

Symmetry Breaking



Hans Lischka

Texas Tech University, USA

Tianjin University, China

What do we mean by symmetry breaking?

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

then every eigenfunction to H is automatically also an eigenfunction of Λ :

In case of a symmetry operation, the exact eigenfunction Ψ 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. 1983, 87, 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).

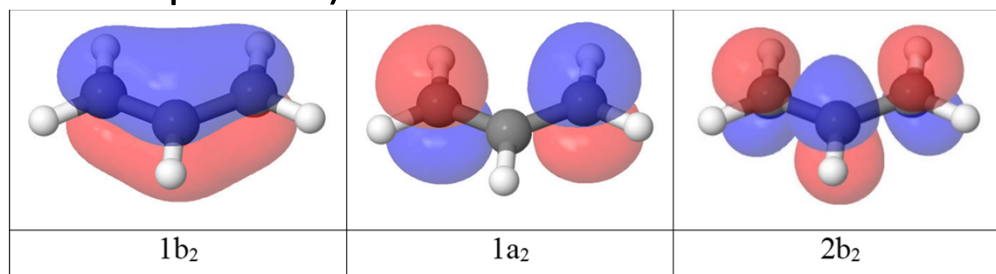
Spin symmetry (as in unrestricted Hartree-Fock (UHF) calculations), time reversal symmetry (leading to complex wave functions even when the Hamiltonian is real), as well as point group symmetry may all be broken. Symmetry can always be imposed as a boundary condition during the optimization of the wave 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

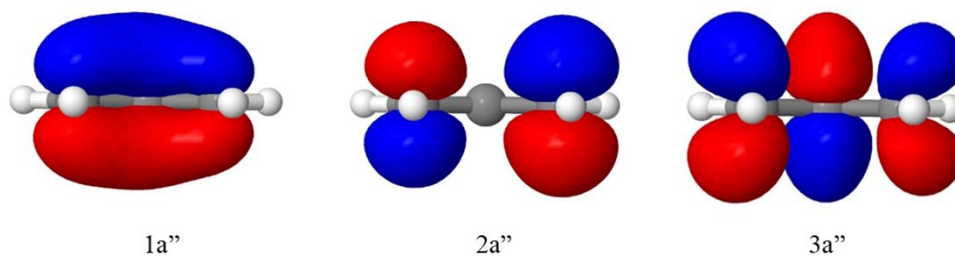
In our tutorial we are going to investigate the symmetry breaking for the allyl radical. We follow the path indicated in the previous slide:

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 σ and π 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)

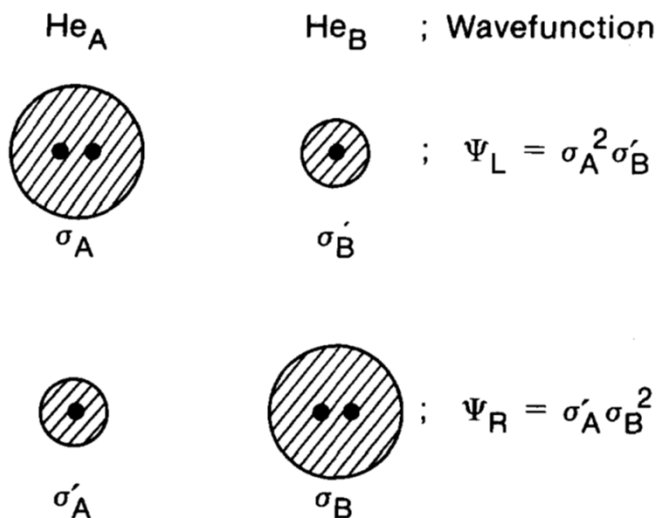


FIG. 1. Resonance structures for He₂⁺.



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

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

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

Orbital size effect: in Ψ_L σ_A is like He atom (more diffuse) than σ_B' (He⁺), vice versa in Ψ_L

Ψ_S represents a compromise

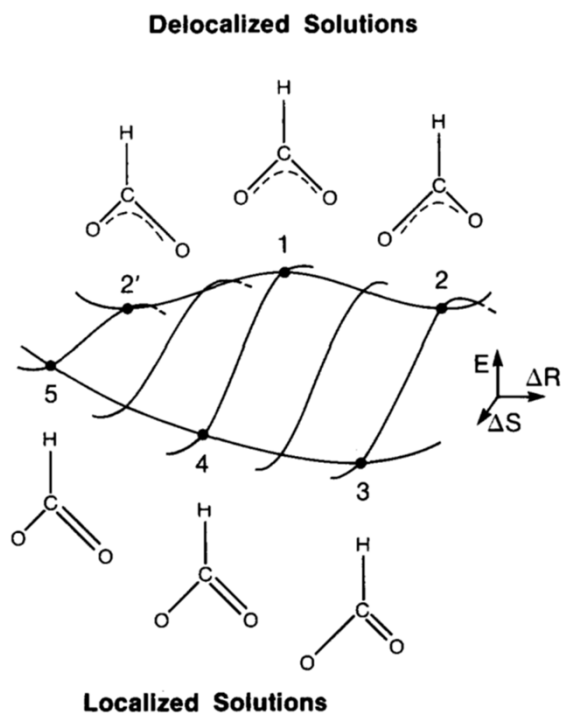
Resonance effect: included in Ψ_S , not in Ψ_L or Ψ_R

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 HCO_2



Generalized potential energy surface:

Two types of coordinates

$\Delta R = (R_{\text{CO1}} - R_{\text{CO2}})$ – asymmetric stretch

ΔS is a symmetry breaking coordinate in the orbitals, b_1 and a_2 π orbitals (C_{2v} symmetry) in this case

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

The valley 543 with positive ΔS , and an equivalent one with negative ΔS behind (not shown)

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

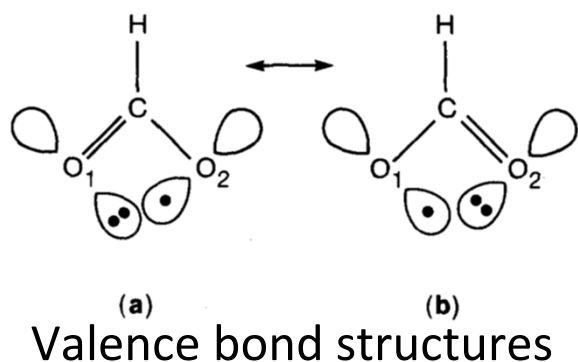
At point 1 the structure and the wavefunction have C_{2v} symmetry; however, this point is instable both with

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

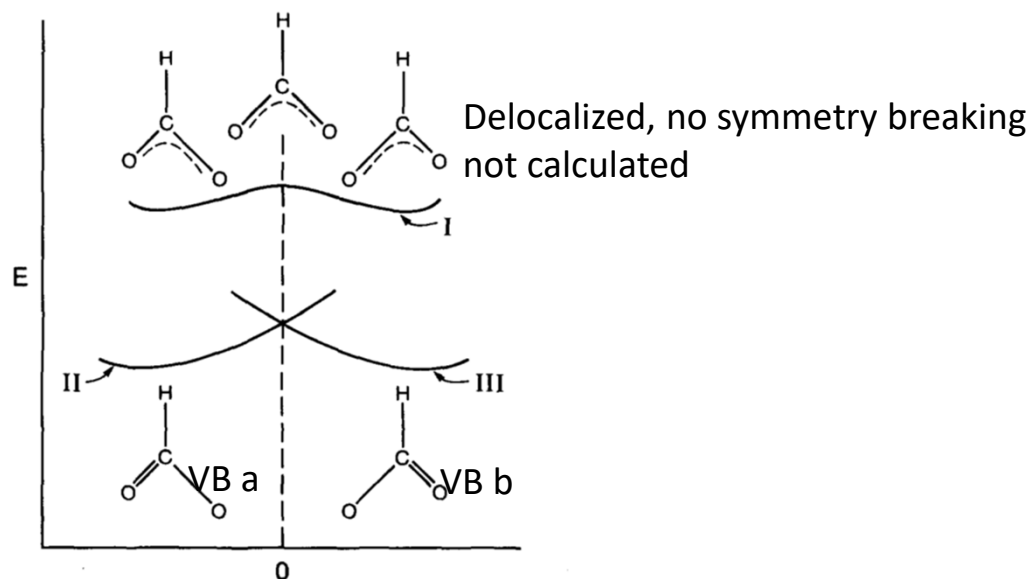
Point 2 is stable as minimum w.r.t. nuclear displacement, but the wavefunction is still

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

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



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



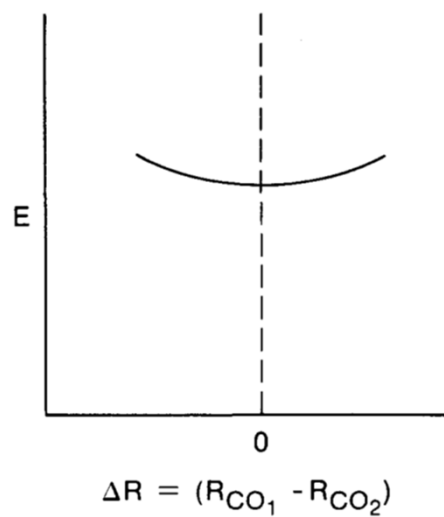
Requirement: starting point: SCF (MCSCF) wavefunctions which **do not** break symmetry, confirmation by MRCI
Wavefunctions I and II not suitable

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⁻, 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⁻¹.

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_{2v}) 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.

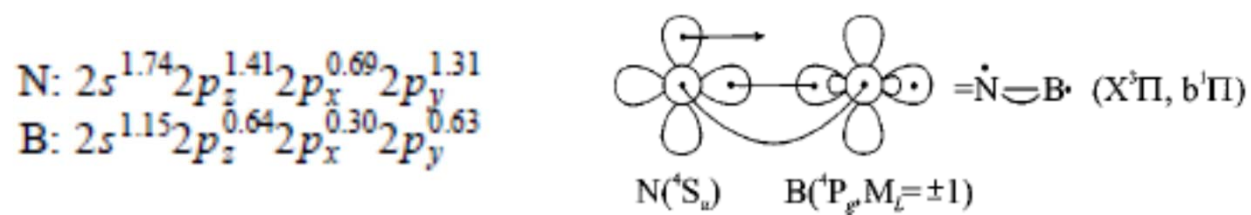
Kalamos, Dunning, and Mavridis, J. Chem. Phys. 120, 1813 (2004)

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 μ_e (D) of the ground $\tilde{X}^2\Sigma_u^+$ state of BNB at various levels of theory.

| Method | E_e | r_e (B ₁ N) | r_e (NB ₂) | μ_e | |
|-------------------------|--------------|--------------------------|--------------------------|---------|------------|
| CASSCF+PT2 ^a | -104.110 217 | 1.275 | 1.381 | 3.58 | asymmetric |
| SACASSCF+PT2 | -104.115 799 | 1.325 | 1.325 | 0.0 | |
| CASSCF+1+2 ^a | -104.113 720 | 1.273 | 1.381 | 3.66 | asymmetric |
| SACASSCF+1+2 | -104.112 996 | 1.324 | 1.324 | 0.0 | |

^a $C_{\infty v}$ 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: $2s^{1.49}2p^{1.36} \sim$ average between 2P and 4P

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

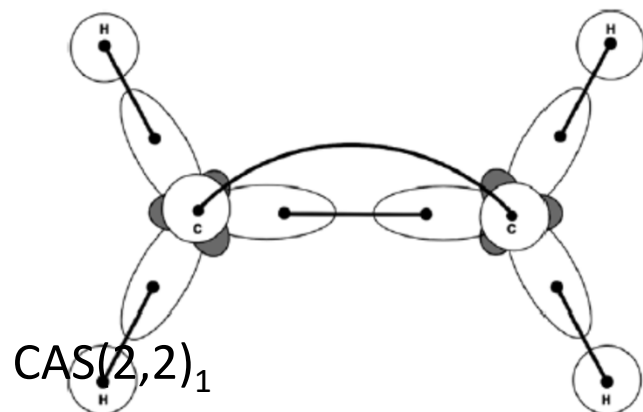
TABLE I. Energy (E_h) and internuclear distances r_{B_1N} , r_{B_2N} (Å) of the $\tilde{X}^2\Sigma_{(u)}^+$ BNB state at the (SA)CASSCF, (SA)CASSCF+1+ 2(= MRCI), ACPF, and MRCI+Q/cc-pVTZ levels of theory.

| 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 ^a | 103.866 236 | 1.3296 | 1.3296 | } symmetric |
| MRCI($9e^-$) ^b | 104.009 545 | 1.3227 | 1.3227 | |
| MRCI($9e^-$)+Q ^c | 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($11e^-$) ^d | 104.099 702 | 1.3845 | 1.2814 | |
| SACASSCF ^a | 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 ^a | 103.908 589 | 1.3606 | 1.3057 | |
| MRCI($11e^-$) ^e | 104.091 809 | 1.3558 | 1.3023 | |
| MRCI($11e^-$) ^f | 104.073 225 | 1.3371 | 1.3371 | Correlation of $2s_N$ is included |
| MRCI($11e^-$) ^g | 104.087 950 | 1.3310 | 1.3310 | |

Generalized Valence Bond (GVB) Theory with COLUMBUS

Example ethylene

R. Shepard, G. S. Kedzior, H. Lischka, I. Shavitt, Th. Müller,
P. G. Szalay, M. Kállay, M. Seth, Chemical Physics **349** (2008) 37



Structure of the GVB wavefunction

GVB wavefunction: direct product of electron-pair
wavefunctions $CAS(2,2)_1 \times CAS(2,2)_2 \times \dots \times CAS(2,2)_6$
Including further occupation and spin restrictions

| | | Cumulative occupancy restrictions | | Cumulative spin restrictions Perfect Pairing (PP) GVB-RCI | | | |
|-----------------------|--|--------------------------------------|--------|-----------------------------------------------------------------|------|-------------------------|------|
| | | occmin | occmax | bmin | bmax | bmin | bmax |
| CAS(2,2) ₆ | | 12 | 12 | 0 | 0 | 0 | 0 |
| | | 10 | 12 | 0 | 0 | 0 | 1 |
| | | 10 | 10 | 0 | 0 | 0 | 2 |
| | | 8 | 10 | 0 | 0 | 0 | 3 |
| | | 8 | 8 | 0 | 0 | 0 | 4 |
| | | 6 | 8 | 0 | 0 | 0 | 5 |
| | | 6 | 6 | 0 | 0 | 0 | 6 |
| | | 4 | 6 | 0 | 0 | 0 | 5 |
| | | 4 | 4 | 0 | 0 | 0 | 4 |
| | | 2 | 4 | 0 | 0 | 0 | 3 |
| CAS(2,2) ₁ | | 2 | 2 | 0 | 0 | 0 | 2 |
| | | 0 | 2 | 0 | 0 | 0 | 1 |
| $b_i = 2S_i$ | | | | | | | |
| | | | | Each pair: | | additional inter pair | |
| | | | | + | | correlation by means of | |
| | | | | intra pair correlation | | high-spin intermediates | |

Invariant subspaces

COLUMBUS input for MCSCF calculation:

mcdrtin.1:

```
:  
:  
1 1 1 2 / doubly occupied orbitals  
1 3 1 14 1 4 1 13 1 5 1 12 1 6 1 11 1 7 1 10 1 8 1 9  
/ active orbitals  
0 2 2 4 4 6 6 8 8 10 10 12 / occmin  
2 2 4 4 6 6 8 8 10 10 12 12 / occmax  
0 0 0 0 0 0 0 0 0 0 0 / bmin  
0 0 0 0 0 0 0 0 0 0 0 / bmax
```

mcscfin:

```
:  
:  
FCIORB= 1,3,0,1,4,0,1,5,0,1,6,0,1,7,0,1,8,0,1,9,0,1,10,0,1,11,0,1,12,0,  
1,13,0,1,14,0
```

GVB-PP Orbitals:

