MOKIT Manual

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1 Introduction

1.1 Introduction to MOKIT

The full name of MOKIT is **Molecular Orbital KIT**. MOKIT offers various utilities and modules to transfer MOs among various quantum chemistry software packages. Besides, the **AutoMR** program in MOKIT can set up and run common multi-reference calculations in a block-box way.

With MOKIT, one can perform multi-reference calculations in a quite simple way, and utilize the best modules of each program, e.g.

```
   UHF(UNO) -> CASSCF -> CASPT2
   Gaussian      PySCF       OpenMolcas
or
   UHF(UNO) -> GVB     -> CASSCF -> NEVPT2
   Gaussian      GAMESS    PySCF       PySCF

   RHF     ->      GVB     -> CASSCF   -> ic-MRCISD+Q
   Gaussian      GAMESS    PySCF       OpenMolcas
```

Negligible energy loss (usually<1e-6 a.u., for the same wave function method in two programs) are ensured during transferring MOs, since the basis order of angular momentum up to H(i.e. *l*=5) is explicitly considered.

Note that although MOKIT aims to make the multi-reference calculations block-box, the users are still required to have practical experiences of quantum chemistry computations (e.g. familiar with routine DFT calculations in Gaussian). You are encouraged to learn how to use Gaussian first if you are a fresh hand. See Appendix A2 for more information.

1.2 How to Cite

If you use any module or utility of MOKIT in your work, you **MUST CITE** the MOKIT in the main body of your paper. Three examples are shown below:

E1. The HF/DFT calculations are performed using Gaussian 16[1] software package, and the MC-PDFT calculation is performed by OpenMolcas[2]. The utility fch2inporb in MOKIT[3] is used to transfer molecular orbitals from Gaussian to OpenMolcas.

E2. The GKS-EDA computations are performed by the XEDA[1] module interfaced with the GAMESS[2] program. For better SCF convergence and accelerating the EDA computation, converged molecular orbitals of each monomer and the complex are taken and converted from Gaussian[3] DFT calculations. This procedure is automatically conducted by the MOKIT[4] package.

E3. The GVB, CASSCF and CASPT2-K computations are performed using the GAMESS[1] and PySCF[2] and ORCA[3] packages, respectively. All the multiconfigurational computations are performed in a black-box way with the help of MOKIT[4].

As for the content of the reference, you should cite like
[4] Jingxiang Zou, MOKIT program, https://gitlab.com/jxzou/mokit (accessed Jul 5, 2022).

where the "Jul 5" should be modified as the version you used. The version number can be found by running "automr --version", or simply "automr -v". Note that citing MOKIT only in the supporting information of a paper is **INSUFFICIENT**, since such citation can hardly be gathered by search engine or database.

If any of the keyword ist=0,1,3 (see Section 4.4.4) in program AutoMR is used, citing the following two papers would be appreciated
[2] J. Chem. Theory Comput. 2019, 15, 141-153. DOI: 10.1021/acs.jctc.8b00854
[3] J. Phys. Chem. A 2020. DOI: 10.1021/acs.jpca.0c05216.

Besides, you need to **CITE** all quantum chemistry software packages called in your AutoMR job(s). For example, the file

mokit/examples/automr/00-h2o_cc-pVDZ_1.5.gjf

is a CASSCF job. 3 software packages will be called:
(1) Gaussian will be called to perform RHF/UHF;
(2) GAMESS will be called to perform GVB;
(3) PySCF will be called to perform CASSCF.

Therefore, in this case you should also **cite** corresponding references of Gaussian, GAMESS and PySCF, as well as possible references of electronic-structure methods and basis sets.

In the future version of MOKIT, there will be a Citation.txt file generated after your computations terminated. You can simply copy citation information in that plain text file.

You can use MOKIT to perform computations for other people. But remember to remind he/she that MOKIT should be properly cited.

2 Installation

The installation of MOKIT does not require any root privilege.

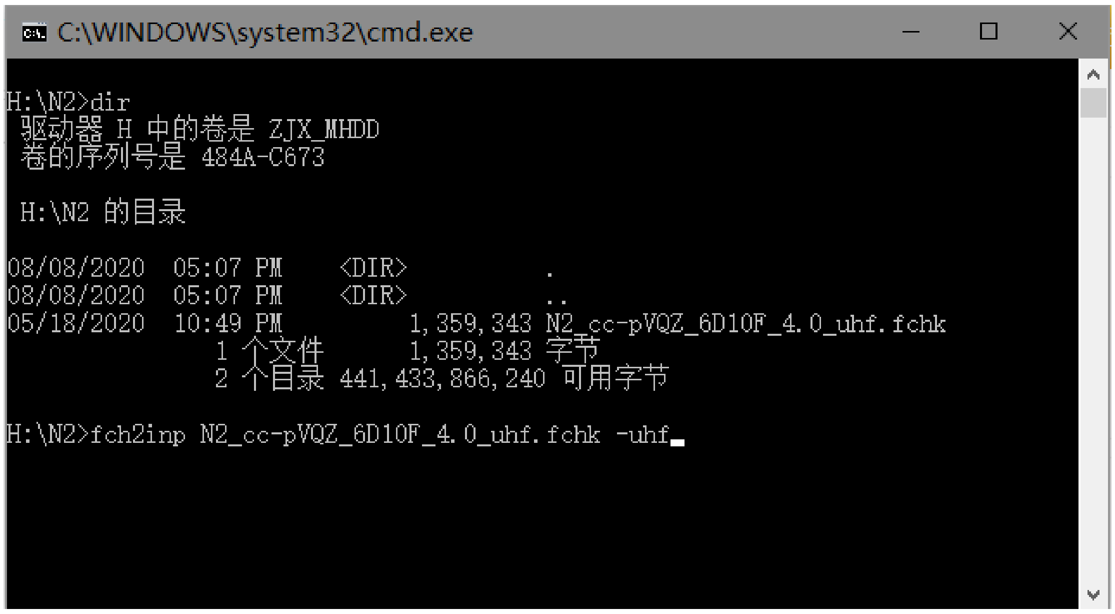
2.1 Pre-built Windows executables

If you only want to use some utilities of MOKIT (e.g. transfer MOs among various programs, generate input files of various programs), the most convenient way is probably to use the pre-built (or pre-compiled) Windows executables. Note that the version of pre-built Windows executables is often older than that of MOKIT source code, so you are recommended to download source code and compile them under Linux.

Only about 23 out of all utilities in MOKIT are provided. These executables are compressed into a .7z file and can be downloaded at Releases. Download, uncompress it, and set the environment variables, then these utilities can used in any directory.

To set the environment variables, search 'environment' ("环境变量" in Chinese) in the Windows search bar, then press Enter and click Edit to edit the PATH variables. Create a new path and type the path of MOKIT \bin into it. For example, on my computer the path is H:\Software\MOKIT\mokit\bin.

Press the combination keys Win+R on the keyboard, type 'cmd' to prompt CMD, and **change into the directory where your .fch(k) file holds**, simply run like



```
H:\N2>dir
 驱动器 H 中的卷是 ZJX_MHDD
 卷的序列号是 484A-C673

 H:\N2 的目录

08/08/2020  05:07 PM    <DIR>          .
08/08/2020  05:07 PM    <DIR>          ..
05/18/2020  10:49 PM         1,359,343 N2_cc-pVQZ_6D10F_4.0_uhf.fchk
               1 个文件      1,359,343 字节
               2 个目录 441,433,866,240 可用字节

H:\N2>fch2inp N2_cc-pVQZ_6D10F_4.0_uhf.fchk -uhf
```

2.2 Installation under Linux

2.2.1 Prerequisite

1. Intel compiler (for ifort compiler and Math Kernel Library(MKL))
2. Anaconda Python3 (for python, f2py, etc)

It is strongly recommended to install **Intel compiler** and **Anaconda Python3** on your computer/node. Although these two packages may be large, they meet all prerequisites of compiling MOKIT. Note that the Intel compiler is free of charge for academic use.

If you do not have the ifort compiler and MKL on your node/computer, you may want to download and install them. There are several versions recommended, you can choose any one of them:
(1) Intel Parallel Studio XE 2017~2020 are all OK (2019 or 2020 preferred).
(2) Since 2021, there is no Parallel Studio XE, but only the Intel® oneAPI. You should download and install both HPC Toolkit and MKL if you want to use 2021 version.

If you want to use any Fortran compiler other than `ifort` (e.g. `gfortran`), you need to install the MKL library (or equivalently, LAPACK/BLAS, OpenBLAS, etc) on your node. And then **uncomment** the first few lines in file mokit/src/Makefile for gfortran settings. And of course, use '#' to comment lines of ifort in that Makefile. The recommended version of gfortran is >= 4.8.5. Gfortran <= 4.7 is outdated and thus not recommended. Even if you can successfully compile all utilities using gfortran<=4.7, they may not work normally or correctly.

If you had compiled MOKIT before, and assuming now you want to use another compiler, REMEMBER to run `make distclean` before re-compiling. Note that if you change the version of Python on your node/machine, the dynamic library files *.so in $MOKIT_ROOT/lib/ will become unrecognized, in which case you have to re-compile MOKIT.

If you want to use Python3 or Miniconda instead of Anaconda Python3, you need to ensure that the `f2py` compiler/wrapper is valid. For example, run `which f2py` in Shell to see whether f2py exists. If your `f2py` comes from psi4conda/bin/, then errors may occur when compiling MOKIT. In such case you are recommended to comment environment variables of PSI4 and use your previous python, e.g. Anaconda Python 3. MOKIT can still call PSI4 even if PSI4 environment variables commented (see Section 2.2.3).

For trouble shooting during compiling, please read Section A1.

The AutoMR program/executable in MOKIT is an integrated interface program connecting common quantum chemistry software packages. The AutoMR itself does not contain any code for computing electron integrals, it just transfers MOs among software, sometimes read one-electron integrals from some package, and call various packages to do specified computations. Therefore, the users are assumed to have successfully installed these common software packages, which are Gaussian, PySCF, GAMESS, OpenMolcas, Molpro, ORCA, BDF, PSI4, and Dalton. Some recommended versions are shown below

Gaussian: >= g09 (>=g16 preferred)
PySCF >= 1.7.4
GAMESS >= 2017 (>= 2019 preferred)
ORCA >= 4.2.1 (>= 5.0 preferred)
OpenMolcas >= v21.02
Molpro >= 2015 (>= 2019 preferred)
BDF >= 0.9.8

PSI4 >= 1.3.2 (>= 1.4 preferred)
Dalton >= 2020.0, OpenMP version

For DMRG related packages:
Block >= 1.5.3
pyblock2 >= preview-0.5.0
QCMaquis >= 3.0.3
CheMPS2 >= 1.8.9

Older versions are not recommended, since (1) they are possibly not tested by the author jxzou, (2) they had been tested but some functionality had not been (correctly) implemented at that time. So that they may work or may not. OpenMolcas v18.09 has also been tested, but you need to take care of a problem, see Section A1, Q5 in Appendix.

Of course, not all packages will be called in an AutoMR job. It depends on the job type and the program specified by users (see Section 4.4.9 ~ 4.4.19 for details). Usually three software packages (Gaussian, PySCF and GAMESS) are extensively used in routine computations. Thus you are recommended to install at least these three packages. If you have any difficulty in installing software, please read their corresponding manuals carefully. Or you can find answers from their official websites, forums, GitHub/GitLab pages:

Gaussian: http://gaussian.com/help
PySCF: https://github.com/pyscf/pyscf/issues
ORCA: https://orcaforum.kofo.mpg.de
OpenMolcas: https://gitlab.com/Molcas/OpenMolcas/-/issues
Molpro: https://groups.google.com/d/forum/molpro-user
GAMESS: https://github.com/gms-bbg/gamess-issues/issues
PSI4: http://forum.psicode.org
Dalton: https://gitlab.com/dalton/dalton

If you can read Chinese, the following installation instructions or tutorials of common software packages on the WeChat Official Accounts 'quantumchemistry' (微信公众号“量子化学”) are strongly recommended:

1. 《Linux 下安装 Intel oneAPI》
2. 《Linux 下 Gaussian 16 安装教程》
3. 《ORCA 5.0 安装及运行》
4. 《GAMESS 简易编译教程》
5. 《离线安装 PySCF-1.7.6》
6. 《PSI4 程序安装及运行》
7. 《量子化学程序 OpenMolcas 的简易安装》
8. 《离线编译 OpenMolcas+QCMaquis》
9. 《Block-1.5 的编译和安装》
10. 《Boost.MPI 的编译》
11. 《安装基于 openmpi 的 mpi4py》
12. 《自动做多参考态计算的程序 MOKIT》

also these installation instructions on GitLab

1. 《离线安装 PySCF-2.0.1》
2. 《离线安装 OpenMolcas-v22.06》
3. 《block2 的编译和安装》

Note that the original GAMESS source code can only deal with GVB up to 12 pairs. To go beyond that (which is routine type of calculation in AutoMR of MOKIT), please read Section 4.4.10 carefully. After re-compiling GAMESS (followed by instructions in Section 4.4.10), an executable 'gamess.01.x' will be generated. This is the executable to be called in automr.

2.2.2 How to compile

Assuming you've already downloaded the MOKIT .zip package, just run

```
unzip mokit-master.zip
```

to uncompress it. Note that do not uncompress the package in Windows* OS, but uncompress it in Linux* OS. Then simply run the following three command lines in Shell

```
mv mokit-master mokit
cd mokit/src
make all
```

to compile MOKIT. This will take about 2 minutes. There is no need to 'make install'. If you do not need automr and only want to compile one or several modules, e.g. fch2inp (for Gaussian -> GAMESS orbital transferring), then you simply need to run

```
make fch2inp
```

Be careful with hints on the screen, some modules depend on other modules, thus a compilation of two or three modules is necessary sometimes.

2.2.3 Environment variables

After successful compilation, you need to add the following environment variables into your ~/.bashrc file:

```
export MOKIT_ROOT=/home/$USER/software/mokit
export PATH=$MOKIT_ROOT/bin:$PATH
export PYTHONPATH=$MOKIT_ROOT/lib:$PYTHONPATH
export GMS=/home/$USER/software/games/rungms
export PSI4=/home/$USER/psi4conda/bin/psi4       # optional
export BDF=/home/$USER/software/bdf-pkg/sbin/run.sh       # optional
```

Note that do not mistake 'PYTHONPATH' for 'LD_LIBRARY_PATH'. Please modify the above paths to **suit your situations**. Since PySCF is run by python, OpenMolcas is run by pymolcas, Molpro is run by molpro, PSI4 is run by psi4 and Dalton is run by dalton, there is no extra environment variable to be exported here. But if you define export PSI4=..., then this variable has priority to the path found by which psi4.

The environment variable BDF are optional, there is no need to write it if you do not want to use BDF. For Dalton, currently only the MKL version of Dalton is supported. The MPI parallel version may be supported in the future.

The configuration file 'program.info' is no longer used since MOKIT 1.2.1. After writing environment variables, a logout and re-login on your terminal is strongly recommended.

The scratch directory (in Chinese, 临时文件存放目录) is not determined by MOKIT or AutoMR, but by each quantum chemistry package (Gaussian, OpenMolcas, GAMESS, etc). Please do not submit two computations with the same input filename (even in different work directories) at the same time, since their temporary files may be overwritten by each other. For example, GAMESS, OpenMolcas and Molpro jobs are sensitive to the files in the scratch directory, while Gaussian, PySCF and ORCA are not that sensitive.

2.2.4 Test

To see the version and help information, you can run
automr -v (or -V, --version)
automr -h (or -help, --help)

To test whether the automr program works, please change into the example directory, and pick up a .gjf file. For example,

```
cd $MOKIT_ROOT/examples/automr/
automr 00-h2o_cc-pVDZ_1.5.gjf >& 00-h2o_cc-pVDZ_1.5.out &
```

If you are running calculations on Ubuntu* OS, where the default sh is probably /bin/dash, not /usr/bin/bash, then you should submit a job like

```
automr 00-h2o_cc-pVDZ_1.5.gjf >00-h2o_cc-pVDZ_1.5.out 2>&1 &
```

If you encounter any errors in output, please search your problem in Section A1 FAQ of Appendix firstly. Some common questions have be listed. For bug reporting, please read Section A3.

It is strongly recommended to create a new directory and put in the input file. Because during computation many files will be generated by AutoMR and those common software packages.

2.3 Installation on Cluster

Installing MOKIT on a cluster (in Chinese, 集群或超算) is somewhat troublesome (also for other software packages). If you can write environment variables freely into ~/.bashrc, then there is nothing different with installation on your local Linux computer.

However, sometimes you are not allowed, or unwilling to modify ~/.bashrc. And usually environment variables of various packages (e.g. ifort, python, etc) are controlled by the 'module' function. For example, if you need some version of python (other than system default), you have to run 'module load python/…' to make it accessible. In such case, you have to firstly load proper versions of Intel compiler and Python before installing MOKIT. For example,

```
module avai                 # find which version you can use
module load intel/2019u5    # load the version you want to use
module load python/3.7.6    # load the version you want to use
make all                    # compile MOKIT
```

The first line finds which versions of software packages you can choose. The 2nd and 3rd lines load the corresponding software. And the 4th line is just the installing of MOKIT. This is just a simple example telling you how to load modules on a cluster. For detailed questions, please consult the administrator of your node, or the cluster. Moreover, a good choice to running automr is that you should create a Shell script, e.g. `run.sh`, with

```
module load intel/2019u5
module load python/3.7.6
gjfname=$1
outname=${gjfname%.*}.out
automr $gjfname >& $outname
```

written in this script. If you are allowed to submit jobs to the current node, then you can run

```
chmod +x run.sh
./run.sh 00-h2o_cc-pVDZ_1.5.gjf &
```

However, usually you are not allowed to submit any job in the main node or login node. And there exists a queue/batch system on your cluster, e.g. 'bsub' in LSF batch or 'qsub' in PBS batch, which distributes your job to a proper computation node. Taking 'bsub' as an example, you should write a Shell script like

```
#!/bin/sh
#BSUB -q …      # queue name
#BSUB -n …      # number of cores
module load intel/2019u5
module load python/3.7.6
gjfname=$1
```

```
outname=${gjfname%.*}.out
automr $gjfname >& $outname
```

Note that do not write '&' symbol after the outname. Then you can run

```
bsub run.sh 00-h2o_cc-pVDZ_1.5.gjf
```

to submit the job. If you still encounter problems of installing or running MOKIT on your cluster, please consult the administrator of your cluster. This is beyond the scope of this manual.

3 Quickstart for MOKIT

See examples in $MOKIT_ROOT/examples/. More details to be added.

3.1 Which method should I use?

For practical use, e.g. to properly compare results with those from experiments, NEVPT2, CASPT2, MC-PDFT or MRCISD is recommended. The GVB and CASSCF methods are often qualitatively correct. For high accuracy results, dynamic correlation is necessary. Additional general recommendations are provided below:
(1) NEVPT2 is free of the intruder-state problem, thus is preferable to CASPT2.
(2) If you find NEVPT2/CASPT2 is too expensive for your system, consider the MC-PDFT method.
(3) If you find the computation cost of NEVPT2/CASPT2 is acceptable for your system and you want higher accuracy, consider ic-MRCISD in OpenMolcas/Molpro. For very small systems such as two or three atoms, the uncontracted MRCISD in ORCA is a good choice.

3.2 Which basis set should I use?

For testing or debug, you can use any type of basis sets. You can, of course, use a small basis set like def2-SVP to test whether AutoMR works. However, for practical use or to obtain publishable data, please use at least triple-zeta basis set, e.g. cc-pVTZ, def-TZVP, def2-TZVP or def2-TZVPP. Results obtained from combinations like MRCISD/def2SVP, NEVPT2/6-31G(d) are almost useless. If, unfortunately, you have very limited computational resource, e.g. less than 8 CPU cores, then the cc-pVDZ basis set is recommended. Additional general recommendations are provided below:

(1) If your system is large, or has complicated electronic structure and you want to see whether AutoMR works, or you just want to see the workflow of AutoMR, you can use a small basis set like def2SVP to go through the computation. After it normally terminates, you can switch to using a larger basis set.

(2) If your system is large (>600 basis functions), you should consider properly simplify your system or use mixed basis sets for different elements/atoms. For example, replace unimportant methyl

group(s) by hydrogen atoms, use cc-pVTZ for important atoms and cc-pVDZ (or even 6-31G(d)) for other atoms, etc. Also/Alternatively you can turn on the RI approximation (see Section 4.4.29) in CASSCF and CASSCF-NEVPT2 computations.

(3) Pople-type basis set like 6-311G(d,p) or 6-31G(d,p) is less recommended, but can be used for unimportant atoms.

(4) If pseudopotential (PP) is desired, better to use cc-pVTZ-PP, def2-TZVP. Be careful with the built-in basis set (with PP) SDD in Gaussian software for elements >= the 4th period. Often there is no *d*, *f* polarization functions in the built-in SDD basis set of Gaussian (although the PP part seem pretty good), but the *d*, *f* polarization functions are usually important for high-accuracy computations. If you insist on using SDD, you should search in previous papers the data of *d*, *f* polarization functions of SDD for your atoms, and add the data to the .gjf file manually.

(5) If your molecule is an anion, e.g. MnO_4^-, it is strongly recommended to use basis set with diffuse functions, such as aug-cc-pVTZ, ma-def2-TZVP. Similar to (1), if your system is large, you can use basis set with diffuse functions for atoms with significant negative charges, and use no diffuse functions for other atoms. If the atoms involving significant negative charges are not so important in your study, you can just use aug-cc-pVDZ or ma-def2-SVP.

(6) If all-electron relativistic calculations are desired (DKH2 or X2C), do remember to use basis sets like cc-pVTZ-DK, x2c-TZVPall or ANO-RCC series. All-electron relativistic computations using CASSCF/cc-pVTZ or cc-pVTZ-PP with DKH2 is almost non-sense.

(7) Remember that def2-TZVP is used formally in papers, but def2TZVP is used as the name of basis set in Gaussian syntax.

(8) If you want to compute the NMR shielding constants, basis sets like pcSseg-1 or pcSseg-2 are strongly recommended. Large basis sets like pcSseg-3, def2-QZVP or cc-pVQZ would be better but they are very time-consuming.

(9) If you only want to obtain the radical indices printed by AutoMR, and accurate electronic energies are not desired, then basis sets cc-pVDZ/6-31G(d,p)/def2SVP are sufficient. There is no need to use triple-zeta basis set like def2TZVP. If your studied molecule is very small (e.g. <10 atoms), then you can still use any triple-zeta basis set.

Currently AutoMR cannot read user-defined basis sets or pseudopotentials in .gjf file, so you have to provide a Gaussian .fch(k) file and use one of the three options ‘readrhf’, ‘readuhf’, ‘readno’. See Section 4.4.1~4.4.3 for related information.

3.3 Do I need to specify the active space?

AutoMR can automatically determine the active space, thus you need not specify that. If you do not want the automatically determined one, you can manually specify it, such as CASSCF(*m*,*n*) or NEVPT2(m,n), with m, n being the number of active electrons and active orbitals, respectively. Currently only m=n is supported (this is very reasonable, see DOI: 10.1021/acs.jctc.0c00123). While for GVB, you may specify GVB(n), where n is the number of pairs. **Manually specifying is only recommended for experienced users**.

Note that usually there is no need to write DMRGCI or DMRGSCF, the users can just write CASCI or CASSCF. Once AutoMR detects the size of active space is larger than (15,15), it will switch from CASCI/CASSCF to DMRGCI/DMRGSCF automatically. Similarly, the NEVPT2/CASPT2/MC-PDFT will be automatically switched into DMRG-NEVPT2/DMRG-CASPT2/DMRG-PDFT when the active space is larger than (15,15). The only exception is that the users just want to perform a DMRG calculation with active space smaller than (15,15), then the DMRGCI or DMRGSCF must be specified.

Usually the automatically determined active space is reasonable. The algorithm in MOKIT is designed to automatically find the minimum active space for a given molecule. However, when you are studying a potential energy curve/surface, the automatically determined active space may be not the same size for each geometry. For example, for N_2 molecule at d(N-N) = 1.15 Å, the CAS(4,4) may be automatically determined by AutoMR, but for for d(N-N) = 4.0 Å, the active space turns into CAS(6,6). Thus, if you want to keep the size to be CAS(6,6), you need to specify CASSCF(6,6), NEVPT2(6,6), MRCISD(6,6), etc.

3.4 Are my computation results reasonable?

(1) You should make sure that your CASSCF initial orbitals and final(i.e. converged) orbitals contain proper active orbitals. Here are two examples: (i) Assuming you are studying the bond breaking of a C-C bond, you use CAS(2,2) at least. And you should make sure that your CASSCF initial orbitals and final orbitals contain the bonding and anti-bonding orbitals this C-C bond. Note that the RHF orbitals or MP2 natural orbitals are usually poor to be used as the initial guess when studying bond breaking or transition-metal-containing molecules. (ii) Assuming you are studying the π->π* excited energies, then your active space is expected to contain desired π and π* orbitals.

(2) If you perform the CASSCF (or CASSCF-based methods like NEVPT2, CASPT2, etc), there would be a file with suffix *CASSCF_NO.fch generated, in which the CASSCF natural orbitals and corresponding occupation numbers are held. You can use GaussView or Multiwfn to open this file and visualize whether these active orbitals are reasonable, if you know your molecule fairly well.

If you perform CASCI (or CASCI-based jobs), the CASCI NOs are held in a *CASCI_NO.fch file. If you only perform GVB computation, the GVB NOs are held in the *gvb2_s.fch file.

(3) If you are comparing relative energies of two target molecules (e.g. two local minima of the same molecule), be sure that you are using the same size of active space for two molecules. For example, it is incorrect(or unfair) to compare two NEVPT2 energies if one is based on CAS(4,4) and the other one is based on CAS(8,8). If, unfortunately, you encounter such special case, you have two options: (i) explicitly specify the active space in the former calculation, i.e. NEVPT2(8,8) in the input file; (ii) if you find there are 4 orbitals not so active in the latter calculation (meaning occupation numbers close to 0 or 2), you can specify NEVPT2(4,4) in the input file.

(4) If you are calculating the bond dissociation energy, you should check whether the sum or combination of active space from two fragments equals to the active space of the original molecule. You are supposed to analyze main components of the active space. For example, assuming the original molecule has a CAS(6,6) active space, and assuming it contains 2 singly occupied orbitals from fragment 1, two bonding orbitals and two anti-bonding orbitals constructed by two fragments. Then quintuplet CAS(4,4) should be used for fragment 1 and triplet CAS(2,2) for fragment 2.

(5) For the rigid/unrelaxed scanning of a chemical bond, you are always recommended to scan the bond from long distance to short distance, rather than from short to long. And you are recommended to write the keyword ‘scan’ in the Gaussian keyword #p line. This will perform the rigid/unrelaxed scan automatically. It is not recommended to calculate each scanned geometry manually.

4 User’s Guide

4.1 Syntax Rules of AutoMR

Syntax rules of the input file of AutoMR is almost identical to those of Gaussian software. Therefore, it takes little time to become familiar with the usage of AutoMR. A simple input (.gjf) example is shown below

```
%mem=4GB
%nprocshared=2
#p CASSCF/cc-pVDZ

mokit{}

0 1
O          -0.23497692       0.90193619      -0.068688
H           1.26502308       0.90193619      -0.068688
H          -0.73568721       2.31589843      -0.068688
```

This is a water molecule with two O-H bonds stretched. CAS(4,4) active space will be automatically determined during computations. One can also provide a .fch(k) file if he/she already performed a UHF job. An example is shown below

```
%mem=4GB
%nprocshared=4
#p CASSCF/cc-pVTZ

mokit{ist=1,readuhf='N2_cc-pVTZ_4.0_uhf.fchk' }
```

For the memory and parallel settings, please read Section **4.2**. For the theoretical method and basis set, please read Section **4.3**. Here we focus on the keywords in mokit{}.

1. All keywords must be written in the curly bracket of 'mokit{}' in the Title Card line of a .gjf file.

2. Using upper or lower case of keywords in AutoMR makes no difference. For example, the following two lines have identical meanings:

(1) MOKIT{readuhf='a,fchk',ist=1,LocalM=Boys}
(2) mokit{readuhf='a,fchk',ist=1,localm=boys}

3. If 'readrhf', 'readuhf', or 'readno' keyword is used, a filename of the provided .fch(k) file must be included in a pair of single quotation marks ''. Do not use double quotation marks "" or no quotation marks.

4. If pure Cartesian functions of basis set are used in the provided .fch(k) file, you need to write keyword 'cart'. The default is pure spherical harmonic functions. And you do not need to write any keyword about this if you provide a .fch(k) file in which pure spherical harmonic functions are used.

5. Use a comma to separate different keywords. Do not use other symbols (like spacing).

6. User-defined basis sets (i.e. gen) and pseudopotentials (i.e. genecp) are not supported in the .gjf file currently. To use that, you can write one of the keywords 'readrhf', 'readuhf', or 'readno', and provided a .fch(k) file (in which the data of basis sets and pseudopotentials are recorded).

4.2 Memory and Parallel Settings

The settings of memory and the number of processors are identical to that in Gaussian. For example, the following syntax

```
%chk=16GB
%nprocshared=8
```

requests a AutoMR calculation use 16GB memory and 8 processors. Note that only the unit GB and %nprocshared is supported. Some DON'T things are listed below:
(1) Do not use unit MB, MW, GW, or %cpu..
(2) Do not write %chk since it is useless for AutoMR.

Since multireference computations often require large memory, it is recommended to use at least %mem=1GB for even a small molecule. It is also recommended to set %mem ⩾ %nproc. Note that memory and parallel settings of OpenMolcas is controlled by variables in your ~/.bashrc (export MOLCAS_NPROCS, export MOLCAS_MEM), not by AutoMR. You should refer to (Open)Molcas manual for details. And the memory and parallel settings of the BDF program is controlled by variables in the Shell script bdf-pkg/sbin/run.sh, you should properly modify the script before doing computations.

The memory and parallel settings are passed into various programs called by AutoMR (e.g. PySCF, Gaussian, etc). The AutoMR itself only needs negligible memory and usually run in a serial mode.

4.3 Keywords of supported methods in AutoMR

Currently, the keywords of all supported methods in AutoMR are: **GVB**, **CASCI**, **CASSCF**, **DMRGCI**, **DMRGSCF**, **NEVPT2**, **CASPT2**, **CASPT2K**, **SDSPT2**, **MRMP2**, **MRCISD**, **MRCISDT**, **MCPDFT**, **DFTCI**, **BCCC2b** and **BCCC3b**. More multi-configurational and multi-reference methods will be supported in the future. These terms should be written in the '#p …' line in the .gjf file.

There must be a '/' symbol between the method and the basis set, e.g. CASSCF/cc-pVTZ. AutoMR does not allow the use of a spacing to separate the method and basis set (which is allowed in Gaussian). When 'readrhf', 'readuhf', or 'readno' is used in mokit{}, the basis set after '/' symbol is usually useless, since the geometry and basis set data will be read from the given .fch(k) file. Note that, however, the user still needs to provide a basis set name, although it is not used in this case.

There is also an exception that the basis set after '/' symbol matters. If RI (see Section 4.4.29) approximation is turned on, the auxiliary basis set will be automatically determined (by AutoMR) according to the basis set. And if F12 (see Section 4.4.31) is turned on, the F12-CABS will be automatically determined (by AutoMR) according to the basis set, too.

4.3.1 GVB

Generalized Valence Bond theory.

Note that the original GAMESS source code can only deal with GVB up to 12 pairs. To go beyond that (which is routine type of calculation in AutoMR of MOKIT), you need to modify the GAMESS source code, please read Section 4.4.10 carefully.

4.3.2 CASSCF

Complete Active Space Self-consistent Field.

Currently excited state computations are not supported. Please read Section A2.3 for comments on excited state computations.

Please read related keyword CASSCF_prog in Section 4.4.12.

4.3.3 CASCI

Complete Active Space Configuration Interaction.

CASCI can be viewed as the 0-th step of the CASSCF step, i.e. CASSCF without orbital optimization. It is always recommended to perform CASSCF rather than CASCI, expect for those who wish to compare the quality of different initial guesses, and/or do not want the CASSCF result.

Please read related keyword CASCI_prog in Section 4.4.11.

4.3.4 DMRGSCF

Here the keyword DMRGSCF actually means the DMRG-CASSCF method. Please also read Section 4.4.14 for related information.

4.3.5 DMRGCI

Here the keyword DMRGCI actually means the DMRG-CASCI method. Please also read Section 4.4.13 for related information.

DMRGCI can be viewed as the 0-th step of the DMRGSCF step, i.e. DMRGSCF without orbital optimization. It is always recommended to perform DMRGSCF rather than DMRGCI, expect for those who wish to compare the quality of different initial guesses, and/or do not want the DMRGSCF result.

4.3.6 NEVPT2

Second order *N*-Electron Valence state Perturbation Theory based on the CASSCF reference.

Please read related keyword NEVPT2_prog in Section 4.4.16.

4.3.7 CASPT2

Second order Perturbation Theory based on CASSCF reference.

Generally speaking, NEVPT2 is more recommended than CASPT2 since there is no need for IP-EA shift, real or imaginary shift in NEVPT2. If you are really a fan of CASPT2, it is recommended to use CASPT2K instead, see Section 4.3.8 CASPT2K.

Please read related keyword CASPT2_prog in Section 4.4.15.

4.3.8 CASPT2K

Second order Perturbation Theory based on CASSCF reference.

This is a new feature since ORCA 5.0. A revised zeroth order Hamiltonian is applied to alleviate the intruder state problem of CASPT2 method. No IP-EA shift is needed in this method.

Note here you can write this keyword as either CASPT2K or CASPT2-K in .gjf file, but you'd better use the method name CASPT2-K in official writing or publishing. The keyword CASPT2_prog will automatically be set as ORCA, since this method is only supported in ORCA currently.

4.3.9 CASPT3

Third order Perturbation Theory based on CASSCF reference.

Only Molpro program can be called to perform CASPT3, and it is default.

4.3.10 SDSPT2

Static-dynamic-static multi-state multi-reference second-order perturbation theory (SDS-MS-MRPT2, or SDSPT2 for short). There are several restrictions when you use this method:
(1) only the single (electronic) state version can be used in automr, since only the ground state is calculated.
(2) SDSPT2 based on the CASCI reference is not supported currently. CASSCF-SDSPT2 is supported.
(3) background point charges are not supported.

This version of SDSPT2 is performed by the Xi'an CI module of BDF program. So you are assumed to have successfully installed BDF. You should cite this paper DOI: 10.1080/00268976.2017.1308029 if you use this method.

4.3.11 MRMP2

Second order Multi-reference Perturbation Theory based on CASSCF reference. After CASSCF converged, AutoMR will call the GAMESS program to perform MRMP2 calculation. No other program is supported. Also, DMRG-MRMP2 is not supported and AutoMR will abort in that case.

4.3.12 OVBMP2

Orthogonal valence bond Møller-Plesset 2 based on CASSCF reference. After CASSCF converged, AutoMR will call the Gaussian program to perform OVB-MP2 calculation. No other program is supported. Also, DMRG-OVB-MP2 is not supported and AutoMR will abort in that case.

Note that OVBMP2 is a keyword in AutoMR but OVB-MP2 is the method name. Do not mix them up. Some literature might call this method as "CASSCF MP2" but that is actually misleading (those authors were fooled by keywords "CASSCF MP2"in Gaussian input file).

4.3.13 MRCISD

Multi-reference Configuration Interaction Singles and Doubles, based on the CASCI/CASSCF reference.

Please read related keyword MRCISD_prog in Section 4.4.17.

4.3.14 MRCISDT

Multi-reference Configuration Interaction Singles, Doubles and Triples, based on the CASCI/CASSCF reference.

The related keyword MRCISDT_prog can only be equal to OpenMolcas/Gaussian/Dalton. No Davidson correction will be provided.

4.3.15 MCPDFT

Multi-configurational Pair Density Functional Theory, based on CASSCF reference. Note that MCPDFT is a keyword in AutoMR but MC-PDFT is the method name. Do not mix them up.

Note that if the active space is larger than (15,15), the MC-PDFT will be automatically switched to DMRG-PDFT. In this special case you need to install the QCMaquis package (interfaced with OpenMolcas) for DMRG computations. DMRG-PDFT is not supported in GAMESS currently.

Please read related keyword MCPDFT_prog in Section 4.4.19. Also note that in GAMESS, the MC-PDFT is only supported for version >= 2019(R2).

4.3.16 DFTCI

The DFT/MRCI method by Stefan Grimme, Mirko Waletzke, and Martin Kleinschmidt *et. al*. Note that the name of this method is DFT/MRCI, but you should write the keyword DFTCI in the input file of AutoMR, in order to perform DFT/MRCI computations.

Currently, to perform DFT/MRCI computations, you should have ORCA and DFT/MRCI program installed on your node/machine.

Note: full implementation of this keyword has not been finished yet.

4.3.17 MRCC

Multi-reference Coupled Cluster theory, based on the CASCI/CASSCF reference. Currently only the FIC-MRCC method in ORCA(>=5.0.0) is supported.

4.3.18 BCCC2b

Block-correlated coupled cluster theory based on the GVB reference. This is in fact a multi-reference coupled cluster theory based on GVB wave function, where 2b means only the two-block excitation operators $\hat{T}_2$ are considered in the cluster expansion. Moreover, this method is a spin-pure coupled-cluster method.

Currently only spin singlet is supported. This program is developed by jxzou during his Ph.D. in Prof. Shuhua Li' research group. Currently this program has not been released yet, but will probably be released after its corresponding paper published.

Currently only correlations between two pairs are taken into consideration (i.e. occ->pair, occ->vir, pair->vir not considered so far). So BCCC2b is just a “rough” theory. Note that the intra-pair excitation operator $\hat{T}_1$ plays little role, so the BCCC2b (i.e. only $\hat{T}_2$) is extremely close to BCCC2 (i.e. $\hat{T}_1 + \hat{T}_2$). For GVB(2), the BCCC2 is equivalent to CASCI(4,4) using GVB orbitals, and thus BCCC2b is extremely close to CASCI(4,4). For GVB(*n*), *n*>2, the GVB(*n*)-BCCC is an approximation method to CASCI(2*n*,2*n*) using GVB orbitals.

This program scales as $O(n^4)$, where *n* is the number of GVB pairs. But the integral transformation needed for the BCCC2b scales as $O(n^5)$, so the overall scaling might behave as $O(n^5)$ for large number of pairs.

4.3.19 BCCC3b

Block-correlated coupled cluster theory based on the GVB reference, where 3b means $\hat{T}_2 + \hat{T}_3$ are considered in the cluster expansion. This means two-pair and three-pair correlations are considered based on the GVB reference. Also, this method is spin-pure. Currently only spin singlet is supported.

For practical computations with desired accuracy, you should use BCCC3b rather than BCCC2b. This program scales as $O(n^5)$, where *n* is the number of GVB pairs. As stated in 4.3.18 BCCC2b, this program has not been released yet.

4.4 List of AutoMR Keywords

If any of the ‘readrhf’, ‘readuhf’, and ‘readno’ keywords is used, there is no need to write Cartesian coordinates in .gjf file (in fact AutoMR will not read coordinates in such case), since the geometry is already provided in the specified .fch(k) file.

4.4.1 readrhf

Read RHF (or ROHF) orbitals from a specified .fch file. Do not provide a UHF-type .fch file using this keyword. This keyword is usually used along with another keyword ist=3 (see Section 4.4.4 ist).

4.4.2 readuhf

Read UHF orbitals from a specified .fch(k) file. AutoMR will firstly check the difference between alpha and beta MOs. If the difference is tiny, the wave function in .fch file will be identified as a RHF one and will call utility fch_u2r to generate a RHF-type .fch file (in which all beta information is deleted). Otherwise (i.e. truly UHF), AutoMR will generate UHF natural orbitals

(UNO) using input UHF orbitals. It is strongly recommended to check the stability of UHF wave function (using keyword ‘stable=opt’ in Gaussian). An instable or not-the-lowest UHF solution sometimes leads to improper GVB or CASSCF results.

The author jxzou does not recommend the usage of UDFT orbitals. But in case you have to do that (e.g. forced by your Boss or driven by your curiosity), remember to add an extra keyword ‘no10cycle’ (see 4.4.24 for no10cycle).

This keyword is usually used along with another keyword ist=1 or 2 (see Section 4.4.4 ist). Note that do not provide a UNO .fch file with this keyword. If you want to use any type of NOs as the initial guess, see ‘readno’ in the following section.

4.4.3 readno

Read natural orbital occupation numbers (NOON) and natural orbitals (NO) from a specified .fch file. In this case, you must ensure that the ‘Alpha Orbital Energies’ section in the .fch file contains occupation numbers, not energy levels or something else, since the size of the active space will be determined according to the (threshold of the) occupation numbers.

With this keyword, you may try different NOs as the initial guess, like MP2 NOs, CCSD NOs, or some type of NOs generated by your own program. You may also use UNOs from UHF as the initial guess. In this case, it is equivalent to use the keyword ‘readuhf’ to read in the UHF orbitals and generate UNOs by MOKIT.

This keyword is usually used along with another keyword ist=5 (see Section 4.4.4 ist).

4.4.4 ist

Request the use of the *i*-th *st*rategy. Default is 0. This means: (1) if the spin of the target molecule is singlet, MOKIT will call the Gaussian software to perform RHF and UHF computations, then determine whether to change ‘ist’ to 1 or 3. If the $E_{\text{UHF}} = E_{\text{RHF}}$, ist will be changed to 3. If $E_{\text{UHF}} < E_{\text{RHF}}$, ist will become 1. (2) if not singlet, ist will be changed to 1 immediately.

For simple organic molecules which have multireference characters (like diradicals), the UHF performed by MOKIT (calling Gaussian) can always find the lowest (and stable) UHF solution. But for complicated systems like binuclear transition metal complex, there often exist multiple UHF solutions. And the UHF solution found by MOKIT is not necessarily the lowest one. In this case you are recommended to do UHF computations by yourself and use ist=1 to read in the Gaussian .fch file. See a practical guide for advanced UHF computations on http://gaussian.com/afc/. If you can read Chinese, you are recommended to read Sobereva’s blog http://sobereva.com/82.

Currently, there are 7 allowed values for ist:
0: meaning that if RHF wave function is stable, use strategy 3; otherwise use strategy 1
1: UHF -> UNO -> associated rotation -> GVB -> CASCI/CASSCF -> ...

2: UHF -> UNO -> (associated rotation ->) CASCI/CASSCF -> ...
3: RHF -> virtual orbital projection -> localization -> pairing -> GVB -> CASCI/CASSCF -> ...
4: RHF -> virtual orbital projection -> CASCI/CASSCF -> ...
5: NOs -> CASCI/CASSCF -> ...
6: minimal basis GVB -> target basis GVB -> CASCI/CASSCF -> …

The value 0 (default) is recommended, if you do not know which one to choose.

4.4.5 LocalM

Specify the orbital localization method. Only the Boys (also called Foster-Boys) localization and Pipek-Mezey (PM) localization method are supported. The corresponding keywords are 'LocalM=Boys' and 'LocalM=PM'. By default, the PM localization is used.

Note: the Boys method will mix σ and π orbitals, while the PM method tends to keep them separated. These two methods make no difference when the target molecule contains only σ bonds (and possibly a few isolated π bonds). But if you are dealing with multiple π bonds or conjugated π systems like oligoacene(benzene, naphthalene, etc), or if you want the active space to contain only π orbitals, better use the PM method. The GVB and CASSCF optimized orbitals will be affected by the localization method sometimes. If you explicitly specify the size of active space which is equal to the π space (note that frontier natural orbitals are usually π orbitals), then using LocalM=Boys is OK since Boys localization among pure π orbitals is safe (no sigma orbital is in the set).

For people who are keen on comparing initial guesses generated from different methods/algorithms, 'Local=Boys' is strongly recommended to be taken into consideration, to see whether a lower GVB, CASCI or CASSCF energy occurs.

4.4.6 CIonly

Skip the CASSCF orbital optimization in the CASPT2 or NEVPT2 job. Obviously, this keyword only applies to CASPT2 or NEVPT2 case. Writing CIonly means a CASCI -> CASPT2 or CASCI -> NEVPT2 job. In fact, the CASSCF orbital optimization is always recommended to be performed, unless it is too time-consuming, or you happen to want this type of result.

Note: if you simply need a CASCI computation, do not use CIonly in a CASSCF job, but simply write CASCI/basis_set in the keyword line of .gjf file.

4.4.7 Force

Request a calculation of the analytical nuclear gradient. Currently this keyword only applies to CASSCF. Geometry optimization is currently not supported, but you can use the generated files to perform optimization using corresponding software. Numerical gradient is not supported.

Note that this keyword do not have any attribute value, i.e. do not write 'force=.True.' but only 'force' in {}. Also keep in mind that force is negative gradient.

4.4.8 Cart

Request the use of Cartesian type atomic basis functions. The default basis type in AutoMR (i.e. spherical harmonic functions) will then be disabled. These two types of basis functions correspond to ‘6D 10F’ (Cartesian functions) and ‘5D 7F’ (spherical harmonic functions) in Gaussian. It is strongly recommended to use spherical harmonic functions, especially in all-electron relativistic computations (DKH2, X2C, etc).

Note that for computations involving the ORCA program, this keyword cannot be used since ORCA only support spherical harmonic functions.

If you don’t know the meaning of 5D or 6D, you are referred to Schlegel and Frisch‘s paper (DOI: 10.1002/qua.560540202), and a good explanation from Chemissian http://www.chemissian.com/ch5. If you can read Chinese, you are recommended to read Sobereva’s blog http://sobereva.com/51.

4.4.9 HF_prog

Specify the program for performing Hartree-Fock (HF) calculations. Supported programs are Gaussian(default), PySCF, PSI4 and ORCA. If the input molecule is singlet, RHF and broken symmetry UHF (plus wave function stability analysis) will be successively performed. If not singlet, only UHF (plus wave function stability analysis) will be performed.

It is strongly recommended to use the default HF_prog (i.e. Gaussian), since the SCF algorithm in Gaussian is the most effect in almost all cases, among all quantum software packages. The only case when you are recommended to use PySCF/PSI4/ORCA, is that if your studied molecule is large and cannot be further simplified ($N_{\text{basis}} > 1500$), you can consider turn on the RI approximation of HF to accelerate computations in PySCF, PSI4 or ORCA. For example, in this special case you are supposed to write

mokit{RI,HF_prog=PySCF} (or PSI4, ORCA if you wish)

in the input file of AutoMR. For small to medium-size molecules ($N_{\text{basis}} < 1500$), better not use PySCF/PSI4/ORCA since their SCF is usually slower or harder to converge than that of Gaussian.

Note: implementation of this keyword for PySCF/PSI4/ORCA has not been finished yet.

4.4.10 GVB_prog

Specify the GVB program. Supported programs are GAMESS(default) and Gaussian. The second-order SCF (SOSCF) algorithm in GAMESS is used to converge the GVB wave function. The GAMESS version >=2017 is strongly recommended. Older versions of GAMESS may work or may not, since they are not tested by the author jxzou. It is always recommended to use the default program GAMESS, rather than Gaussian (due to poor convergence for transition metal).

Note the original GAMESS can only do GVB up to 12 pairs. Nowadays we can do a black-box

GVB computation with hundreds of pairs. So, to go beyond 12 pairs, you need to modify and re-compile the source code of GAMESS.

MOKIT offers a Shell script to help you automatically handle this. Assuming you've compiled GAMESS before (i.e. all *.o files are still in **gamess/object/** directory of GAMESS), now you simply need to copy two files (modify_GMS1.sh and modify_GMS2.f90) from mokit/src/ into **gamess/source/** directory, and run './modify_GMS1.sh'. The script will modify source code and re-compile GAMESS, taking about 2 minutes. The linked GAMESS executable will be gamess.01.x. If you already had an executable named gamess.01.x, please rename it to another filename. Otherwise it will be destroyed and replaced during re-compilation.

Besides, for GAMESS earlier than version 2021-R1, it only supports 32 CPU cores. If your machine has more cores (and if you want to use >32 cores), you need to modify the variable MAXCPUS in file gamess/ddi/compddi. See a simple guide in file src/modify_GMS_beyond32CPU.txt. Since GAMESS 2021, the MAXCPUS is already set to 128, so modification is not needed.

It is strongly recommended to check whether the GAMESS runs normally after modifying. Such check can be done by running './runall 01' in gamess/ directory, where 01 means checking the executable gamess.01.x. This is same as checking for version 00. All tests are supposed to be passed successfully.

4.4.11 CASCI_prog

Specify the program for performing the CASCI calculation, e.g. CASCI_prog=PySCF. Supported programs are PySCF(default), Molpro, GAMESS, OpenMolcas, Gaussian, ORCA, BDF, PSI4 and Dalton.

If you use some old versions of BDF as the CASCI_prog, you may find the NOONs are zero. In that case you should update to the latest version of BDF.

4.4.12 CASSCF_prog

Specify the program for performing the CASSCF calculation, e.g. CASSCF_prog=PySCF. Supported programs are PySCF(default), Molpro, GAMESS, OpenMolcas, Gaussian, ORCA, BDF, PSI4 and Dalton. If you want to use a CASSCF program instead of PySCF, I recommend Molpro, OpenMolcas or GAMESS.

If you use some old versions of BDF as the CASSCF_prog, you may find the NOONs are zero. In that case you should update to the latest version of BDF.

Currently automr cannot run excited state calculations. Please read related comments in Section A2.3.

4.4.13 DMRGCI_prog

Specify the program for performing DMRG-CASCI calculation, e.g. DMRGCI_prog=PySCF.

Currently only PySCF is supported and it is the default program.

Note that in fact the DMRG-CASCI calculations are performed by Block-1.5 and PySCF, not only by PySCF. Thus you should install the Block-1.5 program. And you should also cite corresponding reference of the Block-1.5 program.

Also note that the MPI version used by Block is probably contradicted with MPI version used by ORCA, thus you have to comment one version of MPI environment variables at a time. Or you can use a Shell script to submit the automr job, in which your desired MPI environment variables are written.

4.4.14 DMRGSCF_prog

Specify the program for performing DMRG-CASSCF calculation, e.g. DMRGSCF_prog=PySCF. Currently only PySCF is supported and it is the default program.

Note that in fact the DMRG-CASSCF calculations are performed by Block-1.5 and PySCF, not only by PySCF. Thus you should install the Block-1.5 program. And you should also cite corresponding reference of the Block-1.5 program.

Also note that the MPI version used by Block is probably contradicted with MPI version used by ORCA, thus you have to comment one version of MPI environment variables at a time. Or you can use a Shell script to submit the automr job, in which your desired MPI environment variables are written.

4.4.15 CASPT2_prog

Specify the program for performing CASPT2 calculation, e.g. CASPT2_prog=OpenMolcas. Currently only OpenMolcas(default), Molpro and ORCA are supported. All core orbitals are not frozen. Note that a default IP-EA shift 0.25 a.u. will be applied and it cannot be modified. If your CASPT2 results are sensitive to the IP-EA shift, it implies that CASPT2 is not suitable to your problem. Another two types of shift (the real or imaginary shift) is not supported.

Generally speaking, NEVPT2 is more recommended than CASPT2 since there is no need for IP-EA shift, real or imaginary shift in NEVPT2.

4.4.16 NEVPT2_prog

Specify the program for performing NEVPT2 calculation, e.g. NEVPT2_prog=PySCF. Currently supported programs are PySCF(default), Molpro, ORCA, OpenMolcas and BDF. All core orbitals are not frozen.

Note that there exist at least two variants of the NEVPT2: SC-NEVPT2 and FIC-NEVPT2(aka PC-NEVPT2). By default, for NEVPT2_prog=PySCF/Molpro/ORCA/OpenMolcas, SC-NEVPT2 is chosen; while for NEVPT2_prog=BDF, FIC-NEVPT2 is chosen. To turn on the FIC-NEVPT2 when using PySCF/Molpro/ORCA/OpenMolcas, please read Section 4.4.34. Also note that

(1) When you specify NEVPT2_prog=Molpro or OpenMolcas, both of the SC-NEVPT2 and FIC-

NEVPT2 energies are actually printed in Molpro/OpenMolcas output (.out file). You can open the output file and read it manually, if you need that energy.
(2) If you specify NEVPT2_prog=OpenMolcas, it actually turns into a DMRG-NEVPT2 computation, no matter how large/small the size of active space is. In this special case, you need to install the QCMaquis package (interfaced with OpenMolcas) for DMRG computations.

4.4.17 MRCISD_prog

Specify the program for performing MRCISD calculation. By default, MRCISD_prog=OpenMolcas. You MUST also specify a contraction type, please read Section 4.4.20 carefully.

Currently, AutoMR supports the interfaces of three MRCISD variants:
(1) uncontracted MRCISD
(2) internally contracted MRCISD (ic-MRCISD)
(3) fully internally contracted MRCISD (FIC-MRCISD)

where the computational cost and accuracy is (1)>(2)>(3). The ic- and FIC-MRCISD are both approximations of uncontracted MRCISD. If the Davidson size-consistency correction energy is added, then the method should be denoted as MRCISD+Q. It is recommended to use ic-MRCISD+Q or FIC-MRCISD+Q in practical calculations since the uncontracted MRCISD is often too expensive.

AutoMR is able to call OpenMolcas/Molpro/ORCA/Gaussian/GAMESS/PSI4/Dalton programs to perform MRCISD. Currently all core orbitals are not frozen. MRCISD based on the DMRG reference is not supported currently.

If MRCISD_prog=OpenMolcas, only variants (1) and (2) are supported. The Davidson correction can be provided for both methods.

If MRCISD_prog=ORCA, only (1) and (3) are supported. The Davidson correction can be provided for both methods. However, only spherical harmonic functions of basis sets are supported in ORCA. But this is often not a problem, since it is recommended to use spherical harmonic functions than Cartesian functions.

Note that you should use ORCA>=5.0.0 for FIC-MRCISD+Q computations since older versions have a tiny bug in the Davidson correction.

If MRCISD_prog=Gaussian or Dalton, only (1) is supported and no Davidson correction is given.

If MRCISD_prog=GAMESS or PSI4, only (1) is supported. The Davidson correction energy will also be printed.

If MRCISD_prog=Molpro, only (2) is supported. The Davidson correction energy will also be printed. Note that the MRCIC program of Molpro will be called to perform ic-MRCISD. This ic-MRCISD is not exactly identical to that of OpenMolcas, so their electronic energies are different with (but close to) each other. If you want to compare (relative) electronic energies of two molecules using ic-MRCISD method, please choose the same type, i.e. both using Molpro or both using OpenMolcas.

4.4.18 MRMP2_prog

Specify the program for performing MRMP2 calculation. Only GAMESS is supported and this is the default.

4.4.19 MCPDFT_prog

Specify the program for performing MC-PDFT calculation. Only OpenMolcas(default) and GAMESS are supported.

Note that if the active space is larger than (15,15), the MC-PDFT will be automatically switched to DMRG-PDFT. In this special case you need to install the QCMaquis package (interfaced with OpenMolcas) for DMRG computations. DMRG-PDFT is not supported in GAMESS currently.

Also note that in GAMESS, the MC-PDFT is only supported for version >= 2019(R2), and currently it can only be run in serial.

4.4.20 CtrType

Specify the contraction type of the MRCISD method. The default value is 0. When you specify the MRCISD method and the MRCISD_prog, you must assign an integer for this variable, where
1 for uncontracted MRCISD
2 for ic-MRCISD
3 for FIC-MRCISD.

Generally, the ic- and FIC-MRCISD methods are recommended. If your calculation involves Cartesian-type basis functions, then you cannot use FIC-MRCISD in ORCA. In such case, you can choose ic-MRCISD in OpenMolcas instead.

4.4.21 MaxM

Specify the bond dimension MaxM in DMRG-related calculations. The default values is 1000 (e.g. MaxM=1000). When maxM increases, the DMRG-CASCI energy will become closer to the CASCI energy, but the computational cost increases as well. The value 1000 is suitable for common cases. But do check whether it is valid for your system. For example, three computations using different MaxM (e.g. 500, 1000, 1500) may be conducted to study whether the energy converges with MaxM.

4.4.22 hardwfn

This option can only be applied to CASCI/CASSCF calculations using PySCF, OpenMolcas, GAMESS or PSI4. By specifying ‘hardwfn’, AutoMR will add extra keywords into the CAS input files to ensure a better convergence. Note that normally you do not need this keyword, and it is useless if you specify other programs as the CAS solver.

4.4.23 crazywfn

This option can only be applied to CASCI/CASSCF calculations using PySCF, OpenMolcas, GAMESS or PSI4. By specifying 'crazywfn', AutoMR will add extra keywords (more than those of 'hardwfn') into the CAS input files to ensure a better convergence. Note that usually you do not need this keyword, and it is useless if you specify other programs as the CAS solver.

For example, when the N_2 molecule is stretched to d(N-N) = 4.0 Å, this is a system which features strong correlation and requires a CAS(6,6) active space. The Davidson iterative diagonalization in determinant CASCI (using GAMESS) may not find the singlet state in the lowest 5 states. In this case, specifying 'crazywfn' will increase the NSTATE to 10, so that the singlet state can be found.

4.4.24 no10cycle

Skip the 10 cycles of SCF calculations after importing MOs. By default, AutoMR will do several (up to 10) cycles of RHF or UHF after importing MOs from .fch file. This has two advantages: (1) check whether the SCF converges immediately. If not, the MO in .fch file may be wrong, or there exists some bug of fch2py (which has never been observed by the author). (2) it will slightly improve the orthonormality of the input MOs, although the orthonormality is already good. Thus usually you do not need to write this keyword.

If you start with MOs which are not RHF or UHF MOs (e,g, NOs, UDFT MOs, etc), you must specify 'no10cycle' in mokit{}. Because any iteration of input MOs will change them, which is not what you want.

4.4.25 charge

This keyword has identical meaning with the same keyword in Gaussian software, i.e. including background point charges in calculations. This keyword is supported for almost all methods in AutoMR. Methods which are incompatible with background point charges will signal errors immediately. The charge-charge and charge-nuclei interaction energies are both included in all electronic energies printed (UHF, GVB, CASSCF, NEVPT2, etc).

The including of background point charges is useful for QM/MM calculations or fragmentation-based linear scaling methods (like GEBF, Many-body expansion, etc).

Note: please write this keyword in mokit{}. **DO NOT WRITE** this keyword in the Route Section of .gjf file (i.e. '#p …' line).

4.4.26 OtPDF

The choice of the on-top pair density functional. This keyword has identical meaning with the keyword KSDFT in (Open)Molcas software. Currently available functionals are tPBE(default), tBLYP, tLSDA, trevPBE, tOPBE, ftPBE, ftBLYP, ftLSDA, ftrevPBE and ftOPBE. For more details please refer to the Molcas manual. Note that the available functionals depends on your version of OpenMolcas or GAMESS. Old versions may not support some of the functionals.

Note that for Openmolcas >= v22.02, the on-top pair density functional keywords in .input file of OpenMolcas have been changed to T:PBE, FT:PBE, etc. The user need not worry about this problem in MOKIT, since AutoMR will automatically detect the version of OpenMolcas and change the keyword tPBE into T:PBE if needed.

Note that in GAMESS, the MC-PDFT is only supported for version >= 2019(R2).

4.4.27 DKH2

Request the 2nd order scalar relativistic Douglas–Kroll–Hess (DKH2) correction to the one-electron Hamiltonian. Note that: (1) The two keywords DKH2 and X2C are mutually exclusive, i.e. you can only write one of them. (2) You should use all-electron basis sets like 'cc-pVTZ-DK', 'x2c-TZVPall' or 'ANO-RCC-VDZ' for all-electron relativistic calculations. Pseudopotential should not be used. (3) It is strongly not recommended to use Cartesian-type function of basis set (severe numerical instability observed), please just use the default spherical harmonic functions.

Currently only the point nuclei charge distribution is supported. The DKH0 Hamiltonian is rough and thus not supported. These programs support the DKH2 Hamiltonian: Dalton, Gaussian, GAMESS, OpenMolcas, ORCA, Molpro, PSI4.

4.4.28 X2C

Request the scalar (i.e. spin-free) relativistic X2C (eXact-two-Component) corrections to the one-electron Hamiltonian. Note that: (1) The two keywords DKH2 and X2C are mutually exclusive, i.e. you can only write one of them. (2) You should use all-electron basis sets like 'cc-pVTZ-DK', 'x2c-TZVPall' or 'ANO-RCC-VDZ' for all-electron relativistic calculations. Pseudopotential should not be used. (3) It is strongly not recommended to use Cartesian-type function of basis set (severe numerical instability observed), please just use the default spherical harmonic functions.

Also note that by default, the RHF/UHF is performed using Gaussian called by AutoMR, and GVB is performed using GAMESS called by AutoMR. Since Gaussian and GAMESS do not support X2C, in these steps the X2C will be replaced by DKH2. According to the limited tests of the author jxzou, MOs resulting from DKH2 and X2C are similar and often converge in few cycles.

Currently only the point nuclei charge distribution is supported. These programs support the X2C Hamiltonian: BDF, OpenMolcas, Molpro, PSI4, PySCF. After several months, X2C will be supported in ORCA.

4.4.29 RI

Request to turn on the RI-JK approximation for two-electron integrals in CASSCF. Default is off. Please just write 'mokit{RI}', do not write 'mokit{RI=True}' or 'mokit{RI on}'. The other two types of RI approximations RI-J and RIJCOSX are not supported.

This option currently can only be used in CASSCF computations conducted by PySCF, OpenMolcas, Molpro, ORCA, or PSI4 programs. To learn more about the auxiliary basis set used in RI-JK approximation, see the following Section 4.4.30.

4.4.30 RIJK_bas

Specify an auxiliary basis set for RI-JK approximation in CASSCF computations conducted by ORCA. Usually you do not need to specify this, since the automr program will automatically assign a proper auxiliary basis set according to the basis set (e.g. def2/JK for def2TZVP, cc-pVTZ/JK for cc-pVTZ). You can simply open the output file of automr and see what auxiliary basis set is assigned.

In the current version of OpenMolcas, there is no auxiliary basis set in it. The AutoMR program in MOKIT will automatically transformed the needed basis set file and put that into $MOLCAS/basis_library/jk_Basis/.

4.4.31 F12

Request to turn on the F12 technique in NEVPT2 computations conducted by ORCA. F12 is not used by default. But if you turn on F12, RI (see Section 4.4.29) will be turned on as a byproduct.

This option currently can only be used in CASSCF and CASSCF-NEVPT2 computations conducted by ORCA program, i.e. you need to specify

```
CASSCF_prog=ORCA,NEVPT2_prog=ORCA,F12
```

in mokit{}. To learn more about the near-complete auxiliary basis set used in F12 technique, see the following Section 4.4.32.

4.4.32 F12_cabs

Specify a near-complete auxiliary basis set for the F12 technique in NEVPT2 computations conducted by ORCA. Usually you do not need to specify this, since the automr program will automatically assign a proper auxiliary basis set according to the basis set (e.g. cc-pVTZ-F12-CABS for cc-pVTZ-F12). You can simply open the output file of automr and see what CABS is assigned.

4.4.33 DLPNO

Request to turn on the DLPNO technique in NEVPT2 computations conducted by ORCA. DLPNO is not used by default. But if you turn on DLPNO, RI (see 4.4.29) and FIC (see 4.4.34) will be turned on as byproducts.

This option currently can only be used in CASSCF and CASSCF-NEVPT2 computations conducted by ORCA program, i.e. you need to specify

```
CASSCF_prog=ORCA,NEVPT2_prog=ORCA,DLPNO
```

in mokit{}. Of course it can be combined with F12 to perform RI-DLPNO-FIC-NEVPT2-F12 computations for large systems, where the keywords should be

CASSCF_prog=ORCA,NEVPT2_prog=ORCA,DLPNO,F12

in mokit{}.

4.4.34 FIC

Request the FIC- variant of NEVPT2 (i.e. FIC-NEVPT2) to be used. By default SC-NEVPT2 is invoked if you specify NEVPT2 in route section (#p NEVPT2/…) and use PySCF/Molpro/OpenMolcas/ORCA program as NEVPT2_prog. But if you specify NEVPT2_prog=BDF, this option is turned on as a byproduct and FIC-NEVPT2 will then be performed. SC-NEVPT2 is not supported in BDF. FIC-NEVPT2 is not supported in PySCF.

4.4.35 ON_thres

When ist=5, this parameter is the threshold of natural orbital occupation numbers (NOON) for determining the number of active orbitals. Default value is 0.98, which means orbital occupation numbers 0.02~1.98 will be considered as active orbitals in subsequent CAS/DMRG calculations. Here 0.02=1-0.98, 1.98=1+0.98.

Note that when using ist=5, you should provide a .fch(k) file which contains paired natural orbitals, for example, UNO, UDFT NO, SUHF NO, etc. This is to ensure occupation numbers occur in a pairwise way (1-*x*, 1+*x*). Better not modify the default value unless you are an experienced user.

4.4.36 UNO_thres

When ist=1 or 2, this parameter is the threshold of UNO occupation numbers for determining the number of pairs in GVB computation. The default value is 0.99999 and it means all unoccupied UNOs with occupation numbers >1e-5 will be chosen (as well as their corresponding occupied UNOs) for subsequent orbital localization. The default value often corresponds to a full-valence computation of GVB. Similarly, setting UNO_thres=0.98 corresponds to the fact that any unoccupied UNOs with occupation numbers >0.02 will be chosen.

DO NOT modify the default value unless you are an experienced user.

4.4.37 excludeXH

Request the exclusion of inactive X-H bonds after normal GVB computation finished. For example, a normal GVB computation of the benzene molecule using cc-pVDZ basis set will lead to 15 pairs in total, which contains 9 pairs of C-C bonds and 6 pairs of C-H bonds. If the keyword excludeXH is specified in mokit{}, then a GVB(9) computation containing only C-C bonds will be automatically performed after GVB(15).

4.4.38 NMR

Request the calculation of nuclear shielding constants. Currently only the CASSF method is supported. Gauge-Independent Atomic Orbital (GIAO) method is used to compute the NMR shielding tensors. Note that:
(1) This keyword should be written in mokit{}, not in the Gaussian keyword line (#p …).
(2) The chemical shift of an atom or element is the difference of nuclear shielding constants between the studied molecule and the standard reference molecule. For example, hydrogen atoms in tetramethylsilane(TMS) is usually used as the reference for chemical shifts in ^{1}H-NMR.
(3) For practical computations of chemical shifts, it is recommended to use specially designed basis sets like pcSseg-1 or pcSseg-2. Larger basis sets like pcSseg-3, def2-QZVP or cc-pVQZ would be better but often too expensive.
(4) If you want to calculate NICS, please read tutorial in Section **5.4.2 NICS of cyclobutadiene**. If you want ICSS, please read tutorial in Section **5.4.1 ICSS of cyclobutadiene**.
(5) You should use the OpenMP version of Dalton for this functionality, do not use MPI-parallelized version of Dalton.
(6) This functionality cannot be used for active space >(14,14), since there is no DMRG-GIAO implementation.
(7) MOKIT assumes the user uses 32-bit integer Dalton. The maximum memory allowed for 32-bit integer Dalton is around 16GB. So MOKIT will automatically reduce the memory to 16GB if the user specify >16GB in a NMR job.

4.4.39 ICSS

Request the calculation ICSS (Isochemical Shielding Surfaces). Currently only the CASSF method is supported. Gauge-Independent Atomic Orbital (GIAO) method is used to compute the NMR shieldings. See the example $MOKIT_ROOT/examples/automr/16-C4H4.gjf. Note that:
(1) This keyword should be written in mokit{}, not in the Gaussian keyword line (#p …).
(2) This is an **extremely time-consuming** job. So you'd better have a large node/machine to compute all the generated files. 6-31G(d) or 6-31+G(d) basis set is recommended since larger basis set requires very long time.
(3) After the ICSS computation is accomplished, there would be a file like *_ICSS.cub generated. You can visualized it via GaussView, Multiwfn or VMD.
(4) You should use the OpenMP version of Dalton for this functionality, do not use MPI-parallelized version of Dalton.
(5) This functionality cannot be used for active space >(14,14), since there is no DMRG-GIAO implementation.
(6) MOKIT will submit 2, 3 or 4 Dalton jobs in parallel to accelerate the ICSS computation. The number of Dalton job is determined as three cases: (i) if %nproc is multiples of 4, then 4 jobs will be submitted; (ii) otherwise if %nproc is multiples of 3, then 3 jobs will be submitted; (iii) otherwise 2 jobs will be submitted. In these cases, the allowed maximum total memory is 64GB, 48GB and 32GB, respectively. This is because MOKIT assumes the user uses 32-bit integer of Dalton, which can only utilize up to 16GB.

See a detailed example in Section 5.4 ICSS and NICS of Cyclobutadiene.

4.4.40 Nstates

Specify the number of roots to be averaged in SA-CASSCF computations. For example, Nstates=2 stands for 3 electronic states (ground state + two excited states). The default is to average states with the same spin. If you want to average S_0/T_1, you should also write the keyword Mixed_Spin (see 4.4.41). This keyword is usually used along with DryRun (see 4.4.40).

4.4.41 Mixed_Spin

Specifying this keyword means that allowing electronic states with different spin multiplicities to be averaged in SA-CASSCF. If you want to write this keyword, just write Mixed_Spin. Do not write Mixed_Spin=.True. or Mixed_Spin=True. If this keyword is not specified, the default setting is to average states with the same spin.

4.4.42 GVB_conv

Modify/Set the density matrix convergence criterion in GAMESS GVB to be a desired threshold. The default threshold is 1D-5 (meaning 10^{-5} a.u.). Usually there is no need to modify the default value. But if you want to use a less tight threshold, 1D-4 ~ 5D-4 is recommended, e.g. GVB_conv=5D-4. Note that only 4 characters are allowed for this parameter. Do not write 5.0D-4 since it exceeds the length limit. This keyword is equivalent to the keyword CONV in GAMESS (please read the documentation file docs-input.txt in GAMESS package if you want know more details).

There are two possible cases in which you may want to change the default GVB convergence threshold: (1) When dealing with molecules which have many conjugated π bonds (e.g. acene, zethrene), although the default orbital localization method Pipek-Mezey provides σ-π separated initial guess orbitals for GVB computation, the converged GVB orbitals may still be σ-π mixed. In that case you can specify keywords mokit{LocalM=Boys,GVB_conv=5d-4} and specify exactly the number of π bonds n in Route Section as GVB(n) (this is just a combination of keywords which have been explored by the author jxzou and found often useful). One may wonder why the Boys localization method is used here. This is because we have explicitly specified GVB(n), the n pairs of UNOs near HONO are usually pure π orbitals and it is safe to use Boys localization among π orbitals. (2) When dealing with d transition metal (e.g. Fe) molecules, the GVB orbital optimization often takes many cycles to converge or even diverge in the end, but the first ~30 cycles are often reasonable, so we can use a less tight threshold to converge the GVB wavefuntion.

4.4.43 Skip_UNO

Specify the number of pairs of UNOs to be skipped during orbital localization. Default is 0.

For example, Skip_UNO=1 means that the HONO and LUNO will be kept unchanged when localizing UNOs. And Skip_UNO=2 means that the HONO-1, HONO, LUNO and LUNO+1 will be kept unchanged when localizing UNOs. This is useful when GVB exists multiple SCF solutions. Using Skip_UNO=1 you can probably obtain a biradical-like GVB solution (if the molecule indeed has significant biradical characters). It is recommended to choose the solution with the lowest GVB electronic energies for subsequent post-GVB computations.

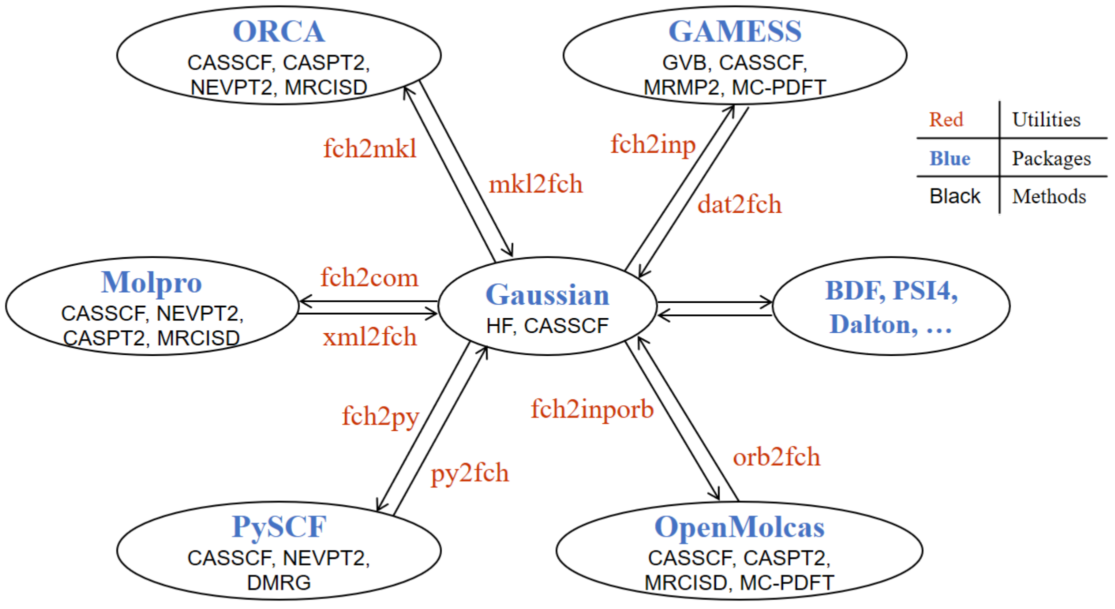
This keyword is invalid for keyword ist=3,4,5. It is also invalid when mokit{ist=6} is specified. But it is valid for keywords mokit{ist=6,inherit} since the keyword inherit will force skip_UNO=*N* to be inherited in the GVB/STO-6G computation.

4.4.44 Inherit

Request to inherit keywords in GVB/STO-6G from target calculations. This keyword can only be used when ist=6. The default is not to inherit keywords. If you want to write this keyword, just write Inherit. Do not write Inherit=.True. or Inherit=True.

4.5 List of Utilities in MOKIT

The utilities of transferring MOs are summarized in the following figure:



For detailed explanations of all utilities, please read the following subsections.

4.5.1 add_bgcharge_to_inp

This utility is designed to add background charges to the input file of various software packages. If you do not use background charges in your computation, you can skip this section. But if you do use them (e.g. in subsystems of fragmentation-based or embedding methods), they are not recorded in any .fch(k) file. This can be viewed as a defect of the .fch(k) file. Therefore, the generated input file by utilities fch2com, fch2inp, fch2iporb, fch2psi or bas_fch2py will contain no background charges either.

To add background charges into the input file, you have to provide a .chg file which contains information of those charges. An example of such file is shown below

```
2
4.0     0.0     0.0       0.1
-4.0     0.0     0.0       0.1
```

The first line holds the number of point charges. While the charges are written starting from the second line, with format *x*, *y*, *z*, *charge*.

Note that in all computations of the AutoMR program, this situation is explicitly considered. This utility will be automatically called if needed. The only situation when you need this utility is merely using utilities fch2com, fch2inp, fch2iporb, fch2psi or bas_fch2py (and of course, with background charges).

4.5.2 bas_fch2py

Generate a PySCF .py file from a Gaussian .fch file. The Cartesian coordinates and basis set data are written in the .py file. Note: AutoMR does not use any built-in basis sets of PySCF, but always generates the basis set data from .fch file. This procedure ensures an (almost) exactly identical setting of basis set in Gaussian and PySCF.

This utility is in fact a wrapper of two utilities 'fch2inp' and 'bas_gms2py'. So if you only want to compile this utility, you have to compile 'fch2inp' and 'bas_gms2py' additionally.

Note that if you use background charges in your studied system, the background charges are not recorded in the .fch(k) file. So there are no background charges in the generated .py file, either. To add background charges, you need to use the utility add_bgcharge_to_inp (see Section 4.5.1).

4.5.3 bas_gau2molcas

Transform a basis set file in Gaussian format to another in (Open)Molcas format. If you turn on RI (see Section 4.4.29) and use OpenMolcas as the CASSCF_prog, there is no RI-JI auxiliary basis set file in current version of OpenMolcas package. Therefore, this utility will be called automatically to transform the auxiliary basis set file in $MOKIT_ROOT/basis/ directory to the (Open)Molcas syntax. And the transformed file will normally be in $MOLCAS/basis_library/jk_Basis/.

You can, of course, use this utility by yourself. An example is shown below

```
bas_gau2molcas def2-universal-jkfit
```

Assuming the basis set file def2-universal-jkfit (in Gaussian format) has been put in the current directory, this command will generate a basis set file named DEF2-UNIVERSAL-JKFIT (in (Open)Molcas format).

4.5.4 bas_gms2bdf

Generate two BDF files (_bdf.inp and .BAS) from a GAMESS .inp/.dat file. Cartesian coordinates are written in the _bdf.inp file, while the basis set data is held in .BAS file. Note that BDF does not support Cartesian-type basis functions, so only spherical harmonic functions will be used. The ‘ISPHER’ keyword in .inp/.dat file (if any) will be ignored. One example is shown below

```
bas_gms2bdf a.inp
```
Generate a_bdf.inp and A.BAS files, for R(O)HF or UHF type wave function.

4.5.5 bas_gms2dal

Generate Dalton .dal and .mol files from a GAMESS .inp/.dat file. The Cartesian coordinates and basis set data are written in the .mol file.

Two examples are shown and explained below

(1) `bas_gms2dal a.inp`
Generate .mol and .dal file, in which the keywords ‘Cartesian’ for all atom are written (in order to use pure Cartesian type of basis functions)

(2) `bas_gms2dal a.inp -sph`
Generate .,mol and .dal file, in which the keywords ‘Cartesian’ of each atom are not written (in order to use pure spherical harmonic type of basis functions).

4.5.6 bas_gms2molcas

Generate an (Open)Molcas .input file from a GAMESS .inp/.dat file. The Cartesian coordinates and basis set data are written in the .input file.

Two examples are shown and explained below

(1) `bas_gms2molcas a.inp`
Generate .inp file, in which the keywords ‘Cartesian’ of each atom are written (in order to use pure Cartesian type of basis functions)

(2) `bas_gms2molcas a.inp -sph`
Generate .inp file, in which the keywords ‘Cartesian’ of each atom are not written (in order to use pure spherical harmonic type of basis functions).

4.5.7 bas_gms2molpro

Generate a Molpro .com file from a GAMESS .inp or .dat file. The Cartesian coordinates and basis set data are written in the .com file.

Two examples are shown and explained below

(1) `bas_gms2molpro a.inp`
Generate .inp file, in which the keyword 'Cartesian' is written (in order to use pure Cartesian type of basis functions)

(2) `bas_gms2molpro a.inp -sph`
Generate .inp file, in which the keyword 'Cartesian' is not written (in order to use pure spherical harmonic type of basis functions).

4.5.8 bas_gms2psi

Generate a PSI4 _psi.inp file from a GAMESS .inp/.dat file. The Cartesian coordinates and basis set data are written in the _psi.inp file.

Two examples are shown and explained below

(1) `bas_gms2psi a.inp`
Generate a_psi.inp file, in which the keyword 'cartesian' is written (in order to use pure Cartesian type of basis functions)

(2) `bas_gms2psi a.inp -sph`
Generate a_psi.inp file, in which the keyword 'spherical' is written (in order to use pure spherical harmonic type of basis functions).

4.5.9 bas_gms2py

Generate a PySCF .py file from a GAMESS .inp/.dat file. The Cartesian coordinates and basis set data are written in the .py file.

Two examples are shown and explained below

(1) `bas_gms2py a.inp`
Generate .inp file, in which the keyword 'mol.cart = True' is written (in order to use pure Cartesian type of basis functions)

(2) `bas_gms2py a.inp -sph`
Generate .inp file, in which the keyword 'mol.cart = True' is not activated (in order to use pure spherical harmonic type of basis functions).

4.5.10 bdf2fch

Transfer MOs from BDF (.scforb/.inporb/.casorb, etc) to Gaussian .fch file. Note that bdf2fch can not generate a .fch file from scratch. The user must provide a .fch(k) file, and MOs in that file will be replaced. Two examples are shown and explained below

(1) `bdf2fch a.scforb a.fch`
This is used for transferring R(O)HF, UHF or CASSCF orbitals.

(2) `bdf2fch a.casorb a.fch -no`
This is used for transferring CASCI or CASSCF NOs and NOONs.

NOTE: the recommended way is to firstly use Gaussian to generate a .fch file (with keywords 'nosymm int=nobasistransform'), then generate the _bdf.inp file from .fch file. After BDF computations finished, you can transfer MOs from .scforb/.casorb back to .fch file. This procedure seems a little bit tedious, but it ensures an exact reproduce of energy in BDF.

This utility supports only spherical harmonic functions. To transfer MOs from Gaussian to BDF, see Section 4.5.16 fch2bdf.

4.5.11 bdf2mkl

Transfer MOs from BDF (.scforb/.inporb/.casorb, etc) to ORCA. The ORCA .inp and .mkl file will be generated. This utility is actually a wrapper of two utilities bdf2fch and fch2mkl. Thus bdf2mkl can not generate a .fch file from scratch, either. The user must provide a .fch(k) file, and MOs in that file will be replaced. Two examples are shown and explained below

(1) `bdf2mkl a.scforb a.fch`
This is used for transferring RHF, ROHF, UHF or CASSCF orbitals.

(2) `bdf2mkl a.casorb a.fch -no`
This is used for transferring CASCI or CASSCF NOs and NOONs.

NOTE: the recommended way is to firstly use Gaussian to generate a .fch file (with keywords 'nosymm int=nobasistransform'), then generate the _bdf.inp file from .fch file. After BDF computations finished, you can transfer MOs from .scforb/.casorb back to .fch file. This procedure seems a little bit tedious, but it ensures an exact reproduce of energy in BDF.

4.5.12 chk2gbw

Convert one (or more) .chk file into .gbw file. The Gaussian utility formchk and ORCA utility orca_2mkl will be called automatically. Multiple chk files are supported. For example,

(1) `chk2gbw a.chk`
Convert a.chk to a.gbw.

(2) `chk2gbw *.chk`
Convert all chk files in the current directory into corresponding gbw files.

4.5.13 dal2fch

Transfer MOs from Dalton (i.e. DALTON.MOPUN file) to Gaussian .fch(k) file. Note that dal2fch can not generate a .fch file from scratch. The user must provide a .fch(k) file, and MOs in that file will be replaced. Two examples are shown and explained below

(1) `dal2fch a.dat a.fch`
This is used for transferring R(O)HF or CASSCF orbitals.

(2) `dal2fch a.dat a.fch -no`
This is used for transferring CASCI/CASSCF natural orbitals and corresponding natural orbital occupation numbers. To transfer MOs from Gaussian to Dalton, see Section 4.5.18 fch2dal.

4.5.14 dat2fch

Transfer MOs from GAMESS (.inp/.dat file) to Gaussian .fch file. Note that dat2fch can not generate a .fch file from scratch. The user must provide a .fch(k) file, and MOs in that file will be replaced. Four examples are shown and explained below

(1) `dat2fch a.dat a.fch`
This is used for transferring R(O)HF, UHF or CASSCF orbitals.

(2) `dat2fch a.dat a.fch -gvb 5`
This is used for transferring GVB orbitals for spin singlet molecule. The order of GVB orbitals is different between Gaussian and GAMESS. Thus you must specify '-gvb [npair]' to tell the utility the number of GVB pairs, so that dat2fch can adjust the order of MOs.

(3) `dat2fch a.dat a.fch -gvb 5 -open 1`
This is used for transferring GVB orbitals for non-singlet molecule. In this way, you tell the utility the number of GVB pairs and singly-occupied orbitals, so that dat2fch can adjust the order of MOs.

(4) `dat2fch a.dat a.fch -no 5 10`
This is used for transferring natural orbitals (NOs) of CASCI/CASSCF. In this way, you tell the utility the beginning index and final index of NOs in .fch file, so that dat2fch can work correctly.

NOTE: the recommended way is to firstly use Gaussian to generate a .fch file (with keywords 'nosymm int=nobasistransform'), then generate the .inp file from .fch file. After GAMESS computations finished, you can transfer MOs from .dat back to .fch file. This procedure seems a little bit tedious, but it ensures an exact reproduce of energy in GAMESS.

This utility supports two types of basis functions: (1) pure spherical harmonic functions; (2) pure Cartesian functions. To transfer MOs from Gaussian to GAMESS, see Section 4.5.19 fch2inp.

4.5.15 extract_noon2fch

Extract natural orbital occupation numbers (NOONs) from the following types of files
(1) .out file of PySCF
(2) .dat file of GAMESS
(3) .gms file of GAMESS
(4) .out file of ORCA
(5) .out file of PSI4
and write NOONs (as the 'Alpha Orbital Energies' section) into a given .fch file. This is for the convenience of visualizing orbitals using GaussView or Multiwfn+VMD.

4.5.16 fch2bdf

Generate three BDF files (_bdf.inp, .BAS, .scforb/.inporb) from a Gaussian .fch(k) file. Cartesian coordinates are written in the _bdf.inp file, while the basis set data is held in .BAS file. The molecular orbitals are written in the .scforb/.inporb file. Note that BDF does not support Cartesian-type basis functions, so only spherical harmonic functions will be used. If there exists any Cartesian-type basis function in .fch(k) file, this utility will signal errors. Two examples are shown and explained below

(1) `fch2bdf a.fch`
This is used for transferring RHF/ROHF/UHF orbitals. Three files will be generated: a_bdf.inp, A.BAS and a.scforb. The data in 'Alpha Orbital Energies' and 'Beta Orbital Energies' sections in .fch file will be read and printed into the a.scforb file.

(2) `fch2bdf a.fch -no`
This is used for transferring NOs. Three files will be generated: a_bdf.inp, A.BAS and a.inporb. Note the data of 'Alpha Orbital Energies' section in .fch file (assumed occupation numbers) will be read and printed into the a.inporb file, but the occupation numbers do not affect subsequent computations.

This utility will call another two utilities 'fch2inp' and 'bas_gms2bdf'. So if you want to compile fch2bdf, you have to compile 'fch2inp' and 'bas_gms2bdf' additionally.

Note that to transfer HF orbitals, the data in 'Alpha Orbital Energies' and 'Beta Orbital Energies' section should be genuine orbital energies, since BDF program will use these values. Random values (like zero) will affect SCF computations and thus it cannot converge in 1 cycle (or even fails to converge). This is totally different with other quantum chemistry software packages where only orbitals are useful and orbital energies are useless. When transferring NOs, the occupation numbers in ‘Alpha Orbital Energies’ section do not affect subsequent computations.

To transfer MOs from BDF back to Gaussian, see Section 4.5.10 bdf2fch.

4.5.17 fch2com

Generate a Molpro .com file from a Gaussian .fch(k) file, with alpha MOs written in a .a file. One example is shown below

```
fch2com a.fch
```

This is used for transferring R(O)HF, UHF or CASSCF orbitals.

This utility will call another two utilities ‘fch2inp’ and ‘bas_gms2molpro’. So if you want to compile fch2com, you have to compile ‘fch2inp’ and ‘bas_gms2molpro’ additionally.

Note that in Windows* OS, any file with .com suffix/extension may be automatically associated with system, in which case double click of the mouse to open this file does not work. You have to right click on the .com file and choose ‘open with’. You can modify the suffix/extension to .inp if you do not like that.

Note that if you use background charges in your studied system, the background charges are not recorded in the .fch(k) file. So there are no background charges in the generated .com file, either. To add background charges, you need to use the utility add_bgcharge_to_inp (see Section 4.5.1).

To transfer MOs from Molpro back to Gaussian, see Section 4.5.35 xml2fch.

4.5.18 fch2dal

Generate Dalton .dal and .mol files from a Gaussian .fch(k) file, where MOs are written in .dal file, and the Cartesian coordinates as well as basis set data are written in .mol file. One example is shown below

```
fch2dal a.fch
```

This is used for transferring R(O)HF or CASSCF orbitals. Note that there is no UHF method (or any methods based on UHF), thus you cannot use a .fch file containing UHF orbitals to transfer orbitals. To transfer MOs from Dalton back to Gaussian, see Section 4.5.13 dal2fch.

4.5.19 fch2inp

Generate a GAMESS .inp file from a Gaussian .fch(k) file, with MOs written in the .inp file. The keywords in .inp file is already suitable for common simple calculations, but do check or modify it if you have additional requirements.

Note that due to the different types of MOs (R(O)HF, UHF, GVB, and CASSCF orbitals), the fch2inp offers different options. Three examples are shown and explained below

(1) fch2inp a.fch
This is used for transferring R(O)HF, UHF or CASSCF orbitals.

(2) fch2inp a.fch -gvb 5
This is used for transferring GVB orbitals for spin singlet molecule. The order of GVB orbitals is different between Gaussian and GAMESS. Thus you must specify '-gvb [npair]' to tell the utility fch2inp the number of GVB pairs, so that fch2inp can adjust the order of MOs.

(3) fch2inp a.fch -gvb 5 -open 1
This is used for transferring GVB orbitals for non-singlet molecule. In this way, you tell the utility fch2inp the number of GVB pairs and singly-occupied orbitals, so that fch2inp can adjust the order of MOs.

This utility supports two types of basis functions: (1) pure spherical harmonic functions; (2) pure Cartesian functions. To transfer MOs from GAMESS back to Gaussian, see Section 4.5.14 dat2fch.

Note that if you use background charges in your studied system, the background charges are not recorded in the .fch(k) file. So there are no background charges in the generated .inp file, either. To add background charges, you need to use the utility add_bgcharge_to_inp (see Section 4.5.1).

4.5.20 fch2inporb

Transfer MOs from Gaussian to (Open)Molcas. A .input file and a .INPORB file will be generated. The .input file is the input file of (Open)Molcas, and it contains the geometry, basis set data and keywords. The .INPORB file contains the MOs. Two examples are shown and explained below

(1) fch2inporb a.fch
This is used for transferring R(O)HF, UHF or CASSCF orbitals.

(2) fch2inporb a.fch -no
This is used for transferring NOs.

The option '-no' means reading NOONs and NOs from .fch(k) file and printing them into the .INPORB file. The NOONs written in the .INPORB file does not affect the calculations in OpenMolcas at all. It just make the file appear more readable.

This utility will call another two utilities 'fch2inp' and 'bas_gms2molcas'. So if you want to compile fch2inporb, you have to compile 'fch2inp' and 'bas_gms2molcas' additionally.

Note: if you use background charges in your studied system, the background charges are not recorded in the .fch(k) file. So there are no background charges in the generated .input file, either. To add background charges, you need to use the utility add_bgcharge_to_inp (see Section 4.5.1).

Note: if you provide a .fch file generated by G09 and this .fch file is generated with DKH2 Hamiltonian in its corresponding .gjf file, the DKH2 information is not recorded in the .fch file. In such case, if you run fch2inporb xxx.fch, the generated xxx.input file will not include keyword Relativistic = R02O, you need to manually add this keyword into the .input file. This is not a problem for G16 since the Route section is recorded in .fch file for G16 so that it can be recognized/identified by fch2inporb.

To transfer MOs from (Open)Molcas back to Gaussian, see Section 4.5.31 orb2fch.

4.5.21 fch2mkl

Transfer MOs from Gaussian to ORCA. One .inp file and one .mkl file will be generated. The .input file of ORCA holds the geometry, basis set data and keywords. The .mkl file contains the MOs. One example is shown below

```
fch2mkl a.fch
```

This is used for transferring R(O)HF, UHF or CASSCF orbitals. Two files will be generated: a_o.inp and a_o.mkl. The '_o' characters are added to avoid file overwritten in case that there is already a xxx.inp file in the current directory (for example, generated by utility fch2inp).

To transfer MOs from ORCA back to Gaussian, see Section 4.5.29 and 4.5.30.

Note 1: Assuming your ORCA input file is a.inp, you need to run 'orca_2mkl a_o -gbw' to generate the ORCA a.gbw file since ORCA cannot read a.mkl file directly.

Note 2: The default keywords in .inp file does not contain any RI approximations, and settings of VeryTightSCF are written (the author does this to ensure an exact reproduce of energy in ORCA). You can modify keywords as you wish, but note that an exact reproduce of energy may not be assured.

Note that if you use background charges in your studied system, the background charges are not recorded in the .fch(k) file. So there are no background charges in the generated .inp or .mkl file, either. To add background charges, you need to use the utility add_bgcharge_to_inp (see Section 4.5.1).

4.5.22 fch2psi

Transfer MOs from Gaussian to PSI4. Two or three files will be generated: *_psi.inp, *.A, and *.B (if Beta MOs exist). The _psi.inp file of PSI4 holds the geometry, basis set data and keywords. The .A (and .B) file contains the Alpha (Beta) MOs. One example is shown below

```
fch2psi a.fch
```

This is used for transferring R(O)HF, UHF or CASSCF orbitals.

Note that this utility will call another two utilities – fch2inp and bas_gms2psi, remember to compile them additionally.

Note that if you use background charges in your studied system, the background charges are not recorded in the .fch(k) file. So there are no background charges in the generated .com file, either. To add background charges, you need to use the utility add_bgcharge_to_inp (see Section 4.5.1).

PSI4 can generate a .fch(k) file after calculation finished, which is equivalent to transferring MOs from PSI4 back to Gaussian.

4.5.23 fch2qm4d

Transfer MOs from Gaussian to QM4D. Input files for QM4D (.xyz, .inp, .xml and basis files for each element) will be generated. One example is shown below

```
fch2qm4d a.fch
```

This is used for transferring RHF or UHF orbitals.

Note 1: Currently QM4D supports only Cartesian-type basis sets. Thus this utility will signal error if you provide a .fch(k) file which has spherical harmonic functions (i.e. 5D 7F).

Note 2: QM4D supports ECP, but currently it seems to use spherical harmonic functions in ECP, so even if you specify '6D 10F' in Gaussian, the electronic energies of Gaussian *v.s.* QM4D will not be equal to each other. This tiny defect does not affect transferring MOs, and SCF can be converged in several cycles with almost no energy change.

Note that if you use background charges in your studied system, the background charges are not recorded in the .fch(k) file. So there are no background charges in the generated .inp file, either. To add background charges, you need to use the utility add_bgcharge_to_inp (see Section 4.5.1).

4.5.24 fch2wfn

Generate .wfn file from a specified .fch(k) file. Two examples are shown below

(1) `fch2wfn a.fch`

For a .fch file in which ground state HF/DFT orbitals are recorded, generate the corresponding a.wfn file.

(2) `fch2wfn a.fch -no`

For a .fch file in which natural orbitals are recorded, generate the corresponding a.wfn file.

4.5.25 fch_mo_copy

Copy MOs from one .fch file into another .fch file. An example is shown below

```
fch_mo_copy a.fch b.fch
```

The default is to copy Alpha MOs in a.fch to Alpha MOs in b.fch. There are 4 optional parameters '-aa', '-ab', '-ba', '-bb'. For example, '-ab' means copying Alpha MOs from a.fch to Beta MOs in b.fch.

4.5.26 fch_u2r

Transform a UHF-type .fch file into a RHF-type one. Only alpha MOs are retained.

4.5.27 frag_guess_wfn

This utility has two functions: (1) perform a SCF (i.e. HF or DFT) computation using initial guess constructed from molecular orbitals of fragments. (2) generate GAMESS .inp file for GKS-EDA or Morokuma-EDA calculation.

The Gaussian software package will be called to perform SCF computation for each fragment. The input file is exactly the Gaussian .gjf file, in which the atoms, charge and spin multiplicities of each fragment are properly defined. See examples in Section 5.3.

Explanations of function (1):

Note: implementation of this function is not yet finished.

The SCF computations of radicals and transition-metal-containing molecules often suffers from multiple UHF/UKS solutions. Using a proper fragment guess (i.e., the 'guess(fragment=*N*)' keyword in Gaussian), one can then obtain a desired SCF solution or a lower energy solution after SCF converged and a check of wavefunction stability of the whole system. However, the wavefunction stability of each fragment in the initial guess cannot be assured in Gaussian, thus not efficient for complicated molecules. This utility – frag_guess_wfn – can ensure the wavefunction stability of each fragment and allow the usage of RHF/UHF (or RKS/UKS) for different fragments, which would improve the quality of initial guess and save time for subsequent SCF computation of the whole system. Examples of the fragment guess can be found at http://gaussian.com/afc. If you can read Chinese, a nice introduction to this topic from Sobereva's blog

《谈谈片段组合波函数与自旋极化单重态》 http://sobereva.com/82

is recommended.

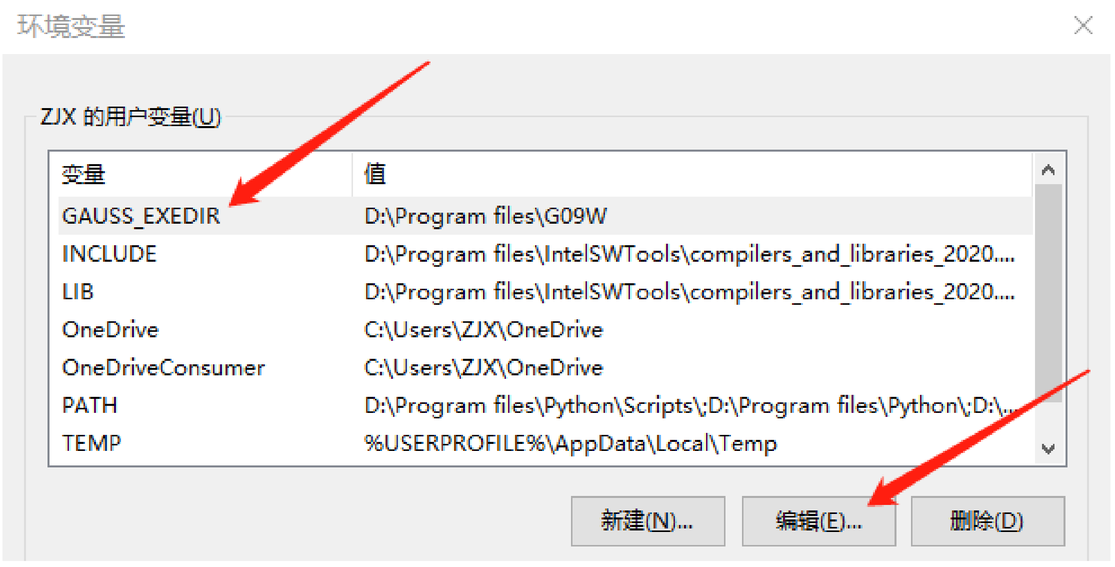
Explanations of function (2):

The Morokuma-EDA calculation is supported by GAMESS-US program, while GKS-EDA calculation is supported by the XEDA program (a modified GAMESS-US program from Prof. Peifeng Su of Xiamen University, supi@xmu.edu.cn). These methods are very useful but often suffer from SCF convergence failure due to the "just so-so" SCF convergence techniques in GAMESS. Even if all SCF converge, their wave function stabilities cannot be checked in GAMESS.

Fortunately, these two methods can read wave function of each fragment (and of total system in GKS-EDA), if we can provide such wave function as initial guess. Therefore, the utility frag_guess_wfn will call Gaussian to perform SCF calculations for each fragment (and for total system in GKS-EDA), then write all MOs into the .inp file, so that all SCF steps during an EDA calculation will converge immediately.

If UHF/UDFT method is specified, wave function stability of each fragment (and of total system in GKS-EDA) will be checked. This is very important for biradical and transition-metal-containing systems. If any fragment is singlet and UHF/UDFT method is specified, broken symmetry initial guess (i.e., guess=mix) will be automatically applied.

The Windows* pre-built executable frag_guess_wfn will be provided at Releases in the near future. Note that you should define the environment variable %GAUSS_EXEDIR% (in Windows* OS) before using this utility, since Gaussian program would be called to perform SCF computations. For example, search “environment variable” in your Windows search bar and click Edit to add a new environment variable, and set it as the correct G03W, G09W or G16W directory. A screenshot is shown below



变量	值
GAUSS_EXEDIR	D:\Program files\G09W
INCLUDE	D:\Program files\IntelSWTools\compilers_and_libraries_2020....
LIB	D:\Program files\IntelSWTools\compilers_and_libraries_2020....
OneDrive	C:\Users\ZJX\OneDrive
OneDriveConsumer	C:\Users\ZJX\OneDrive
PATH	D:\Program files\Python\Scripts\;D:\Program files\Python\;D:\...
TEMP	%USERPROFILE%\AppData\Local\Temp

4.5.28 gvb_sort_pairs

Sort (part of) MOs in descending order of the pair coefficients of the 1st natural orbital in each pair. This utility is designed only for the GAMESS .dat file. A new .dat file will be generated, in which the sorted MOs and pair coefficients are held.

4.5.29 mkl2fch

Transfer MOs from ORCA .mkl file into Gaussian .fch(k) file. A .fch(k) file must be provided by the user, in which the geometry and basis set data are valid (i.e. specifying ‘noysmm int=nobasistransform 5D 7F’ in Gaussian).

Note that the number of digits in .mkl file is only 7, and the scientific notation is not used. Therefore, the transferred MOs will not be very accurate. This should be sufficient for visualizing orbitals and common wavefunction amalysis, but may cause up to 10^{-5} a.u. error on electronic energy in further computations. This can be viewed as a defect of the orca_2mkl utility in ORCA program. You are recommended to bring up an issue or request in the ORCA forum (https://orcaforum.kofo.mpg.de), to suggest ORCA developers to fix this. If the scientific notation is not used, then 10 digits of MO coefficients should be sufficient for further computations.

Two examples are shown and explained below

(1) `mkl2fch a.mkl a.fch`
This is used for transferring R(O)HF or UHF orbitals.

(2) `mkl2fch a.mkl a.fch -no`
This is used for transferring NOs.

To transfer MOs from Gaussian to ORCA, see Section 4.5.21 fch2mkl.

4.5.30 mkl2gjf

Generate the Gaussian .gjf file from the ORCA .mkl file. The Cartesian coordinates, basis set data and MOs (optional) will be printed into the .gjf file. Two examples are shown and explained below

(1) mkl2gjf a.mkl
Generate the Gaussian .gjf file from the ORCA .mkl file. The Cartesian coordinates, basis set data will be printed into the .gjf file. There would be no MOs in it.

(2) mkl2gjf a.mkl -mo
Generate the Gaussian .gjf file from the ORCA .mkl file. The Cartesian coordinates, basis set data plus MOs will be printed into the .gjf file.

Note that the ORCA .mkl file has a defect: it does not contain ECP/PP information. Therefore, if you did not use ECP in your ORCA calculations, there would be no problem. But in case you used ECP, there would be no ECP data in the generated .gjf file (you must add them manually).

4.5.31 orb2fch

Transfer MOs from (Ope)nMolcas *Orb file (e.g. .ScfOrb, .RasOrb.1, .UnaOrb, .UhfOrb, etc) to Gaussian .fch(k) file. A .fch(k) file must be provided by the user, in which the geometry and basis set data are available. Five examples are shown and explained below

(1) `orb2fch a.ScfOrb a.fch`
This is used for transferring RHF orbitals.

(2) `orb2fch a.RasOrb a.fch`
This is used for transferring CASCI/CASSCF or RASCI/RASSCF (pseudo)canonical orbitals.

(3) `orb2fch a.UnaOrb a.fch -no`
This is used for transferring UNOs.

(4) orb2fch a.UhfOrb a.fch
This is used for transferring UHF alpha and beta MOs.

(5) orb2fch a.RasOrb.1 a.fch -no
This is used for transferring CASCI/CASSCF or RASCI/RASSCF NOs.

To transfer MOs from Gaussian to (Open)Molcas, see Section 4.5.20 fch2inporb.

4.5.32 mo_svd

Output the singular values of the overlap matrix between two sets of MOs. This utility will first read the atomic overlap matrix from a given file, then calculate the overlap matrix between two sets of MOs. Finally, perform singular value decomposition (SVD) on the molecular orbital overlap matrix and print information about singular values. The first two command line arguments can be both Gaussian .fch files, or both OpenMolcas orbital files (.INBORB, .RasOrb, etc). The third argument is a Gaussian .log file or a OpenMolcas output file, in which the atomic overlap matrix is written.

The singular values can be used to measure the overlap or similarity of two sets of MOs. If all singular values are close to 1, the compared two sets of MOs are very similar. Any singular value being close to 0 means there exists at least 1 distinct orbital.

4.5.33 solve_ON_matrix

Compute the occupation number matrix (a non-diagonal matrix) of a set of MOs. Assuming you have a .fch(k) file which holds some kind of MOs, and another .fch(k) file which holds some kind of NOs and corresponding NOONs, then this utility can compute the occupation numbers of this set of MOs (transformed from NOs and NOONs). Of course, in this case the occupation number matrix of MOs is not a diagonal matrix, only the diagonal elements are written into the 'Alpha Orbital Energies' section of the file which holds MOs.

4.5.34 replace_xyz_in_inp

Replace the Cartesian coordinates in an input file, by coordinates from a given .xyz file or an output file. For the input/output file, currently only (Open)Molcas and Molpro formats are supported. Other formats will be supported in the near future. Four examples are shown below

(1) replace_xyz_in_inp a.xyz b.input -molcas
Replace the Cartesian coordinates in b.input file, by coordinates from the a.xyz file. A file named b_new.input will be generated.

(2) replace_xyz_in_inp a.out b.input -molcas
Replace the Cartesian coordinates in b.input file, by coordinates from an (Open)Molcas output file.

A file named b_new.input will be generated.

(3) `replace_xyz_in_inp a.xyz b.com -molpro`
Replace the Cartesian coordinates in b.com file, by coordinates from the a.xyz file. A file named b_new.com will be generated.

(4) `replace_xyz_in_inp a.out b.com -molpro`
Replace the Cartesian coordinates in b.com file, by coordinates from a Molpro output file. A file named b_new.com will be generated.

4.5.35 xml2fch

Transfer MOs from Molpro .xml file to Gaussian .fch(k) file. Note that xml2fch cannot generate a .fch file from scratch. The user must provide one .fch file, in which the 'Alpha Orbital Energies' and 'Alpha MOs' sections (and possibly Beta sections) will be replaced by occupation numbers and MOs from Molpro .xml file. Three examples are shown and explained below

(1) `xml2fch a.xml a.fch`
This is used for transferring R(O)HF or UHF orbitals.

(2) `xml2fch a.xml a.fch -no`
This is used for transferring NOs.

To transfer MOs from Gaussian to Molpro, see Section 4.5.17 fch2com.

The utilities below are compiled by **f2py**, which is a Fortran to Python interface generator. These utilities are not binary executable files, but dynamic libraries *.so in $MOKIT_ROOT/lib. They can only be imported in a Python script. And this is the reason that why one of the environment variables of MOKIT is 'PYTHONPATH', not 'LD_LIBRARY_PATH'. These utilities can also be viewed as APIs (Application Programming Interface), but they are described in this section not in Section 4.6, just for better comparison with other utilities of transferring MOs.

4.5.36 fch2py

Transfer MOs from Gaussian to PySCF. By importing fch2py, PySCF Python script is able to read alpha and/or beta MOs from a provided .fch file. All attributes are shown below

```
fch2py(fchname, nbf, nif, ab, mf.mo_coeff)
```

There are 4 parameters required by fch2py: (1) filename of .fch(k) file; (2) the number of basis functions; (3) the number of molecular orbitals; and (4) a character ‘a’/’b’ for reading alpha/beta orbitals. You should write these contents into a Python script, and run that script using the python executable. If you want a more detailed example, just run any AutoMR job and see all *.py files generated.

4.5.37 py2fch

Export MOs from PySCF to a Gaussian .fch file. Note that py2fch cannot generate a .fch file from scratch. The user must provide one .fch file, in which the ‘Alpha Orbital Energies’ and ‘Alpha MOs’ sections (or beta orbital counterpart) will be replaced by occupation numbers and MOs from PySCF.

The provided .fch file must contain exactly the same geometry and basis set data as those data of PySCF. To obtain a valid .fch file, it is strongly recommended to use the bas_fch2py utility to generate a .py file from a .fch file first, and then import py2fch in this generated .py file. These descriptions seem a bit of tedious. But a rigorous transferring of MOs between two programs or two files is ensured. All attributes of py2fch are shown below

```
py2fch('a.fch', nbf, nif, mf.mo_coeff, ab, ev, gen_density)
```

The first few parameters are identical to those in Section 4.5.35 fch2py. The parameter ev means eigenvalues, it is supposed to contain orbital energies or orbital occupation numbers. The last parameter gen_density is a bool variable, where True/False meaning whether or not generating Total SCF Density (as well as writing density into .fch file) using mf.mo_coeff and ev. If gen_density is set to be True, the parameter ev must contain orbital occupation numbers, not orbital energies. Because density would be computed using MOs and occupation numbers. If gen_density is set to be False, you can assign proper values to ev as your wish.

Obviously this utility/module is supposed to used usually along with other three utilities: bas_fch2py (Section 4.5.2), fch2py (Section 4.5.35) and load_mol_from_fch (Section 4.6.1).

4.6 APIs in MOKIT

Currently only Python APIs are provided. C/C++ APIs may be provided in the future. Some commonly used Python APIs are shown below

1. load_mol_from_fch(fchname)
2. loc(fchname, method, idx)
3. read_int1e_from_gau_log(logname, itype, nbf)
4. read_mo_from_fch(fchname, nbf, nif, ab)
5. read_density_from_gau_log(logname, itype, nbf)
6. read_density_from_fch(fchname, itype, nbf)

7. write_pyscf_dm_into_fch(fchname, nbf, dm, itype, force)
8. gen_ao_tdm(logname, nbf, nif, mo, istate)
9. export_mat_into_txt(txtname, n, mat, lower, label)
10. read_natom_from_pdb(pdbname, natom)
11. read_nframe_from_pdb(pdbname, nframe)
12. read_iframe_from_pdb(pdbname, iframe, natom, cell, elem, resname, coor)
13. write_frame_into_pdb(pdbname, iframe, natom, cell, elem, resname, coor, append)
14. calc_unpaired_from_fch(fchname, wfn_type, gen_dm)

Meanings of frequently appeared arguments are
fchname: filename of .fch(k) file
logname: filename of .log/.out file
nbf: the number of basis functions
nif: the number of (linear-independent) MOs

Meanings of other arguments are shown in below subsections.

4.6.1 load_mol_from_fch

Load a PySCF mol object from a Gaussian .fch(k) file. For example, run python in Shell

```
$python
>>>from pyscf import scf
>>>from gaussian import load_mol_from_fch
>>>mol = load_mol_from_fch(fchname='00-h2o_cc-pVDZ_0.96_rhf.fchk')
>>>mf = scf.RHF(mol).run()
```

where the module gaussian is actually the file $MOKIT_ROOT/lib/gaussian.py.

4.6.2 loc

Perform orbital localization for a given .fch(k) file. Two localization methods are supported: Foster-Boys or Pipek-Mezey. For example, run python in Shell

```
$python
>>>from gaussian import loc
>>>loc(fchname='benzene_5D7F_rhf.fchk', method='pm', idx=range(6,21))
```

Only 'boys' or 'pm' is allowed for the 2nd argument. You should specify the orbital indices or range in the 3rd argument. Note that the starting integer index is 0 in Python convention, and the final index cannot be reached. So range(6,21) means orbitals 7-21, which are valence occupied orbitals for benzene. The localized orbitals will be exported/written into a new file with suffix *_LMO.fch (in this case, it is benzene_5D7F_rhf_LMO.fch).

For system containing only σ bonds, these two methods make little difference. While for system containing σ and π bonds, the Boys localization method tends to mix σ and π bonds, which leads to “banana” bonds. The PM localization method tends to keep σ and π separated. If you want to analyze localized π bonds after localization, you should choose method='pm'.

4.6.3 uno

Generate UHF natural orbitals(UNOs) from a given Gaussian .fch(k) file. For example,

```
$python
>>>from gaussian import loc
>>>uno(fchname='benzene_uhf.fch')
```

4.6.4 read_int1e_from_gau_log

Read various one-electron integral matrices from a Gaussian output file. For example, read AO-basis overlap

```
$python
>>>import rwwfn
>>>S = rwwfn.read_int1e_from_gau_log(logname='00-h2o_cc-pVDZ_1.5.log',itype=1,nbf=24)
```

Attribute itype:
The type of one-electron integral matrices. Allowed values are 1,2,3,4 for Overlap, Kinetic Energy, Potential Energy, and Core Hamiltonian, respectively.

4.6.5 read_mo_from_fch

Read MOs from a Gaussian .fch(k) file. For example

```
$python
>>>import rwwfn
>>>mo = rwwfn.read_mo_from_fch(fchname='00-h2o_cc-pVDZ_1.5.fchk',nbf=24,nif=24,ab='a')
```

Attribute ab:
character with length=1, ‘a’/’b’ for reading alpha/beta orbitals.

4.6.6 read_density_from_gau_log

Read various types of density matrix from a Gaussian output file. For example, read the Alpha Density Matrix from a .log file

```
$python
>>>import rwwfn
>>>den = rwwfn.read_density_from_gau_log(logname='00-h2o_cc-pVDZ_1.5.log',
itype=2,nbf=24)
```

Attribute itype:
1/2/3 for Total/Alpha/Beta Density Matrix.

4.6.7 read_density_from_fch

Read various types of density matrix from a Gaussian .fch(k) file. For example, read the Total SCF Density from a .fchk file

```
$python
>>>import rwwfn
>>>den = rwwfn.read_density_from_fch(fchname='00-h2o_cc-pVDZ_1.5.fchk',
itype=1,nbf=24)
```

Attribute itype:

itype	type of density	itype	type of density
1	Total SCF Density	6	Spin MP2 Density
2	Spin SCF Density	7	Total CC Density
3	Total CI Density	8	Spin CC Density
4	Spin CI Density	9	Total CI Rho(1)
5	Total MP2 Density	10	Spin CI Rho(1)

4.6.8 write_pyscf_dm_into_fch

Write a PySCF density matrix into a given Gaussian .fch(k) file. This module does two things: (1) deal with the order of basis functions and their normalization factors, (2) then export density matrix into a given .fch(k) file. All attributes of this module are shown below

```
write_pyscf_dm_into_fch(fchname, nbf, dm, itype, force)
```

where dm is the PySCF density matrix with dimension (nbf,nbf). itype has the same meaning with that in Section 4.6.5. force is a bool variable, and its meaning is:
(1) If the string corresponding to itype (e.g. ‘Total SCF Density’) can be found/located in the given .fch file, this parameter will not be used, i.e. setting True/False does not matter.
(2) If the string corresponding to itype cannot be found, setting force=True will enforce writing density matrix into the given file; setting force=False will stop/abort the program and signal errors immediately (this can be used to check whether desired strings exists in the specified file).

You should use this module via

```
$python
>>>from py2fch import write_pyscf_dm_into_fch
```

Note that this module cannot generate a .fch(k) file from scratch, the user must provide one such file. The recommended approach is firstly using the module bas_fch2py to generate PySCF input file or using load_mol_from_fch to generate proper PySCF object, then do computations in PySCF. Finally using the module write_pyscf_dm_into_fch to export desired density matrix.

4.6.9 gen_ao_tdm

Generate AO-basis ground->excited state Transition Density Matrix for CIS/TDHF/TDDFT from a Gaussian output file. Currently only closed shell is taken into consideration. For example, read the S0->S1 Transition Density Matrix from a Gaussian .log file (with iop(9/40=5) specified in .gjf file)

```
$python
>>>import rwwfn, excited
>>>mo = rwwfn.read_mo_from_fch(fchname='00-h2o_cc-pVDZ_0.96_rhf.fchk',nbf=24,
nif=24,ab='a')
>>>tdm = excited.gen_ao_tdm(logname='00-h2o_cc-pVDZ_0.96_rhf.log',nbf=24,nif=24,
mo=mo,istate=1)
>>>rwwfn.export_mat_into_txt(txtname='h2o_tdm.txt',n=24,mat=tdm,lower=False,label='transiti
on density matrix')
```

Attribute istate:
The i-th excited state. For example, i=1 for the first excited state.

The last python statement means exporting the transition density matrix into a plain text file, see the API below.

4.6.10 export_mat_into_txt

Export a square matrix into a plain text file. The example of exporting transition density matrix is shown in Section 4.6.6. Here I offer one more example – export the lower triangle of a symmetric AO-basis overlap matrix

```
$python
>>>import rwwfn
>>>S = rwwfn.read_int1e_from_gau_log(logname='00-h2o_cc-pVDZ_1.5.log',itype=1,nbf=24)
>>>rwwfn.export_mat_into_txt(txtname='ovlp.txt',n=24,mat=S,lower=True,label='Overlap')
```

Attribute	Explanation

txtname	file name
mat	the square matrix with dimension (n,n)
lower	True/False for whether or not printing only the lower triangle part of a matrix
label	a string, the meaning of exported matrix (provided by yourself)

4.6.11 read_natom_from_pdb

Read the number of atoms from a given pdb file. If there exists more than one frame in the pdb file, only the 1st frame will be detected. See an example in Section 4.6.13.

4.6.12 read_nframe_from_pdb

Read the number of frames from a given pdb file. See an example in Section 4.6.13.

4.6.13 read_iframe_from_pdb

Read the *i*-th frame from a given pdb file. See an example in Section 4.6.13.

4.6.14 write_frame_into_pdb

Write a frame into the given pdb file. A python script is shown below, to illustrate how to use these pdb-related APIs:

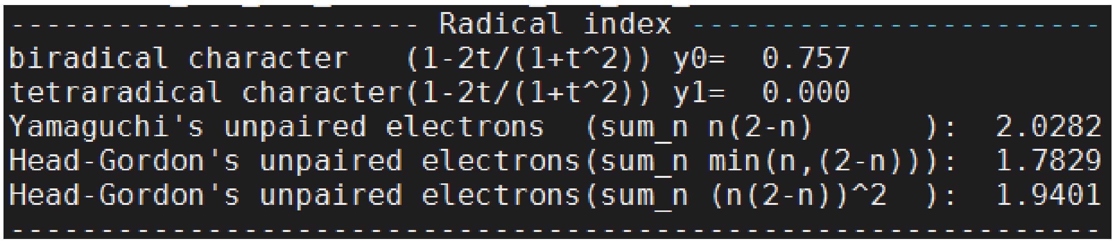
```
import rwgeom as rg
natom = rg.read_natom_from_pdb(pdbname='test.pdb')
cell, elem, resname, coor = rg.read_iframe_from_pdb('test.pdb', 10, natom)
for i in range(0,natom):
   s1 = elem[i][0].decode('utf-8')
   s2 = elem[i][1].decode('utf-8')
   print(s1, s2)
rg.write_frame_into_pdb('a.pdb', 10, natom, cell, elem, resname, coor, False)
```

4.6.15 calc_unpaired_from_fch

Calculate the Yamaguchi's unpaired electrons and Head-Gordon's unpaired electrons using the provided .fch(k) file. Biradical and tetraradical indices are printed as well. This .fch file must include natural orbitals and their corresponding occupation numbers. For example, a UNO, GVB or CASSCF NO .fch file is expected. DO NOT use a UHF .fch file. A python script is shown below:

```
from wfn_analysis import calc_unpaired_from_fch
calc_unpaired_from_fch(fchname='00-h2o_cc-pVDZ_1.5_uhf_uno_asrot2gvb4_s.fch',
wfn_type=2, gen_dm=False)
```

The attribute wfn_type has values 1/2/3 for UNO/GVB/CASSCF NOs, respectively. The example above will print the following



```
----------------------- Radical index -----------------------
biradical character   (1-2t/(1+t^2)) y0=  0.757
tetraradical character(1-2t/(1+t^2)) y1=  0.000
Yamaguchi's unpaired electrons  (sum_n n(2-n)      ):  2.0282
Head-Gordon's unpaired electrons(sum_n min(n,(2-n))):  1.7829
Head-Gordon's unpaired electrons(sum_n (n(2-n))^2  ):  1.9401
-------------------------------------------------------------
```

If the attribute gen_dm is set to True (i.e. gen_dm=True), then a file like *_unpaired.fch will also be generated, in which the unpaired electron density is stored. The unpaired density can be visualized by GaussView or Multiwfn+VMD.

Yamaguchi's biradical index for UHF:

$$t = (n_{\text{HONO}} - n_{\text{LUNO}})/2, y = 1 - \frac{2t}{1+t^2}$$

Yamaguchi's biradical index for CAS(2,2):

$$y = 2c_2^2 = n_{\text{LUNO}}$$

where c_2 is the CI coefficients of the 2nd configurations in CASCI wave function (assuming natural orbitals are used). Note that there is no unique way to define biradical (or tetraradical, etc) index for general cases including CASSCF(*m*,*m*) where *m*>=4, or GVB(*n*) where *n*>=2. The $y_i = n_{\text{LUNO}+i}$ formula is adopted in the module calc_unpaired_from_fch for these general cases.

There are also modules which calculate the number of unpaired electrons of GVB by reading information from GAMESS .dat/.gms file:

```
from wfn_analysis import calc_unpaired_from_gms_dat
calc_unpaired_from_gms_dat(datname='00-h2o_cc-
pVDZ_1.5_uhf_uno_asrot2gvb4_s.fch',mult=1)
```

It requires the user to input the spin multiplicity since there is no spin information in .dat file. Or you can use

```
from wfn_analysis import calc_unpaired_from_gms_out
calc_unpaired_from_gms_out(outname='00-h2o_cc-pVDZ_1.5_uhf_uno_asrot2gvb4.gms')
```

Reference for these two types of unpaired eletrons:
[1] Theoret. Chim. Acta (Berl.) 48, 175-183 (1978). DOI: 10.1007/BF00549017.
[2] Chemical Physics Letters 372 (2003) 508–511. DOI: 10.1016/S0009-2614(03)00422-6.

4.6.16 Other modules in rwwfn

modify_IROHF_in_fch(fchname, k)
read_charge_and_mult_from_fch(fchname, charge, mult)
read_charge_and_mult_from_mkl(mklname, charge, mult)
read_na_and_nb_from_fch(fchname, na, nb)
read_nbf_and_nif_from_fch(fchname, nbf, nif)
read_nbf_and_nif_from_orb(orbname, nbf, nif)
read_nbf_from_dat(datname, nbf)
read_mo_from_chk_txt(txtname, nbf, nif, ab, mo)
read_mo_from_orb(orbname, nbf, nif, ab, mo)
read_mo_from_xml(xmlname, nbf, nif, ab, mo)
read_mo_from_bdf_orb(orbname, nbf, nif, ab, mo)
read_mo_from_dalton_mopun(orbname, nbf, nif, coeff)
read_eigenvalues_from_fch(fchname, nif, ab, noon)
read_on_from_orb(orbname, nif, ab, on)
read_on_from_dat(datname, nmo, on, alive)
read_on_from_xml(xmlname, nmo, ab, on)
read_on_from_bdf_orb(orbname, nif, ab, on)
read_ev_from_bdf_orb(orbname, nif, ab, ev)
read_on_from_dalton_mopun(orbname, nif, on)
read_ncontr_from_fch(fchname, ncontr)
read_shltyp_and_shl2atm_from_fch(fchname, k, shltyp, shl2atm)
read_ovlp_from_molcas_out(outname, nbf, S)
write_eigenvalues_to_fch(fchname, nif, ab, on, replace)
write_on_to_orb(orbname, nif, ab, on, replace)
write_mo_into_fch(fchname, nbf, nif, ab, mo)
write_mo_into_psi_mat(matfile, nbf, nif, mo)
determine_sph_or_cart(fchname, cart)
read_npair_from_uno_out(nbf, nif, ndb, npair, nopen, lin_dep)
read_gvb_energy_from_gms(gmsname, e)
read_cas_energy_from_output(cas_prog, outname, e, scf, spin, dmrg, ptchg_e, nuc_pt_e)
read_cas_energy_from_gaulog(outname, e, scf)
read_cas_energy_from_pyout(outname, e, scf, spin, dmrg)
read_cas_energy_from_gmsgms(outname, e, scf, spin)
read_cas_energy_from_molcas_out(outname, e, scf)
read_cas_energy_from_orca_out(outname, e, scf)
read_cas_energy_from_molpro_out(outname, e, scf)
read_cas_energy_from_bdf_out(outname, e, scf)
read_cas_energy_from_psi4_out(outname, e, scf)
read_cas_energy_from_dalton_out(outname, e, scf)
read_mrpt_energy_from_pyscf_out(outname, ref_e, corr_e)
read_mrpt_energy_from_molcas_out(outname, itype, ref_e, corr_e)

read_mrpt_energy_from_molpro_out(outname, itype, ref_e, corr_e)
read_mrpt_energy_from_orca_out(outname, itype, ref_e, corr_e)
read_mrpt_energy_from_gms_out(outname, ref_e, corr_e)
read_mrpt_energy_from_bdf_out(outname, itype, ref_e, corr_e, dav_e)
read_mrcisd_energy_from_output(CtrType, mrcisd_prog, outname, ptchg_e, nuc_pt_e, davidson_e, e)
read_mcpdft_e_from_output(prog, outname, ref_e, corr_e)
find_npair0_from_dat(datname, npair, npair0)
find_npair0_from_fch(fchname, nopen, npair0)
read_no_info_from_fch(fchname, nbf, nif, ndb, nopen, nacta, nactb, nacto, nacte)
check_cart(fchname, cart)
check_sph(fchname, sph)
write_density_into_fch(fchname, nbf, total, dm)
detect_spin_scf_density_in_fch(fchname, alive)
add_density_str_into_fch(fchname, itype)
update_density_using_mo_in_fch(fchname)
update_density_using_no_and_on(fchname)
check_if_uhf_equal_rhf(fchname, eq)
copy_orb_and_den_in_fch(fchname1, fchname2, deleted)
read_ao_ovlp_from_47(file47, nbf, S)
get_no_from_density_and_ao_ovlp(nbf, nif, P, ao_ovlp, noon, new_coeff)
read_mult_from_fch(fchname, mult)
get_1e_exp_and_sort_pair(mo_fch, no_fch, npair)

5 Examples

5.1 Examples of AutoMR

See examples in $MOKIT_ROOT/examples/automr. More details to be added.

5.2 Examples of Transferring MOs

See examples in $MOKIT_ROOT/examples/utilities. More details to be added.

5.3 Examples of using utility frag_guess_wfn

Introduction of the utility frag_guess_wfn has been provided in Section 4.5.25. Here several examples will be shown to illustrate how this utility is used and how it works.

5.3.1 Construct initial guess wave function from fragments

More details to be added.

5.3.2 Morokuma-EDA

The input file of H_2O-NH_3 complex is shown below

```
%chk=nh3_h2o_m.chk
%mem=16GB
%nprocshared=16
#p RHF/cc-pVDZ guess(fragment=2)

{morokuma}

0 1 0 1 0 1
N(fragment=1)      -1.67861672     -0.49374924     -0.00513612
H(fragment=1)      -1.39223602     -1.00824506      0.80312136
H(fragment=1)      -1.24821305      0.40883590      0.00449440
H(fragment=1)      -1.40093406     -0.98667606     -0.82970600
O(fragment=2)       0.68224018      0.74345713      0.00303850
H(fragment=2)       1.37946396      0.10226230     -0.15300059
H(fragment=2)       0.95548613      1.60139824     -0.32993853
```

This is clearly just a Gaussian .gjf file, and it looks very similar to two other types of calculations: 1) fragment guess calculation in Section 5.3.1; 2) BSSE calculation. The order of fragments is the same as that required in GAMESS. That is to say, you must define atoms in the order of monomer 1, monomer 2, monomer 3, etc. To conveniently add '(fragment=N)' in each row, you may need some advanced text editor like Sublime Text 3, UltraEdit, VSCode, etc.

In Title Card line, {morokuma} must be written to tell the utility frag_guess_wfn you want the input file of Morokuma-EDA. Currently Morokuma-EDA in GAMESS has several restrictions:

(1) Only the RHF method can be used. ROHF, UHF or any DFT methods cannot be used. Both the total system and every fragment should be treated with RHF. This means broken bonds cannot be dealt with.
(2) Spherical harmonic functions cannot be used. The utility frag_guess_wfn will automatically switch to Cartesian fucntions (i.e., 6D 10F) when calling Gaussian to perform SCF computations.

Assuming the filename is nh3_h2o_m.gjf, you simply need to run

```
frag_guess_wfn nh3_h2o_m.gjf
```

Since the molecule is small, you can obtain a file named nh3_h2o_m.inp in seconds. MOs of two fragments will be written into this file. You can submit the file nh3_h2o_m.inp to GAMESS for Morokuma-EDA computations. All SCF of fragments will converge in 1-2 cycles. The initial guess of orbitals of the total system (i.e. supermolecule) is not written in .inp file, but constructed from fragments within GAMESS, and it is supposed to be converged soon.

Simply replacing the {morokuma} by {gks} means you want the input file of GKS-EDA. UHF and UDFT methods can be applied in GKS-EDA. Thus it is powerful, especially when dealing with biradical system, where the symmetry broken UDFT calculations are necessary. See the following section for more examples.

5.3.3 GKS-EDA

To perform GKS-EDA calculations, you need the GAMESS program and xeda-patch script. After you download the required packages, use the xeda-patch script to modify the GAMESS source code. And then compile GAMESS in a usual way. Here is a tutorial written in Chinese 《GKS-EDA 计算简介》.

Here I offer two examples to illustrate how to use the utility frag_wfn_guess to generate the input file of GKS-EDA. The first example: $[Ti(H_2O)_6]^{3+}$ cation, whose input file is shown below

```
%mem=32GB
%nprocshared=16
#p UPBE1PBE/gen guess(fragment=2)

{gks}

3 2 3 2 0 1
Ti(fragment=1)        0.00000000      0.00000000      0.00000000
 H(fragment=2)        0.00000000      2.68428109     -0.78751709
 H(fragment=2)        2.68128062      0.78751744      0.00000000
 H(fragment=2)        0.00000000     -2.68428109      0.78751709
 H(fragment=2)        0.78751709      0.00000000     -2.68228109
 H(fragment=2)       -2.68128062      0.78751744      0.00000000
 H(fragment=2)       -0.78751709      0.00000000      2.68228109
 O(fragment=2)        0.00000000      2.10100000      0.00000000
 H(fragment=2)        0.00000000      2.68428109      0.78751709
 O(fragment=2)        0.00000000      0.00000000      2.09900000
 H(fragment=2)        0.78751709      0.00000000      2.68228109
 O(fragment=2)        0.00000000      0.00000000     -2.09900000
 H(fragment=2)       -0.78751709      0.00000000     -2.68228109
 O(fragment=2)        2.09800000      0.00000000      0.00000000
 H(fragment=2)        2.68128062     -0.78751744      0.00000000
 O(fragment=2)       -2.09800000      0.00000000      0.00000000
 H(fragment=2)       -2.68128062     -0.78751744      0.00000000
 O(fragment=2)        0.00000000     -2.10100000      0.00000000
 H(fragment=2)        0.00000000     -2.68428109     -0.78751709
```

```
Ti 0
def2TZVP
****
H O 0
def2SVP
****
```

Mixed basis set, user-defined basis set or ECP/PP are all supported. DO REMEMBER to type at least 2 blank lines after the basis set data. The only exception of basis set is that definition for each atom tag is unsupported. For example, the following definition

```
1 0
def2TZVP
****
2 0
def2SVP
```

is currently NOT supported for utility frag_guess_wfn. Assuming the filename is Ti.gjf, you simply need to run

```
frag_guess_wfn Ti.gjf &
```

in bash. Electronic energies of fragments will be directly printed onto the screen. You can run instead

```
frag_guess_wfn Ti.gjf >Ti.out 2>&1 &
```

if you do not like things printed on screen. This example may take about 20 min to generate the desired .inp file. Five SCF jobs will be performed in succession:
(1) monomer 1 in its own basis;
(2) monomer 2 in its own basis;
(3) monomer 1 in all basis;
(4) monomer 2 in all basis;
(5) supermolecule in all basis.

Utility frag_guess_wfn will automatically construct the initial guess for job (5) using MOs from job (1) and (2). This will save some time. After all 5 jobs normally terminated, the utility fch2inp will be automatically called to transfer 5 sets of MOs from Gaussian .fch files into one GAMESS .inp file. Proper keywords (including DFT name in DFTTYP, solvent name and radii of solute atoms in $PCM, etc) have been written in the generated .inp file. You can, of course, open this file and modify keywords according to your needs (e.g. dispersion correction).

For HF methods, all 5 SCF jobs during GKS-EDA will converge in 1-2 cycles. While for UDFT, they may take about 10 cycles since the DFT integral grids (and functional implementation details possibly) in GAMESS are not identical to those in Gaussian. Note that when using DFT methods, grid settings '$DFT NRAD=99 NLEB=590 $END' will be automatically added into the .inp file, to mimic the 'int=ultrafine' in Gaussian. If implicit solvent model is also applied, each SCF will take more cycles, since implementation details in GAMESS have differences with those in Gaussian (but the energy usually steadily decreases).

You can write an alias into your ~/.bashrc for convenience of running XEDA, for example,

```
alias xeda='/home/jxzou/software/xeda/rungms'
```

Once the calculation of frag_guess_wfn is done (and you've modified keywords according to your needs), you can simply run in bash

```
xeda Ti.inp 00 16 >& Ti.gms &
```

to perform the GKS-EDA calculation, where the 16 is the number of CPU cores for parallel computation.

Then we come to the second example: the ethane molecule. Assuming we want to see the interaction of two ▪CH3 radicals, such fragmentation will involve **breaking a covalent bond**, which leads to an alpha unpaired electron in one ▪CH3 radical and a beta unpaired electron in another radical. In this case we need to specify **negative spin** in the input file, which represents the beta spin:

```
%mem=4GB
%nprocshared=4
#p UHF/cc-pVTZ guess(fragment=2)

{gks}

0 1 0 2 0 -2
C(fragment=1)     -3.42837266       0.18776078       0.00000000
H(fragment=1)     -3.07171823      -0.82104923       0.00000000
H(fragment=1)     -3.07169982       0.69215897      -0.87365150
H(fragment=1)     -4.49837266       0.18777396       0.00000000
C(fragment=2)     -2.91503044       0.91371705       1.25740497
H(fragment=2)     -1.84503225       0.91200998       1.25838332
H(fragment=2)     -3.27008700       1.92309006       1.25642758
H(fragment=2)     -3.27329940       0.41044905       2.13105517
```

It is equivalent to interchange 2/-2. The coupling of an alpha unpaired electron with a beta unpaired electron leads to the total spin singlet.

The GKS-EDA supports up to 20 fragments. For convenience only examples containing two fragments are shown above.

5.3.4 SAPT

The utility frag_guess_wfn is also able to generate the input file of SAPT computation in PSI4. Currently only SAPT0 (and sSAPT0) is supported. More advanced methods like SAPT2+ and SAPT2+(3)δMP2 will be supported in the near future. Similarly, frag_guess_wfn will first call the Gaussian to perform HF/DFT computations and then generate the input file of SAPT job for PSI4. Be aware that SAPT cannot deal with strong interactions come from two fragments by breaking covalent bonds (in that case you should use the GKS-EDA method).

Here is a SAPT example:

```
%mem=16GB
%nprocshared=8
#p HF/jun-cc-pVDZ guess(fragment=2)

{sapt,bronze}

0 1 0 1 0 1
O(fragment=1)        -1.90937854    1.06610853   -0.05598828
H(fragment=1)        -2.23867796    0.17728177    0.09615925
H(fragment=1)        -0.94953286    1.05932020   -0.04017097
N(fragment=2)        -2.02042680   -1.64298230    0.34416157
H(fragment=2)        -2.28323594   -1.98171649   -0.55927105
H(fragment=2)        -2.67940800   -1.96304329    1.02482651
H(fragment=2)        -1.10944265   -1.98408759    0.57601295
```

Both of SAPT0 and sSAPT0 results can be found in output. The SAPT paper (JCP 140, 094106 (2014)) recommends three levels of theory to be used: (1) bronze: sSAPT0/jun-cc-pVDZ; (2) silver: SAPT2+/aug-cc-pVDZ; (3) gold: SAPT2+(3)δMP2/aug-cc-pVTZ. So far the open shell calculations have not been implemented for silver and gold level in PSI4 (it is OK for sSAPT0). Currently only the bronze level is supported in utility frag_guess_wfn. {sapt} or {sapt,bronze} in the Title Card line will be recognized as the bronze level. You are always recommended to use jun-cc-pVDZ unless there is some element which is out of the range of jun-cc-pVDZ.

5.3.5 Tricks for accelerations in frag_guess_wfn

For some simple fragments (water molecules, organic ligands, etc), if you are sure that they have closed-shell wave function, you can append a character ‘r’ after the Cartesian coordinates of any atom of the fragment. Again, taking the $[Ti(H_2O)_6]^{3+}$ cation as the example,

```
%chk=Ti.chk
%mem=32GB
%nprocshared=16
#p UPBE1PBE/gen guess(fragment=2)
```

```
{gks}

3 2 3 2 0 1
Ti(fragment=1)      0.00000000      0.00000000      0.00000000
H(fragment=2)       0.00000000      2.68428109     -0.78751709 r
H(fragment=2)       2.68128062      0.78751744      0.00000000
```
… (not shown)

Note that there must be a blank between the z-component coordinate and the character 'r'. This will force the use of R(O)HF calculation for this fragment, thus saving computation time. After R(O)HF computation of this fragment is done, beta MOs will be directly copied from alpha MOs, so the net result is that it appears to perform a UHF computation, but with only R(O)HF cost.

If the 'r' is not written, UHF and wave function stability test will be performed for this fragment. In this special case we know that UHF is unnecessary for this fragment.

This trick accelerates computations only when UHF/UDFT is required for the supermolecule so that we can force some fragment(s) to use closed-shell methods. If restricted HF or DFT methods are required for the supermolecule, this trick will not reduce computational time.

5.4 ICSS and NICS of Cyclobutadiene

5.4.1 ICSS of cyclobutadiene

If you are not familiar with ICSS, you are recommended to read Sobereva's blog 《通过Multiwfn绘制等化学屏蔽表面(ICSS)研究芳香性》http://sobereva.com/216. That blog contains necessary information of ICSS using HF/DFT methods.

Here we try to compute ICSS using the CASSCF method. The gjf file of the following example can be found at $MOKIT_ROOT/examples/automr/16-C4H4.gjf. For convenience, here is the content:

```
%mem=32GB
%nprocshared=16
#p CASSCF(4,4)/6-31G(d)

mokit{ICSS}

0 1
 C              0.00000000     0.00000000     0.00000000
 C              0.00000000     0.00000000     1.34900000
 C              1.56200000     0.00000000     1.34894100
 C              1.56200000    -0.00023900    -0.00005900
 H             -0.76022400    -0.00000200    -0.76288200
 H             -0.76022400     0.00013500     2.11188200
 H              2.32222400     0.00000000     2.11182300
```

```
H                          2.32222400    -0.00037400    -0.76294100
```

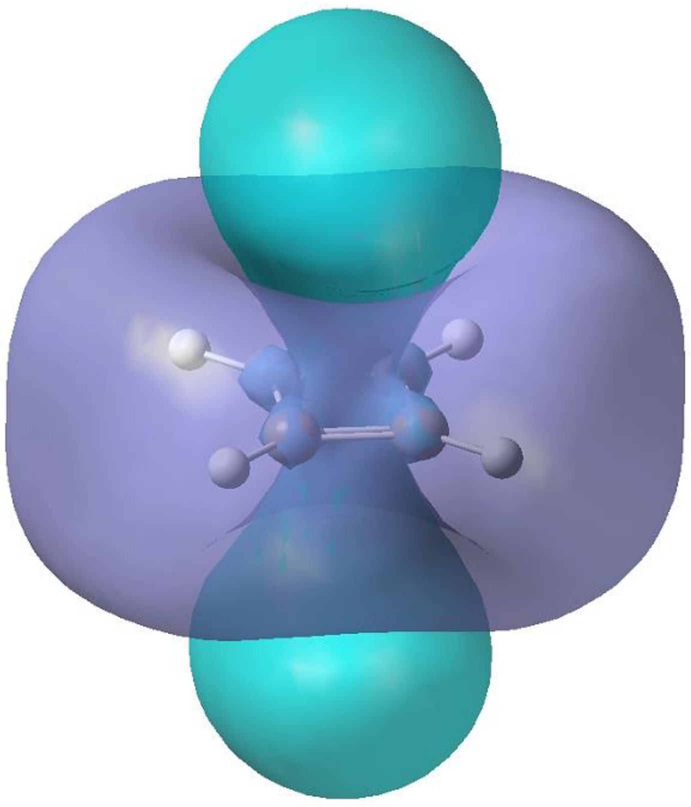
Step 1. Submit the automr job

```
automr 16-C4H4.gjf   >16-C4H4.out   2>&1 &
```

This computation would take about 1 hour. For larger molecules, the computation is very time-consuming and it might take one or two days. The basis set 6-31G(d) or 6-31+G(d) is recommended since larger basis set would cost too much computational time. After the computation is accomplished, there would be a file named 16-C4H4_uhf_gvb10_CASSCF_ICSS.cub. This file can be visualized by GaussView, Multiwfn or VMD.

Step 2. Open the .cub file with GaussView.

You can simply drag the .cub file into GaussView. Next, click the "Results" -> "Surfaces/Contours", set the "Density" to an appropriate value, e.g. 0.2. Finally, click "Surface Actions" -> "New Surface". Then a figure like the following picture would be shown on your screen.



5.4.2 NICS of cyclobutadiene

If you think ICSS computation is too time-consuming, then NICS is a good choice. It usually takes only several seconds or minutes to obtain one or two points of NICS values. Again, we use the cyclobutadiene as the example. The input file is

```
%mem=32GB
%nprocshared=16
#p CASSCF(4,4)/def2TZVP
```

```
mokit{NMR}

0 1
 C                    0.00000000     0.00000000     0.00000000
 C                    0.00000000     0.00000000     1.34900000
 C                    1.56200000     0.00000000     1.34894100
 C                    1.56200000    -0.00023900    -0.00005900
 H                   -0.76022400    -0.00000200    -0.76288200
 H                   -0.76022400     0.00013500     2.11188200
 H                    2.32222400     0.00000000     2.11182300
 H                    2.32222400    -0.00037400    -0.76294100
```

Since NICS computation is cheap, you can use a larger basis set like def2TZVP, rather than 6-31G(d). Note that do not write “NICS” keyword in the input file, “NMR” is enough.

Firstly, you should submit this file to automr. Now assuming you’ve accomplished the CASSCF computation, and next you want to compute NICS(1)_ZZ. Just open the file 16-C4H4_uhf_gvb10_CASSCF_NMR.mol and add the Cartesian coordinates of dummy atom Bq:

```
ATOMBASIS
generated by utility bas_gms2dal in MOKIT
Basis set specified with gen
AtomTypes=9 Integrals=1.0D-14 Charge=0 NoSymmetry Angstrom
Charge=6. Atoms=1 Basis=INTGRL Blocks=3 1 1 1
… (abbreviated for brevity)
           0.8000000000            1.0000000000
Charge=0. Atoms=1 Basis=INTGRL Ghost
Bq     0.7809234989     -1.0000597432      0.6745590841
```

What you need to do is two things: (1) modify the AtomTypes from 8 to 9 (because we add one Bq atom); (2) add coordinates of the Bq dummy atom in the end of the file. The modification is shown in bold text above. The coordinates of Bq can be obtained using Multiwfn, see examples in http://sobereva.com/261. Then submit this job to Dalton, e.g. running the following commands in Shell:

```
dalton -gb 16 -omp 16 -put "SIRIUS.RST" -noarch -ow 16-C4H4_uhf_gvb10_CASSCF_NMR &
```

This only takes 1~2 minutes. After it is finished, open the file 16-C4H4_uhf_gvb10_CASSCF_NMR.out and search “@1 Bq”, you can find the chemical shielding of this Bq atom is -11.9931 ppm. Remember that NICS(1)_ZZ is the negative of the chemical shielding, i.e. 11.9931 ppm.

5.5 Manually making consistent active space

The active space automatically determined by AutoMR of MOKIT may not be the same size for cases involving chemical reactions, different local minima, or different spin states of the same geometry. Or although the active space size remains unchanged, but the active orbitals become substantially different among different geometries. In such cases, if we want to obtain an accurate relative energy, we should pay attention to the following two points:

(1) Different species are required to have the same size of active space.
(2) Active orbitals of different species are supposed to contain the same main components.

Point (2) is merely recommended by the author jxzou, not a rule which you must obey. Taking the singlet-triplet gap of a molecule as an example: if MOKIT automatically determined/recommends the active space of singlet to be CAS(2,2), but triplet to be CAS(4,4), then it would be unfair to directly compare the energies of CASSCF(2,2) *v.s.* CASSCF(4,4). Of course, it would be unfair to simply compare NEVPT2 energies (based on corresponding CASSCF), either. In such cases, the author recommends two approaches:

(i) If we find two orbitals in CAS(4,4) of triplet to be not active, i.e. occupation numbers close to 2 and 0, respectively, we can read CAS(4,4) orbitals, move these two orbitals out of the active space, and perform a CAS(2,2) computation. Then active space size of two spin states are the same.
(ii) If there are similar active orbitals but they are too active to be moved out of the active space, or if we cannot find any similar active orbital between two active space. We should consider to enlarge the size of CAS(2,2) for singlet. The extension target can be CAS(4,4), or can be even larger, depending on the similar extent of two active space.

Obviously the approaches above correspond to intersection set and union set in mathematics. Currently these two approaches have not been implemented in MOKIT, since it requires a lot of techniques to make them become automatic and black-box. Below I will provide two examples to illustrate how to manually make two active space consistent. For comparison of active space from more than two species, the spirit is identical.

5.5.1 The Diels-Alder reaction of 1,3-butadiene and ethane

To be added.

5.5.2 Singlet-Triplet gap of an iron-containing molecule

To be added.

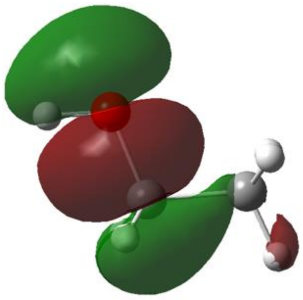
5.5.3 Find a C-C bond for an equilibrium geometry

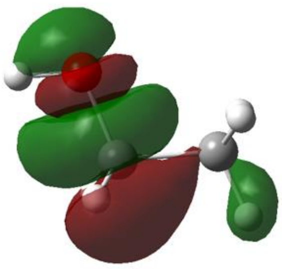
If one studies the C-C bond dissociation in ethanol using multireference computations conducted by AutoMR in MOKIT, he/she may find that when the bond is stretched, AutoMR usually provide desired CAS(2,2) results. However, for the equilibrium geometry (or near that), AutoMR may provide a CAS(2,2) which does not contain the desired chemical bond. This is because there is no multireference character for the equilibrium geometry, AutoMR cannot locate the chemical bond as desired. In fact, in such case the word ‘desired’ has different meanings for different users. Some other users may want the CAS(2,2) to contain the C-O bond, and some users may want the C-H bond.

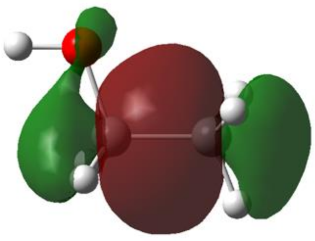
Here I will show how to swap two orbitals to get desired results. Using the ethanol as an example, assuming that we have perform a simple CASPT2(2,2)/cc-pVDZ calculation, the input file ethanol.gjf is shown below

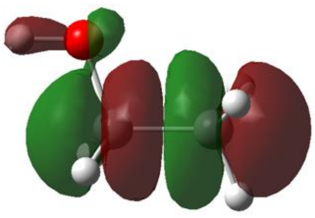
```
%mem=4GB
%nprocshared=4
#p CASPT2(2,2)/cc-pVDZ

mokit{CASPT2_prog=ORCA}

0 1
C          0.00000000    0.00000000    0.00000000
H          0.00000000    0.00000000    1.09270400
H          1.03726900    0.00000000 -0.34698400
H        -0.48033400    0.91954100 -0.34310600
C        -0.73649800 -1.21494100 -0.53167000
H        -0.24338800 -2.13583800 -0.19123400
H        -0.72503400 -1.21412700 -1.63028700
O        -2.08207000 -1.16197400 -0.04736100
H        -2.56286600 -1.92666800 -0.37754100
```

And we find that the HONO and LUNO of CASSCF(2,2) correspond to the C-O bond


HONO


LUNO


6


21

If we want it to be the C-C bond, we should swap/exchange orbitals in GVB NOs since they are the initial guess of CASSCF. To accomplish that, we start python

```
$python
```

```
>>> from gaussian import permute_orb
>>> permute_orb('ethanol_rhf_proj_loc_pair2gvb8_s.fch',6,13)
>>> permute_orb('ethanol_rhf_proj_loc_pair2gvb8_s.fch',14,21)
>>> exit()
```

The orbital indices 13 and 14 are just HONO and LUNO of GVB NOs, while the 6 and 21 are the C-C bonding and anti-bonding orbitals we want. To know the orbital indices, you should visualize MOs in advance. Now the file ethanol_rhf_proj_loc_pair2gvb8_s.fch is updated. We use it as the initial guess of CASSCF(2,2), i.e. submit the job

```
python ethanol_rhf_gvb8_CASSCF.py >ethanol_rhf_gvb8_CASSCF.out 2>&1
```

then we re-open the file ethanol_rhf_gvb8_CASSCF_NO.fch and check whether the HONO and LUNO now correspond to the C-C bond. Finally, we update the .gbw file and re-submit the CASPT2 job

```
fch2gbw ethanol_rhf_gvb8_CASSCF_NO.fch ethanol_rhf_gvb8_CASSCF_CASPT2.gbw
orca ethanol_rhf_gvb8_CASSCF_CASPT2.inp >ethanol_rhf_gvb8_CASSCF_CASPT2.out 2>&1
```

where running the fch2gbw utility is to update the file ethanol_rhf_gvb8_CASSCF_CASPT2.gbw since CASSCF orbitals are stored in this file. Note that you should find CASPT2 energy in file ethanol_rhf_gvb8_CASSCF_CASPT2.out by yourself. It is not in AutoMR output file currently.

5.6 Examples of dinuclear transition metal molecules

5.6.1 $[Fe_2(OH)_2(H_2O)_8]^{4+}$

I downloaded the geometry from some unknown website, so before performing multireference computations, the geometry optimization is necessary. If you obtain the geometry from crystal data, you may only need to optimize the positions of hydrogen atoms. If you get the geometry from previous computational literature (with reasonable computations therein), geometry optimization may be unnecessary.

Assuming we are studying the lowest antiferromagnetic singlet, the Gaussian input file (.gjf) for geometry optimization is shown below

```
%chk=Fe2_ini.chk
%mem=200GB
%nprocshared=48
#p UBP86/TZVP nosymm guess(fragment=5) scf(xqc,maxcycle=500)

title

4 1 3 6 3 -6 -1 1 -1 1 0 1
Fe(Fragment=1)         0.56990000      -0.61710000      -0.77260000
Fe(Fragment=2)         2.46140000      -0.90030000      -3.11630000
O(Fragment=5)           0.83530000       1.50450000      -0.94550000
```

```
O(Fragment=3)        2.42280000     -0.91110000     -0.96240000
O(Fragment=5)        0.24940000     -2.71760000     -0.51100000
O(Fragment=5)       -1.54430000     -0.30870000     -0.63950000
O(Fragment=5)        0.63850000     -0.41510000      1.35780000
O(Fragment=4)        0.58860000     -0.83710000     -2.91460000
H(Fragment=5)        1.26180000      1.66120000     -1.77480000
H(Fragment=5)       -0.63350000     -2.89290000     -0.78630000
H(Fragment=5)       -1.70840000      0.57350000     -0.92580000
H(Fragment=5)        0.18020000      0.37680000      1.58020000
H(Fragment=5)        1.41960000      1.77430000     -0.26000000
H(Fragment=3)        2.55880000     -1.80250000     -0.69740000
H(Fragment=5)        0.30060000     -2.88260000      0.41550000
H(Fragment=5)       -1.77780000     -0.38080000      0.26940000
H(Fragment=5)        1.54020000     -0.32870000      1.61230000
H(Fragment=4)        0.27980000     -1.70780000     -3.08960000
O(Fragment=5)        2.57760000      1.24250000     -3.13070000
O(Fragment=5)        4.59560000     -0.97250000     -3.27840000
O(Fragment=5)        2.39960000     -3.04000000     -3.18650000
O(Fragment=5)        2.40100000     -0.88560000     -5.25630000
H(Fragment=5)        1.50560000     -0.76300000     -5.51910000
H(Fragment=5)        2.41410000      1.52980000     -4.01150000
H(Fragment=5)        4.91230000     -1.68440000     -2.75140000
H(Fragment=5)        3.25730000     -3.36430000     -2.97650000
H(Fragment=5)        3.46380000      1.46430000     -2.89930000
H(Fragment=5)        4.80310000     -1.14140000     -4.18100000
H(Fragment=5)        2.20300000     -3.27960000     -4.07670000
H(Fragment=5)        2.91120000     -0.15440000     -5.55730000

--Link1--
%chk=Fe2_ini.chk
%mem=200GB
%nprocshared=48
#p UBP86 chkbasis nosymm guess=read geom=allcheck scf(xqc,maxcycle=500) stable=opt

--Link1--
%chk=Fe2_ini.chk
%mem=200GB
%nprocshared=48
#p opt=calcfc freq UBP86 chkbasis nosymm guess=read geom=allcheck scf(xqc,maxcycle=500)

--Link1--
%chk=Fe2_ini.chk
%mem=200GB
%nprocshared=48
```

```
#p UBP86 chkbasis nosymm guess=read geom=allcheck stable=opt
```

This is a 4-step job. The 1st step sets up the fragment information of 5 fragments. This is because we need the antiferromagnetic singlet (5 alpha electrons for Fe1 and 5 beta electrons for Fe2) solution. Such an SCF solution is often difficult to be obtained using conventional HF/DFT initial guess, so here we use the fragment guess.

The 2nd step reads MOs from previous step, converges the UBP86 orbitals and checks the stability of UBP86 wavefunction. If not stable, the keyword `stable=opt` will automatically optimize the wavefunction to a stable one. The 3rd step reads MOs from previous step and starts geometry optimizations. Note that the wavefunction stability may change during geometry optimizations, so we need the 4th step to ensure that we get a stable wavefunction finally.

If the UBP86 energy in the 4th step becomes lower (than the electronic energy of the final geometry in the 3rd step), it means that the frequency analysis in the 3rd step is useless since it is based on an instable wavefunction. In that case we need to read MOs from the 4th step and continue geometry optimization. Fortunately, in this example, we obtain the stable *E*(UBP86) = -3289.8489510 a.u. in the 3rd step and it is not lowered in the 4th step.

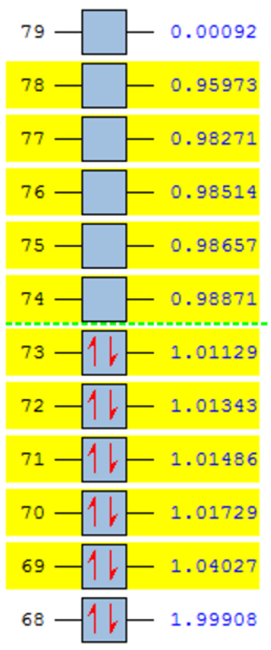
Then we use the optimized geometry to perform multiconfigurational/multireference computations. The AutoMR input file (.gjf) is shown below

```
%mem=200GB
%nprocshared=48
#p CASSCF/TZVP guess(fragment=5)

mokit{GVB_conv=5d-4,hardwfn}

4 1 3 6 3 -6 -1 1 -1 1 0 1
Fe(Fragment=1)        0.525119     -0.497869     -0.708001
Fe(Fragment=2)        2.614048     -0.959498     -3.224439
O(Fragment=5)         0.629061      1.607749     -0.624032
O(Fragment=3)         2.509495     -0.820203     -1.255415
O(Fragment=5)         0.032247     -2.520107     -0.363336
O(Fragment=5)        -1.530291     -0.185439     -0.458412
O(Fragment=5)         0.900278     -0.419588      1.381845
O(Fragment=4)         0.629692     -0.637059     -2.676981
H(Fragment=5)         0.401400      2.259064     -1.321606
H(Fragment=5)        -0.381926     -3.161928     -0.979088
H(Fragment=5)        -1.996364      0.680813     -0.436459
H(Fragment=5)         0.194596     -0.275371      2.052603
H(Fragment=5)         0.786914      2.117185      0.201537
H(Fragment=3)         3.289968     -0.897141     -0.663082
H(Fragment=5)         0.055815     -2.947638      0.521352
H(Fragment=5)        -2.220899     -0.875872     -0.338272
H(Fragment=5)         1.736797     -0.507223      1.890496
H(Fragment=4)        -0.151051     -0.561947     -3.269202
O(Fragment=5)         3.107786      1.062670     -3.567445
```

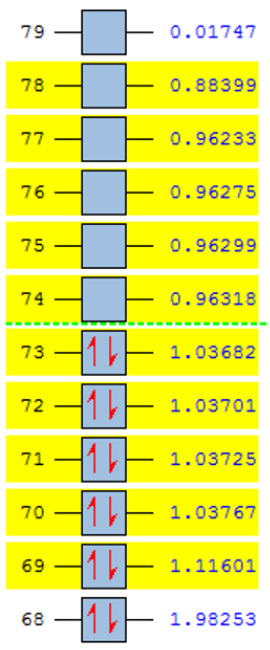
```
O(Fragment=5)          4.669288    -1.273093    -3.474047
O(Fragment=5)          2.508898    -3.065004    -3.309713
O(Fragment=5)          2.239245    -1.036321    -5.314310
H(Fragment=5)          1.403078    -0.946473    -5.823151
H(Fragment=5)          3.085985     1.490862    -4.451860
H(Fragment=5)          5.134581    -2.139729    -3.497196
H(Fragment=5)          2.736911    -3.717012    -2.612900
H(Fragment=5)          3.521488     1.703609    -2.950468
H(Fragment=5)          5.360506    -0.583097    -3.593267
H(Fragment=5)          2.349591    -3.573694    -4.135462
H(Fragment=5)          2.944846    -1.181245    -5.984990
```

This input file will invoke the UHF(fragment guess)->UNO->localization->GVB->CASSCF route. The keyword GVB_conv=5d-4 means using a less tight GVB convergence threshold (see the detailed explanations for GVB_conv in Section 4.4.42). And the keyword hardwfn means extra keywords written into PySCF CASSCF input file to ensure spin pure CASCI wave function since antiferromagnetic singlet with 5 alpha *v.s.* 5 beta electrons is challenging.

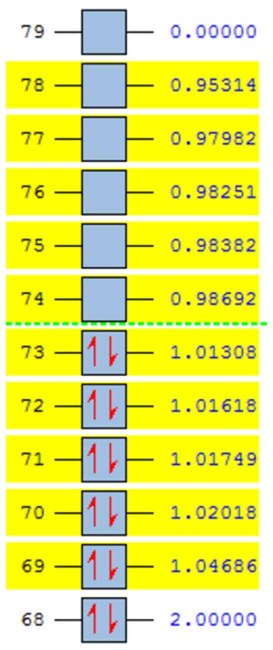
Once the *_uno.fch file is generated, you should open it and see whether there are (at least) 10 UNOs whose occupation numbers are close to 1.0. This is to make sure that we obtain the desired antiferromagnetic singlet UHF solution. Here are my calculated UNO, GVB and CASSCF NOONs:



UNO



GVB



CASSCF

The GVB NOs and CASSCF NOs are stored in *_s.fch and *_CASSCF_NO.fch files, respectively. The figures shown above can be visualized by opening the corresponding .fch file using GaussView. Note that here they are not orbital energies, but natural orbital occupation numbers (NOONs). The automatically determined active space is CAS(10,10), and you can see there are 10 NOs with occupation numbers near 1.0, no matter for UNO, GVB or CASSCF NOs.

The current CAS(10,10) active space is supposed to be adequate for qualitatively correct descriptions of the ground state and d->d transitions. If you perform the SA-CASSCF(10,10) computation based on current CASSCF NOs, you can obtain reasonable excited energies. For quantitatively accurate excited energies, you should perform the state-specific NEVPT2 computations based on each CASCI root. For even better excited energies, QD-NEVPT2 computations can be performed. Here is the AutoMR input file for SA-CASSCF and state-specific NEVPT2 computations:

```
%mem=200GB
%nprocshared=48
#p NEVPT2(10,10)/TZVP

mokit{ist=5,readno='Fe2_uhf_gvb32_CASSCF_NO.fch',nstates=12,hardwfn}
```

If you want larger active space (e.g. which can describe metal-ligand excitations), you should look into GVB NOs (i.e. *_s.fch file) and find which orbitals you want to add in.

Appendix

A1 Frequently Asked Questions (FAQ)

Q1: Find errors like ‘xxx: command not found’. What is the solution?

A1: This is simply because you haven’t installed the corresponding software, or you didn’t write environment variables correctly. Four examples are shown below:

Example 1: error ‘ifort: command not found’ means there is no ifort compiler on your computer, see 2.2.1 Prerequisite for details.
Example 2: error ‘-bash: f2py: command not found’ means there is no f2py on your computer, see Section 2.2.1 Prerequisite for details.
Example 3: assuming you’ve compiled MOKIT successfully, but got the ‘-bash: automr: command not found’ error. Then you should check the MOKIT paths in your ~/.bashrc. See Section 2.2.3 Environment variables for details.
Example 4: errors like ‘/usr/bin/ld: cannot find -lmkl_rt’ or ‘ld: cannot find -lmkl_intel_lp64’ have two possible reasons: (1) there is no MKL installed on your computer; (2) there is MKL on your node but you did not correctly (or you forgot to) write environment variables of MKL.

Q2: Is there any Windows/Mac OS pre-compiled or pre-built version of MOKIT?

A2: The author offers more than 20 utilities of Windows* OS pre-built executables, which are released as a .zip file. See instructions for download and setting environment variables in Section 2.1.

The AutoMR module is not included in pre-compiled executables, since multi-reference calculations are usually performed on high-performance computers/platforms, which usually contain Unix/Linux systems. However, if you really need all modules or utilities under Windows, you can compile the source code on your laptop/computer/node by yourself. The Mac OS pre-compiled executables will never be considered by the author.

Q3: Why the utilities dat2fch, py2fch, mkl2fch, orb2fch xml2fch, bdf2fch and bdf2mkl cannot generate a .fch file from scratch, but require the user to provide one?

A3: Strictly speaking, to correctly transfer MOs between different programs requires 'int=nobasistransform nosymm' (and also possibly '5D 7F' or '6D 10F') keywords in Gaussian, and equivalent keywords in other quantum chemistry programs. This rule also applies to other programs/software which claim they can transfer MOs or support file transformation.

However, the utility/subroutine (which transfers MOs) cannot detect whether the users have truly specified 'int=nobasistransform nosymm' (and also possibly '5D 7F' or '6D 10F') keywords, or equivalent keywords in other programs. Then transferring MOs in such case is very dangerous, i.e. correctness cannot be assured. For example, using the built-in basis sets in other programs instead of basis sets generated by MOKIT is dangerous, since the built-in basis sets in other programs are generally not exactly identical to those generated by MOKIT.

Therefore, the author jxzou has to require the users to provide a .fch file, to remind the users that proper keywords must be used in Gaussian. And the most recommended approach is to use utilities in MOKIT (e.g. fch2inp, bas_fch2py, etc) to generate input files of other quantum chemistry programs. The users use these generated input files to perform their desired computations. After jobs finished, use dat2fch and py2fch to transfer MOs back to the .fch file. Such an approach is already applied in AutoMR.

In the future version of MOKIT, the utility xml2fch will not require the user to provide a .fch file.

Q4: Can MOKIT support more types of files? Transferring MOs between other programs like QChem, NWChem is possible?

A4: The author jxzou wishes to make the MOKIT recognize all kinds of MO files of quantum chemistry programs, but he is not likely to be familiar with all programs. Therefore, if you are very familiar with any program (other than supported ones in MOKIT), and you happens to need a transferring of MOs, please contact jxzou and tell him the information in the MO file of that program. With the help from experienced users, the development will be much easier and quicker.

Q5: Why there is a keyword error in OpenMolcas output when using DKH2 Hamiltonian? Two possible errors are given: (1) ERROR: RELATIVISTIC is not a keyword!, Error in keyword. (2) ERROR: R02O is not a keyword!, Error in keyword.

A5: This is due to a recent update of OpenMolcas. If version <=18.09, the keyword for DKH2 is simply R02O; but for version >=20.10, this keyword become RELAtivistic = R02O. For version >18.09 and <20.10, the author jxzou has no manual and thus it is not tested (but you can test if you like).

If you encounter any of the two errors, you have two choices: (1) update your OpenMolcas to a newer version, e.g. >=20.10; (2) modify the source code of MOKIT and re-compile it. If you choose (2), you will need to modify the words 'RELAtivistic = R02O' to 'R02O' in file src/automr.f90, and run 'make automr' in Shell to re-compile the program automr.

Q6: How does AutoMR read the executable paths of Gaussian, OpenMolcas, PySCF, ORCA, and GAMESS?

A6: For Gaussian, the paths of executable files are read from the environment variables $GAUSS_EXEDIR. For PySCF and OpenMolcas, the 'python' and 'pymolcas' executable files are used directly, assuming the user had installed the corresponding programs correctly. For ORCA, the absolute path is automatically obtained from echo `\which orca`. For GAMESS, the user must define the $GMS environment variable in his/her ~/.bashrc file, such that the automr program can find corresponding paths.

Q7: What are the possible reasons and solutions of the following errors
(1) '*** ERROR **** DIMENSIONS EXCEEDED *****'**
(2) 'PAIR=   xx MAX=   12'
(3) 'DDI Error: Could not initialize xx shared memory segments.'
(4) 'DDI was compiled to support 32 shared memory segments.'
(5) 'The GAMESS executable gamess.01.x or else the DDIKICK executable ddikick.x could not be found in directory…'

in GAMESS .gms file (where xx is an integer >12)?

A7: Please read Section 4.4.10 carefully.

Q8: Errors like 'semget errno=ENOSPC -- check system limit for sysv semaphores' found in the .gms file. Why? How to solve the problem?

A8: Please search the error on this page FAQ of GAMESS.

Q9: I found the error 'DDI Process 0: trapped a floating point error (SIGFPE).' How to solve it?

A9: See this page https://github.com/gms-bbg/gamess-issues/issues/40.

Q10: I found the following error

AttributeError: 'CASSCF' object has no attribute 'mo_occ'

in PySCF output (e.g. .out file). Why? How to solve the problem?

A10: This is because you were using PySCF version < 1.7.4, which has no mo_occ attribute in CASSCF object. Please update to PySCF >=1.7.4.

Q11: I found the following error

FileNotFoundError: [Errno 2] No such file or directory: '/path/to/Block/block.spin_adapted'

in PySCF output (e.g. .out file). Why? How to solve the problem?

A11: This is because you forgot to modify pyscf/dmrgscf/settings.py. You should copy file settings.py.example and rename it as settings.py. Then set the correct path (within the file) for the DMRG solver.

Q12: I found the following error

HDF5-DIAG: Error detected in HDF5 (1.12.0) thread 0:
#000: H5D.c line 435 in H5Dget_type(): invalid dataset identifier
major: Invalid arguments to routine
minor: Inappropriate type

occurs many times in OpenMolcas output, Why? How to solve the problem?

A12: This does not affect the computations. It is just a tiny bug of old versions of OpenMolcas if the QCMaquis support is compiled but not used. You can find this problem here. It is recommended to update your OpenMolcas to the latest version.

Q13: Is 'Total SCF Density' in *_NO.fch file correct? Can it be used to perform wave function analysis?

A13: Yes. The CASCI/CASSCF total densities are correct in generate *_NO.fch files. Besides, the GVB density is in *_s.fch file, and the UHF density are both in *_uhf.fch and *_uno.fch files. Other types of *.fch files (*_asrot.fch, etc) do not have well-defined density. Density and natural orbitals are not calculated for post-CASSCF methods (NEVPT2, CASPT2, MRCISD, etc).

Q14: I found the following error

sh: 1: Syntax error: Bad fd number

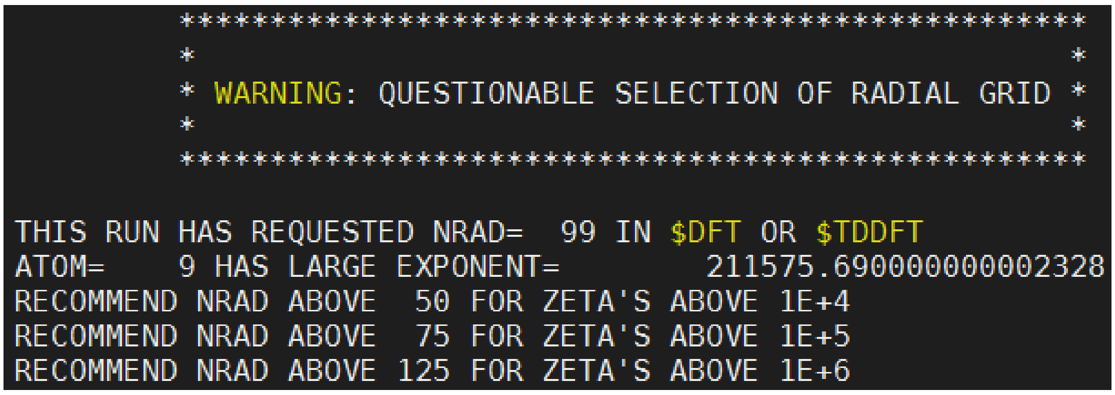
on the terminal/screen. Why? How to solve the problem?

A14: This often occurs on Ubuntu* OS, where the default sh is /bin/dash, not /usr/bin/bash. Please read Section 2.2.4 for details and examples.

Q15: I found the following warnings on terminal/screen, or output of AutoMR
OMP: Warning #181: OMP_STACKSIZE: ignored because KMP_STACKSIZE has been defined
Why? How to make it disappear?

A15: This is simply because both OMP_STACKSIZE and KMP_STACKSIZE environment variables are set. You can comment/delete one of them. Usually you can find these two environment variables in your ~/.bashrc file, or in file bdf-pkg/sbin/run.sh (if you use the BDF program).

Q16: When using the utility frag_guess_wfn to generate GKS-EDA input files, there is a warning (see below) in the GAMESS output file (e.g. xxx.gms file). And SCF does not converge. How to deal with that?



```
          *************************************************
          *                                               *
          * WARNING: QUESTIONABLE SELECTION OF RADIAL GRID *
          *                                               *
          *************************************************

 THIS RUN HAS REQUESTED NRAD=  99 IN $DFT OR $TDDFT
 ATOM=    9 HAS LARGE EXPONENT=        211575.690000000002328
 RECOMMEND NRAD ABOVE  50 FOR ZETA'S ABOVE 1E+4
 RECOMMEND NRAD ABOVE  75 FOR ZETA'S ABOVE 1E+5
 RECOMMEND NRAD ABOVE 125 FOR ZETA'S ABOVE 1E+6
```

A16: As you can see in the screenshot above, GAMESS thinks your radial grid is insufficient for this molecule and recommends the minimum requirement. So, all you need to do is: modify the radial grid in the .inp file to the recommended value. For example, in this example, you should modify NRAD0=99 and NRAD=99 in the .inp file to (at least) NRAD0=126 and NRAD=126, respectively.

Q17: I found the following error in output of running automr
File "h5py/h5.pyx", line 183, in h5py.h5.H5PYConfig.default_file_mode.__set__
ValueError: Using default_file_mode other than 'r' is no longer supported. Pass the mode to h5py.File() instead.
How to solve the problem?

A17: Please check whether your current python is the PSI4 python by running which python in Shell. If yes, and if you do not have to use PSI4 currently, you are recommended to comment/deactivate PSI4's environment variables and use your previous Python (e.g. Anaconda Python 3). Note that .

Q18: I found the following error in output of running automr

```
  File "/home/jxzou/software/pyscf-2.0.1/pyscf/lib/misc.py", line 31, in <module>
    import h5py
ModuleNotFoundError: No module named 'h5py'
```

How to solve the problem?

A18: If you are using python and f2py from PSI4 package, rather than python from Anaconda Python 3, you may encounter this PySCF error. One possible solution is to comment PSI4 variables and write this variable export PSI4=… (see Section 2.2.3). Then exit the terminal and re-login, and you now you are using your previous python, e.g. Anaconda Python 3. Next you should run make distclean and make all to re-compile MOKIT.

Q19: Is it possible that AutoMR takes more (computational) time than that by manually doing multi-reference computations (by chemical intuition, manual inspection, etc) ?

A19: Yes, possible. Note that for some small and well-studied molecules, manually doing multi-reference computations (by chemical intuition, manual inspection, etc) may take less (computational) time than AutoMR. But for general molecules, especially with dozens/hundreds of possible active orbitals, manual inspection is tedious and sometimes chemical intuition is unreliable. AutoMR aims at tackling general and complicated cases.

Besides, to better compare the cost (of time) between the human and automatic approach, the cost of time of human operations must be taken into consideration, since the time of manual inspection and permuting orbitals (when >10 orbitals) is not negligible.

Q20: Why does the GKS-EDA jobs fail even if I used the utility frag_guess_wfn to generate GAMESS .inp file?

A20: Try to modify 'DIIS=.F. SOSCF=.T.' to 'DIIS=.T. SOSCF=.F.' in the .inp file, and re-submit the job (remember to remove temporary files before re-submitting).

Q21: Why does my computation proceed slowly? It took a long time in HF and GVB calculations. Is there any acceleration techniques/tricks?

A21: Firstly, please read Section 3.1 and 3.2 for suggestions on choosing appropriate methods and basis sets. Secondly, assuming your method and basis set is already reasonable, there is no trick to be used currently. The HF step is performed by Gaussian and it does not support RI or density fitting techniques. In the future version of MOKIT, users can specify PSI4 as the HF_prog, where RI is supported. The author jxzou will write a RI-GVB program in a year, then the GVB computation can be greatly accelerated.

A2 Limitations and Suggestions

A2.1 Basic knowledge of multi-reference methods

Although MOKIT is a useful tool for black-box multi-reference computations, the users are assumed to know basic knowledge of multi-reference methods. If he/she does not even know the meaning of CAS(m,n), then the results of MOKIT are meaningless to he/she, and even wrong explanations may be made from the results. Therefore, if you know little about the multi-reference methods, I recommend you the following materials:

(1) the ORCA CASSCF-tutorial (https://orcaforum.kofo.mpg.de/app.php/dlext/?cat=4), which is a quickstart guide (but also detailed) for CASSCF computations. To download this .pdf file, you may need to (register and) login to the forum.

(2) to be added.

If, unfortunately, you are forced by your supervisor/advisor to learn how to perform multireference calculations, but meanwhile you are a totally newbie and you don't even know how to perform routine DFT calculations, it is recommended that you change a task/project as soon as possible (ASAP). Or more radically, you are encouraged to switch to a new supervisor ASAP, since he/she does not know how to teach/train a student properly. This is not your fault, but your supervisor's.

A2.2 Symmetry

Unfortunately, molecular point group symmetry cannot be taken into consideration in any module of MOKIT. This is due to: (1) use of symmetry may change the orientation of the target molecule, and the MO coefficients will be changed accordingly; (2) localized orbitals are used in almost all modules of AutoMR, this usually contradicts with symmetry.

A2.3 Validity of MOs obtained by AutoMR for excited state calculations

When you use AutoMR to perform a ground state CASSCF calculation, the obtained CASSCF MOs (whether pseudo-canonical MOs or NOs) is supposed to be excellent for the ground state electronic structure of the target molecule. And you can use this set of MOs (held in a .fch file) to further conduct excited state calculations like state-averaged CASSCF (SA-CASSCF). And moreover, NEVPT2, CASPT2 or MRCISD, if you wish.

However, the resulting excitation energies and excited state MOs (e.g. state-averaged NOs) are not necessarily excellent. Here 'not necessarily excellent' means for some molecules you may get good results while may be unsatisfactory for some other molecules. The reason is simple: the current algorithms in AutoMR focus on the multi-reference characters in the ground state of the molecule. Thus AutoMR ‘finds’ excellent active orbitals of the ground state. But the active orbitals of excited states are not necessarily the same as those of the ground state. And the orbital optimization in SA-CASSCF does not guarantee leading to good MOs for excited states. This problem actually exists in almost all methods/programs which feature block-box or automatic multi-reference calculations.

There is a solution (although not perfect or elegant) to this problem: (visually) inspect the doubly occupied orbitals, pick up important orbitals (usually the lone-pair orbitals) and add them into the active space. For example, if you obtain a CAS(6e,6o) active space from MOKIT, and assuming you find 4 lone pair orbitals among doubly occupied orbitals, then you can combine them (by interchanging or permuting orbitals) to be a CAS(14e,10o) active space. Because 6+2*4=14 active electrons, and 6+4=10 active orbitals. You can do a SA-CASSCF(14e,10o) computation next. This usually converges in several cycles. Finally you can perform a NEVPT2/CASPT2/MRCISD computation based on SA-CASSCF(14e,10o) orbitals to get more accurate excitation energies.

A2.4 Possible multiple solutions of UHF

There may exist multiple UHF solutions when a covalent bond cleavages homolytically, or in a transition-metal-containing molecule. In these special cases, if you use ist=0, the UHF calculated by AutoMR may be not the lowest UHF solution (but it is stable). You may need to perform several UHF computations (by yourself) using various initial guesses. After you identify the lowest UHF solution, you can use keywords ist=1 and ‘readuhf’ to read in the desired UHF .fch file.

Alternatively, you can simply write the fragment guess information into the .gjf file, exactly as the syntax of Gaussian. See an example in file examples/automr/05-N2_cc-pVTZ_4.0.gjf.

Peter Pulay *et al* suggests that for cases involving multiple UHF solutions, one should use the averaged density (of all possible solutions) to generate UNOs. This approach is not supported in MOKIT currently.

A2.5 Implicit Solvent Model

Currently implicit solvent effect cannot be taken into consideration. But you can use the converged CASSCF wave function *_NO.fch file as an initial guess to your further calculations which takes implicit solvent effect into consideration.

A3 Bug Report

If you find any bug frequently occurs, please go to GitLab (https://gitlab.com/jxzou/mokit) to download the latest version of MOKIT and check whether the bug still exists. If it still exists, you can

(1) contact the author jxzou via E-mail njumath[at]sina.cn, with your input file (.gjf, .fch) and output files attached;

(2) open an issue on GitLab page of MOKIT (https://gitlab.com/jxzou/mokit/-/issues);

(3) (if you can communicate in Chinese) you can join the Tencent QQ group (group number

470745084).

The author may not respond or update code frequently since he is being postponed due to his PhD program.

A4 Acknowledgement

Thanks Mr. Shirong Wang and Tibor Győri for constructive suggestions and bugs report.