A Practical Guide for XMVB Calculations

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Outline

- General introduction
- How to write input files?
- How to get information from output files?

General introduction

An Ab Initio Non-orthogonal Valence Bond Program

Version 2.1

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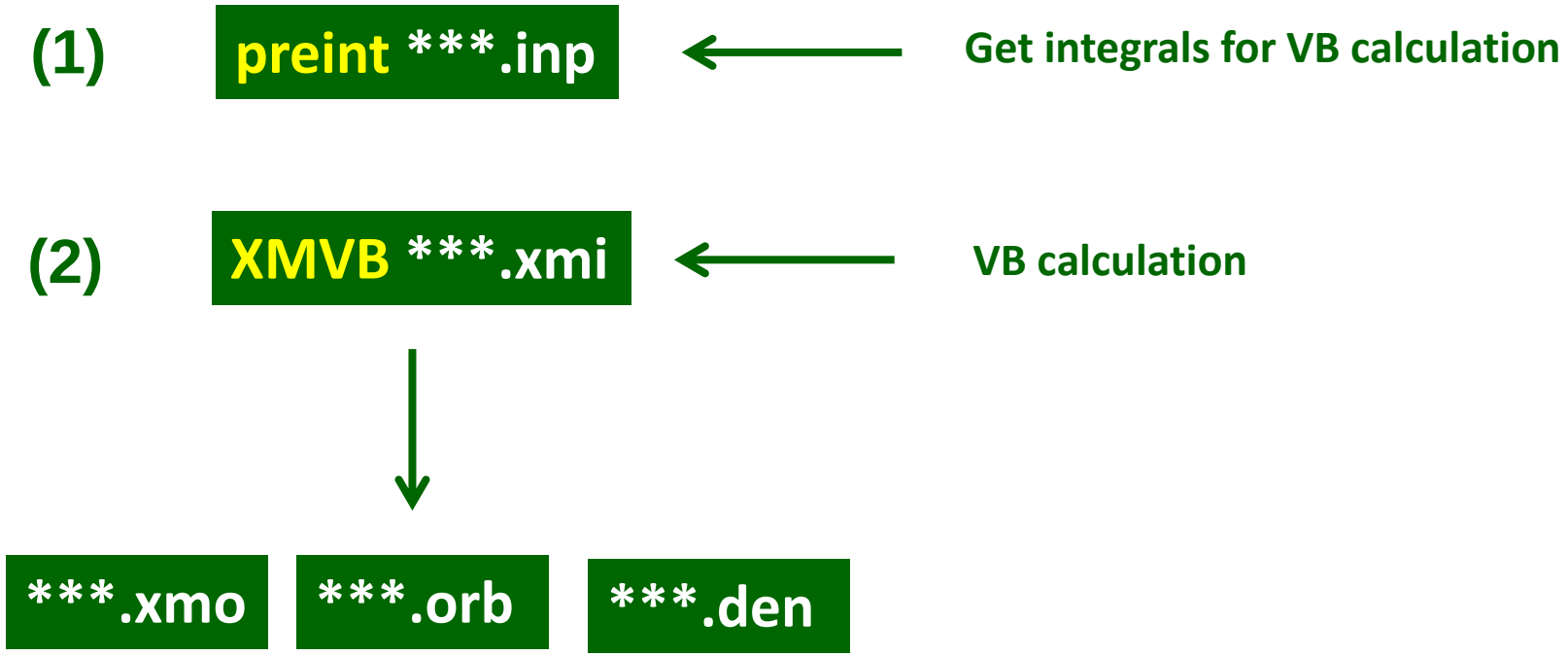
Distributions of XMVB 2.1

Module distribution → A module embedded in GAMESS-US

Stand-alone distribution → A stand-alone program

How to Run An XMVB Job?

For Stand-alone distribution



Useful documents

XMVB manual

http://www.xmvb.org/art.php?id=8

Online Tutorials

http://www.xmvb.org/art.php?id=4

How to write input files?

How to write INT File

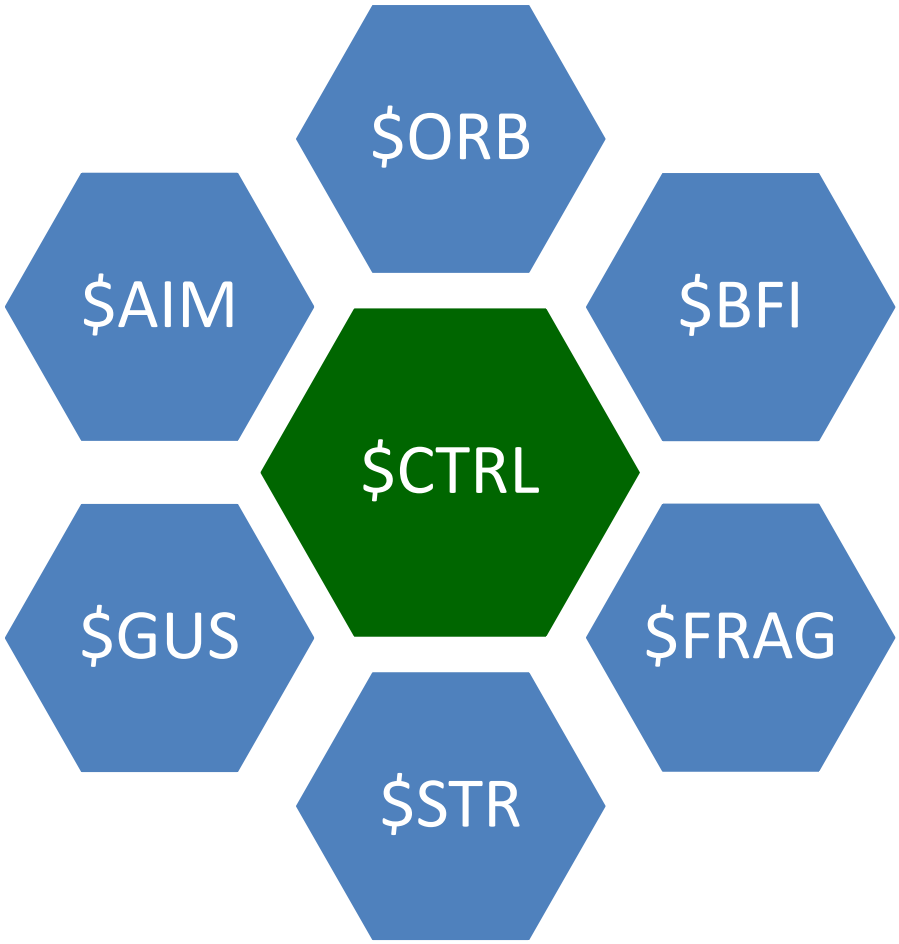
```
RHF cc-pvdz
0 1
H 0.000000  0.000000  0.000000
H 0.000000  0.000000  0.740000
```

← HF Method; basis set

← Charge; multiplicity

← Molecular coordinates

Structure of XMI File

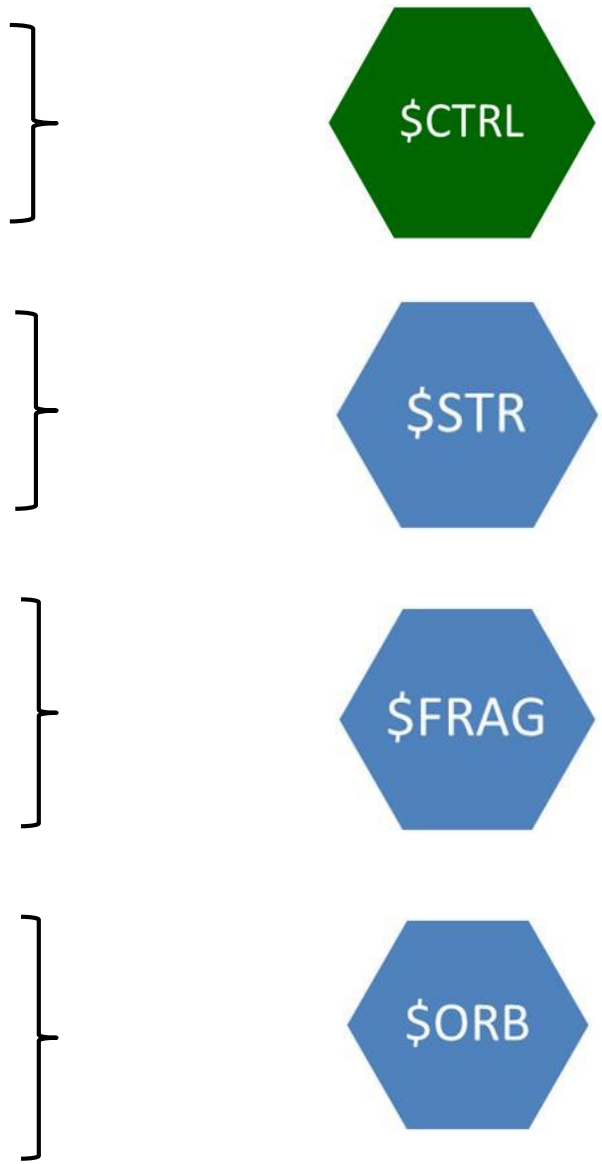


Optional

Necessary

Example 1. H_2 molecule

```
$ctrl
nstr=3  iscf=5 nao=2 nae=2
orbtyp=hao frgtyp=sao
$end
$str
1 2
1 1
2 2
$end
$frag
1 1
spz 1
spz 2
$end
$orb
1 1
1
2
$end
```



```
$ctrl
nstr=3  iscf=5 nao=2 nae=2
orbtyp=hao frgtyp=sao
$end
$str
1 2
1 1
2 2
$end
$frag
1 1
spz 1
spz 2
$end
$orb
1 1
1
2
$end
```

iscf : orbital optimization algorithm (VBSCF, BOVB)
When iscf=5, the two keywords are necessary
nao: number of active orbitals
nae: number of active electrons

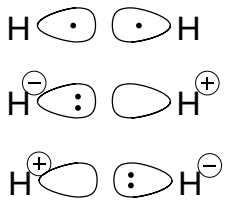
iscf	Gradient	Performance	Required keywords
1	Numerical	Stable, slow	
2	Analytical	Fast	
3	Numerical	Stable, slow	
4	Numerical	Stable, very slow	
5	Analytical	Very Fast	nao, nae
6	Full Hessian	Slow	nao, nae

```
$ctrl
nstr=3  iscf=5 nao=2 nae=2
orbtyp=hao frgtyp=sao
$end
$str
1 2
1 1
2 2
$end
$frag
1 1
spz 1
spz 2
$end
$orb
1 1
1
2
$end
```

nstr =3, the number of structures
$str : describing VB structure or determinant.
In $str, a typical structure is written as:

a a b b c c … m n

a b c : double occupied orbitals (inactive)
m n : single occupied orbitals (active)



1 2 **covalent**

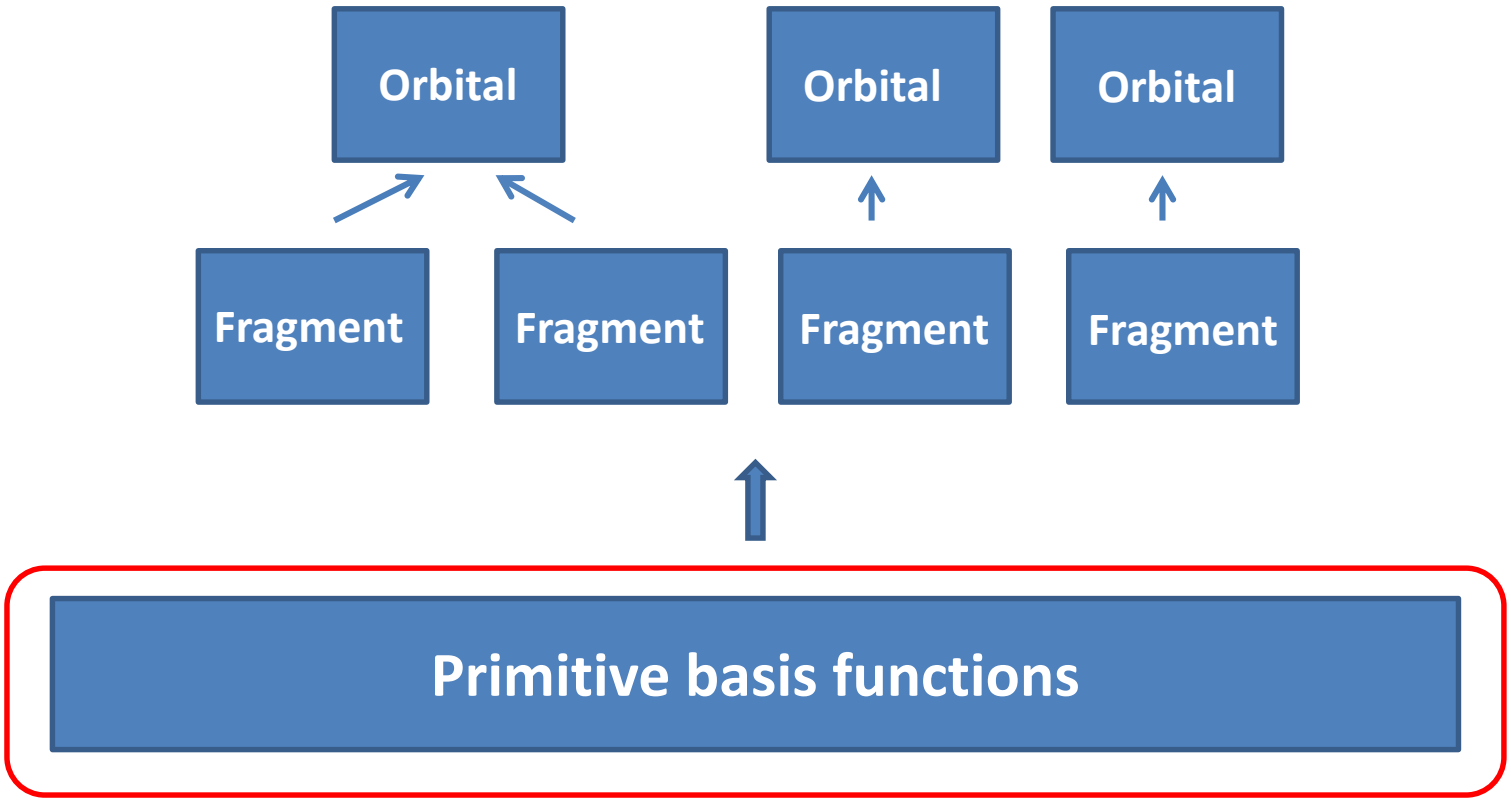
1 1 **ionic**

2 2 **ionic**

```
$ctrl
nstr=3  iscf=5 nao=2 nae=2
orbtyp=hao frgtyp=sao
$end
$str
1 2
1 1
2 2
$end
$frag
1 1
spz 1
spz 2
$end
$orb
1 1
1
2
$end
```

orbtyp=hao,
Hybrid atomic orbitals.
localized non-orthogonal orbitals

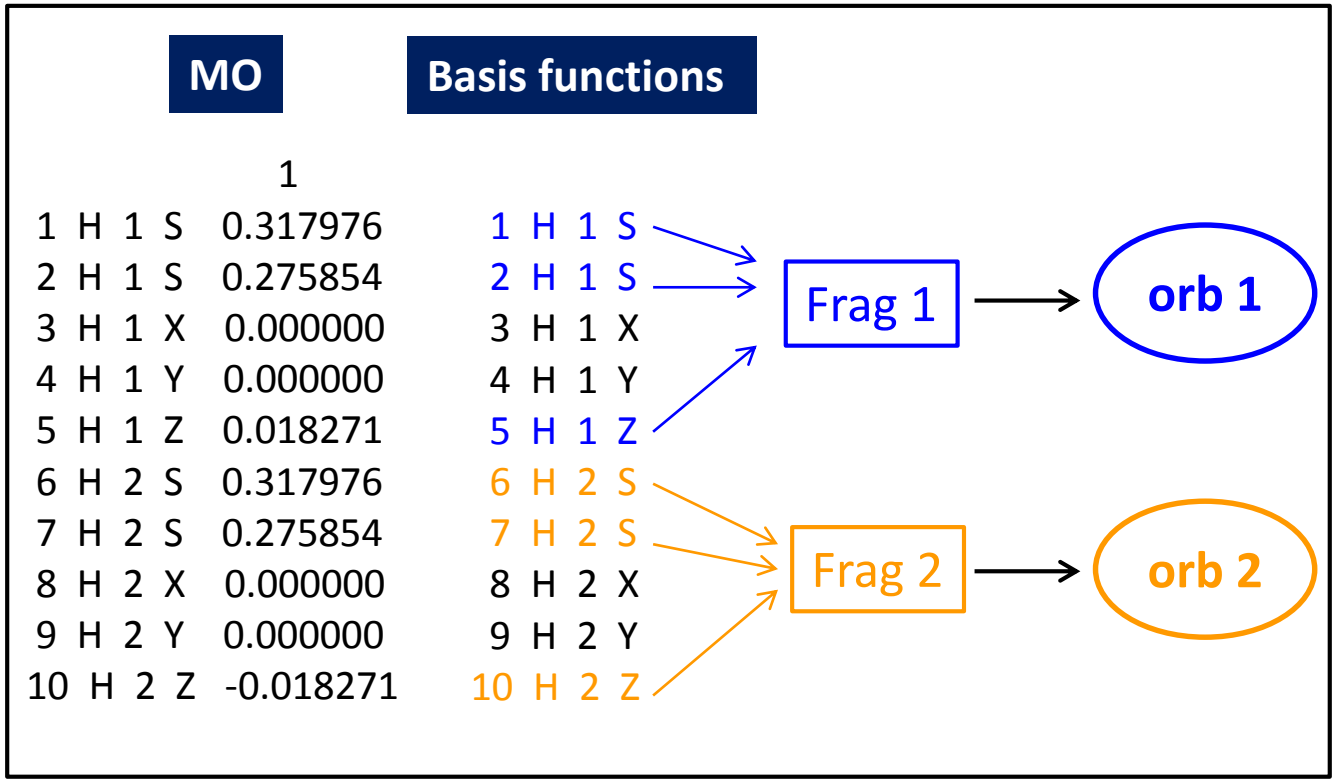
How to define orbitals?



Fragments are a series of basis function sets.

```
$ctrl
nstr=3 iscf=5 nao=2 nae=2
orbtyp=hao frgtyp=sao
$end
$str
1 2
1 1
2 2
$end
$frag
1 1
spz 1
spz 2
$end
$orb
1 1
1
2
$end
```

frgtyp=sao, fragments are defined with **s**ymmetrized **a**tomic **o**rbitals.



```
$ctrl
nstr=3 iscf=5 nao=2 nae=2
orbtyp=hao frgtyp=sao
$end
$str
1 2
1 1
2 2
$end
$frag
1 1
spz 1
spz 2
$end
$orb
1 1
1
2
$end
```

$frag: description for fragments
Line 1: the number of atoms in each fragment.
Line 2 : the basis functions of s and pz in atom 1
Line 3 : the basis functions of s and pz in atom 2.

$orb: description for VB orbitals
Line 1: the number of fragments in each orbital.
Line 2: orbital 1 is described by fragment 1
Line 3: orbital 2 is described by fragment 2.

Summary (1)

1. The assignment of orbital optimization algorithm (iscf)
2. The writing of VB structures with $str
3. The determination of VB orbitals with ‘Frgtyp=sao’

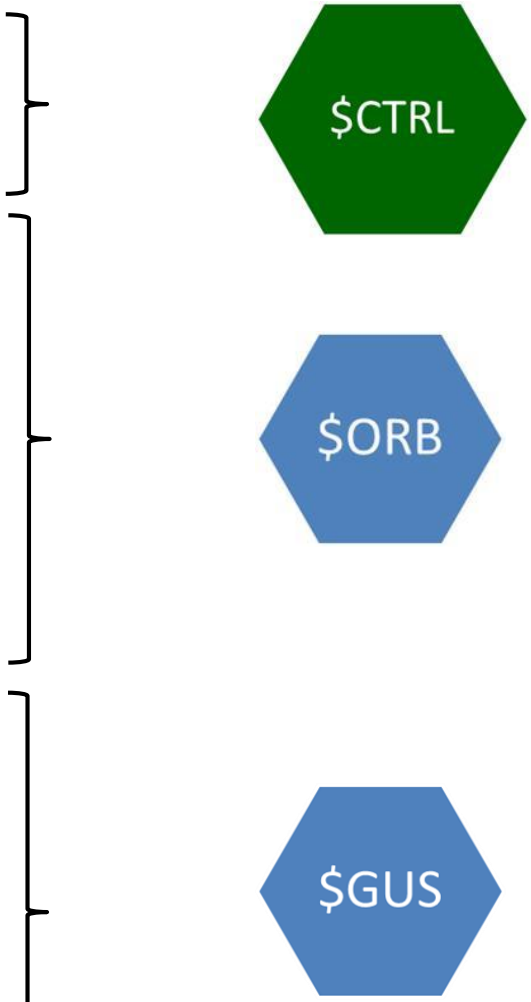
Example 2. HF molecule

hf.int

```
RHF basis set
 0 1
 H    0.000000  0.000000  0.000000
 F    0.000000  0.000000  0.917000
```

HF molecule, 3 structures hf.xmi

```
$ctrl
str=full nae=2 nao=2 iprint=3 orbtyp=hao
frgtyp=atom iscf=5 guess=mo
$end
$orb
1 1 1 1 1 1
2
2
2
2
2
1
$end
$gus
1 1
2 2
3 4
4 5
5 3
6 3
$end
```



HF molecule, 3 structures

hf.xmi

```
$ctrl
str=full nae=2 nao=2 iprint=3 orbtyp=hao
frgtyp=atom iscf=5 guess=mo
$end
$orb
1 1 1 1 1 1
2
2
2
2
2
1
$end
$gus
1 1
2 2
3 4
4 5
5 3
6 3
$end
```

Automatically generate structures based on the active orbitals and electrons.

str = full => generate all VB structures

cov => only covalence

Ion => only ionic structures

nao = m, the final m orbitals are selected as active orbitals.

nae = n, the number of active VB electrons

Iprint=3, full print-out message.

Using str, $str can be absent.

HF molecule, 3 structures

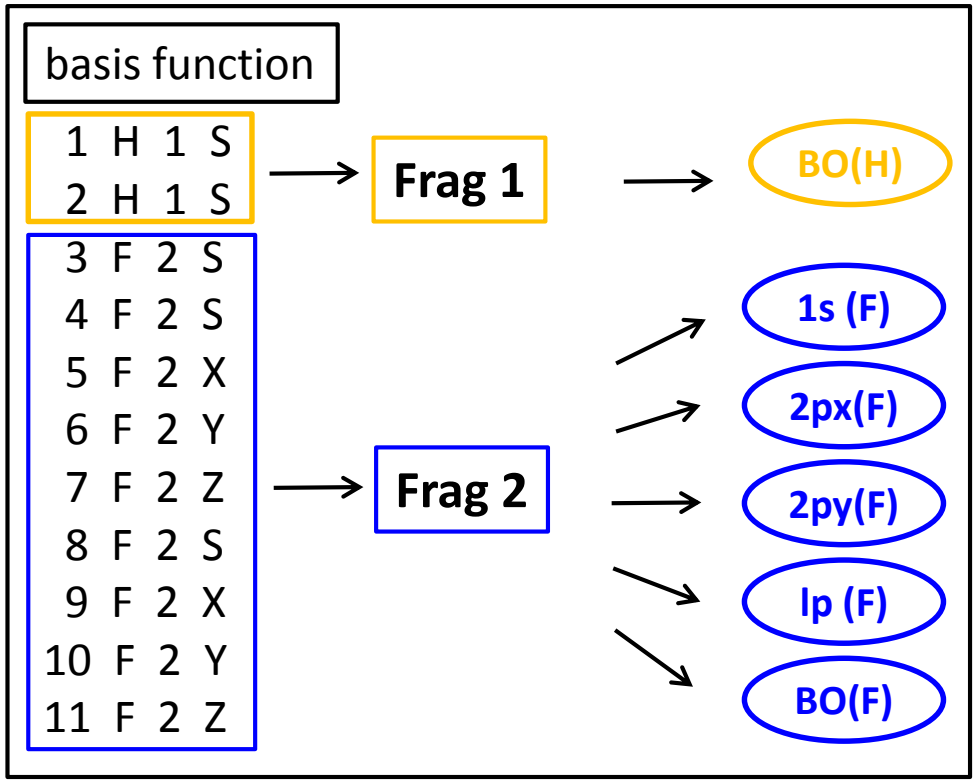
hf.xmi

```
$ctrl
str=full nae=2 nao=2 iprint=3 orbtyp=hao
frgtyp=atom iscf=5 guess=mo
$end
$orb
1 1 1 1 1 1
2
2
2
2
2
1
$end
$gus
1 1
2 2
3 4
4 5
5 3
6 3
$end
```

frgtyp=atom

The fragments of system are defined with atoms.

Fragtyp=atom and without $frag means that the orbitals will be determined by the atom directly.

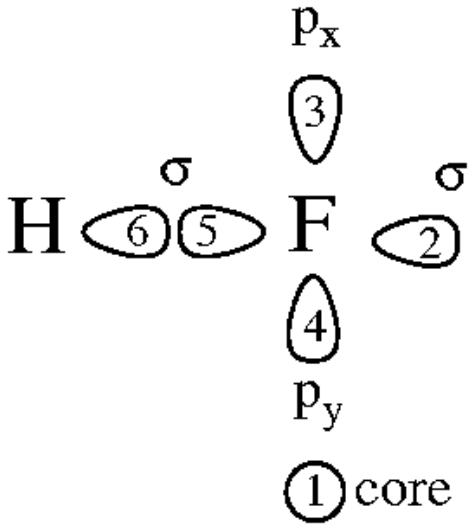


HF molecule, 3 structures hf.xmi

```
$ctrl
str=full nae=2 nao=2 iprint=3 orbtyp=hao
frgtyp=atom iscf=5 guess=mo
$end
$orb
1 1 1 1 1 1
2
2
2
2
2
1
$end
$gus
1 1
2 2
3 4
4 5
5 3
6 3
$end
```

VB orb
1 => frag 2
2 => frag 2
3 => frag 2
4 => frag 2
5 => frag 2
6 => frag 1

$orb is required when orbtyp=hao
Line 1 shows that there are six orbitals.
While the first 5 orbitals are described by the basis functions of F atom. (**frag 2**)
The last orbitals are described by the basis functions of H atom. (frag 1)



HF molecule, 3 structures

hf.xmi

```
$ctrl
str=full nae=2 nao=2 iprint=3 orbtyp=hao
frgtyp=atom iscf=5 guess=mo
$end
$orb
1 1 1 1 1 1
2
2
2
2
2
1
$end
$gus
1 1
2 2
3 4
4 5
5 3
6 3
$end
```

←

guess=mo : Initial guess of VB orbitals will be obtained directly from molecular orbitals

VB orb		MO
1	1s orbital of F atom	1
2	Lone pair of F atom	2
3	px pair of F atom	4
4	py pair of F atom	5
5	H-F bonding orbital on F atom	3
6	H-F bonding orbital on H atom	3

				1	2	3	4	5
				-26.2757	-1.5897	-0.7391	-0.631	-0.631
				A	A	A	A	A
1	H	1	S	0.000301	0.132423	-0.293056	0.000000	0.000000
2	H	1	S	0.001771	-0.013969	-0.107756	0.000000	0.000000
3	F	2	S	0.995513	-0.230516	-0.061755	0.000000	0.000000
4	F	2	S	0.021368	0.497220	0.137028	0.000000	0.000000
5	F	2	X	0.000000	0.000000	0.000000	0.654168	0.091145
6	F	2	Y	0.000000	0.000000	0.000000	-0.091145	0.654168
7	F	2	Z	-0.001488	-0.084307	0.548328	0.000000	0.000000
8	F	2	S	-0.005826	0.529428	0.244193	0.000000	0.000000
9	F	2	X	0.000000	0.000000	0.000000	0.485512	0.067646
10	F	2	Y	0.000000	0.000000	0.000000	-0.067646	0.485512
11	F	2	Z	0.001400	-0.047087	0.349640	0.000000	0.000000

Summary (2)

1. Automatically generate structures (str)
2. The determination of VB orbitals with ‘Frgtyp=atom’
3. The usage of ‘guess=mo’ with $gus.

Example 3. L-BOVB calculation for HF

Using VBSCF orbitals as guess orbitals

cp hf.orb hf-bovb.gus

Preparing GAMESS and XMVB input files for BOVB

hf-bovb.xmi

Running XMVB

hf-bovb.xmi

```
HF molecule, 3 structures
$ctrl
str=full nae=2 nao=2 bovb
iprint=3 orbtyp=hao frgtyp=atom iscf=2
guess=read
$end
$orb
1 1 1 1 1 1
2
2
2
2
2
1
$end
```

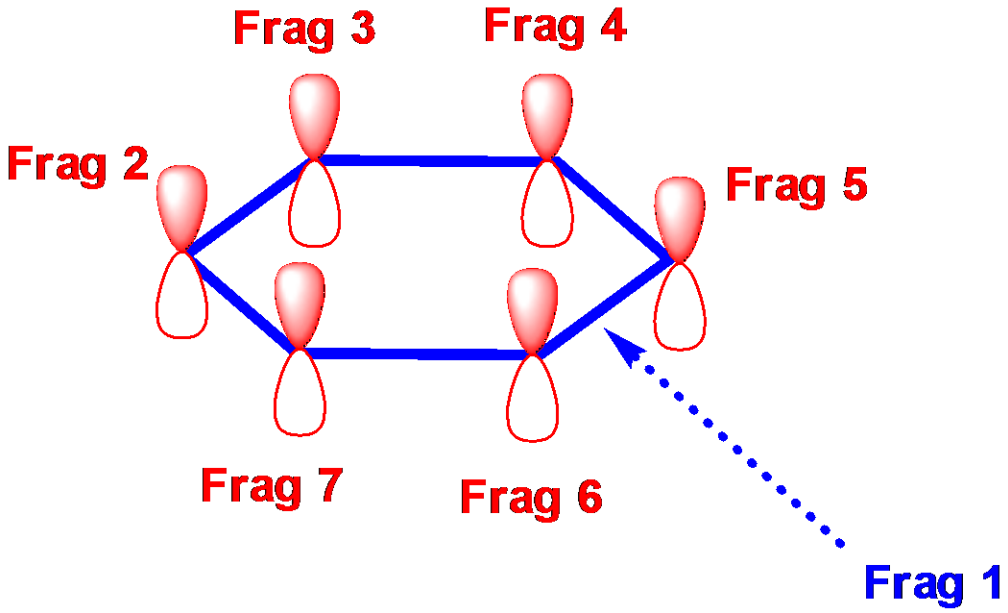
iscf = 4, 5,6 can not be used for BOVB calculations.
iscf=2 is recommended for BOVB

Example 4, benzene molecule

ben.int

```
RHF 6-31G*
 0  1
 C              0.6993466831   1.2113039873   0.0000000000
 C             -0.6993466831   1.2113039873   0.0000000000
 C             -1.3986933663   0.0000000000   0.0000000000
 C             -0.6993466831  -1.2113039873   0.0000000000
 C              0.6993466831  -1.2113039873   0.0000000000
 C              1.3986933663   0.0000000000   0.0000000000
 H              1.2427030147   2.1524247602   0.0000000000
 H             -1.2427030147   2.1524247602   0.0000000000
 H             -2.4854060294   0.0000000000   0.0000000000
 H             -1.2427030147  -2.1524247602   0.0000000000
 H              1.2427030147  -2.1524247602   0.0000000000
 H              2.4854060294   0.0000000000   0.0000000000
```

For C6H6, If the π bonding is focused, the orbitals for the bonding in XY plane (σ bonding), can be considered as one fragment. The π bonding can be considered as six fragments.



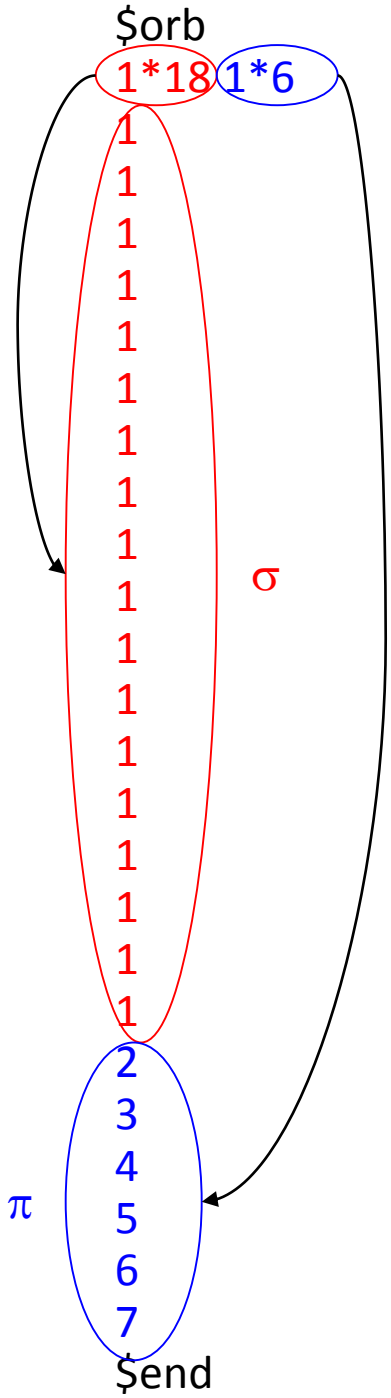
ben.xmi (part1)

```
benzene
$ctrl
str=full nao=6 nae=6
iscf=5 iprint=3 guess=auto
orbtyp=hao frgtyp=sao
$end
$frag
12 1*6
spxpydxxdyydzzdxy 1-12
pzdxzdyz 1
pzdxzdyz 2
pzdxzdyz 3
pzdxzdyz 4
pzdxzdyz 5
pzdxzdyz 6
$end
```

nao =6, the final 6 orbitals are selected as active orbitals.
nae=6, the number of active VB electrons
str = full => generate all VB structures
cov => only covalence
Ion => only ionic structures

frgtyp=sao, fragments are defined with symmetrized atomic orbitals.

Here “s” means basis function S, “pxy” means basis function Px and Py. “dxxdyy” means Dxx, Dyy,.
1-12 means the appointed basis sets of atoms 1~12



ben.xmi (part2)

There are 24 VB orbitals, the first 18 orbitals are described by frag 1; the remain 6 orbitals are described by frag 2 ~ frag 7 respectively.

How to get information from output files?

Information of XMO file

Input message → Input file, Integrals, Guess etc

SCF iterative procedure (final energy) →
Iteration ** E = **.** DE = **
VBSCF converged in ** iterations
Total Energy: **

S_{ij} and H_{ij} Matrices

Information of VB wavefunction →
Coefficients of structures and determinants
Weights of structures
Optimized orbitals

Properties and analysis → Bond order, atomic charge, dipole moments

Optional

Default

The VB calculation message in gamess output file is not correct

hf.xmo

Total Energy: -100.03252880
First Excited: -98.677762
The Last Change in Energy: -0.000000
Number of Iteration: 32

SCF procedures (final energy)

****** MATRIX OF OVERLAP ******

	1	2	3
1	1.000000	-0.694887	-0.694887
2	-0.694887	1.000000	0.318276
3	-0.694887	0.318276	1.000000

****** MATRIX OF HAMILTONIAN ******

	1	2	3
1	-2.554856	2.041815	1.827629
2	2.041815	-2.247238	-1.090411
3	1.827629	-1.090411	-1.685275

S_{ij} and H_{ij} matrices

If iscf =5, the S_{ij} and H_{ij} matrices only contain the information of active electrons. If you want to obtain the total H_{ij} of all electrons, please use iscf = 1, 2 and 3

****** WEIGHTS OF STRUCTURES ******

1	0.64395	******	1:4	5	6
2	0.30554	******	1:4	5	5
3	0.05051	******	1:4	6	6

Weights of VB structures

	1	2	3	4	5	6
1	0.000000	0.000000	0.000000	0.000000	0.000000	-0.835424
2	0.000000	0.000000	0.000000	0.000000	0.000000	-0.227552
3	1.012748	-0.084340	0.084340	-0.084340	0.049531	0.000000
4	-0.025976	0.300588	-0.300588	0.300588	-0.165593	0.000000
5	0.000000	-0.020440	-0.477373	-0.456933	0.000000	0.000000
6	0.000000	0.539422	0.252010	-0.287413	0.000000	0.000000
7	-0.010873	0.069765	-0.069765	0.069765	0.701583	0.000000
8	-0.054032	0.316476	-0.316475	0.316476	-0.042957	0.000000
9	0.000000	-0.015134	-0.353442	-0.338309	0.000000	0.000000
10	0.000000	0.399383	0.186585	-0.212797	0.000000	0.000000
11	-0.006949	0.056493	-0.056493	0.056493	0.419452	0.000000

Optimized orbitals

****** POPULATION AND CHARGE ******

ATOM	MULL.POP.	CHARGE	LOW.POP.	CHARGE
1 H	0.744964	0.255036	0.855733	0.144267
2 F	9.255036	-0.255036	9.144267	-0.144267

****** BOND ORDER ******

ATOM 1	ATOM 2	DIST	BOND ORDER
1 H	2 F	0.900	0.899

XMVB atomic population analysis


XMVB - GUI
A Graphical User Interface for XMVB Program