厦门能量分解分析程序(XEDA)使用介绍

谷俊井
厦门大学化学系
2022/04/23

1 使用入门

使用举例

使用建议

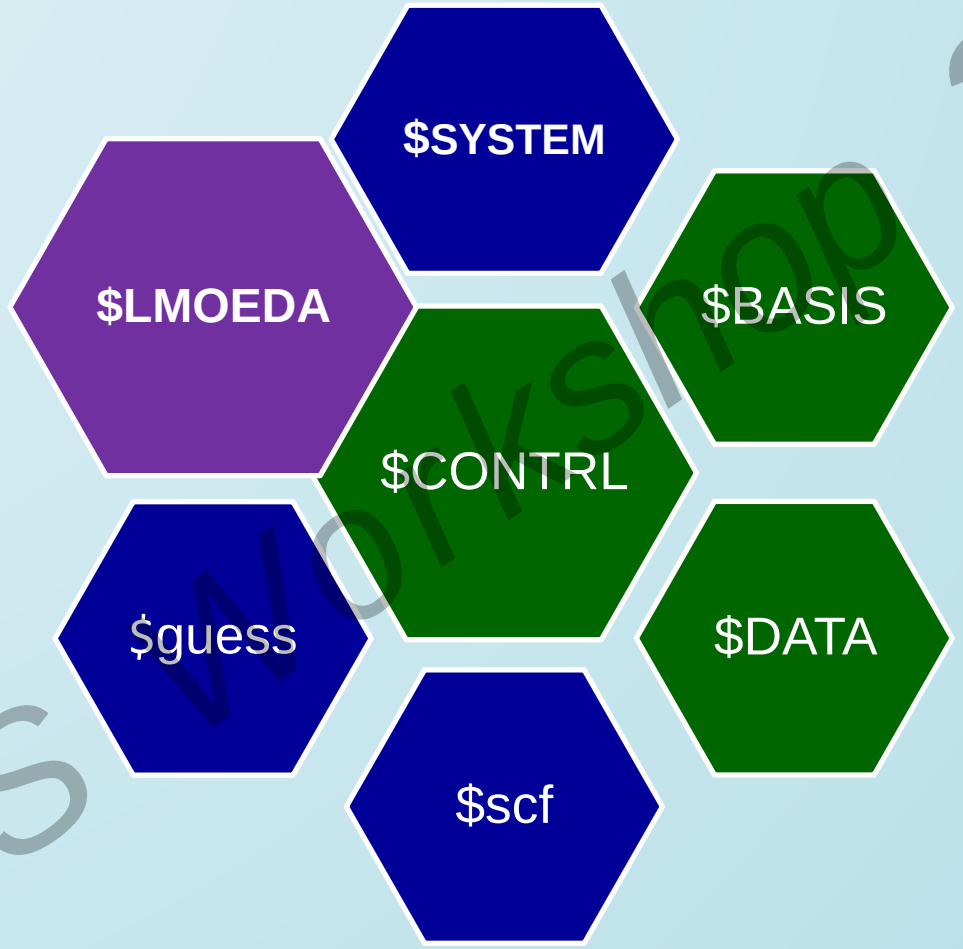
总结

使用方式

XEDA程序需要通过GAMESS获取积分和波函数，
因此输入输出文件格式和GAMESS一样。

GAMESS:
General Atomic and Molecular Electronic Structure System
https://www.msg.chem.iastate.edu/index.html

输入文件



Necessary

Optional

XEDA calculation

计算方法书写

```
SCFTYP = RHF
DFTTYP = B3LYP
```

```
SCFTYP = ROHF
DFTTYP = B3LYP
MULT = 3
```

```
SCFTYP = UHF
DFTTYP = B3LYP
MULT = 3
```

基组书写

Gaussian	GAMESS
6-31G	gbasis=n31 ngauss=6
6-31G*	gbasis=n31 ngauss=6 ndfunc=1
6-311+G*	gbasis=n311 ngauss=6 ndfunc=1 diffsp=.t.
6-311++G**	gbasis=n311 ngauss=6 ndfunc=1 npfunc=1 diffsp=.t. diffs = .t.
aug-cc-pVTZ	gbasis =acct (ispher=1 is necessary in $CONTRL)

单点计算

```
$contrl runtyp=energy scftyp=rhf $end
$basis gbasis=n31 ngauss=6 $end
$data
F2 molecule
C1
F   9.0   0.000000  0.000000 -0.724000
F   9.0   0.000000  0.000000  0.724000
 $end
```

rhf for mult=1
rohf or uhf for mult >1

basis set: 6-31G

$DATA group
– Title line
– Symmetry group
– Atom input: NAME, nuclear charge, X, Y, Z

The molecular geometry from GAMESS or GAUSSIAN optimization.

Note:

- '$' sign specifying group must be in column 2
- All groups must terminate with $END (this $ can be anywhere except column 1)

XEDA关键词

$CONTRL … **RUNTYP=EDA DFTTYP=B3LYP** … $end
$LMOEDA … $end

MATOM	单体原子个数
MCHARG	单体电荷
MMULT	单体多重度
RDVECM	读取初始猜测
EDATYP	• GKS, will do GKS-EDA calculation • BSEDA, will run GKS-EDA(BS) on open shell singlet

$SCF DIIS=.T. SOSCF=.F. DIRSCF=.T. FDIFF=.F. NPUNCH=1 $END

DIIS: Pulay's DIIS interpolation, SOSCF: 2nd order SCF orbital optimization

Only one of DIIS or SOSCF may be .TRUE. in any run.

DIRSCF: direct SCF calculation which stores integrals on disk storage when false

FDIFF: to compute only the change in Fock matrices, to turn this parameter off for cases with many diffuse functions in the basis set, or large molecules.

NPUNCH: to punch out the occupied orbitals

使用入门

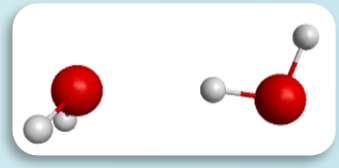
2 使用举例

使用建议

总结

(1) water dimer输入文件

氢键



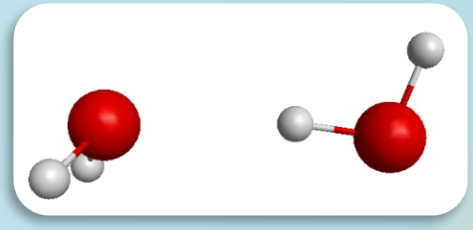
```
!water-dimer single-point calculation
 $CONTRL SCFTYP=RHF ICHARG=0 MULT=1 ispher=1 $end
 $BASIS GBASIS=ccd $END
 $SCF DIIS=.t. DIRSCF=.T. SOSCF=.f. FDIFF=.F. NPUNCH=1 $END
 $SYSTEM MWORDS=100 memddi=100 $END
 $DATA
  water-dimer
  C1
  O      8.0     -1.4144282139   0.0586474087   0.0000582983
  H      1.0     -1.7584849734  -0.4192312817  -0.7610094201
  H      1.0     -1.7586293132  -0.4192344610   0.7610625431
  O      8.0      1.4895241886  -0.0665781904  -0.0001866907
  H      1.0      0.5304648330   0.0689840578  -0.0000513225
  H      1.0      1.8575560391   0.8205325366   0.0001265917
 $end
```

(1) water dimer输入文件

氢键

The 1st line of comments is necessary for cloud computing.

```
!water-dimer XEDA calculation
 $CONTRL SCFTYP=RHF RUNTYP=eda dfttyp=wb97x-d ICHARG=0 ispher=1 $end
 $LMOEDA MATOM(1)=3 3                                    EDATYP=gks $END
 $BASIS GBASIS=ccd $END
 $SCF DIIS=.t. SOSCF=.f. DIRSCF=.T. FDIFF=.F. NPUNCH=1 $END
 $SYSTEM MWORDS=100 memddi=100 $END
 $DATA
  water-dimer
  C1
  O      8.0    -1.4144282139   0.0586474087   0.0000582983
  H      1.0    -1.7584849734  -0.4192312817  -0.7610094201
  H      1.0    -1.7586293132  -0.4192344610   0.7610625431
  O      8.0     1.4895241886  -0.0665781904  -0.0001866907
  H      1.0     0.5304648330   0.0689840578  -0.0000513225
  H      1.0     1.8575560391   0.8205325366   0.0001265917
 $end
```

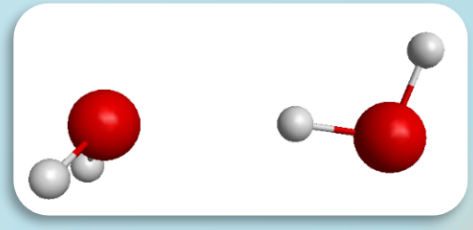


(1) water dimer输入文件

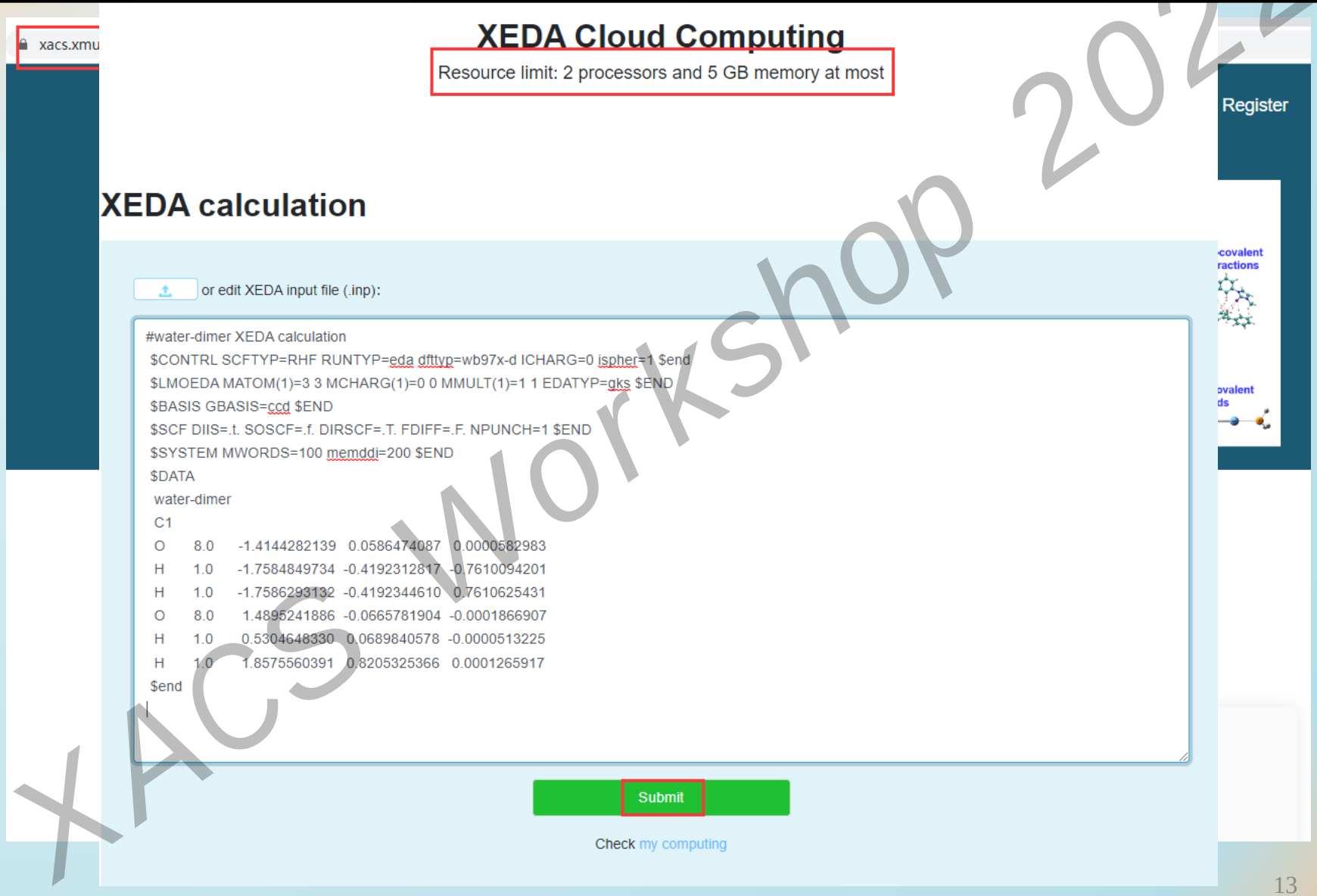
氢键

The 1st line of comments is necessary for cloud computing.

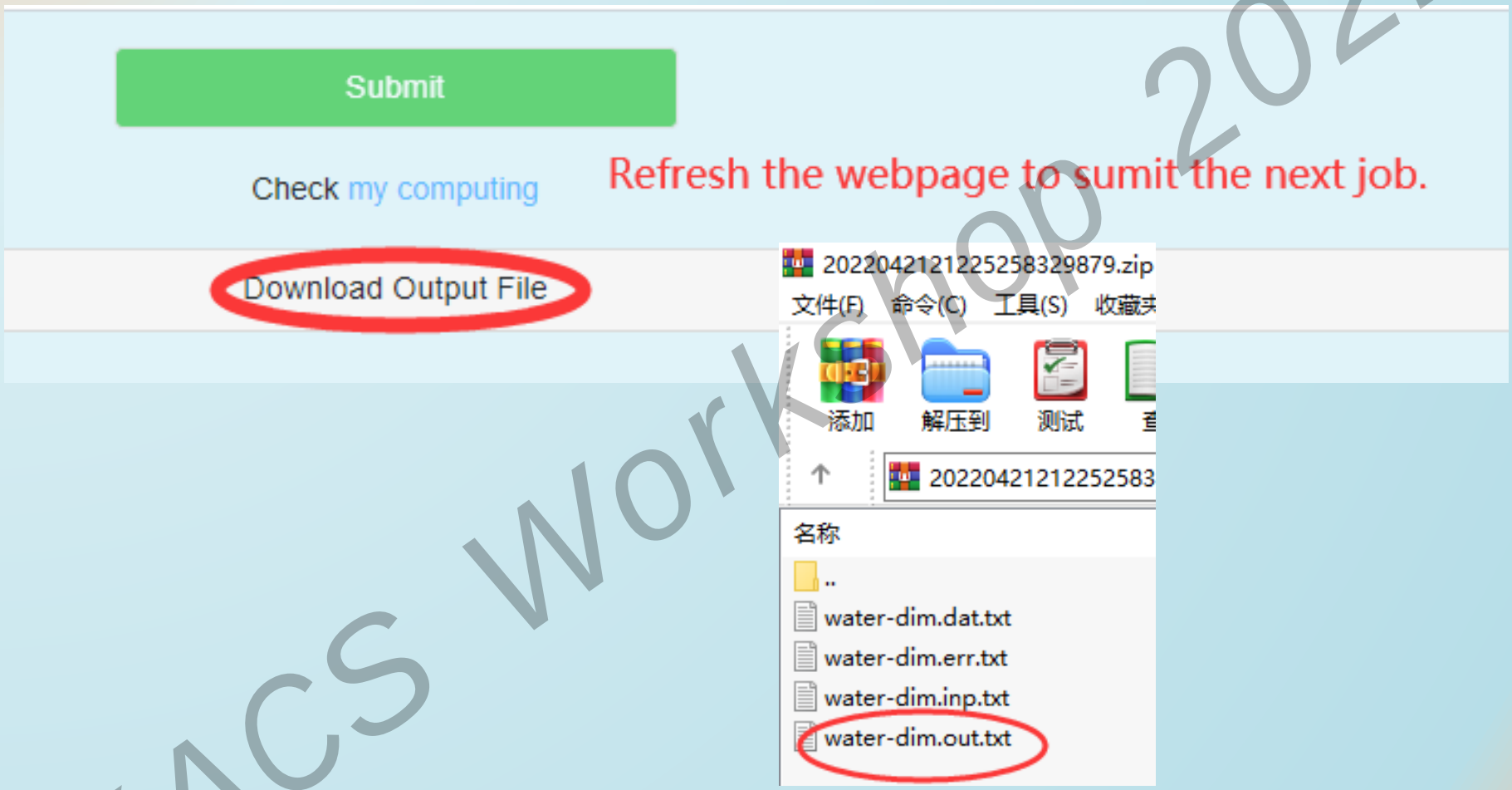
```
!water-dimer XEDA calculation
 $CONTRL SCFTYP=RHF RUNTYP=eda dfttyp=wb97x-d ICHARG=0 ispher=1 $end
 $LMOEDA MATOM(1)=3 3 MCHARG(1)=0 0 MMULT(1)=1 1 EDATYP=gks $END
 $BASIS GBASIS=ccd $END
 $SCF DIIS=.t. SOSCF=.f. DIRSCF=.T. FDIFF=.F. NPUNCH=1 $END
 $SYSTEM MWORDS=100 memddi=100 $END
 $DATA
  water-dimer
  C1
  O      8.0    -1.4144282139   0.0586474087   0.0000582983
  H      1.0    -1.7584849734  -0.4192312817  -0.7610094201
  H      1.0    -1.7586293132  -0.4192344610   0.7610625431
  O      8.0     1.4895241886  -0.0665781904  -0.0001866907
  H      1.0     0.5304648330   0.0689840578  -0.0000513225
  H      1.0     1.8575560391   0.8205325366   0.0001265917
 $end
```



(1) water dimer输出文件



(1) water dimer输出文件



(1) water dimer输出文件

```
*******************************
SUMMARY OF INTERACTION ENERGIES
  XEDA IN XIAMEN UNIVERSITY
 - ZHEN TANG AND PEIFENG SU -
*******************************
```

OWN BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.011912	-7.48
EXCHANGE ENERGY	EX=	-0.010438	-6.55
REPULSION ENERGY	REP=	0.019678	12.35
POLARIZATION ENERGY	POL=	-0.005740	-3.60
GRIMME DISP CORRECTION	DC=	-0.000753	-0.47
ELECTRON CORRELATION	CORR=	-0.003373	-2.12
TOTAL INTERACTION ENERGY	E=	-0.012538	-7.87

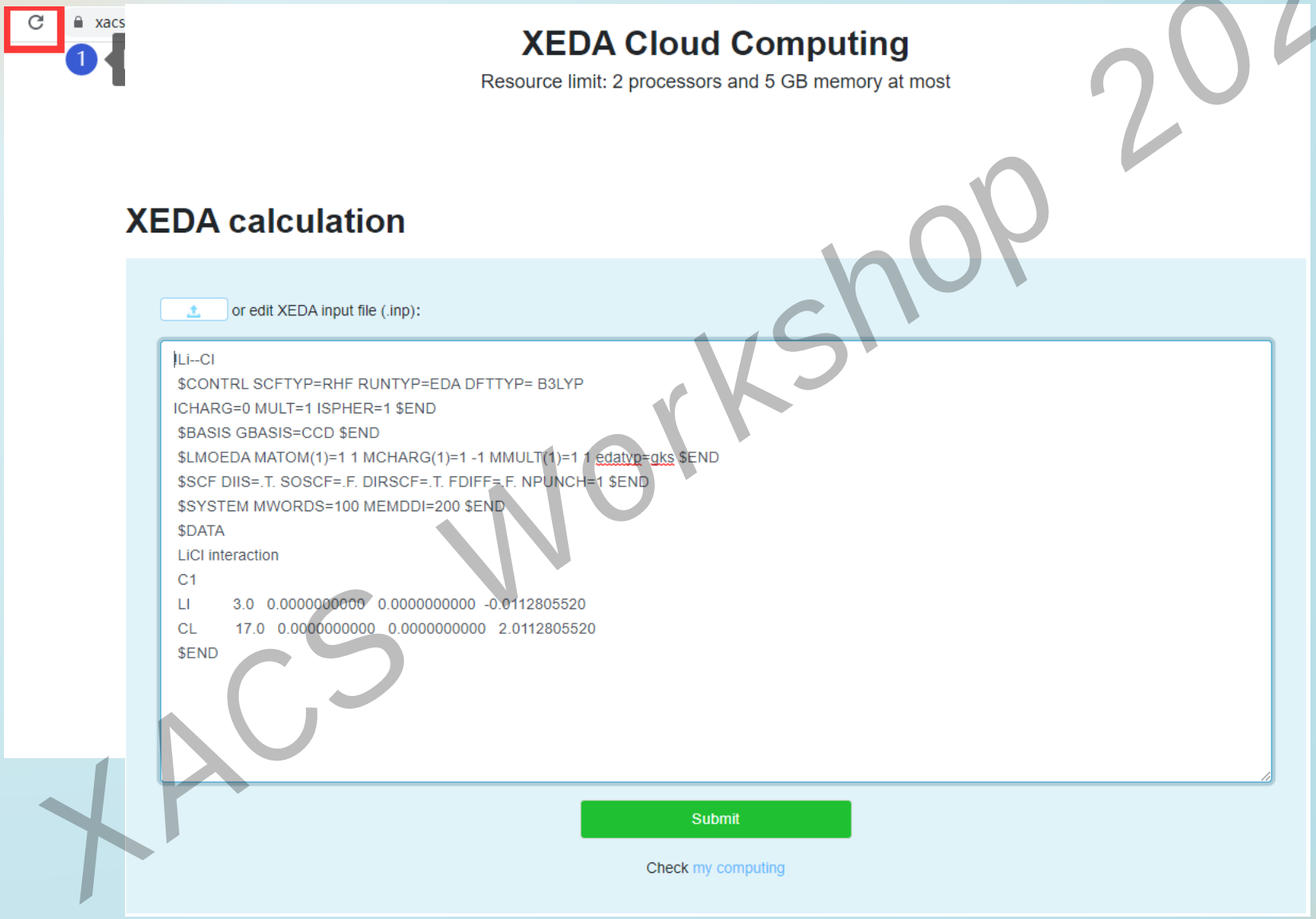
ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.014554	-9.13
EXCHANGE ENERGY	EX=	-0.017726	-11.12
REPULSION ENERGY	REP=	0.030986	19.44
POLARIZATION ENERGY	POL=	-0.004060	-2.55
GRIMME DISP CORRECTION	DC=	-0.000753	-0.47
ELECTRON CORRELATION	CORR=	-0.001920	-1.20
TOTAL INTERACTION ENERGY	E=	-0.008027	-5.04

(2) Li^+…Cl^-输入文件

离子键

```
!Li--Cl
 $CONTRL SCFTYP=RHF RUNTYP=EDA DFTTYP= B3LYP
ICHARG=0 MULT=1 ISPHER=1 $END
 $BASIS GBASIS=CCD $END
 $LMOEDA MATOM(1)=1 1 MCHARG(1)=1 -1 MMULT(1)=1 1 edatyp=gks $END
 $SCF DIIS=.T. SOSCF=.F. DIRSCF=.T. FDIFF=.F. NPUNCH=1 $END
 $SYSTEM MWORDS=100 MEMDDI=100 $END
 $DATA
 LiCl interaction
 C1
 LI         3.0   0.0000000000   0.0000000000  -0.0112805520
 CL        17.0   0.0000000000   0.0000000000   2.0112805520
 $END
```

(1) water dimer输出文件



(2) Li^+…Cl^-输出文件

```
*******************************
SUMMARY OF INTERACTION ENERGIES
  XEDA IN XIAMEN UNIVERSITY
 - ZHEN TANG AND PEIFENG SU -
*******************************
```

OWN BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.261244	-163.93
EXCHANGE ENERGY	EX=	-0.021811	-13.69
REPULSION ENERGY	REP=	0.064614	40.55
POLARIZATION ENERGY	POL=	-0.034185	-21.45
ELECTRON CORRELATION	CORR=	-0.015566	-9.77
TOTAL INTERACTION ENERGY	E=	-0.268192	-168.29

ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.262932	-164.99
EXCHANGE ENERGY	EX=	-0.025402	-15.94
REPULSION ENERGY	REP=	0.076015	47.70
POLARIZATION ENERGY	POL=	-0.031170	-19.56
ELECTRON CORRELATION	CORR=	-0.005754	-3.61
TOTAL INTERACTION ENERGY	E=	-0.249243	-156.40

(3) CH3---CH3输入文件

共价键

```
!ethane
 $CONTRL SCFTYP=ROHF RUNTYP=EDA DFTTYP=PBE ICHARG=0 $END
 $LMOEDA MATOM(1)=4 4 MCHARG(1)=0 0 MMULT(1)=2 -2 edatyp=gks $END
 $BASIS GBASIS=N311 NGAUSS=6 NDFUNC=1 DIFFSP=.T. $END
 $SCF DIIS=.T. SOSCF=.F. DIRSCF=.T. FDIFF=.F. NPUNCH=1 $END
 $SYSTEM MWORDS=100 MEMDDI=100 $END
 $DATA
 CH3-CH3 interaction
 C1
 C    6.0   -0.49027225   0.46910772  -0.00444996
 H    1.0   -0.22655283   1.07803512   0.85698873
 H    1.0   -1.10423672  -0.35536841   0.35016090
 H    1.0   -1.10425293   1.07811451  -0.66366345
 C    6.0    0.75166166  -0.03806581  -0.72153479
 H    1.0    0.78037816  -1.12496066  -0.73800385
 H    1.0    1.65830922   0.30850673  -0.23127511
 H    1.0    0.78075457   0.30863136  -1.75175524
 $END
```

(3) CH3---CH3输出文件

```
*******************************
SUMMARY OF INTERACTION ENERGIES
  XEDA IN XIAMEN UNIVERSITY
 - ZHEN TANG AND PEIFENG SU -
*******************************
```

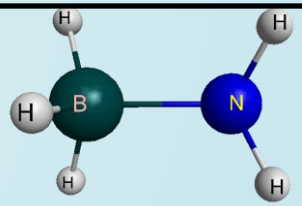
OWN BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.228817	-143.58
EXCHANGE ENERGY	EX=	-0.337435	-211.74
REPULSION ENERGY	REP=	0.694323	435.69
POLARIZATION ENERGY	POL=	-0.259811	-163.03
ELECTRON CORRELATION	CORR=	-0.049390	-30.99
TOTAL INTERACTION ENERGY	E=	-0.181130	-113.66

ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC ENERGY	ES=	-0.218824	-137.31
EXCHANGE ENERGY	EX=	-0.321252	-201.59
REPULSION ENERGY	REP=	0.667551	**418.90**
POLARIZATION ENERGY	POL=	-0.258182	-162.01
ELECTRON CORRELATION	CORR=	-0.048814	-30.63
TOTAL INTERACTION ENERGY	E=	-0.179520	-112.65

eclipsed conformer

(4) BH_3…NH_3输入文件

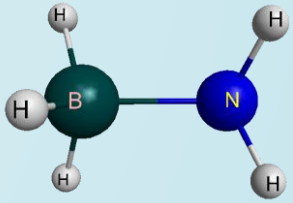
EDA-PCM




```
!BH3-NH3 in gas phase
 $CONTRL SCFTYP=RHF RUNTYP=EDA DFTTYP=B3LYP ICHARG=0 MULT=1 $END
 $LMOEDA MATOM(1)=4 4 MCHARG(1)=0 0 MMULT(1)=1 1 edatyp=gks $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
 $SCF DIIS=.T. SOSCF=.F. DIRSCF=.T. FDIFF=.F. NPUNCH=1 $END
 $SYSTEM MWORDS=50 MEMDDI=500 $END
 $DATA
 BH3-NH3 in water solution
 C1
 B         5.0  -1.4930097404  -0.5082255173   0.1193861744
 H         1.0  -0.2909569897  -0.6053374650   0.0759344076
 H         1.0  -1.9156069781   0.5145748522  -0.3618103786
 H         1.0  -2.0743035096  -1.4976304007  -0.2543430610
 N         7.0  -1.8483952471  -0.3946836719   1.7286231427
 H         1.0  -2.8481727853  -0.3078087733   1.8739751783
 H         1.0  -1.4009475344   0.4155452945   2.1428980703
 H         1.0  -1.5302644453  -1.2172120485   2.2291780163
 $END
```

(5) BH_3…NH_3 in water输入文件

EDA-PCM



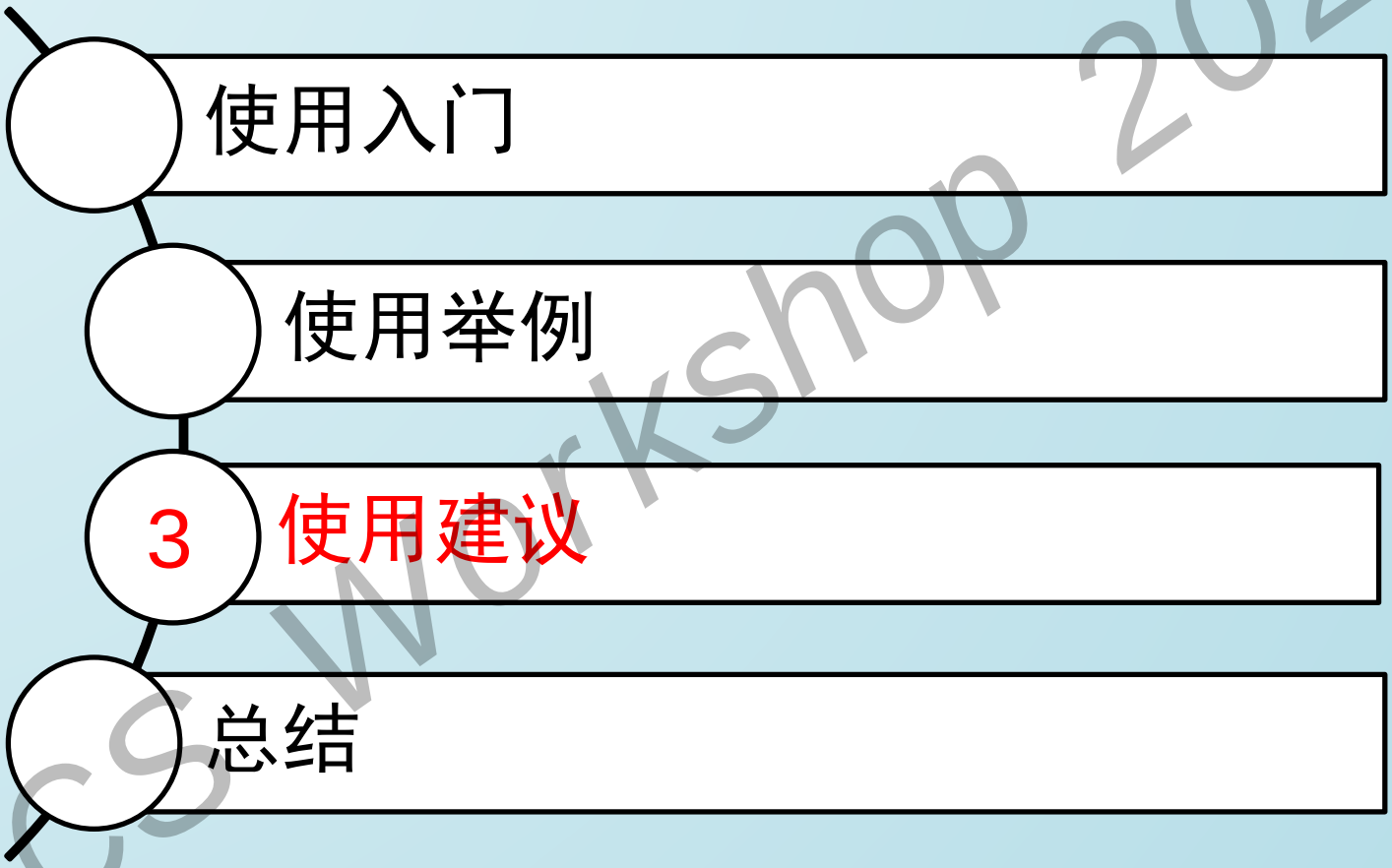

```
!BH3-NH3 in water phase
 $CONTRL SCFTYP=RHF RUNTYP=EDA DFTTYP=B3LYP ICHARG=0 MULT=1 $END
 $LMOEDA MATOM(1)=4 4 MCHARG(1)=0 0 MMULT(1)=1 1 edatyp=gks $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
 $PCM SOLVNT=WATER $END
 $SCF DIIS=.T. SOSCF=.F. DIRSCF=.T. FDIFF=.F. NPUNCH=1 $END
 $SYSTEM MWORDS=50 MEMDDI=500 $END
 $DATA
 BH3-NH3 in water solution
 C1
 B         5.0  -1.4930097404  -0.5082255173   0.1193861744
 H         1.0  -0.2909569897  -0.6053374650   0.0759344076
 H         1.0  -1.9156069781   0.5145748522  -0.3618103786
 H         1.0  -2.0743035096  -1.4976304007  -0.2543430610
 N         7.0  -1.8483952471  -0.3946836719   1.7286231427
 H         1.0  -2.8481727853  -0.3078087733   1.8739751783
 H         1.0  -1.4009475344   0.4155452945   2.1428980703
 H         1.0  -1.5302644453  -1.2172120485   2.2291780163
 $END
```

(5) BH_3…NH_3 in water输出文件

OWN BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC FREE ENERGY	ES=	-0.151984	-95.37
EXCHANGE FREE ENERGY	EX=	-0.195901	-122.93
REPULSION FREE ENERGY	REP=	0.375813	235.83
POLARIZATION FREE ENERGY	POL=	-0.084157	-52.81
DESOLVATION FREE ENERGY	DESOL=	-0.017224	-10.81
ELECTRON CORRELATION	CORR=	-0.014261	-8.95
TOTAL INTERACTION ENERGY	E=	-0.087714	-55.04

ALL BASIS SET		HARTREE	KCAL/MOL
ELECTROSTATIC FREE ENERGY	ES=	-0.146578	-91.98
EXCHANGE FREE ENERGY	EX=	-0.224589	-140.93
REPULSION FREE ENERGY	REP=	0.425172	266.80
POLARIZATION FREE ENERGY	POL=	-0.107240	**-67.29**
DESOLVATION FREE ENERGY	DESOL=	-0.016774	-10.53
ELECTRON CORRELATION	CORR=	-0.012260	-7.69
TOTAL INTERACTION ENERGY	E=	-0.082269	**-51.62**

VB conclusion: Charge-Shift Bond



如何判断计算是否正常结束？

失败例子

```
MONOMER    2

                    OWN BASIS              ALL BASIS

T              1638.08371271          1637.96077132
V             -3901.02170315         -3900.47724347
X               -11.37252651           -11.36907602
J               636.52341747           636.09306286
N                 0.00000000             0.00000000
EC               -2.13193258            -2.13911992
DC               -0.00000000            -0.00000000
E                 0.00000000             0.00890608
```

```
------------
ALL BASIS SET                                HARTREE          KCAL/MOL
-------------
ELECTROSTATIC ENERGY                  ES=      -0.213882          -134.21
EXCHANGE ENERGY                       EX=      -0.066621           -41.81
REPULSION ENERGY                     REP=       0.170784           107.17
POLARIZATION ENERGY                  POL=     122.031345         76575.89
GRIMME DISP CORRECTION                DC=      -0.004427            -2.78
DFT CORRELATION                     CORR=     104.050198         65292.54
TOTAL INTERACTION ENERGY HF OR DFT     E=     225.967398        141796.80
```

计算不收敛怎么办？-定义初始猜测

RDVECM=.TRUE.

默认为.FALSE.，适用于RHF，UHF，ROHF

读入初始猜测

给出每个或部分单体的初始猜测（$VEC1，$VEC2，...）

超分子的初始猜测由$VEC0提供，为可选项

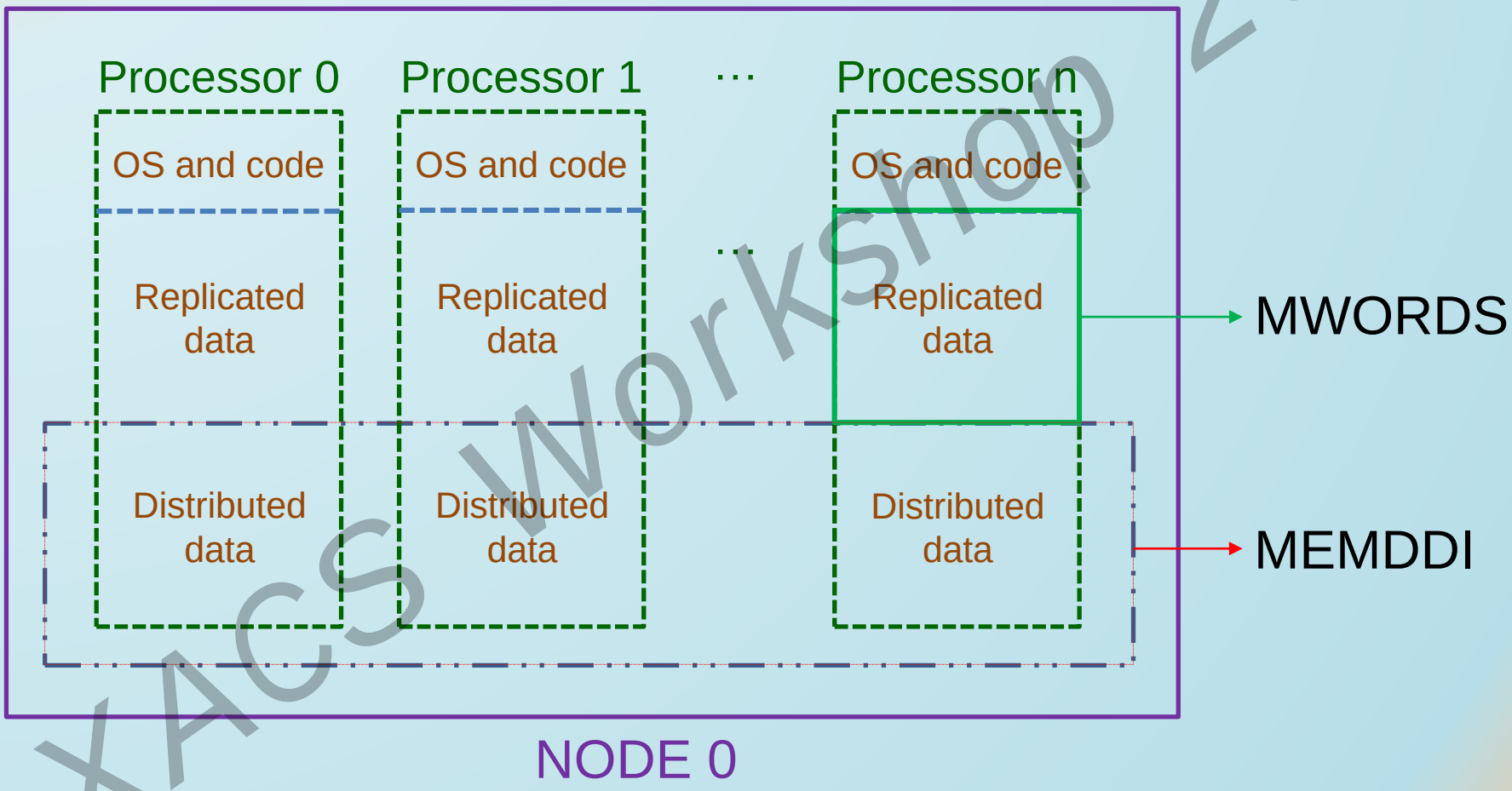
VEC可由Gaussian或GAMESS的输出文件得到

计算不收敛怎么办？定义初始猜测

```
 $CONTRL SCFTYP=RHF RUNTYP=EDA ICHARG=0 dfttyp=blyp $end
 $LMOEDA MATOM(1)=12 3 MCHARG(1)=0 0 MMULT(1)=1 1
edatyp=gks RDVECM=.T. $END
 $BASIS GBASIS=n31 ngauss=6 $END
 $system …
 $DATA
…
 $END
 $VEC1  (单体1的波函数)
…
 $END
 $VEC2  (单体2的波函数)
…
 $end
```

自定义运行内存

$SYSTEM MWORDS=XX MEMDDI=YY $END



自定义运行内存

$SYSTEM MWORDS=**100** MEMDDI=**100** $END

MWORDS: Replicated memory for one core.
MEMDDI: Total distributed memory for parallel jobs.
UNIT IN MWORDS, 1word=8bytes

TOTAL MEMORY=MWORDS*(CORE NUMBER)+MEMDDI

GAMESS建模与可视化

MacMolPlt

可显示GAMESS输出结果，
如结构、反应路径、分子轨道、电子密度、振动模式等。
包括基本的分子建模。

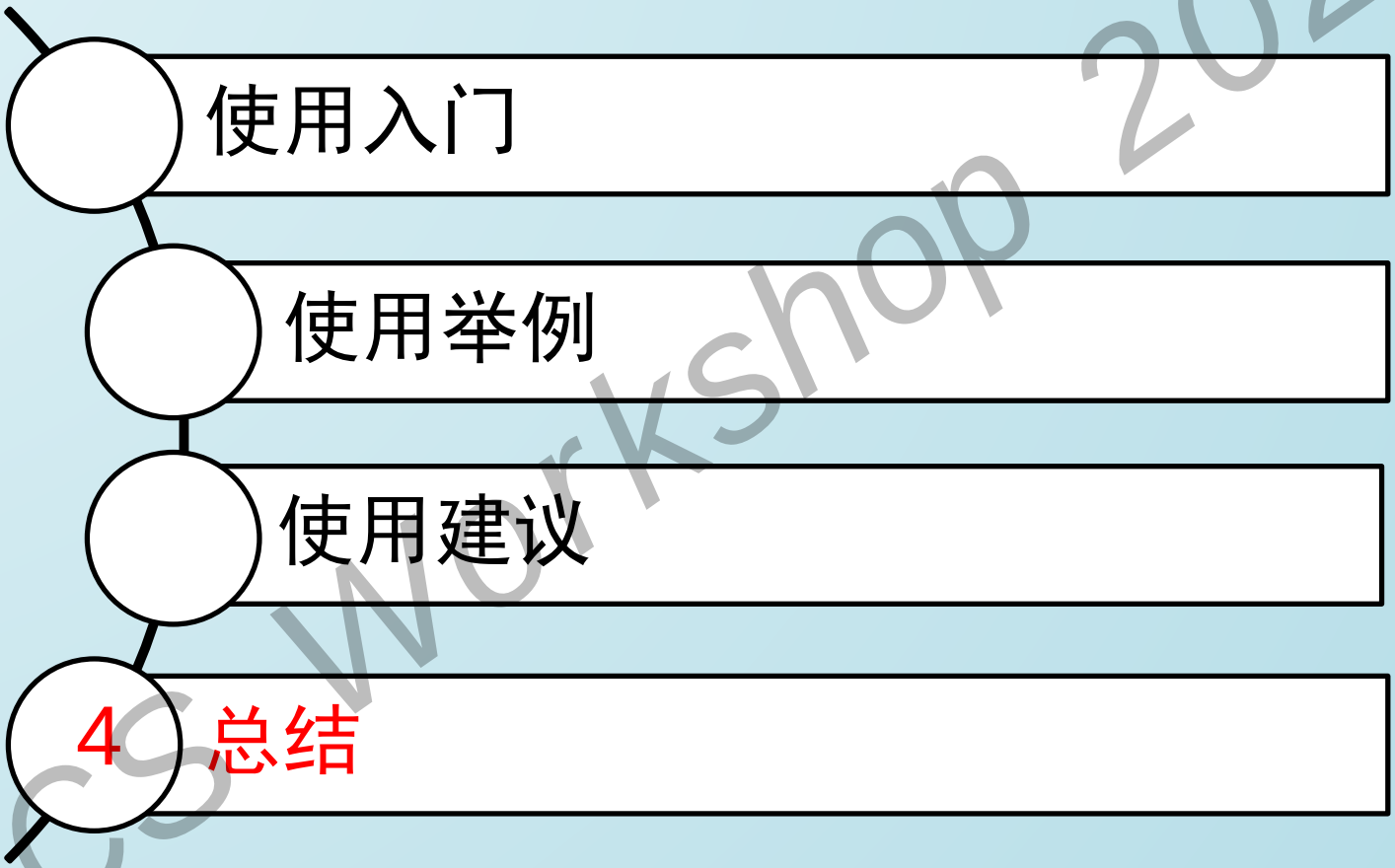
https://www.msg.chem.iastate.edu/graphics/programs.html

GAMESS手册

重点关注的关键词:

- $SCF
- $DFT

https://www.msg.chem.iastate.edu/gamess/documentation.html



总结

1. 只需要指定每个单体几何构型、电荷和多重度，就能计算出单体间的相互作用信息。
2. 通过每个相互作用分项的相对大小和比重，就能理解相互作用的本质。

Free to get &

Welcome to contact us:

xmvb@xmu.edu.cn

Chemistry: Chem Is Try.
I Chem, so I try.