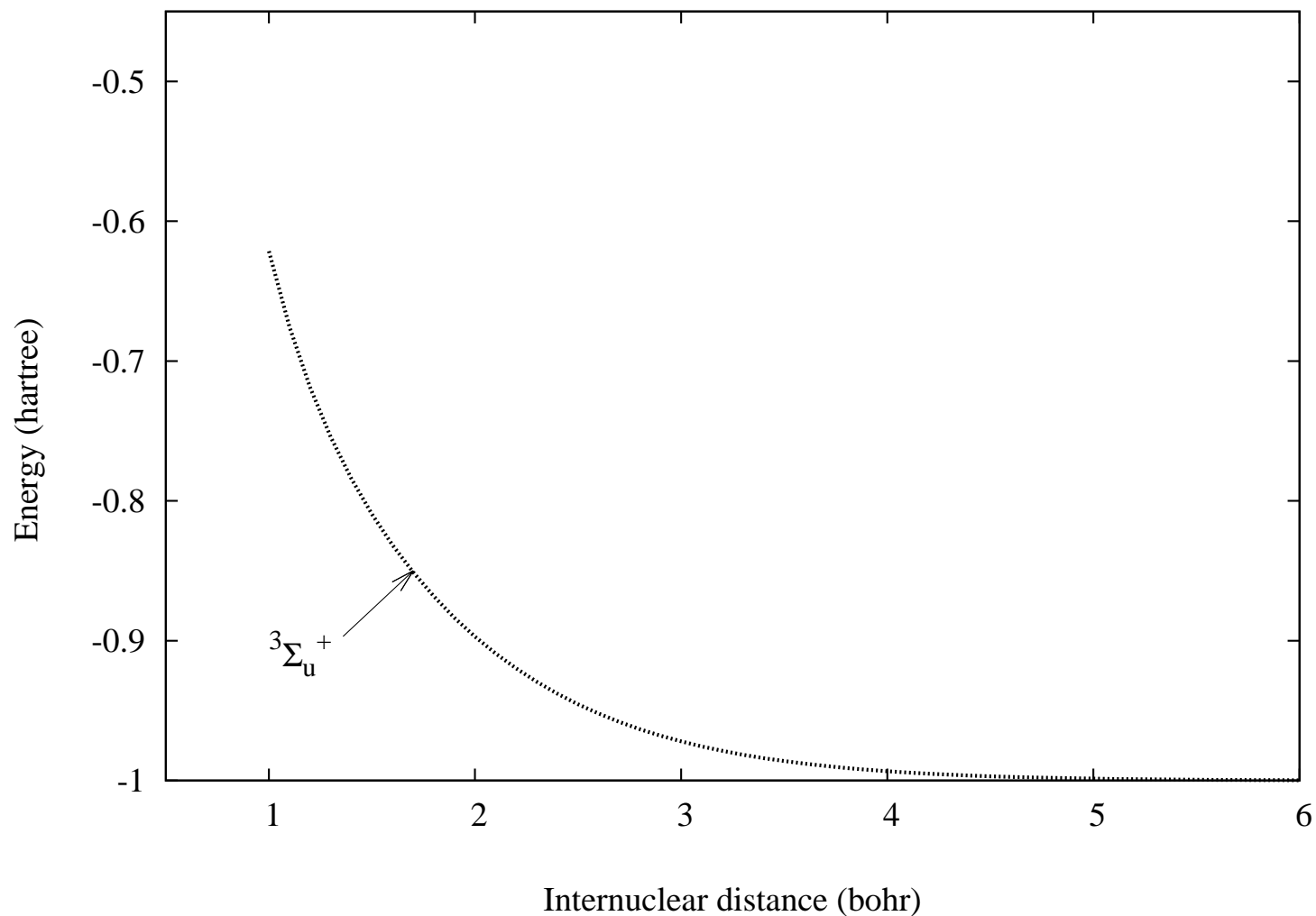
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# A comparison of VB and OVB: OVB and the $\Sigma_u$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

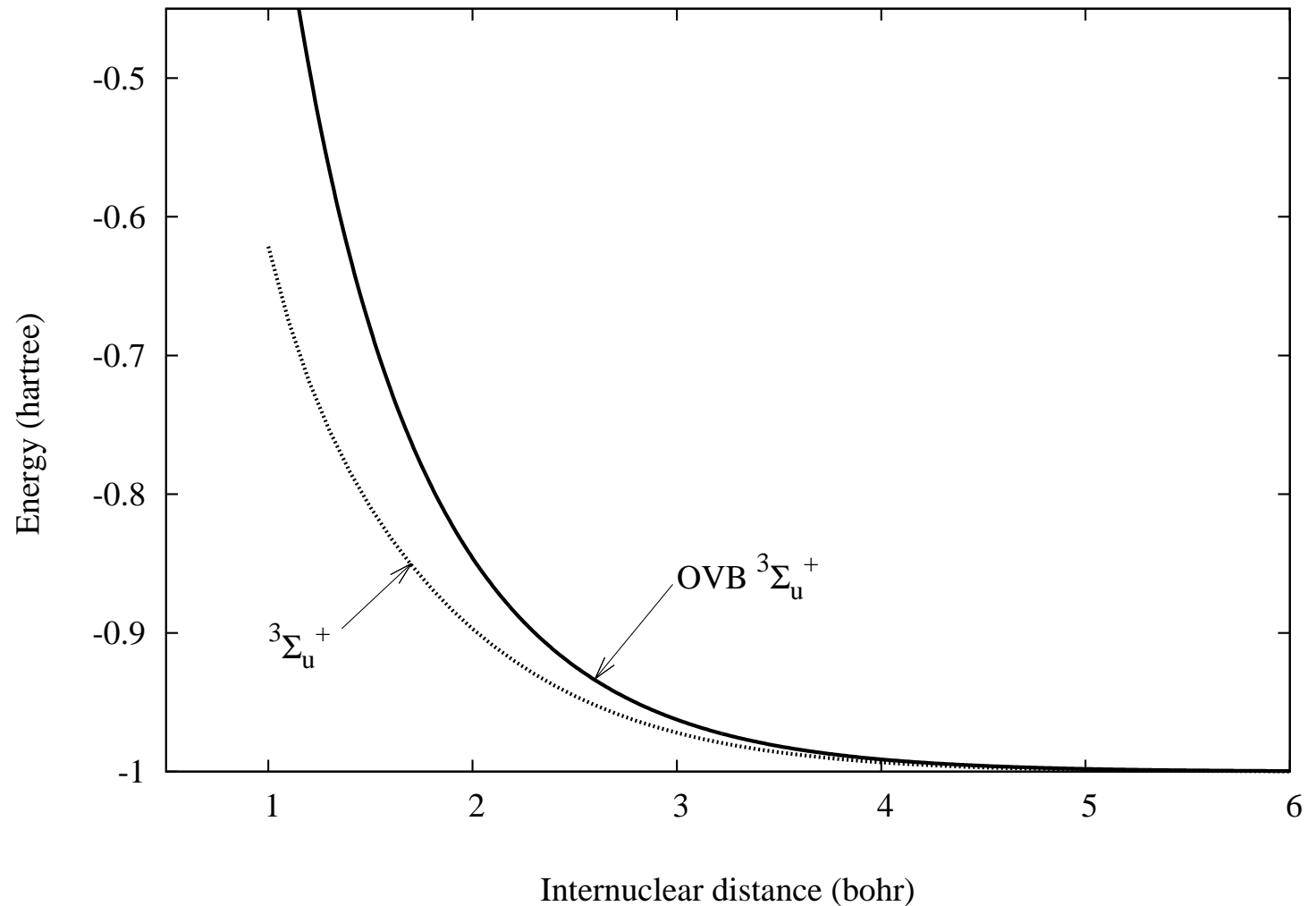
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# A comparison of VB and OVB: OVB and the $\Sigma_u$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

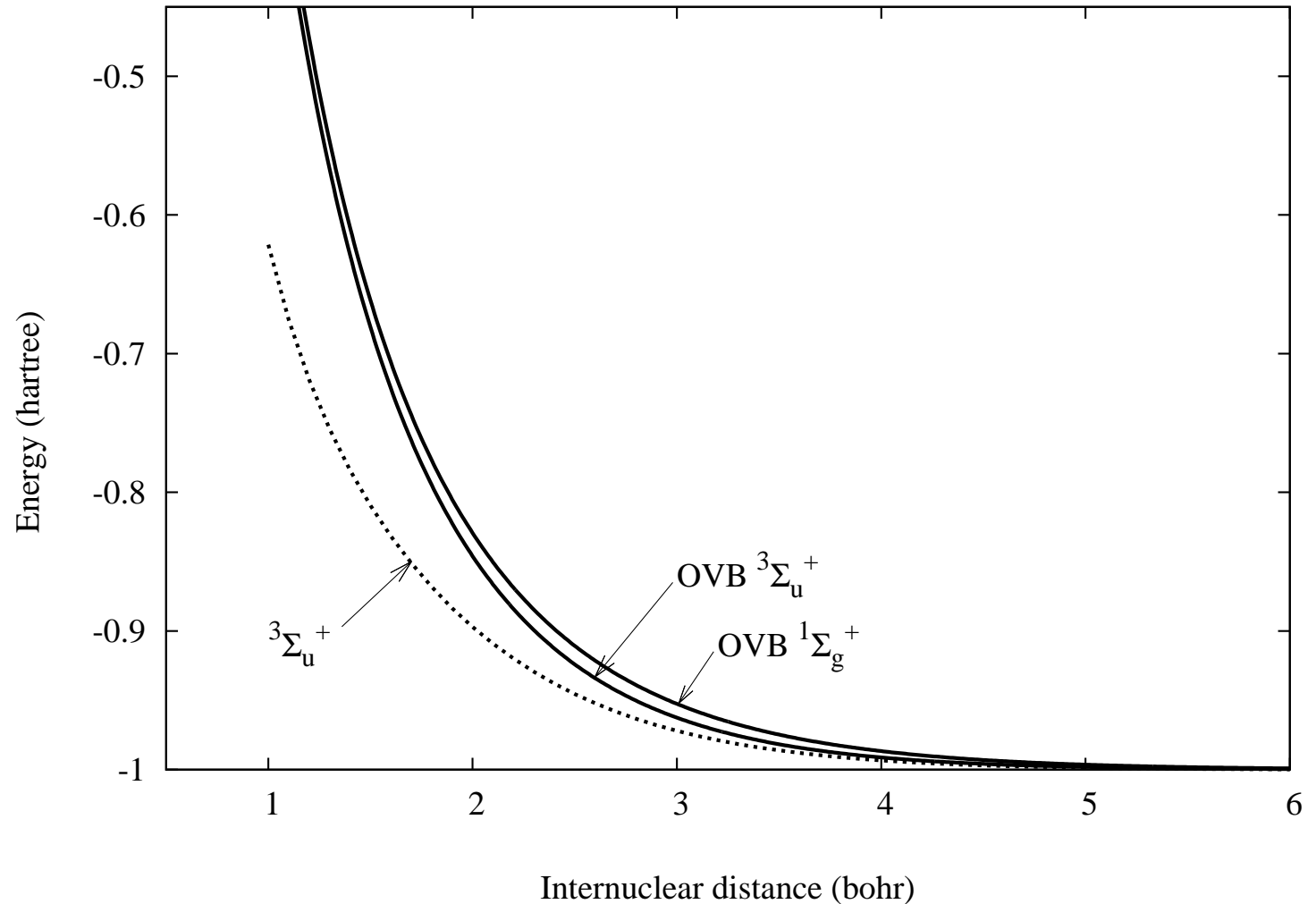
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# A comparison of VB and OVB: OVB and the $\Sigma_u$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

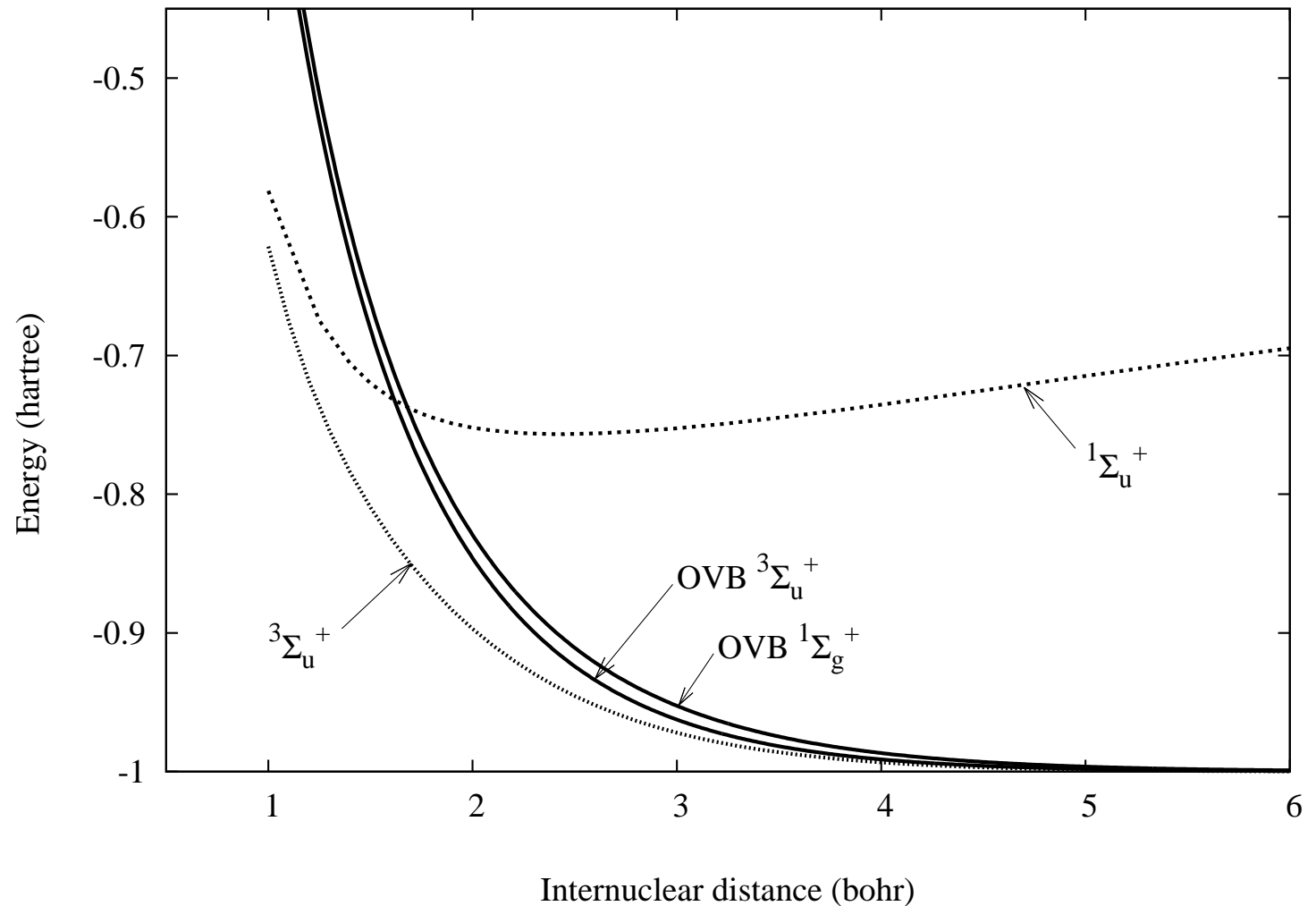
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# A comparison of VB and OVB: OVB and the $\Sigma_u$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

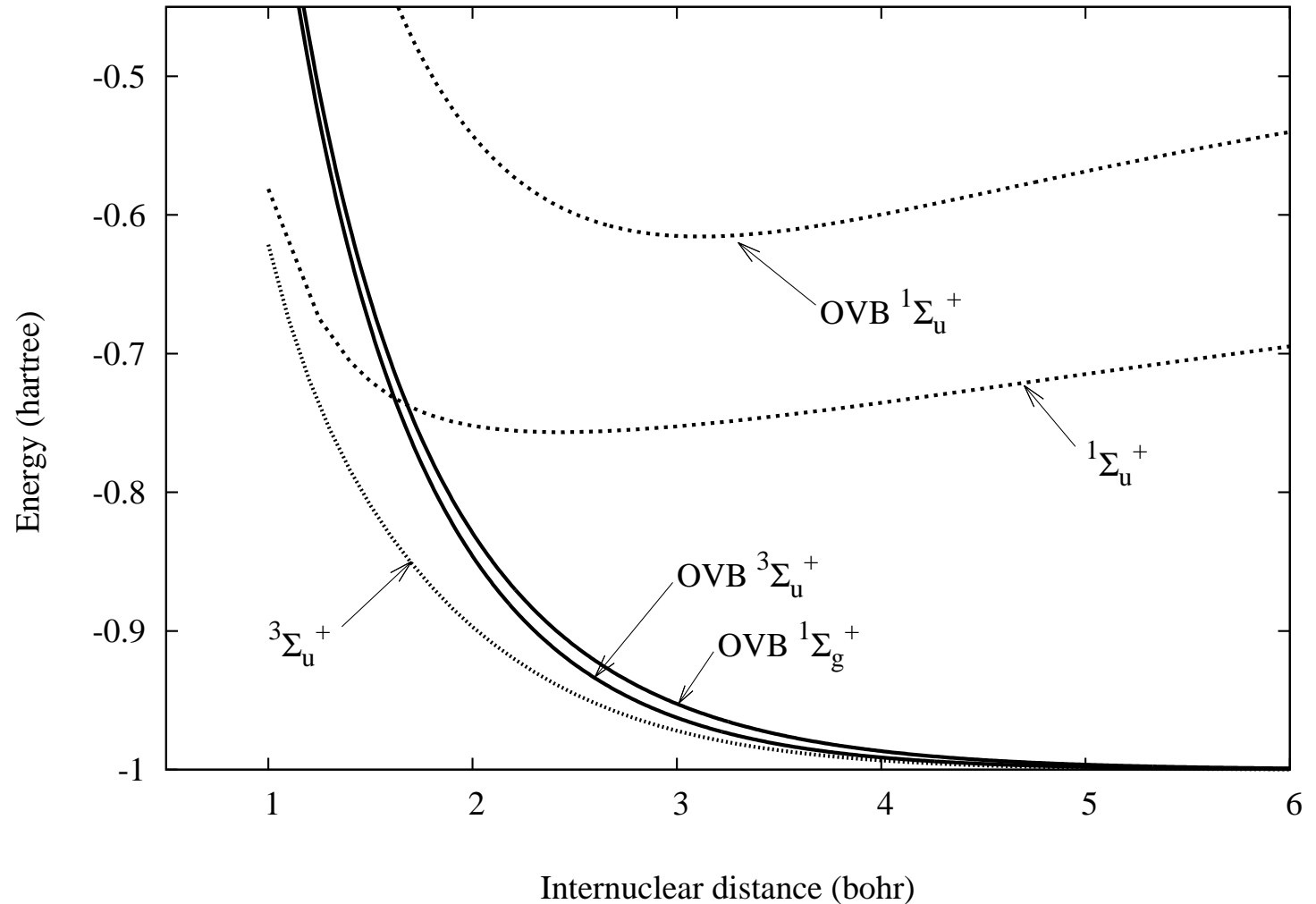
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# A comparison of VB and OVB: OVB and the $\Sigma_u$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

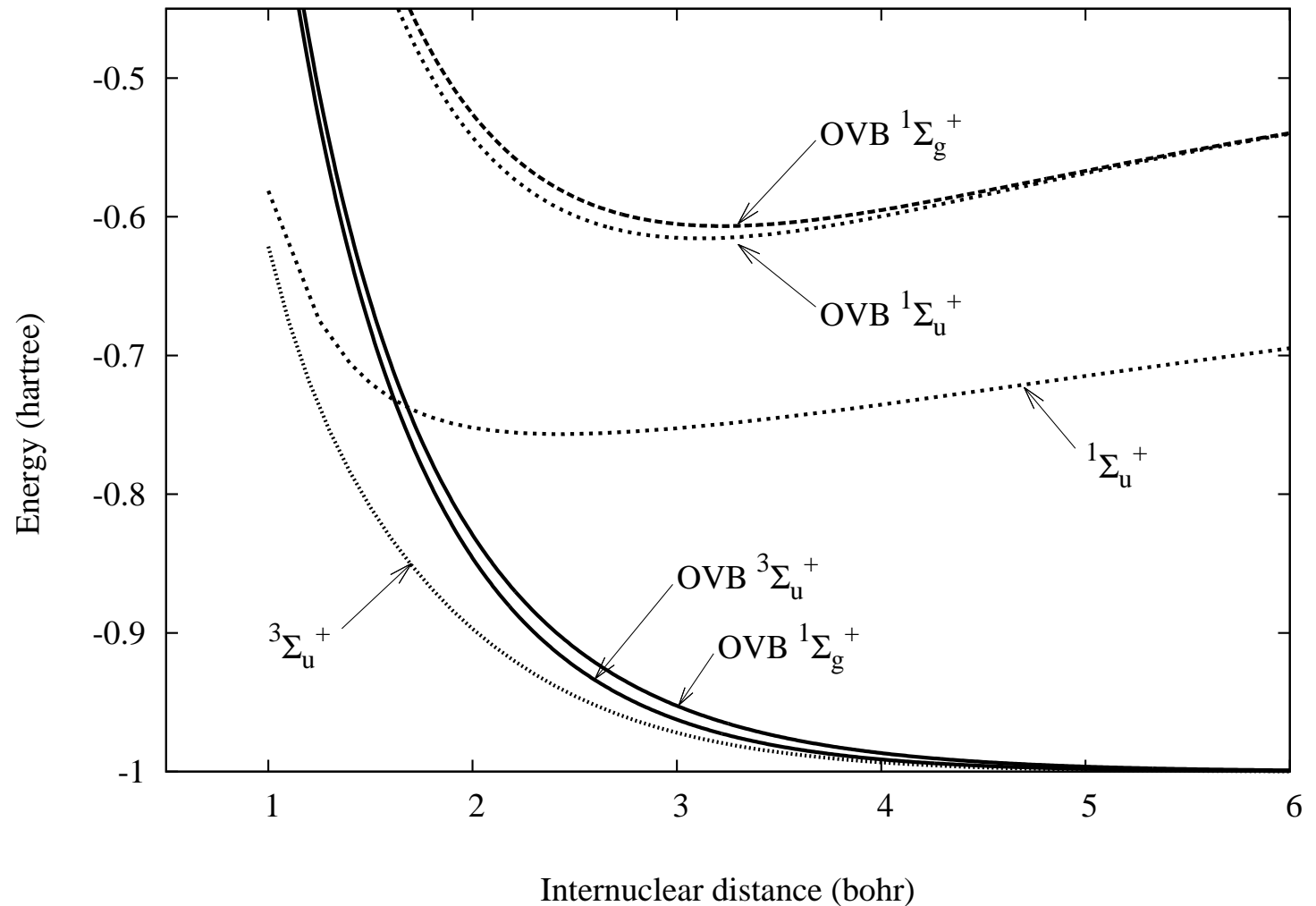
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical





# A comparison of VB and OVB: VB and the $\Sigma_u$ states.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

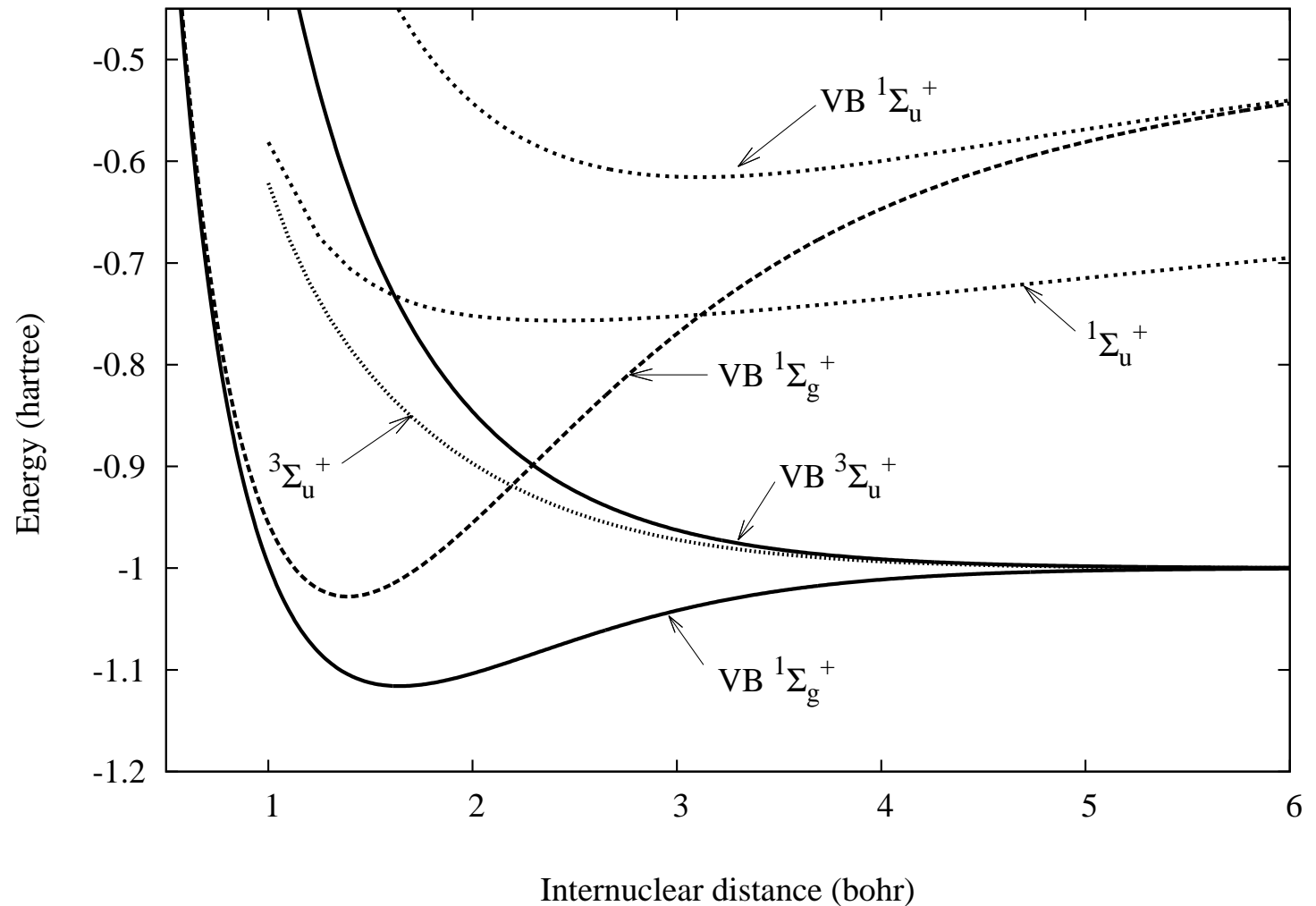
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# Graphical representation of the wavefunction composition.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

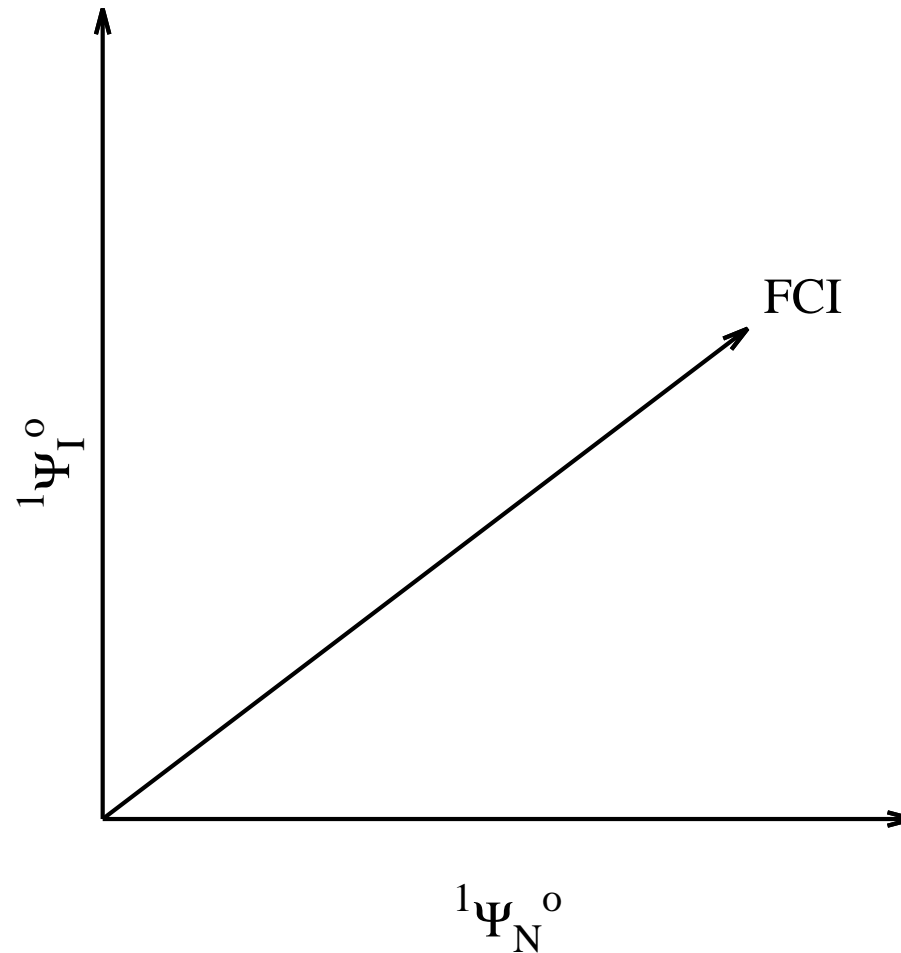
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# Graphical representation of the wavefunction composition.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

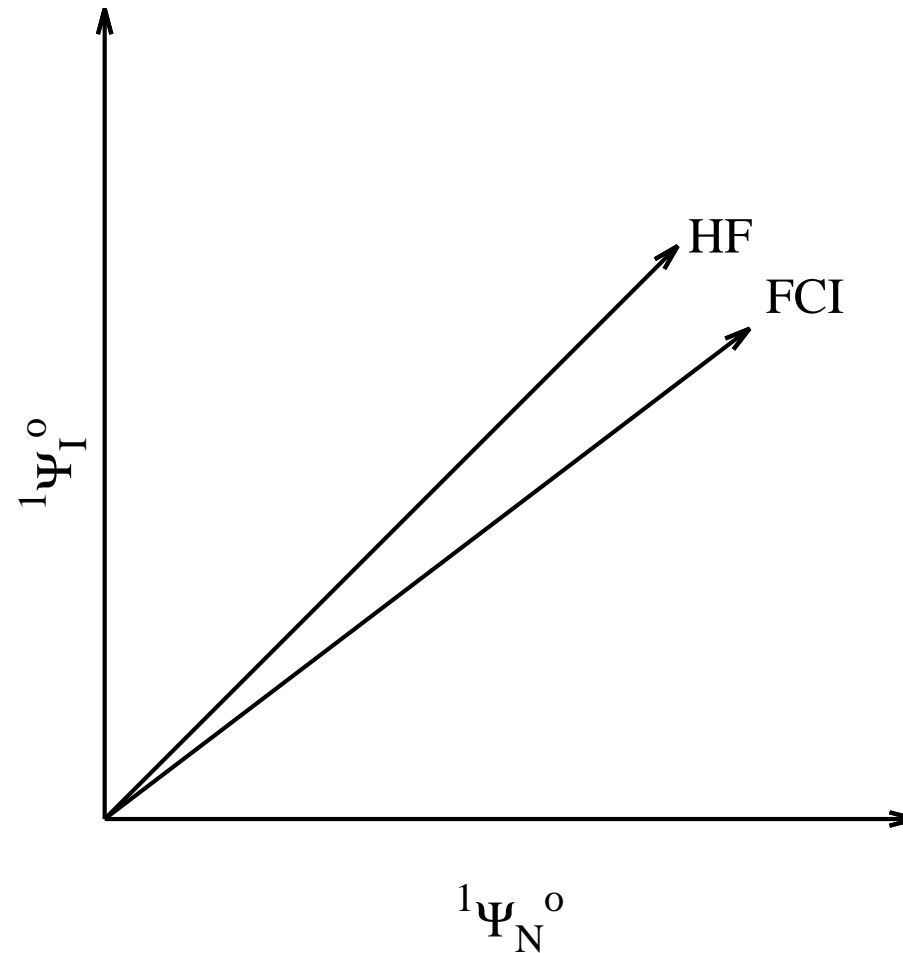
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# Graphical representation of the wavefunction composition.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

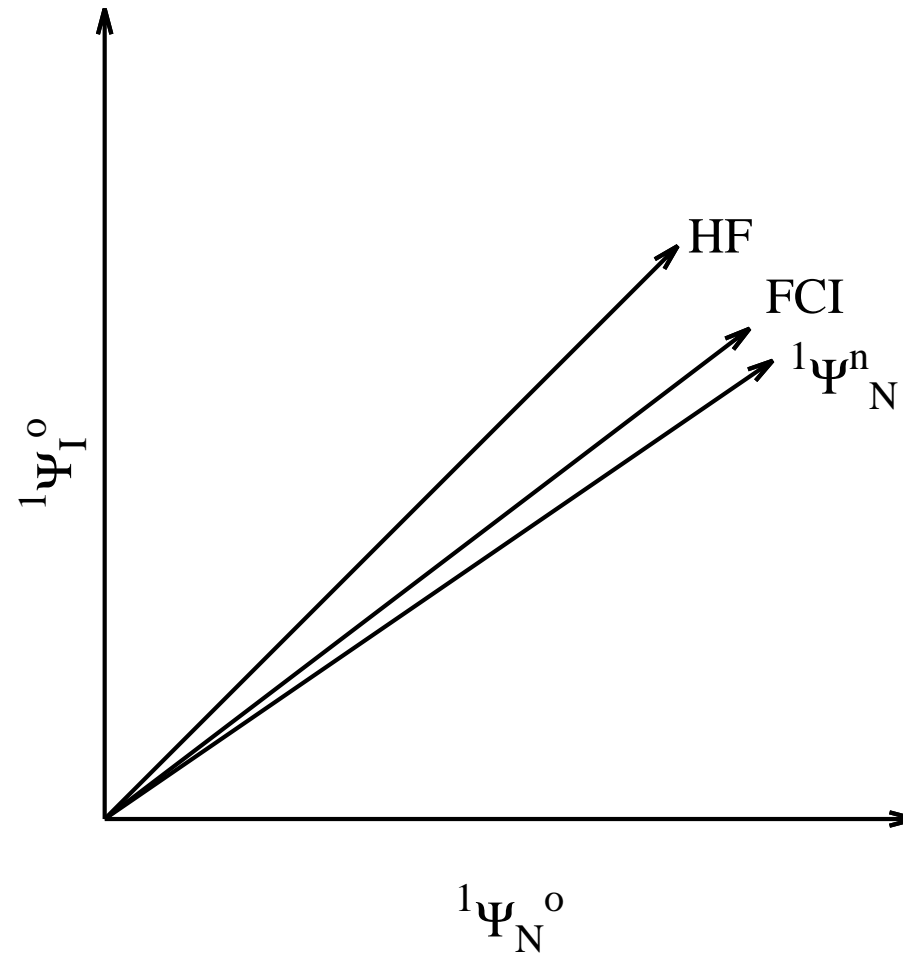
Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical



# Graphical representation of the wavefunction composition.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

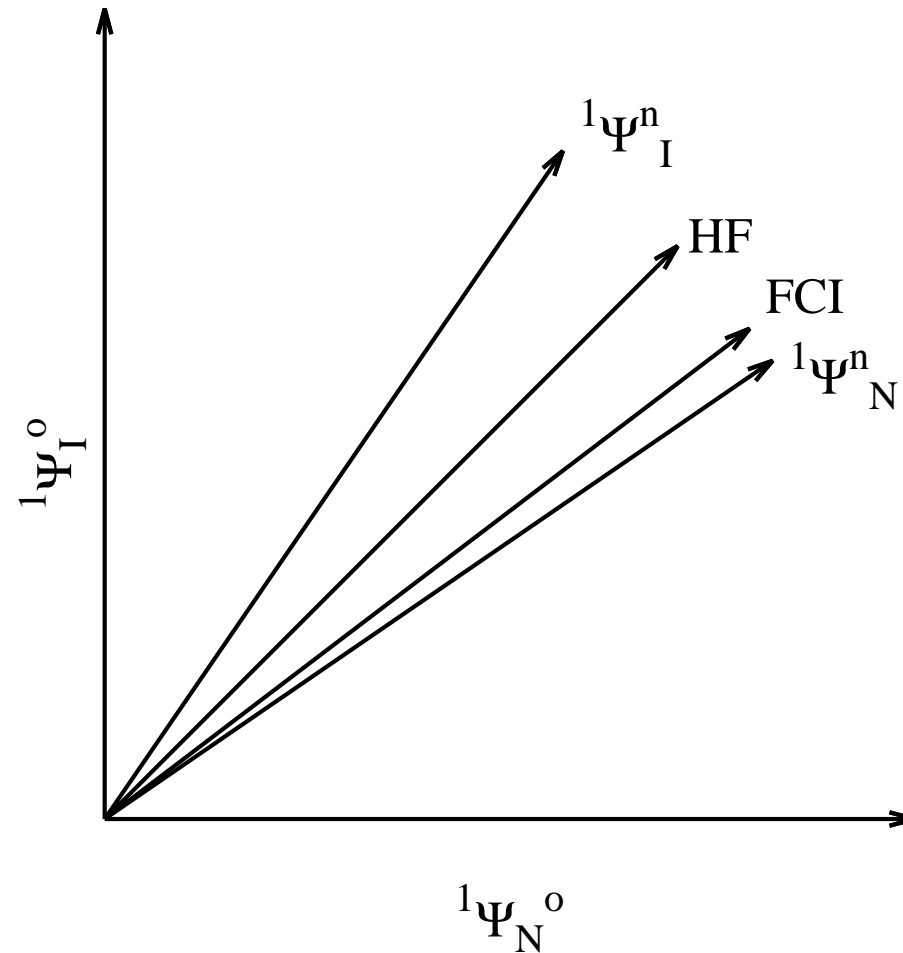
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



# Graphical representation of the wavefunction composition.

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

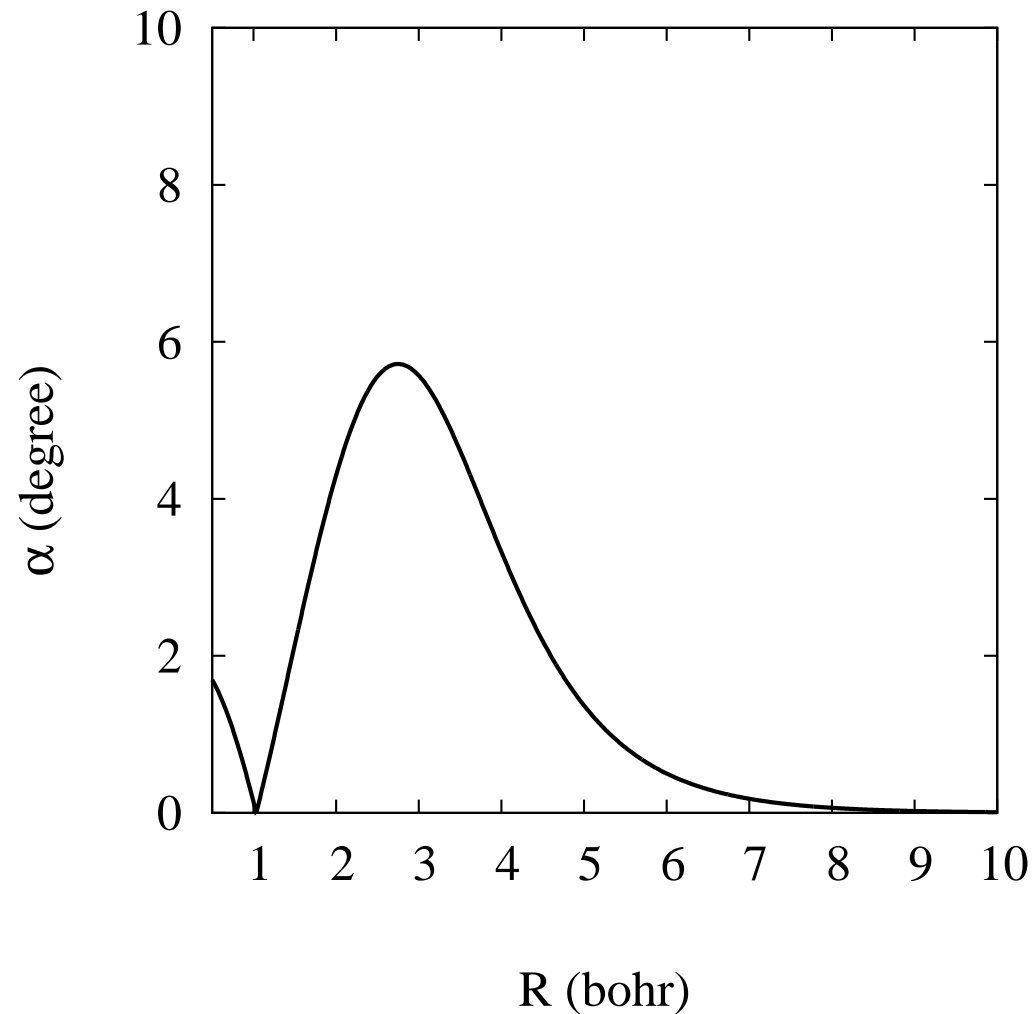
Comparison of VB and OVB

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



# Conclusions

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

---

A different approach  
to benzene

---

Polyenes

---

Singlet-Triplet  
splitting in Ullman's  
diradical

---

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

# Conclusions

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

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

OVB gives a coherent description of the neutral and ionic configurations (even if there is the “tail problem”) but it requires the explicit inclusion of the ionic structures.



# Conclusions

VB and OVB: H<sub>2</sub>

Standard VB

Orthogonal VB

Comparison of VB  
and OVB

OVB analysis of  
ethylene

A different approach  
to benzene

Polyenes

Singlet-Triplet  
splitting in Ullman's  
diradical

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

OVB gives a coherent description of the neutral and ionic configurations (even if there is the “tail problem”) but it requires the explicit inclusion of the ionic structures.

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 wavefunction.

VB and OVB: H<sub>2</sub>

**OVB analysis of ethylene**

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

# An OVB analysis of the V state of ethylene.

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(1)**, 35-50, (2007).

C. Angeli, "On the nature of the  $\pi \rightarrow \pi^*$  ionic excited states: the V state of ethene as a prototype. *J. Comp. Chem.*, **30(8)**, 1319-1333, (2009).

C. Angeli, "An analysis of the dynamic  $\sigma$  polarization in the V state of ethene", *Int. J. Quant. Chem.*, **110(13)**, 2436-2447, (2010).

# Standard MO calculations

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

The vertical excitation energy for the V state of ethylene is a challenge for MO methods:

✓ experimental band maximum: 7.66 eV

# Standard MO calculations

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

The vertical excitation energy for the V state of ethylene is a challenge for MO methods:

- ✓ experimental band maximum: 7.66 eV
- ✓ very expensive MRCI calculations: 7.7 eV

# Standard MO calculations

VB and OVB: H<sub>2</sub>

**OVB analysis of ethylene**

**V state**

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

The vertical excitation energy for the V state of ethylene is a challenge for MO methods:

- ✓ experimental band maximum: 7.66 eV
- ✓ very expensive MRCI calculations: 7.7 eV
- ✓ CASSCF 12/12 + MRPT2 + MRPT3: > 8.2 eV

# Standard MO calculations

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

The vertical excitation energy for the V state of ethylene is a challenge for MO methods:

- ✓ experimental band maximum: 7.66 eV
- ✓ very expensive MRCI calculations: 7.7 eV
- ✓ CASSCF 12/12 + MRPT2 + MRPT3: > 8.2 eV
- ✓ many other problems (diffuseness, slow convergence, etc.)

Where is the source of these difficulties for such a “simple” state ( $\pi \rightarrow \pi^*$ ) of such a small molecule?

# The analysis in the $\pi$ manifold: the V state is ionic

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

The V state is described by the singlet  $\pi \rightarrow \pi^*$  excitation (CASSCF 2/2) on the GS. Focusing on the  $\pi$  space

$${}^1\Psi_{B_{1u}} = \frac{\|\pi\bar{\pi}^*\| + \|\pi^*\bar{\pi}\|}{\sqrt{2}}$$

Introducing two  $p$  OAOs (localized in the two C atoms)

$$\pi = \frac{p_a + p_b}{\sqrt{2}} \quad \pi^* = \frac{p_a - p_b}{\sqrt{2}} \quad \Rightarrow \quad p_a = \frac{\pi + \pi^*}{\sqrt{2}} \quad p_b = \frac{\pi - \pi^*}{\sqrt{2}}$$

one has

$${}^1\Psi_{B_{1u}} = \frac{p_a p_a - p_b p_b}{\sqrt{2}} = \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \rightarrow \text{ionic}$$

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

σ C-C + π

σ polarization

σ pol in GS and T

The *p* contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

Note that the triplet  $\pi \rightarrow \pi^*$  state (T state)

$${}^3\Psi_{B_{1u}} = \frac{\|\pi\bar{\pi}^*\| - \|\pi^*\bar{\pi}\|}{\sqrt{2}}$$

becomes

$${}^3\Psi_{B_{1u}} = \frac{p_a p_b - p_b p_a}{\sqrt{2}} \frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \rightarrow \text{neutral}$$

Such interpretation of the V and T wavefunctions, is completely hidden in the MO language where the V and T states have both open-shell nature and differs only for the spin coupling of the two unpaired electrons.



# OVB decomposition: the $\pi$ and $\sigma$ C-C orbitals.

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

Considering explicitly the  $\sigma$  C-C bond in the wf,

$${}^1\Psi_{B_{1u}} = \frac{\|\sigma\bar{\sigma}\pi\bar{\pi}^*\| + \|\sigma\bar{\sigma}\pi^*\bar{\pi}\|}{\sqrt{2}}$$

$$\sigma_a = \frac{\sigma + \sigma^*}{\sqrt{2}} \quad \sigma_b = \frac{\sigma - \sigma^*}{\sqrt{2}}$$

one has

$$\begin{aligned} {}^1\Psi_{B_{1u}} = \frac{1}{2\sqrt{2}} & \left( \|\sigma_a\bar{\sigma}_b p_a \bar{p}_a\| + \|\sigma_b\bar{\sigma}_a p_a \bar{p}_a\| - \|\sigma_a\bar{\sigma}_b p_b \bar{p}_b\| + \right. \\ & - \|\sigma_b\bar{\sigma}_a p_b \bar{p}_b\| + \|\sigma_a\bar{\sigma}_a p_a \bar{p}_a\| - \|\sigma_b\bar{\sigma}_b p_b \bar{p}_b\| + \\ & \left. + \|\sigma_b\bar{\sigma}_b p_a \bar{p}_a\| - \|\sigma_a\bar{\sigma}_a p_b \bar{p}_b\| \right) \end{aligned}$$

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

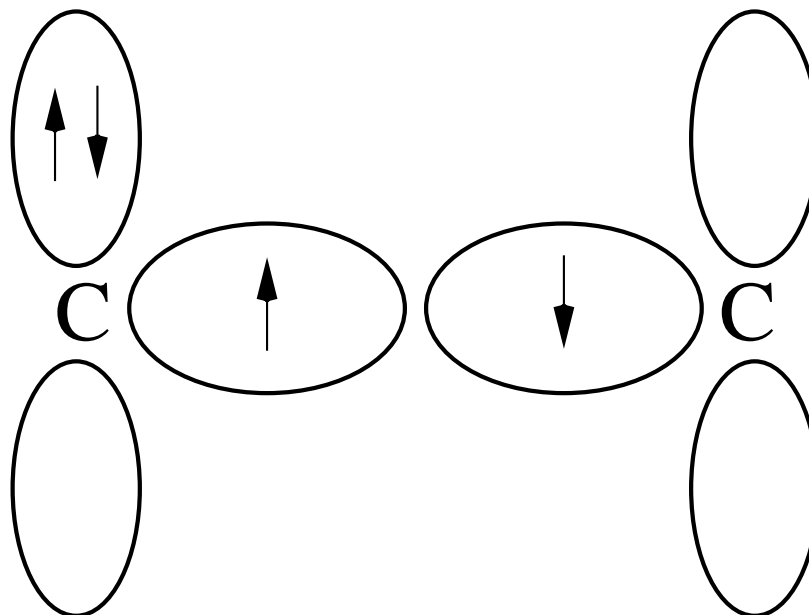
Polyenes

Singlet-Triplet splitting in Ullman's diradical

The structures:

$$\|\sigma_a \bar{\sigma}_b p_a \bar{p}_a\|, \|\sigma_b \bar{\sigma}_a p_a \bar{p}_a\|, \|\sigma_a \bar{\sigma}_b p_b \bar{p}_b\|, \|\sigma_b \bar{\sigma}_a p_b \bar{p}_b\|$$

are ionic in the  $\pi$  manifold and neutral in the  $\sigma$  one.



VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

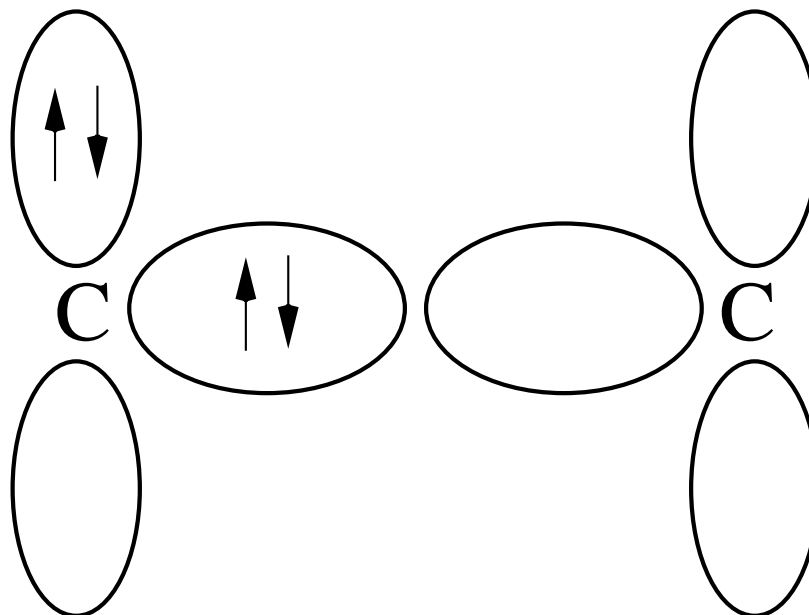
Polyenes

Singlet-Triplet splitting in Ullman's diradical

The structures:

$$\|\sigma_a \bar{\sigma}_a p_a \bar{p}_a\|, \|\sigma_b \bar{\sigma}_b p_b \bar{p}_b\|$$

are ionic in both manifolds, ( $C^{-2}-C^{+2}$  and  $C^{+2}-C^{-2}$ ).



VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

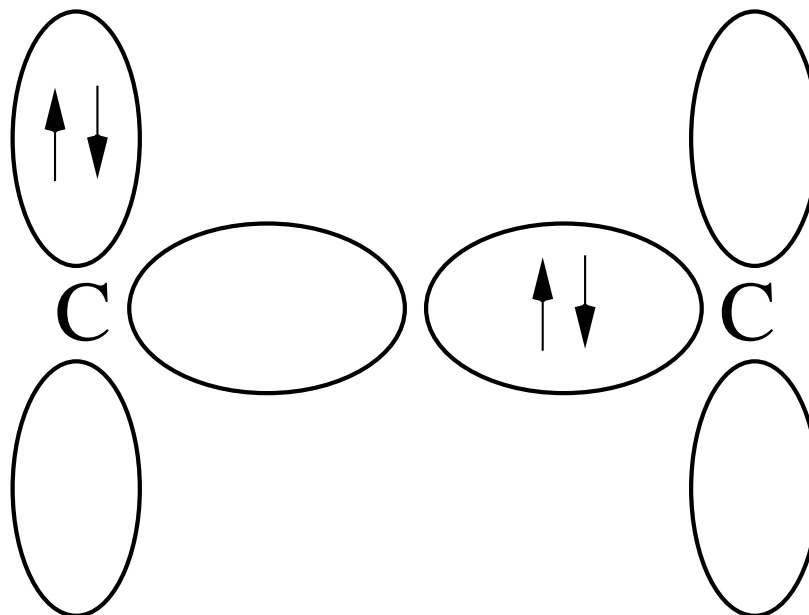
Polyenes

Singlet-Triplet splitting in Ullman's diradical

The structures:

$$\|\sigma_b \bar{\sigma}_b p_a \bar{p}_a\|, \|\sigma_a \bar{\sigma}_a p_b \bar{p}_b\|$$

are ionic in both manifolds, but globally neutral.



# The $\sigma$ polarization: the OVB description

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

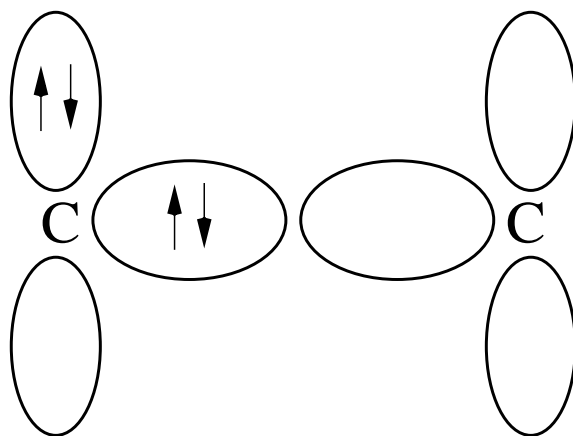
A different approach to benzene

Polyenes

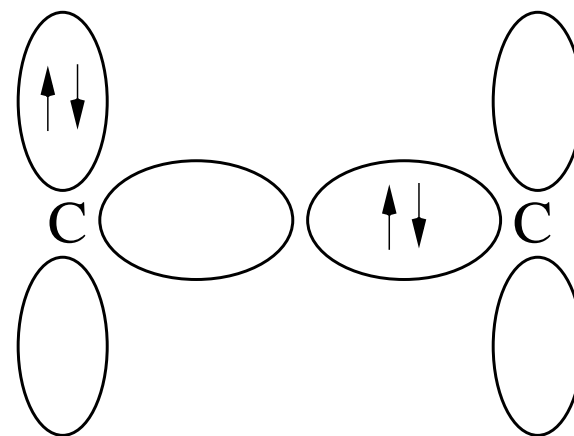
Singlet-Triplet splitting in Ullman's diradical

All the OVB structures have the same weight in the CASSCF 2/2 wf, but  $\|\sigma_a\bar{\sigma}_ap_a\bar{p}_a\|$  and  $\|\sigma_b\bar{\sigma}_bp_b\bar{p}_b\|$  are much higher in energy. To improve the wf, one has to decrease their weight and to improve the one of the  $\|\sigma_b\bar{\sigma}_bp_a\bar{p}_a\|$  and  $\|\sigma_a\bar{\sigma}_ap_b\bar{p}_b\|$  structure  $\rightarrow$  dynamical  $\sigma$  polarization.

DECREASE



INCREASE



# The $\sigma$ polarization: the MO description.

VB and OVB: H<sub>2</sub>

**OVB analysis of ethylene**

V state

T state

$\sigma$  C-C +  $\pi$

**$\sigma$  polarization**

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

By an OVB analysis of the double excitations, one can show that the  $\sigma$  polarization is described by the mixing of the  $\|\sigma\bar{\sigma}\pi\bar{\pi}^*\|$  and  $\|\sigma\bar{\sigma}\pi^*\bar{\pi}\|$  CASSCF 2/2 determinants with the  $\|\sigma\bar{\sigma}^*\pi\bar{\pi}\|$ ,  $\|\sigma^*\bar{\sigma}\pi\bar{\pi}\|$ ,  $\|\sigma\bar{\sigma}^*\pi^*\bar{\pi}^*\|$  and  $\|\sigma^*\bar{\sigma}\pi^*\bar{\pi}^*\|$  determinants.

These are  $\sigma\pi^* \rightarrow \sigma^*\pi$  and  $\sigma\pi \rightarrow \sigma^*\pi^*$  double excitations with respect to the determinants describing the V state or  $\sigma \rightarrow \sigma^*$  single excitations with respect to the determinants describing the GS.

Indeed in a MR-CI wf these are the double excitations with the largest weight.

Such an analysis is almost impossible in the MO frame!

# The $\sigma$ polarization: the the GS case.

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

In the T state the dynamical  $\sigma$  polarization is not important!

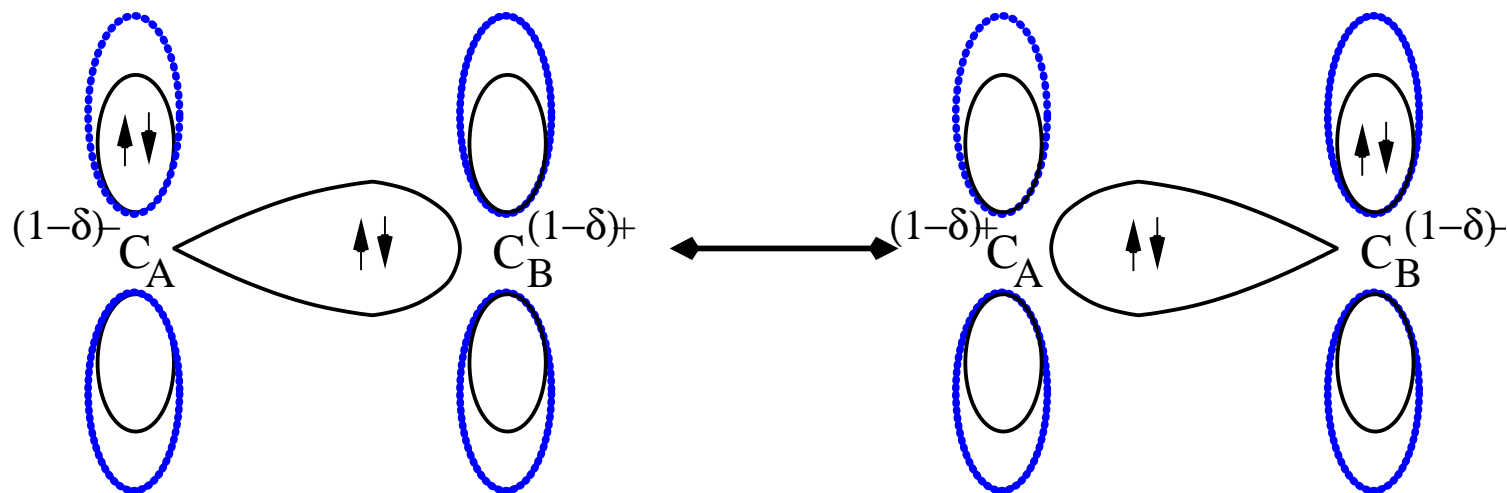
In the GS, the dynamical  $\sigma$  polarization has a small effect.

Therefore it has a strong differential contribution to the transition energy for the singlet but not for the triplet.

This effect is considered in a CAS(2/2) + MRPT2 calculation. The problem is not there ....

# The contraction of the $p$ OAOs.

Actually, besides the dynamic  $\sigma$  polarization, another effect is important and it is the contraction of the  $p$  orbitals due to the reduction of ionicity originated by the dynamic  $\sigma$  polarization:



VB and OVB:  $H_2$

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

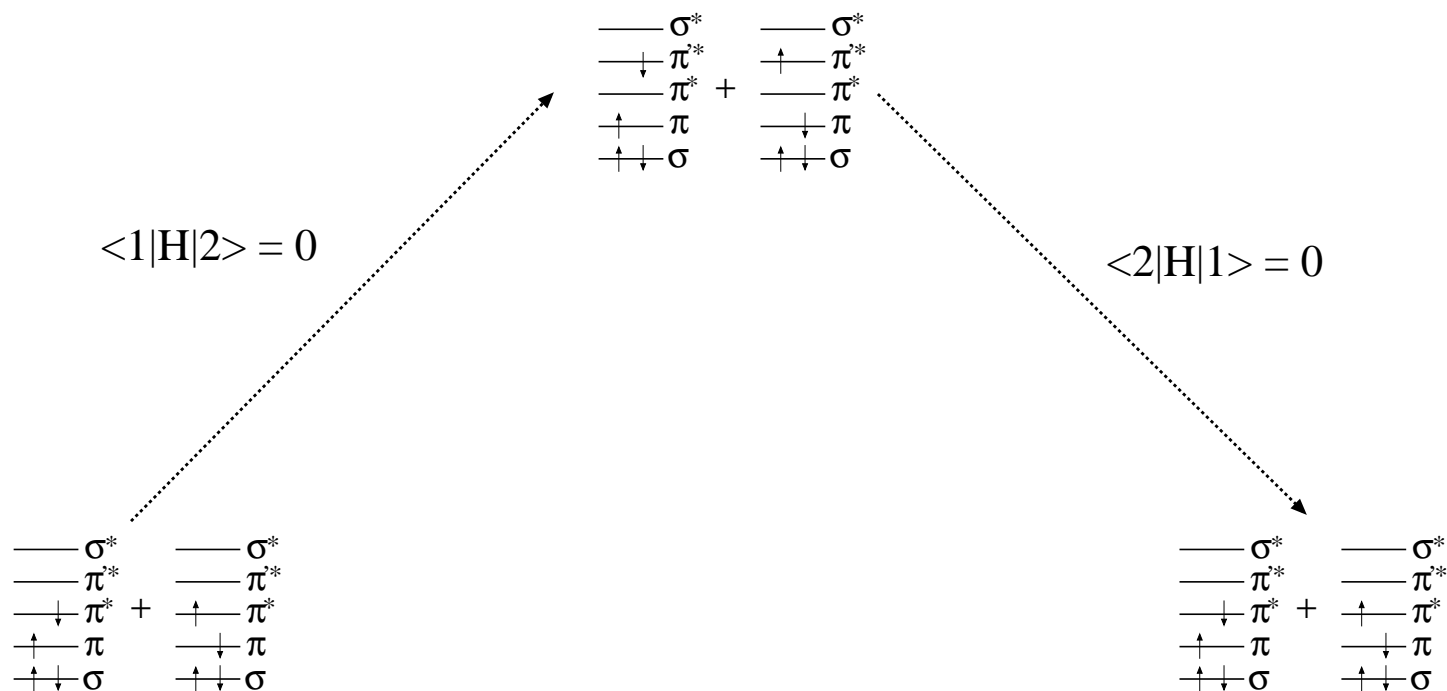
$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

V state

T state

$\sigma$  C-C +  $\pi$

$\sigma$  polarization

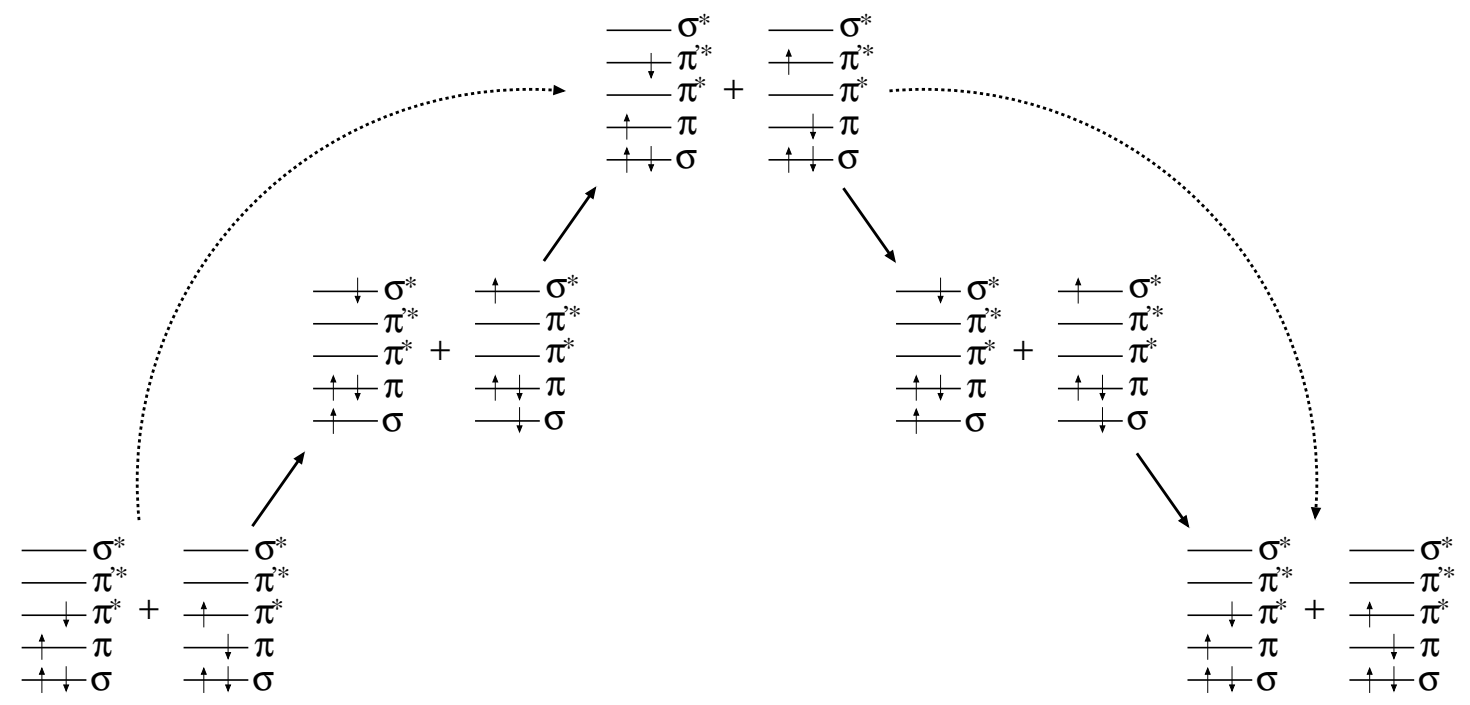
$\sigma$  pol in GS and T

The  $p$  contraction

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical



VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

**A different approach to benzene**

Kekulé OBO

$\pi$  correlation

$\pi$  delocalization

Cyclic deloc.

Polyenes

Singlet-Triplet splitting in Ullman's diradical

# The description of benzene using localized bond orbitals.

J.-P. Malrieu, C. Angeli,

**"Aromaticity: an ab Initio Evaluation of the Properly Cyclic Delocalization Energy and the  $\pi$ -Delocalization Energy Distortivity of Benzene",**

*J. Phys. Chem. A*, **112**, 11481, (2008).

# The localized bond orbitals.

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

**A different approach to benzene**

**Kekulé OBO**

$\pi$  correlation

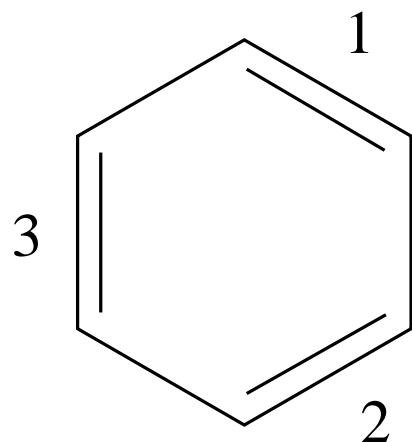
$\pi$  delocalization

Cyclic deloc.

Polyenes

Singlet-Triplet splitting in Ullman's diradical

One can consider a localization of the  $\pi$  orbitals on three bonds (OBOs). In this case one of the Kekulé structure is:



$$= \|\pi_1 \bar{\pi}_1 \pi_2 \bar{\pi}_2 \pi_3 \bar{\pi}_3\|$$

The energy of this determinant is -230.501456 a.u., 9.0 eV higher than the CASSCF energy. It represents 30.8 % of the CASSCF wavefunction.

# Static correlation energy: the local $\pi\bar{\pi} \rightarrow \pi^*\bar{\pi}^*$ excitations.

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Kekulé OBO

$\pi$  correlation

$\pi$  delocalization

Cyclic deloc.

Polyenes

Singlet-Triplet splitting in Ullman's diradical

The  $\pi\bar{\pi} \rightarrow \pi^*\bar{\pi}^*$  excitations on each bond

$$\left\| \pi_1^* \bar{\pi}_1^* \pi_2 \bar{\pi}_2 \pi_3 \bar{\pi}_3 \right\|$$

$$\left\| \pi_1 \bar{\pi}_1 \pi_2^* \bar{\pi}_2^* \pi_3 \bar{\pi}_3 \right\|$$

$$\left\| \pi_1 \bar{\pi}_1 \pi_2 \bar{\pi}_2 \pi_3^* \bar{\pi}_3^* \right\|$$

describe the static correlation inside a  $\pi$  bond.

Their energy is -229.960712 a.u. (23.7 eV) and their weight in the CASSCF wf is  $3 \times 1.5 \%$ .

# Static correlation energy: single excitation from one bond to another.

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

**A different approach to benzene**

Kekulé OBO

$\pi$  correlation

**$\pi$  delocalization**

Cyclic deloc.

Polyenes

Singlet-Triplet splitting in Ullman's diradical

The  $\pi_i \rightarrow \pi_j^*$  ( $i \neq j$ ) excitations on each bond, such as for instance

$$\|\pi_1 \bar{\pi}_2^* \pi_2 \bar{\pi}_2 \pi_3 \bar{\pi}_3\|$$

describe the intrabond delocalization. They have an energy of -230.150731 a.u. (18.5 eV) and their weight in the CASSCF wf is  $12 \times 2.5 \%$ .

# Static correlation energy: the cyclic delocalization energy.

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Kekulé OBO

π correlation

π delocalization

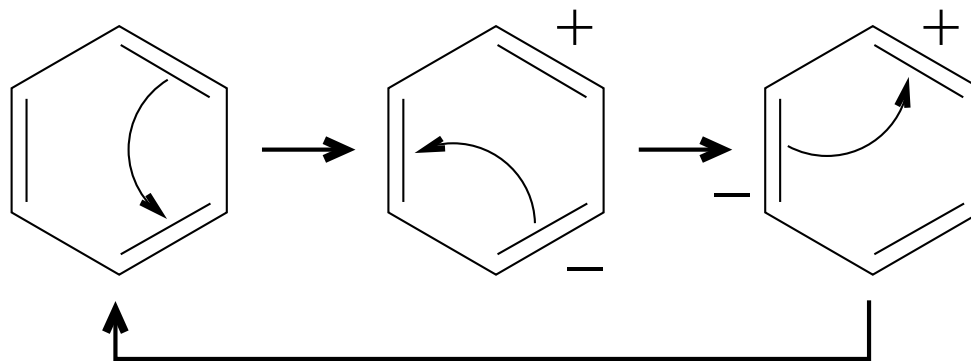
Cyclic deloc.

Polyenes

Singlet-Triplet splitting in Ullman's diradical

Among other effects (next neighbor delocalization) they account for the cyclic delocalization energy, which is a third order contribution of the form ( $\Psi_K = \text{Kekulé det.}$ )

$$\frac{\langle \Psi_K | \hat{H} | a_{\pi_2}^\dagger a_{\pi_1} \Psi_K \rangle \langle a_{\pi_2}^\dagger a_{\pi_1} \Psi_K | \hat{H} | a_{\pi_3}^\dagger a_{\pi_1} \Psi_K \rangle \langle a_{\pi_3}^\dagger a_{\pi_1} \Psi_K | \hat{H} | \Psi_K \rangle}{(\varepsilon_{\pi^*} - \varepsilon_{\pi}) (\varepsilon_{\pi^*} - \varepsilon_{\pi})}$$



An analog expression can be written for the delocalization of “holes”. These are “aromatic” contributions!

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

**Polyenes**

MO/OAO/LMO

Singlet-Triplet splitting in Ullman's diradical

# The analysis of the linear polyenes using localized bond orbitals.



# CASSCF molecular orbitals

VB and OVB: H<sub>2</sub>

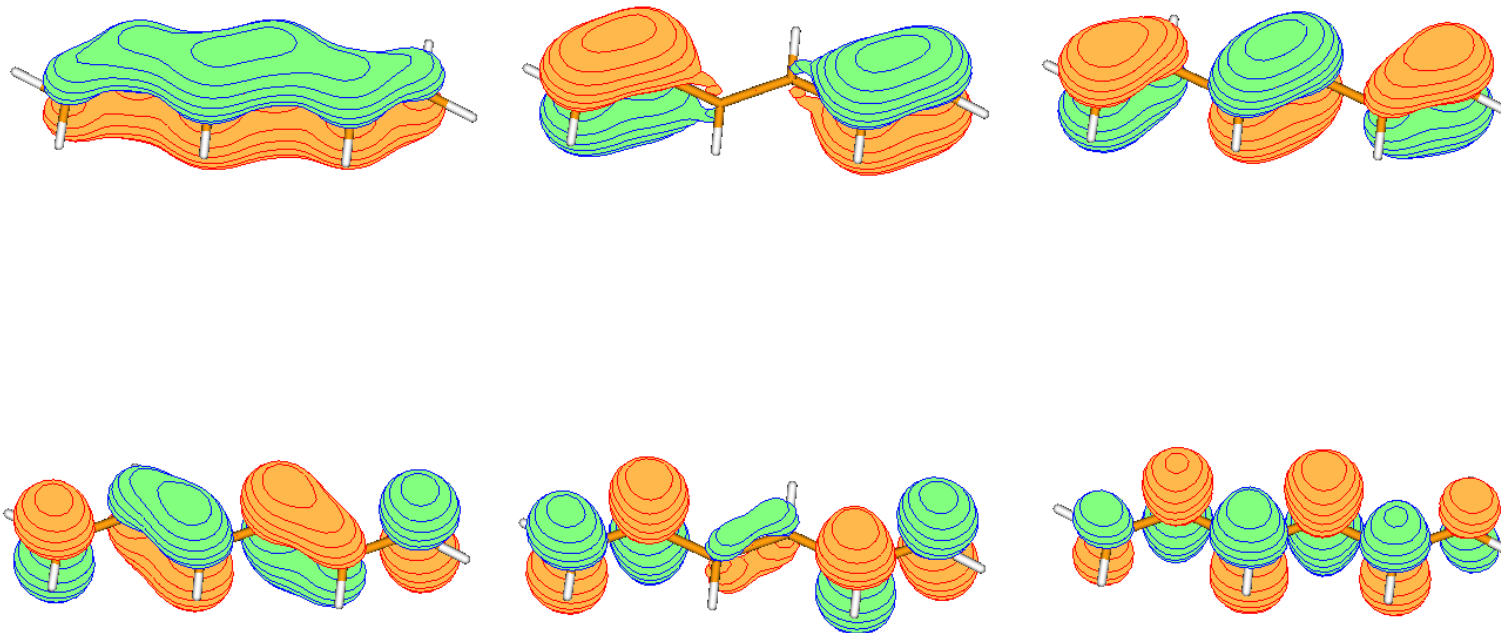
OVB analysis of ethylene

A different approach to benzene

Polyenes

MO/OAO/LMO

Singlet-Triplet splitting in Ullman's diradical



CASSCF delocalized molecular orbitals of hexatriene.

# CASSCF molecular orbitals

VB and OVB: H<sub>2</sub>

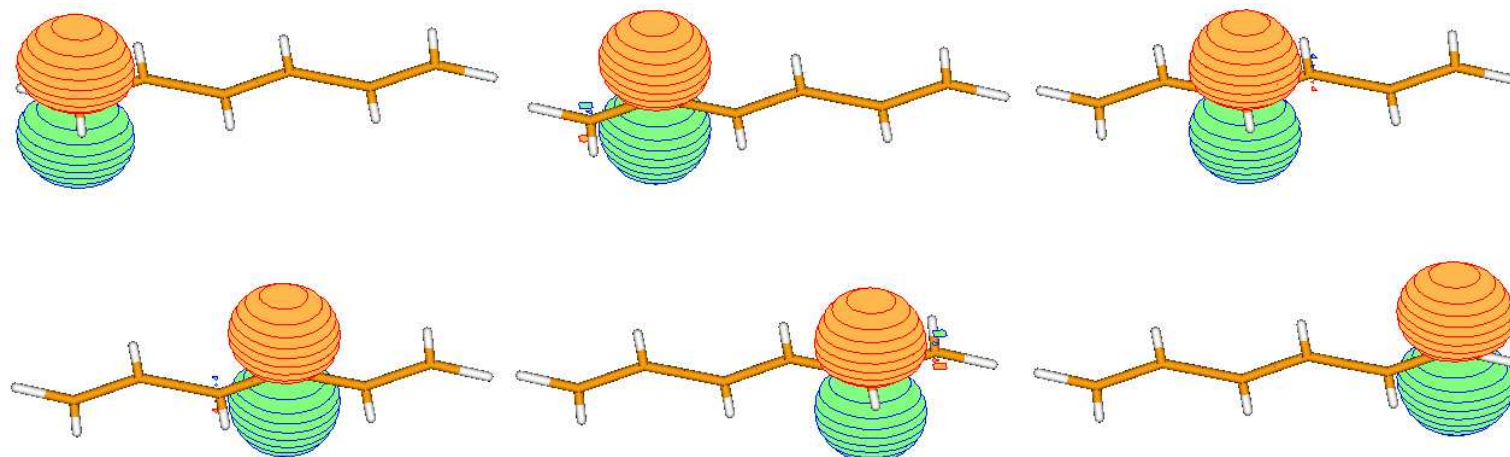
OVB analysis of ethylene

A different approach to benzene

Polyenes

MO/OAO/LMO

Singlet-Triplet splitting in Ullman's diradical



CASSCF localized orthogonal atomic orbitals of hexatriene.

# CASSCF molecular orbitals

VB and OVB: H<sub>2</sub>

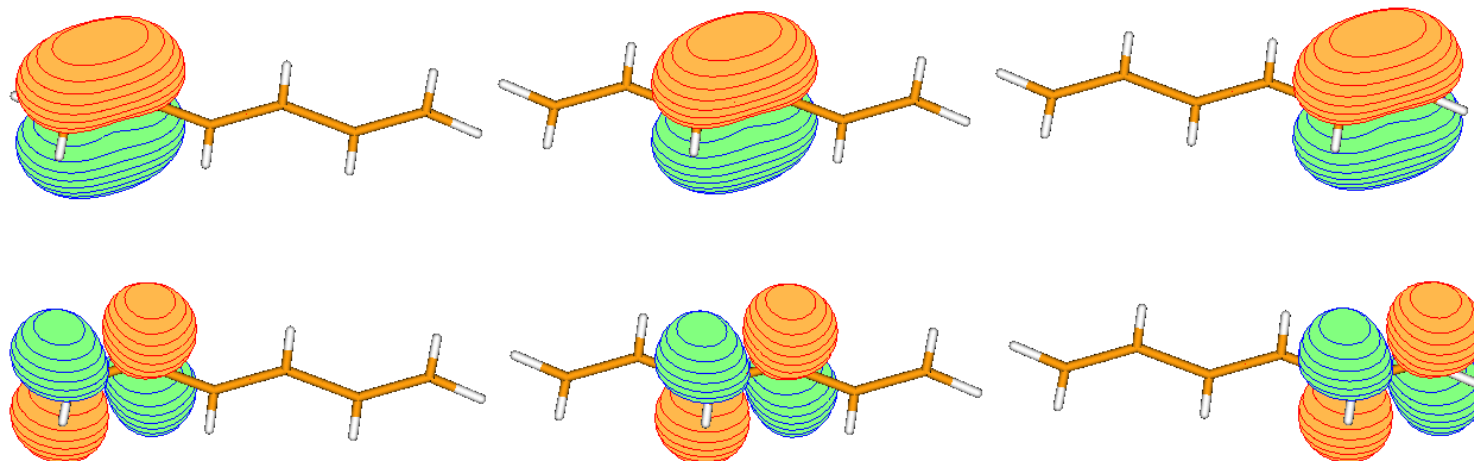
OVB analysis of ethylene

A different approach to benzene

Polyenes

MO/OAO/LMO

Singlet-Triplet splitting in Ullman's diradical



CASSCF localized molecular (bond) orbitals of hexatriene.

# OVB reading of the CASSCF wf based on LMOs

VB and OVB: H<sub>2</sub>


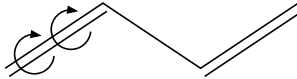
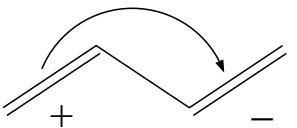
OVB analysis of ethylene

A different approach to benzene

**Polyenes**  
**MO/OAO/LMO**

Singlet-Triplet splitting in Ullman's diradical

The ground state of the butadiene molecule.

Degen.	Structure	Energy (eV)	Weight
1		0.00	0.847
2		16.68	0.038
4		11.11	0.015

More than 98 % of the wavefunction is represented by these structures.

# OVB reading of the CASSCF wf based on LMOs

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Polyenes  
MO/OAO/LMO

Singlet-Triplet splitting in Ullman's diradical

The ground state of the hexatriene molecule.

Degen.	Structure	Energy (eV)	Weight
1		0.00	0.740
2		16.63	0.033
1		16.96	0.033
4		11.39	0.013
4		10.97	0.014

More than 94 % of the wavefunction is represented by these structures.

# OVB reading of the CASSCF wf based on LMOs

VB and OVB: H<sub>2</sub>






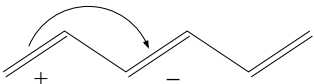

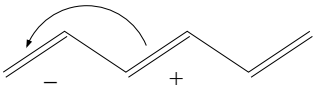
OVB analysis of ethylene

A different approach to benzene

Polyenes

MO/OAO/LMO

Singlet-Triplet splitting in Ullman's diradical

$\Psi_1$	$\Psi_2$	$\langle \Psi_1   \hat{H}   \Psi_2 \rangle$ (eV)
		3.72
		3.81
		1.55
		1.61

The same parameters have been computed also for butadiene and octatetraene. An very good level of transferability has been observed.

⇒ ab initio parameters for excitonic model Hamiltonians.

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Polyenes

**Singlet-Triplet splitting in Ullman's diradical**

Ullman's diradical

# Singlet-Triplet splitting in Ullman's diradical

C. Angeli, C. J. Calzado, C. de Graaf, R. Caballol,  
"The electronic structure of Ullman's biradicals: an orthogonal valence bond interpretation",

*Phys. Chem. Chem. Phys.*, **13**, 14617, (2011).

# The nitronylnitroxide diradical

VB and OVB: H<sub>2</sub>

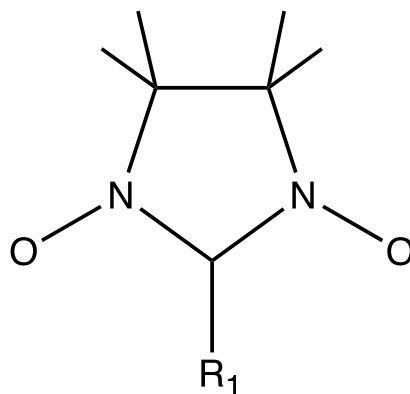
OVB analysis of ethylene

A different approach to benzene

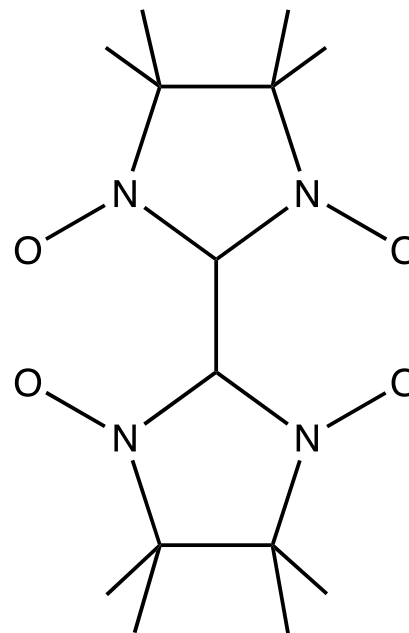
Polyenes

**Singlet-Triplet splitting in Ullman's diradical**

**Ullman's diradical**



(a)



(b)

The nitronylnitroxide radical and Ullman's diradical → strange behavior of the S-T splitting with "standard" MO methods (CAS(2/2) + DDCI).



# The nitronylnitroxide diradical

VB and OVB: H<sub>2</sub>

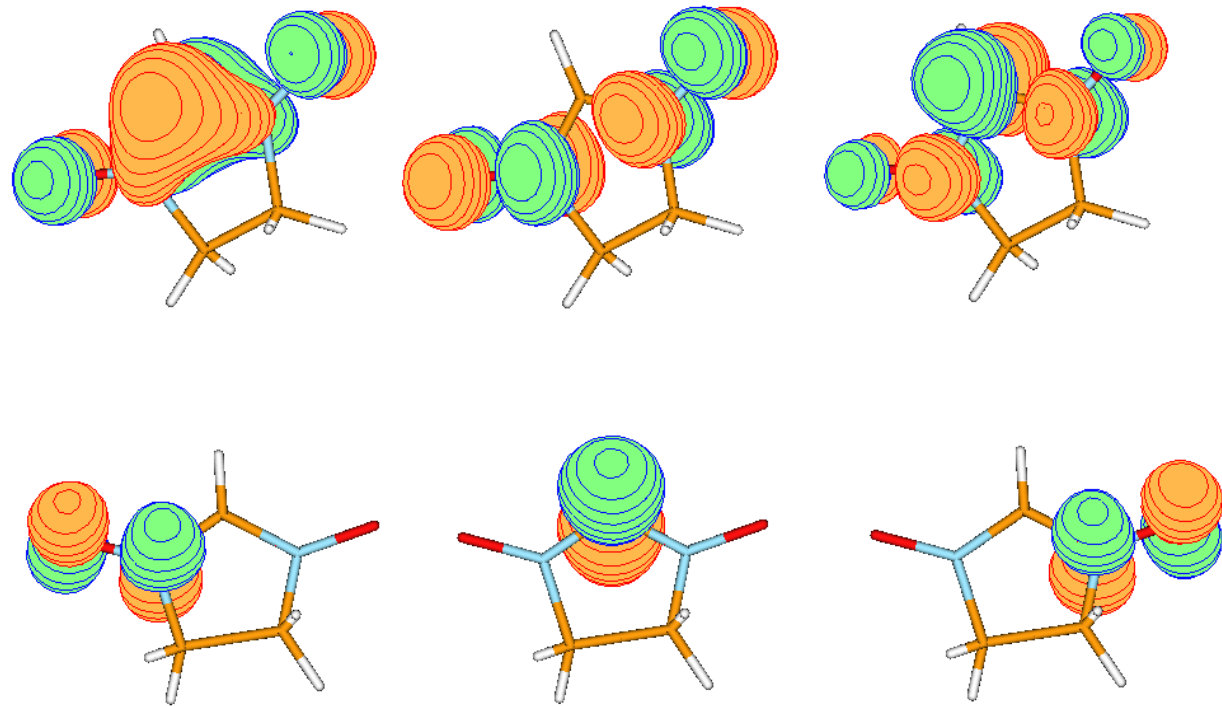
OVB analysis of ethylene

A different approach to benzene

Polyenes

**Singlet-Triplet splitting in Ullman's diradical**

Ullman's diradical



Delocalized and localized CASCF (3/3) MOs.

# The nitronylnitroxide diradical

Table 1: Weights of the various OVB structures.

Structure	ROHF	+SPm	+SPd	+SPmd	CASSCF
$\begin{array}{c} \uparrow \quad \downarrow \quad \uparrow \\ \text{NO} - \text{C} - \text{NO} \end{array}$	0.244	0.453	0.226	0.339	0.444
$\begin{array}{c} \uparrow \quad \uparrow \quad \downarrow \\ \text{NO} - \text{C} - \text{NO} \end{array}$	0.122	0.040	0.278	0.170	0.222
$\begin{array}{c} \uparrow \downarrow \quad \uparrow \\ \text{NO} - \text{C} - \text{NO} \\ \oplus \quad \ominus \end{array}$	0.336	0.296	0.312	0.304	0.224
$\begin{array}{c} \uparrow \downarrow \quad \uparrow \\ \text{NO} - \text{C} - \text{NO} \\ \ominus \quad \oplus \end{array}$	0.176	0.172	0.162	0.174	0.086
$\begin{array}{c} \uparrow \downarrow \quad \uparrow \\ \text{NO} - \text{C} - \text{NO} \\ \ominus \quad \oplus \end{array}$	0.122	0.040	0.022	0.014	0.022
C SD (MPA)	0.000				-0.189
C SD (VBA)	0.000	-0.375	0.073	-0.155	-0.200

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

Ullman's diradical

# The nitronylnitroxide diradical

Table 2: Matrix elements (in eV) of the OVB structures

$\Psi_1$	$\Psi_2$	Symbol	$\langle \Psi_1   \hat{H}   \Psi_2 \rangle$
		$K_{\text{CNO}}$	0.27
		$t_{\text{NOC}}$	3.73
		$t_{\text{NOC}}$	3.75
		$t'_{\text{NOC}}$	3.31
		$t_{\text{CNO}}$	2.45

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Polyenes

Singlet-Triplet splitting in Ullman's diradical

Ullman's diradical

# Conclusions

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Polyenes

**Singlet-Triplet splitting in Ullman's diradical**

Ullman's diradical

The OVB analysis of a wf

- ✓ is a very powerful tool: it gives an information complementary to that given in the MO frame (as happens with pictures from different viewpoints of a solid object);

# Conclusions

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Polyenes

**Singlet-Triplet splitting in Ullman's diradical**

Ullman's diradical

## The OVB analysis of a wf

- ✓ is a very powerful tool: it gives an information complementary to that given in the MO frame (as happens with pictures from different viewpoints of a solid object);
- ✓ allows the identification of the main physical effects (they emerge in a rather intuitive way);

# Conclusions

VB and OVB: H<sub>2</sub>

OVB analysis of ethylene

A different approach to benzene

Polyenes

**Singlet-Triplet splitting in Ullman's diradical**

Ullman's diradical

## The OVB analysis of a wf

- ✓ is a very powerful tool: it gives an information complementary to that given in the MO frame (as happens with pictures from different viewpoints of a solid object);
- ✓ allows the identification of the main physical effects (they emerge in a rather intuitive way);
- ✓ helps to identify effective computational strategies for non standard or pathological problems.