

Valence-Bond method

An Overview

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Two-Electron wavefunction – general remarks

- Let $a(1) \equiv a(\mathbf{r}_1, \sigma_1)$ and $\bar{b}(2) \equiv b(\mathbf{r}_2, \sigma_2)$ be two spin-orbitals with different S_z values:

$$a(1) \equiv a(\mathbf{r}_1, \sigma_1) = a(\mathbf{r}_1)\alpha(\sigma_1)$$

$$\langle \hat{S}^2 \rangle = 3/4, \langle \hat{S}_z \rangle = +1/2$$

$$\bar{b}(2) \equiv b(\mathbf{r}_2, \sigma_2) = b(\mathbf{r}_2)\beta(\sigma_2)$$

$$\langle \hat{S}^2 \rangle = 3/4, \langle \hat{S}_z \rangle = -1/2$$

- Let us construct an anti-symmetric two-electron wavefunction (a Slater determinant) from them:

$$\begin{aligned} \Psi(1,2) &= \hat{A}(ab) = | a \bar{b} | = \begin{vmatrix} a(1) & a(2) \\ \bar{b}(1) & \bar{b}(2) \end{vmatrix} = a(1)\bar{b}(2) - a(2)\bar{b}(1) = \\ &= a(\mathbf{r}_1)\alpha(1)b(\mathbf{r}_2)\beta(2) - a(\mathbf{r}_2)\alpha(2)b(\mathbf{r}_1)\beta(1) \end{aligned}$$

where $\hat{A}(1,2)$ is the antisymmetrizing operator. Such $\Psi(1,2)$ is not a pure singlet, unless $a(\mathbf{r}_1) = b(\mathbf{r}_1)$! See next page 3 for detail.

- If we want our wavefunction to have a pure spin, then the spatial *or* the spin part has to be *antisymmetric*, the other being symmetric with respect to $1 \leftrightarrow 2$ interchange. This gives rise to the following **singlet** wavefunction:

$$^1\Psi(1,2) = (a(\mathbf{r}_1)b(\mathbf{r}_2) + a(\mathbf{r}_2)b(\mathbf{r}_1))(\alpha(1)\beta(2) - \alpha(2)\beta(1)) \quad \langle \hat{S}^2 \rangle = 0, \langle \hat{S}_z \rangle = 0$$

and to the following **triplet** wavefunctions:

$$^3\Psi_0(1,2) = (a(\mathbf{r}_1)b(\mathbf{r}_2) - a(\mathbf{r}_2)b(\mathbf{r}_1))(\alpha(1)\beta(2) + \alpha(2)\beta(1)) \quad \langle \hat{S}^2 \rangle = 2, \langle \hat{S}_z \rangle = 0$$

$$^3\Psi_{+1}(1,2) = (a(\mathbf{r}_1)b(\mathbf{r}_2) - a(\mathbf{r}_2)b(\mathbf{r}_1))\alpha(1)\alpha(2) \quad \langle \hat{S}^2 \rangle = 2, \langle \hat{S}_z \rangle = +1$$

$$^3\Psi_{-1}(1,2) = (a(\mathbf{r}_1)b(\mathbf{r}_2) - a(\mathbf{r}_2)b(\mathbf{r}_1))\beta(1)\beta(2) \quad \langle \hat{S}^2 \rangle = 2, \langle \hat{S}_z \rangle = -1$$

Two-Electron wavefunction – general remarks

- Note that ${}^1\Psi_0(1,2)$ and ${}^3\Psi_0(1,2)$ are *not* single Slater determinants, but can be expressed through two Slater determinants:

$${}^1\Psi(1,2) = |a\bar{b}| - |\bar{a}b|$$

$${}^3\Psi_0(1,2) = |a\bar{b}| + |\bar{a}b|$$

$${}^3\Psi_{+1}(1,2) = |ab|$$

$${}^3\Psi_{-1}(1,2) = |\bar{a}\bar{b}|$$

- If the two electrons form a *pair*, the spatial orbitals are identical:

$$\alpha(\mathbf{r}) = b(\mathbf{r}). \text{ Then, } |a\bar{a}| = -|\bar{a}a| \Rightarrow {}^1\Psi(1,2) = 2|a\bar{a}| = \\ = 2\alpha(\mathbf{r}_1)\alpha(\mathbf{r}_2)(\alpha(1)\beta(2) - \alpha(2)\beta(1)).$$

► No triplet wavefunction would be possible in such a situation, since ${}^3\Psi(1,2)$ would be zero \Rightarrow Pauli principle how we know it from the high school.

► Singlet spin functions for an electron pair is always the same:

$$\Theta(1,2) = \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

It is antisymmetric with respect to $1 \leftrightarrow 2$ interchange.

- VB description of the H₂ molecule.

► Let a and b now be *atomic* orbitals of two H atoms in the H₂ molecule:

$${}^1\Psi_{\text{VB}}(1,2) = |a\bar{b}| - |\bar{a}b| = (a(\mathbf{r}_1)b(\mathbf{r}_2) + a(\mathbf{r}_2)b(\mathbf{r}_1)) \Theta(1,2)$$

$$E = \langle {}^1\Psi_{\text{VB}} | \hat{\mathbf{H}} | {}^1\Psi_{\text{VB}} \rangle$$

$$E = \int N (a(1)b(2) + a(2)b(1)) \hat{\mathbf{H}} N (a(1)b(2) + a(2)b(1)) d\mathbf{r}_1 d\mathbf{r}_2 =$$

$$\begin{aligned} &= E_a + E_b + \frac{Z_a Z_b}{R_{ab}} + 2N^2 \left(\int a(1)b(2) \left(\frac{1}{r_{12}} \right) a(1)b(2) d\mathbf{r}_1 d\mathbf{r}_2 + \int a(1) \left(-\frac{1}{r_{1b}} \right) a(1) d\mathbf{r}_1 + \right. \\ &\quad \left. + \int b(2) \left(-\frac{1}{r_{2a}} \right) b(2) d\mathbf{r}_2 + \int a(1)b(1) \left(\frac{1}{r_{12}} \right) a(2)b(2) d\mathbf{r}_1 d\mathbf{r}_2 + \right. \\ &\quad \left. + S \int b(2) \left(-\frac{1}{r_{2b}} \right) a(2) d\mathbf{r}_2 + S \int a(1) \left(-\frac{1}{r_{1a}} \right) b(1) d\mathbf{r}_1 \right) \end{aligned}$$

► A dissociation energy of ~72 kcal·mol⁻¹ is obtained in this way.

- Still, much of the dissociation energy is missing. Improvement is needed! We should include *ionic terms* in order to correct the situation.

► Possible ansätze:

Ionic terms:

$|a\bar{a}| = a(1)a(2)\Theta(1,2)$: both electrons are on atom A;

and

$|b\bar{b}| = b(1)b(2)\Theta(1,2)$: both electrons are on atom B.

Note: all the wavefunctions include the antisymmetric spin function $\Theta(1,2)$ (see page 3).

- A wavefunction $\Psi_{\text{cov-ion}}$ including covalent and ionic terms (covalent-ionic resonance):

$$\Psi_{\text{cov-ion}}(1,2) = N (\Psi_{\text{cov}} + k\Psi_{\text{ion}}) = N(a(1)b(2) + a(2)b(1) + ka(1)a(2) + kb(1)b(2))\Theta(1,2)$$

where k is some variationally adjustable parameter. $k \approx 0.13$



- When atomic orbitals are fixed, there is a one-to-one correspondence between the resonance structures and the form of the VB wavefunction!

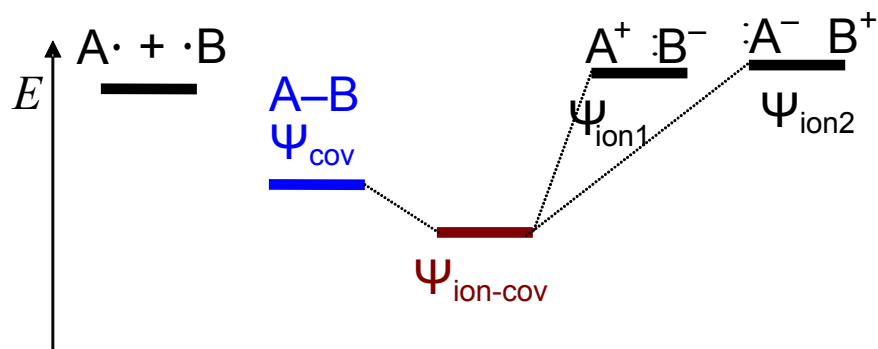
$\Psi_{\text{cov-ion}}$ is equivalent to the minimal-basis CI-Doubles wavefunction

$\Psi_{\text{CI}}(1,2)$ built on molecular orbitals $\sigma = a+b$, $\sigma^* = a-b$:

$$\Psi_{\text{CI}}(1,2) = N'(\sigma(1)\sigma(2) + \mu \sigma^*(1)\sigma^*(2)), \text{ where } \mu = k/(1+k) \text{ if } k = (1+\mu)/(1-\mu)$$

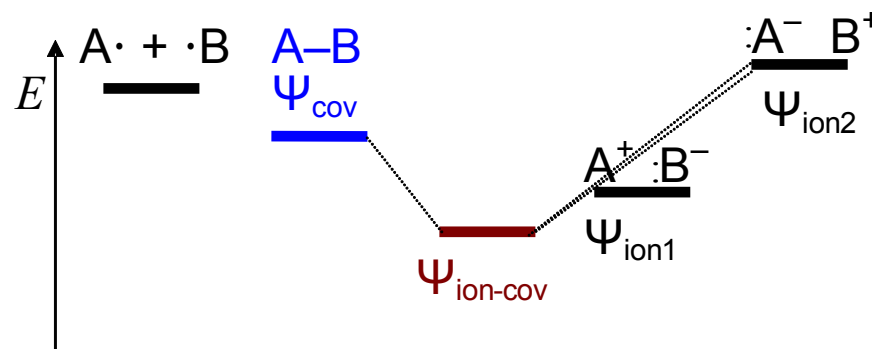
Valence-Bond theory – importance of ionic terms

► Typical *covalent* situation:



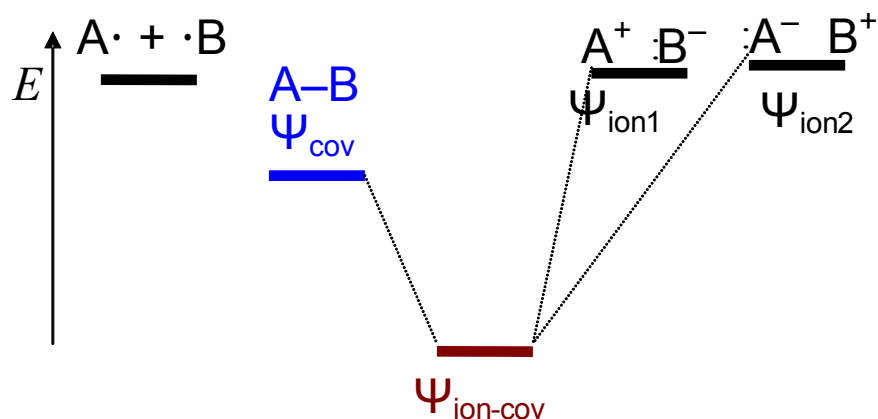
Examples: H_2 , $C-H$, $B-H\cdots$

► Typical *ionic* situation:



Examples: NaF , $NaCl$

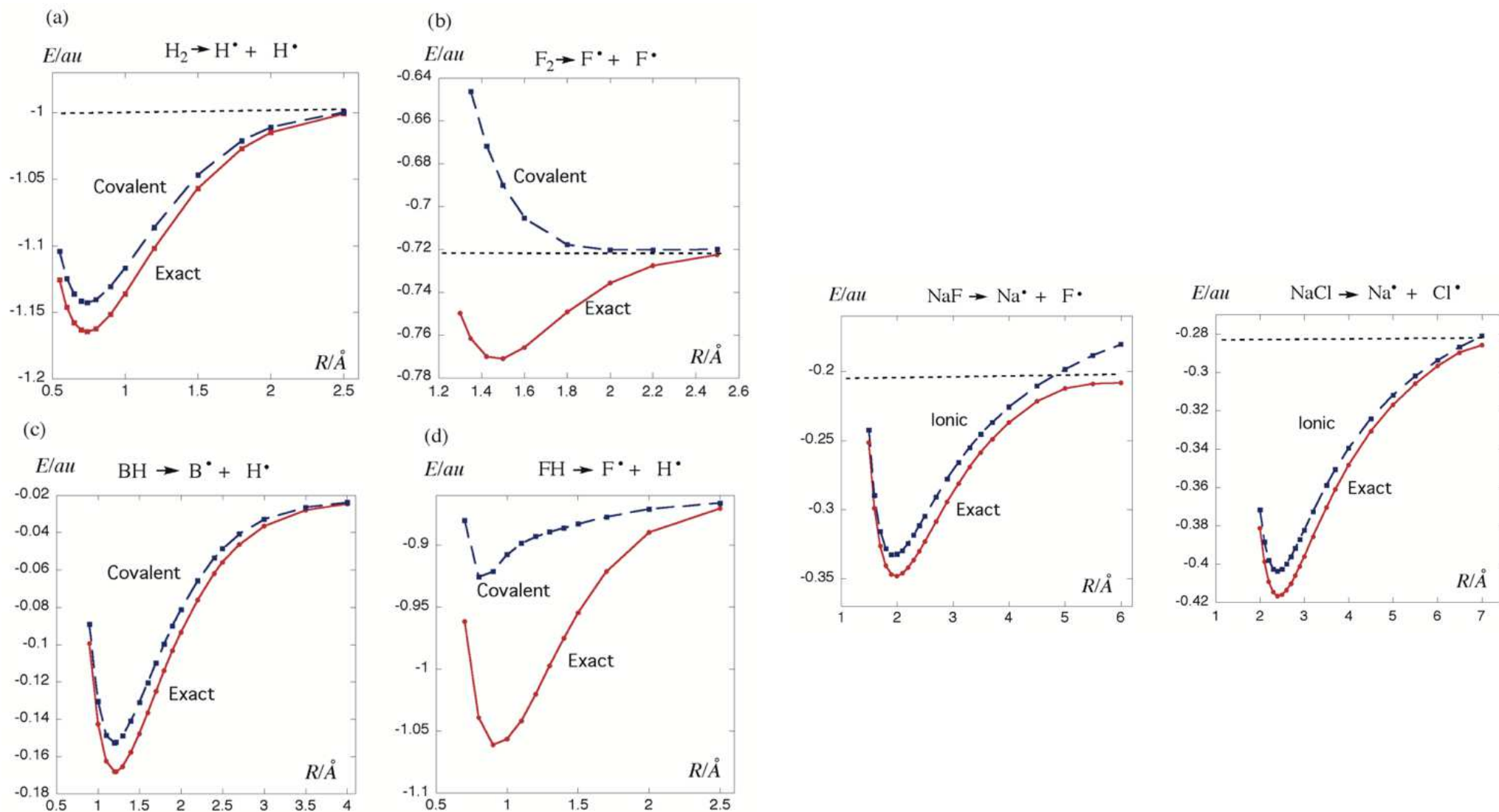
► Typical *charge-shift* situation (see Shaik *et al.* DOI: 10.1002/anie.201910085)



Examples: F_2 , HF , $C-F$, Cl_2 , $O-O$, $S-S$ – when many lone pairs are present.

- A ***charge-shift*** bond: a bond for which the largest part of the bonding energy comes from the covalent-ionic resonance, not from the covalent structure alone.

Valence-Bond theory – role of various terms



► Charge-shift bonds typically appear when there many lone pairs

► 2) Coulson–Fischer wavefunction (1949):

$\Psi_{\text{C-F}}(1,2) = N''(a'(1)b'(2) + a'(2)b'(1))\Theta(1,2)$, where $a' = a + \lambda b$, $b' = b + \lambda a$, where λ is a variationally adjustable parameter \Rightarrow atomic orbitals are *not* fixed in this approach.

$$\lambda = 0: \Psi_{\text{C-F}} = \Psi_{\text{VB}}$$

$$\lambda = 1: \Psi_{\text{C-F}} = \Psi_{\text{MO}}$$

$$k = \frac{2\lambda}{\lambda^2 + 1} : \Psi_{\text{C-F}} = \Psi_{\text{cov-ion}}$$

• More general approach (Goddard *et al.* 1973; Wilson–Gerratt 1975):

$$a'(\mathbf{r}_1) = \sum_k c_{ak} \chi_k(\mathbf{r}_1)$$

$$b'(\mathbf{r}_2) = \sum_k c_{bk} \chi_k(\mathbf{r}_2)$$

where $\chi_k(\mathbf{r}_1)$ are some basis functions and c_{ak} , c_{bk} are variationally adjustable coefficients (normally the usual Gaussian-type functions).

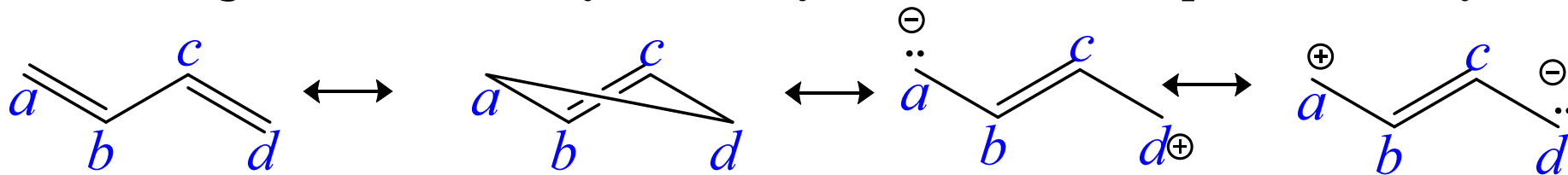
► Note that $a'(\mathbf{r})$ and $b'(\mathbf{r})$ are still *atomic* (not molecular) orbitals, but may include admixture of other atoms' basis functions.

► Note that $\Psi_{\text{C-F}}$ can be represented through the anti-symmetrizer:

$$\Psi_{\text{C-F}}(1,2) = \hat{A}(a'(1)b'(2)\Theta(1,2)).$$

Valence-Bond theory – polyatomic molecules

- Consider e.g. butadiene (π -system only, i.e. one atomic per atom only):



Two latter structures are referred to as *zwitterionic*.

$${}^1\Psi_{\text{VB1}}(1,2,3,4) = \hat{A}((|a\bar{b}| - |\bar{a}b|)(|c\bar{d}| - |\bar{c}d|)) = |a\bar{b}c\bar{d}| - |\bar{a}b c\bar{d}| - |a\bar{b} \bar{c}d| + |\bar{a}b \bar{c}d|$$

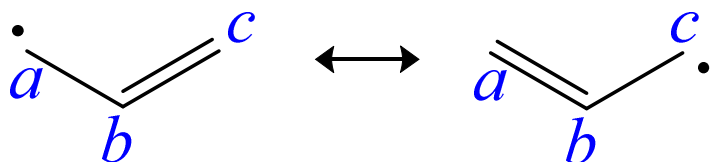
$${}^1\Psi_{\text{VB2}}(1,2,3,4) = \hat{A}((|a\bar{d}| - |\bar{a}d|)(|b\bar{c}| - |\bar{b}c|)) = |a\bar{d}b\bar{c}| - |\bar{a}d b\bar{c}| - |a\bar{d} \bar{b}c| + |\bar{a}d \bar{b}c|$$

$${}^1\Psi_{\text{VB3}}(1,2,3,4) = \hat{A}(|a\bar{a}|(|b\bar{c}| - |\bar{b}c|)) = |a\bar{a}b\bar{c}| - |\bar{a}a \bar{b}c|$$

$${}^1\Psi_{\text{VB4}}(1,2,3,4) = \hat{A}((|b\bar{c}| - |\bar{b}c|)|d\bar{d}|) = |b\bar{c}d\bar{d}| - |\bar{b}c d\bar{d}|$$

(Note that the above determinants are not orthogonal).

- Wavefunction with unpaired electrons (doublet states):



For the “spin-up” ($\langle \hat{S}^2 \rangle = 3/4$, $\langle \hat{S}_z \rangle = +1/2$):

$${}^2\Psi_{\text{VB1}}(1,2,3) = \hat{A}(a \cdot (|b\bar{c}| - |\bar{b}c|)) = |a b \bar{c}| - |a \bar{b} c|$$

$${}^2\Psi_{\text{VB2}}(1,2,3) = \hat{A}((|a\bar{b}| - |\bar{a}b|) \cdot c) = |a \bar{b} c| - |\bar{a} b c|$$

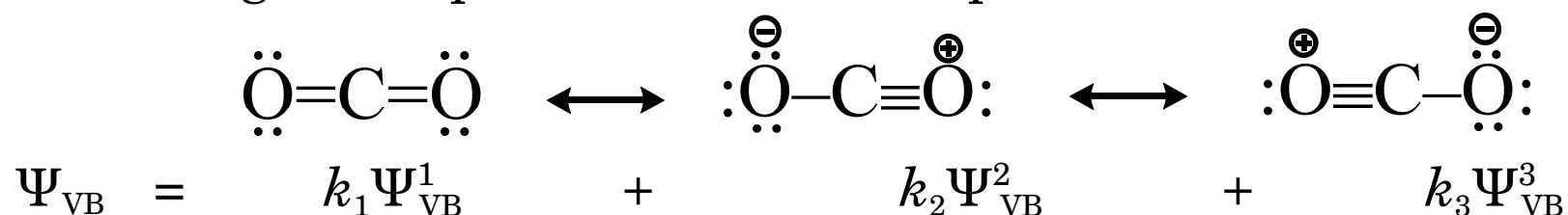
For the “spin-down” ($\langle \hat{S}^2 \rangle = 3/4$, $\langle \hat{S}_z \rangle = -1/2$):

$${}^2\Psi_{\text{VB1}}(1,2,3) = \hat{A}(\bar{a} \cdot (|b\bar{c}| - |\bar{b}c|)) = |\bar{a} b \bar{c}| - |\bar{a} \bar{b} c|$$

$${}^2\Psi_{\text{VB2}}(1,2,3) = \hat{A}((|a\bar{b}| - |\bar{a}b|) \cdot \bar{c}) = |a \bar{b} \bar{c}| - |\bar{a} b \bar{c}|$$

- When atomic orbitals are defined, each Lewis structure (a covalent, ionic, or zwitter-ionic) corresponds to a certain multielectron VB wavefunction constructed as shown above. The total wavefunction will be a variationally optimized linear combination of these Lewis structures ("**resonance**"). Note that the spin must be conserved, i.e. Lewis structures with different spins do not mix.

In principle, we can consider as many resonance structures as we wish, but we must have enough atomic orbitals (basis functions) for this. From a given covalent structure, we can generate ionic or zwitter-ionic ones by making a lone pair from a covalent pair:



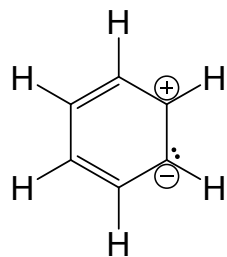
Obviously, $k_2 = k_3$ due to symmetry. The coefficients k_1, k_2, k_3 are variationally adjusted.

Some “unreasonable” resonance structures (with high formal charges etc.) can be included, but their contribution to the total Ψ_{VB} will be minor.

Exercise

Draw possible Lewis structures for the following molecules. Include ionic structures whenever appropriate. Think which Lewis structures are symmetrically equivalent, which are not:

- C_6H_6 (benzene). Please consider, in addition to two Kekulé structures, also Dewar structures. Also consider ionic and zwitterionic structures such as the following one:

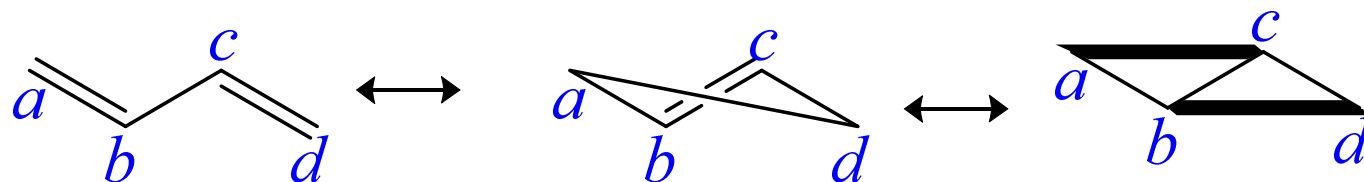


- HF ; HNO_3 ; NO_3^- ; H_2CO_3 ; CO_3^{2-} ; HF_2^- ; $(\text{H}_2\text{O})_2$.
- SF_6 ; PF_5 ; I_3^- ; I_5^- . Do *not* include any *d* orbitals.

Note: A Hartree–Fock or a CI wavefunction can be mapped (projected) to a VB wavefunction (Hiberty, Leforestier, 1978)

Valence-Bond theory – Rumer diagrams

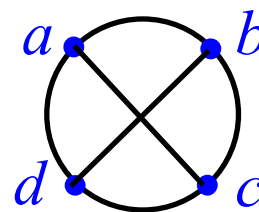
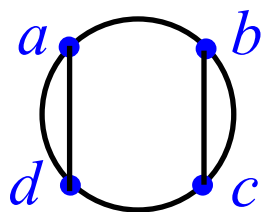
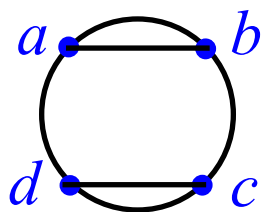
- Actually, some of the Lewis structures may correspond to linearly dependent wavefunctions. For instance, for the above butadiene example, one could add another structure (VB5, with A–C and B–D linked):



$${}^1\Psi_{\text{VB5}}(1,2,3,4) = \hat{A}((|a\bar{c}| - |\bar{a}c|)(|b\bar{d}| - |\bar{b}d|)) = |a\bar{b}c\bar{d}| - |\bar{a}b\bar{c}d| - |a\bar{b}\bar{c}d| + |\bar{a}b\bar{c}d|$$

As we see, ${}^1\Psi_{\text{VB5}} = {}^1\Psi_{\text{VB1}}$ and is thus not linear independent.

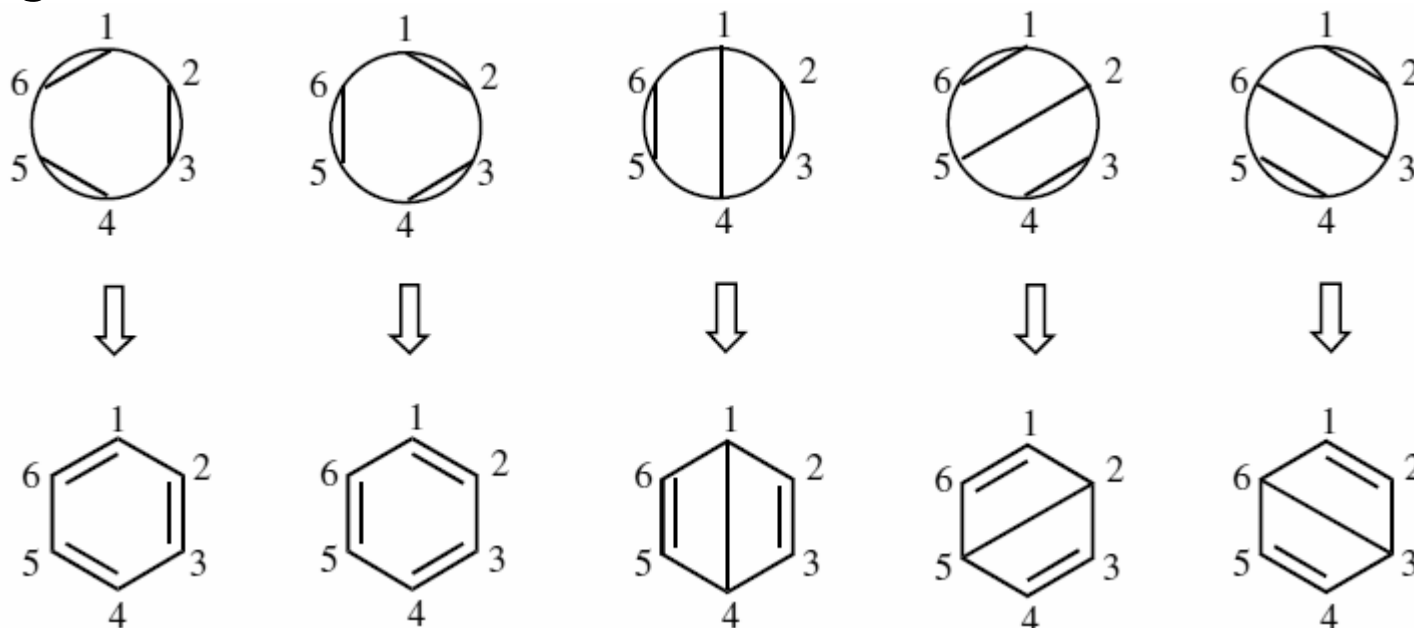
There is a simple rule allowing to filter out linearly dependent Lewis structures – so-called **Rumer's rule**: one should put all the orbitals involved on a circle. For instance, the Rumer diagrams for the above butadiene Lewis structures are:



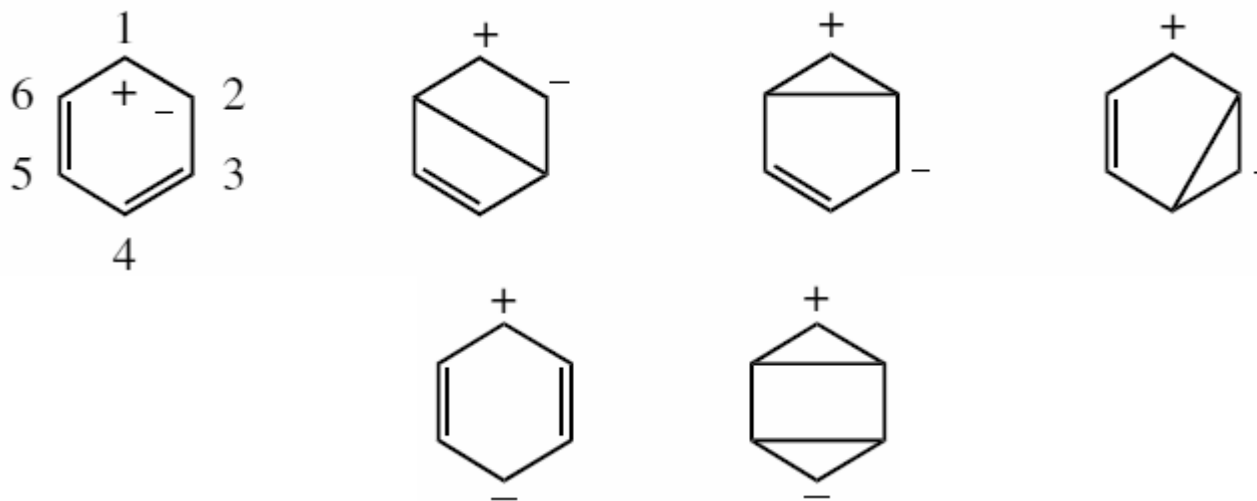
The diagrams containing crossing lines are *forbidden* according to Rumer's rule. This means that the corresponding wavefunctions are linear dependent.

Valence-Bond theory – Rumer diagrams for benzene

- Rumer diagrams for benzene (covalent Kekulé and Dewar structures)



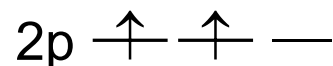
- Rumer diagrams for ionic VB structures can also be generated.
For instance:



Valence-Bond theory – hybridization

- Hybridization was invented by L. Pauling within the VB theory to explain the geometry of molecules such as CH_4 .
 - Unlike the MO theory, AOs are not mixed automatically in the standard VB theory \Rightarrow hybridization does not appear automatically. If we want to use hybrid orbitals, we have to construct them before we construct the VB wavefunction.

► CH_4 example:

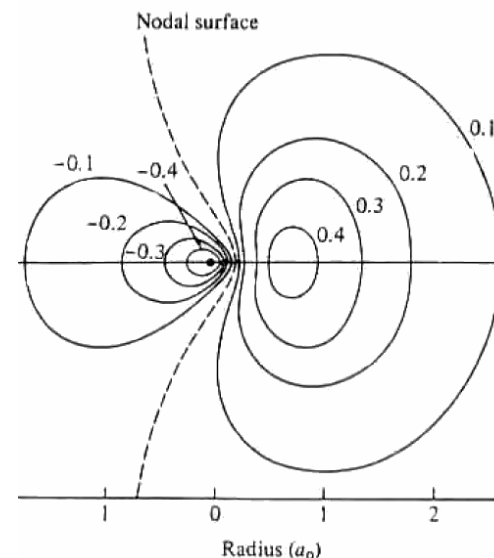


$$sp^3 \text{ hybrids: } \psi_1 = \frac{1}{2} (s + p_x + p_y + p_z)$$

$$\psi_2 = \frac{1}{2} (s - p_x - p_y + p_z)$$

$$\psi_3 = \frac{1}{2} (s + p_x - p_y - p_z)$$

$$\psi_4 = \frac{1}{2} (s - p_x + p_y - p_z)$$



Exercise: *demonstrate that the sp^3 hybrids are orthonormal.*

- Hybrid orbitals are not eigenfunctions of the single-atomic Fockian. Still, they can be used for constructing VB wavefunctions.
- Don't say " CH_4 is tetrahedral because carbon is sp^3 -hybridized". This is distorted logic!

Valence-Bond theory – hybridization

- There exists a systematic procedure for obtaining hybrid orbitals for various cases. It is a kind of inversion of the projection method. This procedure is beyond the scope of our course for now.

sp^2 hybrids:

$$\psi_1 = (1/\sqrt{3})s + (2/\sqrt{6})p_x$$

$$\psi_2 = (1/\sqrt{3})s - (1/\sqrt{6})p_x + (1/\sqrt{2})p_y$$

$$\psi_3 = (1/\sqrt{3})s - (1/\sqrt{6})p_x - (1/\sqrt{2})p_y$$

Exercise: *demonstrate that the sp^2 hybrids are orthonormal.*

- Various hybridizations:

Main-group elements: sp (linear), sp^2 (trigonal-planar), sp^3 (tetrahedral)

Main-group, hypervalent molecules: sp^3d (trigonal-bipyramidal), sp^3d^2 (octahedral), sp^3d^3 (pentagonal-bipyramidal)

Note: contribution of such Lewis structures involving d -containing hybrids is minor for main-groups element and not possible at all for 1st and 2nd periods (no d orbitals).

Exercise: *discuss the octet rule in this context.*

Transition metals: sd (bent 90°), sd^2 (trigonal-pyramidal), sd^3 (tetrahedral), sd^4 (square-pyramidal), sd^5 (trigonal prismatic);
 sp^3 (tetrahedral), dsp^2 (square-planar), d^2sp^3 (octahedral).