



Kylin: Ab-Initio DMRG Package

User Guide

Version 1.2.0

The Group of Prof. Haibo Ma

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1 Introduction

1.1 Overview

Kylin is an *ab-initio* quantum chemistry software package for evaluating electronic structures of molecular systems with high precision and efficiency. The *ab-initio* methods are fundamental and powerful tools in quantum chemistry researches. Because their dependence on artificial assumptions and parameter fittings is less than many other popular methods such as the density functional theory (DFT), the *ab-initio* methods are usually more reliable, but more expensive at the same time, in the study of electronic structures of complex systems such as radicals, transition metal compounds, and large conjugated molecules. Energies, properties, and many interesting chemical reactions of these systems are strongly influenced by their near-degenerate electronic configurations, as well as the fast movements and interactions of electrons. Kylin can be used for precisely measuring electronic correlations in these systems, and predicting energies, properties and reactions with extensive treatment.

The heart of Kylin is an efficient implementation of the density matrix renormalisation group (DMRG) method, which is an accurate approximation of the classical full configuration interaction (Full-CI) method but can be applied on large active spaces with more than 100 active orbitals. Besides, Kylin also features extensive capabilities in pre- and post-DMRG treatments, including Hartree-Fock self-consistent field (HF-SCF), complete active space SCF (CASSCF), single-reference and multi-reference CI, single-reference and multi-reference perturbation theories (PT), as well as DMRG wave function analysis and geometry optimization. Therefore, Kylin can also be used as an independent quantum chemical software, with no necessity to involve additional packages.

1.2 Features

The developers of Kylin aim to provide an efficient implementation of the *ab-initio* quantum chemistry DMRG method. Beyond that, the developers also want to create a complete package for general *ab-initio* quantum chemistry researches, which includes all necessary procedures in a typical wave-function-based calculation. The following methods are available in the 1.0 version of Kylin:

- Hartree-Fock SCF, including the restricted approach for closed-shell systems and the unrestricted one for open-shell systems;
- Second-order Møller-Plesset perturbation theory;
- Full-CI, CASCI and CISD with the graphical unitary group approach (GUGA);

- DMRG based on the matrix product states (MPS);
- CASSCF and DMRG-SCF, based on the second-order Werner-Meyer-Kowles method;
- Multi-reference CI, with CASSCF/DMRG-SCF reference wave function;
- Multi-reference Epstein-Nesbet perturbation theory, with CASSCF/DMRG-SCF reference wave function.

The available methods are also listed in Figure.1. Besides, there are also some practical functions in Kylin package, including

- population analysis for both classical CI-type wave functions and DMRG wave functions;
- geometry optimization in Hartree-Fock, CASSCF and DMRG-SCF calculations.

More methods and functions will be introduced in further releases.

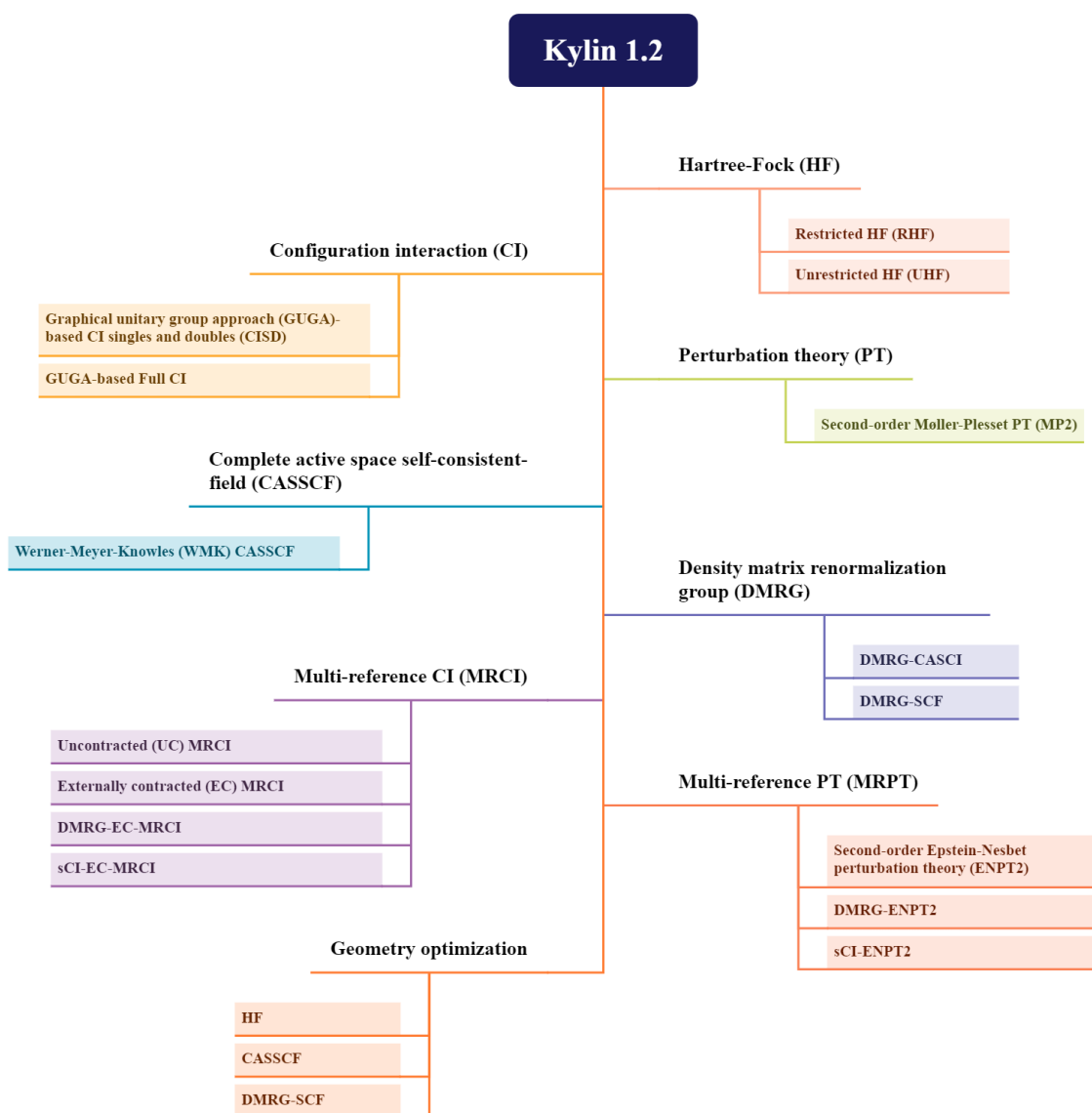


Figure 1: Available methods in Kylin 1.2.

1.3 Copyright and Citation

The Kylin package is developed by the research group of Prof. Dr. Haibo Ma at Nanjing University. The copyright has been certified by the National Copyright Administration of the People's Republic of China.

Any publication resulting from use of this program must acknowledge the following article:

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Matrix Renormalization Group Quantum Chemistry Program. **Journal of Computational Chemistry.** 2023, 44(13), 1316. <https://doi.org/10.1002/jcc.27085>

2 Installation and Running

2.1 Installation

The latest version of Kylin is distributed as a pre-compiled binary. After your download request is approved, a download link will be sent to your email address. See the [official website](#)¹ for more information.

It is easy to install Kylin on your computer: firstly you need to download the zip file, then extract this file and set the required environment variables. After that, the Kylin program is ready for work. For example, you can extract the zipped file as

```
unzip kylin-latest.zip
```

Then a new directory `kylin` appears, which containing two sub-directories `bin` and `share`. Note the two sub-directories must be always placed in the same directory. You can put the `kylin` directory wherever you want (e.g. `Applications/kylin` in your home directory, as shown in the following examples).

The binary is compiled on an intel platform running Ubuntu 20.04 and the AVX2 instructions must be enabled.

2.2 Environment

The only environment required by Kylin is `KYLIN`, which is the absolute path of Kylin directory. The environment can be automatically initialized by adding the following two lines into your `.bashrc` file.

```
export KYLIN=$HOME/Applications/kylin
export PATH=$KYLIN/bin:$PATH
```

Note that `$HOME/Applications/kylin` is the directory of Kylin. Besides, to run Kylin parallely, the `OMP_NUM_THREADS` must be declared. The value of this environment variable should be the number of CPU cores.

```
export OMP_NUM_THREADS=24
```

2.3 Running

Once the environment variable `KYLIN` is successfully loaded, and the `kylin` command could be found in your `PATH`, the Kylin program can be used as

¹<https://kylin-qc.com>


```
kylin INPUT_FILE
```

Then all output will be printed on the screen, which can be redirected to a file, as

```
kylin INPUT_FILE > OUTPUT_FILE
```

Since all temporary files, such as the molecular orbital integrals, will be stored in the `tmp` folder in the current working directory, we recommend to place your working directory on a disk with fast I/O, for example, on a solid state drive.

3 Input and Output Files

3.1 Input File

The syntax of Kylin's input file is simple. Currently there are only 4 kinds of entries in the input file, which are

1. module, surrounded by a pair of square brackets “[” and “]”;
2. keyword and its value(s), which should be separated by at least one separator (space or "="), for example, keyword = value. Input keywords do not have case or underscore sensitivity, which means that InputKeyword and input_keyword are regarded as exactly the same.
3. comment, which is similar to python. The single-line comment starts with hashtag symbol (#), while the multi-line comment is surrounded by triple quotes (“”).
4. line break. If there are too many values which can not be put in one line, the backslash character (\) can be put at the end of the line.

Note that the calculation of a certain method (eg. METHOD) can only be initialized with the [METHOD] label, and all the necessary keywords used in the METHOD must be put under its label.

Here is an example input file.

```
[info]
  # coordination file
  coord = example.xyz

  # multiple basis sets
  basis = 6-31g C cc-pvtz N cc-pvdz \
          0 S cc-pvqz

  pg = c1 # not use point group symmetry

'''
multi-line comment
'''

[integral]
```

[hf]

The case of the module names and keywords are ignored. However, the case of some values, such as the value of the `coord` in the above example, must be specified clearly, because it denotes the name of another file, and file names in Linux are case-sensitive.

The detailed keywords in each module are listed in the following sections.

3.2 Output File(s)

When running a calculation, a temporary folder `tmp` will be created in the working directory, which stores atomic orbital integrals and some other scratch files. Besides, some useful output will also be stored in this folder, including the molecular orbital file and the related `molten` file.

To visualize molecular orbitals with `molten` file, we recommend to use the `Multiwfn` software.

4 Geometry and Basis Set

As we can see in the input example in the last section, a calculation should always start with the [info] module, which defines the basic information of the system, including the geometry, basis set and point group of the molecule. Kylin can also read such information from a MOLDEN file, but point group symmetry will not be used when using a MOLDEN file as input.

Keyword	Description
Basis	(case-insensitive string) Basis sets for the calculation
Coord	(case-sensitive string) The path to an XYZ file.
InputType	(case-insensitive string) default: normal The type of the input file. This keyword should be set as normal or molden.
MoldenFile	(case-sensitive string) The path to an Molden file. This keyword is incompatible with keywords "Coord" "Basis" "RotCoord" and "PG", because only C1 molden are allowed and all information are already in molden file.
PG	(case-insensitive string) The symmetry of the molecular system. When set as C1, point group symmetry will not be used.
RotCoord	(bool) default: true Whether to rotate molecular coordinates when using point group symmetry. If the coordinates has been rotated, they can be used directly to do calculations under point group symmetry by setting it to false.
SymThresh	(double) default: 1e-5

Keyword	Description
	Threshold for symmetry point group symmetry recognition. It can be loosen to 1e-2 at most, or the accuracy of Single Point Calculation maybe affected.

Table 1: Keywords in Info.

4.1 Geometry

Molecular geometry in Kylin is set by the keyword `coord`, as

```
coord = XYZ_FILE
```

where `XYZ_FILE` is the relative path to a standard XYZ file defining the cartesian coordinates (default in Ångstrom units). Usually we put the XYZ file in the same directory of our input file, in this case `XYZ_FILE` is the name of this XYZ file. For example, the following is a XYZ file defining the structure of a naphthalene molecule.

```
18
unit or comment
C      0.00000000  -0.70070000  0.00000000
C     -1.21364800  -1.40140000  0.00000000
C      1.21364800  -1.40140000  0.00000000
C     -2.42729600  -0.70070000  0.00000000
H     -1.21364800  -2.47140000  0.00000000
C     -0.00000000   0.70070000  0.00000000
C      2.42729600  -0.70070000  0.00000000
H      1.21364800  -2.47140000  0.00000000
C     -2.42729600   0.70070000  0.00000000
H     -3.35394318  -1.23570000  0.00000000
C     -1.21364800   1.40140000  0.00000000
C      1.21364800   1.40140000  0.00000000
C      2.42729600   0.70070000  0.00000000
H      3.35394318  -1.23570000  0.00000000
H     -3.35394318   1.23570000  0.00000000
```

H	-1.21364800	2.47140000	0.00000000
H	1.21364800	2.47140000	0.00000000
H	3.35394318	1.23570000	0.00000000

In the first line the number of atoms in this molecule is declared. If atomic unit is used, "a.u." or "bohr" should be put at the beginning of second line. Other strings in the second line are recognized as comment and ignored.

4.2 Basis Set

There are four ways to specify basis set with basis keyword.

1. single basis set

```
basis = 6-31g
```

2. multiple basis set

```
basis = 6-31g C O cc-pvtz N cc-pvqz
```

(C and O with cc-pVTZ, N with cc-pVQZ, other atoms with 6-31G)

3. multiple basis set

```
basis = C O cc-pvtz N cc-pvqz
```

(C and O with cc-pVTZ, N with cc-pVQZ)

4. multiple basis set

```
basis = specified
```

Then the basis sets are specified in coordination file, for example

```
3
o      1.8926600      0.6524290      0.0      cc-pvqz
h      2.8385790      0.3622590      0.0      cc-pvtz
h      2.0138280      1.6344200      0.0      cc-pvdz
```

The available basis sets are listed in the file `$KYLIN/share/basis/basis_list`. This file actually provides indices of the basis set files in the same directory.

If the basis name contains space character, the space character should be replaced by underscore character in input file. For example, if using "Ahlichs pVDZ" basis set, the basis keyword should be set as

```
basis = Ahlichs_pVDZ
```

You can add new basis sets into this directory if necessary, by putting a Molcas-style basis set file into this directory and adding its name to the `basis_list` file. Please visit the [Basis Set Exchange](#)² website for more basis sets.

The ECP basis sets are not supported currently.

Only spherical basis functions are used in Kylin currently.

4.3 Point Group Symmetry

The point group symmetry will be automatically determined, unless the keyword `pg` is set to `C1`. The supported point groups and the numbering of their irreducible representations (irreps) are listed in Table 2. Note that currently point group symmetries are not supported in some modules.

²<http://www.basissetexchange.org>

Point group	irrep							
	1	2	3	4	5	6	7	8
C_1	A							
C_i	A_g	A_u						
C_s	A'	A''						
C_2	A	B						
C_{2v}	A_1	B_2	B_1	A_2				
C_{2h} (main C_2 axis is $C_2(z)$)	A_g	A_u	B_u	B_g				
C_{2h} (main C_2 axis is not $C_2(z)$)	A_g	B_u	A_u	B_g				
D_2	A	B_1	B_2	B_3				
D_{2h}	A_g	B_{3u}	B_{2u}	B_{1g}	B_{1u}	B_{2g}	B_{3g}	A_u

Table 2: Supported point groups and the numbering of their irreps.

5 Hartree-Fock SCF

The Hartree-Fock module [hf] in Kylin supports both the restricted and the unrestricted Hartree-Fock methods with acceleration techniques like direct inversion of the iterative subspace (DIIS). When a Hartree-Fock calculation is successfully converged, a set of canonical molecular orbitals is saved to the tmp/hf.ScfOrb file, which is a standard Molcas-style orbital file and can be used independently. The corresponding molden file is saved as tmp/hf.molden, which can be visualized with the Multiwfn software. Besides, population analysis will be automatically performed at the end of Hartree-Fock calculations.

The keywords in the Hartree-Fock module are listed in Table 3. Note that the point group symmetry of the molecule is directly taken from the [info] module and can not be changed in the Hartree-Fock module.

Keyword	Description
2S	(integer) default: 0 The value of spin multiplicity $2S$.
AccConv	(case-insensitive string) default: cdiis options: cdiis, c2diis, ediis, mixed, off Acceleration technique to be used in the self-consistent field procedure.
CalMOIntegrals	(bool) default: true aliases: CalMOInt, CalMOIntegral, MOInt, MOIntegral, MOIntegrals Whether to generate molecular orbital integrals at the end of the Hartree-Fock calculation.
Charge	(integer) default: 0 Charge of the system.
DIISspace	(integer) default: 10 Size of the DIIS space. This option is valid only if a DIIS-type accelerator is enabled.

Keyword	Description
Guess	(bool) default: true Whether to use an optimized matrix for initial guess.
MaxIter	(integer) default: 500 Maximum number of Hartree-Fock iterations.
PopulationAnalysis	(case-insensitive string) default: mulliken alias: PopAnalysis options: cspa, mulliken Population analysis method.
Tol	(double) default: 1.0e-6 Energy convergence tolerance of the Hartree-Fock iterations.
UHF	(bool) default: false Whether use the unrestricted Hartree-Fock method. This option must be set to true manually if UHF is required.

Table 3: Keywords in Hartree-Fock.

6 Configuration Interaction

The configuration interaction (CI) calculations are performed by the graphical unitary group approach (GUGA). [1–6] The full CI (FCI) method are implemented in module [GUGACI], while the CI singles-and-doubles (CISD) method will be implemented in next version. The CISD wavefunction includes HF configuration as well as its single and double excitation configurations, while the FCI wavefunction further includes all other higher excitation configurations. The keywords are listed in Table 4.

Keyword	Description
CISD	Perform CISD calculation (will be implemented in next version). Default is <code>false</code> and FCI calculation will be performed.
2S	Spin ($2S$), default 0 for singlet.
docc	Number of doubly-occupied orbitals in each irrep.
active	Number of active orbitals in each irrep.
charge	Charge, default 0.
irrep	Irreducible representation of target state(s) (start from 1), default 1.
nstate	Number of states to calculate, default 1.
eigensolver	Algorithm of eigensolver. <code>lanzcos</code> , <code> davidson</code> and <code> jacdav</code> for Lanczos, Davidson and Jacobi-Davidson algorithms respectively. Default is <code> davidson</code> .
dump	Print active MO integrals to file FCIDUMP and not perform CI calculation, default <code> false</code> .
dumpAll	Print all of MO integrals to file FCIDUMP and not perform CI calculation, default <code> false</code> .

Table 4: Keywords in GUGACI.

7 Møller-Plesset Perturbation Theory

The MP2 method in Kylin requests a restricted Hartree-Fock calculation, which is followed by a second-order Møller-Plesset correction on energy. [7] Unrestricted MP2 calculation will be supported in the future.

The MP2 module can be initialized with [mp2]. Keywords of the [mp2] module are listed in Table. 5.

Keyword	Description
frozen	Total number of frozen orbitals.
frozen_irrep	Number of frozen orbitals in each irreducible representation.
full	Whether all of occupied orbitals are taken into consideration. If true, no orbitals are frozen. The default value is false.

Table 5: Keywords in MP2.

The MP2 module regards non-valence orbitals as frozen by default. Keywords frozen, frozen_irrep and full can be used to specify the number of frozen orbitals. To avoid conflict, only one of them can be valid. The following is an example of MP2 calculation of C₆H₆ benzene with point group symmetry.

```
[info]
  coord = benzene.xyz
  basis = 6-31g

[integral]

[hf]

[mp2]
  # frozen = 6
  frozen_irrep = 2 0 2 0 1 0 1 0
  # full
```

8 DMRG

In Kylin package, the implemented DMRG method is based on the matrix-product state (MPS) ansatz. The symmetry-protected DMRG method is implemented as the [DMRG] module. The [DMRG] module support the $U(1)$ and $SU(2)$ spin symmetry and the point group symmetry listed in Table 2. The [DMRG] module can run in double-precision and mixed-precision. The mixed-precision DMRG is suggested when the truncation dimension M is larger than 1500. The keywords of the [DMRG] module are listed in Table 6.

Keyword	Description
2S	Spin, default 0 for singlet.
active	Number of active orbitals in each irrep.
charge	Charge, default 0.
docc	Number of doubly-occupied orbitals in each irrep.
dump	Print active MO integrals to file FCIDUMP and not perform CI calculation, default false.
dumpAll	Print all of MO integrals to file FCIDUMP and not perform CI calculation, default false.
eigsolver	Algorithm of eigensolver. lanczos, davidson and jacdav for Lanczos, Davidson and Jacobi-Davidson algorithms respectively. Default is davidson.
ENV_GT_MEM	Set if the size of the two largest ENVs lager than the computer memory, default false.
independent	Run independent DMRG with existing MO integral file, default false.
init_MPS_from_file	Use existing MPS file as the initial guess to run DMRG, default false.
init_MPS_path	The path to the existing file, when use existing MPS file as the initial guess (<code>init_MPS_from_file=true</code>), default tmp.
MPS_only	Only read MPS files and not perform DMRG calculation, default false.

Keyword	Description
initial_guess	Method for initial guess. 0: no initial guess. 1: use *** initial guess.
InitialConfig	Initial configuration. Required when using the point group symmetry EXCEPT C_1 . For detailed usage, see Chapter Examples.
integral	Name of the MO integral file.
irrep	Irreducible representation of target state(s) (start from 1), default 1.
M	Number of reserved states. Need three input integer as final reserved states, step increment, starting number of reserved states, delimited with space.
maxCycle	Max number of diagonalization iteration, default 100.
maxSpace	Max space of diagonalization, default 10.
mixed_double	Using mixed-precision diagonalization in the double-precision sweeps, default true.
nelec	Number of active electrons.
nstate	Number of states to calculate, default 1.
nsweeps	Maximal number of DMRG sweeps.
nsweeps_d	Maximal number of double-precision DMRG sweeps. Active when using mixed precision DMRG.
nsweeps_f	Maximal number of single-precision DMRG sweeps. Active when using mixed precision DMRG.
nsweeps_screen	Maximal number of screen sweeps.
pg	Point group symmetry.
reorder_method	Orbital reorder method, default 0. Available input are: 0 (no reorder) and 1 (Fiedler orbital reordering).
store_ENV	Store ENV to disk, default false.
store_MPO	Store MPO to disk, default false.

Keyword	Description
store_MPS	Store MPS to disk, default false.
sweep_precision	The precision for the DMRG sweep. Available input are: double, mix and float. The float perform full single-precision DMRG, may generate unreliable results. For feasible single-precision DMRG, run sweep_precision=mix, nsweeps_d=0.
symm	Spin symmetry. Available input are: 2u1 and su2u1 for $U(1)$ and $SU(2)$ spin symmetry respectively.
tol_davidson	Tolerance for diagonalization. Need two input as the starting tolerance and final tolerance.
tol_E	Tolerance for DMRG, default 1e-8.
tol_svd	Tolerance for SVD. Need two input as the starting tolerance and final tolerance.
use_cadmrq	Use DMRG with continuous address storage in memory, default true.
MPO_first	Contract MPO first rather than MPS for calculating $\hat{H} \Psi\rangle$ when use_cadmrq is true, default true.
twoSite	Perform two-site algorithm DMRG, default true. If false, perform one-site algorithm DMRG.
2sitePlus1site	Perform one-site algorithm DMRG after two-site algorithm DMRG finished, default true.

Table 6: Keywords in DMRG.

9 CASSCF and DMRG-SCF

The CASSCF and DMRG-SCF modules in Kylin are based on the second-order Werner-Meyer-Knowles method. [8–13] In these two modules, both CI coefficients and molecular orbital coefficients are optimized simultaneously. These two methods are widely applied to evaluate static electronic correlations in molecular systems, and their wave functions are essential for multi-reference dynamic electronic correlation calculations.

The CASSCF method applies to small active spaces with less than 16 active orbitals. For larger active spaces, we recommend using the DMRG-SCF method. Note: Neither [casscf] nor [dmrgscf] requires molecular integral from precedent modules.

9.1 CASSCF

The CASSCF module can be initialized with either [mcscf] or [casscf]. Before initializing the [casscf] module, a set of initial molecular orbitals and integrals must be accessible, which are usually generated by Hartree-Fock calculations. Therefore, in most cases the [info], [integral] and [hf] modules should be finished before using [casscf]. The keywords in CASSCF calculations are listed in Table.7.

Keyword	Description
2S	The value of spin multiplicity $2S$, default 0 (singlet).
pg	Point group symmetry. If running standalone MCSCF with keyword "independent", pg required except "c1", default c1.
irrep	Irrep index of the target state, default 1.
frozen	Number of frozen orbitals in each irreducible representation of the point group symmetry (irrep).
docc	Number of doubly-occupied orbitals in each irrep.
active	Number of active orbitals in each irrep.
nactel	Number of active electrons (all electrons minus twice the number of inactive and frozen orbitals). This keyword mustn't be omitted if running standalone MCSCF with keyword "independent".

Keyword	Description
charge	Charge of the system, default 0. It is incompatible with keywords "nactel" and "independent". Because you can destroy the system's neutrality by setting "nactel" directly. Default 0.
rotate	The indices of molecular orbitals to be swapped. This option is helpful if the indices of active orbitals are discontinuous. For example, rotate = 1 3 2 4 indicates exchanging the orbital 1 with 3, and 2 with 4. Default None. Note: only orbitals with the same irreducible representation allow for exchange
nstate	Number of state to be solved, default 1.
weights	Weights of different states from state 1 to state n in the average energy. For example, if nstate = 3 and weights = 1 1 3, the average is taken over three states from state 1 to state 3 with weights 20%, 20% and 60%, respectively. NOTE: if you set nstate no less than 2 without specifying weights, all states's weights will be set to 1/n automatically. Default None.
max_macro	Maximal number of the macro-iterations, default 100.
max_micro	Maximal number of the micro-iterations in each macro-iteration, default 50.
tol_macro	Convergence threshold of macro-iterations, default 1.0E-6.
tol_micro	Convergence threshold of micro-iterations, default 1.0E-6.
tol_davidson	Convergence threshold in matrix diagonalization, default 1.0E-6.
independent	Run a standalone [MCSCF] calculation with a complete integral file(not only active orbitals) specified by keyword "integral". Default false. NOTE: it is incompatible with [geoopt] module.
integral	a complete integral file name to run a standalone MCSCF calculation. Default None.
dump_all	Generate full integral when MCSCF converged, which can be used for standalone MCSCF calculation, default false.

Keyword	Description
continue	resume MCSCF calculation from latest [dmrgscf/casscf]-exported integral specified with keyword "integral" or [dmrgscf/casscf]-exported orbital(NOT Hartree-Fock's orbital!!!) specified with keyword "fileorb", default <code>false</code> .
fileorb	External orbital file name from HF or itself. You can use it to directly start MCSCF from Hartree-Fock orbital or resume MCSCF from latest MCSCF orbitals by setting keyword "continue" to true at the same time. Default None.
rlx_state	Specify which state to be relaxed in a geometry optimization of a state average wave function, default 1.

Table 7: Keywords in CASSCF.

9.2 DMRG-SCF

The DMRG-SCF module is initialized with [dmrgscf]. As the CASSCF and DMRG-SCF methods share the similar orbital optimization procedures, all keywords in Table 7 are also valid in DMRG-SCF module. Besides, the DMRG-SCF module also inherits all DMRG keywords in Table 6.

Keyword	Description
2S	The value of spin multiplicity $2S$, default 0 (singlet).
pg	Point group symmetry. If running standalone MCSCF with keyword "independent", pg required except "c1", default c1.
irrep	Irrep index of the target state, default 1.
frozen	Number of frozen orbitals in each irreducible representation of the point group symmetry (irrep).
docc	Number of doubly-occupied orbitals in each irrep.
active	Number of active orbitals in each irrep.

Keyword	Description
nactel	Number of active electrons (all electrons minus twice the number of inactive and frozen orbitals). This keyword mustn't be omitted if running standalone MCSCF with keyword "independent".
charge	Charge of the system, default 0. It is incompatible with keywords "nactel" and "independent". Because you can destroy the system's neutrality by setting "nactel" directly. Default 0.
rotate	The indices of molecular orbitals to be swapped. This option is helpful if the indices of active orbitals are discontinuous. For example, rotate = 1 3 2 4 indicates exchanging the orbital 1 with 3, and 2 with 4. Default None. Note: only orbitals with the same irreducible representation allow for exchange
nstate	Number of state to be solved, default 1.
weights	Weights of different states from state 1 to state n in the average energy. For example, if nstate = 3 and weights = 1 1 3, the average is taken over three states from state 1 to state 3 with weights 20%, 20% and 60%, respectively. NOTE: if you set nstate no less than 2 without specifying weights, all states's weights will be set to 1/n automatically. Default None.
max_macro	Maximal number of the macro-iterations, default 100.
max_micro	Maximal number of the micro-iterations in each macro-iteration, default 50.
tol_macro	Convergence threshold of macro-iterations, default 1.0E-6.
tol_micro	Convergence threshold of micro-iterations, default 1.0E-6.
tol_davidson	Convergence threshold in matrix diagonalization, default 1.0E-6.
independent	Run a standalone [MCSCF] calculation with a complete integral file (not only active orbitals) specified by keyword "integral". Default false. NOTE: it is incompatible with [geoopt] module.

Keyword	Description
integral	a complete integral file name to run a standalone MCSCF calculation. Default None.
dump_all	Generate full integral when MCSCF converged, which can be used for standalone MCSCF calculation, default <code>false</code> .
continue	resume MCSCF calculation from latest [dmrgscf/casscf]-exported integral specified with keyword "integral" or [dmrgscf/casscf]-exported orbital (NOT Hartree-Fock's orbital!!!) specified with keyword "fileorb", default <code>false</code> .
fileorb	External orbital file name from HF or itself. You can use it to directly start MCSCF from Hartree-Fock orbital or resume MCSCF from latest MCSCF orbitals by setting keyword "continue" to true at the same time. Default None.
rlx_state	Specify which state to be relaxed in a geometry optimization of a state average wave function, default 1.
eigensolver	Algorithm of eigensolver. lanczos, davidson and jacdav for Lanczos, Davidson and Jacobi-Davidson algorithms respectively. Default is davidson.
ENV_GT_MEM	Set if the size of the two largest ENVs larger than the computer memory, default <code>false</code> .
init_MPS_from_file	Use existing MPS file as the initial guess to run DMRG, default <code>false</code> .
init_MPS_path	The path to the existing file, when use existing MPS file as the initial guess (<code>init_MPS_from_file=true</code>), default <code>tmp</code> .
initial_guess	Method for initial guess. 0: no initial guess. 1: use *** initial guess.
InitialConfig	Initial configuration. Required when using the point group symmetry instead of C_1 . For detailed usage, see Chapter Examples.
M	Number of reserved states. Need three input integer as final reserved states, step increment, starting number of reserved states, delimited with space.

Keyword	Description
maxCycle	Max number of diagonalization iteration, default 100.
maxSpace	Max space of diagonalization, default 10.
mixed_double	Using mixed-precision diagonalization in the double-precision sweeps, default true.
nsweeps	Maximal number of DMRG sweeps.
nsweeps_d	Maximal number of double-precision DMRG sweeps. Active when using mixed precision DMRG.
nsweeps_f	Maximal number of single-precision DMRG sweeps. Active when using mixed precision DMRG.
nsweeps_screen	Maximal number of screen sweeps.
reorder_method	Orbital reorder method, default 1. Available input are: 0 (no reorder) and 1 (Fiedler orbital reordering).
store_ENV	Store ENV to disk, default false.
store_MPO	Store MPO to disk, default false.
store_MPS	Store MPS to disk, default false.
sweep_precision	The precision for the DMRG sweep. Available input are: double, mix and float. The float perform full single-precision DMRG, may generate unreliable results. For feasible single-precision DMRG, run sweep_precision=mix, nsweeps_d=0.
symm	Spin symmetry. Available input are: 2u1 and su2u1 for $U(1)$ and $SU(2)$ spin symmetry respectively. Default su2u1. Note: 2u1 doesn't work now.
tol_E	Tolerance for DMRG, default 1e-8.
tol_svd	Tolerance for SVD. Need two input as the starting tolerance and final tolerance.

Table 8: Keywords in DMRG-SCF.

9.3 Start from Hartree-Fock Orbital

If Hartree-Fock calculation has finished, an orbital file named "HFOrbForMCSCF" occurs under "tmp" path, you can start MCSCF directly using keyword "fileorb".

(1) c1 Hartree-Fock calculation input file:

```
[info]
basis = sto-3g
coord = benzene.xyz
pg = c1

[integral]

[hf]
guess = true
moint = false
acc_conv = cdiis
tol = 1e-5
```

(2) start c1 MCSCF calculation from Hartree-Fock orbital:

```
[info]
basis = sto-3g
coord = benzene.xyz
pg = c1

[dmrgscf]
fileorb = tmp/HFOrbForMCSCF
irrep = 1
2S = 0
frozen = 0
docc = 18 #first 18 orbitals set as docc
active = 6 # [19, 24]orbitals set as active orbitals
rotate = 17 19 #because 17 is PI orbital but 19 not
print_mo_indices #you can check orbital index and irreps in output
```

9.4 Start from [casscf/dmrgscf] Exported Orbital

The latest MCSCF orbital is saved in a file named "MCSCFOrb" under "tmp" path, you can resume MCSCF directly using keywords "continue" and "fileorb".

(1) D2h Hartree-Fock calculation input file:

```
[info]
basis = sto-3g
coord = benzene.xyz
[integral]

[hf]
guess = true
moint = false
acc_conv = cdiis
tol = 1e-5
```

(2) start D2h MCSCF calculation from Hartree-Fock orbital:

```
[info]
basis = sto-3g
coord = benzene.xyz

[dmrgscf]
fileorb = tmp/HFOrbForMCSCF
irrep = 1
2S = 0
frozen = 0 0 0 0 0 0 0 0
docc = 6 5 4 3 0 0 0 0
active = 0 0 0 0 2 2 1 1
print_mo_indices
```

(3) resume D2h MCSCF calculation from MCSCF exported orbital:

```
[info]
basis = sto-3g
```

```

coord = benzene.xyz

[dmrgscf]
continue = true
fileorb = tmp/MCSCF/MCSCFOrb
irrep = 1
2S = 0
frozen = 0 0 0 0 0 0 0 0
docc = 6 5 4 3 0 0 0 0
active = 0 0 0 0 2 2 1 1
print_mo_indices

```

9.5 Start from External Integrals

The CASSCF and DMRG-SCF modules in Kylin can be used as stand-alone MCSCF solvers, as long as the initial molecular orbital integrals are provided. In this case, the initial molecular orbitals and integrals are directly loaded from external files, while the [info], [integral] and [hf] modules are not necessary. The standalone MCSCF solvers do not directly update the input molecular orbitals, instead the update matrix U will be printed. The MCSCF orbitals C can be simply obtained by

$$C = C_0U,$$

in which C_0 is the initial molecular orbital coefficient matrix, which is not required in the standalone MCSCF calculation.

To start a MCSCF calculation independently, the option `independent` must be enabled, and the initial molecular orbital integrals must be provided by setting the `integral` keyword to a FCIDUMP file. The FCIDUMP is a standard format to store one- and two-electron integrals, and can be generated by many quantum chemistry softwares such as Molpro, Molcas as well as Kylin(in modules [dmrg]/[MCSCF], full integral can be dumped to running path by setting keyword "dumpAll"/"dump_all" to true).

Note: in the standalone MCSCF calculations in Kylin, the input FCIDUMP file must contain integrals of all the molecular orbitals, not only in the active space; standalone MCSCF is incompatible with geometry optimization, because geometry optimization requires orbitals

(1) standalone MCSCF from full integral which is not generated by [casscf/dmrgscf] module


```
[dmrgscf]
independent = true
integral = FCIDUMP_full
pg = d2h #specify its point group
2S = 0
irrep = 1
M = 200 50 50 #use a less M
frozen = 0 0 0 0 0 0 0 0
docc = 6 5 4 3 0 0 0 0
active = 0 0 0 0 2 2 1 1
nactel = 6 #must specify active electrons in standalone mcscf
print_mo_indices
dump_all #dump FCIDUMP for next calculation with larger M
```

(2) resume standalone MCSCF from full integral which is generated by [casscf/dmrgscf] module

```
[dmrgscf]
continue = true
independent = true
integral = FCIDUMP_full
pg = d2h #specify its point group
irrep = 1
2S = 0
M = 1000 500 100 #revoke MCSCF with a greater M
frozen = 0 0 0 0 0 0 0 0
docc = 6 5 4 3 0 0 0 0
active = 0 0 0 0 2 2 1 1
nactel = 6 #specify active electrons
print_mo_indices
dump_all #dump FCIDUMP for next calculation with larger M
```

9.6 Tips to Flexibly Modify Active Space

(1) If a molecule's point group is C_i , C_s or C_2 , target active orbitals with the same irreducible representation may be not consecutive. Then, we need to use keyword

"rotate" to make such active orbitals consecutive. Take t-Bu-DHP as example, it has a total of 14 π orbitals, 7 with Ag symmetry and 7 with Au symmetry respectively. However, 7 Ag-symmetry π orbitals are not consecutive, so we need to exchange corresponding orbitals like C1.

```
[info]
basis = sto-3g
coord = t-Bu-DHP.xyz
[integral]
[hf]
guess = true
moint = false
acc_conv = cdiis
tol = 1e-5
```

Check tmp/hf.molden, you will find 45th and 46th Ag-orbitals are not π orbitals, while 43th and 44th orbitals is target active orbitals. So you need to exchange them in input file.

```
[info]
basis = sto-3g
coord = t-Bu-DHP.xyz

[dmrghscf]
fileorb = tmp/HF0rbForMCSCF
irrep = 2#calculate ${S_1}$ state
2S = 0
frozen = 0 0
#Ag docc is [1,44] based 1
#Au docc is [82,124] based 1
docc = 44 43
#Ag active is [45,51] based 1
#Au active is [125,131] based 1
active = 7 7
M = 400 100 50
reorder_method = 0 #for set to 0 for this system
print_mo_indices
```

```

#45th and 46th Ag-orbital NOT PI orbital
#43th and 44th Ag-orbital PI orbital
#exchange 43th with 45th
#exchange 44th with 46th
rotate = 43 45 44 46 #orbital indice is from 1 to total orbitals
nstate = 1
InitialConfig = 222u000222d000

```

t-BU-DHP's coordinate is as follows:

```

58
C          -0.39668597  -0.02744447  -0.65873403
C           0.39668597   0.02744447   0.65873403
C          -0.14351483   1.24303820  -1.45453423
C           0.14351483  -1.24303820   1.45453423
C          -0.07845264   1.17751650  -2.84603458
C           0.07845264  -1.17751650   2.84603458
H          -0.02339864   2.11063091  -3.38954979
H           0.02339864  -2.11063091   3.38954979
C          -0.02509317  -0.04573561  -3.56251181
C           0.02509317   0.04573561   3.56251181
C           0.04000741  -1.24699573  -2.82539697
C          -0.04000741   1.24699573   2.82539697
H           0.18242851  -2.18532038  -3.33946693
H          -0.18242851   2.18532038   3.33946693
C          -0.01639678  -1.28341779  -1.42636429
C           0.01639678   1.28341779   1.42636429
C          -0.12350483   2.45130409  -0.72852912
C           0.12350483  -2.45130409   0.72852912
H          -0.12564084   3.39028916  -1.26792587
H           0.12564084  -3.39028916   1.26792587
C           0.12700405  -2.46525785  -0.67603421
C          -0.12700405   2.46525785   0.67603421
H           0.22365383  -3.41061023  -1.19544466
H          -0.22365383   3.41061023   1.19544466
C          -1.94772146  -0.10294841  -0.42346602

```

C	1.94772146	0.10294841	0.42346602
H	-2.29696970	0.77389983	0.11134380
H	2.29696970	-0.77389983	-0.11134380
H	-2.20638827	-0.99375824	0.13912937
H	2.20638827	0.99375824	-0.13912937
H	-2.44117512	-0.14335268	-1.39038684
H	2.44117512	0.14335268	1.39038684
C	0.03604340	-0.00629190	-5.11185247
C	-0.03604340	0.00629190	5.11185247
C	0.06438152	-1.42874150	-5.72743436
C	-0.06438152	1.42874150	5.72743436
H	-0.81128771	-1.99962865	-5.43833498
H	0.81128771	1.99962865	5.43833498
H	0.95410090	-1.97122984	-5.42672932
H	-0.95410090	1.97122984	5.42672932
H	0.07186991	-1.34539685	-6.81117308
H	-0.07186991	1.34539685	6.81117308
C	-1.22015181	0.73246756	-5.64745601
C	1.22015181	-0.73246756	5.64745601
H	-2.12360242	0.21678959	-5.33870497
H	2.12360242	-0.21678959	5.33870497
H	-1.19217071	0.76567274	-6.73358800
H	1.19217071	-0.76567274	6.73358800
H	-1.26622974	1.75189581	-5.27903986
H	1.26622974	-1.75189581	5.27903986
C	1.31899155	0.74712126	-5.55531477
C	-1.31899155	-0.74712126	5.55531477
H	1.37412414	0.77315315	-6.64056002
H	-1.37412414	-0.77315315	6.64056002
H	2.20290197	0.24631275	-5.17407267
H	-2.20290197	-0.24631275	5.17407267
H	1.32237489	1.76932657	-5.19186592
H	-1.32237489	-1.76932657	5.19186592

(2) [MCSCF] module always print out chkmcscf.molden under tmp path, you can check active space as soon as possible(this molden's occupation numbers are fixed to RHF, you can ignore it).

(3) Latest orbitals are saved to MCSCFOrb and MCSCFOrb.molden under tmp/MC-

SCF path, you can use it to resume MCSCF calculation with keywords "continue = true" and "fileorb = tmp/MCSCF/MCSCFOrb". Since orbitals have been rotated according to keyword "rotate" in former input file(if "rotate" is not specified, you can skip this tip), the updated input file should remove keyword "rotate" to resume MCSCF. For example, resume benzene's dmrgcf calculation with latest MCSCFOrb with point group = C1:

```
[info]
basis = sto-3g
coord = benzene.xyz
pg = c1

[dmrgscf]
continue = true
fileorb = tmp/MCSCF/MCSCFOrb
irrep = 1
2S = 0
frozen = 0
docc = 18
active = 6
'''
#because 17 has exchanged with 19 in former mcsf calculation
#so remove keyword "rotate"
#rotate = 17 19
'''
print_mo_indices
```

Similarly, MCSCF calculation can also be resumed by hf.molden/MCSCFOrb.molden or other molden files generated by other softwares if point group = C1:

a. start mcsf calculation with hf.molden

```
[info]
inputType = molden
moldenfile = tmp/hf.molden
[integral]

[dmrgscf]
irrep = 1
```

```

2S = 0
frozen = 0
docc = 18
active = 6
rotate = 17 19
print_mo_indices

```

b. resume mcscf calculation with MCSCFOrb.molden

```

[info]
inputType = molden
moldenfile = tmp/MCSCF/MCSCFOrb.molden
[integral]

[dmrgscf]
irrep = 1
2S = 0
frozen = 0
docc = 18
active = 6
'''
#because 17 has exchanged with 19 in former mcscf calculation
#so remove keyword "rotate"
#rotate = 17 19
'''
print_mo_indice

```

(4) Latest orbitals are also saved to mcscfStatex.molden and mcscfAverage.molden under tmp/MCSCF path, so you can use MULTIWFN to check optimized orbitals in time. If you find additional docc- or virtual-type orbitals should be covered in active space, you can use latest MCSCFOrb to resume MCSCF calculation by updating corresponding parameters your input file:

- a. modify the orbital number corresponding to irreducible representation in docc/active or only active(if only virtual orbitals need to be covered) domain;
- b. exchange target orbitals with outside orbitals of updated active space if necessary with keyword "rotate" like C1 dmrscf calculation.

(5) Latest orbitals are also saved to `molcas.mcscfStatex` and `molcas.mcscfAverage` under `tmp/MCSCF` path. If point group = C1, these molcas orbital files can be imported to openMOLCAS or other softwares via MOKIT, but attention should be paid to the consistency of basis sets.

10 MRCI

The multi-reference configuration interaction (MRCI) module in Kylin supports the uncontracted (UC) and the externally contracted (EC) MRCI methods. This module can be initialized with the label [mrci].

Since the second order Epstein-Nesbet perturbation theory (ENPT2) energy could be obtained during the EC-MRCI calculation, this module could also perform ENPT2 calculation.

Currently, the configuration state function (CSF) which is the eigenfunction of operator \hat{S}^2 is used as wavefunction basis. Moreover, the electron excitations from doubly-occupied (or core) orbitals to other orbitals are not considered.

The keywords in the MRCI module are listed in Table 9.

Keyword	Description
method	Which method to be performed, should be uc, ec or enpt2, default ec. Note that if method = ec, the ENPT2 energy could also be obtained.
ref	Reference configurations, default all for all CAS configurations. If reference configurations are selected, these selected configurations ("2", "u", "d" and "0" represent double, positively spin-coupled, negatively spin-coupled and zero occupation respectively) should be written in a file (one configuration on each line) and the file name should be passed to this keyword.
2S	The value of spin multiplicity $2S$, default 0 (singlet).
frozen	Number of frozen orbitals in each irreducible representation of the point group symmetry (irrep). The frozen orbitals are doubly-occupied and the electron excitations from frozen orbitals to other orbitals are not allowed.
active	Number of active orbitals in each irrep.
external	Number of external orbitals in each irrep, default all of external orbitals in each irrep.
charge	Charge of the system, default 0.
irrep	Irrep index of the target state(s), default 1.

nstate	Number of state(s) to be solved, default 1.
directCI	Perform direct CI calculation, default false.
eigsolver_cas	Eigsolver for reference space CI calculation before MRCI, should be lanczos, davidson or jacdav for Lanczos, Davidson and Jacob-Davidson algorithms respectively, default lanczos.
eigsolver	Eigsolver for MRCI calculation, should be lanczos, davidson or jacdav for Lanczos, Davidson and Jacobi-Davidson algorithms respectively, default davidson.
refGuess	User specified initial guess for reference Hamiltonian diagonalization, default empty. For example, a singlet system using CAS(2e, 2o) as reference space, if refGuess = 20 02 and assuming that index(20) = 0 (C-style, starting from 0) and index(02) = 2, then [1, 0, 1] will be used as initial guess.
initH0	Initial guess for reference Hamiltonian (H0, not \hat{H}_0 of ENPT2) diagonalization (only valid when refGuess is empty), should be 0 for [[1, 0, 0, ...], [0, 1, 0, ...]], 1 for [1, 1, 1, ...], 2 for [diagElem(H0)] or 3 for [random numbers and, 1000 * thisvector[maxIndex(diagElem(H0))]], default 3.
tol_H	Threshold value of saving Hamiltonian matrix elements when directCI = false, default 1.0E-8.
tol_E	Threshold value of diagonalization convergence, default 1.0E-10. If directCI = true, 1.0E-7 is recommended for balanced precision and cost.
tol_C	Threshold value of contraction coefficients for EC-MRCI, default 1.0E-6.
tol_O	Threshold value of orthogonalization for EC-MRCI when nstate > 1, default 1.0E-10.
actOrbOrder	Order of active orbitals when ref \neq all, default empty. For example, if reference configurations are obtained from DMRG wavefunction with Fiedler order, actOrbOrder should be specified with Fiedler order.

actExc	Allow electron excitations in active space when ref \neq all, default false.
verbose	Print level, default 1.
printWfn	Print CI coefficients to file MRCICoef- n (n is the state index), default false. If verbose ≥ 3 , printWfn will be set to true automatically.

Table 9: Keywords in MRCI.

Here is an example of N₂.

```
[info]
coord = n2.xyz
basis = cc-pvdz
pg = c1

[integral]

[hf]
rhf

[mrci]
method = ec
2S = 0
frozen = 4
active = 6
```

10.1 Computation with External Integrals

The MRCI module in Kylin could be used as a stand-alone program if the molecular orbital integrals are provided. Some extra required parameters are listed in Table 10.

Keyword	Description
independent	Perform stand-alone MRCI calculation, default <code>false</code> .
integral	FCIDUMP file name. In this file, the irreps and orbital indices both start from 1.
nelec	Number of total electrons. If FCIDUMP file does not contain doubly-occupied orbitals, <code>nelec</code> = number of active electrons and <code>frozen</code> should be 0 for each irrep.
pg	Point group symmetry of the system, default <code>c1</code> .

Table 10: Extra required keywords for stand-alone MRCI.

Here is an example of hexacene. The FCIDUMP file contains active and external orbital integrals. The `CollectedCFGs.txt` contains the selected reference CSFs.

```
[mrci]
independent
method = ec
integral = FCIDUMP
ref = CollectedCFGs.txt
2S = 0
active = 26
nelec = 26
pg = c1
irrep = 1
```

The `ref` file (`CollectedCFGs.txt`) supports two formats.

First, one CSF and the corresponding coefficient a line (this format is the same as the output file of EDGA module)

```
22222222222220000000000000 0.93
```

Second, one CSF a line

222222222222000000000000

11 MRPT

Currently, Kylin only supports the second order Epstein-Nesbet perturbation theory (ENPT2) using CASCI/CASSCF/sCI/DMRG2sCI wavefunction as reference. Since the ENPT2 energy could be obtained during the EC-MRCI calculation, the ENPT2 calculation is implemented in MRCI module (see Section 10).

12 Geometry Optimization

Geometry Optimization module [geoopt] in Kylin supports the localization of equilibrium structure in redundant internal coordinates. Currently, only the following methods are available:

- (1) restricted Hartree-Fock;
- (2) state-specific CASSCF without frozen orbitals;
- (3) state-specific DMRGSCF without frozen orbitals.

This version has several limitations:

- (1) only support Abelian point group, non-Abelian point group can't be sustained with 100% confidence;
- (2) can't deal with the degradation of structural symmetry.

Ways to smash above limitations, Z_mat format, constrained optimization and other functions will be supported in the future.

Besides, attention must be paid to the memory requirement in MCSCF geometry optimization: Twice the memory of two-electron atomic integrals is required by MCSCF while four times the memory of two-electron atomic integrals is required by MCSCF geometry optimization, so you'd better select a suitable machine to do MCSCF geometry optimization.

The Geometry Optimization module can be started with [geoopt]. The keywords in this module are listed in Table 11.

Keyword	Description
method	The method used to do single point calculation, default hf.
optimizer	Optimization method used to locate suitable structures, rfo, gdiis and gediis for Rational Functional optimization, geometry-based and energy-based direct inversion in the iterative subspace algorithms respectively. Default is rfo.
hess_type	Option to specify the type of guess hessian which will be updated by Broyden-Fletcher-Goldfarb-Shanno formula, including schlegel and model. Default schlegel.
max_opt_iter	Max number of optimization iterations, default 50.
max_opt_step	Max step length of each optimization iteration, default 0.3(Angstrom). If an atom's step overshoots this value, actual optimization step length will be scaled.

Keyword	Description
max_force	Threshold for maximum force in redundant internal coordinates of an optimal structure, default 0.00045(hartree/bohr or hartree/rad).
rms_force	Threshold for root-mean-square deviation(RMSD) of force in Cartesian coordinates of an optimal structure, default 0.0003(hartree/bohr).
max_displace	Threshold for maximum displacement in Cartesian coordinates of an optimal structure, default 0.0018(Angstrom).
rms_displace	Threshold for root-mean-square deviation(RMSD) of displacement in Cartesian coordinates of an optimal structure, default 0.0012(Angstrom).
diis_size	Size of the GDIIS/GEDIIS space, default 3.
numeric_hess	Option to calculate numeric hessian matrix of optimal structure, default false. Note: this is only for point group = C1

Table 11: Keywords in Geometry Optimization.

12.1 Output Norm of Geometry Optimization

(1) During geometry optimization, energy, max_force, rms_force, max_displace and rms_displace of each structure is updated in a text file named "GeooptList.txt" in the current working directory, so you can check the progress of geometry optimization directly. If max_opt_iter is too small, the end of GeooptList.txt won't tell if geometry optimization converged or not.

(2) All structures generated in geometry optimization are saved to a folder with the same name of `***.xyz` or `***.molden` you specify in [info]. This folder is created under tmp path.

(3) Cartesian coordinates, Cartesian gradient and steps are all written in x.xyz file (0.xyz is the initial guess structure specified in [info], 1.xyz is the first structure produced by geometry optimization) and saved to the above folder. If abortion occurs during MCSCF geometry optimization, you can use x.xyz and corresponding MCSCFOrb with keyword "continue = true" to resume geometry optimization directly.

(4) For visualization, each structure has a copy of x.gjf file generated at the same time.

(5) If numeric hessian is calculated, hessian matrix will be updated in text file numHess.txt in time. And all frequencies as well as zero point energy will be output at the tail of your log file.

12.2 Start MCSCF Geometry Optimization from [hf] Module

(1) If a molecular's active space has been picked out, you can run MCSCF geometry optimization from [hf] module, as following input file shows:

```
[info]
basis = sto-3g
coord = c18h18.xyz

[integral]

[hf]
guess = true
moint = false
acc_conv = cdiis
tol = 5e-5

[dmrgscf]
irrep = 1
2S = 0
frozen = 0 0 0 0
docc = 28 26 0 0
active = 0 0 9 9
M = 500 300 50
print_mo_indices
tol_macro = 1e-5
nstate = 1
InitialConfig = 222220000222200000

[geoopt]
method = dmrgscf
optimizer = gediis
```



```
hess_type = schlegel
```

The geometry of C₁₈H₁₈ polyacetylene is defined in the file [c8h18.xyz](#) in chapter Examples.

(2) Start MCSCF geometry optimization from saved HFOrbForMCSCF file, if you have generated Hartree-Fork orbitals:

```
[info]
basis = sto-3g
coord = c18h18.xyz

[dmrgscf]
fileorb = tmp/HFOrbForMCSCF
irrep = 1
2S = 0
frozen = 0 0 0 0
docc = 28 26 0 0
active = 0 0 9 9
M = 400 200 50
#reorder_method=0
print_mo_indices
tol_macro = 1e-5
nstate = 1
InitialConfig = 222220000222200000

[geopt]
method = dmrgscf
optimizer = gdiis
hess_type = schlegel
```

12.3 Start MCSCF Geometry Optimization from MCSCF Orbitals

(1) You can resume MCSCF geometry optimization from any external molden if point group = C1. Take ben's geometry optimization with point group = C1 as example:

```

[info]
inputtype = molden
moldenfile = tmp/MCSCF/MCSCF0rb.molden

[integral]

[dmrgscf]
irrep = 1
2S = 0
frozen = 0
docc = 18
active = 6
'''
#because 17 has exchanged with 19 in former mcscf calculation
#so remove keyword "rotate"
#rotate = 17 19
'''
print_mo_indices

[geopt]
method = dmrgscf
optimizer = gediis
hess_type = schlegel

```

(2) You can resume MCSCF geometry optimization from MCSCF exported orbitals of initial guess structure:

```

[info]
basis = sto-3g
coord = t-Bu-DHP.xyz

[dmrgscf]
continue = true
fileorb = tmp/MCSCF/MCSCF0rb
irrep = 2
2S = 0
frozen = 0 0

```

```

docc = 44 43
active = 7 7
M = 400 100 50
reorder_method = 0
print_mo_indices
'''
#because active space has been made consecutive
#in former mcscf calculation
#so remove keyword "rotate"
#rotate = 43 45 44 46
'''
nstate = 1
InitialConfig = 222u000222d000
[geopt]
method = dmrgscf
optimizer = gediis
hess_type = schlegel

```

(3) You can resume MCSCF geometry optimization from MCSCF exported orbitals of latest generated structure if abortion occurs:

```

[info]
basis = sto-3g
coord = tmp/c8h18/3.xyz
#because coordinates has been rotated in single point calculation
#we have to maintain the consistency of orbitals and coordinates
rotcoord = false

[dmrgscf]
continue = true
fileorb = tmp/MCSCF/MCSCSF0rb
irrep = 1
2S = 0
frozen = 0 0 0 0
docc = 28 26 0 0
active = 0 0 9 9
M = 400 200 50

```

```
#reorder_method=0
print_mo_indices
tol_macro = 1e-5
nstate = 1
InitialConfig = 222220000222200000

[geopt]
method = dmrgscf
optimizer = gdiis
hess_type = schlegel
```

13 Examples

In this section, we give some practical examples to show how to use Kylin in quantum chemistry researches.

13.1 CASSCF and DMRG-SCF

The following is an example of CASSCF calculation of $C_{12}H_{14}$ polyacetylene.

```
[info]
  coord = c12h14.xyz
  basis = 6-31g
  pg = c1

[integral]

[hf]
  guess = true
  moint = false #because moint can be generated in MCSCF
[casscf]
  2S = 0
  frozen = 0
  docc = 37
  active = 12
  tol_davidson = 1e-7
  nstate = 1
  nactel = 12
  rotate = 47 53 48 54
```

The geometry of $C_{12}H_{14}$ polyacetylene is defined in the file `c12h14.xyz`, as

```
26
Angstrom
C          -0.08389600   4.32582500   0.00000000
H          -1.17875300   4.39409800   0.00000000
C           0.49694800   3.09580500   0.00000000
H           1.59237900   3.03292300   0.00000000
```

C	-0.22577000	1.85266800	0.00000000
H	-1.32108200	1.91302100	0.00000000
C	0.36008900	0.62116400	0.00000000
H	1.45554400	0.56169500	0.00000000
C	-0.36008900	-0.62116400	0.00000000
H	-1.45554400	-0.56169500	0.00000000
C	0.22577000	-1.85266800	0.00000000
H	1.32108200	-1.91302100	0.00000000
C	-0.49694800	-3.09580500	0.00000000
H	-1.59237900	-3.03292300	0.00000000
C	0.08389600	-4.32582500	0.00000000
H	1.17875300	-4.39409800	0.00000000
C	-0.65094200	-5.57286900	0.00000000
H	-1.74484800	-5.49307100	0.00000000
C	-0.08389600	-6.79496400	0.00000000
H	1.00336100	-6.91703400	0.00000000
H	-0.68811500	-7.70416700	0.00000000
C	0.65094200	5.57286900	0.00000000
H	1.74484800	5.49307100	0.00000000
C	0.08389600	6.79496400	0.00000000
H	-1.00336100	6.91703400	0.00000000
H	0.68811500	7.70416700	0.00000000

As shown above, if running CASSCF/DMRGSCF calculation directly from [hf] module, keyword "moint" in [hf] module should be set to false, because molecular integral can be generated in MCSCF calculation. The active space used in the CASSCF calculation consists of 12 π orbitals and 12 π electrons. However, the indices of the π orbitals are not consecutive. We use the rotation option to exchange the 47-th molecular orbital with the 53, and 48 with 54.

We can also use DMRG-SCF method to perform MCSCF calculation. However, if there are less than 16 active orbitals, the classical CASSCF method are usually much cheaper, faster but more accurate than the DMRG-SCF method. The accuracy of DMRG-related methods are controlled by the number of reserved states M.

13.2 InitialConfig in DMRG and DMRGSCF

A suitable initial configuration should be given in input file when running [dmrg] and [dmrgscf] to calculate molecular systems with point group symmetry higher than

C1 in Kylin. The keyword "InitialConfig" is only used to describe the configuration in active space, and it should be declared in the form of "2ud0", among which 2 denotes doubly occupied, u, singly occupied by a spin-up active electron, d, singly occupied by a spin-down active electron, and 0, an empty active orbital. A suitable initial configuration MUST meet TWO requirements:

(1) The direct product of irreducible representations of all active electrons MUST EQUAL to the value of keyword "irrep" you specified, which means you should know all active orbitals' irreducible representation in advance. Note: Direct product rules can refer to [Point Group Symmetry Table³](#) website.

(2) The spin number(2S) of active space MUST EQUAL to the value of keyword "2S" you specified.

Otherwise, an assertion related to quantum number error may occur like "system_qn == Q0". The following are examples to illustrate how to specify keyword "InitialConfig" in [dmrgscf](the same is with [dmrg]):

(1) Ground state of benzene with point group symmetry = D2h:

```
[info]
basis = sto-3g
coord = benzene.xyz

[integral]

[hf]
guess = true
moint = false
acc_conv = cdiis
tol = 1e-5

[dmrgscf]
#ground state
irrep = 1
2S = 0
frozen = 0 0 0 0 0 0 0 0
docc = 6 5 4 3 0 0 0 0
active = 0 0 0 0 2 2 1 1
M = 200 50 50
print_mo_indices
```

³<https://zh.webqc.org/symmetry.php>

```

#In tmp/hf.molden, six active PI orbitals'
#irreducible representation as well as
#occupation numbers are
#B1u B1u B2g B2g B3g Au
# 2 0 2 0 2 0
#According to direct product rules
#of electronic configuration and 2S = 0
#202020 is suitable
initialconfig = 202020

```

(2) 1^1B_{2u} state of benzene with point group symmetry = D_{2h}:

```

[info]
basis = sto-3g
coord = benzene.xyz

[integral]

[hf]
guess = true
moint = false
acc_conv = cdiis
tol = 1e-5

[dmrgscf]
#B2u's first singlet state
irrep = 3
2S = 0
frozen = 0 0 0 0 0 0 0 0
docc = 6 5 4 3 0 0 0 0
active = 0 0 0 0 2 2 1 1
M = 200 50 50
print_mo_indices
#In tmp/hf.molden, six active PI orbitals'
#irreducible representation as well as
#occupation numbers are
#B1u B1u B2g B2g B3g Au

```



```
# 2 0 2 0 2 0
#According to direct product rules
#of electronic configuration
#B2u = B1u * B3g
#as well as 2S = 0
#2u20d0 is suitable
InitialConfig = 2u20d0
```

13.3 Mixed-Precision DMRG

The following is an example of mixed-precision DMRG calculation of benzene molecule. Note that do not use `sweep_precision = single` to run single-precision sweeps in DMRG calculations because they may lead to unreliable results. To run reliable single-precision, use `sweep_precision = mix` and `nsweep_d = 0`.

```
[info]
basis = 6-31g
coord = benzene.xyz
pg = c1

[integral]

[hf]
2S = 0
guess = true

[dmrg]
2S = 0
docc = 11
active = 20
M = 2000 400 400
tol_davidson = 1e-3 1e-5
tol_svd = 1e-50 1e-7
sweep_precision = mix
mixed_double = true
symm = su2u1
```

The geometry of benzene molecule is defined in the file `benzene.xyz`, as

```
12
6      1.21364800  0.70070000  0.00000000
6      0.00000000  1.40140000  0.00000000
6     -1.21364800  0.70070000  0.00000000
6     -1.21364800 -0.70070000  0.00000000
6      0.00000000 -1.40140000  0.00000000
6      1.21364800 -0.70070000  0.00000000
1      2.14029518  1.23570000  0.00000000
1      0.00000000  2.47140000  0.00000000
1     -2.14029518  1.23570000  0.00000000
1     -2.14029518 -1.23570000  0.00000000
1      0.00000000 -2.47140000  0.00000000
1      2.14029518 -1.23570000  0.00000000
```

13.4 HF geometry optimization

The following is an example of Hartree-Fock geometry optimization of $C_{18}H_{18}$ polyacetylene.

```
[info]
basis = sto-3g
coord = c18h18.xyz

[integral]

[hf]
guess = true
moint = false #molecular integral is not required in hf geoopt
acc_conv = cdiis
tol = 1e-5

[geoopt]
method = hf
optimizer = rfo
```

```
hess_type = schlegel
max_opt_iter = 20
```

The geometry of C₁₈H₁₈ polyacetylene is defined in the file c18h18.xyz, as

```
36
C      0.00000000  0.00000000  0.00000000
C      0.00000000  0.00000000  3.03674316
C      0.13922104  0.00000000 -1.30314036
C      0.13922104  0.00000000  4.33988352
C      1.41586478  0.00000000 -2.04606030
C      1.41586478  0.00000000  5.08280346
C      2.61089088  0.00000000 -1.50951328
C      2.61089088  0.00000000  4.54625644
C      3.94052985 -0.00000000 -2.12894389
C      3.94052985 -0.00000000  5.16568705
C      5.09745163  0.00000000 -1.45518376
C      5.09745163  0.00000000  4.49192692
C      5.23384423  0.00000000  0.00391420
C      5.23384423  0.00000000  3.03282896
C      6.28517534  0.00000000  0.78068273
C      6.28517534  0.00000000  2.25606043
C     -1.19423177  0.00000000  2.18675605
C     -1.19423177  0.00000000  0.84998712
H      0.91974131  0.00000000  0.54928970
H      0.91974131  0.00000000  2.48745346
H     -0.75703156  0.00000000 -1.91246154
H     -0.75703156  0.00000000  4.94920470
H      1.33618480 -0.00000000 -3.12702166
H      1.33618480 -0.00000000  6.16376482
H      2.62506861  0.00000000 -0.43885687
H      2.62506861  0.00000000  3.47560003
H      3.98182577 -0.00000000 -3.21228061
H      3.98182577 -0.00000000  6.24902377
H      6.01512073  0.00000000 -2.03216572
H      6.01512073  0.00000000  5.06890888
```

H	4.29879649	0.00000000	0.52406896
H	4.29879649	0.00000000	2.51267420
H	7.26231500	0.00000000	0.31190553
H	7.26231500	0.00000000	2.72483763
H	-2.15318908	0.00000000	0.34445811
H	-2.15318908	0.00000000	2.69228505

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