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DMRG-CASPT2 with Molcas-CheMPS2 interface

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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

INPORB

canonical orbitals

natural orbitals

FCIDUMP

fcidump_output.f90

FOCK

fckpt2.f

chemps2.input

chemps2ctl.f

CheMPS2_canorb_MPSx.h5

molcas_canorb_fiedler.txt

binary called OMP

chemps2.log

molcas_2rdm.h5.rx

molcas_3rdm.h5.rx

molcas_f4rdm.h5.rx

chemp2_util

fcidump_output.f90

chemps2_load2pdm.f90

chemps2_densi_rasscf.f

chemps2_load3pdm.f90

chemps2ctl.f

$$\mathrm{Che}[\mathcal{M}][\mathcal{P}][\mathcal{S}]\ 2$$

E(DMRG)

chemps2_load2pdm.f90

chemps2_densi_rasscf.f

```
&RASSCF
  DMRG = 1000
  3RDM
  OUTOrbitals = CANOnical

&CASPT2
   CHEMps2
```

E(CASPT2)

chemps2_load2pdm.f90

chemps2_load3pdm.f90

mkfg3chemps2.f

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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
```

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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
```

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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,…)

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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
```

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`

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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
```

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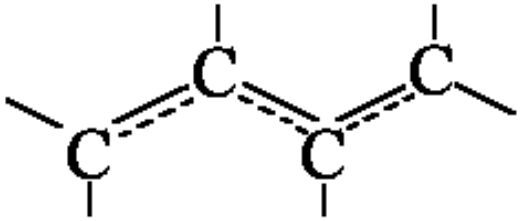
Examples

- DMRG calculations with C_nH_{n+2}
- Active space CAS(n,n) n = 4, 6, 8, 10



`https://github.com/quanp/polyene`

Log in Dirac

- Connect your laptop to eduroam
- All the information about the accounts is put on `https://quantchem.kuleuven.be/owncloud`

  userid:
  password:

- Register using the URLs in `b_network_registration_vouchers.txt`

- Connect to the B-zone using the **pulse-client**

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Log in Dirac

- Connect to dirac, password provided

```
ssh tccmx@dirac.quantchem.kuleuven.be                x=2,3,etc.
git clone https://github.com/quanp/polyene
ssh node87
```

- Molcas-CheMPS2 installed at `/home/tccm1/source`
- interactively run `molcas.sh on node87` (64 CPUs)

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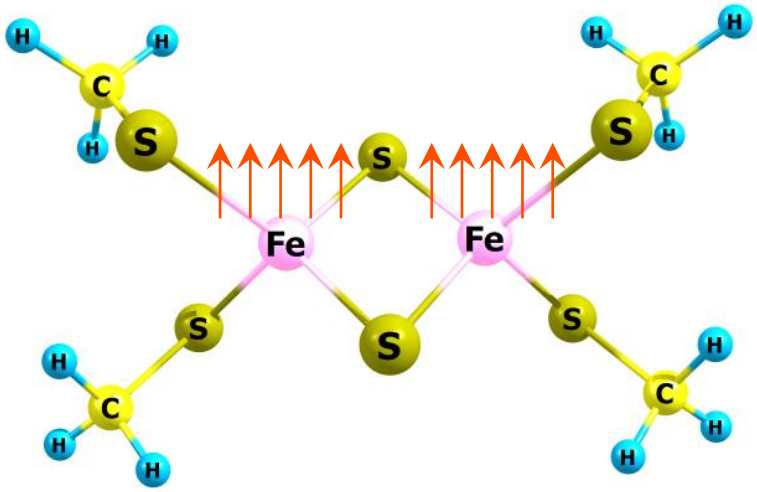
Larger example: $[Fe_2S_2(SCH_3)_4]^{2-}$



HS

C_{2h}

Minimal ANO-RCC basis sets

Low CD

INPORB: RASSCF orbitals

DAVTolerance = 1.0E-5

DMRG = 500 or 2000

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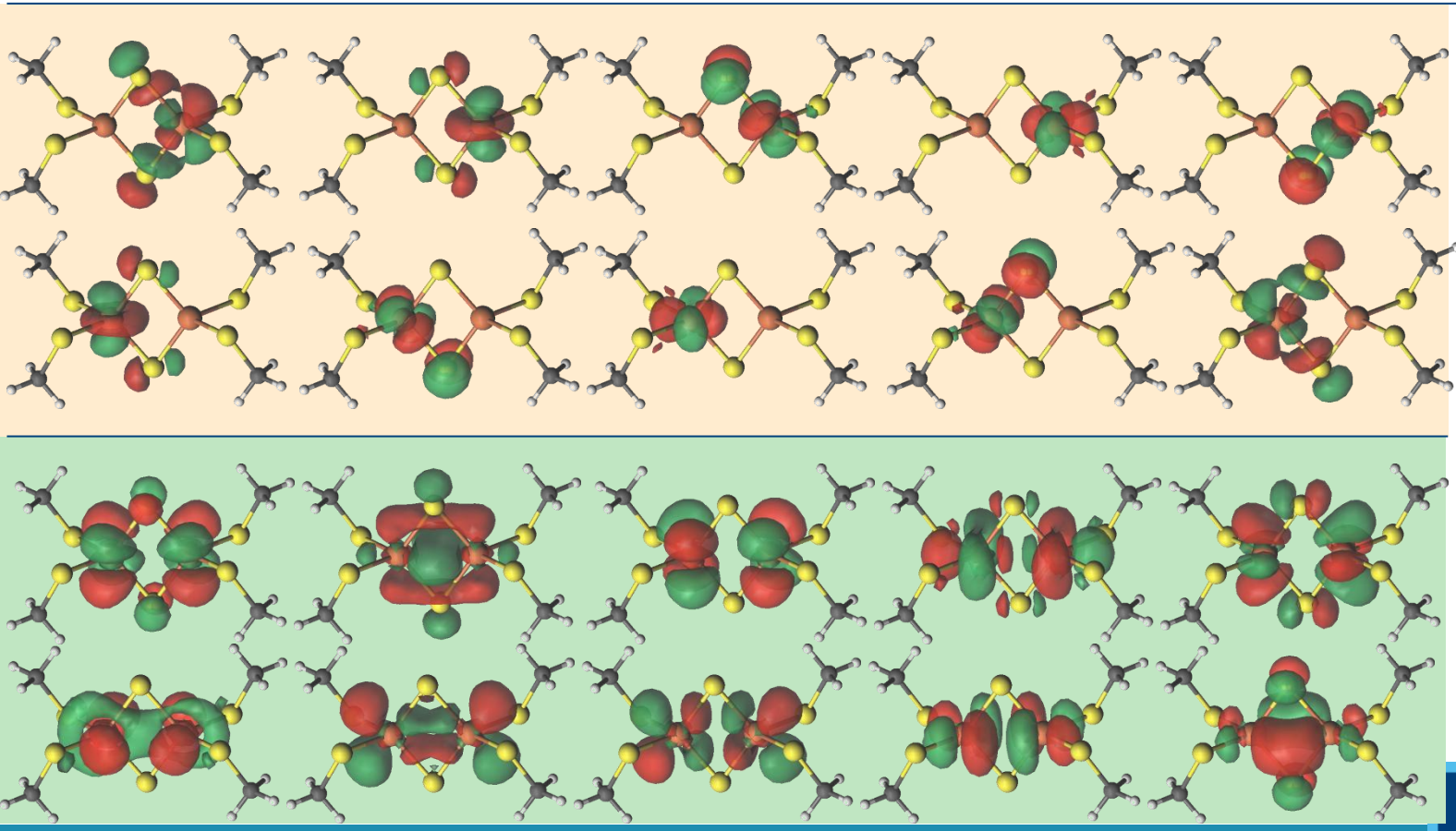
Active space of $[Fe_2S_2(SCH_3)_4]^{2-}$



CAS(10,20)