The 2^{nd} Valence Bond Workshop

Last updated on June 13, 2015

WELCOME TO

THE 2nd VALENCE BOND WORKSHOP

XMVB 2.1 is the program for computer exercises.

For details of XMVB, see

http://www.xmvb.org

B

LECTURERS FOR VB WORKSHOP

Lecture 1	Philippe C. Hiberty
Lecture 2	Peifeng Su
Lecture 3	Sason Shaik
Lecture 4	Wei Wu

TUTORS FOR VB WORKSHOP

Benoît Braïda	Université Pierre et Marie Curie, France
Zhenhua Chen	Xiamen University, China
David Danovich	Hebrew University, Israel
John Galbraith	Marist College, USA
Philippe C. Hiberty	Université Paris-Sud 11, France
Stéphane Humbel	Aix Marseille Université, France
Sason Shaik	Hebrew University, Israel
Avital Shurki	Hebrew University, Israel
Jinshuai Song	Xiamen University, China
Peifeng Su	Xiamen University, China
Wei Wu	Xiamen University, China
Fuming Ying	Xiamen University, China

PROGRAM OF THE 2ND VB WORKSHOP

14:00-15:00, Jun 16	VB Lecture 1	Chemistry Conference Hall
15:00-15:45, Jun 16	VB Lecture 2	Chemistry Conference Hall
16:05-17:45, Jun 16	VB Tutorial 1	Room 601 & 602 No. 5 Jiageng Building
14:00-15:00, Jun 17	VB Lecture 3	Chemistry Conference Hall
15:00-15:45, Jun 17	VB Lecture 4	Chemistry Conference Hall
16:05-17:45, Jun 17	VB Tutorial 2	Room 601 & 602 No. 5 Jiageng Building
09:00-12:35, Jun 18	VB Tutorial 3	Room 601 & 602 No. 5 Jiageng Building
14:00-17:45, Jun 18	VB Tutorial 4	Room 601 & 602 No. 5 Jiageng Building

Contents

I Quickstart Guide to XMVB 2.1 1
0.1 The New features in XMVB 2.1 3
0.2 How to run an XMVB job? 3
  0.2.1 XMVB as a stand-alone program 3
  0.2.2 XMVB as a GAMESS-US module 5
0.3 Keywords in XMVB 2.1 for this tutorial . . . 5
  0.3.1 Global keywords 5
  0.3.2 Structure specification 7
  0.3.3 Keywords for VBSCF 7
  0.3.4 Keywords for BOVB 8
  0.3.5 Keywords for VBCI 9

II Tutorial for XMVB 2.1 11

1 BASICS OF THE XMVB PROGRAM AND CHARGE-SHIFT BONDING 13
Exercise 1.1 Calculations on H_2 13
Exercise 1.2 Calculations on HF molecule 14
Exercise 1.3 Calculations of F_2 15
Exercise 1.4 BOVB bonding energies, and ”Charge-Shift Bonding” (CSB) resonance energies 17
Exercise O1 Reactivity of CH_3Cl vs. SiH_3Cl 19
Exercise O2 Calculations on Au_2 20

2 Π SYSTEMS AND MULTIPLE BONDING 21

Exercise 2.1 Ozone and sulfer dioxide 21
Exercise 2.2 Benzene and anthracene 23
Exercise O3 The triplet and singlet states of O_2 25
Exercise O4 Full and partial calculation of N_2 26

3 CHEMICAL REACTIVITY **27**
Exercise 3.1 Identity hydrogen abstraction reaction 27
Exercise O5 Cope Rearrangement 30

4 OPTIONAL PAPER EXERCISES **33**
Exercise 4.1 H_2 33
Exercise 4.2 The lone pairs of H_2O 34
Exercise 4.3 S_N2 reaction 35
Exercise 4.4 Allyl radical 35
Exercise 4.5 Rumer basis set of VB structures 37

ANSWERS TO THE PAPER EXERCISES **39**
Answer 4.1 H_2 39
Answer 4.2 The lone pairs of H_2O 40
Answer 4.3 S_N2 reaction 42
Answer 4.4 Allyl radical 43
Answer 4.5 Rumer basis set of VB structures 47

Part I

Quickstart Guide to XMVB 2.1

0.1 The New features in XMVB 2.1

XMVB 2.1 includes the following new features/improvements:

1. Fixed bugs found in XMVB 2.0 in structure generation, BOVB calculations, etc.
2. Stand-alone XMVB is now implemented in Fortran 90 and supports dynamic memory allocation.
3. A new VBSCF algorithm with full hessian matrix is implementedf in stand-alone XMVB 2.1.
4. Prallelizations is supproted in stand-alone XMVB by intorducing OpenMP into XMVB 2.1.

0.2 How to run an XMVB job?

This section may introduce a brief procedure to run an XMVB job. For detials, please refer to XMVB manual at http://www.xmvb.org/art.php?id=8.

0.2.1 XMVB as a stand-alone program

A complete XMVB job includes follwoign steps:

0.2.1.1 Integral preparation

If you have already had the integrals from previous XMVB jobs, you may skip this to the next directly.

The integrals for XMVB job are obtained from other programs, such as PREINT, a program written by Wei Wus group for XMVB, and GAMESS-US. For PREINT, one may just prepare the input file input.inp and type command

```
preint input.inp
```

For GAMESS-US, you may need a GAMESS-US module for XMVB (see 0.2.2) first. After linking the module into GAMESS-US, you may prepare an input file input.inp with keyword VBTYP=XMVB specified in $CONTRL section. Then just run the GAMESS-US as

```
rungms input.inp mygms 1 >& output.out
```

Replace *mygms* with your own GAMESS-US program with XMVB implemented and keep the CPU number 1 unchanged since XMVB cannot be run in parallel with GAMESS-US. After this step, you may get three files: 1-e integral file **x1e.int**, 2-e integral file **x2e.int**, and a file **INFO** with coordinates and basis function information.

0.2.1.2 Run XMVB job

After obtaining the integrals, create an input file file.xmi for your job (for details, see section 0.3). Then run the XMVB job by typing command

```
xmvb file.xmi
```

Then an output file with name file.xmo will be obtained.

By default, the above command may run the XMVB job with ***ALL*** processors in your computer. Set the variable OMP_NUM_THREADS as

```
export OMP NUM THREADS=N
```

if you just need a certain number N of CPUs for your job.

For large systems, parallel XMVB may proceed a strange segmentation fault. This is because the stack size of threads is not large enough. Set the variable OMP_STACKSIZE to a certain number to avoid this error. For example, command

```
export OMP_STACKSIZE=1G
```

will set OMP_STACKSIZE to 1GB and then each thread may have 1GB stack size for the computation.

0.2.2 XMVB as a GAMESS-US module

An object file xmvb.o is essential in this situation. You may run XMVB as a GAMESS-US module after linking the object file into GAMESS-US. You may prepare two files, file.inp and file.xmi, for GAMESS-US and XMVB respectively, sharing the same filename. Then just type the command

```
rungms file mygms 1 >& file.out
```

to run the GAMESS-US. GAMESS-US will first run a HF calculation then XMVB automatically.

Tips:

1. By default, XMVB guess and input files will not be copied into the $SCR directory, which is the real directory where GAMESS-US is doing the calculation. Please copy these files into your $SCR directory *BEFORE* the calculation. Otherwise an error may occur.

2. After the calculation, the integral files and XMVB outputs will also be left in $SCR. Integral files may be used for XMVB calculations with stand-alone XMVB program (see 0.2.1.1). Please remember to get them if you need them later for stand-alone XMVB.

0.3 Keywords in XMVB 2.1 for this tutorial

0.3.1 Global keywords

NMUL=*n*: The multiplicity of the system. The default value is 1, which means the singlet.

ORBTYP=*OPTION*: Orbital type. Available options are:

GEN: The general case. Orbitals will be described as the list of basis function numbers on which the orbital expands. This is the default value.

HAO: Hybrid atomic orbitals. Orbitals will be described according to either atoms or SAOs. See FRGTYP for details.

BDO: Bond distorted orbitals. Localized orbitals will be described as ORBTYP=GEN and XMVB will delocalize them according to the bondings described in $STR.

OEO: Overlap enhance orbitals. Orbitals will delocalize in the whole system. In this case $ORB is not needed.

FRGTYP=*OPTION*: Fragment type. Available options are:

ATOM: The basis functions are fragmented according to atoms. $FRAG is relavent in this case. This is the default value.

SAO: Symmetrized atomic orbitals. The fragments are built according to the symmetries (s, p_x , p_y , $\ldots$). $FRAG is needed.

GUESS=*OPTION*: Describes the way to generate or read the initial guess for a VB computation. Valid options can be:

AUTO: The program automatically provides guess orbitals by diagonalizing a fragment-localized Fock matrix. This is the default option.

UNIT: The first basis function of an orbital in $ORB is set to be the guess for the orbital.

READ: Guess orbitals are read from external file, which should be provided by user.

MO: Initial guess of VB orbitals will be obtained directly from molecular orbitals. A $GUS section in the input file is needed.

RDCI: Initial guess in VBCI type will be given by users.

Note that GUESS=AUTO generally works when the active and inactive sets of orbital expand on disjoint subset of basis functions (like in σ/π separation for instanfce.)

0.3.2 Structure specification

NSTR=*n*: Number of VB structures specified in $STR.

STR=*OPTION*: Automatically generate VB structures according to NAO and NAE (see below) specified. Available options are:

COV:	Covalent structures will be generated.
ION[(*n*-*m*)]:	Ionic structures will be generated. A simple ION will generate all ionic structures; ION(*n*,*m*) will generate only the *n*-th and *m*-th order ionic structures and ION(*n*-*m*) will generate ionic structures from the *n*-th to the *m*-th order.
FULL:	All VB structures will be generated.

NAO=*n*: Number of active orbitals.

NAE=*n*: Number of active electrons.

0.3.3 Keywords for VBSCF

VBSCF: Run VBSCF calculation. This is the default choice and hence can be neglected.

ISCF=*n*: Specifies orbital optimization algorithm. The value *n* can be:

1. Numerical gradients with forward-difference approximation are used with the DFP-BFS algorithm. This is the default option of XMVB.

2. Analytical gradients in terms of basis functions with the L-BFGS algorithm. This algorithm involves only the first-order density matrix and is not suitable in cases displaying structures that are orthogonal to each other.

3. Numerical gradients with central-difference approximation are used with the DFP-BFS algorithm.

4. Optimization with Generalized Brillouin Theory(GBT)is requested.
5. Analytical gradients in terms of VB orbitals with the L-BFGS algorithm. This is the most efficient algorithm so far. NAO and NAE are needed.
6. VBSCF with full hessian matrix. NAO and NAE are needed. This algorithm is potentially faster and more robus than ISCF=5, but it is still under development and thus shall not be used in the current version of the program.

BOYS: Boys localization will be proceeded. This is essential if VBSCF result is used as the initial guess of VBCI.

0.3.4 Keywords for BOVB

BOVB: Run BOVB calculation.

NCOR=*n*: Number of core orbitals. The first *n* orbitals will keep the same as VBSCF in all structures.

ISCF=*n*: Specifies orbital optimization algorithm. The value *n* can be:

1. Numerical gradients with forward-difference approximation are used with the DFP-BFS algorithm. This is the default option of XMVB.
2. Analytical gradients in terms of basis functions with the L-BFGS algorithm. This algorithm involves only the first-order density matrix. This is recommended option for BOVB, except in cases where some structures are orthogonal to each other which cannot be handled properly by this algorithm.
3. Numerical gradients with central-difference approximation are used with the DFP-BFS algorithm.

0.3.5 Keywords for VBCI

VBCIS: VBCI with only singly excitation.

VBCISD: VBCI with both singly and doubly excitation.

NCOR=*n*: Number of core orbitals. Electrons in the first *n* orbitals will not be excited .

Part II

Tutorial for XMVB 2.1

LESSON 1

BASICS OF THE XMVB PROGRAM AND CHARGE-SHIFT BONDING

Exercise 1.1 Calculations on H_2

The simplest example in VB theory is the H_2 molecule. In this exercise all the input files have been prepared and commented by the tutors, so the participants will only have to read the .xmi input files to understand its format, run VBSCF, L-BOVB and D-BOVB calculations, and analyze the .xmo outputs.

Basis set: cc-pVDZ
Orbitals: HAOs with FRGTYP=ATOM
GUESS=AUTO (VBSCF) and GUESS=READ (BOVB)

Steps in the exercise:

1. Prepare the integrals with PREINT for the H_2 molecule
   preint h2-int.inp
   with $r_{\text{H-H}} = 0.74\text{Å}$.

2. Examine the h2-lvbscf.xmi input. Do L-VBSCF calculation for H_2 with command:
   xmvb h2-lvbscf.xmi

3. Copy VBSCF optimized orbitals to BOVB guess orbital file[1]:
   cp h2-lvbscf.orb h2-lbovb.gus

4. Examine the h2-lbovb.xmi input and see the differences with the h2-lvbscf.xmi input. Do L-BOVB claculaiton for H_2 with command:
   xmvb h2-lbovb.xmi

5. Analyze the XMO outputs, and get from them:

   - the total energy;
   - the weights of structures;
   - the overlap between covalent and ionic structures.

Exercise 1.2 Calculations on HF molecule

In this exercise also all the input files have been prepared and commented by the tutors, so the participants will only have to read the .xmi input files to understand its format, run VBSCF, L-BOVB and D-BOVB calculations, and analyze the .xmo outputs.

Basis set: cc-pVDZ
Orbitals: HAOs with FRGTYP=SAO

---

[1] Albeit not necessary for such a simple molecule, in the general case we *strong* recommand to *systematically* do L-BOVB calculation taking converged L-VBSCF orbitals as a guess. For doing that you have to copy the converged L-VBSCF orbitals (h2-lvbscf.orb file) to the guess orbital file for the L-BOVB calculations (h2-lbovb.gus file), and put "*GUESS=READ*" in the $CTRL section.

GUESS=AUTO (VBSCF) and GUESS=READ (BOVB)

Steps in this exercise:

1. Prepare the integrals with PREINT for the HF molecule at $r_{\text{H-F}} =$ 0.917Å.
2. Examin the hf-lvbscf.xmi input. Do L-VBSCF calculation for HF with command:
   xmvb hf-lvbscf.xmi
3. Examine the hf-lbovb.xmi input, and see the differences with the hf-lvbscf.xmi input. Do L-BOVB calculation for HF (hf-lbovb.xmi file) using the orbitals obtained at the previous step as a guess[2].
4. Do D-BOVB calculation (hf-dbovb.xmi file) using the orbitals obtained at the previous step as a guess[3]. At the D-BOVB level the active orbitals are kept localized and frozen, while the inactive orbitals are let delocalize over the entire basis of functions.
5. Analyze the XMO outputs, and get from it:
   - the total energy;
   - the weights of structures;
   - the overlap between covalent and ionic structures.

Exercise 1.3 Calculations of F_2

In this exercise, the participants will be asked to prepare themselves all the input files, using the input files from the previous HF calculation as a template.

---

[2] Copy the converged L-VBSCF orbitals (hf-lvbscf.orb file) to the guess orbital file for the L-BOVB calculations (hf-lbovb.gus file), and put "*GUESS=READ*" in the $CTRL section in the L-BOVB input file.

[3] D-BOVB calculations are *necessarily* done by taking converged L-BOVB orbitals as a guess, as the active orbitals are frozen in this step.

Basis set: cc-pVDZ
Orbitals: HAOs with FRGTYP=SAO
GUESS=AUTO
Steps in the exercise:

1. Prepare the integrals with PREINT at $r_{\text{F-F}} = 1.41\text{Å}$.

2. Prepare the input for the L-VBSCF wave function including three structures: one covalent and two ionics, and run the calculation[4].

3. Prepare input of the full L-BOVB wave function and run the calculation[5].

4. Prepare input of the full D-BOVB wave function and run the calculation[6].

5. Analysis of the structures weights:

    - Comment the evolution of the structure covalent vs. ionic weights between the different levels of theory (L-VBSCF, L-BOVB and D-BOVB) for the F_2 molecule.
    - Compare the values of the L-BOVB structure weights of H_2, HF and F_2 molecules.

---

[4] To input a selection of structures, you should add a "$STR" section in the .xmi file specifying your structures one by one (see VBSCF output for the HF molecule as an example), and replace "STR=FULL" by "NSTR=X" in the $CTRL section, where "X" is the number of structures in your $STR section.

[5] *Always* use the orbitals obtained at the previous step as initial guess. If you use the L-VBSCF input file as a template, don't forget to change "ISCF=5" to "ISCF=2" in the $CTRL section (The "ISCF=5" algorithm is more advanced and much faster than the "ISCF=2" algorithm, but it cannot be used with BOVB).

[6] *Always* use converged L-BOVB orbitals as a guess for D-BOVB calculations where the active orbitals are frozen.

Exercise 1.4 BOVB bonding energies, and ”Charge-Shift Bonding” (CSB) resonance energies

In this exercise, the bond dissociation energies of the H_2, HF and F_2 molecules will first be calculated at the BOVB level, and compared with the reference values. Then in the optional part, the CSB resonance energies will be computed for the three molecules, and participants will conclude for each bond whether it should be classified as a standard polar-covalent bond, or as a charge-shift bond.

Basis set: cc-pVDZ
Orbitals: HAOs with FRGTYP=SAO
GUESS=AUTO

Steps in the exercise:

1. Bond dissociation energies (D_e).
   Here we will learn how to calculate the bonding energy with XMVB using the molecules we used in the previous sections. The bonding energy D_e of a molecule AB is defined as the energy difference between the molecule at equilibrium geometry adn the separate fragments A and B:

$$D_e = (E_A + E_B) - E_{AB} \tag{1.1}$$

   I Compute the Restricted Open-Shell Hartree-Fock (ROHF) energies for the hydrogen and fluorine atoms with the PREINT program.

   II Calculate, using results of question 1I of this exercise and results of the previous exercises, the bond dissociation energies (D_e) of H_2 at the L-BOVB level, and of HF and F_2 at the D-BOVB level, respectively. *Hint: for these molecules* *the dissociation limit of the L/D-BOVB wave function corresponds to the atoms calculted at the ROHF level.*

2. OPTIONAL PART: CSB resonance energies. For the H_2, HF and F_2 molecules, do the following calculations in the folders of the previous exercises:

   I Prepare an input for a ONE-structure L-VBSCF wave function including only the covalent structure, and run the calculation. *Hint: you may use the L-VBSCF inputs prepared in previous exercises, and specify only one covalent structure in the $STR section (together with NSTR=1 in the $CTRL section).*

   II Prepare an input of the one-structure (covalent) D-VBSCF wave function for HF and F_2, and run the calculation, using the L-VBSCF orbitals, obtained at the previous step as initial guess.

   III Calculate the CSB resonance energies (RE_{CS}) for H_2 by taking the difference between the L-BOVB total energy obtained in the Exercise 1.1 and the L-VBSCF covalent energy obtained in the previous question[7].

   IV Calculate the CSB resonance energies (RE_{CS}) for HF and F_2, by taking the difference between the D-BOVB total energies obtained in the Exercise 1.2 and Exercise 1.3, and the D-VBSCF covalent structure energies obtained in the previous question[7].

3. Compute for the three molecules the percentage of RE_{CS} relative to the D_e, and conclude to the character of each of these three bonds (is it a normal polar-covalent bond, or a CSB).*Hint: A bond is considered as "Charge-Shift" when the RE_{CS} represents more than 50% of the total D_e.*

Reference: *Nat. Chem.* **2009**, 1, 443.

---

[7] Hint: in one-structure calculations, the VBSCF and BOVB levels are identical.

Exercise O1 Reactivity of CH_3Cl vs. SiH_3Cl

In this exercise, we will compare the reactivities of CH_3Cl and SiH_3Cl. First, D-BOVB calculations of these 2 molecules will be proceeded. Then we will analyze the result, find the nature of C−Cl and Si−Cl bonds and the difference of reactivity between these molecules in S_N1 reactions.

Basis set: 6-31G*
Orbitals: HAOs with FRGTYP=ATOM
GUESS=MO (VBSCF) and GUESS=READ (BOVB)

Perform the calculations of CH_3Cl and SiH_3Cl in different subfolders to avoid any confusion with the integral files.

The L-VBSCF input files and orbital guess are provided for the CH_3Cl and SiH_3Cl molecules.

1. Following the same procedure as in Exercise 1.2, compute the three-structure D-BOVB wave function for the CH_3Cl and SiH_3Cl molecules. Compare the values of the D-BOVB structure weights between the two molecules.

2. Following the same procedure as in Exercise 1.4, compute the CSB resonance energies of the CH_3Cl and SiH_3Cl molecules. Conclusion for the nature of the C−Cl and Si−Cl bonds.

3. What do the results of the previous questions imply in terms of the compared reactivity of CH_3Cl and SiH_3Cl molecules (in a S_N1 reaction for instance)?

For a more detailed treatment including solvent VB calculations, see reference:

J. Phys. Chem. A **2008**, 112, 2988.

Exercise O2 Calculations on Au_2

In this exercise, the Au_2 will be calculated with VBSCF & BOVB method. The integrals and input files are already prepared for the participants.

Basis set: Lanl2DZ
Orbitals: HAOs with FRGTYP=SAO

Steps in the exercise:

1. Run the VBSCF calculation with prepared input file.
2. Run the L-BOVB and D-BOVB calculations with prepared input file.
3. Analyze the XMO outputs, and get from it:
    - the total energy;
    - the weights of structures;
    - the overlap between covalent and ionic structures.

LESSON 2

Π SYSTEMS AND MULTIPLE BONDING

Exercise 2.1 Ozone and sulfer dioxide

In this exercise, the π systems of O_3 and SO_2 will be computed, analyzed and compared, at the σ-D-VBSCF and σ-D-BOVB levels. All π-type electrons/orbitals are taken as active (and thus localized), and all σ-type electrons/orbitals are inactive and delocalized over the whole molecule. Because the active and inactive sets of orbitals expand on different basis functions, in this exercise the D-VBSCF and D-BOVB calculations can each be done in a single step in which both active and inactive orbitals are optimized simultaneously, because the inactive σ orbitals and the active π orbitals expand on disjoint subsets of basis functions. So there is no need to freeze any orbital. We will refer to these calculations as σ-D-VBSCF and σ-D-BOVB to distinguish them from standard D-VBSCF and D-BOVB levels. The ”σ-D” label indicates that the σ orbitals are inactive and delocalized over the whole molecule. Using ”FRGTYP=SAO” is necessary. The σ-D-VBSCF input files are provided.

The contrasted reactivity of O_3 vs. SO_2 will then be explained from the VB analysis.

Basis set: cc-pVDZ
Orbitals: HAOs with FRGTYP=SAO
GUESS=AUTO

Steps in the exercises:

1. Analysis:

   I Analyze the σ-D-VBSCF input files, and in particular see that the π system only is described at the VB level using orbitals localized on one atom, while the σ system is described as inactive using delocalized MOs.

   II What is the Rumer basis for the description of the π system of O_3 and SO_2 at the VB level[1]? Which structures should we neglect in the BOVB calculation? Run the VBSCF calculations using ”STR=FULL” keyword to check your result. Don’t forget to use NCOR=X, where X is the number of core orbitals in the calculations.

2. Run the σ-D-BOVB calculation for O_3 and SO_2 using a selection of structures[2,3], and, as usual, the orbitals obtained from the previous VBSCF calculation as a guess[4].

3. Reactivity: Compare the structure weights for O_3 and SO_2. How could you explain the high reactivity of ozone, vs. the very low reactivity of SO_2[5]?

---

[1] Hint: this is a 4-electron/3-active-orbital problem.

[2] We will retain in this exercise only the structures that have a weight larger than 2% in at least one of the two molecules (O_3 or SO_2) at the VBSCF level. In any case, you should *never* include in a BOVB calculation structures that have a weight lower than 1%, as this may lead to convergence issue.

[3] You may copy-paste the structures description from the VBSCF output file.

[4] Don’t forget to change ”GUESS=AUTO” by ”GUESS=READ” in the $CTRL section, and to change ISCF=5 by ISCF=2

[5] In the references below, it is shown that the reaction barriers of dipolor cycloadditions correlate well with the biradical character in the 1,3 dipole.

References:

- *J. Am. Chem. Soc.*, **2010**, 132, 7631.

- *J. Chem. Theory Comput.*, **2011**, 7(7), 2104.

Exercise 2.2 Benzene and anthracene

Benzene and anthracene are also famous π systems. In this exercise, we may do the VBSCF calculations with covalent structures. Both localized and delocalized π orbitals will be used in the calculations.

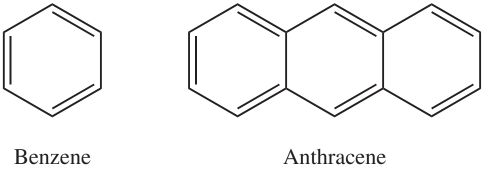


Figure 2.1: Benzene and anthracene

Basis set: 6-31G*
Orbitals: HAOs and OEOs, FRGTYP=SAO
GUESS=AUTO

Steps in the exercise:

1. Benzene:

   I Use the Rumer's diagram rule to derive the Rumer basis of covalent structures for benzene. These structures will be used in the following calculations.

- II Compute a D-VBSCF wave function for benzene using the structures selected in the previous question (π orbitals are localized AOs, σ orbitals are delocalized MOs).
- III Compute a VBSCF wave function starting from the guess orbitals at the previous step, and delocalizing the π orbitals using Overlap Enhance Orbitals (”ORBTYP=OEO” keyword in the $CTRL section)[6]. Compare the weights and energies with the wave functions computed at the previous step.
- IV Repeat step 1II and 1III for a wave function containing only the two Kekulé structures of Benzene. Compare the difference in total energies for the full covalent and 2-structure calculations:
  - i When AOs are used;
  - ii When OEOs are used.
- V What do you conclude concerning VB calculations including OEOs?

2. Anthracene:
   - I Propose a complete set of Kekulé structures for Anthracene[7].
   - II Compute a D-VBSCF wave function for anthracene using the structures selected at the previous question. Fully delocalized MOs are used for the σ space (inactive), and strictly localized AOs in the π space (active).
   - III Compute a VBSCF wave function starting from the guess orbitals obtained at the previous step, and delocalizing the π orbitals using OEO orbitals[6].
   - IV Compare the total energies of the two wave functions, and explain the differences.

---

[6] When ”ORBTYP=OEO” is specified, no”FRGTYP” keyword is needed, and no $ORB section is needed.

[7] Kekulé structures shall only display covalent π bonds between two neighboring atoms (two atoms also connected by a σ bond).

Exercise O3 The triplet and singlet states of O_2

In this exercise, the triplet and singlet states of O_2 will be computed, analyzed and compared, at the σ-D-BOVB level, with the π system taken as active and σ system as inactive. Thus, as in Exercise 2.1, the σ-D-VBSCF and σ-D-BOVB calculations will be done in a single step, with both active and inactive orbitals being optimized simultaneously. The σ-D-VBSCF input files are provided, together with the σ-D-BOVB file and orbital guess for the singlet state.

Basis set: cc-pVTZ
Orbitals: HAOs with FRGTYP=SAO
GUESS=AUTO

Steps in the exercise:

1. Paperwork for the triplet O_2:

   I For each VB structure in the $STR section of the σ-D-VBSCF input file: draw a picture corresponding to it (using the usual convention of drawing of VB structures), and write below the mathematical expression of this structure considering the active system only. Which type of bonding do these structures describe?

   II Guess what would be the ranking of the different structures in terms of decreasing weights.

2. Compute the σ-D-VBSCF, and then σ-D-BOVB wave function for triplet O_2. Compare the ranking of the different structures in terms of decreasing weights coming out from the σ-D-BOVB calculations, with your guess from previous question.

3. Repeat questions 1 and 2 for the singlet O_2. In that case both σ-D-VBSCF and σ-D-BOVB input files are provided, so you

just need to run the calculations[8].

4. Compare the σ-D-BOVB energies for the triplet and singlet states of O_2. To which of the two states does the O=O Lewis structure correspond?

Exercise O4 Full and partial calculation of N_2

In this exercise, the full basis set of structures for the N_2 molecule will be computed at the L-VBSCF level, and then a structure selection will be made. This will teach the participants a systematic method to make a selection of structures out of a full basis L-VBSCF calculation. The L-VBSCF input files are provided.

Basis set: cc-pVTZ
Orbitals: HAOs with FRGTYP=SAO
GUESS=MO

Steps in the exercise:

1. Examine the L-VBSCF input file and understand it. Run the calculation.

2. Using the output of the previous calculation, make a selection of structures by retaining only the structures that has a weight larger than 1%. Run a new L-VBSCF using this subset of structures.

3. Compare the difference in total energies obtained at step 1 and 2, and comment.

---

[8] The O_2 singlet state belongs to the very rare cases displaying structures that are orthogonal to each other, so the much slower ISCF=1 algorithm has to be used. A good initial guess is thus provided to the participants.

LESSON 3

CHEMICAL REACTIVITY

In this lesson, barrier heights of various chemical reactions will be computed, and VBSCD diagrams will also be plotted.

Exercise 3.1 Identity hydrogen abstraction reaction

Chemical reaction in this exercise:

$$H_3C\bullet + H{-}CH_3 \longrightarrow [H_3C\cdots H\cdots CH_3] \longrightarrow H_3C{-}H + \bullet CH_3 \quad (3.1)$$

The geometries for the reactant and TS states are provided.

A template xmi input file is provided, without the structure block which has to be filled by the participants.

Basis set: 6-31G*
Orbitals: HAOs with FRGTYP=ATOM
GUESS=MO & GUESS=READ

Steps in the exercise:

1. Basis set of structures (this is a 3-electron/3-orbital problem):
    - I Examine the input files. What are the active orbitals? How many electrons occupy them?
    - II Propose a complete basis set of structures, draw a picture corresponding to each of them (using the usual convention of drawing of VB structures) and writing below their mathematical experssion. *Hint: you can check your result by performing a VBSCF calculation using the "STR=FULL" keyword.*
    - III Which combination of structures describes the reactant (R) electronic structure ($H_3C\bullet + H{-}CH_3$)? Which combination of structures describes the product (P) electronic structure ($H_3C{-}H + \bullet CH_3$)?
2. Compute VBSCF wave functions **at the reactant geometry**, for, respectively:
    - I A VBSCF function including only the structures corresponding to R;
    - II A VBSCF function including only the structures corresponding to P, and deduce from this value and the previous one the value of the gap "G" of the VBSCD diagrams;
    - III A VBSCF function including to the full basis set of structures (F).
3. Same question as step 2 **at the TS geometry**. Deduce from these values the value of the parameter "B" in the VBSCD diagrams.
4. Using results of questions 2 and 3, compute the reaction barrier for the identity hydrogen abstraction reaction at the VBSCF level. Compare with the Coupled-Cluster CCSD value of 22.9

kcal/mol and CCSD(T) value of 21.6 kcal/mol in the same basis set.

5. Repeat questions 2 to 4 at the VBCIS level[1].

6. Qualitatively draw the VBSCD diagram corresponding to the identity hydrogen abstraction reaction at the VBCIS level. *Hint: the VBSCD diagrams correspond to separate curves for R, P and F wave functions, at the reactant - TS - and product geometries.*

7. Rationalization of the barrier heights in the $H_3X-H-XH_3$ series of hydrogen abstraction reactions with X=C, Si, Ge, Pb:

   I Recall the simplest VBSCD theory expression for the energy barrier of any reaction as a function of the three fundamental parameters f, G and B. Briefly recall the definition of these three parameters.

   II Experimental and high level computed vertical bond energies (D) and Bond Dissociation Energies (BDE) are provided in Table 3.1. In the case of the identity hydrogen abstraction reactions, what are the expressions of the parameters G and B as functions of D and BDE?

   III The experimental and high level computed reaction barriers are provided in the Table 3.2. Calculate the VBSCD predicted energy barriers using the expressions recalled in questions 7I and 7II, and the data provided in Table 3.1. How does these predicted energy barriers compare with the experimental ones provided in Table 3.2?

   IV Rationalize the trend in the $H_3X-H-XH_3$ reaction barrier using VBSCD analysis.

---

[1] Hint: you should just add the keyword ”VBCIS” in the $CTRL section as compared with corresponding VBSCF input and use the corresponding converged VBSCF orbitals as a guess. Add also the keyword ”NCOR=2” to specify that the first 2 orbitals (which are inactive in the chemical process studied) will not be correlated at the VBCI level. The ”Davidson Corrected Energy” should be used to compute the reaction barries and draw the VBSCD diagram

Table 3.1: Experimental and CCSD(T)/CBS energy barriers (in kcal/mol) of the HAT reaction $X{-}H + {\bullet}X \longrightarrow X{\bullet} + H{-}X$

X	$E^{\ddagger}_{\mathrm{CCSD(T)/CBS}}$	$E^{\ddagger}_{\mathrm{exp}}$
CH_3	16.7	14.9
SiH_3	8.4	
GeH_3	5.8	
SnH_3	4.2	
PbH_3	1.8	

Table 3.2: CCSD(T)/CBS Bond Dissociation Energies (BDE) and vertical bond strength energies (D) (in kcal/mol) for the X−H bonds

X	BDE	D
C	103.2	110.0
Si	90.1	90.3
Ge	82.7	82.9
Sn	74.1	74.3
Pb	64.9	64.2

References:

- *Chem. Soc. Rev.*, **2014**, 43, 4968.
- *Angew. Chem. Int. Ed.*, **2012**, 51, 5556.

Exercise O5 Cope Rearrangement

The VBSCF and BOVB calculations of Cope rearrangement reaction (see fig 3.1) will be proceeded in this exercise. The geometries of reactant, product and TS are provided, along with orbital guess.

Basis set: 6-31G*
Orbitals: localized HAOs.

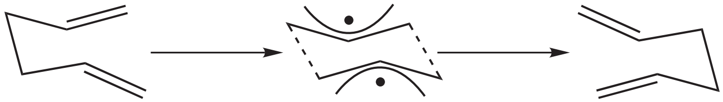


Figure 3.1: Cope Rearrangement

Steps in the exercise:

1. Compute VBSCF wave functions for the reactant, product and TS geometries, and calculate the barrier height.
2. Same question as 1 at the BOVB level. Compare the barrier heights with these two methods.

LESSON 4

OPTIONAL PAPER EXERCISES

Exercise 4.1 H_2

This exercise aims at learning the basics of VB theory. The participants will try to compare the descriptions of H_2 in both VB and MO way, and try to get the connection between VB and MO.

1. Develop the Heitler-London wave function for H_2 (include its usual expression with atomic orbitals *a* and *b*) in terms of spin-orbital products, and factorize it in terms of spatial part times a spin part, to show that it corresponds to a singlet state.

2. Propose a similar VB wave function for the triplet state.

3. Expand the Hartree-Fock configuration and the doubly excited configuration with a doubly occupied σ^* orbital for H_2 (Hund-Mulliken) in the basis of VB determinants (built on the atomic orbitals *a* and *b*). Make the correspondance with Pauling's VB wave function for H_2 including covalent/ionic superposition.

Exercise 4.2 The lone pairs of H_2O

This exercise aims at comparing two descriptions of the lone pair of H_2O: (i) the MO description in terms of non-equivalent canonical MOs and (ii) the ”rabbit-ear” VB description in terms of two equivalent hybrid orbitals. For further reading, see S. Shaik and P.C. Hiberty, ”The Chemist’s Guide to VB theory”, Wiley, Hoboken, New Jersey, 2008, pp. 107-109.

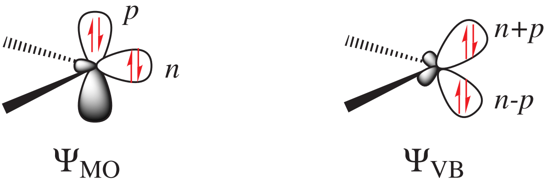


Figure 4.1: Lone pairs of H_2O represented in MO and VB theory

1. Focusing on the lone pairs only, write the four-electron single-determinants Ψ_{MO} and Ψ_{VB}.

2. Expand Ψ_{VB} into elementary determinants containing only n and p orbitals, eliminate determinants having two identical spinorbitals, and show the equivalence between Ψ_{MO} and Ψ_{VB}.

3. We now remove one electron from H_2O. Write the two possible VB structures Φ_1 and Φ_2 in the VB framework. By convention, one may write the doubly occupied lone pair first, then the singly occupied one.

4. The two ionized states are the symmetry-adapted conbinations $\frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2)$ and $\frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)$. Knowing that the sign of the hamiltonian matrix element $\langle \Phi_1 | \hat{H} | \Phi_2 \rangle$ is negative, give the energy ordering of the two ionized states.

5. By expanding the two ionized states into elementary determinants (dropping the normalization constants), show that they are equivalent, respectively, to the MO configurations $|n\bar{n}p|$ and $|p\bar{p}n|$.

Exercise 4.3 S$_N$2 reaction

We want to study the following S$_N$2 reaction using VB theory:

$$X\!:^- + A{-}X \longrightarrow X{-}A + :\!X^- \tag{4.1}$$

1. How many active electron and orbitals do we have to consider?
2. Write a complet basis of Lewis structures for this problem.
3. Write the mathematical expression of the corresponding VB structures, letting alone the inactive orbitals.
4. What structures describe the reactant electronic structure? The product electronic structure?
5. What will be the major structure(s) at the transition state geometry, for the S$_N$2 reaction on the carbon (A=CMe$_3$ for instance)? On the silicon (A=SiMe$_3$)?
6. Propose an expression for the gap G in the VBSCD theory function of experimental parameters. *Hint,: the expression involves vertical Ionization Energy(ies) and/or vertical Electron Attachement Energy(ies).*

Exercise 4.4 Allyl radical

In this exercise, the participants will try to write the VB structures of allyl radical, understand the spin density polarization of allyl radical with VB theory, and try to select a subset of VB structures from the complete set.

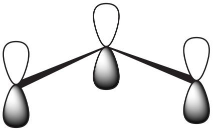


Figure 4.2: Allyl Radical

1. Covalent structures of the allyl radical:
   - I What are the three possible covalent structures for the allyl radical molecule?
   - II Show that the third structure can be expressed as a linear combination of the first two structures, and thus that only two of the three covalent structures form a complete basis of non-redundant structures (Rumer basis).
2. Understanding the pattern of spin density distributions in the allyl radical as found in EPR spectroscopy.
   - I Express the wave functions of the non-redundant structures (from 1I) of allyl radical in terms of the VB determinants. Write the wave function of the ground state of the allyl radical as a negative combination of the wave function of the non-redundant structures. Based on the expression of the spin density ρ_s

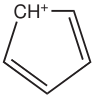
     $$\rho_k^s = N^2 \sum_i c_i^2 \delta_{ki} \tag{4.2}$$

     propose the spin density distribution in the allyl radical. In the above equation N is a normalization constant, c is the coefficient of the VB determinant in the wave function and δ is either $+1$ or -1 depending on whether the electron which is located on atom k in the i^{th} determinant is α or β spin, respectively.
   - II Show pictorially:

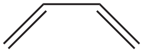
    a Why your spin density is polarized?
    b What would be the spin density in the excited state of ally radical (taking into account that resulting wave function is a positive combination of the Φ_L and Φ_R wave function)?
    c What would be the spin density pattern in pentadienyl radical? *Hint: reason on the total spin-alterned determinants as being the major one.*

3. What are the possible ionic structures for the allyl radical? Based on your chemical knowledge, propose a selection subset of the most chemical meaningful covalent + ionic structures.

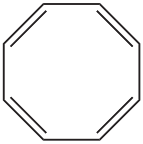
Exercise 4.5 Rumer basis set of VB structures



cyclopentadienyl cation



1,3-butadiene



cyclooctatetraene

1. Draw the Rumer basis set of covalent VB structures for cyclopentadienyl cation.

2. For 1,3-butadiene, draw the Rumer basis set of covalent VB structures, then the full basis set of covalent + ionic VB structures.

3. Draw the Rumer basis set of covalent VB structures for cyclooctatetraene.

ANSWERS TO THE PAPER EXERCISES

Answer 4.1 H_2

1.
$$\begin{aligned}\Psi_\mathrm{s} &= [a(1)\alpha(1)b(2)\beta(2) - a(1)\beta(1)b(2)\alpha(2)] \\ &= a(1)b(2)\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= a(1)b(2)\begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix}\end{aligned}$$

   The spatial part of Ψ_s is symmetric while the spin part is antisymmetric, so the wave function represents a singlet system.

2.
$$\begin{aligned}\Psi_\mathrm{t} &= [a(1)\alpha(1)b(2)\beta(2) - a(2)\beta(2)b(1)\alpha(1)] \\ &= [a(1)b(2) - b(1)a(2)]\,\alpha(1)\beta(2) \\ &= \begin{vmatrix} a(1) & b(1) \\ a(2) & b(2) \end{vmatrix}\alpha(1)\beta(2)\end{aligned}$$

   The spin part of Ψ_t is symmetric while the spacial part is antisymmetric, so the wave function represents a triplet system.

3. Assume that $\sigma = N_\sigma(a+b)$ and $\sigma^* = N_{\sigma^*}(a-b)$ where N_σ and N_{σ^*} are the normalization coefficients for MOs σ and σ^*.

The covalent and ionic wave functions in VB representation are:

$$\Psi_{\text{cov}} = |a\bar{b}| - |\bar{a}b|$$
$$\Psi_{\text{ion}} = |a\bar{a}| + |b\bar{b}|$$

And the HF wave functions can be represented as

$$\begin{aligned}
\Psi_{\text{HF}} &= |\sigma\bar{\sigma}| \\
&= N_{\sigma}^{2}|(a+b)\overline{(a+b)}| \\
&= N_{\sigma}^{2}\left(|a\bar{b}| + |b\bar{a}| + |a\bar{a}| + |b\bar{b}|\right) \\
&= N_{\sigma}^{2}\left(|a\bar{b}| - |\bar{a}b| + |a\bar{a}| + |b\bar{b}|\right) \\
&= N_{\sigma}^{2}\left(\Psi_{\text{cov}} + \Psi_{\text{ion}}\right)
\end{aligned}$$

$$\begin{aligned}
\Psi_{\text{HF}}^{*} &= |\sigma^{*}\bar{\sigma}^{*}| \\
&= N_{\sigma^{*}}^{2}|(a-b)\overline{(a-b)}| \\
&= N_{\sigma^{*}}^{2}\left(-(|a\bar{b}| + |b\bar{a}|) + |a\bar{a}| + |b\bar{b}|\right) \\
&= N_{\sigma^{*}}^{2}\left(-(|a\bar{b}| - |\bar{a}b|) + |a\bar{a}| + |b\bar{b}|\right) \\
&= N_{\sigma^{*}}^{2}\left(-\Psi_{\text{cov}} + \Psi_{\text{ion}}\right)
\end{aligned}$$

Answer 4.2 The lone pairs of H_2O

1.

$$\Psi_{\text{MO}} = |n\bar{n}p\bar{p}|$$

$$\Psi_{\text{VB}} = |\,(n-p)\,(\bar{n}-\bar{p})\,(n+p)\,(\bar{n}+\bar{p})\,|$$

2.

$$\begin{aligned}
\Psi_{\text{VB}} = &\,|\,(n\bar{n} - p\bar{n} - n\bar{p} + p\bar{p})\,(n\bar{n} + p\bar{n} + n\bar{p} + p\bar{p})\,| \\
= &\,|n\bar{n}n\bar{n}| + |n\bar{n}p\bar{n}| + |n\bar{n}n\bar{p}| + |n\bar{n}p\bar{p}| - |p\bar{n}n\bar{n}| \\
&- |p\bar{n}p\bar{n}| - |p\bar{n}n\bar{p}| - |p\bar{n}p\bar{p}| - |n\bar{p}n\bar{n}| - |n\bar{p}p\bar{n}| \\
&- |n\bar{p}n\bar{p}| - |n\bar{p}p\bar{p}| + |p\bar{p}n\bar{n}| + |p\bar{p}p\bar{n}| + |p\bar{p}n\bar{p}| \\
&+ |p\bar{p}p\bar{p}|
\end{aligned}$$

After eliminating all determinants having two orbitals with the same spin, there remains :

$$\Psi_{\mathrm{VB}} = |n\bar{n}p\bar{p}| - |p\bar{n}n\bar{p}| - |n\bar{p}p\bar{n}| + |p\bar{p}n\bar{n}|$$

After permuting the columns and changing signs accordingly, there remains : $\Psi_{\mathrm{VB}} = 4|n\bar{n}p\bar{p}| = \Psi_{\mathrm{MO}}$ (if one includes normalization factors).

3. $\Phi_1 = |\,(n-p)\,(\bar{n}-\bar{p})\,(n+p)\,|$, $\Phi_2 = |\,(n+p)\,(\bar{n}+\bar{p})\,(n-p)\,|$ Permuting the first and third orbitals in Φ_2 and changing the sign accordingly, we get $-\Phi_2$ that has maximum orbital correspondence with Φ_1 : $-\Phi_2 = |\,(n-p)\,(\bar{n}+\bar{p})\,(n+p)\,|$.

4. Φ_1 and $-\Phi_2$ differ by only one orbital, $(\bar{n}-\bar{p})$ in Φ_1 which becomes $(\bar{n}+\bar{p})$ in $-\Phi_2$. Therefore the matrix element $\langle\Phi_1|\hat{H}|-\Phi_2\rangle$ is a simple β integral, necessarily negative. Hence, the lowest ionized state is $\frac{1}{\sqrt{2}}(\Phi_1-\Phi_2)$ while the higher ionized state is $\frac{1}{\sqrt{2}}(\Phi_1+\Phi_2)$.

5.

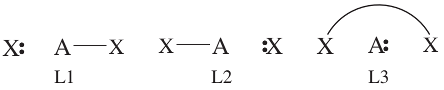
$$\begin{aligned}\Phi_1 &= |n\bar{n}n| - |p\bar{n}n| - |n\bar{p}n| + |p\bar{p}n| + |n\bar{n}p| \\ &\quad - |p\bar{n}p| - |n\bar{p}p| + |\bar{p}p| \\ &= +2|p\bar{p}n| + 2|n\bar{n}p|\end{aligned}$$

In the same way, one shows that $\Phi_2 = +2|p\bar{p}n| - 2|n\bar{n}p|$. It follows that :
$(\Phi_1 - \Phi_2) \propto |n\bar{n}p|$ (lowest ionized state in MO theory)
$(\Phi_1 + \Phi_2) \propto |p\bar{p}n|$ (higher ionized state in MO theory).
It is concluded that 1) VB theory yields two ionization potentials for H_2O, in agreement with experiment, and 2) that these ionization potentials are exactly the same as the ones found in elementary MO theory.

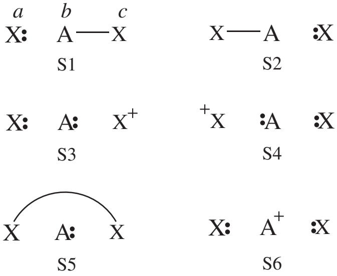
Answer 4.3 S_N2 reaction

1. We need to consider 4 active electrons and 3 active orbitals in this problem.

2. There are 3 Lewis structures in this problem, as shown below:



3. There are 6 VB structures in this problem, as shown below:



Assume that 3 orbitals are a, b and c, as shown above in S1. The 6 VB structures can be expressed as:

$$
\begin{aligned}
\Psi_{\mathrm{S1}} &= |a\bar{a}b\bar{c}| - |a\bar{a}\bar{b}c| \\
\Psi_{\mathrm{S2}} &= |c\bar{c}a\bar{b}| - |c\bar{c}b\bar{a}| \\
\Psi_{\mathrm{S3}} &= |a\bar{a}b\bar{b}| \\
\Psi_{\mathrm{S4}} &= |b\bar{b}c\bar{c}| \\
\Psi_{\mathrm{S5}} &= |b\bar{b}a\bar{c}| - |b\bar{b}\bar{a}c| \\
\Psi_{\mathrm{S6}} &= |a\bar{a}c\bar{c}|
\end{aligned}
$$

4. Structures S1, S3 and S6 describe the reactant state, and structures S2, S4 and S6 describe the product state.

5. Since the electronegativity of silicon is lower than that of carbon, the major structures will be S1 and S2 for when A=CMe$_3$ and S6 will be the major structure for A=SiMe$_3$.

6. The gap G can be expressed as

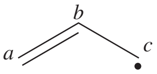
$$G = IE_{\mathrm{X}\colon^{-}} - EA_{\mathrm{AX}}$$

where $IE_{\mathrm{X}\colon^{-}}$ is the vertical ionization Energy of the nucleophile $\mathrm{X}\colon^{-}$, and EA_{AX} is the vertical electron attachment energy (electron affinity) of the A−X molecule.

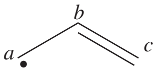
Answer 4.4 Allyl radical

1. Covalent structures of the allyl radical:

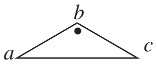
   I The following are the three possible covalent structures:



Φ_1



Φ_2



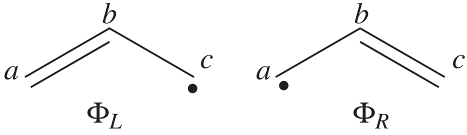
Φ_3

   II

$$\Phi_1 = |a\bar{b}c| - |\bar{a}bc|$$
$$\Phi_2 = |ab\bar{c}| - |a\bar{b}c|$$
$$\Phi_3 = |ab\bar{c}| - |\bar{a}bc| = \Phi_1 + \Phi_2$$

   Since Φ_3 is the positive combination of Φ_1 and Φ_2, the two first structures form a complete basis of non-redundant structures.

2. Understanding the pattern of spin density distributions in the allyl radical as found in EPR spectroscopy



I The wave functions of the non-redundant structures are

$$\Phi_L = \frac{1}{\sqrt{2}}\left[|a\bar{b}c| - |\bar{a}bc|\right]$$

$$\Phi_R = \frac{1}{\sqrt{2}}\left[|ab\bar{c}| - |a\bar{b}c|\right]$$

The negative combination of these two wave functions determines the ground state wave-function of allyl radical

$$\Phi_{\text{GS}} = \Phi_L - \Phi_R = \frac{1}{sqrt6}\left[2|a\bar{b}c| - |\bar{a}bc| - |ab\bar{c}|\right]$$

We note with that respect that the determinant with the largest coefficient in the ground state is the spin-alternant determinant. We can see that the weight of this spin-alternant determinant is four times larger than the corresponding weights of the two other determinants. This, as we will show later can explain the polarization of the spin density. Now, let's use the following expression for the spin density: $\rho_k = N^2\sum_i {c_i}^2\delta_{ki}$ to calculate the spin density distribution in the allyl radical:

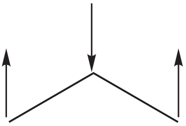
$$\rho_a = \frac{1}{6}[4-1+1] = \frac{2}{3}$$

$$\rho_b = \frac{1}{6}[-4+1+1] = -\frac{1}{3}$$

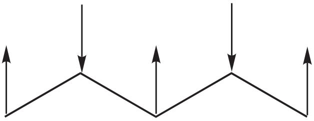
$$\rho_c = \frac{1}{6}[4+1-1] = \frac{2}{3}$$

II Since Φ_{GS} is dominated by the spin-alternant determinant $|a\bar{b}c|$, (as mentioned before, it has the largest coefficient in the ground state), the spin distribution properties could in fact be predicted without any calculation, but just by looking at the spin-alternant determinant.

  a Here is a pictorial representation of the spin-alternant determinant. It is clear that it predicts spin polarization with a spin-down on the central carbon atom and spin-up on the two terminals. As such, (since it dominates the ground state wave-function) it is predicted that the ground state wave function will exhibit the same spin distribution. In other words, in principle, in this case it could be sufficient to look at this spin-alternant determinant to get a qualitative correct estimate of the spin distribution.

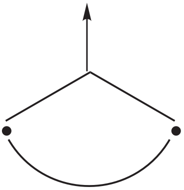


  b The spin-alternant determinant will generally dominate the wave function of the ground state for the entire series of conjugated radicals. For example, if we wish to predict/understand the spin density patterns of the pentadienyl radical, all we have to do is draw the spin-alternant determinant. Thus, as shown below for pentadienyl the central carbon atom has spin up, and the spins alternate in direction on both sides.



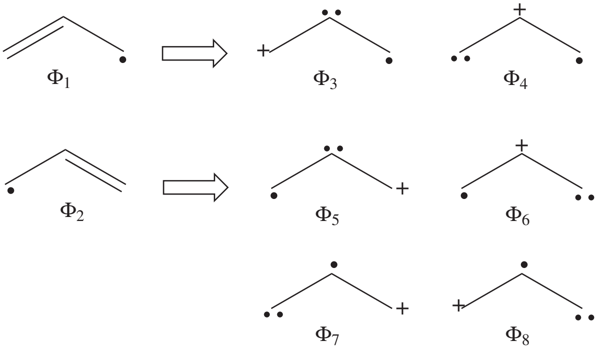
The next radical in line (with 7 carbons) will have a similar spin distribution as in allyl, with spin-down in the center flanked by spin-ups on both sides, etc.

c Lets turn now to the excited state of allyl radical. Since the ground state is the negative combination of the Φ_L and Φ_R structures above, the excited state is the corresponding positive combination. This positive combination eliminates the spin-alternant determinant, and we remain with: $\Phi_{\mathrm{EXS}} = \Phi_L + \Phi_R = \frac{1}{\sqrt{2}}\left[|ab\bar{c}| - |\bar{a}bc|\right]$. Pictorially, this is simply the cyclopropyl structure with spin density localized only on the central carbon:



Note how the spin switches from the ground- to the excited state. It is generally true that in the first excited state of the polyenyl radicals, the spin alternant determinant vanishes and the spin density is determined by the long bond structures.

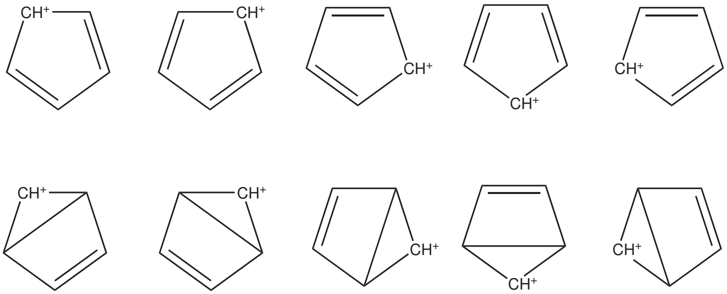
3. Covalent and ionic structures of the allyl radical:
   From each covalent structure we can get two ionic structures. Additional two ionic structures are obtained from the redundant structure. Therefore overall there are 6 different ionic structures:


Φ1
Φ3
Φ4
Φ2
Φ5
Φ6
Φ7
Φ8

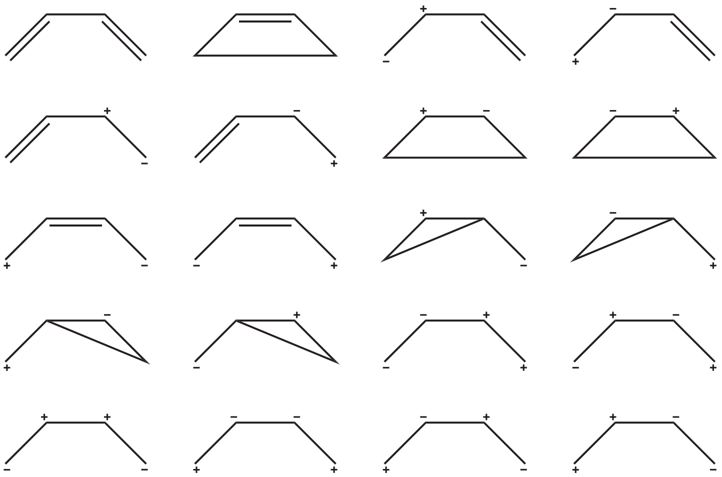
In the two ionic structures (Φ_7, Φ_8) that are based on the redundant structure the charges are farther from each other compared with the other ionic structures and are therefore, expected to be higher in energy. These two structures will therefore not be included in our chosen sub-set of structures.

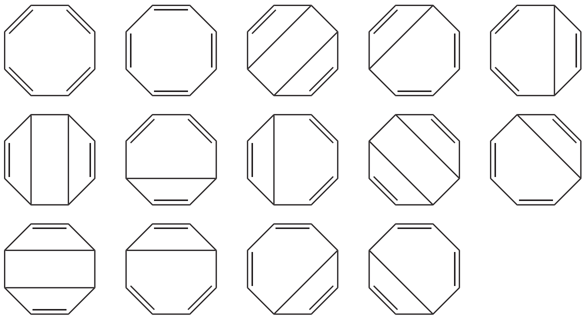
Answer 4.5 Rumer basis set of VB structures

1.


CH+
CH+
CH+
CH+
CH+
CH+
CH+
CH+
CH+
CH+

2.



3.