

# Symmetry Breaking



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# What do we mean by symmetry breaking?

- The symmetry of the wavefunction at a high-symmetry molecular structure is broken
- Löwdin “Symmetry dilemma”
- If  $\Lambda$  is a normal constant of motion, i.e.  $H\Lambda = \Lambda H$

then every eigenfunction to  $H$  is automatically also an eigenfunction of  $\Lambda$ :

In case of a symmetry operation, the exact eigenfunction  $\Psi$  is automatically symmetry adapted:  $H\Psi = E\Psi$ ,  $\Lambda\Psi = \lambda\Psi$

In case of an expectation value, the consequence of symmetry is not automatically given

Löwdin, P. O. In Lykos, P.; Pratt, G. W. Discussion on The Hartree-Fock Approximation. Rev. Mod. Phys. 1963, 35, 496–501

Two cases for:

(i)  $\delta \langle D | H | D \rangle = 0$ ; and  $\Lambda D = \lambda D$  is enforced

(ii) The symmetry constraint is dropped and only the variational calculation is performed without further constraint:  $\delta \langle D | H | D = 0 \rangle$

$D$  is e.g. a Hartree-Fock determinant.

This procedure was termed *nonrestricted* Hartree-Fock scheme. The solution  $D$  corresponding to the absolute minimum can have lost its symmetry adaptation. Such symmetry broken situations can already be observed for the dissociation process of  $H_2$ .

The main question in practice is: how can one find out whether an observed symmetry breaking is “real” or induced by an artificial bias of the approximate wavefunction toward symmetry breaking.

## Symmetry Breaking in Polyatomic Molecules: Real and Artifactual

Ernest R. Davidson and Weston Thatcher Borden

J. Phys. Chem. 1963, 67, 4783-4790

Broken symmetry structures may appear as minima on a calculated potential surface for several reasons. One of the most common is that the calculation is "wrong". That is, the form assumed for the wave function is oversimplified and leads to artifactual structure on the potential surface.

It is easily demonstrated that any exact eigenfunction of an electronic Hamiltonian in the Born-Oppenheimer approximation must belong to an irreducible representation of the point group of the Hamiltonian. If an approximate functional form (such as a single Slater determinant) is assumed for the wave function, optimization of the average energy of this function may lead to a function that does not have pure symmetry (i.e., which does not transform like any irreducible representation under the operations of the group).

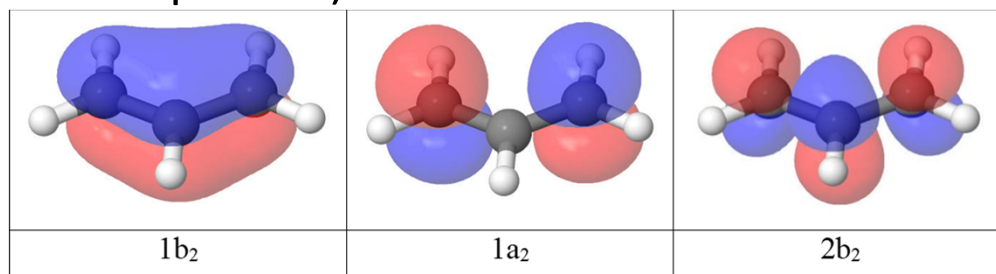
Spin symmetry (as in unrestricted Hartree-Fock (UHF) calculations), time reversal symmetry (leading to complex wave functions even when the Hamiltonian is real), as well as point group symmetry may all be broken. Symmetry can always be imposed as a boundary condition during the optimization of the wave function. This is commonly done for spin and time reversal symmetry. Imposition of spatial symmetry, however, often leads to discontinuities on the potential surface since only certain geometrical arrangements have any symmetry. In order to obtain a continuous potential surface, the same prescription for obtaining the energy must be used at every point.

Note: Correct treatment of symmetry breaking is crucial for correct treatment of Jahn-Teller and pseudo Jahn-Teller systems

# Allyl Radical

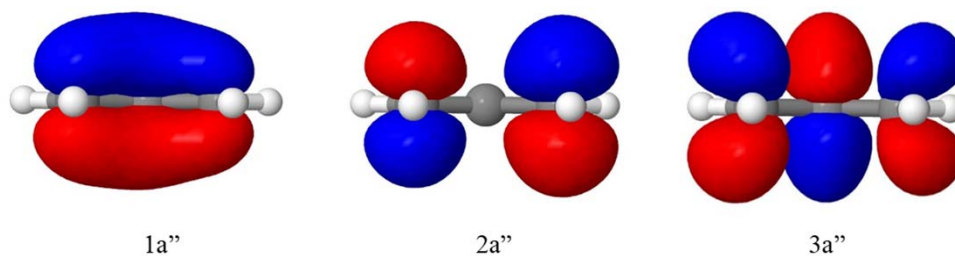
In our tutorial we are going to investigate the symmetry breaking for the allyl radical. We follow the path indicated in the previous slide:

1. Calculation under  $C_{2v}$  symmetry constraint (we use CASSCF(3,3) and restricted open shell RO-SCF for comparison):



2. Calculation with  $C_s$  symmetry (molecular plane, to distinguish easily  $\sigma$  and  $\pi$  symmetry), but without restriction of left-right symmetry. The results are: Geometry optimization at CASSCF(3,3) level of the initially distorted structure (the two CC bonds are not equivalent anymore) leads back to the original  $C_{2v}$  symmetry. The same calculation at RO-SCF level keeps the distorted structure, thus the symmetry is broken. One can see this also from the symmetry broken orbitals obtained even at the symmetric  $C_{2v}$  structure.

The orbitals look as follows



If we increase the CAS(3,3) to CAS(3,4), the respective CASSCF result is also symmetry broken! Thus, the symmetry breaking is not restricted to SCF alone. A CAS(3,5) recovers the symmetry again. For more details see Ref. 1.

P. G. Szalay, A. G. Császár, G. Fogarasi, A. Karpfen, and H. Lischka, J. Chem. Phys. **93**, 1246 (1990)

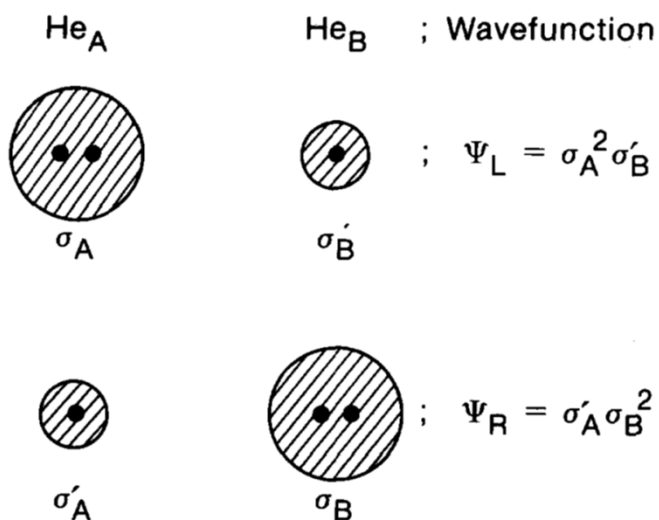
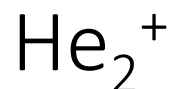


FIG. 1. Resonance structures for He<sub>2</sub><sup>+</sup>.



$$\Psi_L = \sigma_A^2 \sigma_B' \quad \text{symmetry broken}$$

$$\Psi_R = \sigma_A' \sigma_B^2 \quad \text{symmetry broken}$$

$$\Psi_S = (\sigma_A'' + \sigma_B'')^2 (\sigma_A''' - \sigma_B''')^1 \quad \text{not symmetry broken}$$

**Orbital size effect:** in  $\Psi_L$   $\sigma_A$  is like He atom (more diffuse) than  $\sigma_B'$  (He<sup>+</sup>), vice versa in  $\Psi_L$

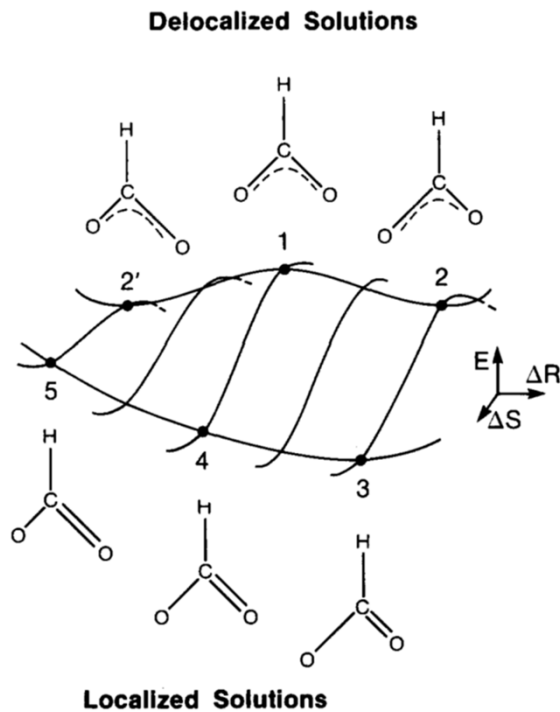
$\Psi_S$  represents a compromise

**Resonance effect:** included in  $\Psi_S$ , not in  $\Psi_L$  or  $\Psi_R$

One possible solution:  $\Psi_L + \Psi_R$ , four orbitals, 2x2 nonorthogonal CI

In orthogonal orbitals: 3 electrons in the four orbitals obtained by orthogonalizing  $\sigma_A, \sigma_A', \sigma_B, \sigma_B' \Rightarrow$  **orbital doubling**

# The Formyloxyl radical $\text{HCO}_2$



Generalized potential energy surface:

Two types of coordinates

$\Delta R = (R_{\text{CO}_1} - R_{\text{CO}_2})$  – asymmetric stretch

$\Delta S$  is a symmetry breaking coordinate in the orbitals,  $b_1$  and  $a_2$   $\pi$  orbitals ( $C_{2v}$  symmetry) in this case

The ridge 2'12 contains orbitals with  $\Delta S = 0$

The valley 543 with positive  $\Delta S$ , and an equivalent one with negative  $\Delta S$  behind (not shown)

The surface contains 4 minima: 2, 2' and 3 and 3'

At point 1 the structure and the wavefunction have  $C_{2v}$  symmetry; however, this point is instable both with

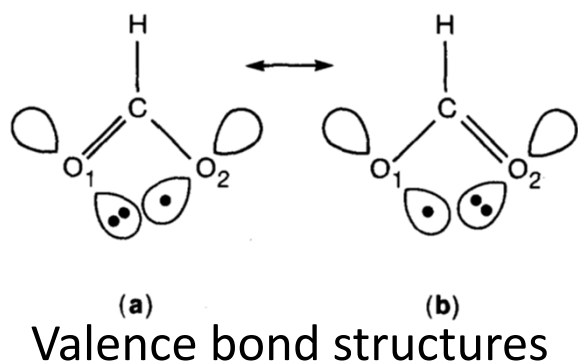
respect of breaking the nuclear symmetry as well as the symmetry of the wavefunction.

Point 2 is stable is a minimum w.r.t. nuclear displacement, but the wavefunction is still

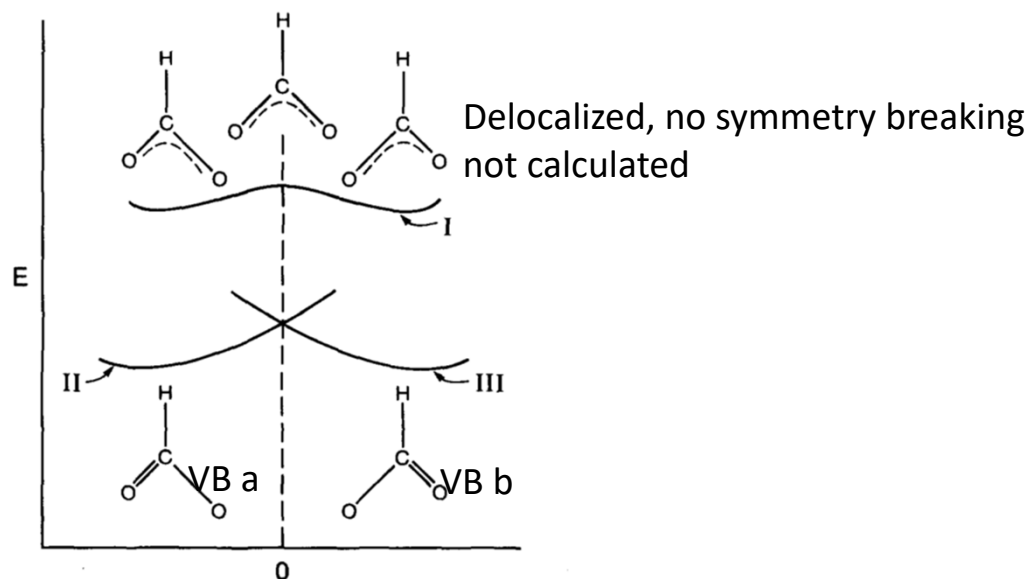
unstable. Point 4: wavefunction stable, but the nuclear frame not; point 3 is table in both aspects



Series of calculations to find out the real topography of the energy surface



Wavefunction A:  $KKKs_{O_1}^2 s_{O_2}^2 CO_1^2 CO_2^2 CH^2 \sigma^2 \sigma'^2 \pi_1^2 \pi_2^2$



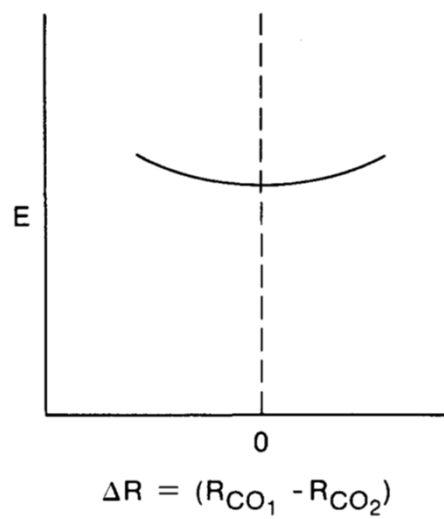
**Requirement:** starting point: SCF (MCSCF) wavefunctions which **do not** break symmetry, confirmation by MRCI  
Wavefunctions I and II not suitable

Wavefunction D:  $KKKs_{O_1}^2 s_{O_2}^2 (CO_1 CO_1^*)^2 (CO_2 CO_2^*)^2 (CHCH^*)^2 (p_{O_1} p_{O_1}^* p_{O_2} p_{O_2}^*)^3 (\pi\pi\pi)^4$

Wavefunction D' (more economic, S stands for singlet coupling):

$$KKKs_{O_1}^2 s_{O_2}^2 (CO_1 CO_1^*)_S (CO_2 CO_2^*)_S (CHCH^*)_{SS} \left[ (p_{O_1} p_{O_1}^*)_S (p_{O_2} p_{O_2}^*)^1 + (p_{O_2} p_{O_2}^*)_S (p_{O_1} p_{O_1}^*)^1 \right] (\pi\pi\pi)_S^4$$

Wavefunction  $D'$  does not break the symmetry; symmetric minimum confirmed by large scale CI



# The $\tilde{X}^2\Sigma_u^+$ state of BNB

This system is a prototype for studying symmetry breaking

Questions: linear or not, symmetric or not

A long history of investigations, selected examples:

CASSCF(7,8) and CASSCF(11,12) by Martin et al. Phys. 85, 527 (1995): BNB  
asymmetric

Almost all of the following investigations also find a linear, asymmetric structure,  
e.g.

Gwaltney and Head-Gordon, Phys. Chem. Chem. Phys. 3, 4495, (2001) Coupled  
cluster calculations

Li and J. Paldus, J. Chem. Phys. 126, 224304 (2007), reduced multireference (RMR)  
CCSD(T)

Stanton, J. Chem. Phys. 133, 174309 (2010), EOMIP-CCSDT based on BNB<sup>-</sup>, linear vibronic coupling (LVC) model, second order Jahn-Teller (SOJT) analysis.

Statement: « That is, for this molecule, it is equally—and perhaps more—important to treat the phenomena of nonadiabatic coupling than it is to do better and better old-fashioned quantum chemistry. ...These calculations avoid the symmetry breaking problem associated with orbital optimization (an arcane topic that is entirely peripheral to the current discussion)...

Al-Saidi, Chem. Phys. Lett. 543, 41 (2012), Diffusion Monte Carlo (DMC), asymmetric structure is lower than the symmetric one by 22 cm<sup>-1</sup>.

Experimental investigations:

Matrix isolation ESR (Knight, Jr., Hill, Kirk, and Arrington, J. Phys. Chem. 96, 555 (1992),  $\tilde{X}^2\Sigma_u^+$  ground state

Matrix infrared study (Andrews, Hassanzadeh, Burkholder, and Martin, J. Chem. Phys. 98, 922 (1993), identify a cyclic (C<sub>2v</sub>) and linear, symmetric BNB

Anion photoelectron spectroscopy (12K. R. Asmis, T. R. Taylor, and D. M. Neumark, J. Chem. Phys. 111, 8838 (1999): various vibrational modes

Spectroscopic results also not conclusive since their interpretation relies in part on theoretical calculations which are uncertain.

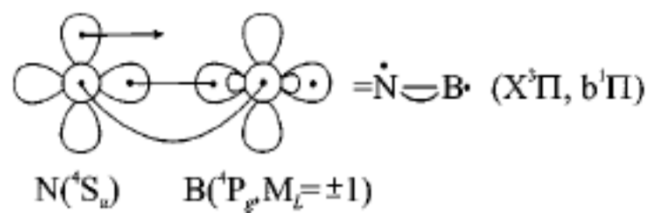
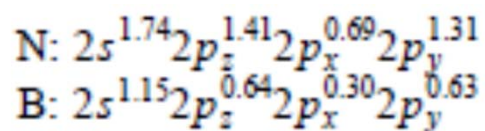
Kalamos, Dunning, and Mavridis, J. Chem. Phys. 120, 1813 (2004)

Kalamos, J. Chem. Phys. 138, 224302 (2013), state-averaged (SA) CASSCF/MRCI calculations, BNB is linear and symmetric

Comment to Stanton

he mysteriously claimed the greatest importance of nonadiabatic effects in the BNB case than “. . . to do better and better old-fashioned quantum chemistry”

The main argument in the work of Kalemios comes from the analysis of the different states of BN with another B atom in the ground state  $^2P$ . There are several states to be considered, but all show the same feature: the electronic configuration of B is  $^4P$ , derived from a Mulliken population analysis, and leading to the VB diagram below



The incoming, reacting B atom is doublet ( $^2P$ ), so that there will be two types of B atoms in BNB,  $^4P$  and  $^2P$

CASSCF in all valence orbitals

TABLE IV. Total energies  $E_e$  (hartree), equilibrium bond lengths  $r_e$  (Å), and dipole moments  $\mu_e$  (D) of the ground  $\tilde{X}^2\Sigma_u^+$  state of BNB at various levels of theory.

Method	$E_e$	$r_e$ (B <sub>1</sub> N)	$r_e$ (NB <sub>2</sub> )	$\mu_e$
CASSCF+PT2 <sup>a</sup>	-104.110 217	1.275	1.381	3.58 asymmetric
SACASSCF+PT2	-104.115 799	1.325	1.325	0.0
CASSCF+1+2 <sup>a</sup>	-104.113 720	1.273	1.381	3.66 asymmetric
SACASSCF+1+2	-104.112 996	1.324	1.324	0.0

<sup>a</sup> $C_{\infty v}$  point group symmetry.

Mulliken population for CASSCF

$$\text{N: } 2s^{1.35}2p_z^{1.09}2p_x^{1.32}2p_y^{1.32},$$

$$\text{B}_1: 2s^{1.13}2p_z^{0.71}2p_x^{0.43}2p_y^{0.43},$$

$$\text{B}_2: 2s^{1.77}2p_z^{0.78}2p_x^{0.22}2p_y^{0.22}.$$

One B is in  $2s^{1.13}2p^{1.57} \sim 4p$   
The other  $2s^{1.77}2p^{1.22} \sim 2p$

Mulliken population for SA-CASSCF

$$\text{N: } 2s^{1.37}2p_z^{1.10}2p_x^{1.30}2p_y^{1.30},$$

$$\text{B}_1: 2s^{1.49}2p_z^{0.70}2p_x^{0.33}2p_y^{0.33},$$

$$\text{B}_2: 2s^{1.49}2p_z^{0.70}2p_x^{0.33}2p_y^{0.33}.$$

B:  $2s^{1.49}2p^{1.36} \sim \text{average between } 2P \text{ and } 4P$

State-averaging is important to describe both states of B in BNB equally

TABLE I. Energy ( $E_h$ ) and internuclear distances  $r_{B_1N}$ ,  $r_{B_2N}$  (Å) of the  $\tilde{X}^2\Sigma_{(u)}^+$  BNB state at the (SA)CASSCF, (SA)CASSCF+1+ 2(= MRCI), ACPF, and MRCI+Q/cc-pVTZ levels of theory.

Method	-E	$r_{B_1N}$	$r_{B_2N}$	
$9e^-/11orb[ = (2s + 2p)_B \times 2 + (2p)_N]$				
CASSCF	103.878 400	1.3854	1.2716	
SACASSCF <sup>a</sup>	103.866 236	1.3296	1.3296	} symmetric
MRCI( $9e^-$ ) <sup>b</sup>	104.009 545	1.3227	1.3227	
MRCI( $9e^-$ )+Q <sup>c</sup>	104.018 967	1.3213	1.3213	
$11e^-/12orb[ = (2s + 2p)_B \times 2 + (2s + 2p)_N]$				
CASSCF	103.904 481	1.4030	1.2744	
MRCI( $11e^-$ )	104.089 343	1.3861	1.2787	
MRCI( $11e^-$ )+Q	104.101 130	1.3845	1.2815	
ACPF( $11e^-$ ) <sup>d</sup>	104.099 702	1.3845	1.2814	
SACASSCF <sup>a</sup>	103.894 051	1.3739	1.3006	Unsymmetric! Correlation of $2s_N$ is missing
$11e^-/13orb[ = (2s + 2p)_B \times 2 + (2s + 2p + s')_N]$				
CASSCF	103.917 461	1.3976	1.2745	
SACASSCF <sup>a</sup>	103.908 589	1.3606	1.3057	
MRCI( $11e^-$ ) <sup>e</sup>	104.091 809	1.3558	1.3023	
MRCI( $11e^-$ ) <sup>f</sup>	104.073 225	1.3371	1.3371	Correlation of $2s_N$ is included
MRCI( $11e^-$ ) <sup>g</sup>	104.087 950	1.3310	1.3310	