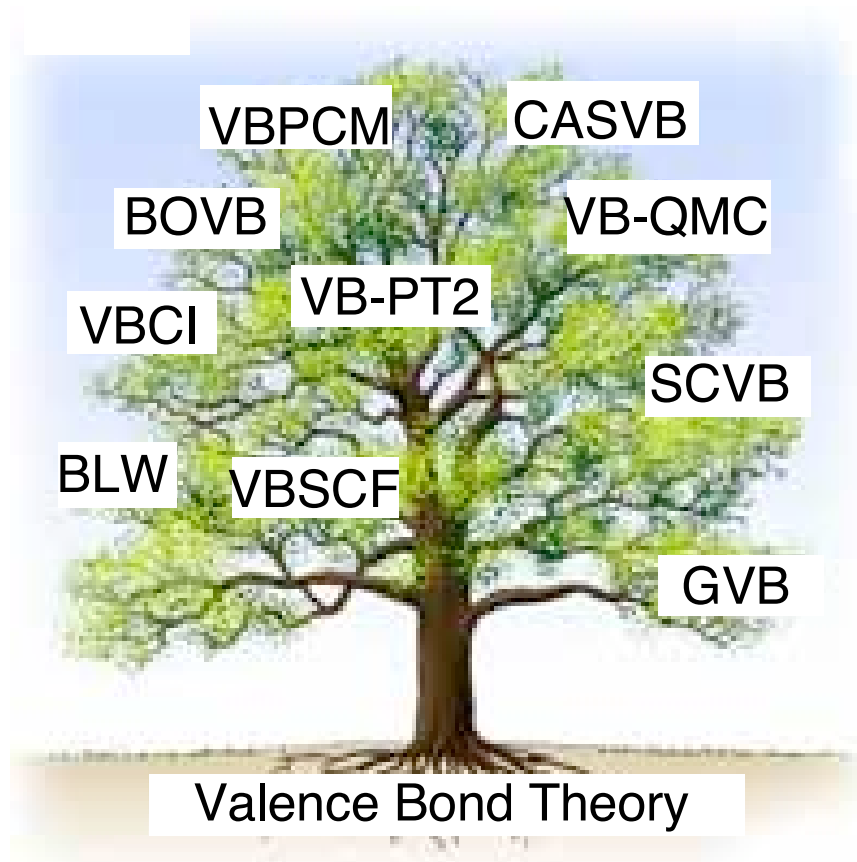


An overview of modern ab initio Valence bond methods



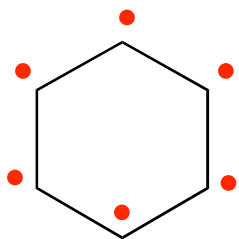
An overview of modern ab initio Valence bond methods

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 VB structures (not linearly independent)

Which ones to choose?

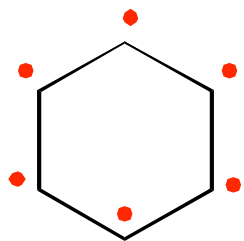
An overview of modern ab initio Valence bond methods

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

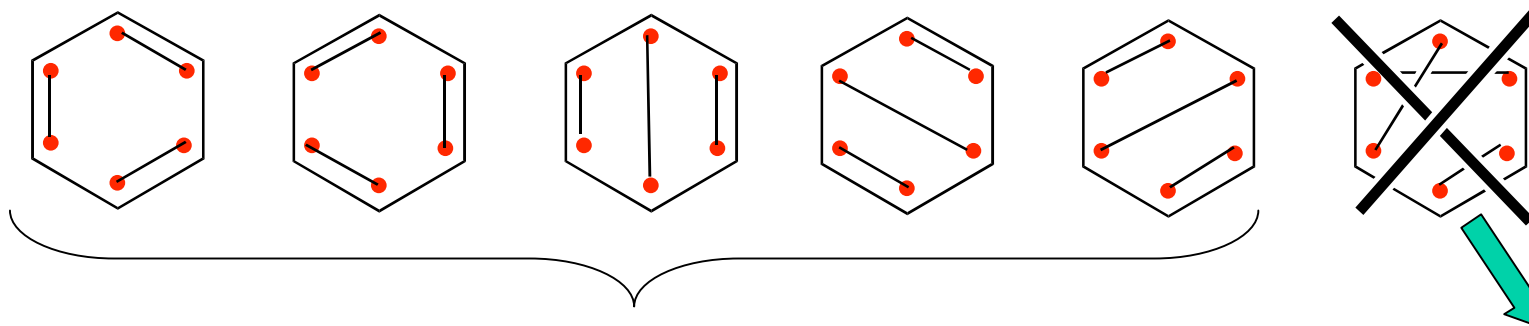
² : H. Weyl. The Theory of Groups and Quantum Mechanics; Dover: New York, 1956.

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



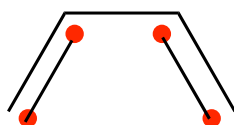
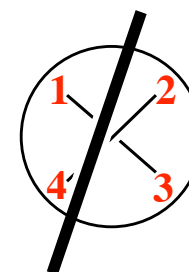
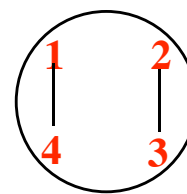
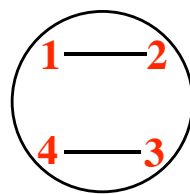
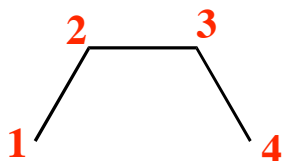
- Complete and **non-redundant** set of VB structures
- VB structures are chemically meaningful

-Redundant
-Chemically
meaningless

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

1,3-Butadiene:

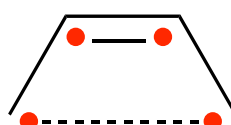
Put the orbitals around an imaginary circle, *even if the molecule is not a ring*



1



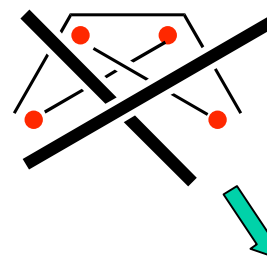
Major
VB structure



2



Explains the
barrier to rotation

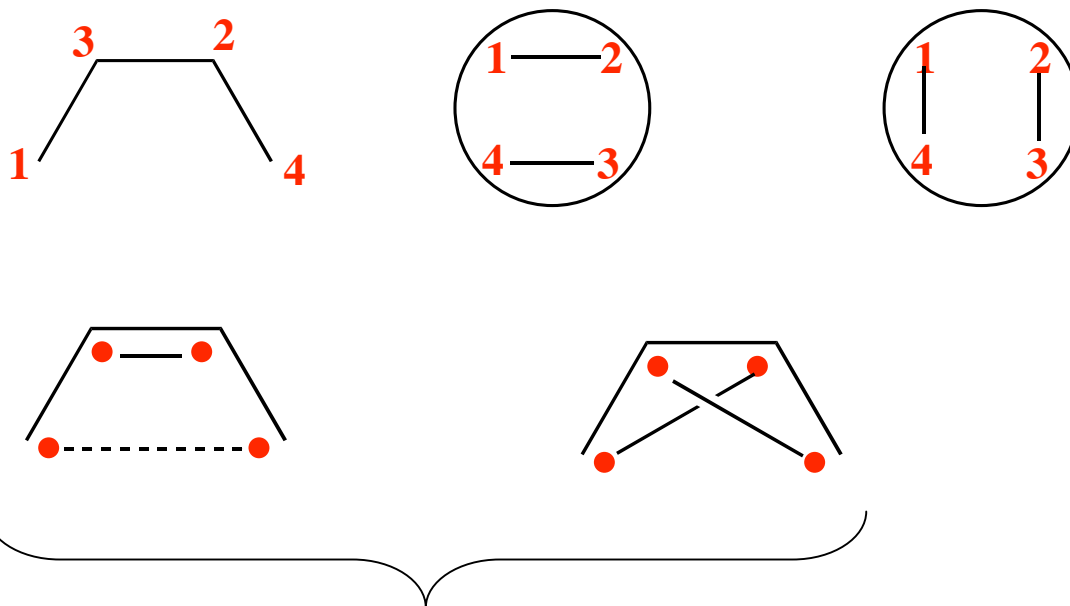


= 1 + 2

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

1,3-Butadiene:

Other possible (but stupid!) choice:

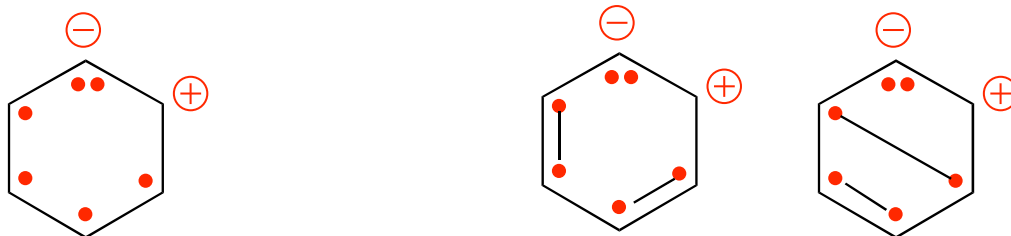


- Complete and non-redundant set of VB structures
- **Chemically meaningless !!**

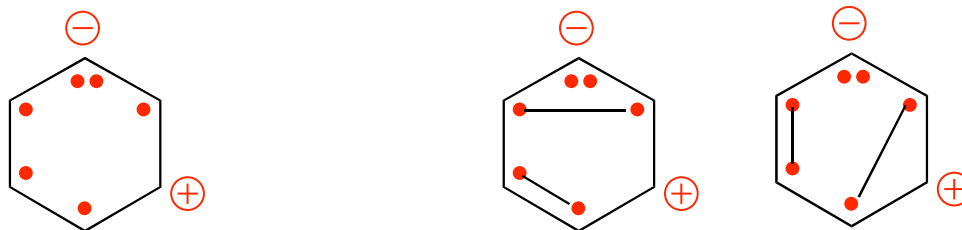
Rumer's rule for n -center/ n -electron ionic structures

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...

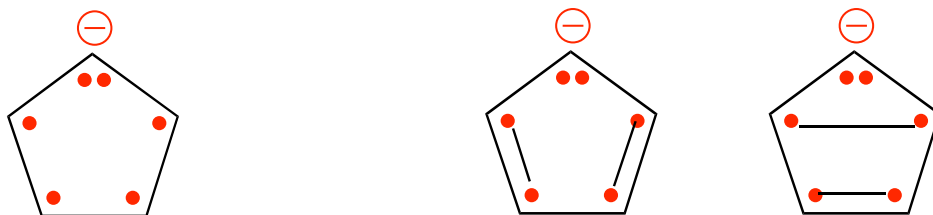


... and so on...

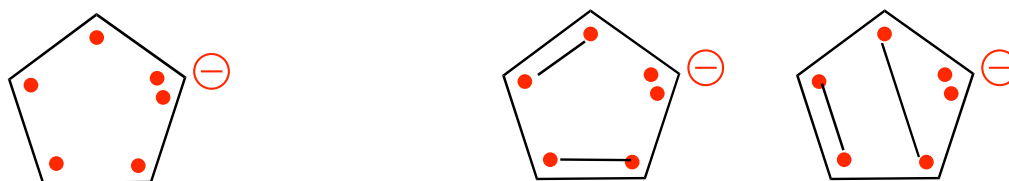
Rumer's rule for m -center/ n -electron covalent structures

Example cyclopentadienyl 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...



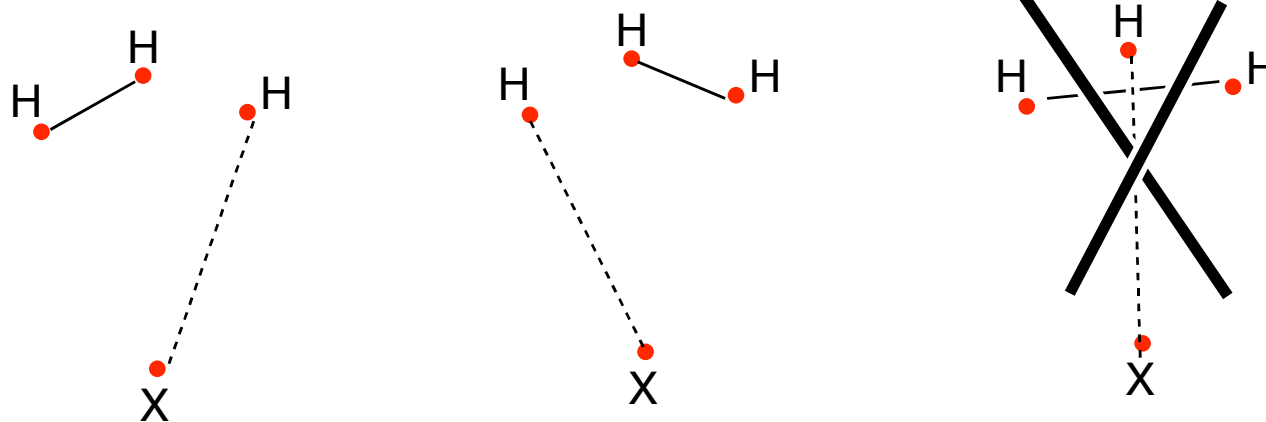
And so on...

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



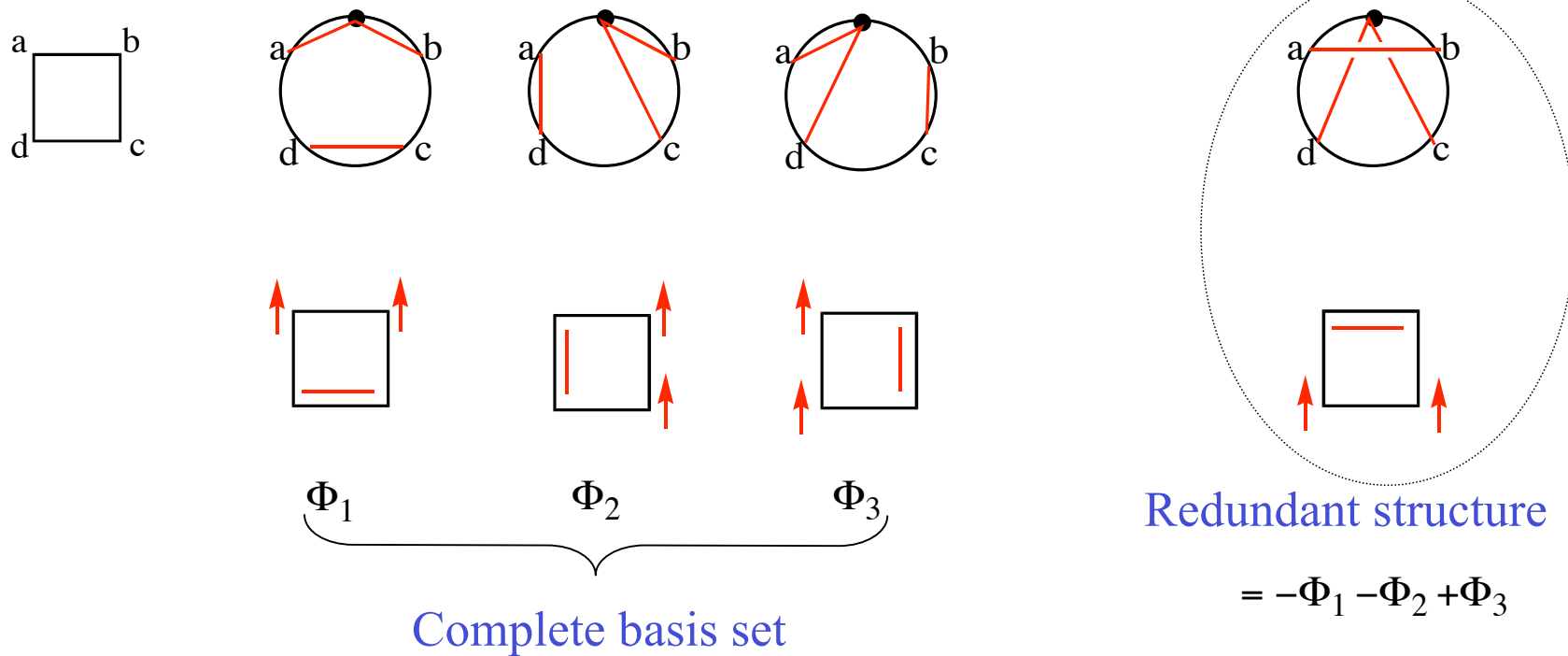
Same number of structures as in the $(m+1)$ -e/ $(m+1)$ -c system

Application on allyl radical: see tutorials

Rumer's rule for triplets

- 1) Insert the atoms + a fictitious center in the circle
- 2) Link the fictitious center to two atoms
- 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:
$$f_S^N = \frac{(2S + 1)N!}{(\frac{1}{2}N + S + 1)!(\frac{1}{2}N - S)!}$$

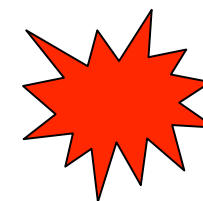
N	4	6	8	10	12	...
f_S^N	2	5	14	42	121	...



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

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

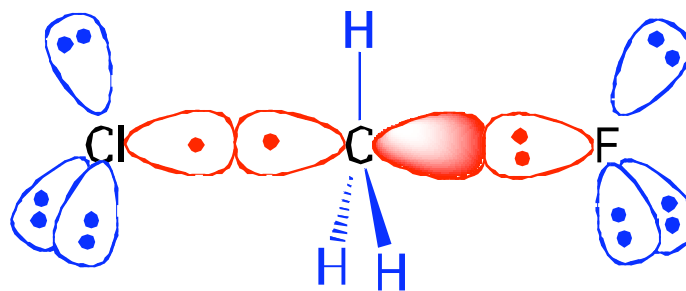
$N=m$	4	6	8	14	28
f_S^N	20	175	1764	2.76×10^6	2.07×10^{14}



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

Example:

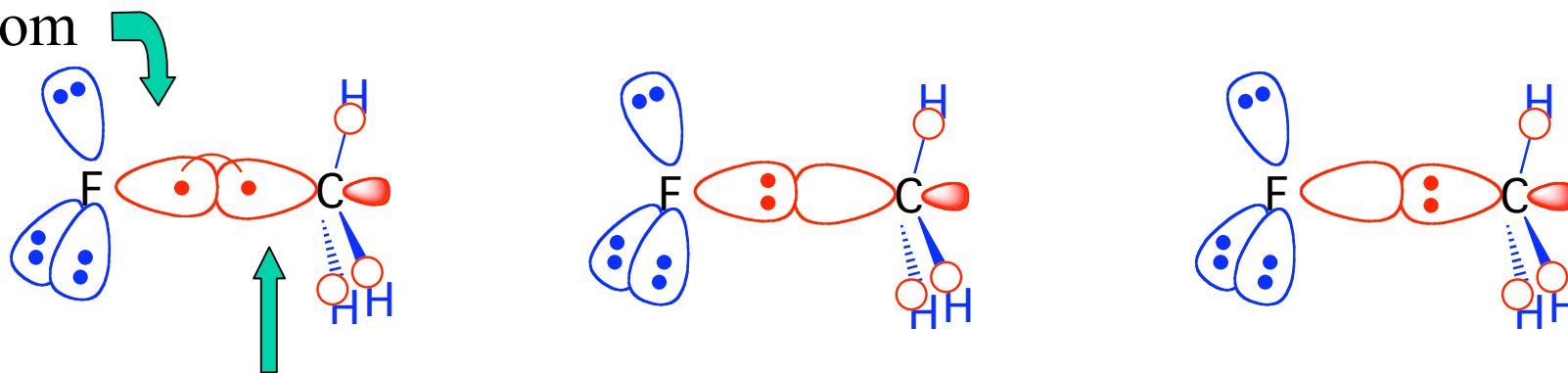
S_N2 Transition state:
a 4-e/3-orbital VB system
only 6 VB structures



Orbitals in VB structures: localized or semi-localized?

The **localized** orbital option

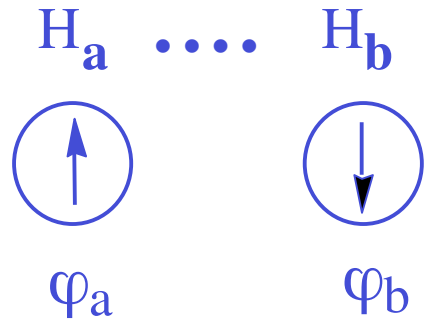
Active orbitals are strictly localized on a single atom



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

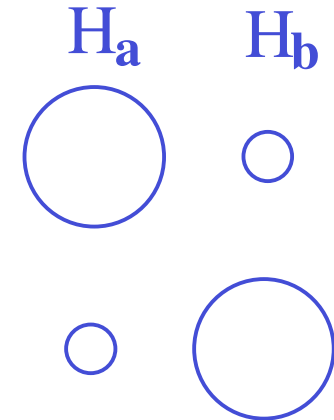
The semi-localized orbital option: Coulson-Fischer orbitals



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

$$\Phi_a = \varphi_a + \epsilon \varphi_b$$

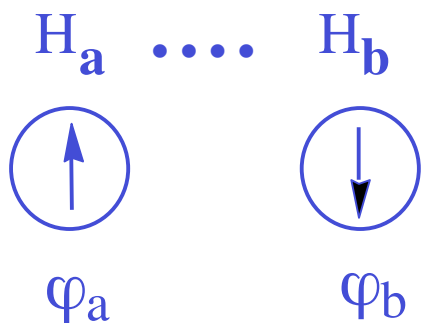
$$\Phi_b = \varphi_b + \epsilon \varphi_a$$



Used in:

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

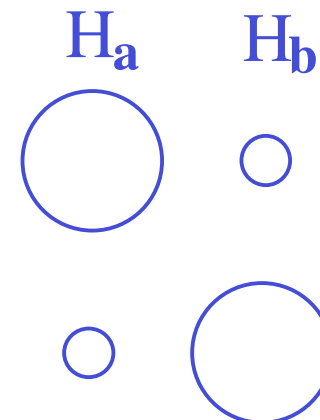
The Generalized Valence Bond Method (GVB)



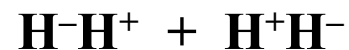
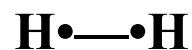
$$\Psi_{\text{GVB}} = |\Phi_a \bar{\Phi}_b| + |\Phi_b \bar{\Phi}_a|$$

$$\Phi_a = \varphi_a + \epsilon \varphi_b$$

$$\Phi_b = \varphi_b + \epsilon \varphi_a$$



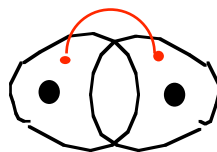
$$\Psi_{\text{GVB}} = (1 + \epsilon^2) (|\varphi_a \bar{\varphi}_b| + |\varphi_b \bar{\varphi}_a|) + 2\epsilon (|\varphi_a \bar{\varphi}_a| + |\varphi_b \bar{\varphi}_b|)$$



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

The Generalized Valence Bond Method (GVB)

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

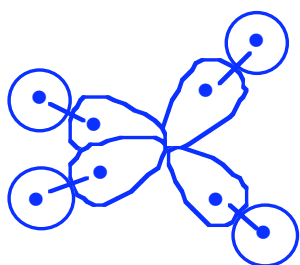


« **GVB pair** »
Overlapping distorted AOs

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

Generalization:

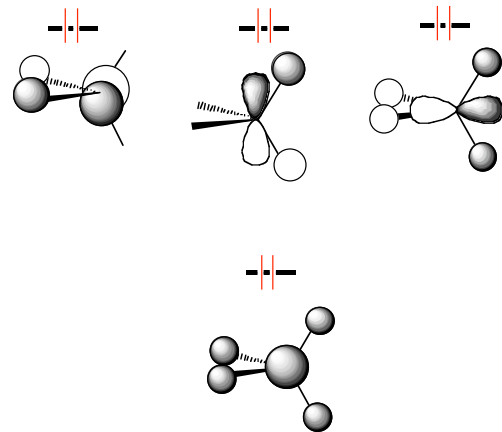
$$\Psi_{\text{GVB}} = \left| (\phi_{1a} \bar{\phi}_{1b} + \phi_{1b} \bar{\phi}_{1a}) (\phi_{2a} \bar{\phi}_{2b} + \phi_{2b} \bar{\phi}_{2a}) (\dots\dots\dots) \right|$$



Four GVB pairs

- GVB:** - Perfect-pairing (only one spin-coupling)
 - Orthogonality of GVB pairs
- Spin-coupled VB:** no restrictions

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



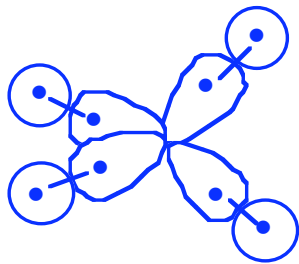
SCF

« *Is it time to retire the hybrid atomic orbitals?* »

Significant experimental evidence and theoretical advances indicate that hybrid atomic orbitals do not exist and do not appropriately describe molecular bonding...

A. Grushow, *J. Chem. Educ.* **2011**, 88, 860

80%



Best possible single-configuration wave function

GVB

20%

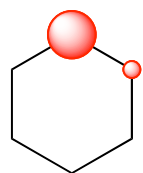
CASSCF (1764 conf)

localized or semi-localized orbitals...

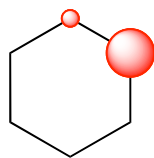
To what extent do we (semi-)delocalize the orbitals?

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

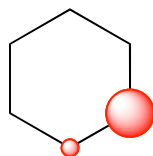
Example: BDOs for a Kekulé structure of benzene



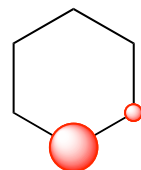
Φ_1



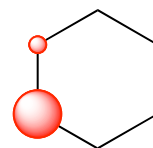
Φ_2



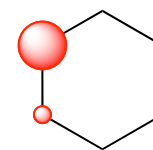
Φ_3



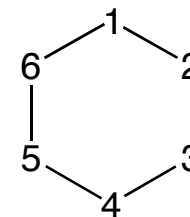
Φ_4



Φ_5

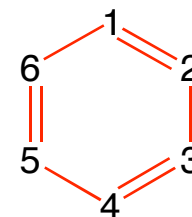


Φ_6



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

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



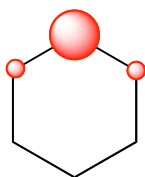
localized or semi-localized orbitals...

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

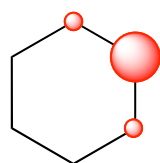
- 2) Fully allowed to delocalize: overlap-enhanced orbitals (OEOs)
(Option used in GVB or SCVB methods)

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

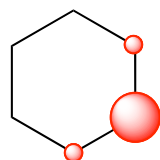
$$\Psi^{GVB} \propto \left| (\Phi_1 \bar{\Phi}_2 + \Phi_2 \bar{\Phi}_1)(\Phi_3 \bar{\Phi}_4 + \Phi_4 \bar{\Phi}_3)(\Phi_5 \bar{\Phi}_6 + \Phi_6 \bar{\Phi}_5) \right| \\ + \left| (\Phi_2 \bar{\Phi}_3 + \Phi_3 \bar{\Phi}_2)(\Phi_4 \bar{\Phi}_5 + \Phi_5 \bar{\Phi}_4)(\Phi_6 \bar{\Phi}_1 + \Phi_1 \bar{\Phi}_6)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



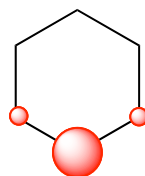
Φ_1



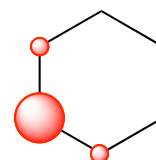
Φ_2



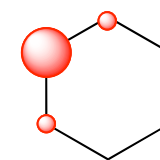
Φ_3



Φ_4



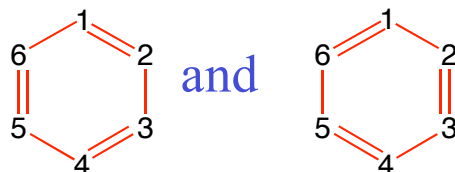
Φ_5



Φ_6

Orbitals are delocalized on 3 centers

The relationship to



and

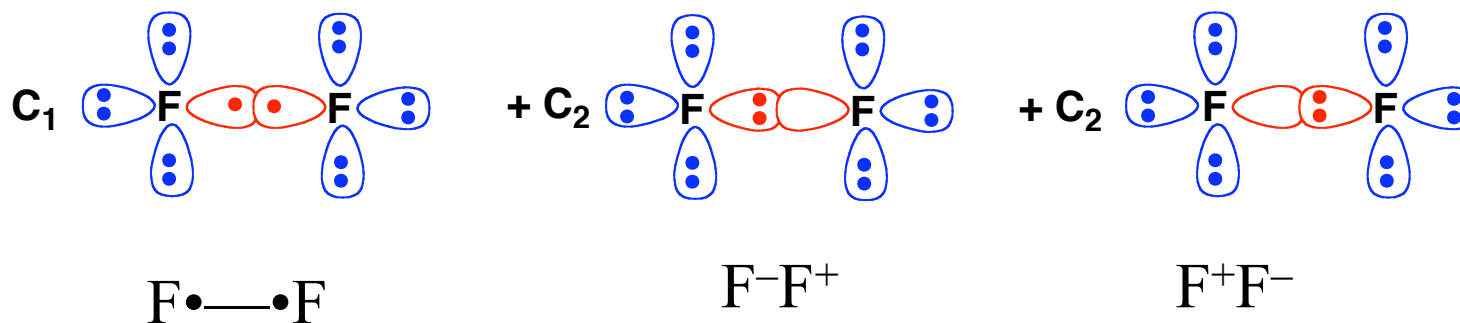
is less obvious

How does one calculate VB wave functions with localized orbitals ?

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

The VBSCF method (Balint-Kurti & van Lenthe)

Example: the F_2 molecule



Coefficients C_i and orbitals optimized simultaneously (like MCSCF)

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

GVB, SCVB ~ equivalent to VBSCF

Accuracy of the various methods



Calculation of ΔE for $F-F=1.43\text{\AA}$, 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**

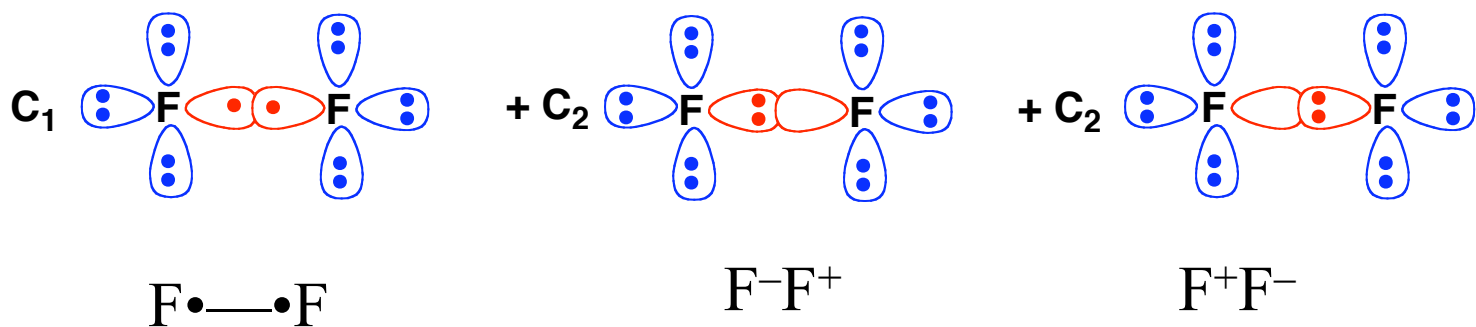
- GVB, VBSCF, CASSCF **Only ~ 15kcal/mol**

Reason: we miss dynamic correlation.

What does this physically mean?

What is missing in GVB and VBSCF?

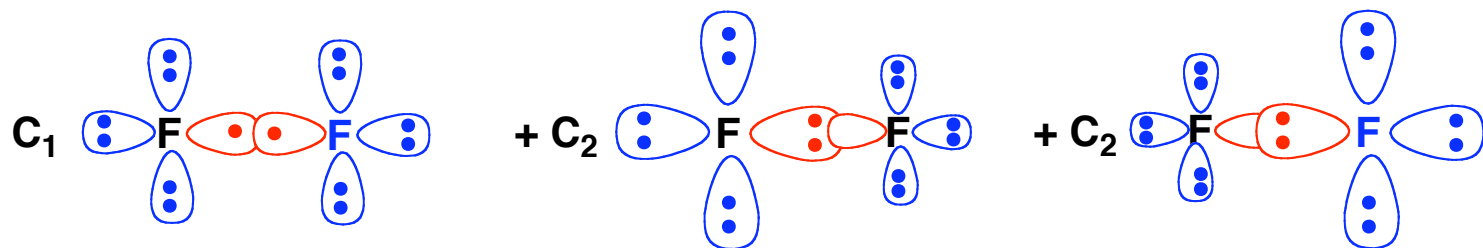
GVB/VBSCF: a closer examination



The coefficients and orbitals are optimized, but...

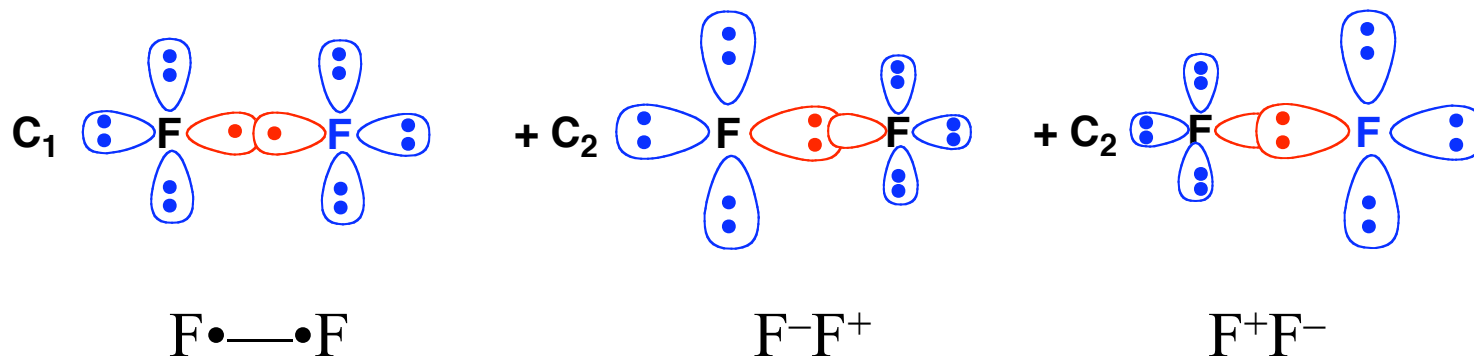
- The same set of AOs is used for all VB structures:
optimized for a mean neutral situation

A better wave function:



The « Breathing-Orbital » VB method (BOVB)

- Provides optimized covalent-ionic coefficients (like GVB)



- **Different orbitals for different VB structures**
 - Orbitals for $F\cdot\text{---}\cdot F$ 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 F₂



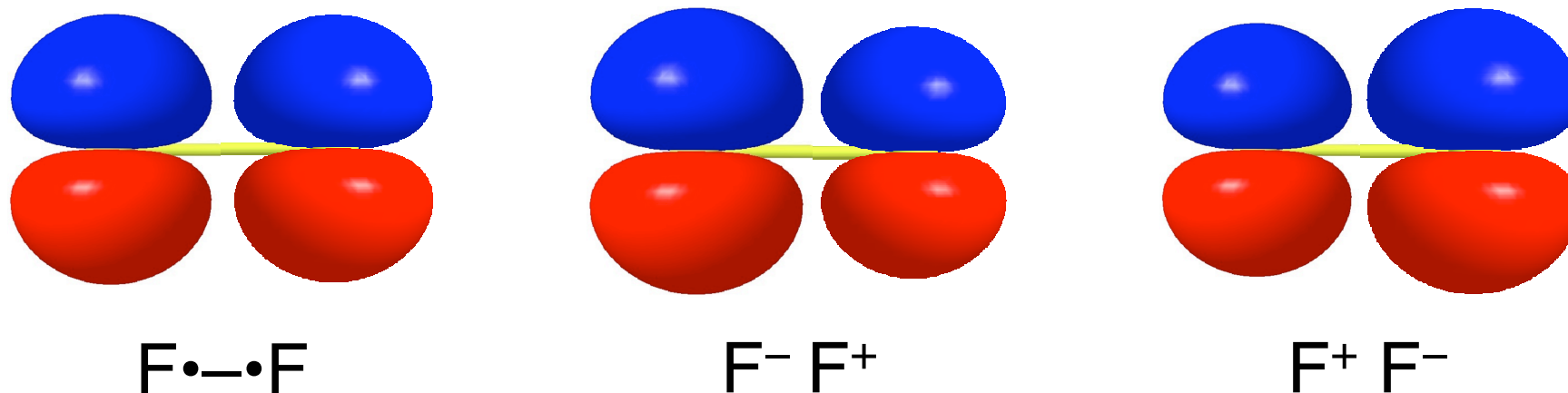
Calculation of ΔE for F-F=1.43Å, 6-31G(d) basis:

Iteration	De(kcal)	F•-•F	F ⁺ F ⁻ ↔ F-F ⁺
Classical VB	-4.6	0.813	0.187
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:

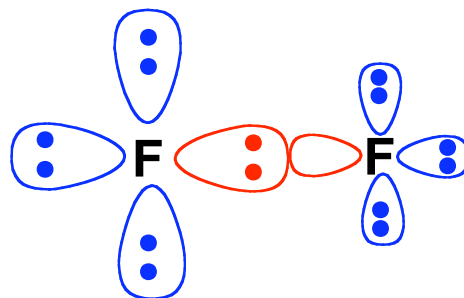


Small difference in shape, significant effect in energy

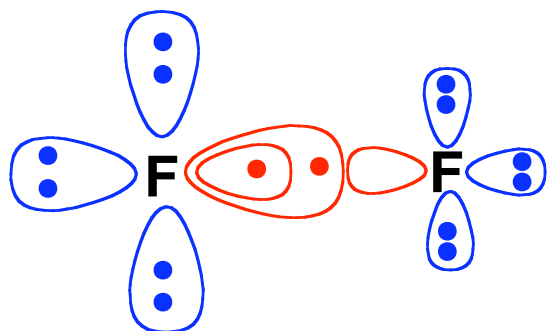
Improvements of the BOVB method

- **Improvement of the ionic VB structures**

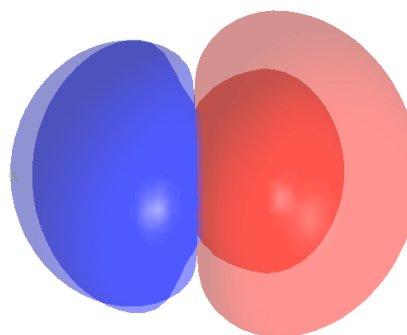
- basic level:



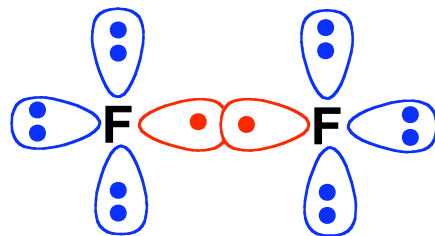
- improved level (« split-level » or **S**)



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

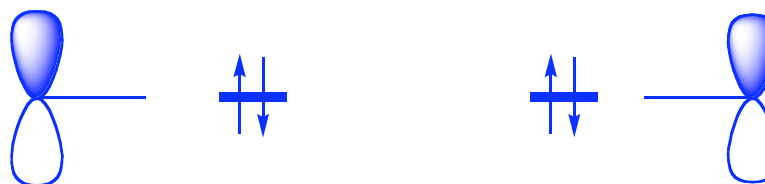


- **Improvement of the interactions between spectator orbitals**

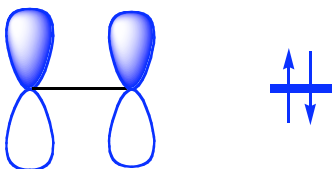
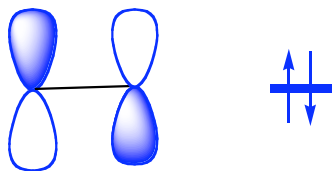


- **Spectator orbitals can be:**

- local atomic orbitals



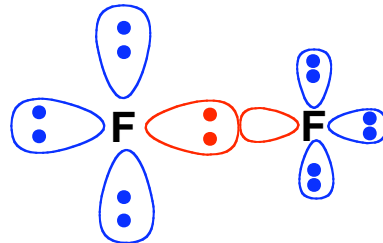
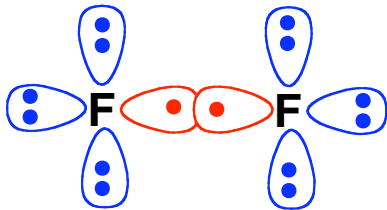
- bonding and antibonding combinations



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

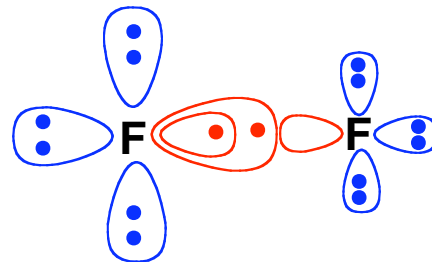
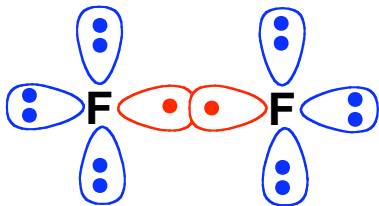
The various levels of the BOVB method

- **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

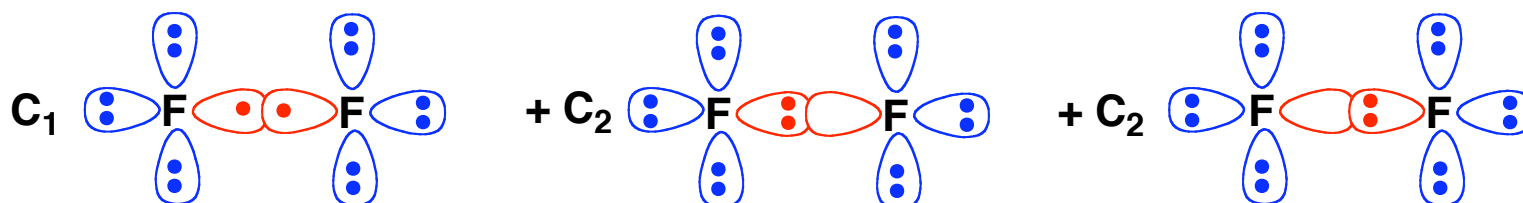
- **D-BOVB**

Spectator orbitals are **delocalized** in all structures

Electron correlation in BOVB

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

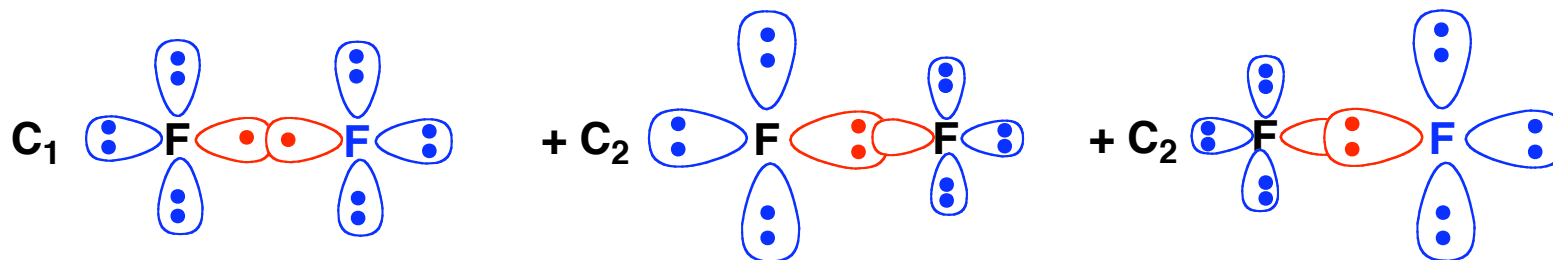
- Non dynamic correlation gives the correct ionic/covalent ratio



- **Dynamic correlation**

- All the rest. This is what is missing in VBSCF-CASSCF-GVB.

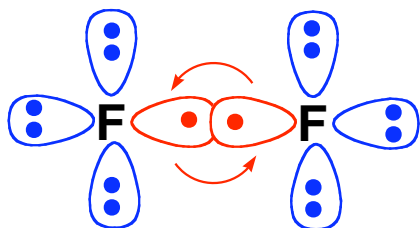
- BOVB brings **that part of dynamic correlation that varies** in the reaction



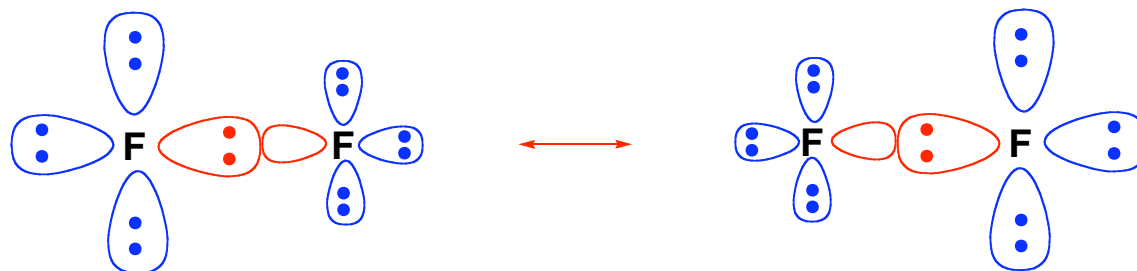
What is an accurate description of two-electron bonding?

- **Spin exchange between two atomic orbitals**

- Electrons are on different atoms and they exchange their positions



- **Charge fluctuation**



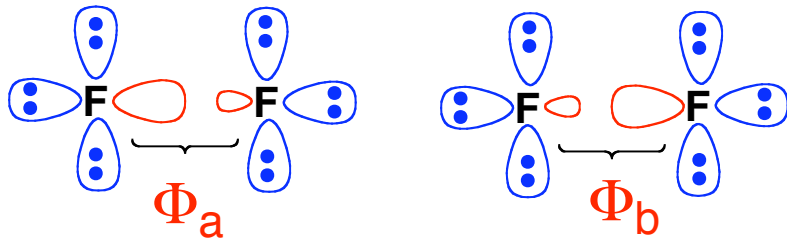
- Sometimes both electrons are on the same atom.
- There is some charge fluctuation. All orbitals instantaneously rearrange in size and shape to follow the charge fluctuation (orbitals « breathe »).

This is **differential dynamic correlation**

Delocalizing also the *active orbitals* in BOVB ?

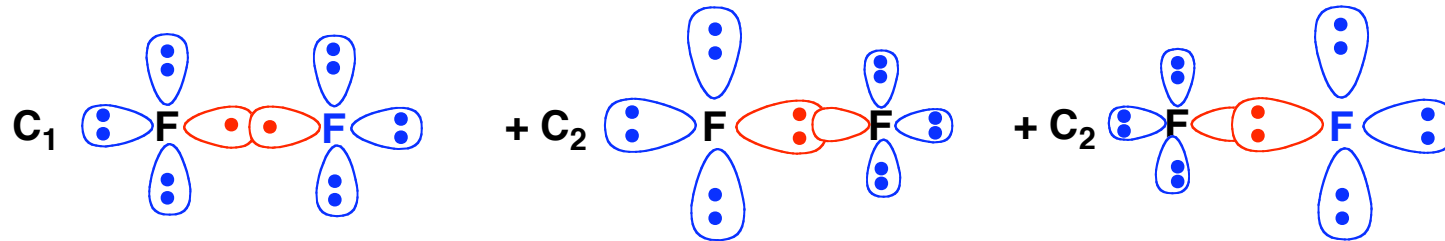
No ! Never ! No way ! By no means!

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



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

- 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 F₂

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

Alternative means to include dynamic correlation into VB

The VBCI method

- 1) Start from VBSCF $\Psi_{VB} = \sum C_i \Phi_i$
- 2) For each Φ_i , define a set of i strictly localized virtual orbitals (localized on the same centers as the occupied orbitals of Φ_i)
- 3) Improve Φ_i by post-VBSCF configuration interaction:

$$\Phi_K^{CI} = \sum_i C_K^i \Phi_K^i$$

All Φ_K^i are excitations that correspond to the same VB structure

Φ_K^{CI} is a multi-determinant description of a unique VB structure

- 4) Do the configuration interaction: $\Psi^{VBCI} = \sum_K C_K^{CI} \Phi_K^{CI}$

Alternative means to include dynamic correlation into VB

- **The VBPT2 method**

- 1) Start from VBSCF $\Psi_{VB} = \sum_i C_i \Phi_i$
- 2) Same principle as VBCI, but 2nd-order perturbation instead of CI

VBCI and VBPT2 will be taught in
VB lecture III by Prof. Wei Wu

- **The VB-QMC method** (QMC = Quantum Monte Carlo)

- 1) Start from VBSCF $\Psi_{VB} = \sum_i C_i \Phi_i$
- 2) Each determinant is multiplied by a Jastrow factor

Summary : the two great families of VB methods

Example: the H₂ molecule

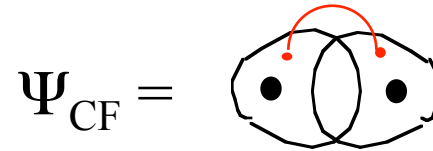
Static correlation

Classical VB
Local approach

$$\Psi_{\text{VB}} = \text{H}\cdot\text{---}\cdot\text{H} + \text{H}^-\text{H}^+ + \text{H}^+\text{H}^-$$

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

Coulson-Fischer
Semi-delocal approach



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

Dynamic correlation

BOVB, VB CI, VBPT2, VB-QMC

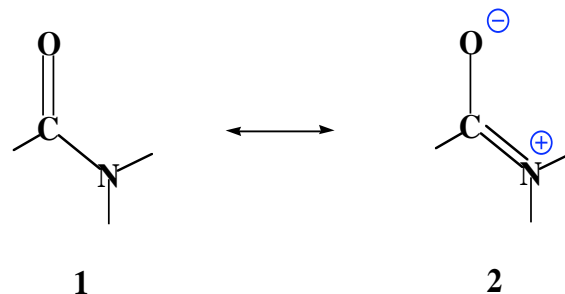
CCCI, VB-QMC

Calculation of diabatic energies

What for?

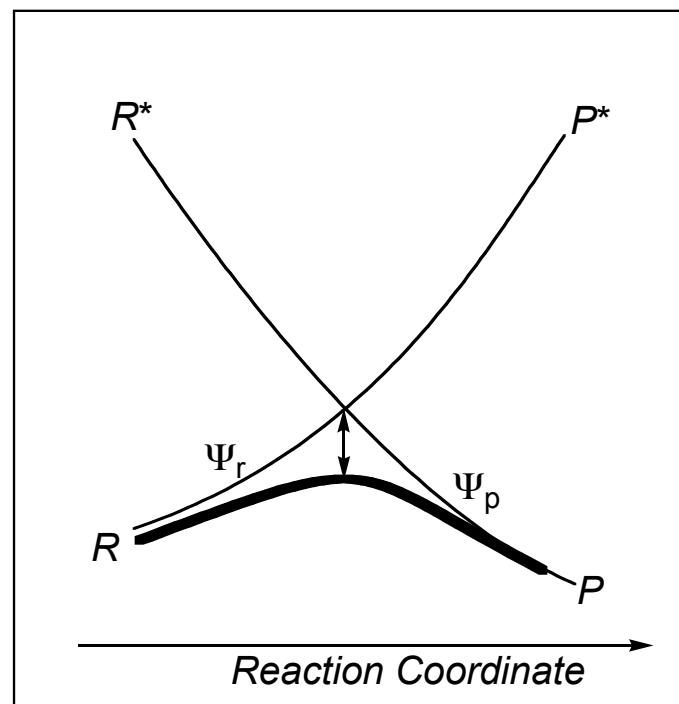
Resonance energies

$$RE = E(1) - E(1 \leftrightarrow 2)$$



VB-state-crossing diagrams

See VB lecture V
by Prof. S. Shaik



Calculation of diabatic energies

Example: Covalent-ionic resonance energy in H₂


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

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

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

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

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

$$\text{RE}(\text{CDC}) = -1.85388 + 1.86452 = 0.01064 \text{ au} = 6.7 \text{ kcal/mol}$$

Calculation of diabatic energies

Example: Covalent-ionic resonance energy in H₂

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

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

Second method: « Variational Diabatic Configuration »

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

$\Rightarrow \Phi_{\text{cov}}$ 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

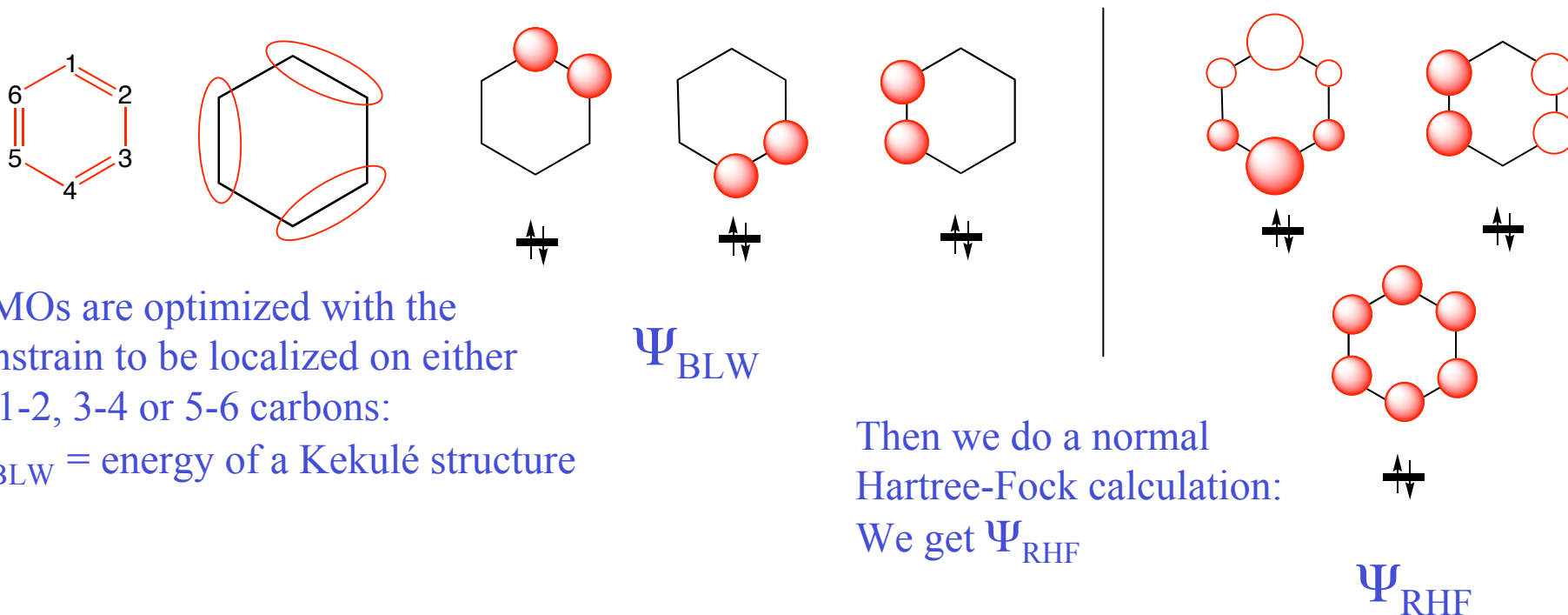
$$E(\Psi_{\text{VB}}) = -1.86452 \text{ au}$$

$$\text{RE(VDC)} = -1.85778 + 1.86452 = 0.00674 \text{ au} = 4.2 \text{ kcal/mol}$$

(< RE(CDC))

An alternative way to calculate diabatic energies: The block-localized wave function (BLW) method

Example: Energy of a single Kekulé structure of benzene



π -MOs are optimized with the constrain to be localized on either of 1-2, 3-4 or 5-6 carbons:

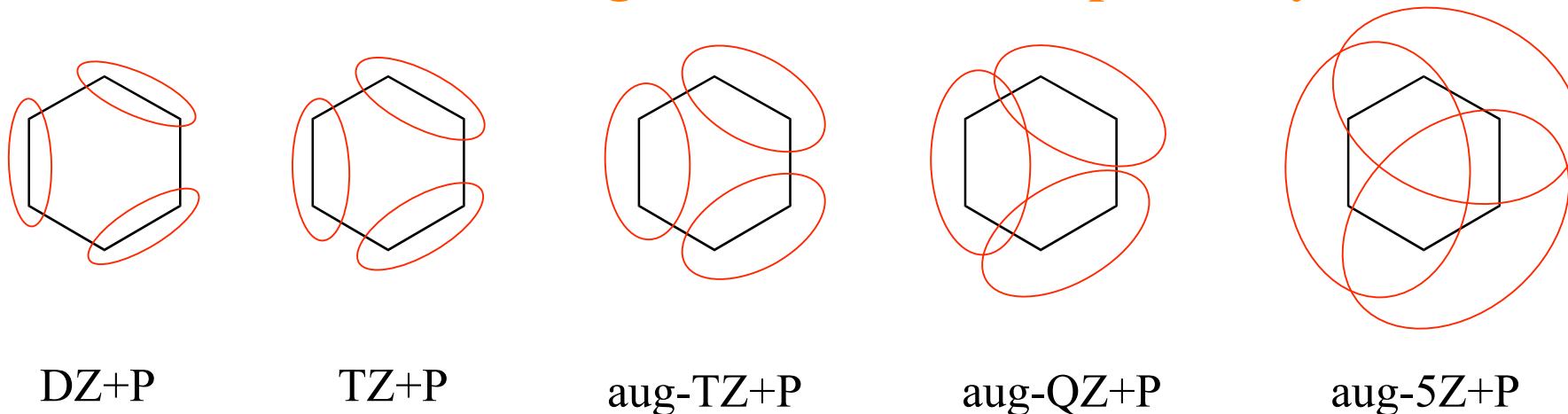
Ψ_{BLW} = energy of a Kekulé structure

Resonance energy = $E(\Psi_{\text{BLW}}) - E(\Psi_{\text{RHF}})$

Exists also at the DFT level

See VB lecture VIII
by Prof. Yirong Mo

Variational diabatic energies and basis set dependency: a warning



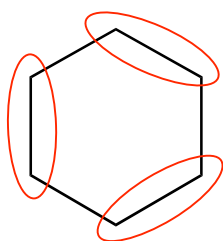
In infinite basis set, any one-center AO can take the shape of a fully delocalized MO

- ⇒ The concepts of localized AO and of VB structure become meaningless
- ⇒ Variational diabatic energies (BLW method, VB calculation of VDC type) tend to collapse to the energy of the ground state
- ⇒ Resonance energies tend to collapse to unrealistic small values

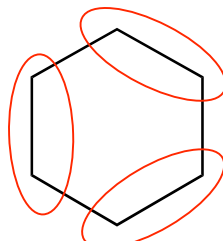
Example: variational calculation of the vertical resonance energy of benzene

Block-localized wave function method:

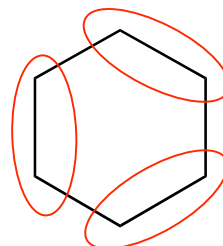
$$\text{VRE} = E(\text{Kekulé}) - E(\text{ground state})$$



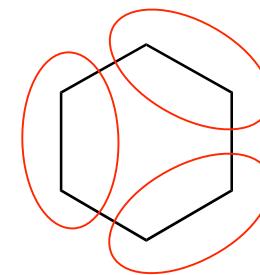
6-31G(d)



6-311+G(d)



cc-pVTZ



aug-cc-pVTZ

VRE (kcal/mol):

BLW-RHF

87.9

91.6

90.7

79.0

BLW-DFT

88.8

92.2

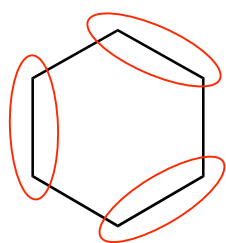
89.1

80.9

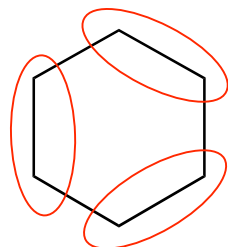
Moderate basis sets => consistent values,
Match experimentally measured quantities

too small
values...

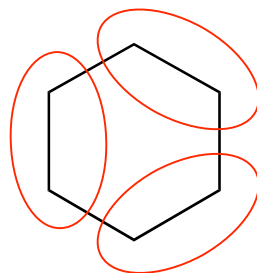
Variational diabatic energies: which basis set to choose?



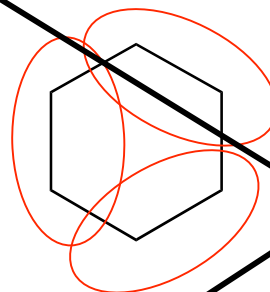
DZ+P



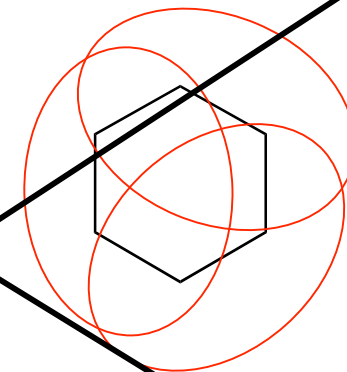
TZ+P



aug-TZ+P



~~aug-QZ+P~~



~~aug-5Z+P~~

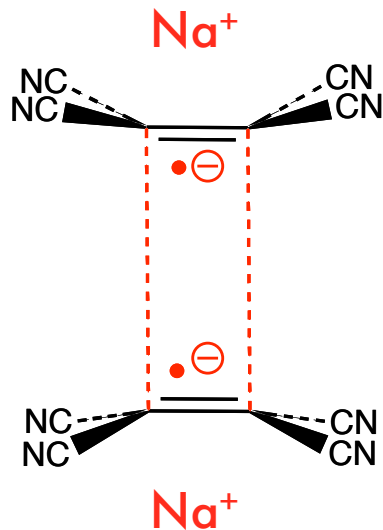
Strategy:

- Avoid diffuse orbitals if not necessary (keep only for anions)
- **Choose a basis set** sufficiently large to yield good energetics (bonding energies, reaction energies, reaction barriers, etc.), but no larger (typically DZ+P or TZ+P)
- Calculate the diabatic states and resonance energies in the **same basis set**

Current capabilities of the XMVB code

Can do: classical VB, GVB, SCVB, BLW, VBCI, VBPT2, + solvent effects

Current size limitations: Recent VB-QMC study:



- 22 non-hydrogen atoms
- 90 valence electrons
- accuracy matching CASPT2 or CCSD(T)

To be implemented in the very near future: CAS-VBSCF

- millions of VB structures allowed
- same cost and computational scaling as CASSCF

And now do it yourself !
(hands-on labs)