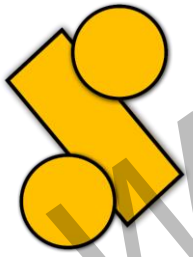
Computations with



XMVB

Fuming Ying

Apr. 22, 2022

OUTLINE

- Introduction to XMVB
- Construct XMVB Input file
- Example of output file
- Utilities
- Procedures for BOVB and VBCI
- Introduction to XGUI

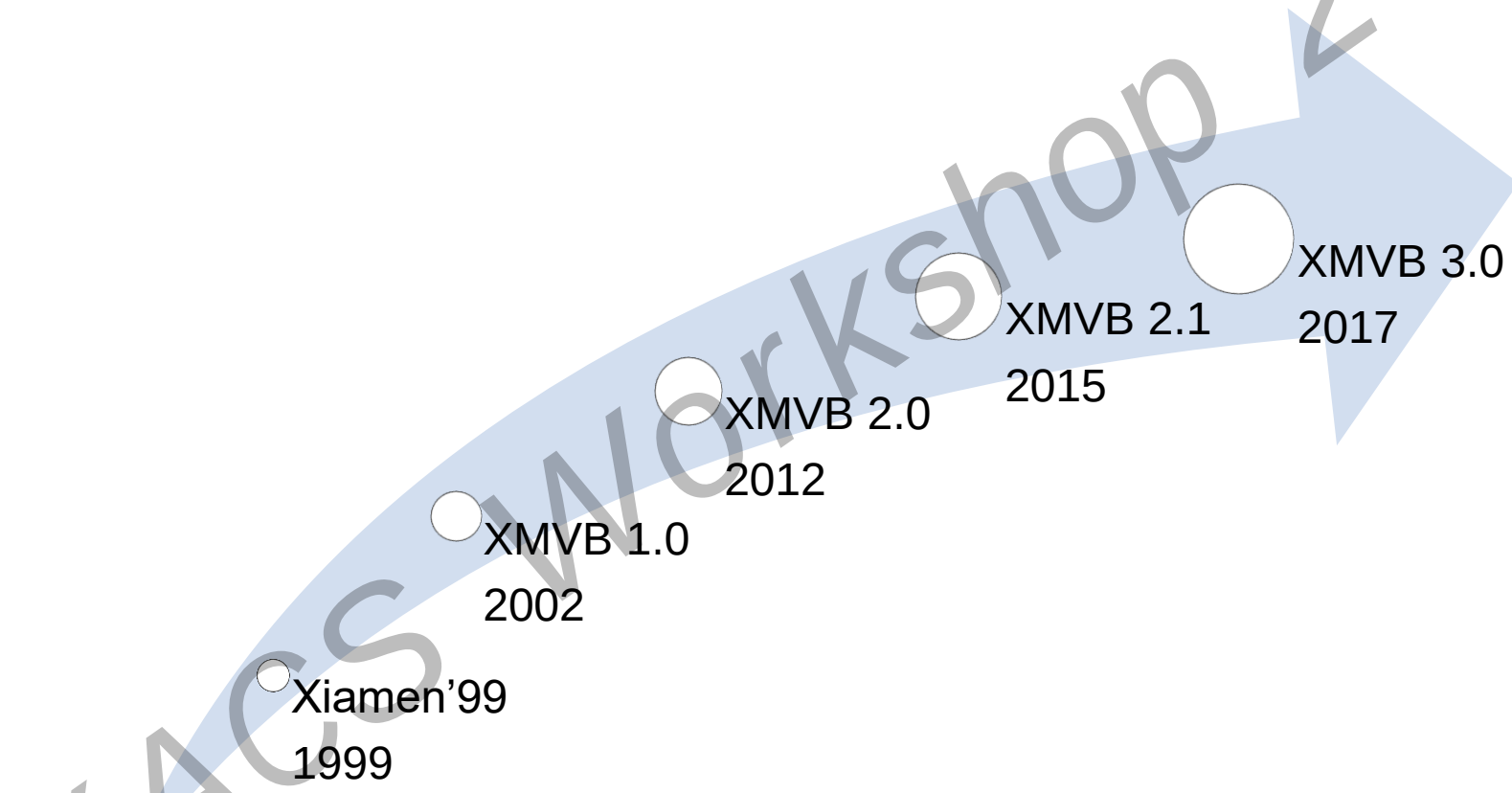
PART I

- Introduction to XMVB
- Construct XMVB Input file
- Example of output file
- Utilities
- Procedures for BOVB and VBCI
- Introduction to XGUI

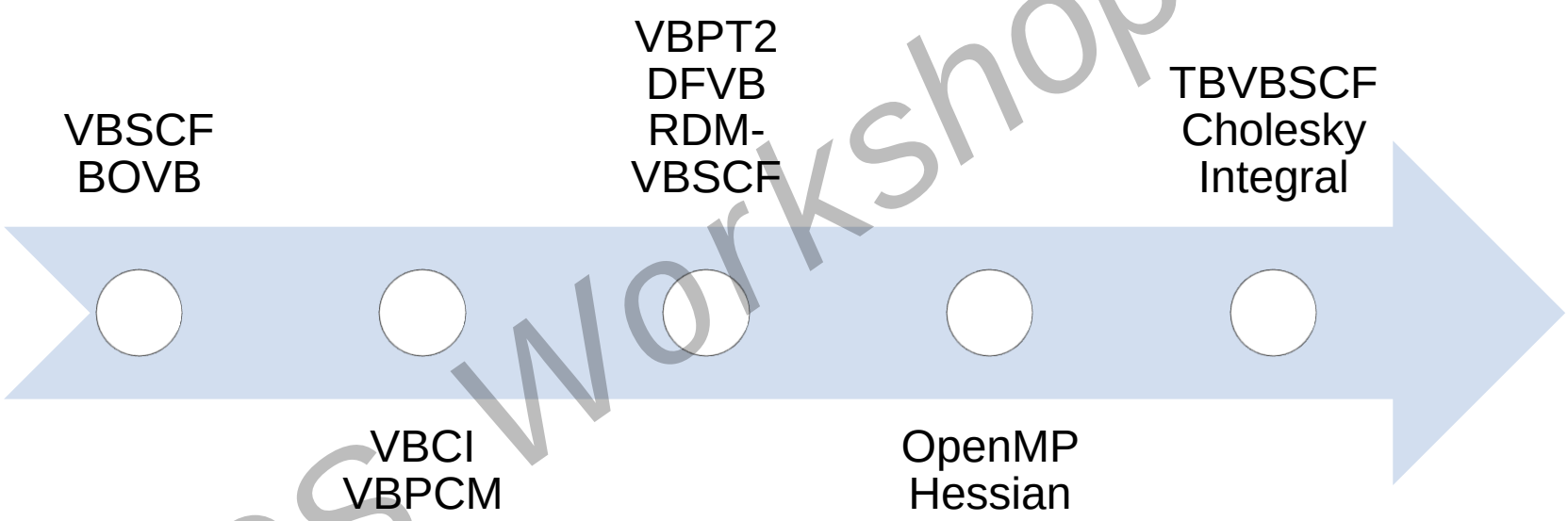
What's XMVB?

- XMVB=XiaMen Valence Bond
- Supports Windows (with cmd) and *NIX
- Distributed as standalone program or module of GAMESS-US
- Free of Charge for academic and non-commercial usage

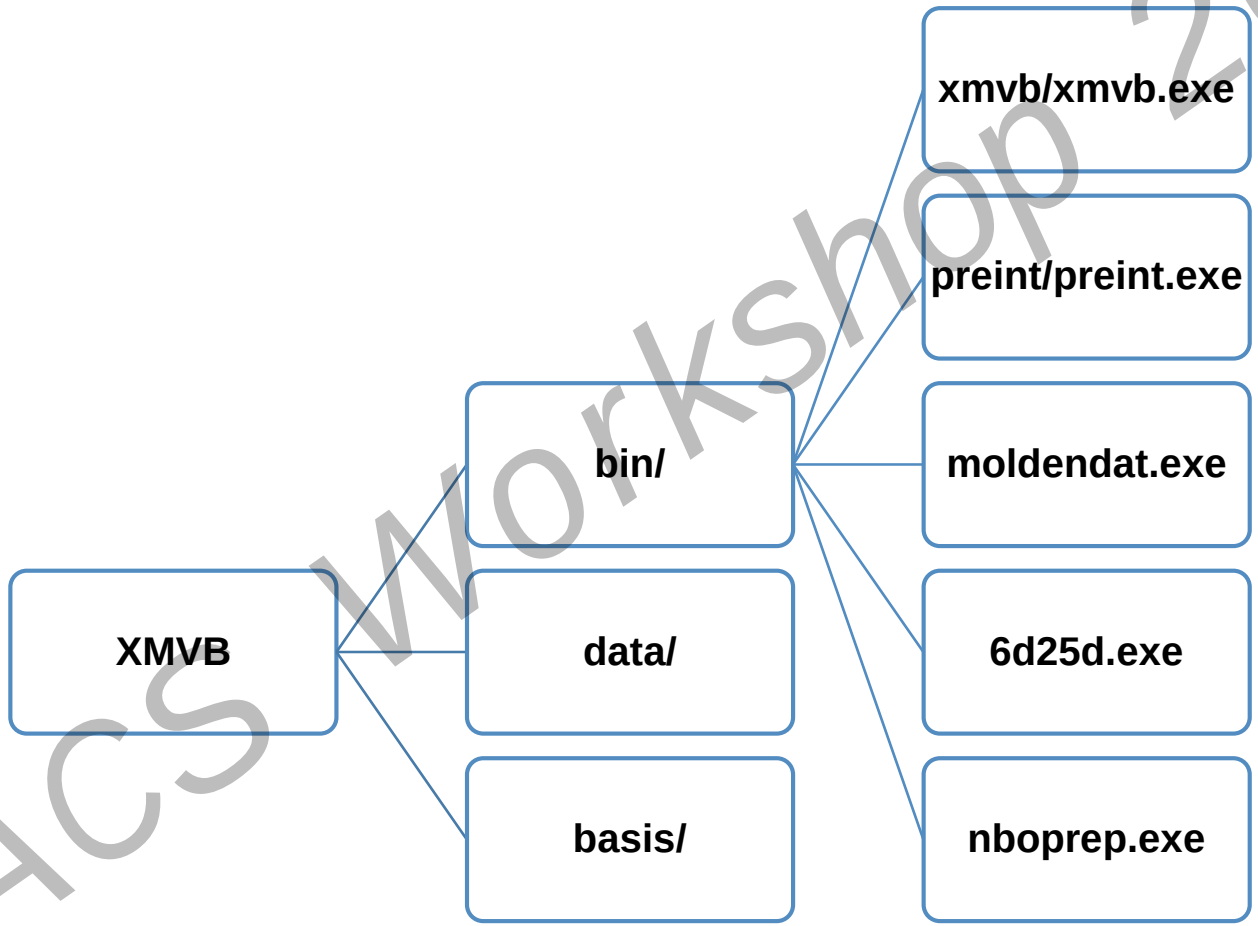
History of XMVB: Versions



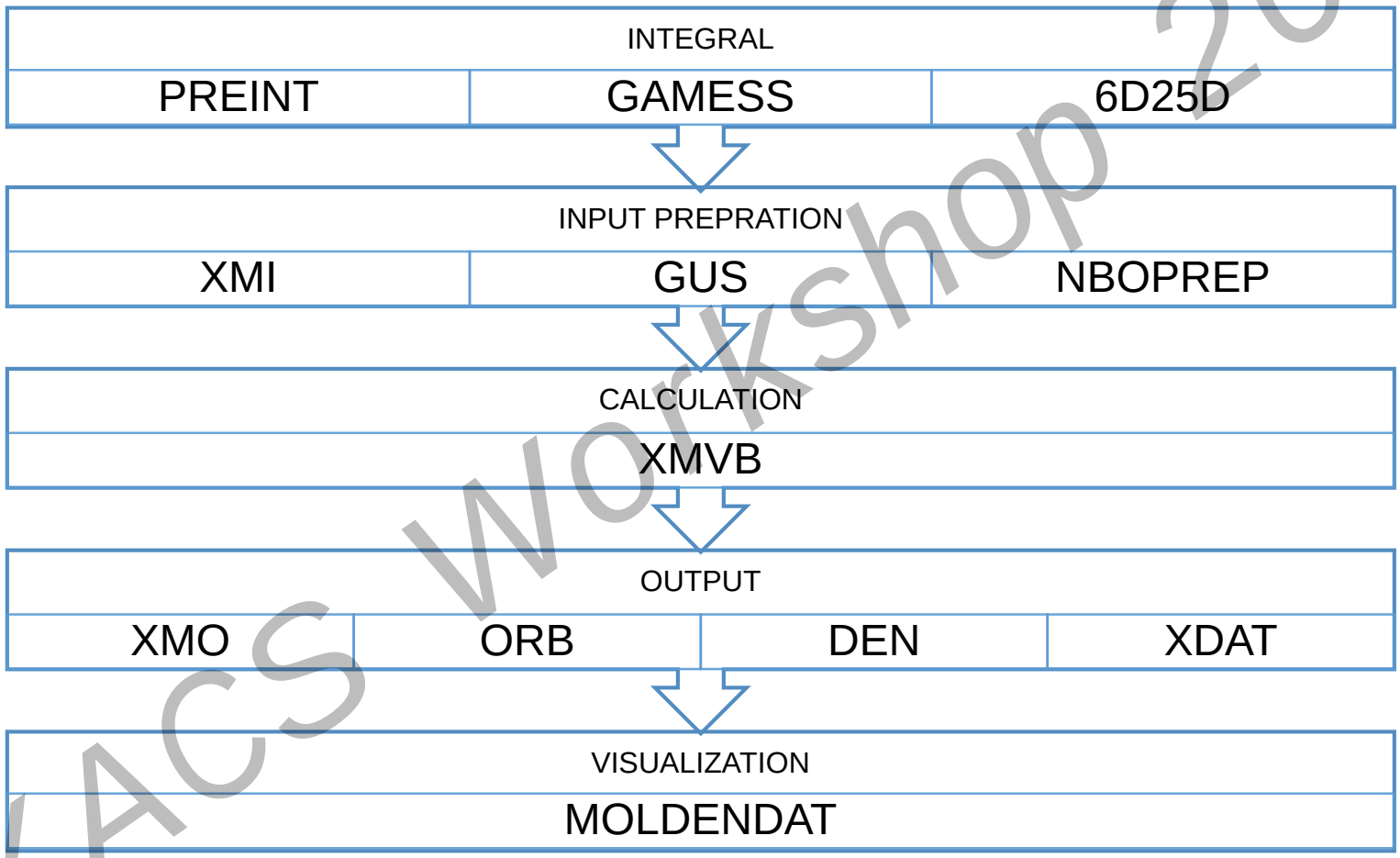
History of XMVB: Functions



Structure of XMVB Package



Running an XMVB Job



Running an XMVB Job

- GAMESS-US Module

  rungms job.inp [verno] [1]

- Standalone XMVB

  /path/to/xmvb/bin/xmvb job.xmi

Useful Websites

- XACS Homepage

  http://xacs.xmu.edu.cn
- XMVB Homepage

  http://xacs.xmu.edu.cn/program/xmvb
- Google Group

  https://groups.google.com/forum/#!forum/xmvb-user
- GAMESS Homepage

  http://www.msg.ameslab.gov/GAMESS/

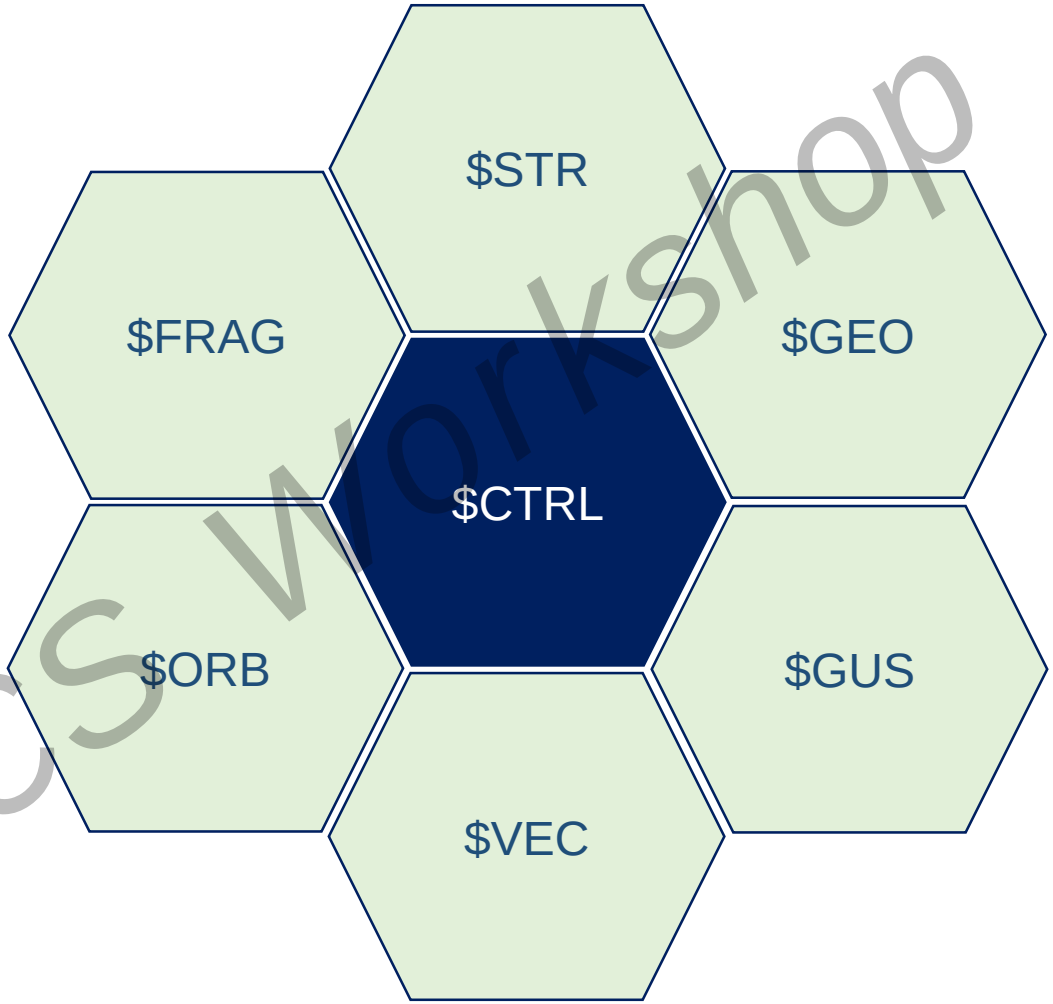
PART II

- Introduction to XMVB
- Construct XMVB Input file
- Example of output file
- Utilities
- Procedures for BOVB and VBCI
- Introduction to XGUI

Common Notes

- Case insensitive
- 400 characters at most in a single line
- First line is treated as title of the job
- Contents after “#” or “;” are comments

Structure of Input



Before constructing, We need…

- Choose methods and algorithms
  - Which method do I need?
  - Which algorithm is better?
- Describe structures and wavefunction
  - Multiplicity
  - Active orbitals and electrons
  - Number of electrons (charge)
  - How many structures?
  - Wavefunction/Structures expanded into structures/determinants/PPDs
- Describe orbitals
- Choose proper initial guess
- Choose output level
  - Hamilton/overlap matrices
  - Population analysis

Example

```
H2 VBSCF
$CTRL
NSTR=1 ISCF=3
$END
$STR
1 2
$END
$ORB
5*2
1-5
6-10
$END
```

Title, essential

Global keywords

Description of VB strctures

Description of VB orbitals

Commonly Used Keywords in $CTRL

- Method & Algorithm:
  - ✓VBSCF, BOVB, VBCIS, VBCISD, VBPT2, ISCF
- Strcture & Wavefunction:
  - ✓NSTR, STR, NAO, NAE, WFNTYP, VBFTYP, NMUL
- Orbital Definition:
  - ✓ORBTYP, FRGTYP
- Output:
  - ✓IPRINT
- Initial Guess:
  - ✓GUESS
- Integral:
  - ✓INT, BASIS, CHARGE

Description of Methods and Algorithms

ISCF	Gradient	Performance	Note
1	Numerical	Stable, slow	
2	Analytical	Fast	
3	Numerical	Stable, slow	
4	Numerical	Stable, very slow	VBSCF Only
5	Analytical	Fast	VBSCF Only with NAO and NAE
6	Full Hessian	Slow	

```
$CTRL
ISCF=1 VBCISD
$END
```

```
$CTRL
ISCF=2 BOVB
$END
```

```
$CTRL
ISCF=5 NAO=2 NAE=2
$END
```

Description of Structures and Wavefunctions

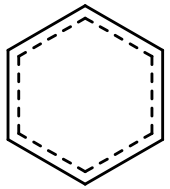
Describe structures manually: NSTR (with $STR)
Generate structures automatically: STR, NAO, NAE

STR: Level to generate VB structures automatically
- **COV:** Covalent structures only
- **ION:** Ionic structures only
- **FULL:** All structures, COV+ION

Requirements: NAO and NAE

STR=FULL NAO=6 NAE=6

NSTR=5



STR=COV NAO=3 NAE=3 NMUL=2

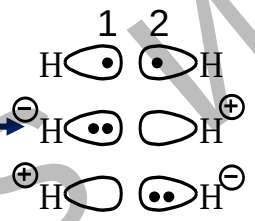
Description of Structures and Wavefunctions

A typical VB structure is defined in the form

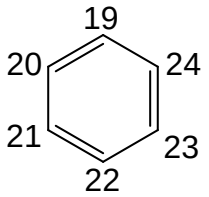
$$\underbrace{1\ 2\ \cdots\ (m-1)\ m}_{\text{LP/bonding}}\ \underbrace{(m+1)\ \cdots\ (n-1)\ n}_{\text{high spin}}$$

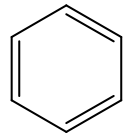
Digit: # of orbital
Position of digit: # of electron
1:4 = 1 1 2 2 3 3 4 4

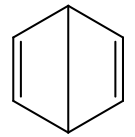
$STR
1 2
1 1
2 2
$END

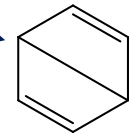


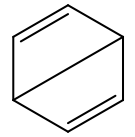
$STR
1:18 19 20 21 22 23 24
1:18 19 24 20 21 22 23
1:18 19 22 20 21 23 24
1:18 20 23 19 24 21 22
1:18 21 24 19 20 22 23
$END











Description of Orbitals

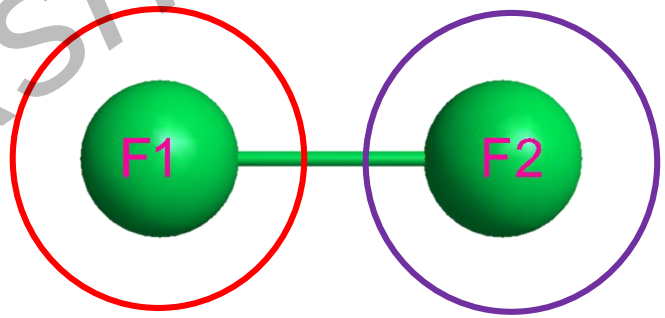
$ORB
15*10
1-15
16-30
1-15
16-30
1-15
16-30
1-15
16-30
1-15
16-30
$END

Number of BFs in each orbital, 15*10=15 15 … 15

BFs in orbital 1

BFs in orbital 2

BFs in the last orbital



Initial Guess

GUESS: The way to get initial guess

AUTO : Default option, initial guess by diagonalizing Fock matrices

UNIT : The first BF in each orbital to 1, others to 0

READ : Initial guess from a previous XMVB calculation

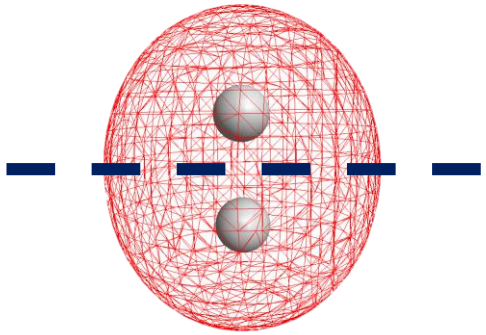
RDCI : Initial guess from a previous VBCI calculation

MO : Initial guess from MOs, need $GUS

NBO : Initial guess from NBO, need $GUS

```
$CTRL
GUESS=MO
$END
$ORB
5 5
1-5
6-10
$END
```

```
$GUS
1 1
2 1
$END
```

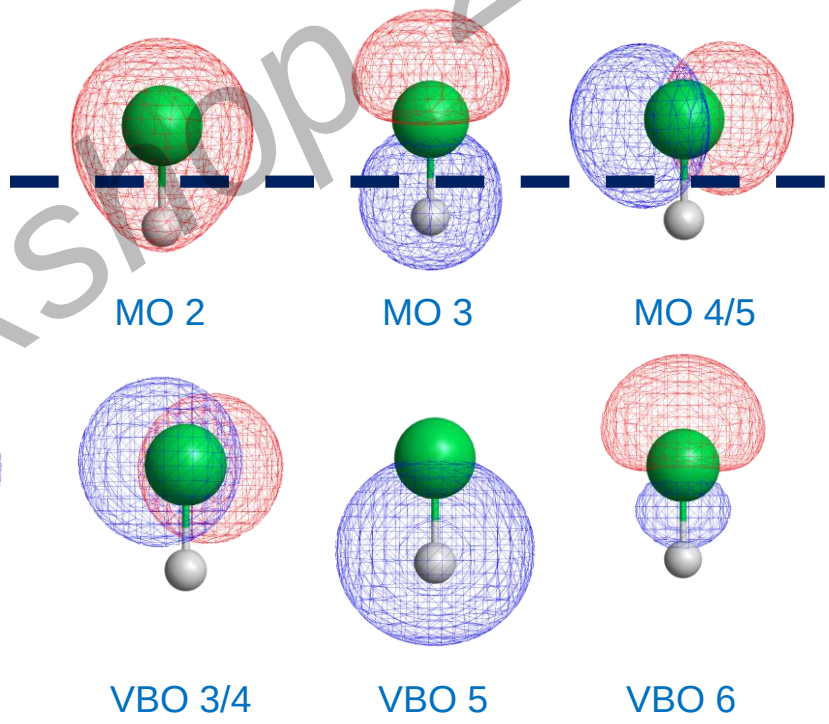


MO 1

Initial Guess: HF

```
$CTRL
GUESS=MO
$END
$ORB
15*4 5 15
6-20
6-20
6-20
6-20
1-5
6-20
$END
```

```
$GUS
1 1
2 2
3 4
4 5
5 3
6 3
$END
```



PART III

- Introduction to XMVB
- Construct XMVB Input file
- Example of output file
- Utilities
- Procedures for BOVB and VBCI
- Introduction to XGUI

- Recall of XMI
- Structure and initial guess
- Calculation procedure and final energy
- Structure overlap and Hamiltonian matrix
  - For IPRINT>=2
- Coefficients and weights of VB structures
- Optimized orbitals
- Orbital overlap matrix
  - for IPRINT=3
- Density matrix and population analysis
  - for IPRINT>=2

Calculation Procedure and Final Energy

ITER	ENERGY	DE	GNORM
1	-198.4777622814	-198.4777622814	0.8618538151
2	-198.5868705995	-0.1091083180	1.0764782459
	…		
20	-198.7163628825	-0.0000015413	0.0017946573
21	-198.7163632277	-0.0000003452	0.0006872325

VBSCF converged in 21 iterations

Total Energy: -198.71636328

Coefficients and Weights

```
******  COEFFICIENTS OF STRUCTURES  ******
  1    0.81645  ******  1:8    9  10
  2    0.20731  ******  1:8    9   9
  3    0.20731  ******  1:8   10  10
...
******  WEIGHTS OF STRUCTURES ******
    1    0.78740  ******  1:8    9  10
    2    0.10630  ******  1:8    9   9
    3    0.10630  ******  1:8   10  10
...
```

Population Analysis


```
==========================================
                XMVB ATOMIC POPULATION ANALYSIS
==========================================

                ******  POPULATION AND CHARGE  ******
   ATOM        MULL.POP.    CHARGE     LOW.POP.     CHARGE
    1 F         9.000000   -0.000000     9.000000   -0.000000
    2 F         9.000000    0.000000     9.000000    0.000000

                ******  BOND ORDER  ******
        ATOM 1       ATOM 2         DIST     BOND ORDER
          1 F          2 F          1.400         0.748
...
```

PART IV

- Introduction to XMVB
- Construct XMVB Input file
- Example of output file
- Utilities
- Procedures for BOVB and VBCI
- Introduction to XGUI

PRECAL

- PRECAL=PREliminary CALculation
- Hartree-Fock orbitals and integral preparation for XMVB
- DFT is implemented
  - B88, LYP, Slater, VWN
  - BLYP, BHHLYP, B3LYP
- Cartesian basis functions up to F are supported
- $ /path/to/xmvb/bin/precal file.inp

Syntax of PREINT Input

RHF 6-31G*	Method and Basis Set
0 1	Charge Multiplicity
F 0.0 0.0 0.0	Geometry (Cartesian)
F 0.0 0.0 1.4	

B3LYP 6-31G*	Method and Basis Set
0 1	Charge Multiplicity
F	Geometry (ZMT)
F 1 1.40	

6D25D.EXE

- Transform Cartesian basis functions to spherical/harmonic basis functions
- Cartesian integrals and MOs are replaced by spherical ones
- Supports basis functions till F shell
- $ /path/to/xmvb/bin/6d25d.exe

MOLDENDAT.EXE

- Prepare file to visualizing VB orbitals
- Need a corresponding GAMESS-US output file
- Output on the screen
- $ /path/to/xmvb/bin/moldendat gms.out vb.xdat >& vb.out

NBOPREP.EXE

- Prepare NBOs in proper format for GUESS=NBO
- Need a previous NBO calculation with FILE.36 and FILE.37 generated
- New file “orb.nbo” will be generated
- $ /path/to/xmvb/bin/nboprep.exe file.log [NBO/PNBO]

  file.log is the output of Gaussian or GAMESS-US

PART V

- Introduction to XMVB
- Construct XMVB Input file
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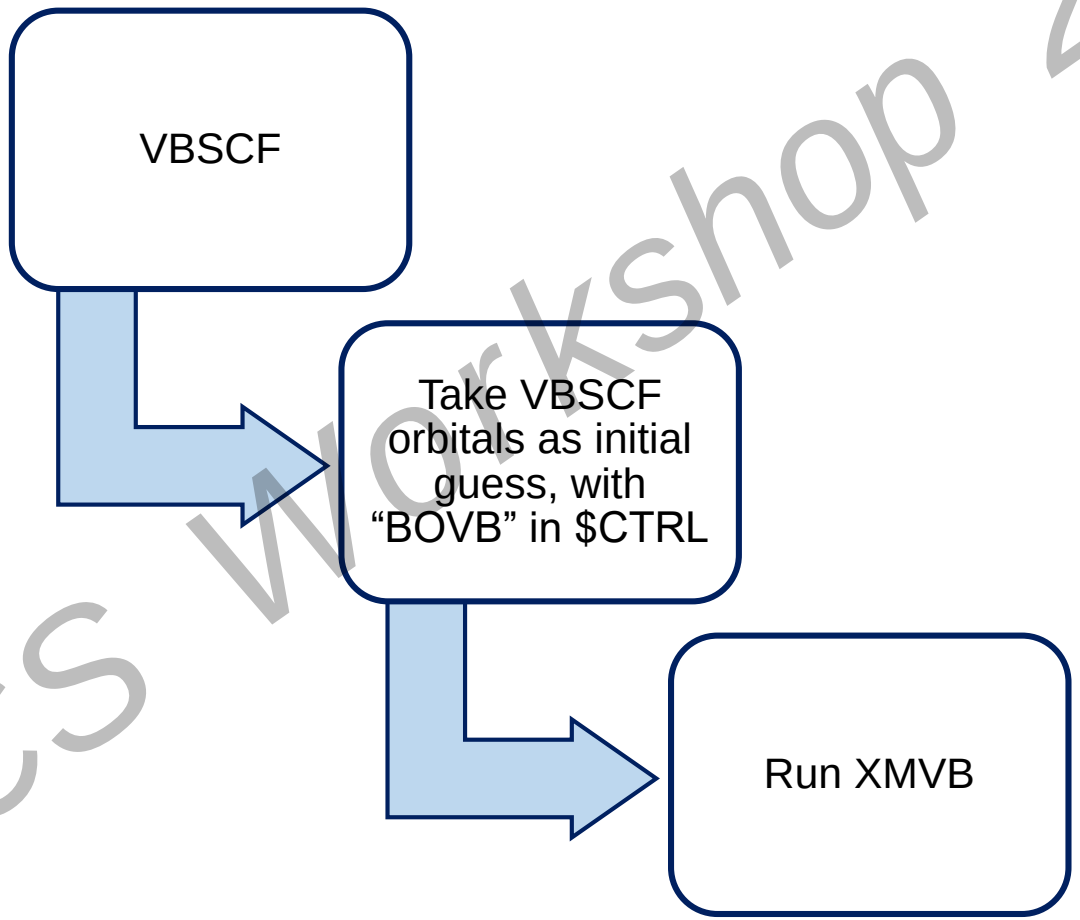
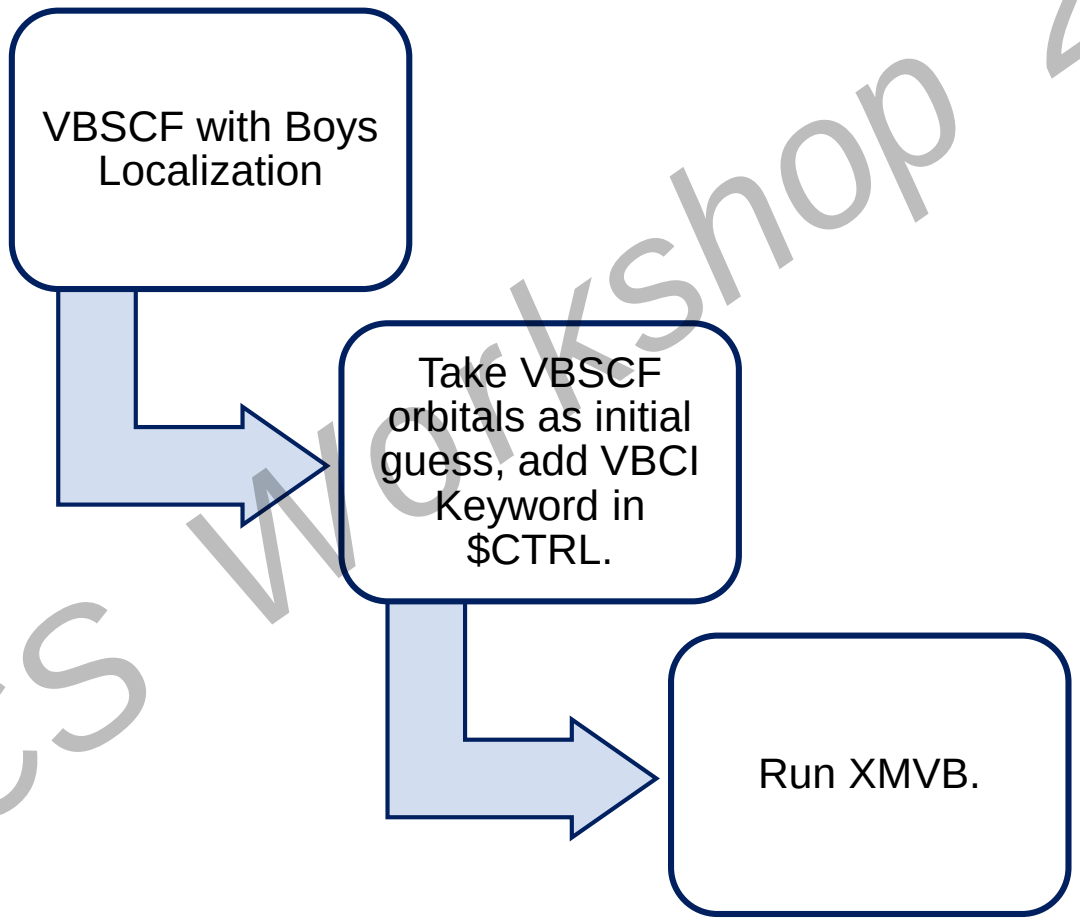
To Run BOVB



To Run VBCI



PART V

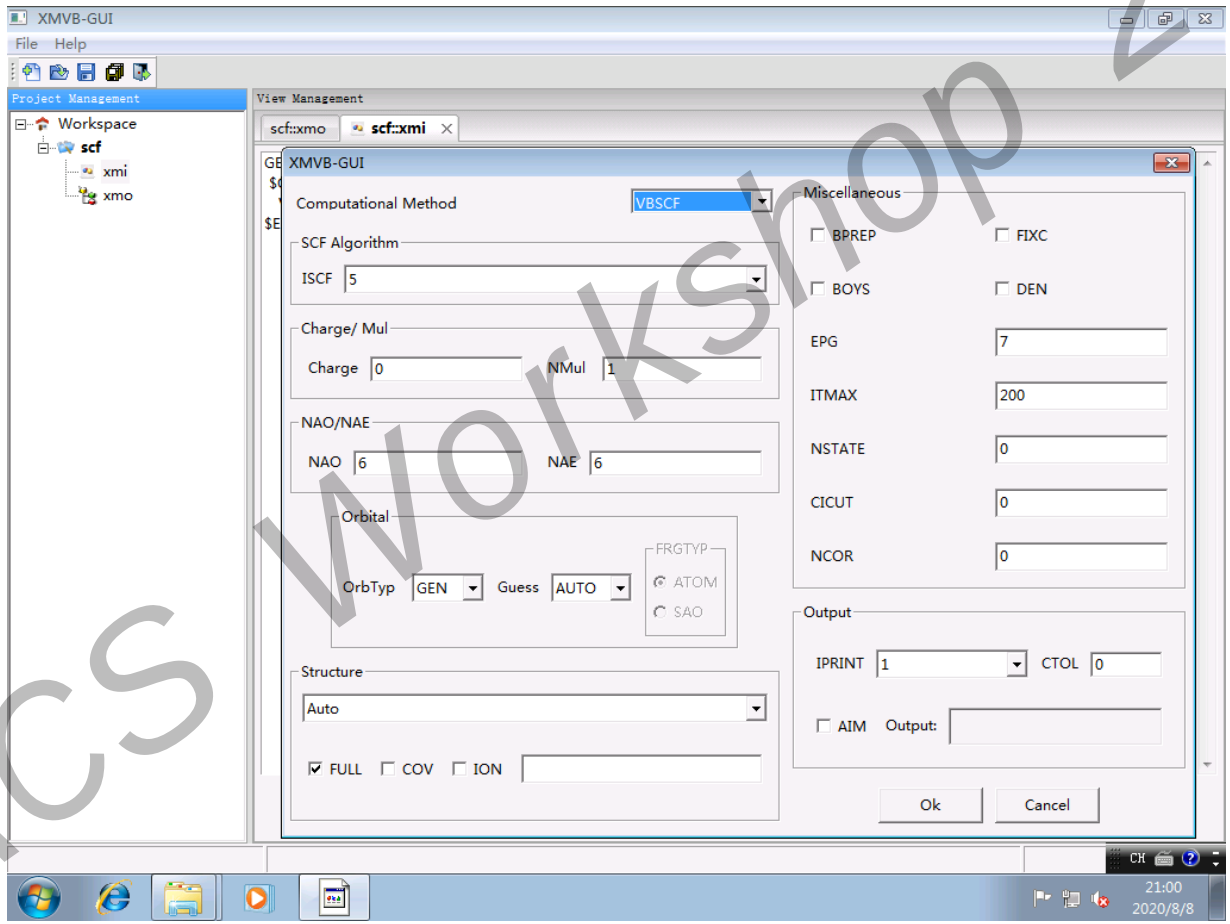
- Introduction to XMVB
- Construct XMVB Input file
- Example of output file
- Utilities

- Introduction to XGUI

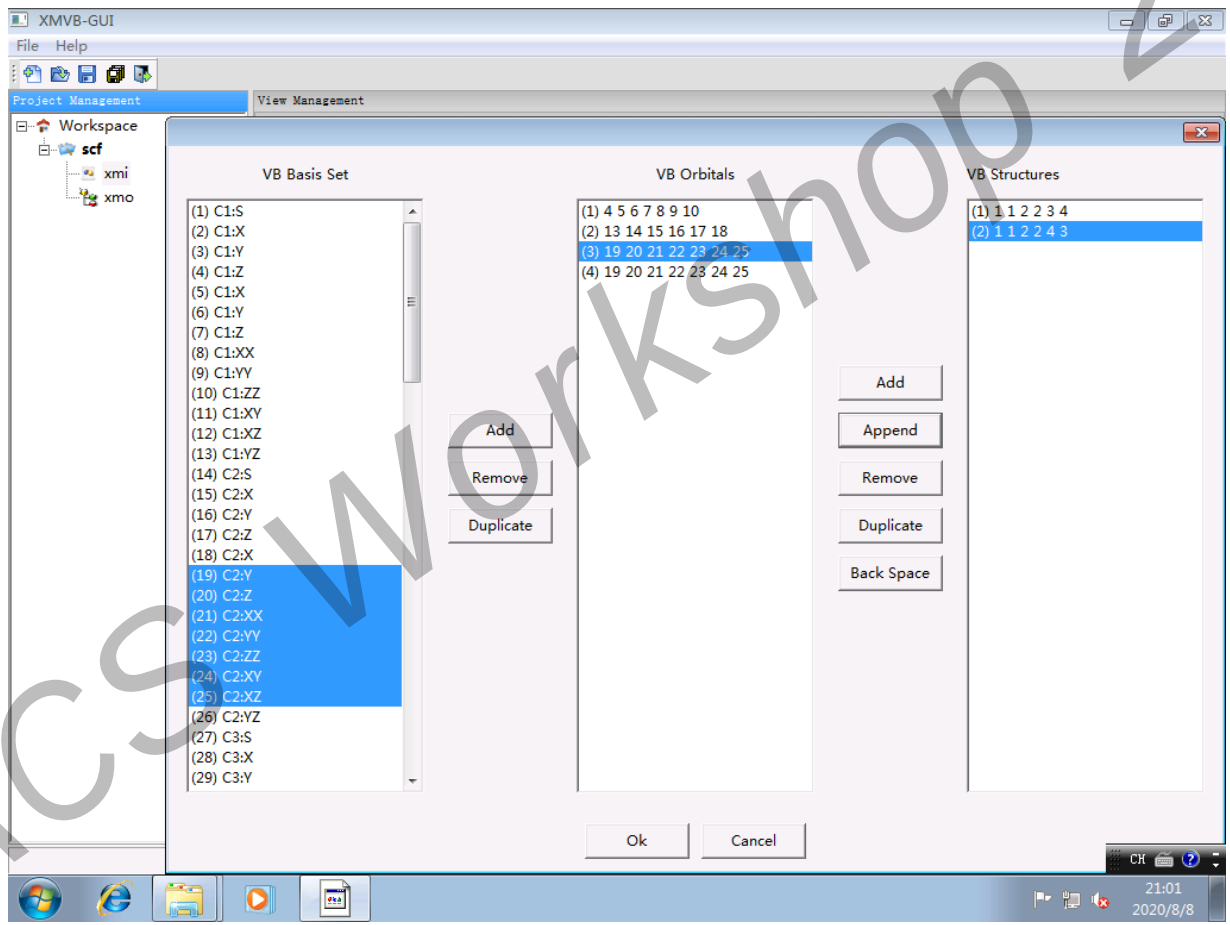
Introduction to XGUI

- A Graphical User Interface (GUI) for XMVB users to
  - Generate input files
  - Visualize orbitals and structures in the output
- Supported OS:
  - Windows, 32 & 64 bit
  - Mac OS X
- Available at:
  - http://xacs.xmu.edu.cn/downloads

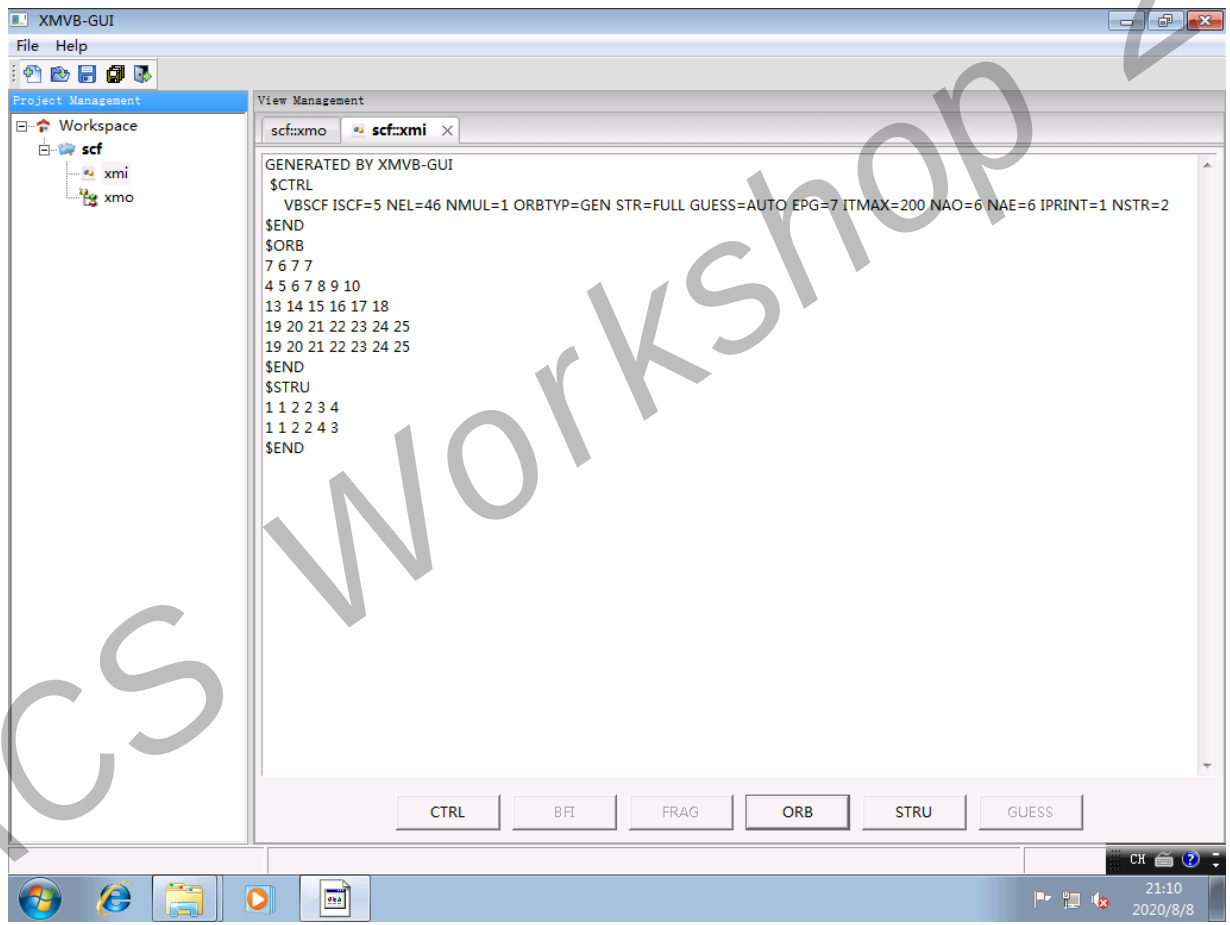
Generate XMI: Keywords in $CTRL



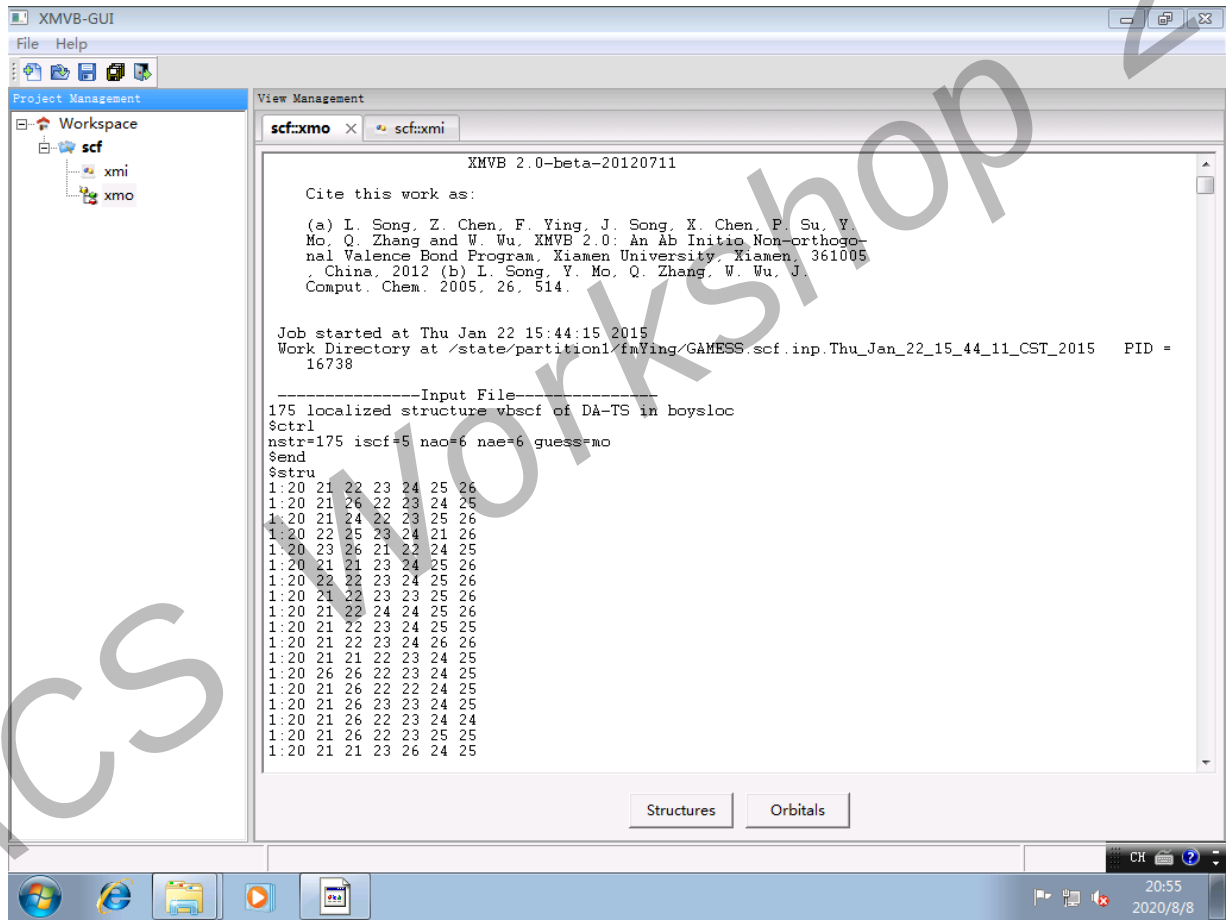
Generate XMI: $ORB and $STR



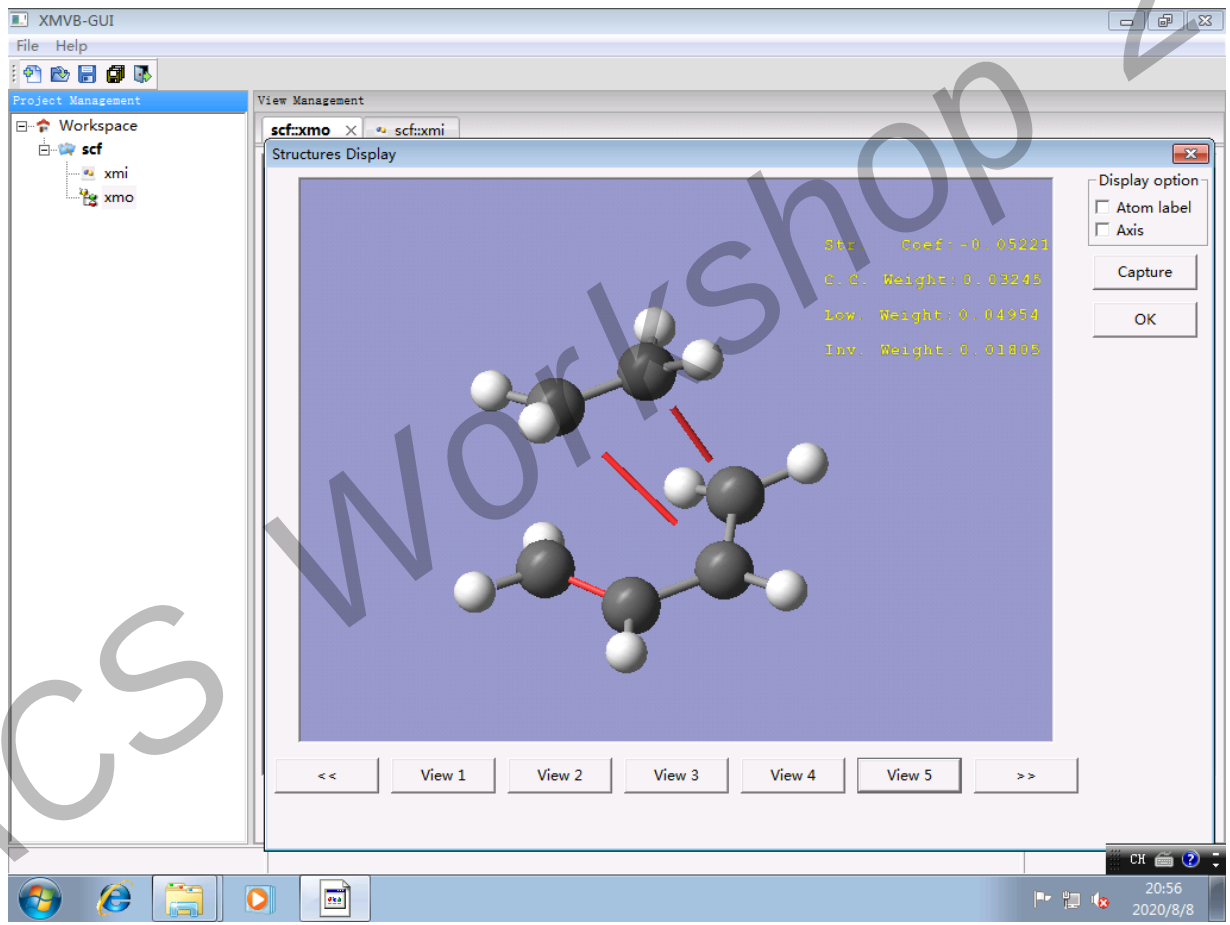
Generate XMI: Overview



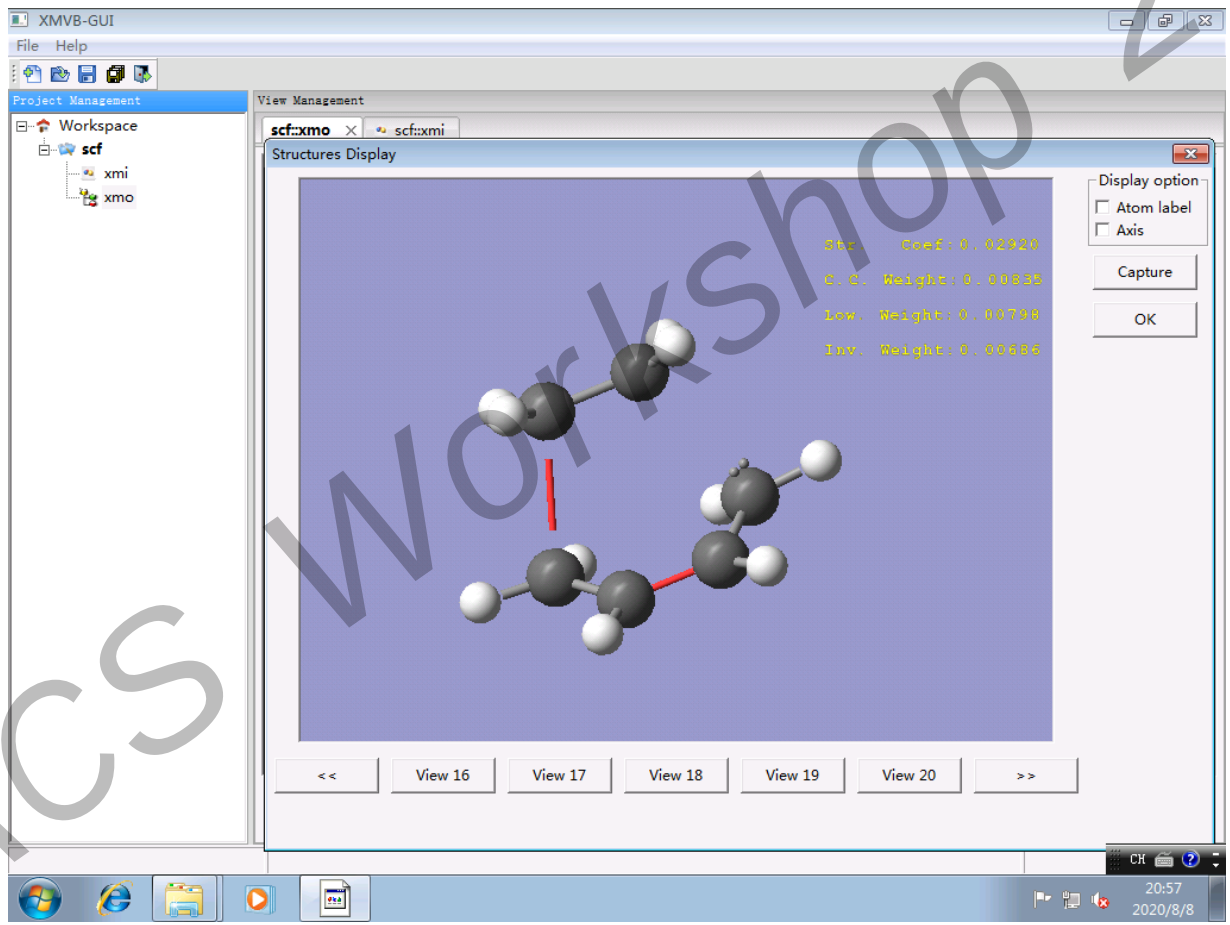
Visualize XMO: Overview



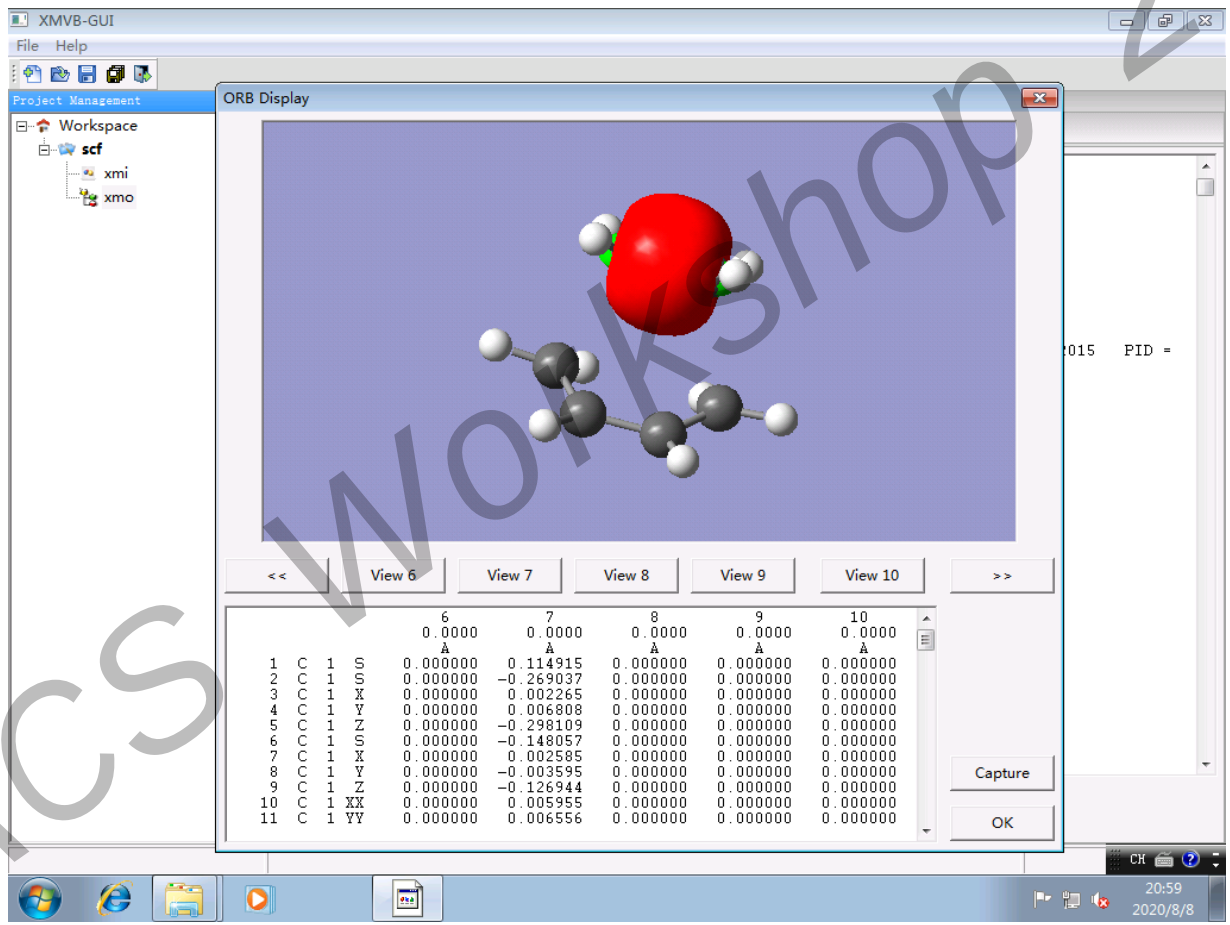
Visualize XMO: Structures



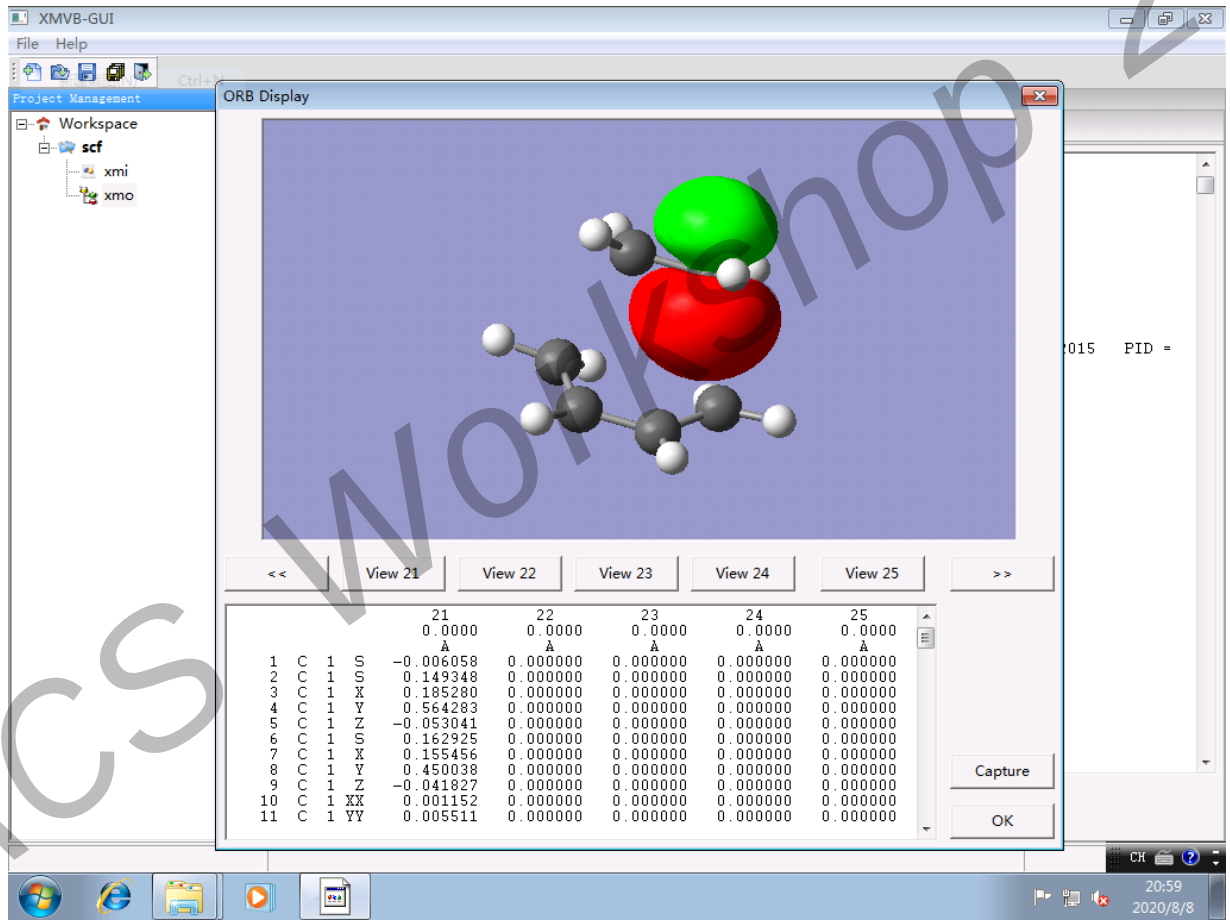
Visualize XMO: Structures

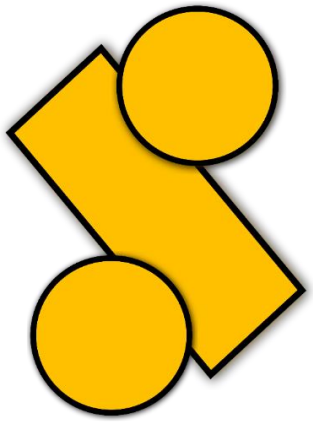


Visualize XMO: Orbitals



Visualize XMO: Orbitals





Thank You!