Valence Bond

Joop van Lenthe
Theoretical Chemistry Group
Utrecht University

joop@chem.uu.nl

```
    t                        t       l
    t                        t       l
  tttt    u   u   rrrr   tttt        l            eee
    t     u   u   r   r    t         l          eeeee
    t   t u   u   r        t   t   l   l    l      e
    ttt     uu       r           ttt       lll       eee


  ----              ----              ----         )))))
      ----                      ----        _ _ _  { o o }
                          ----          _(_)_(_)_   ( ^  )
  ----        ----                    _(_)_(_)_(_)_/ /
      ----                  ---- _(_)_(_)_(_)_(_)/
                                (_)_(_)_(_)_(_)_(_)
  ----        ----        ----     /7   /7    7/   7/
```
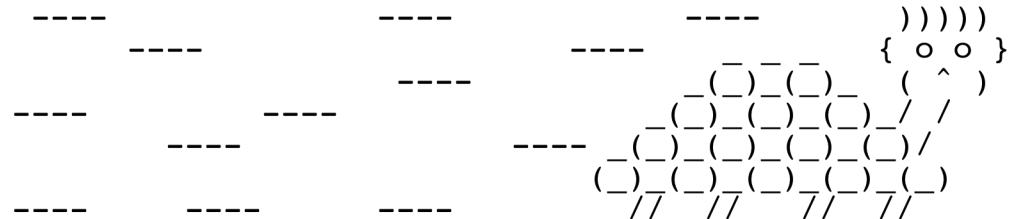
Contents

- What is VB / Spinfunctions/Bonds
- Orbital Optimisation / Brillouin Theorem
- Energies and Gradients - Matrix elements
- Applications/Illustrations
    - Is the BSSE problem solved by using Non-orthogonal Orbitals ?
    - What is a π system in a bent benzene ?
    - Resonance and aromaticity
    - Local Resonance
    - Do VB structures mean something ?
    - What about O_2

VB techniques are like Orthogonal methods

What Universe are we in:

- Time independent
- Electronic Structure
- Born Oppenheimer
- Only scalar relativity
- The Answer is 42
- The Question ??

$$H = \sum_i h(i) + \sum_{i<j} \frac{1}{r_{ij}} + N.R. + \sim$$

1-electron

2-electron

VB

Starting from : Atoms
Bonding :   Spin-pairing
Orbitals :   Non-Orthogonal
              (historically) fixed
Simplest :   1 structure, more determinants
In general :   Multi-structure
Extend :   Add Ionic.. structures
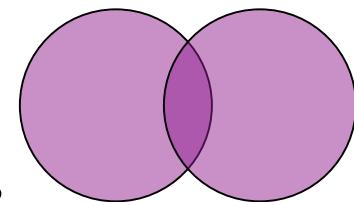
MO

Starting from : Molecules
Bonding :   Sharing Orbitals
Orbitals :   Orthogonal
              Optimised
In general :   1 configuration, 1 determinant
Extend :   Add configurations (CI)

VB-atoms

H_2O

$$O \quad {}^3\Sigma_g^- \quad \begin{cases} 1s^2 2s^2 2p_z^2 2p_x 2p_y \\ 1s^2 2s^2 2p_x^2 2p_z 2p_y \\ 1s^2 2s^2 2p_y^2 2p_z 2p_x \end{cases}$$

$$H_a \quad {}^2S \quad 1s_a$$

$$H_b \quad {}^2S \quad 1s_b$$

$$H_2O = O \otimes H \otimes H$$

and

or
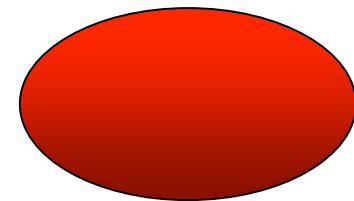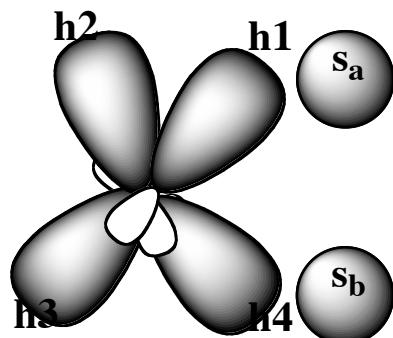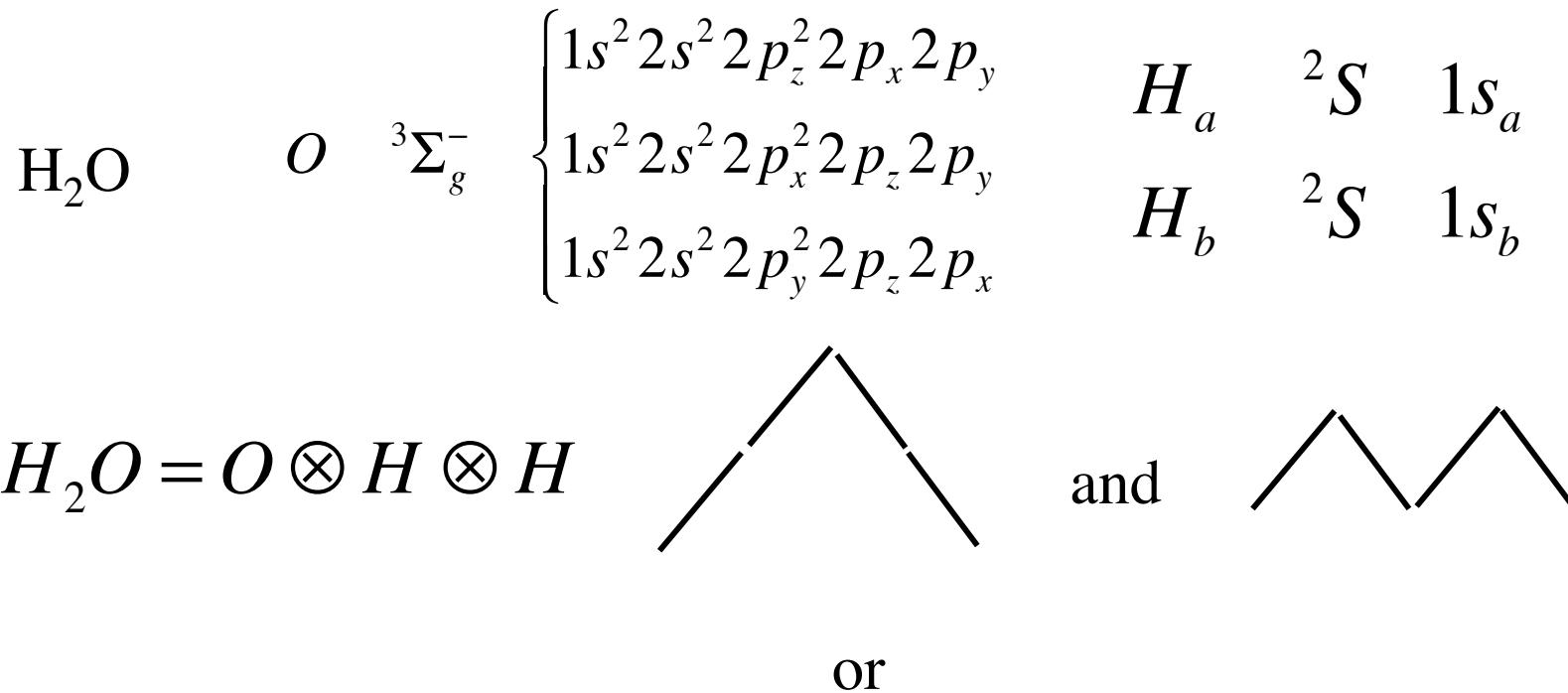
$$\Psi = 1s^2 h_2^2 h_3^2 h_1 s_a h_4 s_b$$
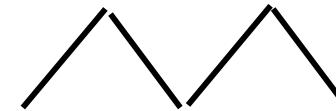
SPIN COUPLING

Perfect pairing - two orbitals are coupled to a singlet (bond)

$$\Psi = N\left(\left|\varphi_1\bar{\varphi}_2\right| - \left|\bar{\varphi}_1\varphi_2\right|\right)$$

$$\Psi = \left(\widehat{\varphi_1\varphi_2}\right)$$

Two Bonds
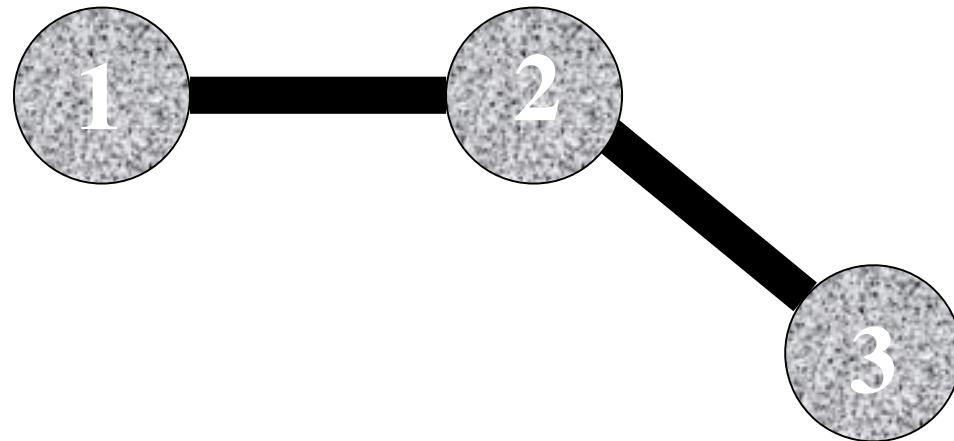
$$\Psi = N \; \mathbb{A}\left(\left|\varphi_1\overline{\varphi}_{2a}\right| - \left|\overline{\varphi}_1\varphi_{2a}\right|\right)\left(\left|\varphi_{2b}\overline{\varphi}_3\right| - \left|\overline{\varphi}_{2b}\varphi_3\right|\right) = \left(\widehat{\varphi_1\varphi_{2a}}\right)\left(\widehat{\varphi_{2b}\varphi_3}\right)$$

$$\Psi = \left(\widehat{\varphi_1\varphi_3}\right)\left(\widehat{\varphi_{2a}\varphi_{2b}}\right)$$
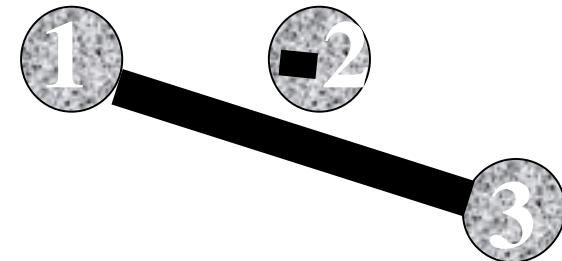
VB-2 H$_2$ vergeet spin

$$\Psi(1,2) = c_1 \underbrace{\left(s_a(1)s_b(2) + s_a(2)s_b(1)\right)}_{Covalent}$$

$$+c_2 \underbrace{\left(s_a(1)s_a(2)\right)}_{ionisch} + c_3 \underbrace{\left(s_b(1)s_b(2)\right)}_{ionisch}$$
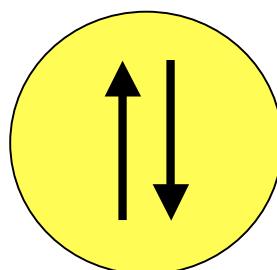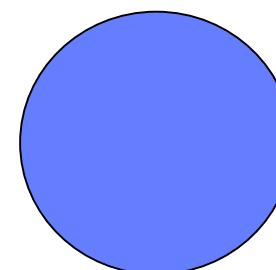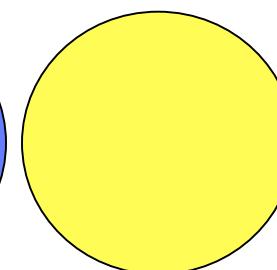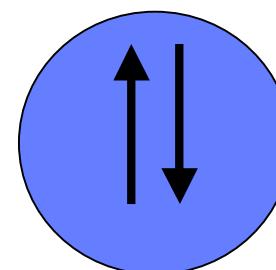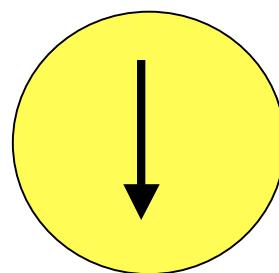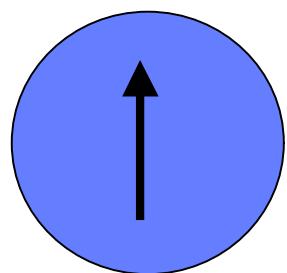
Covalent   ionisch   ionisch

H$_2$ VB possibilities

$$\Psi_{singlet} = \frac{1}{2}\left(1s_A 1s_B + 1s_B 1s_A\right)\left(\alpha\beta - \beta\alpha\right) \quad m_s = 0, s = 0 \quad (singlet \uparrow\downarrow)$$

$$\Psi_{triplet} = \begin{cases} \frac{1}{2}\left(1s_A 1s_B - 1s_B 1s_A\right)\left(\alpha\beta + \beta\alpha\right) & m_s = 0, s = 1 \quad (triplet \uparrow\uparrow) \\ \frac{1}{\sqrt{2}}\left(1s_A 1s_B - 1s_B 1s_A\right)\left(\alpha\alpha\right) & m_s = 1, s = 1 \quad (triplet \uparrow\uparrow) \\ \frac{1}{\sqrt{2}}\left(1s_A 1s_B - 1s_B 1s_A\right)\left(\beta\beta\right) & m_s = -1, s = 1 \quad (triplet \uparrow\uparrow) \end{cases}$$

Volgorde elektronen - 1..2 1..2

Kunt $\langle E \rangle = \dfrac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$ berekenen; Grondtoestand is natuurlijk singlet

De Hamiltoniaan bevat (bij ons) enkel ruimte afhankelijke
termen. Dus wordt de energie door het ruimte deel bepaald.

VB energy H_2 - 3

$$\Psi_{singlet} : \frac{1}{2}\left(1s_A 1s_B + 1s_B 1s_A\right) \quad (singlet \uparrow\downarrow) \quad E \approx E_1 + J + K$$

gives bonding

$$\Psi_{triplet} : \begin{cases} \frac{1}{2}\left(1s_A 1s_B - 1s_B 1s_A\right) & (triplet \uparrow\uparrow) \\[2ex] \frac{1}{\sqrt{2}}\left(1s_A 1s_B - 1s_B 1s_A\right) & (triplet \uparrow\uparrow) \quad E \approx E_1 + J - K \\[2ex] \frac{1}{\sqrt{2}}\left(1s_A 1s_B - 1s_B 1s_A\right) & (triplet \uparrow\uparrow) \end{cases}$$

J en K : Bevoordelen triplet (denk He* / Regel van Hund)
VB attractief door 1-elektron term (niet orthogonaal)
But J,K,E are different

Can we use orthogonal Orbitals in VB ??

H_2(STO6G)
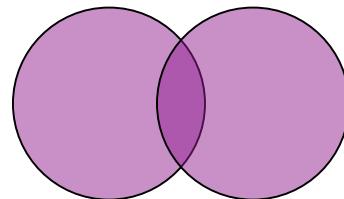
$$\Psi = \frac{1}{\sqrt{2}}\left[\left|a\overline{b}\right| + \left|b\overline{a}\right|\right]$$

fixed orbitals   optimised orbitals

VB: Heitler-London :	0.70 Å	120.6 Kcal/mol
VB: Coulson-Fischer: (full CI)	0.73 Å	128.0 Kcal/mol
Hartree-Fock :	0.71 Å	115.6 Kcal/mol
Orthogonal VB :	>5.9 Å	0 Kcal/mol
Experimental (WWW):	0.74 Å	104 Kcal/mol

NO

Atomic Population Analysis (cf. McWeeny (1953))

H2 (STO6G/0.70 Å)

	Orb-overlap	q_a	q_{ab}	Energy
VB: H-L	0.69	0.68	0.32	-1.134187
VB: C-F	0.81	0.62	0.38	-1.144979
HF :	0.0	0.60	0.40	-1.126100
Orthog VB :	0.0	1.89	-0.89	-0.463516
VB:C-F (+p)	0.81	0.61	0.39	-1.148056

VB-hierarchy

$$\Psi = \sum C_i \Phi_i \qquad \text{L} \qquad \text{Wavefunction}$$

$(H - ES)C = 0 \;\text{or}\; \textit{fixed}$

$$\Phi = \sum s_d \Delta_d \qquad \text{L} \qquad \text{Structure}$$

Spin-projection

$$\Delta = \left| \psi_1 \psi_2 \ldots \psi_n \right| \qquad \text{L} \qquad \text{Determinant}$$

$$\psi = \sum c_i \varphi_i \qquad \text{L} \qquad \textit{Orbital}$$

Optimised or fixed

basis-function

Spin-Functions(1)

Rumer functions : Different orbitals spin-paired
Benzene (6-31G)

| -230.6614 | -230.6326 | -230.6326 | -230.6614 | -230.6326 |

| 0.44 | -0.07 | -0.07 | 0.44 | -0.07 |

C
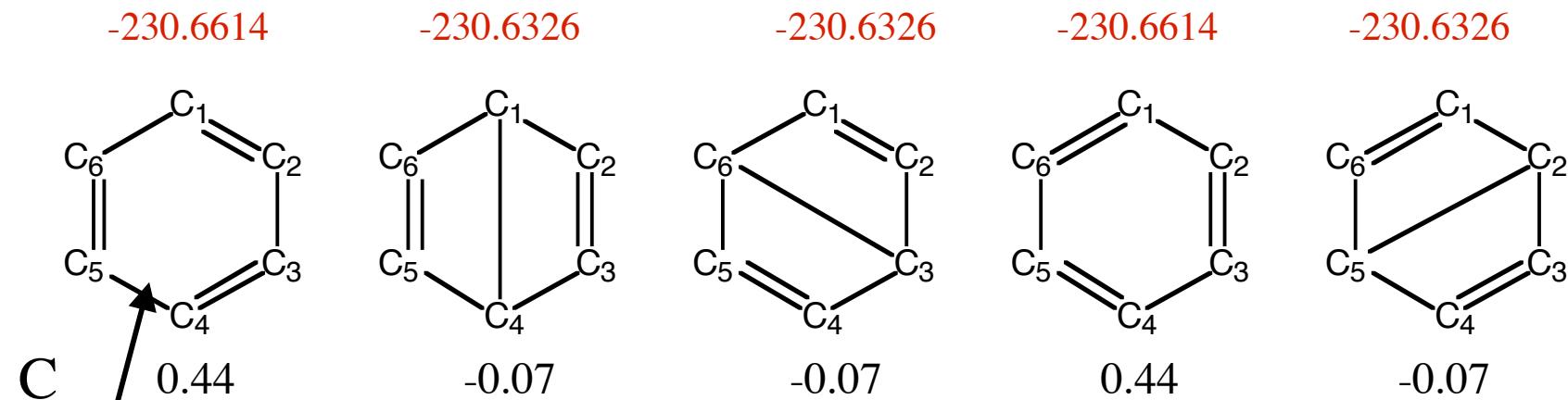
$$E = -230.6938$$

$$\Psi_1 = N\left(\left|\varphi_1\overline{\varphi}_2\right| - \left|\overline{\varphi}_1\varphi_2\right|\right)\left(\left|\varphi_3\overline{\varphi}_4\right| - \left|\overline{\varphi}_3\varphi_4\right|\right)\left(\left|\varphi_5\overline{\varphi}_6\right| - \left|\overline{\varphi}_5\varphi_6\right|\right)$$

Spin-functions non-orthogonal

$$\langle\psi_1|\psi_2\rangle = 0.52$$

$$\langle\Psi_1|\Psi_4\rangle_{spin} = 0.25 \qquad \langle\Psi_1|\Psi_3\rangle_{spin} = 0.5$$

$$\langle\Psi_1|\Psi_4\rangle \;\;= 0.66 \qquad \langle\Psi_1|\Psi_3\rangle \;\;= 0.82$$

Spin-Functions(2)

## Branching Diagrams : Orbitals in standard order
### Different spin-functions
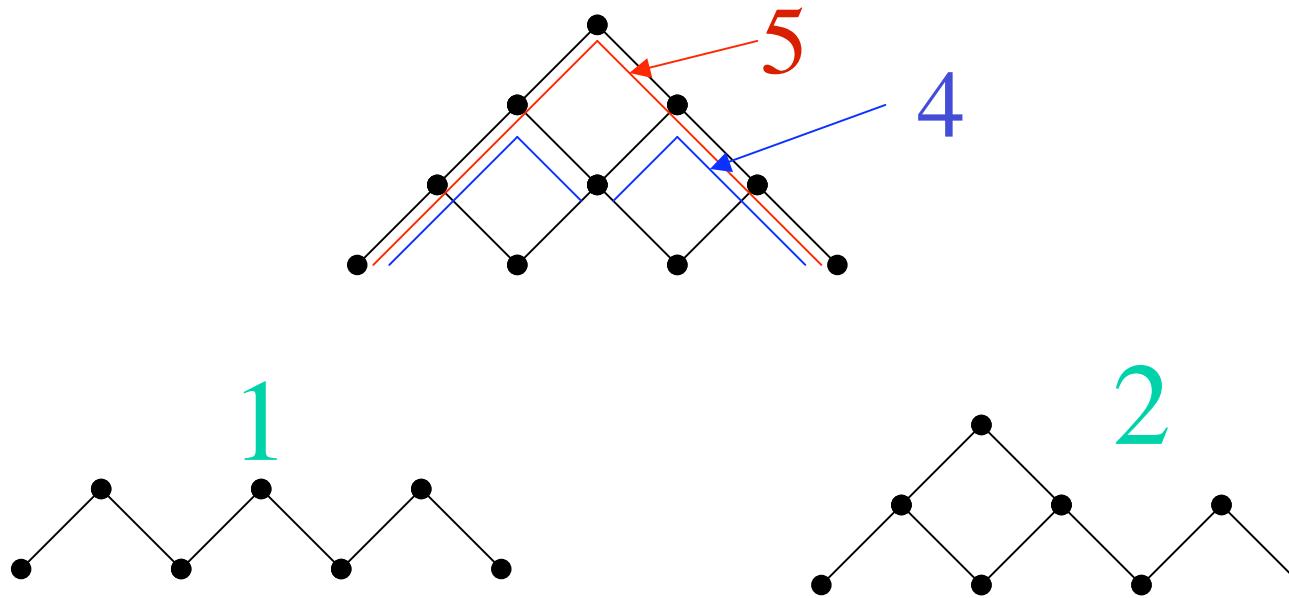
Spin-functions orthogonal;
Obtain by e.g Schmidt orthogonalising Rumer functions

Spin-Functions(3) $\otimes$

Branching Diagrams are often considered less informative
OH ($^2\Pi$) (JHvL, G.G.Balint-Kurti (1980) DZP, Atomic Opt

#	Atomic states	Configuration	spin	Coefficient
1	O(^{3}P) H(^{2}S)	$1s^22s^2y^2xzh$		-0.235
2	O(^{1}D) H(^{2}S)	$1s^22s^2y^2xyz$		0.191
3	O$^+$(^{2}D^0) H$^-$(^{1}S)	$1s^22s^2(z^2-y^2)xh^2$		0.053
4	O$^+$(^{2}P^0) H$^-$(^{1}S)	$1s^22s^2(z^2+y^2)xh^2$		-0.028
5	O$^-$(^{2}P^0)H$^+$	$1s^22s^2z^2y^2x$		0.327
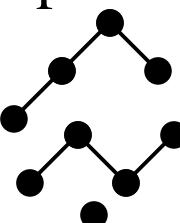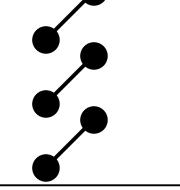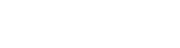
- Oxygen ^{1}D mixes in
- O$^-$ ionic structure important due to atomic orbitals
- O(z) => hybrid on bond formation

- Spin-function may be transformed from one basis to another

VB=MCSCF

$$\Psi = N\left(c_1\left|\varphi_3\bar{\varphi}_3\right| - c_2\left|\bar{\varphi}_4\varphi_4\right|\right) =$$

$$with \begin{cases} \varphi_1 = \left(\sqrt{c_1}\varphi_3 + \sqrt{c_2}\varphi_4\right)\Big/\left(c_1 + c_2\right) \\[2em] \varphi_2 = \left(\sqrt{c_1}\varphi_3 - \sqrt{c_2}\varphi_4\right)\Big/\left(c_1 + c_2\right) \end{cases}$$

$$= N\left(\left|\varphi_1\bar{\varphi}_2\right| - \left|\bar{\varphi}_1\varphi_2\right|\right) = \left(\varphi_1\varphi_2\right)$$

$$\left\langle\varphi_1\middle|\varphi_2\right\rangle = \frac{c_1 - c_2}{c_1 + c_2} \qquad \left\langle\varphi_3\middle|\varphi_4\right\rangle = 0$$

$$\left(\widehat{\varphi_1 \varphi_2}\right)\left(\widehat{\varphi_3 \varphi_4}\right) = \left(2 - MCSCF\right) * \left(2 - MCSCF\right)$$

Only if $(\phi_1\phi_2)$ orthogonal to $(\phi_3\phi_4)$:**Strong Orthogonality**

GVB : W.A. Goddard III et al (1972 - ..)

Original version: general

Popular version : GVB-PP

strong orthogonality

perfect pairing

uses Fock-operators (N^4)

size extensive

1999 : GVB-RP

Spincoupled / Spincoupled VB
J. Gerratt[†], M. Raimondi, D.L. Cooper - "The gang of Three"

Spincoupled : 1 configuration all spincouplings, optimised

$$\Psi = \sum_{k}^{f_S^N} c_{Sk} \left(N!\right)^{\frac{1}{2}} A\left\{\psi_1\psi_2\psi_3...\psi_N\Theta_{S,M;k}^N\right\}$$

This function can be obtained by restricting a CASSCF function : **CASVB**

Each ψ_i satisfies her own $\quad F_i^{eff}\psi_i = \varepsilon_i\psi_i$
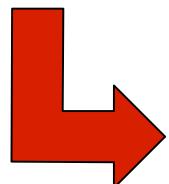
"stack" of virtual orbitals $(\psi_i^1, \psi_i^2, ...)$

Generate excited structures by applying excitations :

$$C_{i\rightarrow i1}\, or\, C_{i\rightarrow i2}, ... (singles), C_{i\rightarrow i1, j\rightarrow ij1}\, (double)$$

Spincoupled-VB

Orbital models

Fixed (VB)

Optimised

   Atomic
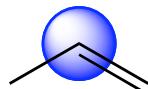
   Partial Delocal
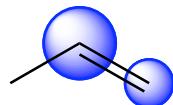
   Delocal
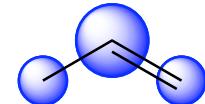
   (overlaps to 99 %)

   Breathing
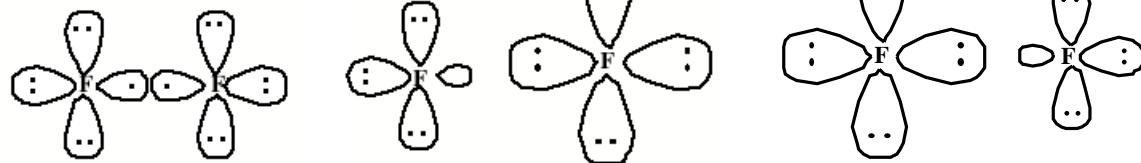
covalent   ionic A   ionic B

I-20

+

G. Balint-Kurti, G. Gallup, R. McWeeny, J. van Lenthe,
M. Raimondi, Y. Mo, W.Wu, R. Harcourt, D. Cooper, J.Gerratt,
R. Braam, , P-A Malmquist, R. Havenith,
S. Shaik, P. Hiberty, S. Humbel, P. Karadov
 + ...
and a lot of Physics (superconductivity, crystals)
 e.g.
Masafumi Tamura, Akiko Nakao, Reizo Kato,
"*Frustration-induced valence - bond ordering*
 *in a new quantum triangular antiferromagnet based on [Pd(dmit)2].* "

XMVB, CASVB, TURTLE, VB2000, CRUNCH,...

(Core)-hole states / Broken symmetry

He_2^+

A B Hit 1s **e** A B

$$\Psi = \Psi_A^{\frac{1}{2}+} \Psi_B^{\frac{1}{2}+}$$

$$\Psi = \Psi_A \Psi_B^+$$

$$\Psi = \Psi_A \Psi_B^+ - \Psi_B \Psi_A^+$$

$$\langle \Psi_A \Psi_B^+ | \Psi_A^+ \Psi_B \rangle > 0.9$$

Ria Broer - GNOME

Glyoxaal$^+$

$$\left(\begin{array}{c} O \\ \| \\ HC - CH \\ \| \\ O \end{array} \right)^+$$

Paul Ruttink

I-22
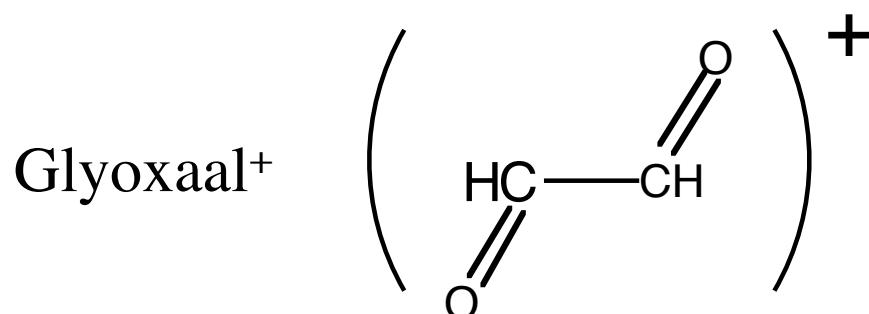
NH ($^3\Sigma^-$) dimer

G.Dhont, G. Groenenboom,A. vd Avoird

VB allows states to remain "themselves"
as interaction (and overlap) kicks in
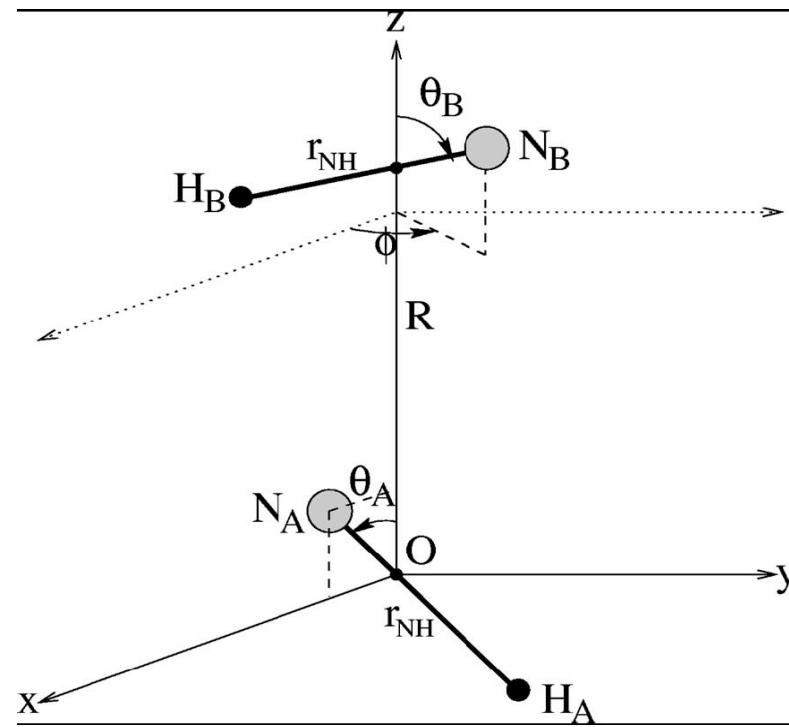
Some wise (edited) remarks by
J.N. Murrell, S.F.A. Kettle and J.M. Tedder
The Chemical Bond
(Wiley, 1985)

Valence bond theory relies on chemical intuition for finding suitable valence structures. In some respect, this may seem an advantage in that chemical experience can be directly introduced into a quantum-chemical calculation. In another respect, however, it is a weakness because it assumes some knowledge of the answer at the start. If chemical intuition is wrong, the VB calculation is wrong. The most valuable calculations are often those whose results refute intuition. In contrast, molecular orbital theory does not make any assumption about the way orbitals are paired in a molecule.

Probably the most misunderstood concept of the theory is "resonance energy". From resonance theory we deduce that a resonance hybrid will have a lower energy than any single canonical form. The theory tells us nothing about the absolute stability of one species relative to another.