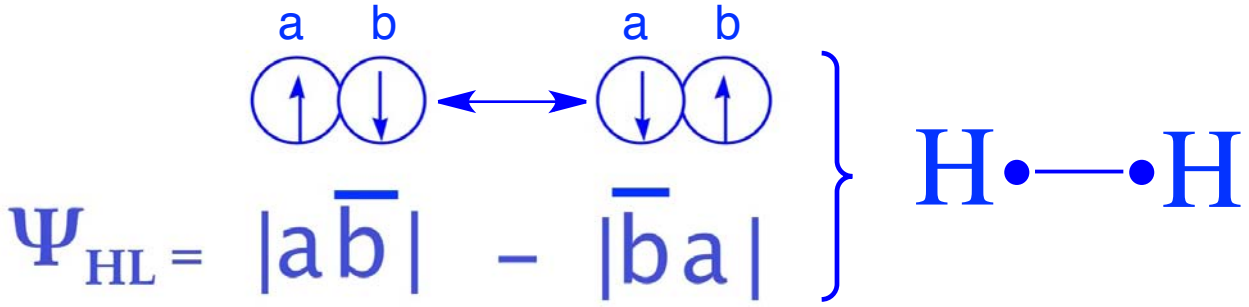
"Classical" VB theory

- Basis of VB theory:

The Heitler-London wave function (1927) for H_2



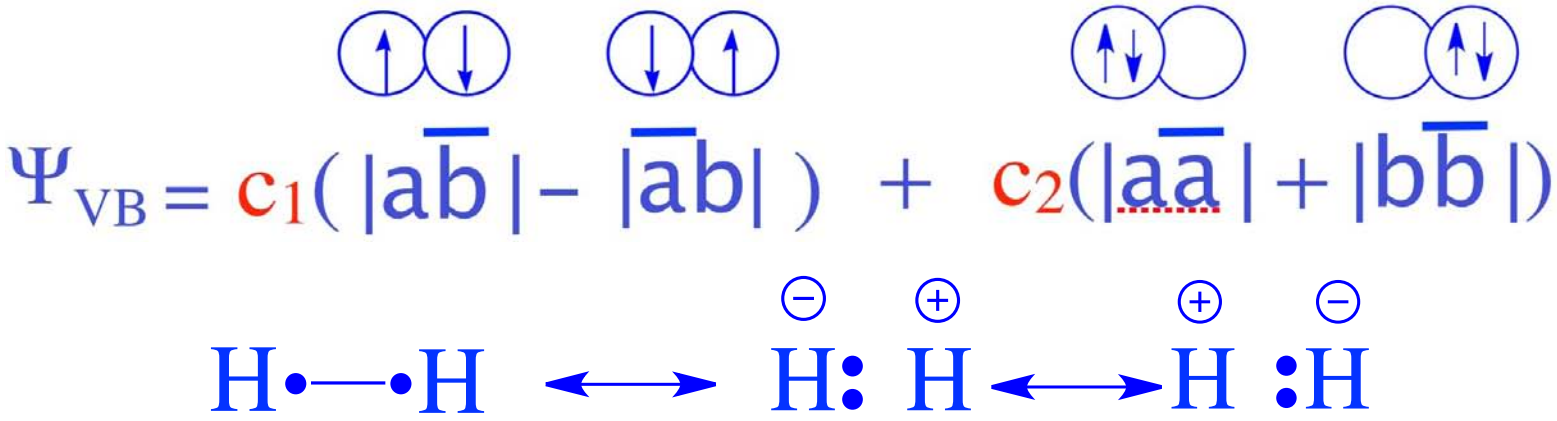
A two electron **covalent bond** is described by :

- electrons occupying **localized atomic orbitals**
- **singlet coupling** between the two spins

"Classical" VB theory

- Basis of classical VB theory:

Pauling (1930-33) : covalent-ionic superposition



A two electron **covalent bond** in **classical VB** described by :

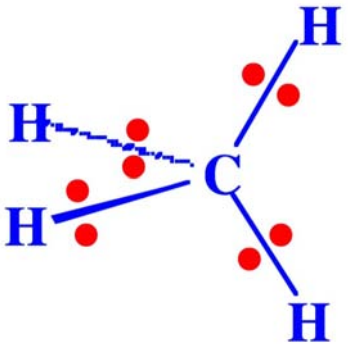
- electrons occupying **"strictly" localized (atom-centered) orbitals**
- **singlet coupling** between the two spins
- Classical VB: **covalent/ionic supperposition**

"Classical" VB theory

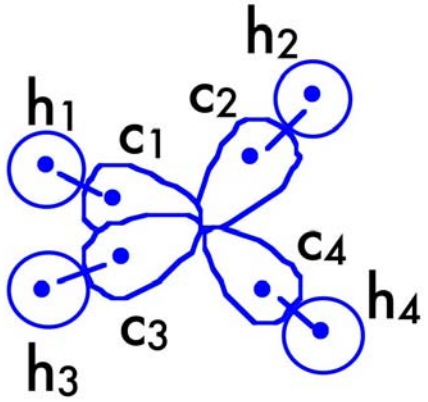
- Basis of classical VB theory:

Generalization to multiple bonds

Lewis :



VB :



$$\Psi_{HL} = \left|(c_1\overline{h_1} - \overline{c_1}h_1)(c_2\overline{h_2} - \overline{c_2}h_2)(c_3\overline{h_3} - \overline{c_3}h_3)(c_4\overline{h_4} - \overline{c_4}h_4)\right|$$

$\Longrightarrow$ Thanks to the use of "strictly" localized orbitals

"classical" VB achieves a quantum dressing of Lewis structures

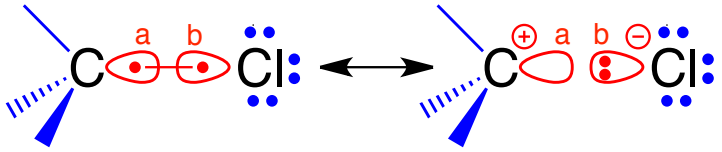
"Classical" VB theory

- Basis of classical VB theory:

Practical case : **inactive** / **active** separation

$$\psi_{VB} = \mathcal{A}\left[\{inactives\} \bullet \{actives\}\right]$$

Example:

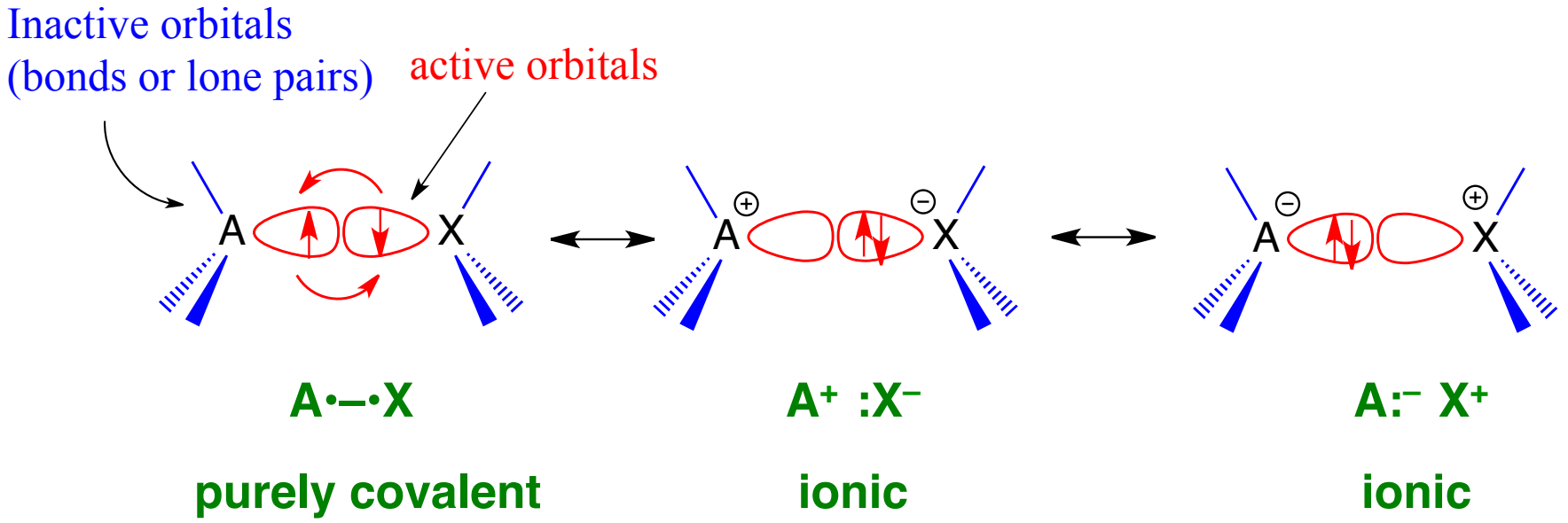


$$\psi_{VB} = \left| \underbrace{\sigma_1\sigma_2 ..\sigma_n}_{\text{delocalized MOs}} \left(a\bar{b} - \bar{a}b\right) \right| + \left| \underbrace{\sigma_1\sigma_2 ..\sigma_n}_{\text{delocalized MOs}} b\bar{b} \right|$$

$\Rightarrow$ **Only active orbitals/e⁻ are described at the VB level**

Quantifying the « classical » paradigm of a two-electron bond

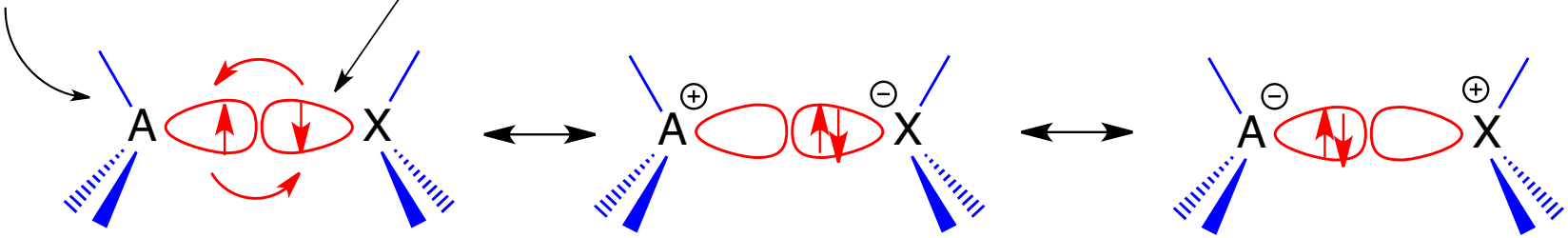
1) Orbitals are localized on single atom or fragment
2) The covalent and ionic components of the bond are explicitly considered



Quantifying the classical paradigm of a two-electron bond

Inactive orbitals
(bonds or lone pairs)

active orbitals



A•–•X **A^+ $:X^-$** **$A:^-$ X^+**

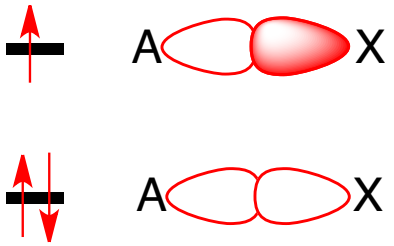
$$\Psi_{A\text{-}X} = c_1(A\bullet\!-\!\bullet X) + c_2(A^+ :X^-) + c_3(A:^- X^+)$$

In modern ab initio valence bond methods,

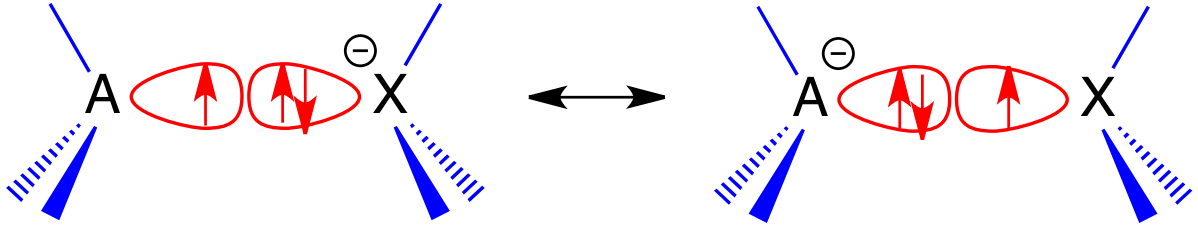
orbitals and ci coefficients are simultaneously optimized

Another common type of bond: the three-electron bond

The Hartree-Fock picture of the $[A\therefore X]^-$ bond:



The Valence Bond picture:



A· :X⁻ ⟷ **A:⁻ ·X⁺**

$$\Psi(A\therefore X)^- = c_1(A\cdot\ :X^-) + c_2(A:^-\ \cdot X)$$

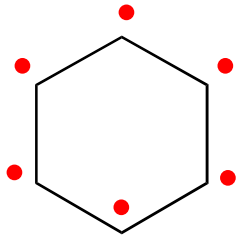
Conjugated molecules with interacting VB structures

Ψ_{VB} is a multistructure wave function

$$\Psi_{VB} = \sum_i C_i \Phi_i$$

where each Φ_i is a VB structure

Example: the π system of benzene



6 electrons, 6 centers

15 possible covalent VB structures
(not linearly independent)

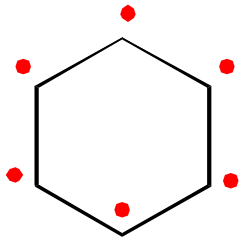
Which ones to choose?

Conjugated molecules with interacting VB structures

Ψ_{VB} is a multistructure wave function : $\Psi_{VB} = \sum_i C_i \Phi_i$

where each Ψ_i is a VB structure

Exemple: the π system of benzene



6 electrons, 6 centers

15 possible VB structures (not linearly independent)

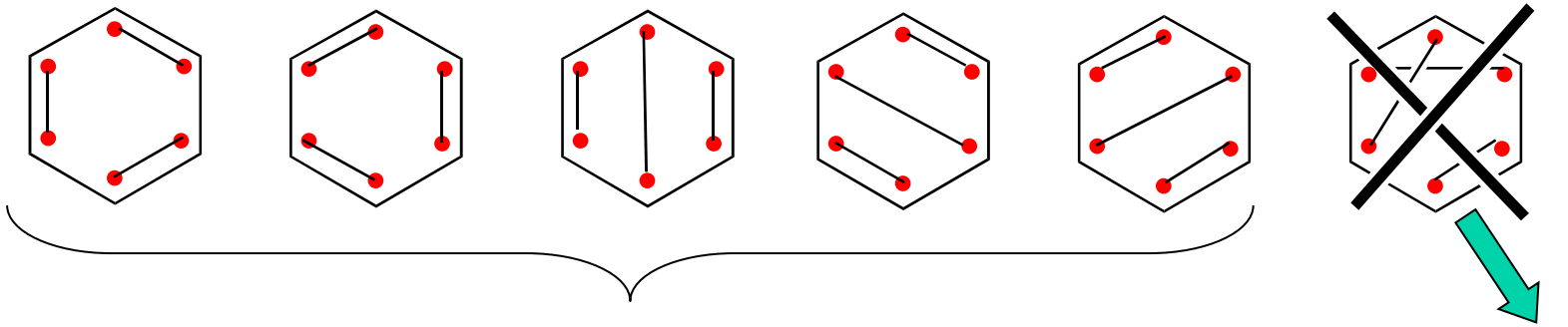
Which ones to choose : - Rumer's Rules [1]
- Weyl tableaux [2]
- Young tableaux and operators [1,3]

[1] : Pauncz book
[2] : H. Weyl. The Theory of Groups and Quantum Mechanics; Dover: New York, 1956.
[3] : McWeeny

An overview of modern ab initio Valence bond methods

Rumer's rule for a covalent *n*-electron/*n*-orbital system:

1) Put the orbitals around an imaginary circle (doesn't need to have the shape of the molecule)
2) Generate all possible VB structures * *not displaying* * crossing bonds



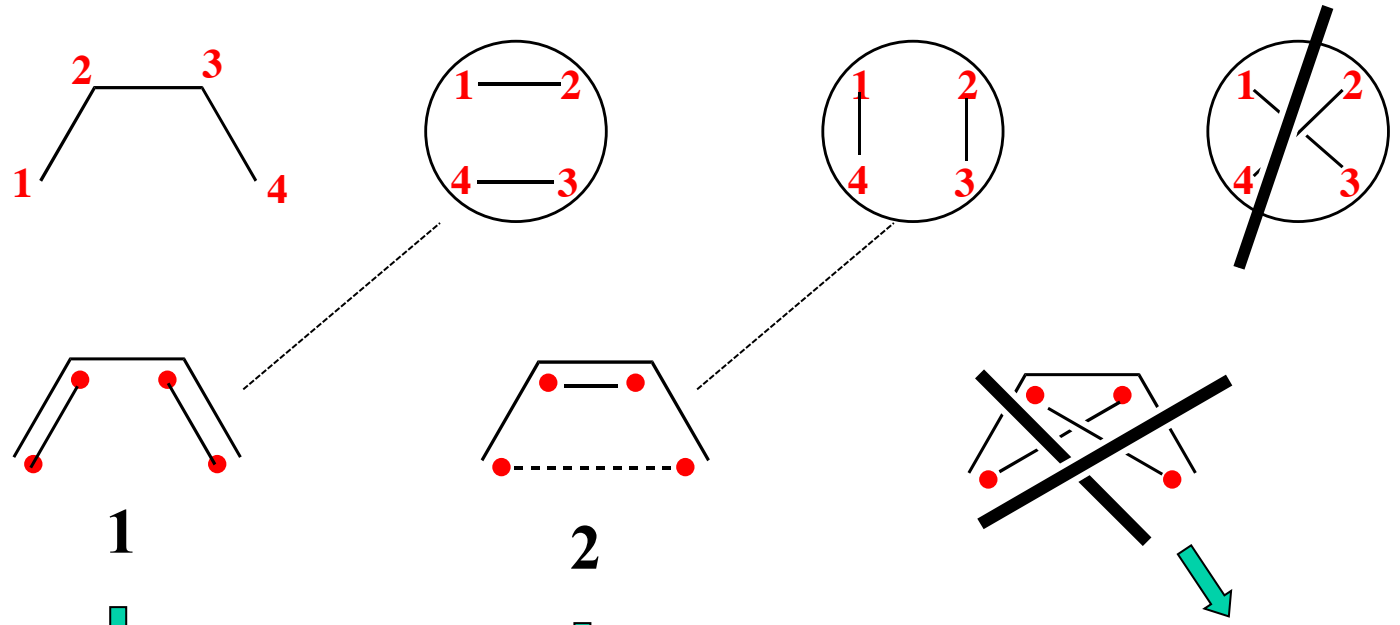
- Complete and **non-redundant** set of VB structures
- VB structures are chemically meaningful

-Redundant
-Chemically meaningless

Rumer's rule for covalent *n*-center/*n*-electron systems

1,3-Butadiene:

Put the orbitals around an imaginary circle, ***even if the molecule is not a ring***



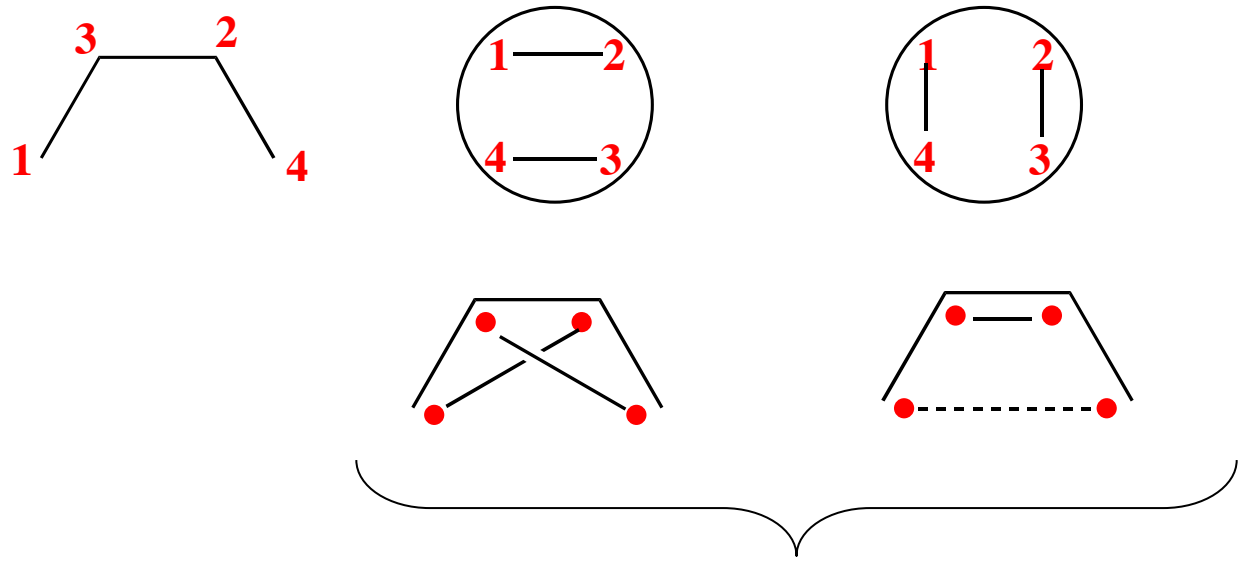
Major VB structure

Explains the barrier to rotation

Rumer's rule for covalent *n*-center/*n*-electron systems

1,3-Butadiene:

Other possible (but unphysical!) choice:

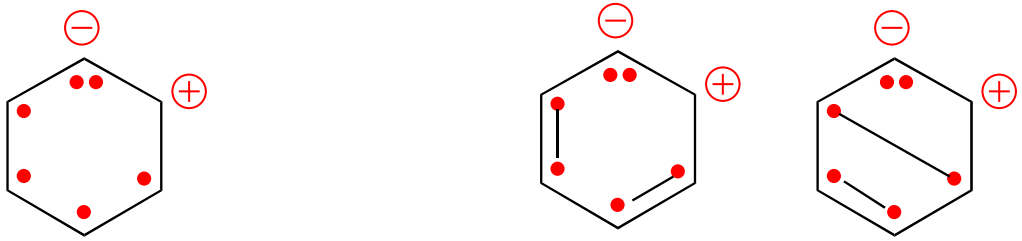


- Complete and non-redundant set of VB structures
- **Chemically meaningless !!**

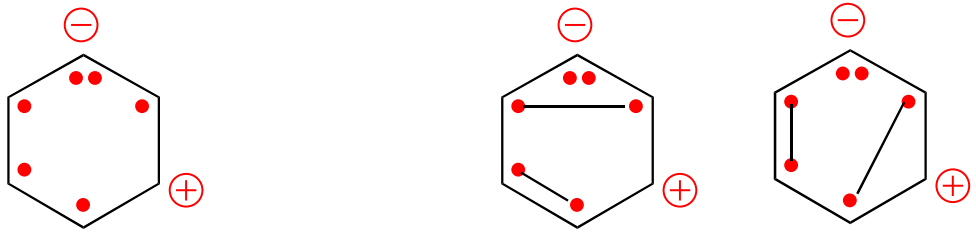
Rumer's rule for *n*-center/*n*-electron ionic structures

Example benzene:

1) Choose a distribution of charges
2) Apply Rumer's rules on the rest of the system



3) Choose another distribution of charges…

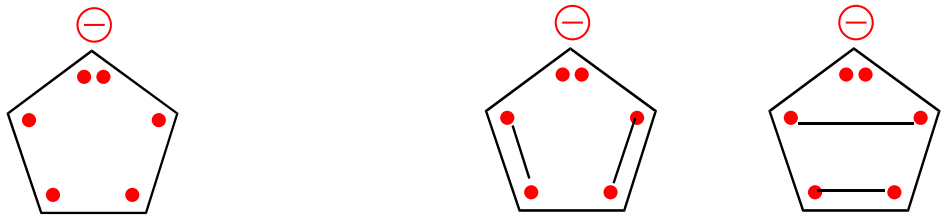


… and so on…

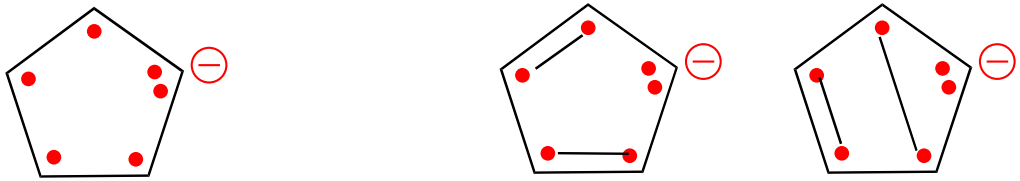
Rumer's rule for *m*-center/*n*-electron covalent structures

Example cycopentadienyl anion, *m*>*n*

1) Choose a center for the lone pair
2) Apply Rumer's rules on the rest of the system



3) Choose another center for the lone pair…



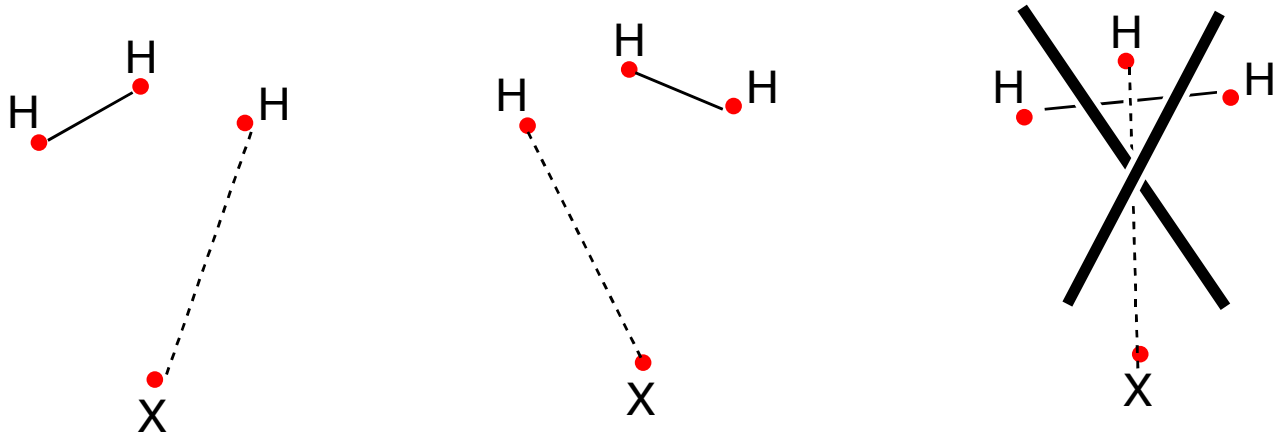
And so on…

Application on ozone: see tutorials

Rumer's rule for **radicals (*m*-e/*m*-c, *m* odd)**

Exemple : [H---H---H]•

1) Add a fictitious center with one electron
2) Treat the system as a singlet



Same number of structures as in the (*m*+1)-e/(*m*+1)-c system

Application on allyl radical: see tutorials

Rumer's rule for **radicals (*m*-e/*m*-c, *m* odd)**

Exemple : [H---H---H]•

3) Then wipe out the fictitious atom

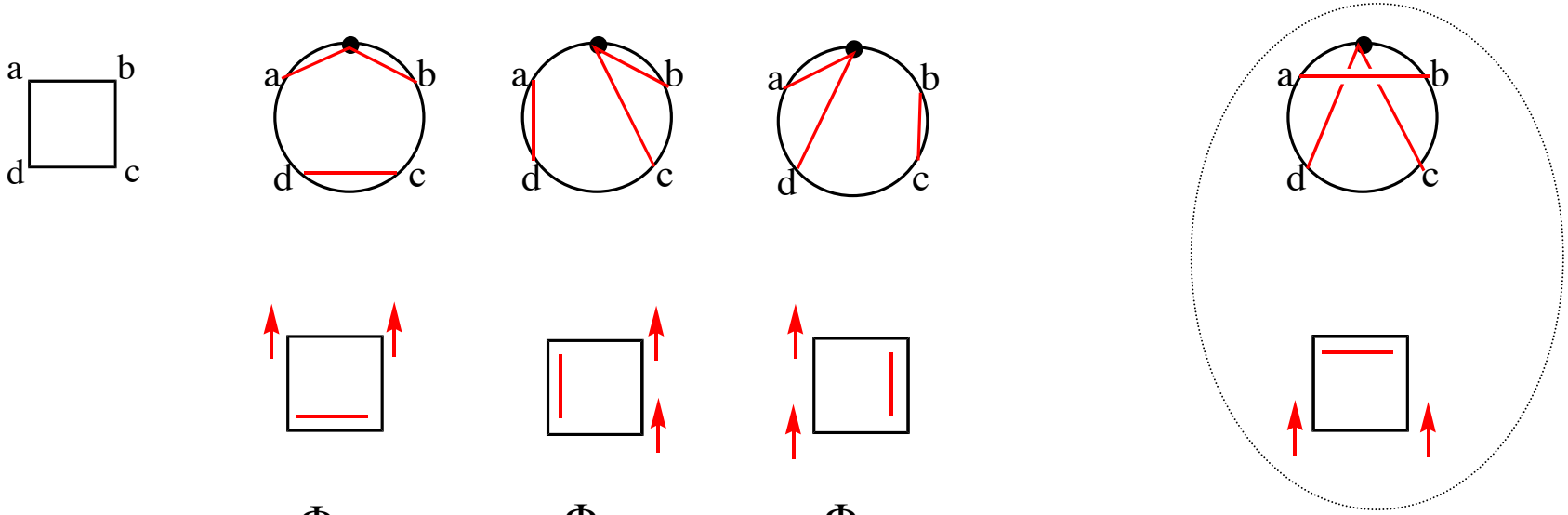
Same number of structures as in the (*m*+1)-e/(*m*+1)-c system

Application on allyl radical: see tutorials

Rumer's rule for **triplets**

1) Insert the atoms + a fictitious center in the circle
2) Link the fictitious center to two atoms (they will have ↑ ↑ spins)
3) Link the other atoms 2 by 2, applying the non-crossing rule

Exemple : butadiene



Number of covalent structures for *N*-e/*N*-c systems)

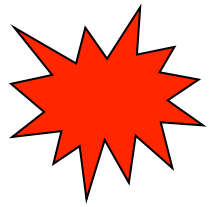
Weyl's formula: $$f_S^N = \frac{(2S+1)N!}{(\frac{1}{2}N+S+1)!(\frac{1}{2}N-S)!}.$$

N	4	6	8	10	12	…
f_S^N	2	5	14	42	132	…

Number of covalent+ionic structures for *N*-e/*m*-c systems)

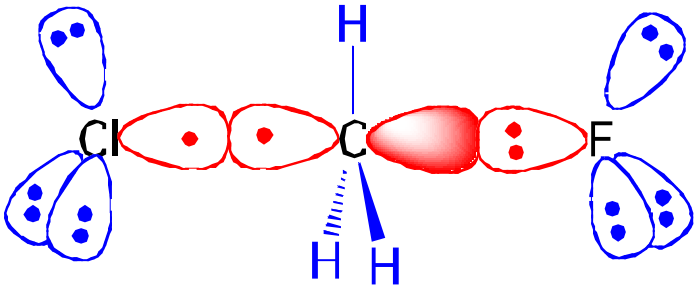
Weyl's formula : $g_S^{N,m} = \frac{2S+1}{m+1}\binom{m+1}{\frac{N}{2}+S+1}\binom{m+1}{\frac{N}{2}-S}$

$N=m$	4	6	8	14	28
f_S^N	20	175	1764	2.76×10^6	2.07×10^{14}



Solution: treating an **active space** at the VB level (the bonds that form/break), and **the rest** as MOs (« spectator orbitals »).

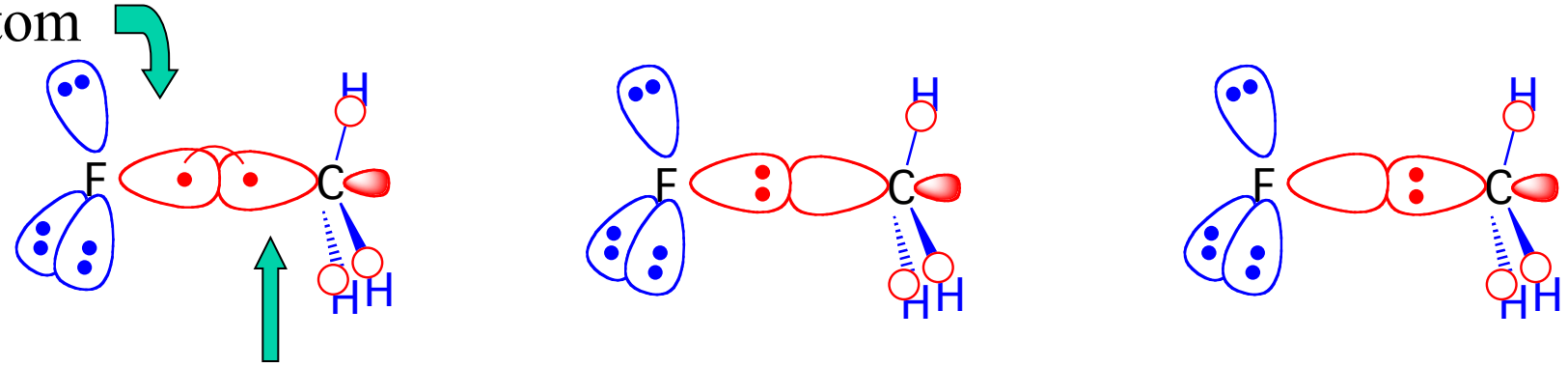
Example:
S_N2 Transition state:
a 4-e/3-orbital VB system
only 6 VB structures



Orbitals in VB structures: localized or semi-localized?

The localized orbital option (so-called « classical » VB)

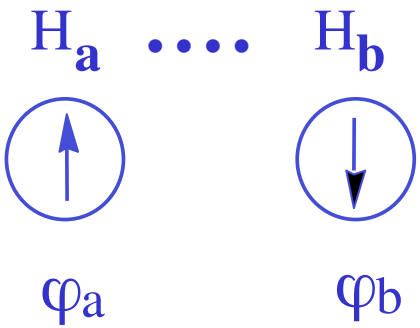
Active orbitals are strictly localized on a single atom



or on a single fragment

- An active orbital ***must not*** ***be delocalized on a center to which it is bonded***
- Covalent and ionic structures must be explicitly generated

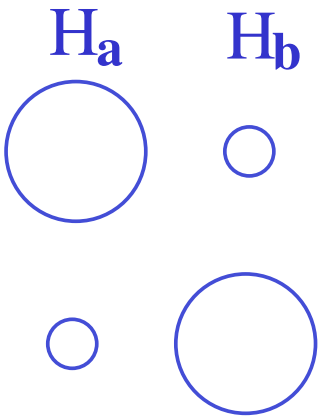
The semi-localized orbital option: Coulson-Fischer orbitals



$$\Psi_{GVB} = |\Phi_a \bar{\Phi}_b| + |\Phi_b \bar{\Phi}_a|$$

$$\Phi_a = \varphi_a + \varepsilon\varphi_b$$

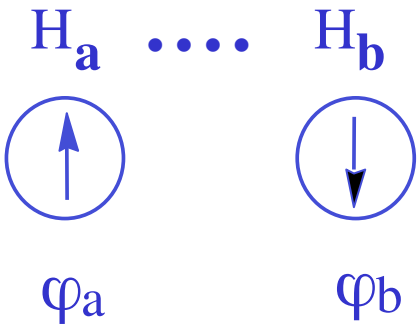
$$\Phi_b = \varphi_b + \varepsilon\varphi_a$$



Used in:

- Generalized Valence Bond (GVB, W. A. Goddard)
- Spin-Coupled valence Bond (J. Gerratt, D. L. Cooper)

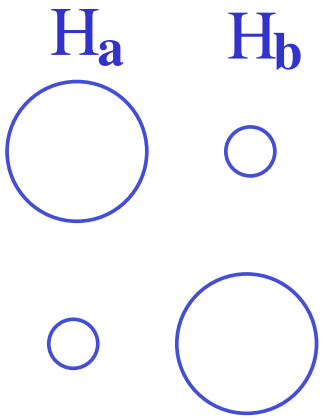
The Generalized Valence Bond Method (GVB)



$$\Psi_{GVB} = |\Phi_a \bar{\Phi}_b| + |\Phi_b \bar{\Phi}_a|$$

$$\Phi_a = \varphi_a + \varepsilon\varphi_b$$

$$\Phi_b = \varphi_b + \varepsilon\varphi_a$$



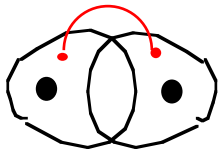
$$\Psi_{GVB} = (1+\varepsilon^2)(|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|) + 2\varepsilon\,(|\varphi_a \bar{\varphi}_a| + |\varphi_b \bar{\varphi}_b|)$$

H•—•H **$H^-H^+ + H^+H^-$**

Ψ_{GVB} is *formally* covalent, but *physically* covalent-ionic optimized

The Generalized Valence Bond Method (GVB)

$$\Psi_{GVB} = |\, \Phi_a \bar{\Phi}_b \,| + |\, \Phi_b \bar{\Phi}_a \,|$$

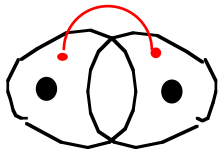


« GVB pair »
Overlapping distorted AOs

*Ionic structures are implicitely included => they **must not** be explicitly introduced in the GVB wave function*

The Generalized Valence Bond Method (GVB)

$$\Psi_{GVB} = |\, \Phi_a \bar{\Phi}_b \,| + |\, \Phi_b \bar{\Phi}_a \,|$$

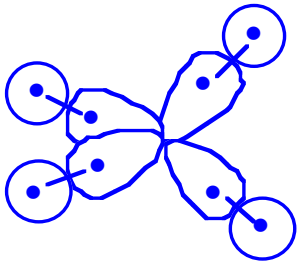


« GVB pair »
Overlapping distorted AOs

*Ionic structures are implicitely included => they **must not** be explicitly introduced in the GVB wave function*

Generalization:

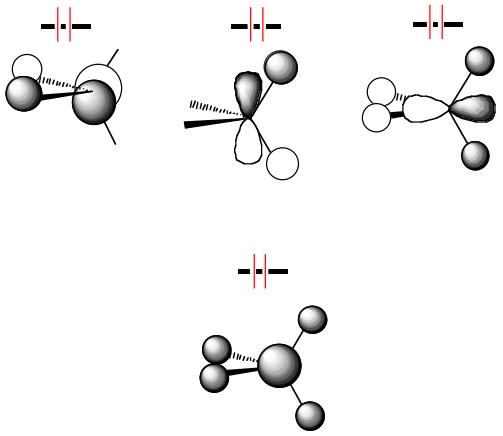
$$\Psi_{GVB} = |(\phi_{1a}\bar{\phi}_{1b} + \phi_{1b}\bar{\phi}_{1a})(\phi_{2a}\bar{\phi}_{2b} + \phi_{2b}\bar{\phi}_{2a})(.....)|$$



Four GVB pairs

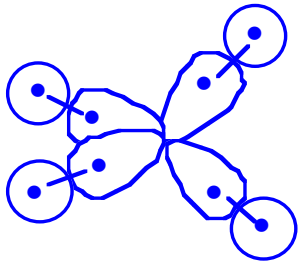
Albeit full orbital delocalization is allowed, orbitals appear as fairly localized

Hartree-Fock, GVB, CASSCF … and static correlation energy



SCF

80%



GVB

20%

CASSCF (1764 conf)

Best possible single-configuration wave function

GVB: - one spin-coupling
- Orthogonality of GVB pairs

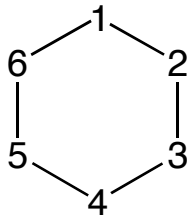
Spin-coupled VB: no restrictions

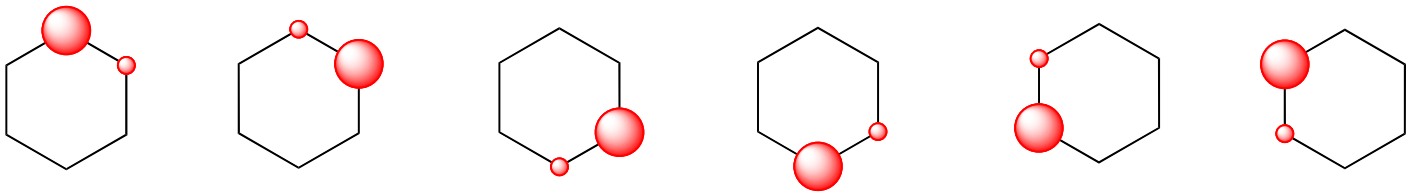
localized or semi-localized orbitals…

To what extent do we (semi-)delocalize the orbitals?

1) On 2 centers only: bond-distorted orbitals (BDOs)

Example: BDOs for a Kekulé structure of benzene

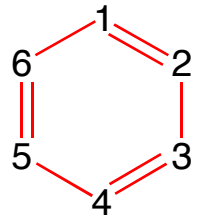




Φ_1 Φ_2 Φ_3 Φ_4 Φ_5 Φ_6

$$\Psi_{BDOs}^{VB} \propto \left|(\Phi_1\overline{\Phi}_2 + \Phi_2\overline{\Phi}_1)(\Phi_3\overline{\Phi}_4 + \Phi_4\overline{\Phi}_3)(\Phi_5\overline{\Phi}_6 + \Phi_6\overline{\Phi}_5)\right|$$

describes a Kekulé structure « stricto sensu »,
with 3 fully localized π bonds



localized or semi-localized orbitals…

To what extent do we (semi-)delocalize the orbitals?

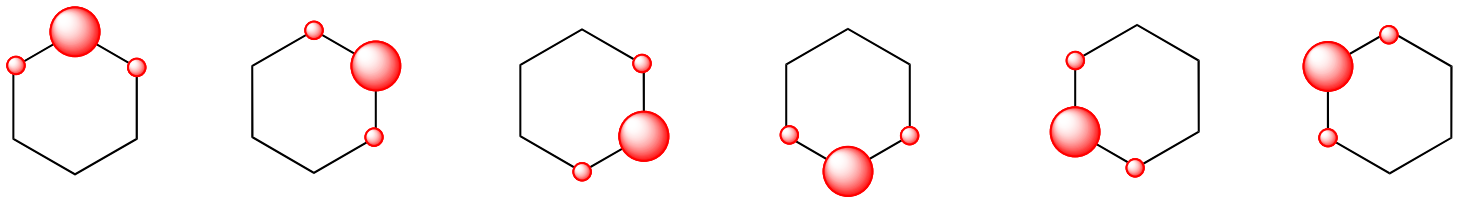
2) Fully allowed to delocalize: overlap-enhanced orbitals (OEOs)

(Option used in GVB or SCVB methods)

Example: GVB or SCVB description of benzene with two Kekulé structures

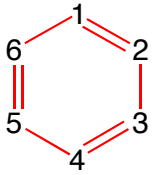
$$\Psi^{GVB} \propto \left|(\Phi_1\overline{\Phi}_2 + \Phi_2\overline{\Phi}_1)(\Phi_3\overline{\Phi}_4 + \Phi_4\overline{\Phi}_3)(\Phi_5\overline{\Phi}_6 + \Phi_6\overline{\Phi}_5)\right|$$

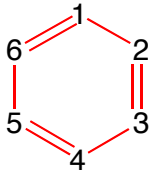
$$+ \left|(\Phi_2\overline{\Phi}_3 + \Phi_3\overline{\Phi}_2)(\Phi_4\overline{\Phi}_5 + \Phi_5\overline{\Phi}_4)(\Phi_6\overline{\Phi}_1 + \Phi_1\overline{\Phi}_6)\right|$$



Φ_1 Φ_2 Φ_3 Φ_4 Φ_5 Φ_6

Orbitals are delocalized on 3 centers

The relationship to 

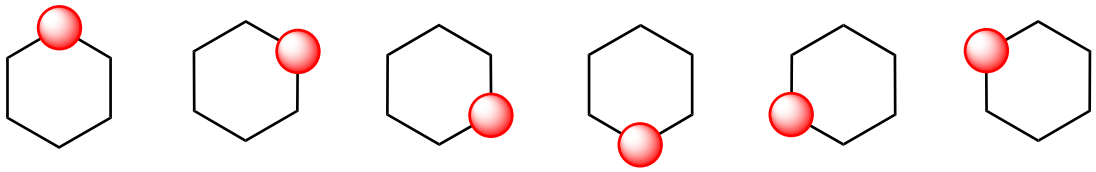
and 

is less obvious

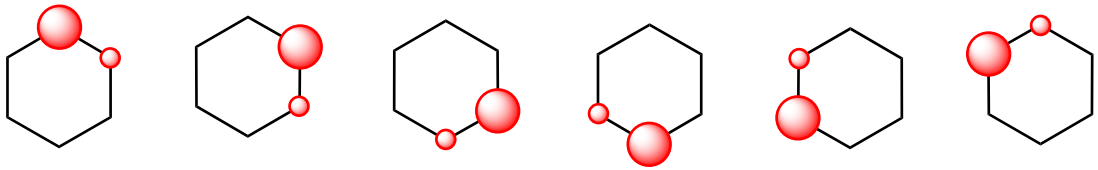
Summary (exemplifed on benzene π bonds)

Three options:

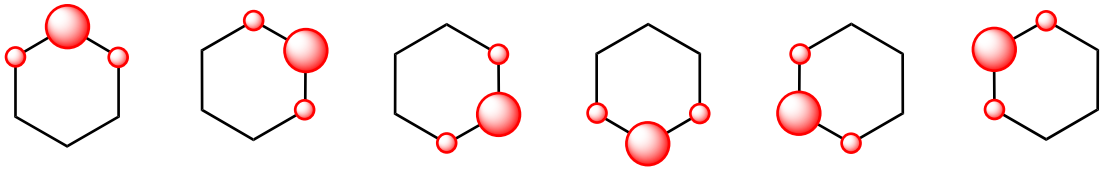
Localized orbitals



Bond-distorted orbitals (BDOs)



Overlap-enhanced orbitals (OEOs)

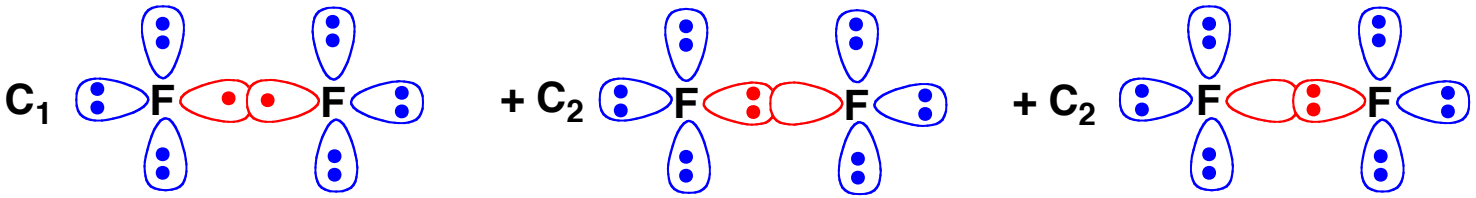


How does one calculate VB wave functions with localized orbitals ?

$$\Psi_{VB} = \sum_i C_i \Phi_i$$ where each Φ_i is a VB structure

Basic method: VBSCF (Balint-Kurti & van Lenthe)

Example: the F_2 molecule



F•—•F $\quad F^-F^+ \quad F^+F^-$

Coefficients C_i and orbitals optimized simultaneously (like MCSCF)

All orbitals are optimized (active as well as spectator ones)

VBSCF ~ equivalent to GVB, SCVB

Accuracy of the various methods

Test case: the dissociation of F_2

Calculation of ΔE for F-F=1.43Å, 6-31G(d) basis:

- **Hartree-Fock: − 37 kcal/mol (repulsive!)**

  Reason: too much ionic

- **Full configuration interaction** (6-31G(d) basis) **30-33 kcal/mol**

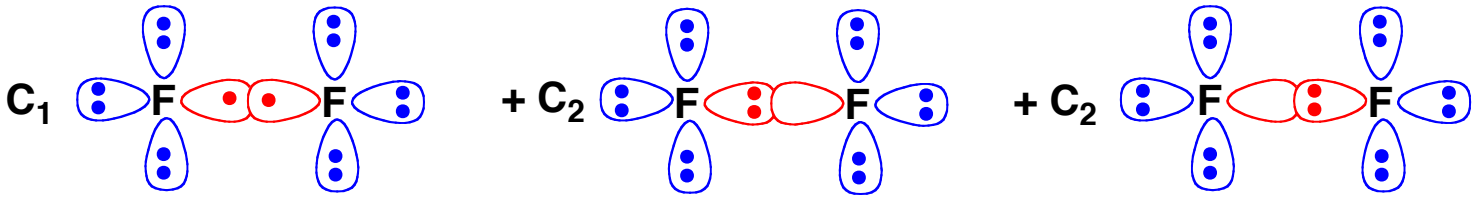
- **GVB, VBSCF, CASSCF** **Only ~ 15kcal/mol**

  Reason: we miss dynamic correlation.

  What does this physically mean?

What is missing in GVB and VBSCF?

GVB/VBSCF: a closer examination



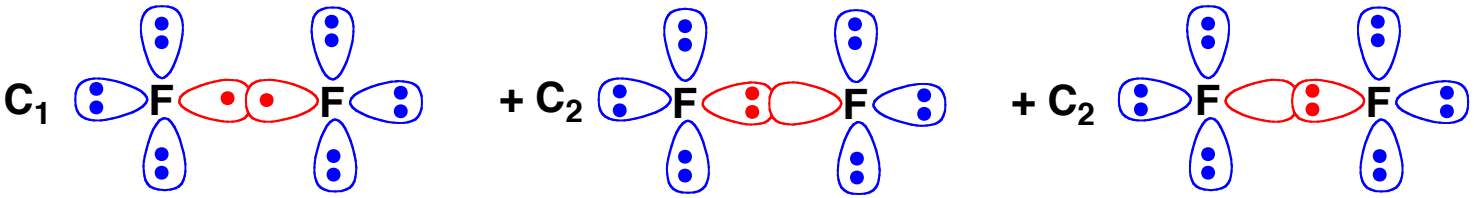
F•—•F F^-F^+ F^+F^-

The coefficients and orbitals are optimized, but…

- The same set of AOs is used for all VB structures:
  optimized for a mean neutral situation

What is missing in GVB and VBSCF?

GVB/VBSCF: a closer examination

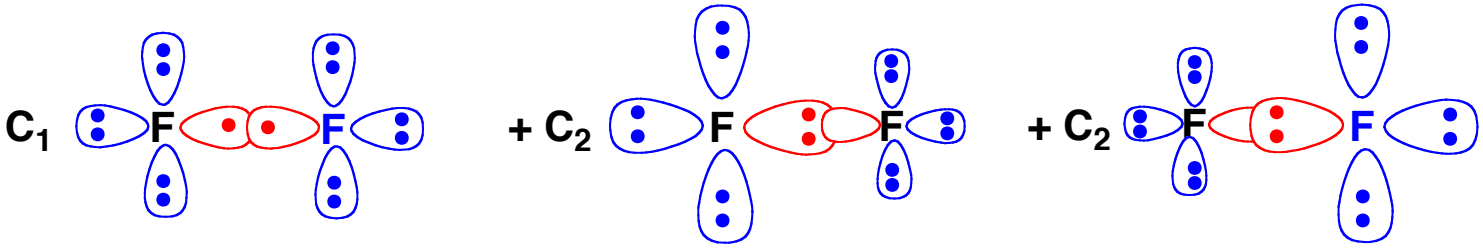


F•—•F F^-F^+ F^+F^-

The coefficients and orbitals are optimized, but…

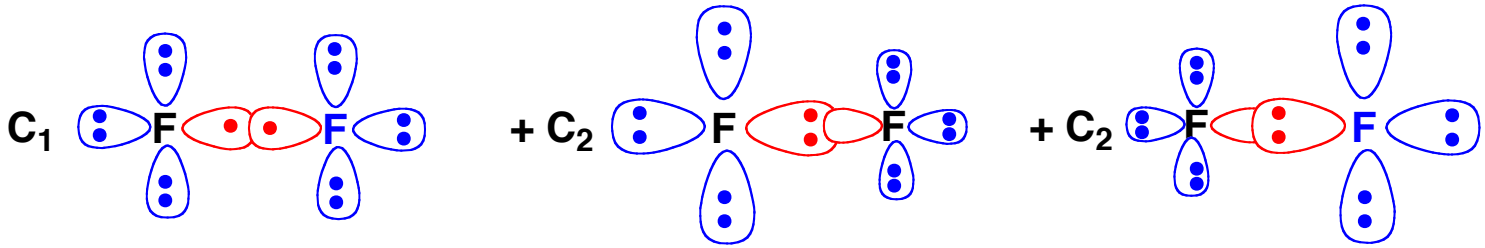
- The same set of AOs is used for all VB structures:
  optimized for a mean neutral situation

A better wave function:



The « Breathing-Orbital » VB method (L-BOVB)

- **Provides optimized covalent-ionic coefficients** (like GVB)



F•—•F F^-F^+ F^+F^-

- **Different orbitals for different VB structures**

- Orbitals for F•—•F will be the same as VBSCF
- Orbitals for ionic structures will be much improved

- **One expects**

- A better description of ionic structures
- A better bonding energy

Test case: the dissociation of F_2

$$F\text{–}F \xrightarrow{\Delta E} F\bullet + F\bullet$$

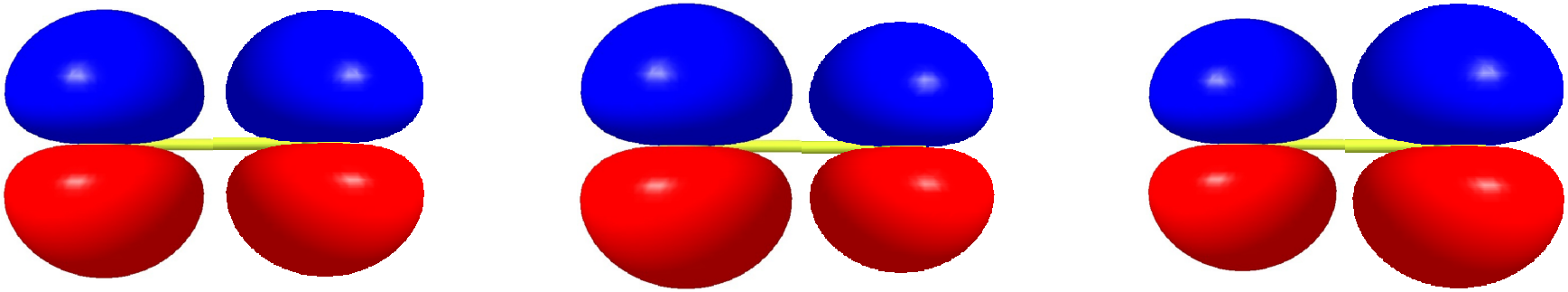
Calculation of ΔE for F-F=1.43Å, 6-31G(d) basis:

Iteration		De(kcal)	F•–•F	$F^+F^- \leftrightarrow F^-F^+$
GVB,VBSCF		~ 15	0.768	0.232
BOVB	1	24.6	0.731	0.269
	2	27.9	0.712	0.288
	3	28.4	0.709	0.291
	4	28.5	0.710	0.290
	5	28.6	0.707	0.293
Full CI		30-33		

The « Breathing-Orbital » VB method (BOVB)

Different orbitals for different VB structures:
How different are the orbitals?

The π lone pairs of F_2 in BOVB:

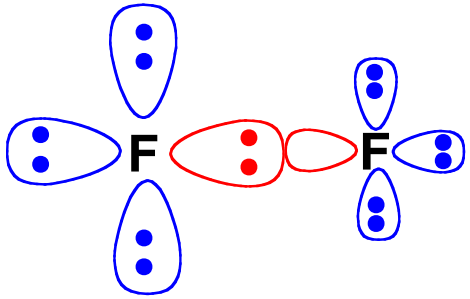


F•—•F F^- F^+ F^+ F^-

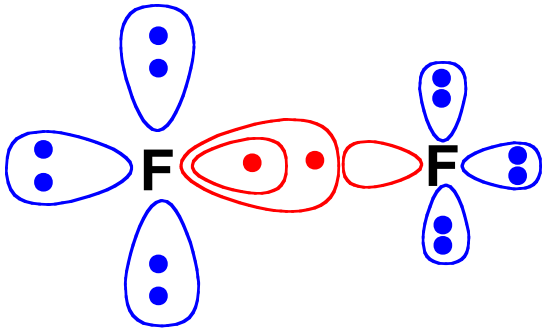
Small difference in shape, significant effect in energy

Improvements of the BOVB method

- **Improvement of the ionic VB structures**
  - basic level:



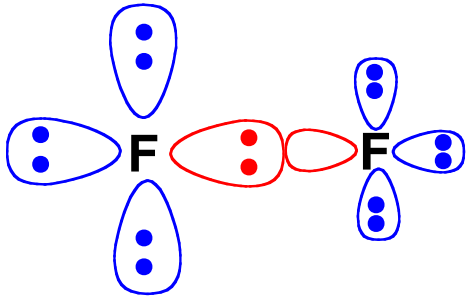
- improved level (« split-level » or **S**)



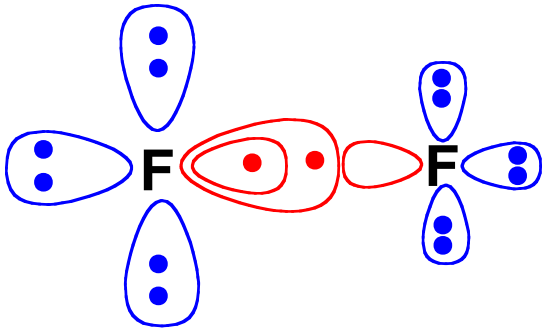
The « active » orbital is split.
This brings radial electron correlation

Improvements of the BOVB method

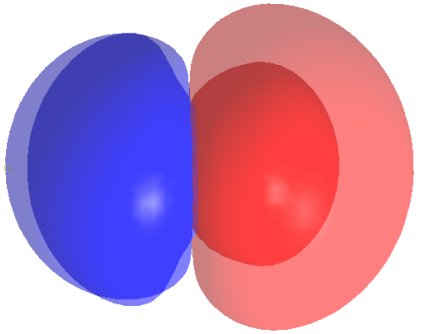
- **Improvement of the ionic VB structures**
  - basic level:



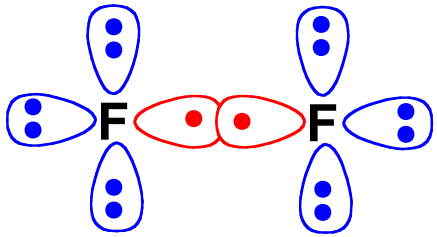
- improved level (« split-level » or **S**)



Actual shapes of the split orbitals:



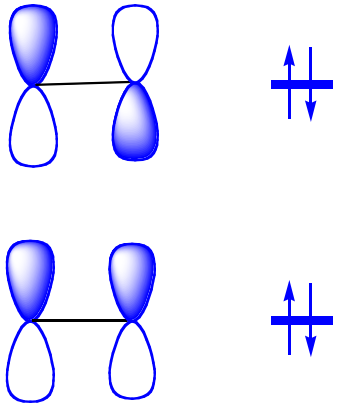
- **Improvement of the interactions between spectator orbitals**



- **Spectator orbitals can be:**

  - local atomic orbitals

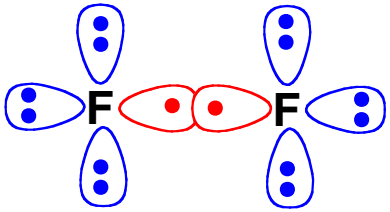
  - bonding and antibonding combinations

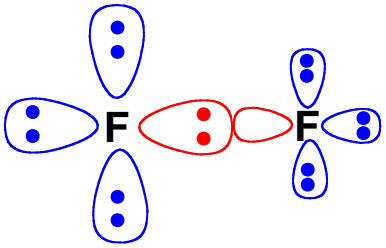


Slightly better (« Delocalized » level or **D**)

The various levels of the BOVB method

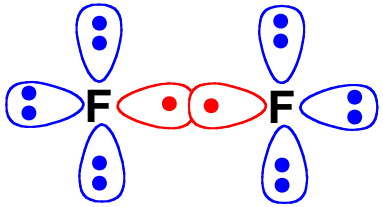
- **Basic: L-BOVB**

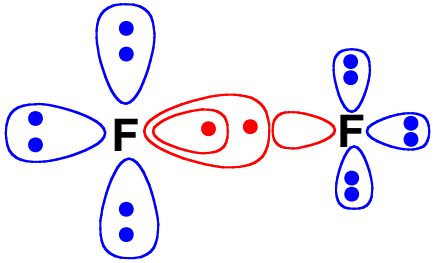




All orbitals are localized,
ionics are closed-shell

- **SL-BOVB**





All orbitals are localized, but
active orbitals in ionics are split

- **SD-BOVB**

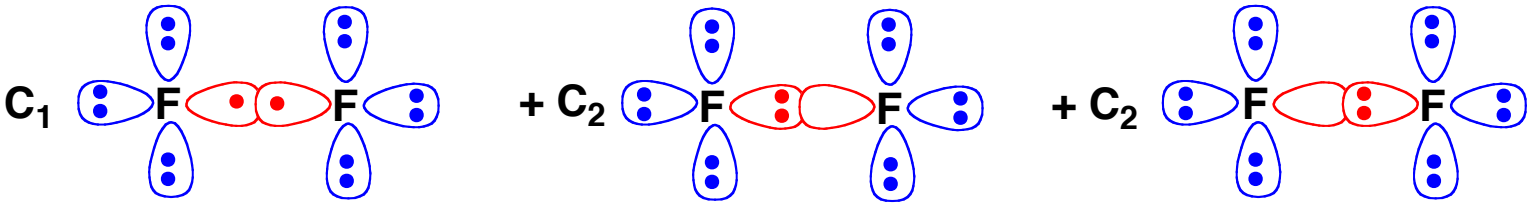
- Active orbitals are split in ionics
- Spectator orbitals are delocalized in all structures

- **D-BOVB** Spectator orbitals are delocalized in all structures

Electron correlation in BOVB

- **Non-dynamic correlation (VBSCF, CASSCF,GVB)**

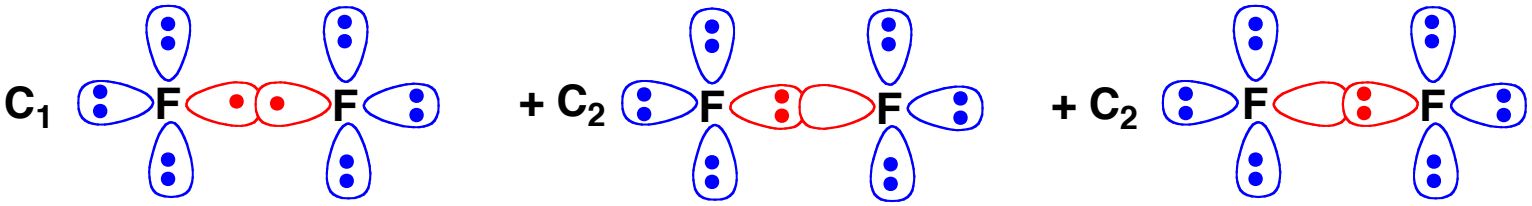
  - Non dynamic correlation gives the correct ionic/covalent ratio



Electron correlation in BOVB

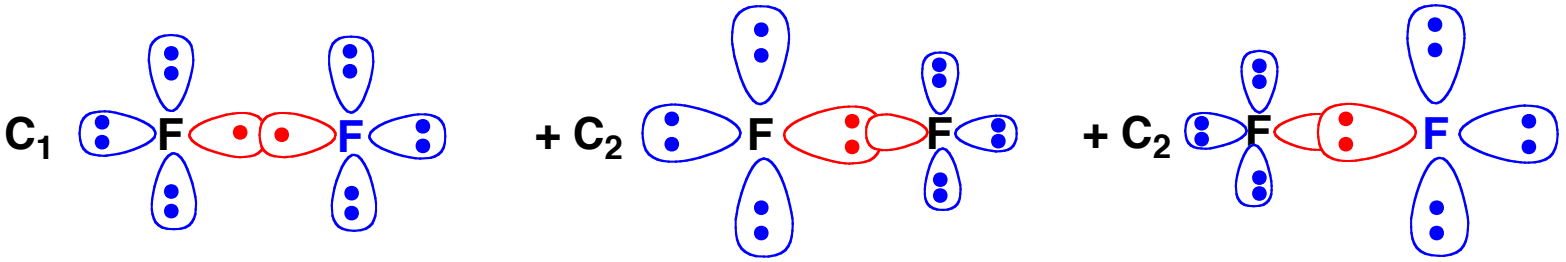
- **Non-dynamic correlation (VBSCF, CASSCF,GVB)**

  - Non dynamic correlation gives the correct ionic/covalent ratio



- **Dynamic correlation**

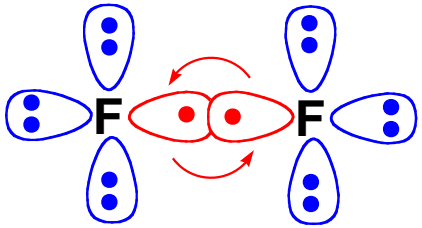
  - All the rest. This is what is missing in VBSCF-CASSCF-GVB.
  - BOVB brings that part of dynamic correlation that varies in the reaction



What is an accurate description of two-electron bonding?

- **Spin exchange between two atomic orbitals**

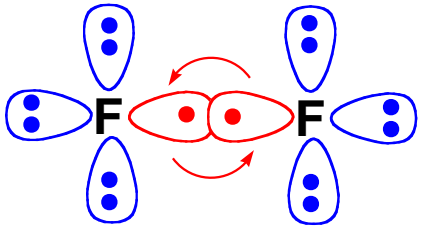
  - Electrons are on different atoms and they exchange their positions



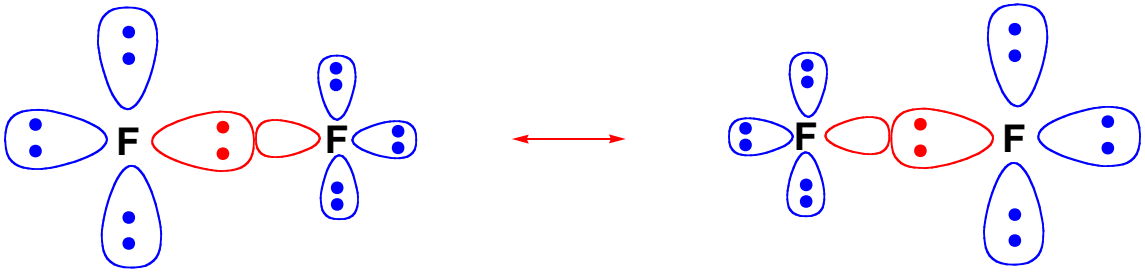
What is an accurate description of two-electron bonding?

- **Spin exchange between two atomic orbitals**

  - Electrons are on different atoms and they exchange their positions



- **Charge fluctuation**



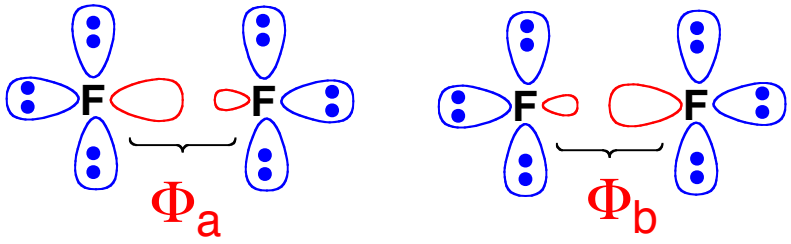
- Sometimes both electrons are on the same atom.
- There is some charge fluctuation. All orbitals instantaneously rearrange in size and shape to follow the charge fluctuation (orbitals « breathe »).

This is differential dynamic correlation

Delocalizing also the *active orbitals* in BOVB ?

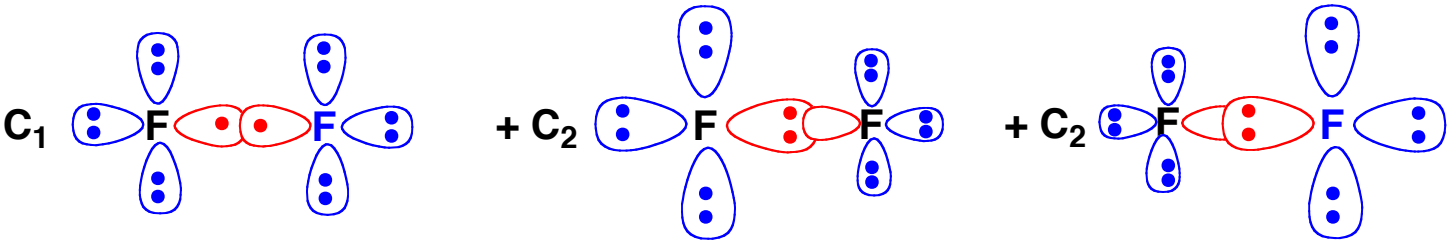
No ! Never ! No way ! By no means!

- Delocalizing the active orbitals in a formally covalent function is ***one way*** of taking care of ionic structures



$$\Psi_{GVB} = \left|...\Phi_a\overline{\Phi}_b\right| + \left|...\Phi_b\overline{\Phi}_a\right|$$

- Explicitly writing covalent and ionic structures with localized orbitals is ***another way***:



- Combining ***both ways*** leads to ***redundancy***
  - no consequences in VBSCF
  - artefactual energy lowering in BOVB

Delocalizing also the active orbitals in BOVB ?

No ! Never ! No way ! By no means!

Test case: the dissociation of F_2

1) BOVB with *strictly local* active orbitals

L-BOVB De = 29.1 kcal/mol

SD-BOVB De = 36.3 kcal/mol

2) BOVB with delocalized active orbitals

L-BOVB De = 51.5 kcal/mol

SD-BOVB De = 102 kcal/mol (!)

Experiment

De = 38 kcal/mol

Faraday Discuss., **2007**, *135*, 369-371

Delocalizing also the active orbitals in BOVB ?

No ! Never ! No way ! By no means!

Test case: the dissociation of F_2

1) BOVB with *strictly local* active orbitals

L-BOVB De = 29.1 kcal/mol

SD-BOVB De = 36.2 kcal/mol

~~**2) BOVB with delocalized active orbitals**~~

~~L-BOVB De = 51.5 kcal/mol~~

~~SD-BOVB De = 102 kcal/mol (!)~~

Faraday Discuss., **2007**, *135*, 369-371

Experiment

De = 38 kcal/mol

Summary : the two great families of VB methods

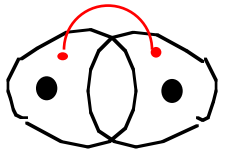
Exemple: the H_2 molecule

Static correlation

Classical VB
Local approach

Coulson-Fischer
Semi-delocal approach

$\Psi_{VB} = H\bullet\!\!-\!\!\bullet H + H^{-}H^{+} + H^{+}H^{-}$

$\Psi_{CF} =$ 

- *Keep strictly local orbitals*
- *Explicit inclusion of ionic structures*

- *Use semi-delocalized orbitals*
- *Implicit inclusion of ionic structures*

Dynamic correlation

BOVB, VBCI, VBPT2, VB-QMC

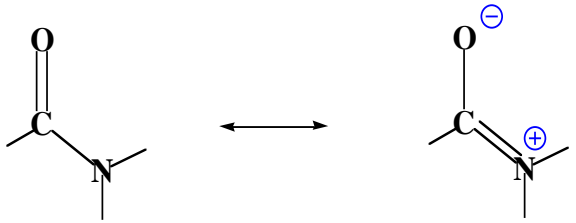
CCCI, VB-QMC

Calculation of diabatic energies

What for?

Resonance energies

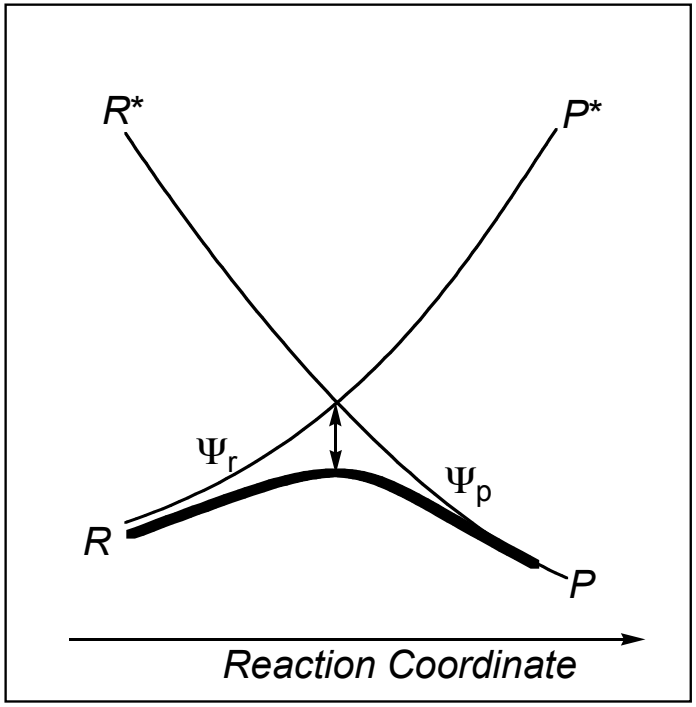
RE = E(**1**) - E(**1** ⟷ **2**)



1 **2**

VB-state-crossing diagrams

See VB lecture III
by Prof. S. Shaik



Calculation of diabatic energies

Example: Covalent-ionic resonance energy in H_2

$$\Psi_{VB} = C_1\Phi_{cov} + C_2\Phi_{ion\text{-}1} + C_2\Phi_{ion\text{-}2}$$

$$RE = E(\Phi_{cov}) - E(\Psi_{VB})$$

How does one calculate $E(\Phi_{cov})$?

First method: « Consistent Diabatic Configuration »

Φ_{cov} is simply extracted from the Hamiltonian matrix

	1	2	3
1	-1.853879	-1.579215	-1.579215
2	-1.579215	-1.578592	-1.163000
3	-1.579215	-1.163000	-1.578592

$E(\Psi_{VB})$ = -1.86452 au

RE(CDC) = -1.85388 + 1.86452 = 0.01064 au = 6.7 kcal/mol

Calculation of diabatic energies

Example: Covalent-ionic resonance energy in H_2

$$\Psi_{VB} = C_1\Phi_{cov} + C_2\Phi_{ion\text{-}1} + C_2\Phi_{ion\text{-}2}$$

$$RE = E(\Phi_{cov}) - E(\Psi_{VB})$$

Second method: « Variational Diabatic Configuration »

Φ_{cov} is calculated separately: $E(\Phi_{cov})$ = -1.85778 au

=> Φ_{cov} is ***variationally optimized***

	1	2	3
1	-1.853879	-1.579215	-1.579215
2	-1.579215	-1.578592	-1.163000
3	-1.579215	-1.163000	-1.578592

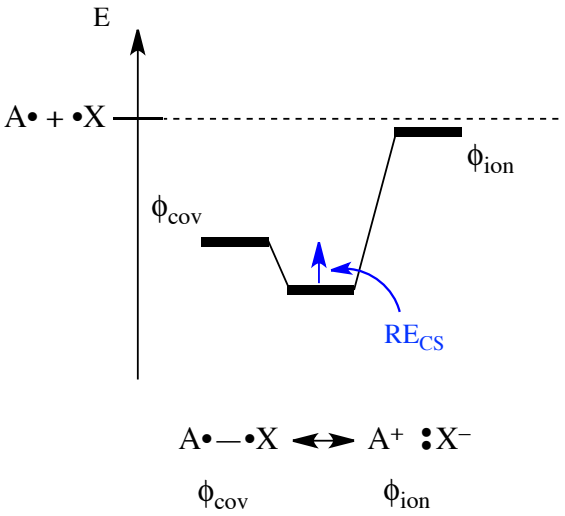
$E(\Psi_{VB})$ = -1.86452 au

RE(VDC) = -1.85778 + 1.86452 = 0.00674 au = 4.2 kcal/mol

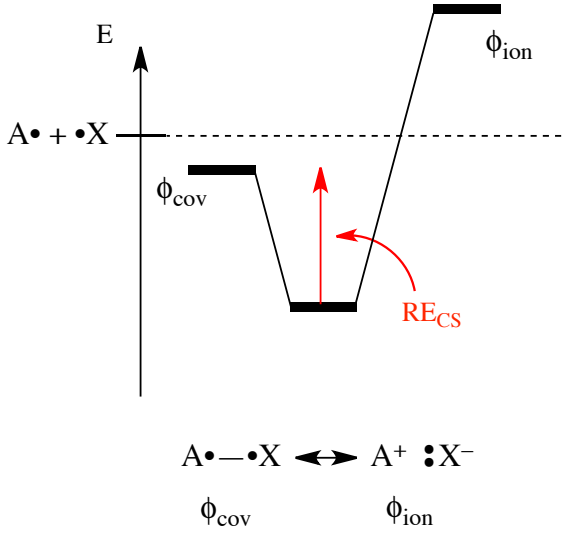
(< RE(CDC))

"Charge shift" bond

- What is a Charge Shift bond*?



Polar-Covalent bond



"Charge-Shift" bond

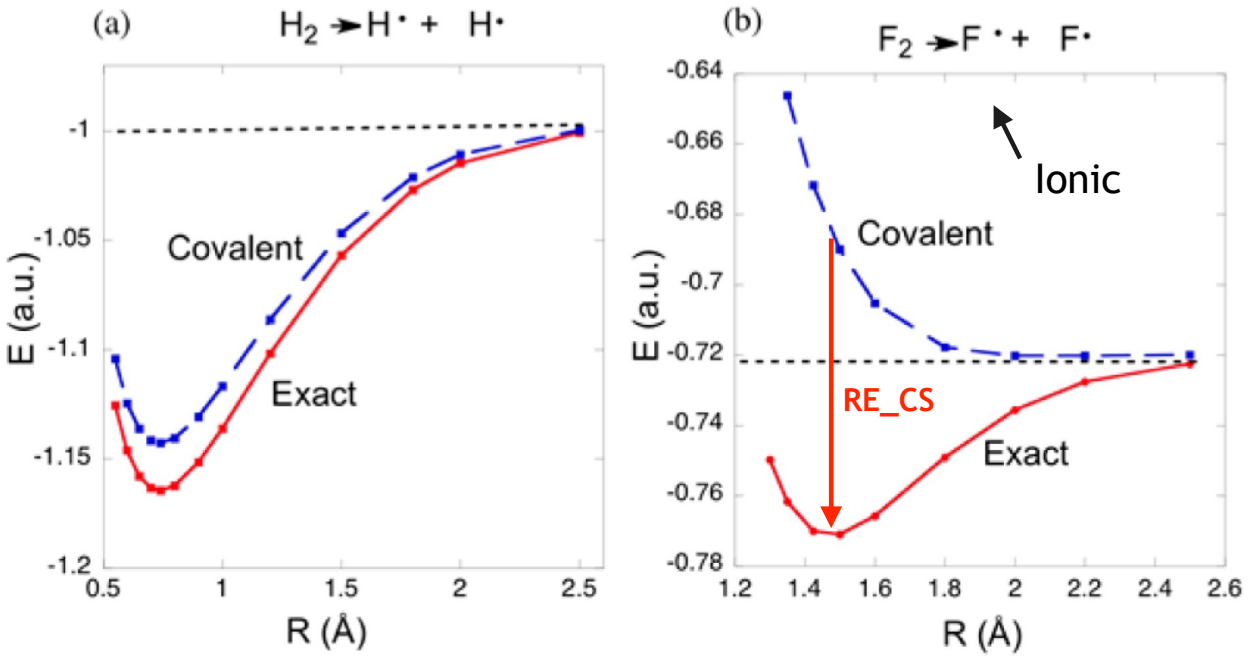
A bond is called "charge shift" when it owes its stability to the **resonance energy** between the **covalent** and **ionic** states of the bond

* Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. Nat. Chem. 2009, 1, 443–449.
Zhang H., Danovich, D.; Wu, W.; Braïda B.; Hiberty, P. C.; Shaik S. JCTC 2014, 10, 2410–2418

"Charge shift" bond

- Prototype examples of charge-shift bond : F_2 :

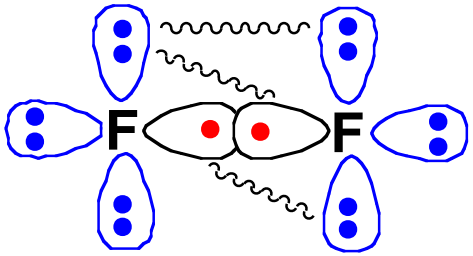
H_2 and F_2 both ~80% covalent and 20% ionic !



* Shaik, S.; Danovich, D.; Wu, W.; Hiberty, P. C. Nat. Chem. 2009, 1, 443–449.
Zhang H., Danovich, D.; Wu, W.; Braïda B.; Hiberty, P. C.; Shaik S. JCTC 2014, 10, 2410–2418

"Charge shift" bond

- Condition for charge-shift bonding:



CS-bonding appears when there is much Pauli repulsion around the bond (high T)

Necessary condition for charge-shift bonding :
at least one of the atoms involved in the bond should bear **lone pair(s)**