



DMRG-CASPT2 with Molcas-CheMPS2 interface

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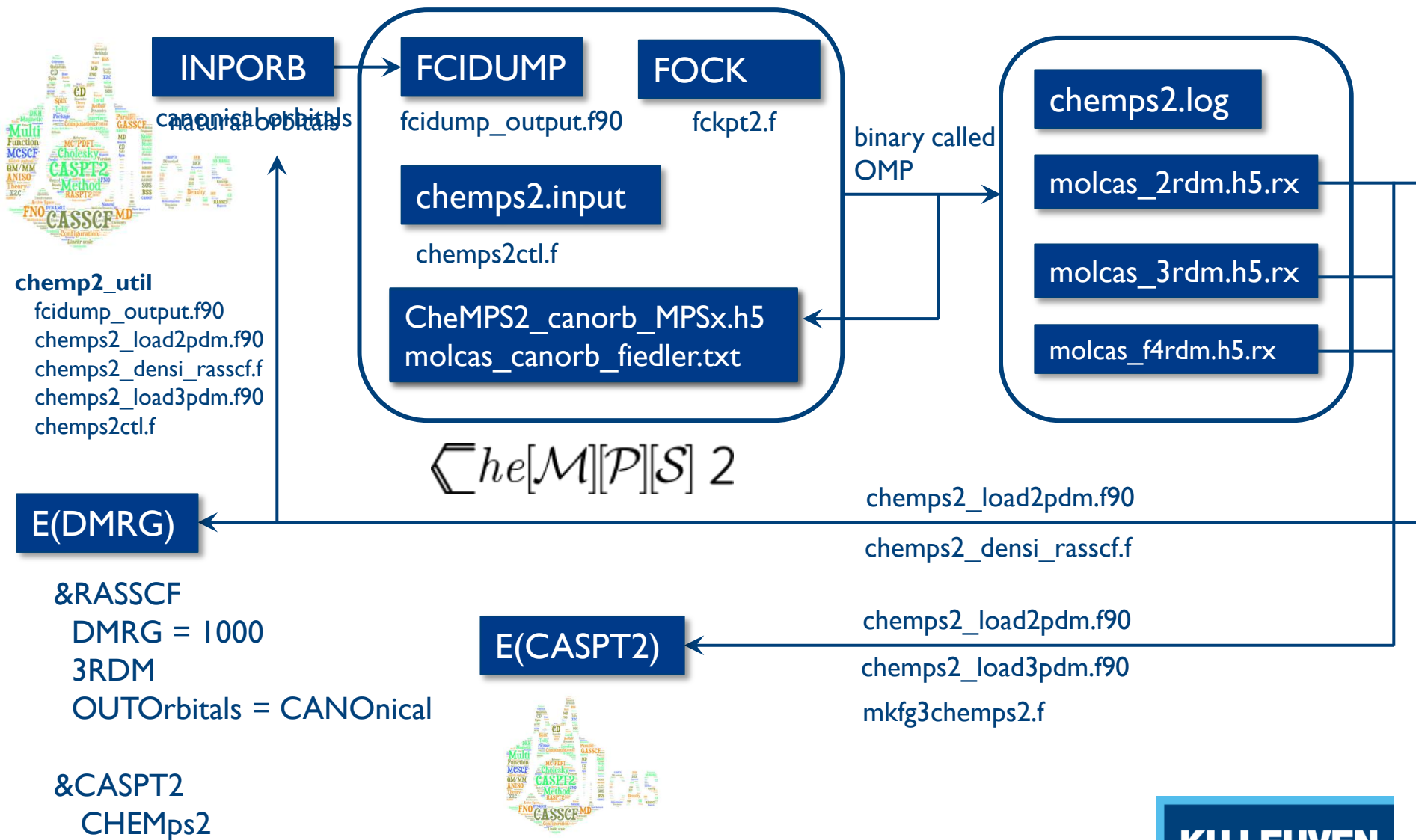
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Molcas-CheMPS2 main features

CheMPS2

- ✓ DMRG-SCF with PCM
- ✓ SS- and SA- with DMRG-SCF calculations
- ✓ DMRG-CASPT2 with pseudocanonical basis
 - ✓ Not bad choice for compact molecules, e.g. TM complexes
 - ✓ Construction of F.4-RDM is simplified
 - × Not the optimal type of orbital for DMRG
- ✓ DMRG-CASPT2 with non-pseudocanonical basis implemented

DMRG-CASPT2 calculation with Molcas-CheMPS2



Installation

Cmake > 3.0

HDF5

<https://support.hdfgroup.org/HDF5>

must be configured with Fortran, Fortran 2003, and C++ enabled:

```
CC=icc CXX=icpc FC=ifort ./configure --enable-fortran  
--enable-fortran2003 --enable-cxx
```

Installation

CheMPS2

<https://github.com/SebWouters/CheMPS2>

only Open Multi-Processing (OpenMP) is supported:

```
CC=icc CXX=icpc FC=ifort
```

```
CMAKE_INCLUDE_PATH=/path/to/hdf5/include
```

```
CMAKE_LIBRARY_PATH=/path/to/hdf5/lib cmake .. -DMKL=ON
```

```
-DWITH_MPI=OFF
```

Installation

Molcas

parallel Molcas supported

```
FC=ifort CC=icc CXX=icpc  
cmake .. -DCMAKE_BUILD_TYPE=Release -DMPI=ON -DLINALG=MKL  
-DMKLROOT=/path/to/intel/mkl -DMPI_C_COMPILER=mpicc  
-DMPI_Fortran_COMPILER=mpif90 -DMPI_CXX_COMPILER=mpicxx  
-DOPENMOLCAS_DIR=/path/to/OpenMolcas -DHDF5=ON  
-DHDF5_LIBRARIES=/path/to/hdf5/lib  
-DHDF5_INCLUDE_DIRS=/path/to/hdf5/include  
-DCHEMPS2=ON -DCHEMPS2_DIR=/path/to/CheMPS2/bin
```

verification

```
molcas verify 850 851 --keep
```

850

Input:

&RASSCF

DMRG = 1000

3RDM

Dependencies:

- RUNFILE, **INPORB**
- molcas_natorb_fiedler.txt, CheMPS2_natorb_MPSx.h5
(x=0,1,...)
- molcas_canorb_fiedler.txt, CheMPS2_canorb_MPSx.h5
(x=0,1,...)

850

Log

++ DMRG sweep specifications:

Number of renormalized basis	1000	(DMRG)
Number of root(s) required	1	(CIROot)
Maximum number of sweeps	8	(MXSweep)
Maximum number of sweeps in RDM	40	(MXCAnonical)
Threshold for restarting	0.500E-02	(CHBLb)
Minimum Davidson tolerance	0.100E-06	(DAVTolerance)
DMRG convergence threshold	0.500E-08	
Noise prefactor	0.500E-01	(NOISe)
Restart from previous calculation	F	(CHREstart)
Calculate 3-RDM and F.4-RDM	T	(3RDM)
Restart scheme in 3-RDM and F.4-RDM	0	(DMREstart)
Root chosen for geometry opt.	1	

850

Output files

- log file
- chemps2.input chemps2.log chemps2.log.total
- FCIDUMP_CHEMPS2
- molcas_natorb_fiedler.txt molcas_canorb_fiedler.txt
- CheMPS2_natorb_MPSx.h5 CheMPS2_canorb_MPSx.h5
- molcas_2rdm.h5.rx
- molcas_3rdm.h5.rx
- molcas_f4rdm.h5.rx
- FOCK_CHEMPS2

850

Input:

&CASPT2

CHEMps2

Dependencies:

- RUNFILE, JOBIPH
- molcas_2rdm.h5.rx
- molcas_3rdm.h5.rx
- molcas_f4rdm.h5.rx

Log: very similar to conventional CASPT2 calculations

```

*****
Multi-State initialization phase begins for group  1
-----
CHEMPS2> MKRPTORB assumes PSEUDOCANONICAL orbitals!
*****
Compute H0 matrices for state  2
-----
-----
H0 matrices have been computed.
*****
CASPT2 EQUATION SOLUTION
-----

Total nr of CASPT2 parameters:
Before reduction: 5658
After reduction:  5586

The contributions to the second order correlation energy in atomic units.
-----

```

IT.	VJTU	VJTI	ATVX	AIVX	VJAI	BVAT	BJAT	BJAI	TOTAL	RNORM
1	-0.001863	-0.004705	0.000000	-0.046445	-0.025930	-0.001014	-0.001069	-0.126817	-0.207844	0.001367
2	-0.001866	-0.004760	0.000000	-0.046475	-0.025995	-0.001016	-0.001073	-0.126819	-0.208004	0.000145
3	-0.001866	-0.004761	0.000000	-0.046475	-0.025996	-0.001016	-0.001073	-0.126819	-0.208006	0.000017

```

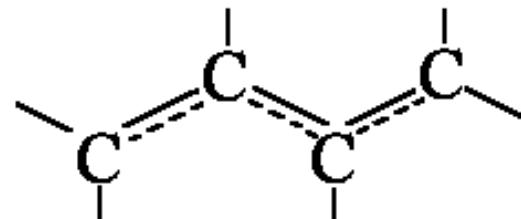
-----
FINAL CASPT2 RESULT:

Reference energy:      -191.8232886709
E2 (Non-variational): -0.2080040379
E2 (Variational):     -0.2080040493
Total energy:         -192.0312927202
Residual norm:        0.0000006831
Reference weight:      0.91044

```

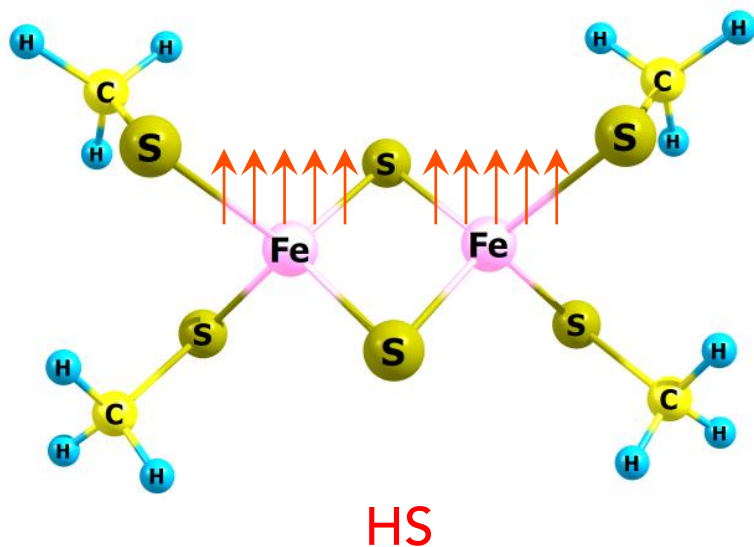
Examples

- DMRG calculations with C_nH_{n+2}
- Active space $CAS(n,n)$ $n = 4, 6, 8, 10$
- Natural delocalized or localized orbitals



<https://github.com/quanp/polyene>

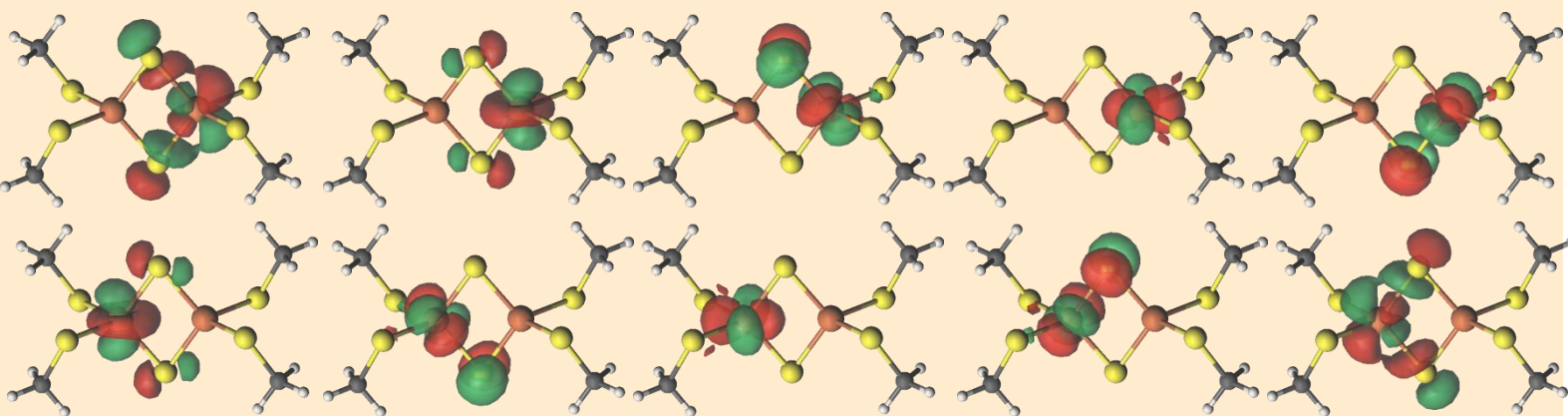
Larger example: $[\text{Fe}_2\text{S}_2(\text{SCH}_3)_4]^{2-}$



C_{2h}
Minimal ANO-RCC basis sets
Low CD
INPORB: RASSCF orbitals

DAVTolerance = 1.0E-5
DMRG = 500 or 2000

Active space of $[\text{Fe}_2\text{S}_2(\text{SCH}_3)_4]^{2-}$



CAS(10,20)

