Supporting information for: OpenMolcas: From Source Code to Insight

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Contents

Stochastic-CASSCF in Action

A test case is described here to show how to prepare OpenMolcas and NECI inputs to perform Stochastic-CASSCF calculations. In the OpenMolcas input the `NECI` keyword is necessary (within the RASSCF module) to enable the FCIQMC as CI eigensolver. By default the *uncoupled* mode is used, which is available in a standard compilation of OpenMolcas (the user is responsible to download and compile NECI program externally). When OpenMolcas is compiled with the embedded NECI (as a git submodule), the input keyword `EMBD` switches to the *embedded* mode. The keyword `DMPO` is used to generate the `DUMPFILE` related to the chosen active space and input orbitals (the ones linked to the INPORB). The keywords for controlling the NECI run from OpenMolcas are chosen to match as closely as possible the corresponding ones in NECI. The keyword `TOTAlwalkers` sets the target number of walkers. The use of the `DEFInedet` keyword is also adviced to set an initial reference determinant for the FCIQMC dynamics. It is an array of integers indicating the occupied alpha and beta spin-orbitals in the MO orbitals as ordered in the `INPORB` file. If the population on the user specified reference determinant is reduced with respect to some other determinant within a given ratio, the reference determinant is automatically changed by the NECI program. The keyword `RDMSamplingiters` defines the number of iterations for accumulating RMDs. The keyword `CALCrdmonfly` takes two integers: the first entry specifies equilibration delay before RDM sampling is started, the second entry is the period for averaging RDM and RDM energy. Other keywords are optional.

```
&RASSCF
  spin
```

```
    1
  Symmetry
    1
  nactel
    26 0 0
  inactive
    20 17 17 14 0 0 0 0
  ras2
     0  0  0  0 7 6 6 5
  * DMPOnly
      * This will generate the DMPFILE and quit OpenMolcas
  NECI
      * It enables FCIQMC as CI eigensolver
  * EMBD
      * This keyword would allow to run in embedded mode, which requires compilation
          ↪ of OpenMolcas with -DNECI=ON.
      * For active spaces correlating more than 20 electrons and 20
      * orbitals it is recommended to use the decoupled Stochastic-CASSCF mode.
    totalwalkers = 5000000
      * Walker population will grow until this selected walker population target.
          ↪ Larger value ensure better CI convergence.
    nmcyc = 200000
      * Total number of FCIQMC iterations. The convergence of the FCIQMC method
          ↪ varies from system to system.
    rdmsamplingiters = 5000
      * Number of iterations during which RDMs are sampled
    calcrdmonfly = 100000  1000
      * First entry specifies equilibration delay before RDM sampling is started.
      * Second entry is the period for averaging RDM and RDM energy.
```

Listing S1: A possible OpenMolcas input for the porphyrin molecule within the D_{2h} point group.

```
System read
  electrons  26
  nonuniformrandexcits 4ind-weighted
  nobrillouintheorem
endsys
calc
  methods
    method vertex fcimc
  endmethods
  totalwalkers 5000000
  shiftdamp 0.02
  nmcyc     200000
  stepsshift 10
  proje-changeref 1.2
  truncinitiator
  addtoinitiator 3
  allrealcoeff
  realspawncutoff 0.30
  jump-shift
  tau 0.01 search
  max-tau 0.02
  maxwalkerbloom 1
  memoryfacspawn 4.0
  memoryfacpart 5.0
  time 2000
  startsinglepart 10
  semi-stochastic 1000
  pops-core 10000
  rdmsamplingiters 5000
endcalc
logging
  printonerdm
  print-spin-resolved-RDMS
  hdf5-pops
  calcrdmonfly  3  100000  1000
endlog
end
```

Listing S2: List of relevant input keywords used by the FCIQMC program.

DMRG-CASPT2 Input Example

In listing S3, we present an input example to perform a geometry optimization calculation of benzene using DMRG-CASPT2 numerical gradients on a 12-core (24 threads) CPU. In the RASSCF module, the keyword DMRG specifies the maximum number of renormalized states (or virtual bond dimension m) in each microiteration. With the keyword `3RDM`, the three-particle and Fock matrix contracted with the four-particle reduced density matrices (3-RDM and F.4-RDM) are evaluated. In the CASPT2 module, the keyword `CHEMps2` activates the DMRG-CASPT2 calculation and OpenMolcas will skip the calculations of the reduced density matrices. Note that only state-specific calculations are supported.

Because the effective number of displacements in this example is 12, we used `MOLCAS_NPROCS=12`. The number of CheMPS2 threads can be set using the environment variable `OMP_NUM_THREADS`.

```
>> export MOLCAS_NPROCS=12

&GATEWAY
 Coord = 12

  C     1.21172447   0.69959384   0.00000000
  C     0.00000000  -1.39919781   0.00000000
  C    -1.21172447   0.69959384   0.00000000
  C     1.21172447  -0.69959384   0.00000000
  C    -1.21172447  -0.69959384   0.00000000
  C     0.00000000   1.39919781   0.00000000
  H     2.15120407   1.24196780   0.00000000
  H     0.00000000  -2.48402224   0.00000000
  H    -2.15120407   1.24196780   0.00000000
  H     2.15120407  -1.24196780   0.00000000
  H    -2.15120407  -1.24196780   0.00000000
  H     0.00000000   2.48402224   0.00000000
 Basis = ANO-RCC-VDZP

>>> Do while

&SEWARD
 Medium Cholesky

>> export OMP_NUM_THREADS=12
&RASSCF
 Spin = 1
 Symmetry = 1
 NActEl = 6 0 0
 Inactive = 6 4 5 3 0 0 0 0
 RAS2     = 0 0 0 0 2 1 2 1
 LumOrb
 DMRG = 1000
 3RDM

&CASPT2
 Multistate = 1 1
 Imaginary = 0.1
 CHEMps2

>> export OMP_NUM_THREADS=2
&SLAPAF

>>> End do
```

Listing S3: Geometry optimization of benzene using DMRG-CASPT2 numerical gradients.

QCMaquis Input Examples

Listings S4 to S6 provide input examples for DMRG-SCF, MPSSI and DMRG-NEVPT2 calculations performed with the OpenMOLCAS–QCMaquis interface. For more information and a detailled documentation, the reader may consult the QCMaquis interface manual (https://scine.ethz.ch/static/download/qcmaquis_manual.pdf).

In listing S4, the DMRGSCF module is employed to drive the DMRG-SCF optimization with the keyword `ActiveSpaceOptimizer=QCMaquis`. Its input is similar to the input of the RASSCF module, but contains an additional `DMRGSettings...EndDMRGSettings` block. Two settings are mandatory to perform a DMRG calculation, namely the maximum bond dimension specified in the `max_bond_dimension` option and the maximum number of sweeps, denoted `nsweeps`. Non DMRG-specific options (corresponding to the "old-style" RASSCF input) are specified in the `OOptimizationSettings` block and are otherwise identical to the RASSCF input for an analogous CASSCF calculation.

```
&GATEWAY
 coord = 2
  Angstrom
 N       0.000000  0.000000  -0.54880
 N       0.000000  0.000000   0.54880
 Basis = cc-pVDZ

&SEWARD

&SCF

&DMRGSCF
 ActiveSpaceOptimizer = QCMaquis
 DMRGSettings
  nsweeps            = 4
  max_bond_dimension = 100
 EndDMRGSettings
 OOptimizationSettings
  inactive = 2 0 0 0 2 0 0 0
  RAS2     = 1 1 1 0 1 1 1 0
  linear
 EndOOptimizationSettings
```

Listing S4: MRG-SCF optimization of the ground state of N_2, with a (6,6) active space.

In listing S5, we show an example of MPSSI input. First, we perform a singlet and a triplet DMRG-SCF optimization with the DMRGSCF module. We save the HDF5 output files of the singlet and triplet calculation to prevent them from being overwritten, and, additionally, save also the QCMaquis MPS, which is stored in a separate folder `$Project.checkpoint_state.0.h5`. The information about the QCMaquis checkpoint folder name which is required for the MPSSI calculation is stored in the DMRGSCF HDF5 file `$Project.dmrgscf.h5`, but as the QCMaquis checkpoint folder has been renamed, the new name must be stored in the DMRGSCF HDF5 file too. This is accomplished with a call to the `qcm_checkpoint_rename.py` script. Finally, MPSSI is run, with an input identical to a RASSI input.

```
* CH2 triplet-singlet spin-orbit couplings with MPS-SI
```

```
&GATEWAY
 Coord = 3
  CH2 Triplet coordinates in Angstrom
 C 0.000000 0.000000 0.000000
 H 0.000000 0.000000 1.077500
 H 0.784304 0.000000 -0.738832
 Basis = ANO-RCC-MB
 Group = Nosym
 AMFI
 ANGMOM = 0.0 0.0 0.0

&SEWARD

** perform a triplet calculation
&DMRGSCF
 ActiveSpaceOptimizer = QCMaquis
 DMRGSettings
  max_bond_dimension = 1024
  nsweeps = 10
 EndDMRGSettings
 OOptimizationSettings
  Spin = 3
  Inactive = 1
  Ras2 =6
  NActEl = 6 0 0
 EndOOptimizationSettings

* save triplet JobIph and QCMaquis checkpoint files
>> COPY $Project.JobIph JOBOLD
>> COPY $Project.dmrgscf.h5 $Project.trip.h5
>> EXEC mv $CurrDir/$Project.checkpoint_state.0.h5
    ↪ $CurrDir/$Project.trip.checkpoint_state.0.h5
>> EXEC $MOLCAS/pytools/qcm_checkpoint_rename.py $Project.trip.h5 -q

* perform a singlet calculation
&DMRGSCF
 ActiveSpaceOptimizer = QCMaquis
 DMRGSettings
  max_bond_dimension = 1024
  nsweeps = 10
 EndDMRGSettings
 OOptimizationSettings
  Spin = 1
  Inactive = 1
  Ras2 = 6
  NActEl = 6,0,0
  JobIph
 EndOOptimizationSettings

* save singlet JobIph and QCMaquis checkpoint files
>> COPY $Project.dmrgscf.h5 $Project.sing.h5
>> EXEC mv $CurrDir/$Project.checkpoint_state.0.h5
    ↪ $CurrDir/$Project.sing.checkpoint_state.0.h5
>> EXEC $MOLCAS/pytools/qcm_checkpoint_rename.py $Project.sing.h5 -q

* run MPSSI
&MPSSI
 Nrof
 2 1 1
 1
 1
 File
 2
 $Project.trip.h5
 $Project.sing.h5
 EJob
 SOCoupling
 0.0001
 Spin
```

Listing S5: Spin–orbit couplings calculation with MPSSI between the lowest singlet and triplet state of methylene for a (6,6) active space.

Listing S6 shows a DMRG-NEVPT2 example. The DMRGSCF module gains two additional options, `NEVPT2Prep`, which prepares a NEVPT2 calculation, and `EvRDM`, which explicitly evaluates the four-particle reduced density matrix (4-RDM). For active spaces larger than 10–11 orbitals, an external distributed parallel 4-RDM evaluation, as described in the QCMaquis interface manual is recommended. Afterwards, a MOTRA call with the HDF5 option is required, and, if Cholesky decomposition of two-electron integrals is employed, also options `CTOnly` and `Kpq`. We conclude the input with the call to the NEVPT2 module.

```
&GATEWAY
 Coord = 3
  CH2 Triplet coordinates in Angstrom
 C      0.000000  0.000000  0.000000
 H      0.000000  0.000000  1.077500
 H      0.784304  0.000000 -0.738832
 Basis = cc-pVTZ
 Group = NoSym
 RICD
 CDThreshold = 1.0e-7

&SEWARD

&DMRGSCF
 ActiveSpaceOptimizer = QCMaquis
 DMRGSettings
  max_bond_dimension = 128
  nsweeps = 5
 EndDMRGSettings
 OOptimizationSettings
  Spin = 3
  Inactive = 1
  Ras2 = 6
  NActEl = 6 0 0
  NEVPT2Prep
  EvRDM
 EndOOptimizationSettings

&MOTRA
 Frozen = 0
 CTOnly
 Kpq
 HDF5

&NEVPT2
```

Listing S6: A DMRG-SC-NEVPT2 and DMRG-PC-NEVPT2 calculation of the lowest triplet state in methylene with a (6,6) active space.

Spin State Energetics of Iron(II) Porphyrin with OpenMolcas–CheMPS2

Computational Details of FeP

- Active space: CAS(8,11) and CAS(26,27), see fig. S1.
- Cartesian coordinates from PBE0/def2-TZVP, see tables S2 and S3.

- Symmetry: D_{2h}.
- Basis set: ANO-RCC, contractions are [7s6p5d3f2g1h] for Fe, [4s3p2d1f] for C, N; and [3s1p] for H.
- Cholesky decomposition technique for the two-electron integrals with a threshold of 10^{-6} a u
- Scalar relativistic effect with standard second-order Douglas–Kroll–Hess (DKH) Hamiltonian.
- DMRG calculations: Fiedler orbital ordering, perturbative noise (noise prefactor of 0.05), residual norm threshold 10^{-7} for the Davidson algorithm.
- CASPT2 calculations: standard ionization potential electron affinity (IPEA) shift of 0.25 E_h, imaginary shift of 0.1 E_h. All valence electrons (but not the Fe 3s and 3p electrons) were correlated.

Table S1: Total energies (in E_h) obtained from CASSCF/CASPT2 and DMRG/CASPT2[$m = 10000$].

	CASSCF[a]	CASPT2[a]	DMRG[b]	DMRG-CASPT2[b]
$^3A_{2g}$	−2254.391 028	−2258.538 810	−2254.556 156	−2258.506 297
$^5A_{1g}$	−2254.417 218	−2258.546 312	−2254.582 257	−2258.513 704

[a]CAS(8,11).
[b]CAS(26,27).

Active Orbitals of FeP

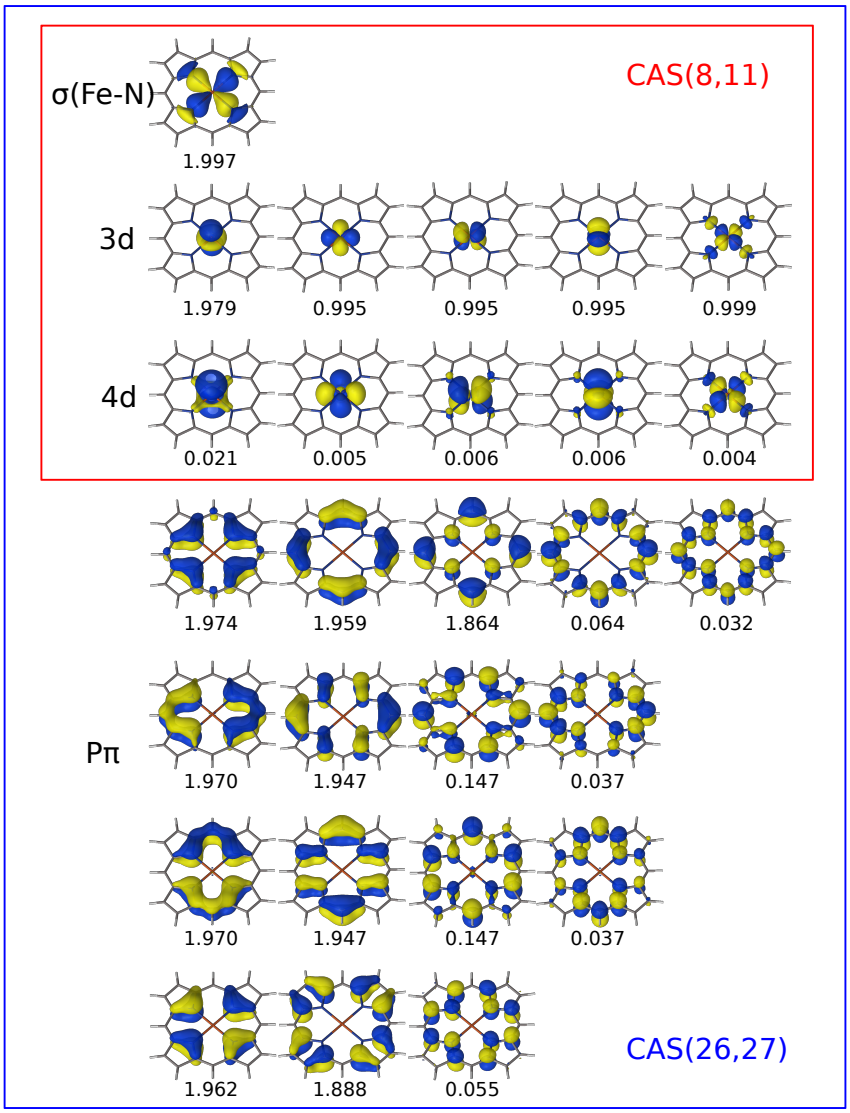


Figure S1: Active natural orbitals and natural orbital occupation numbers of $^5A_{1g}$ FeP.

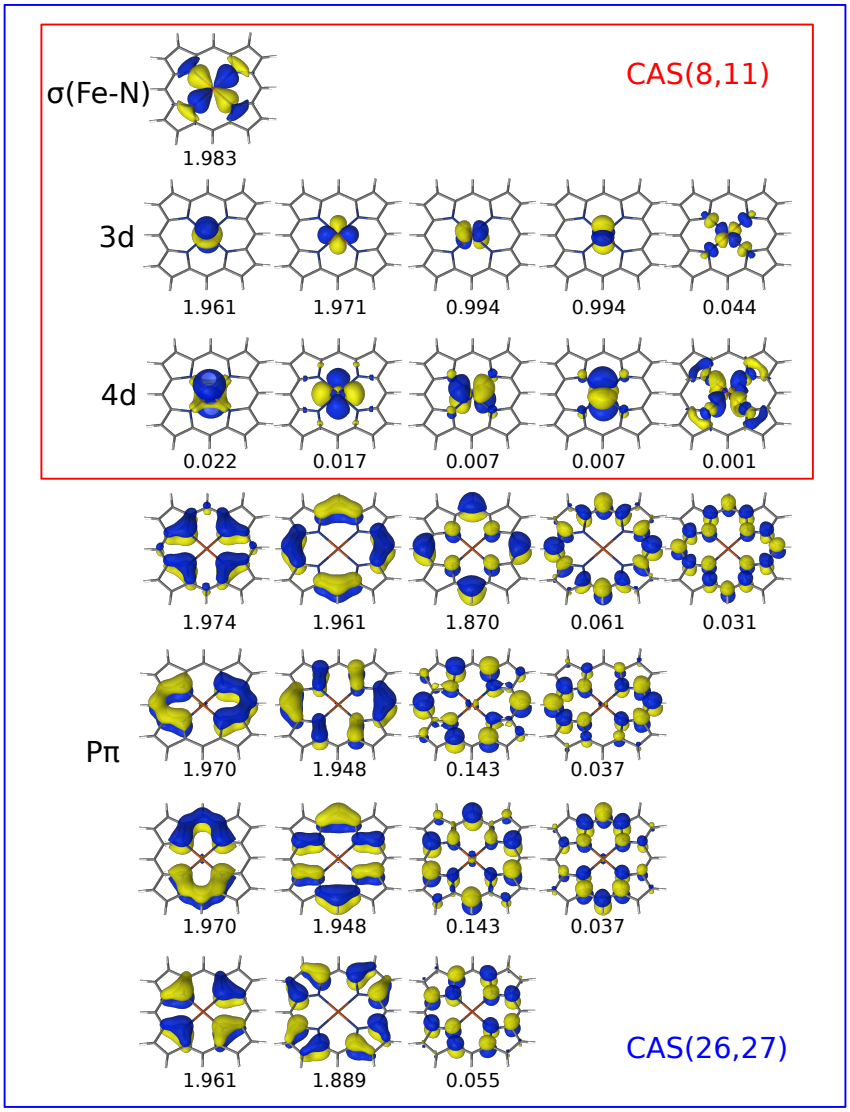


Figure S2: Active natural orbitals and natural orbital occupation numbers of $^3A_{2g}$ FeP.

Cartesian coordinates of FeP

Table S2: PBE0/def2-TZVP structure (in Å) of FeP $^3A_{2g}$.

37 atoms			
Fe	0.000 000	0.000 000	0.000 000
N	1.406 727	1.406 727	0.000 000
N	−1.406 727	1.406 727	0.000 000
N	1.406 727	−1.406 727	0.000 000
N	−1.406 727	−1.406 727	0.000 000
C	0.000 000	3.400 142	0.000 000
C	0.000 000	−3.400 142	0.000 000
C	3.400 142	0.000 000	0.000 000
C	−3.400 142	0.000 000	0.000 000
C	2.483 151	3.440 698	0.000 000
C	−2.483 151	3.440 698	0.000 000

C	2.483 151	−3.440 698	0.000 000
C	−2.483 151	−3.440 698	0.000 000
C	3.440 698	2.483 151	0.000 000
C	−3.440 698	2.483 151	0.000 000
C	3.440 698	−2.483 151	0.000 000
C	−3.440 698	−2.483 151	0.000 000
C	1.222 770	2.760 387	0.000 000
C	−1.222 770	2.760 387	0.000 000
C	1.222 770	−2.760 387	0.000 000
C	−1.222 770	−2.760 387	0.000 000
C	2.760 387	1.222 770	0.000 000
C	−2.760 387	1.222 770	0.000 000
C	2.760 387	−1.222 770	0.000 000
C	−2.760 387	−1.222 770	0.000 000
H	0.000 000	4.482 672	0.000 000
H	0.000 000	−4.482 672	0.000 000
H	4.482 672	0.000 000	0.000 000
H	−4.482 672	0.000 000	0.000 000
H	4.513 532	2.603 261	0.000 000
H	−4.513 532	2.603 261	0.000 000
H	4.513 532	−2.603 261	0.000 000
H	−4.513 532	−2.603 261	0.000 000
H	2.603 261	4.513 532	0.000 000
H	−2.603 261	4.513 532	0.000 000
H	2.603 261	−4.513 532	0.000 000
H	−2.603 261	−4.513 532	0.000 000

Table S3: PBE0/def2-TZVP structure (in Å) of FeP $^5A_{1g}$.

37 atoms			
Fe	0.000 000	0.000 000	0.000 000
N	1.451 412	1.451 412	0.000 000
N	−1.451 412	1.451 412	0.000 000
N	1.451 412	−1.451 412	0.000 000
N	−1.451 412	−1.451 412	0.000 000
C	0.000 000	3.417 223	0.000 000
C	0.000 000	−3.417 223	0.000 000
C	3.417 223	0.000 000	0.000 000
C	−3.417 223	0.000 000	0.000 000
C	2.513 686	3.473 694	0.000 000
C	−2.513 686	3.473 694	0.000 000
C	2.513 686	−3.473 694	0.000 000
C	−2.513 686	−3.473 694	0.000 000
C	3.473 694	2.513 686	0.000 000
C	−3.473 694	2.513 686	0.000 000
C	3.473 694	−2.513 686	0.000 000
C	−3.473 694	−2.513 686	0.000 000
C	1.245 363	2.796 785	0.000 000

C	−1.245 363	2.796 785	0.000 000
C	1.245 363	−2.796 785	0.000 000
C	−1.245 363	−2.796 785	0.000 000
C	2.796 785	1.245 363	0.000 000
C	−2.796 785	1.245 363	0.000 000
C	2.796 785	−1.245 363	0.000 000
C	−2.796 785	−1.245 363	0.000 000
H	0.000 000	4.500 641	0.000 000
H	0.000 000	−4.500 641	0.000 000
H	4.500 641	0.000 000	0.000 000
H	−4.500 641	0.000 000	0.000 000
H	4.545 432	2.645 246	0.000 000
H	−4.545 432	2.645 246	0.000 000
H	4.545 432	−2.645 246	0.000 000
H	−4.545 432	−2.645 246	0.000 000
H	2.645 246	4.545 432	0.000 000
H	−2.645 246	4.545 432	0.000 000
H	2.645 246	−4.545 432	0.000 000
H	−2.645 246	−4.545 432	0.000 000

Convergence and Performance

In fig. S3, we present the error of the quintet–triplet relative energy calculated at different m values, using the data at $m = 10000$ as a reference. The results show that both DMRG-SCF and DMRG-CASPT2 results converge quickly with m. Even at the smallest m value ($m = 2000$), the errors do not exceed 0.5 kcal/mol (2 kJ/mol). At $m = 5000$–6000, the relative energies have already converged to within 0.1 kcal/mol (0.4 kJ/mol).

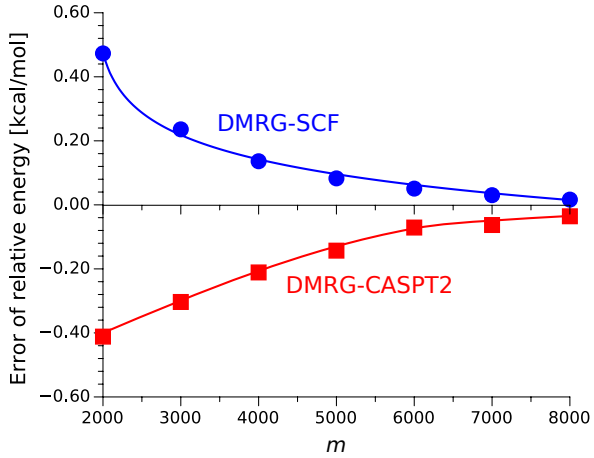


Figure S3: Error of the ${}^3A_{2g}-{}^5A_{1g}$ relative energy ΔE calculated at different m. The results at $m = 10000$ are used as references, ΔE(DMRG-SCF) $= -68.53$ kJ/mol, ΔE(DMRG-CASPT2) $= -19.46$ kJ/mol. All valence electrons (but not Fe (3s, 3p) were correlated in the PT2 treatment.

In fig. S4, we report the computing time of the F.4-RDM and 3-RDM, the most time consuming part of these calculations, as well as the required computational resources (memory and temporary disk space). All calculations were done on a single node with an

Intel(R) Xeon(R) CPU 6140 @ 2.3 GHz, 768 GB of memory, and 4 MPI processes. The computational complexity of the DMRG-CASPT2 calculations and the required computer resources grow quickly, though polynomially, with the number of active orbitals n and number of renormalized states m.[S1,S2] At $m = 10000$, the calculations demand almost 120 hours computing time for the F.4-RDM (fig. S4(a)), a very large amount of RAM (up to 700 GB) and modest temporary disk space (see fig. S4(b)). However as shown above, one does not have to raise m to 10000 in order to achieve converged results. In the present case, $m = 5000$–6000, requiring only moderate computational resources, already provides converged results to $\sim$0.4 kJ/mol.

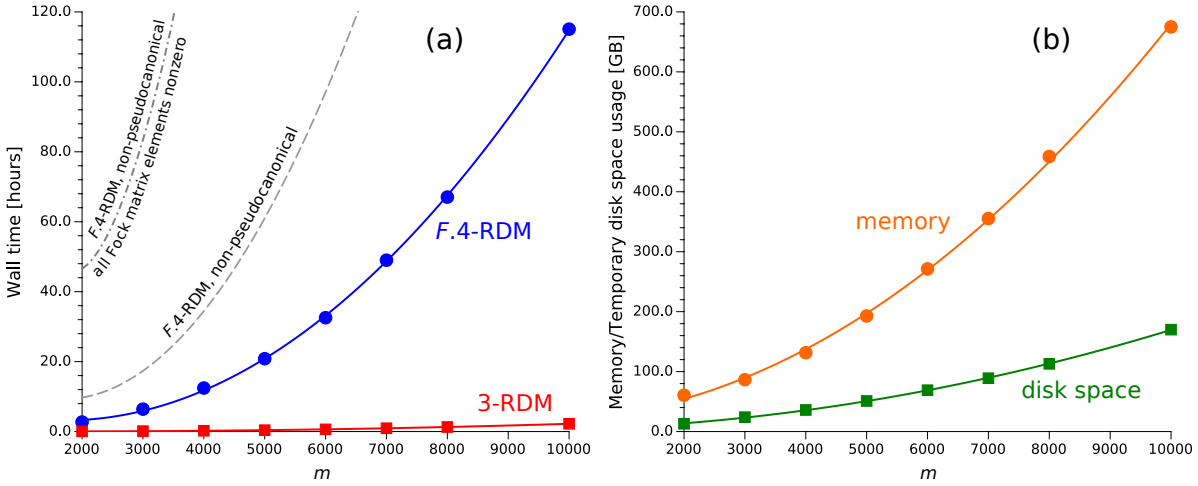


Figure S4: (a) Computing time (in hours) of the reduced density matrices (3-RDM and F.4-RDM) using pseudocanonical orbital basis and (b) computational resources needed (memory and disk storage) (in GB) at different number of renormalized states m. The data in gray lines are estimated based on the number of nonzero Fock matrix elements: dashed line – block diagonal Fock matrix; dash-dotted line – all Fock matrix elements are nonzero.

Finally, we illustrate the advantage of using the pseudocanonical orbital basis (diagonal Fock matrix) in the calculation of the F.4-RDM (fig. S4(a)). The wall-time of F.4-RDM is proportional to the number of nonzero Fock matrix elements.

For pseudocanonical orbitals, it only scales as $\mathcal{O}(n^5m^3 + n^7m^2)$ (with n the number of active orbitals, see also fig. S5) and is almost 3 times smaller than using a nonpseudocanonical orbital basis (block diagonal Fock matrix, gray dashed line). Without molecular symmetry, all Fock matrix elements have to be considered (gray dash-dotted line), and we expect a significantly longer wall-time to calculate the F.4-RDM.

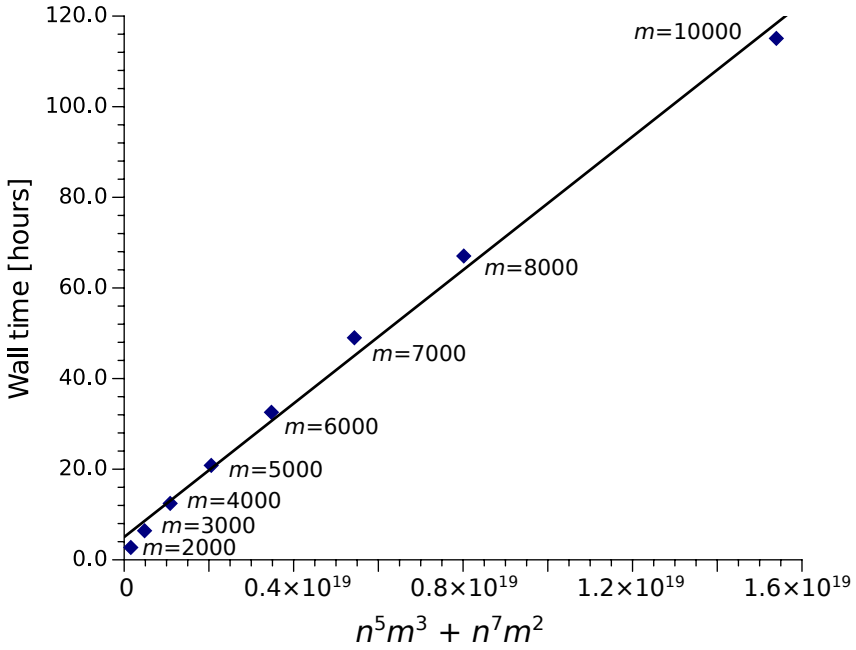


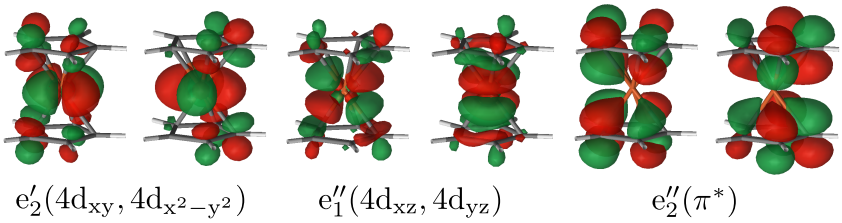
Figure S5: Computing time (in hours) for the $F.4$-RDM as a function of $n^5m^3 + n^7m^2$, $n = 27$.

Equilibrium Structure of Ferrocene

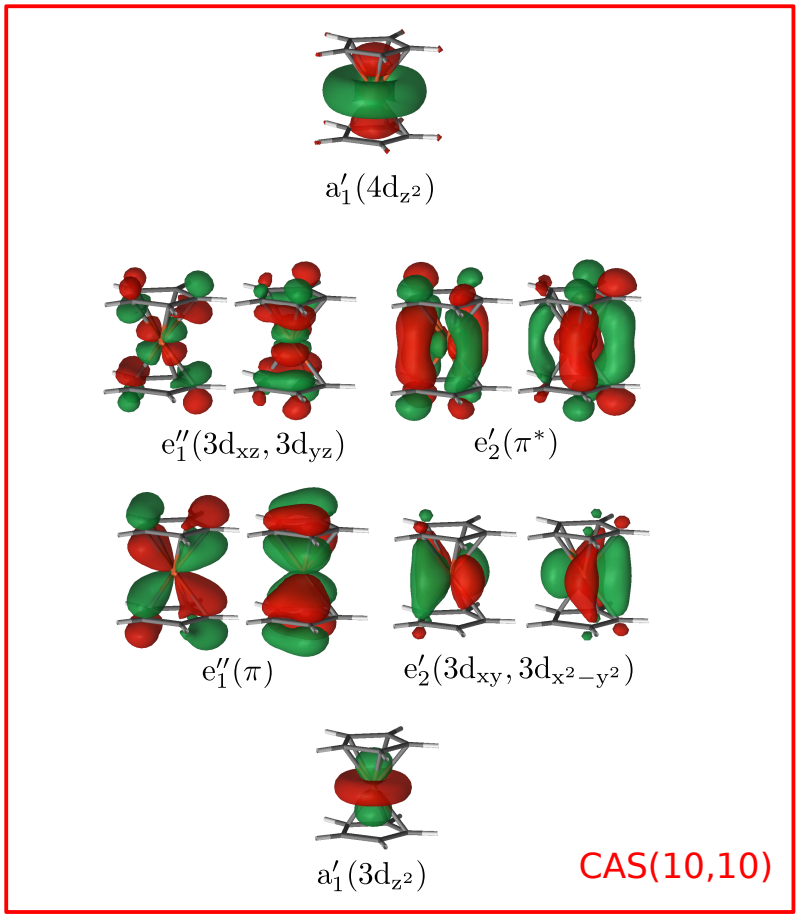
Computational Details

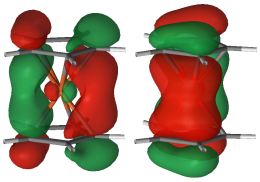
- Active space: CAS(10,10) and CAS(14,18), see fig. S6.
- Cartesian coordinates optimized with CASPT2 and DMRG-CASPT2, see tables S4 and S5.
- Symmetry: C_{2v}.
- Basis set: cc-pwCVTZ, is the same as used before in the work of Harding et al.[S3]
- Cholesky decomposition technique for the two-electron integrals with a threshold of $10^{-6}\,E_\mathrm{h}$
- DMRG calculations: $m = 1000$, Fiedler orbital ordering, perturbative noise (noise prefactor of 0.05), residual norm threshold 10^{-4} for the Davidson algorithm.
- CASPT2 calculations: standard ionization potential electron affinity (IPEA) shift of $0.25\,E_\mathrm{h}$, imaginary shift of $0.1\,E_\mathrm{h}$. All 96 electrons were correlated, which was used in the work of Harding et al.[S3]
- NUMERICAL_GRADIENT module: the number of displacements is 32.
- SLAPAF module: Convergence criteria with respect to the energy change and the norm of the gradient are $1.0 \times 10^{-5}\,E_\mathrm{h}$ and $1.0 \times 10^{-3}\,E_\mathrm{h}/a_0$, respectively.

Active Orbitals of Ferrocene



$e_2'(4d_{xy}, 4d_{x^2-y^2})$ $e_1''(4d_{xz}, 4d_{yz})$ $e_2''(\pi^*)$





$e_1'(\pi)$

Figure S6: Active natural orbitals of ferrocene.

Cartesian Coordinates of Ferrocene

Table S4: Equilibrium structure (in Å) of ferrocene calculated with CASPT2.

21 atoms			
Fe	0.000 000 00	−0.000 828 75	0.000 000 00

C	0.000 000 00	1.212 802 72	1.609 557 91
C	1.153 937 51	0.374 399 76	1.609 711 90
C	0.713 185 36	−0.982 181 37	1.609 969 93
H	0.000 000 00	2.289 321 49	1.596 057 80
H	2.177 709 32	0.707 131 34	1.595 898 50
H	1.345 932 05	−1.853 097 25	1.596 418 61
C	0.000 000 00	1.212 802 72	−1.609 557 91
C	−1.153 937 51	0.374 399 76	−1.609 711 90
C	1.153 937 51	0.374 399 76	−1.609 711 90
C	−1.153 937 51	0.374 399 76	1.609 711 90
C	−0.713 185 36	−0.982 181 37	−1.609 969 93
C	0.713 185 36	−0.982 181 37	−1.609 969 93
C	−0.713 185 36	−0.982 181 37	1.609 969 93
H	0.000 000 00	2.289 321 49	−1.596 057 80
H	−2.177 709 32	0.707 131 34	−1.595 898 50
H	2.177 709 32	0.707 131 34	−1.595 898 50
H	−2.177 709 32	0.707 131 34	1.595 898 50
H	−1.345 932 05	−1.853 097 25	−1.596 418 61
H	1.345 932 05	−1.853 097 25	−1.596 418 61
H	−1.345 932 05	−1.853 097 25	1.596 418 61

Table S5: Equilibrium structure (in Å) of ferrocene calculated with DMRG-CASPT2.

21 atoms			
Fe	0.000 000 00	−0.000 836 82	0.000 000 00
C	0.000 000 00	1.212 757 57	1.614 880 82
C	1.154 098 20	0.373 992 05	1.615 439 11
C	0.713 137 28	−0.982 183 00	1.615 400 35
H	0.000 000 00	2.288 729 50	1.599 915 55
H	2.177 165 70	0.707 425 66	1.598 886 43
H	1.345 890 32	−1.852 337 01	1.598 237 07
C	0.000 000 00	1.212 757 57	−1.614 880 82
C	−1.154 098 20	0.373 992 05	−1.615 439 11
C	1.154 098 20	0.373 992 05	−1.615 439 11
C	−1.154 098 20	0.373 992 05	1.615 439 11
C	−0.713 137 28	−0.982 183 00	−1.615 400 35
C	0.713 137 28	−0.982 183 00	−1.615 400 35
C	−0.713 137 28	−0.982 183 00	1.615 400 35
H	0.000 000 00	2.288 729 50	−1.599 915 55
H	−2.177 165 70	0.707 425 66	−1.598 886 43
H	2.177 165 70	0.707 425 66	−1.598 886 43
H	−2.177 165 70	0.707 425 66	1.598 886 43
H	−1.345 890 32	−1.852 337 01	−1.598 237 07
H	1.345 890 32	−1.852 337 01	−1.598 237 07
H	−1.345 890 32	−1.852 337 01	1.598 237 07

Computational Details for the DMRG-NEVPT2 Example

The Cartesian coordinates for all three states were the same and were taken from ref. S4. The all-electron ANO-RCC[S5] basis set with the valence quadruple-zeta polarized (ANO-RCC-VQZP) contraction scheme was chosen for the Fe atom and the valence double-zeta polarized (ANO-RCC-VDZP) contraction scheme for other atoms, resulting in a total of 1595 basis functions. Two-electron integrals were calculated with the atomic compact Cholesky decomposition approach (acCD)[S6–S8] with a decomposition threshold of 10^{-4} E_h. Scalar-relativistic effects were accounted for through the second-order scalar-relativistic Douglas–Kroll–Hess one-electron Hamiltonian.[S9–S11]

Multiconfiguration Pair-Density Functional Theory. Input examples

General Input for Single-Point MC-PDFT Calculations

MC-PDFT calculation of the N_2 molecule using tPBE, ftPBE, and tOPBE:

```
&SEWARD
 Coord = 2
  Angstrom
  N 0.00 0.00 -0.55
  N 0.00 0.00 0.55
 Basis = cc-pVDZ
 Group = XY YZ XYZ
 NoDeleted
 Grid input
  Grid = ultrafine
 End of grid input

&SCF

&RASSCF
 Linear
 nAct = 10 0 0
 Inactive = 2 0 0 0 2 0 0 0
 RAS2 = 1 1 1 0 1 1 1 0

>> foreach DFT in (TPBE, FTPBE, TOPBE)
&MCPDFT
 KSDFT = $DFT
>> enddo
```

SS-CAS-PDFT Gradient

Geometry optimization of the N_2 molecule using SS-CAS-PDFT with the tPBE on-top functional:

```
&SEWARD
 coord = 2
  Angstrom
  N 0.0 0.0 0.60
  N 0.0 0.0 -0.60
 Basis
 N.ANO-RCC-VDZP
 Group
```

```
 Full
 NoDeleted
 Grid input
 Grid=Ultrafine
 End of grid input
 NoCD

&RASSCF &END
 Linear
 nActEl = 5 0 0
 Frozen = 0 0 0 0 0 0 0 0
 Inactive = 2 0 0 0 2 0 0 0
 RAS2 = 3 3 3 0 1 1 1 0
 Deleted = 0 0 0 0 0 0 0 0
 Symmetry = 1
 Spin = 2

&MCPDFT
 KSDFT = TPBE
 Gradient

&ALASKA
```

Scaling Exchange and Correlation Terms in MC-PDFT and KS-DFT

Geometry optimization of the N_2 molecule using SS-CAS-PDFT with an HLE-type functional constructed from scaling the exchange term and the correlation term of tPBE by 1.25 and 0.5, respectively.

```
&GATEWAY
 Coord = 2
  Angstrom
  N 0.0 0.0 0.60
  N 0.0 0.0 -0.60
 Basis = N.ANO-RCC-VDZP
 Group = Full

>> do while

&SEWARD
 NoDeleted
 Grid input
  Grid = ultrafine
 End of grid input

&RASSCF
 Linear
 nActEl = 5 0 0
 Frozen = 0 0 0 0 0 0 0 0
 Inactive = 2 0 0 0 2 0 0 0
 RAS2 = 3 3 3 0 1 1 1 0
 Deleted = 0 0 0 0 0 0 0 0
 Symmetry = 1
 Spin = 2

&MCPDFT
 KSDFT = TPBE
 DfCf = 1.25 0.5
 Gradient

&SLAPAF

>> enddo
```

Kohn-Sham density functional theory calculation of the N_2 molecule using the B3LYP functional with the correlation terms scaled by a factor of 0.8.

```
&SEWARD
 coord = 2
  Angstrom
  N 0.0 0.0 0.60
  N 0.0 0.0 -0.60
 Basis = N.ANO-RCC-VDZP

&SCF
 KSDFT = B3LYP
 DfCf = 1.0 0.8
```

SI-PDFT

The following is an example SI-PDFT run for the dissociation of LiF:

```
>> export XX=2.9

>> foreach L in ( 1 .. 30 )
>> eval XX = $XX + 0.1

&SEWARD
 Coord = 2
  Angstrom
  F 0.000 0.000 $XX
  Li 0.000 0.000 0.00
 Group = Full
 Basis set = Li.cc-pVDZ,F.aug-cc-pVDZ
 Grid input
  Grid = Ultrafine
 End of grid input

&SCF

>> COPY $Project.ScfOrb INPORB

* This is the first RASSCF run. This is the multistate calculation.
* The JOBIPH generated by this run must be copied to JobIph01.

&RASSCF
 Linear
 LumOrb
 nActEl = 6 0 0
 Inactive = 3 0 0 0
 RAS2 = 4 2 0 2
 Symmetry = 1
 Spin = 1
 OrbListing = All
 PrWf = 0.000001
 CIRoot = 2 2 1

>> COPY $Project.JobIph $Project.JobIph01
>> RM $Project.JobIph

* This is the second RASSCF run. This is the single state used as the reference
* in performing the GS-like orthogonalization. The JOBIPH generated by this run must
* be copied to JobIph02.

&RASSCF
 Linear
 nActEl = 6 0 0
 Inactive = 3 0 0 0
 RAS2 = 4 2 0 2
 Symmetry = 1
 Spin = 1
 OrbListing = All
```

```
 PrWf = 0.000001

>> COPY $Project.JobIph $Project.JobIph02
>> RM $Project.JobIph

* This is the first RASSI call. It generates the new SI states and
* creates a JOBIPH file called JOBGS. This first RASSI run requires the
* GSORthog keyword.

&RASSI
 NrOf = 2 2 1
  1 2
  1
 IphN = JobIph01; JobIph02
 GSORthog

* The JOBGS must be copied to JobIph prior to the MC-PDFT calculation,
* as that is where the information for the MC-PDFT calculation is taken
* from.

>> COPY JOBGS $Project.JobIph

* The MC-PDFT calculation requires a few special keywords:
* GSOR toggles the generation of new density matrices
* NOGRadient is to turn off the calculation of potentials (not needed).
* Since this calculation loops over geometries, MC-PDFT thinks this might be
* a gradient calculation and will calculate potentials, unless explicitly
* prevented through the use of NOGRadient.

&MCPDFT
 KSDFT = tPBE
 GSOR
 NoGradient

>> RM $Project.JobIph01
>> RM $Project.JobIph02
>> RM $Project.JobIph

* The JOBGS (which was modified in the MCPDFT part) must be copied
* to JobIph01

>> COPY JOBGS $Project.JobIph01

*The SECOnd keyword must be used in the second call to RASSI

&RASSI
 NROF = 1 2
  1 2
 IphN = JobIph01
 SECOnd

>> RM JOBGS

>> enddo
```

General Input for a Single-Point DMRG-PDFT Calculation

```
&GATEWAY
 Coord = 2
  Angstrom
  N 0.00 0.00 -0.55
  N 0.00 0.00 0.55
 Basis = cc-pVDZ

&SEWARD
 Grid input
  Grid = Ultrafine
 End of grid input
```

```
&SCF

&DMRGSCF
 ActiveSpaceOptimizer = QCMaquis
 DMRGSettings
  nsweeps = 4
  max_bond_dimension = 100
 EndDMRGSettings
 OOptimizationSettings
  Inactive = 2 0 0 0 2 0 0 0
  RAS2 = 1 1 1 0 1 1 1 0
  Linear
 EndOptimizationSettings

&MCPDFT
 KSDFT = TPBE
```

Conical Intersection Optimization and Characterization

```
&GATEWAY
  Coord = 12
    Benzene
    C  0.00000  0.00000  0.00000
    C  1.39000  0.00000  0.00000
    C  2.03441  0.00000  1.32123
    C  1.46393 -0.93565  2.28597
    C  0.38195  0.04158  2.36298
    C -0.53215  0.04837  1.21178
    H -0.53500  0.00000 -0.92665
    H  1.98517 -0.08076 -0.88552
    H  2.99189  0.44075  1.50522
    H  2.03615 -1.24240  3.13648
    H  0.15152  0.51223  3.29587
    H -1.58992  0.00920  1.36830
  Basis = STO-3G
  Group = NoSymm
  Constraints
    E = Ediff 1 2
  Values
    E = 0.0
  End of constraints

>>> Do While

&SEWARD

>>> If (Iter = 1)
&SCF
&RASSCF
  FileOrb = $Project.scf.h5
  Charge  = 0
  NActEl  = 6
  Ras2    = 6
  CIRoot  = 2 2 1
>>> End If

&RASSCF
  FileOrb = $Project.rasscf.h5
  CIRestart
  NActEl  = 6
  CIRoot  = 2 2 1

&SLAPAF
  Tolerance = 1.0D-5

>>> End Do
```

Listing S7: Input example for optimization of a conical intersection between the two lowest singlet states of benzene.

```
    Pitch (delta_gh):                   1.56682E-01 Eh/a0
    Asymmetry (Delta_gh):               2.76223E-01
    Relative tilt (sigma=s/delta_gh):   5.97519E-01
    Tilt heading (theta_s):             1.56953E+00

    P:    4.93286E-01
    B:    9.59395E-01
    Type: peaked (P<1) bifurcating (B<1)
```

Listing S8: Characterization parameters at the converged structure from listing S7.

Setup for a Single SHARC Trajectory

This quick tutorial presents how to setup a single SHARC trajectory using OpenMolcas as quantum chemistry program. To this end, we use the interface script `$SHARC/SHARC_MOLCAS.py`, which fully supports OpenMolcas. Note that typically, SHARC trajectories are not setup manually, but using the tools of the SHARC suite. Hence, for a more complete overview over the SHARC suite, please see the manual and tutorial of SHARC at http://www.sharc-md.org/.

The files that need to be prepared and the relevant directory structure are presented in fig. S7. The contents of the files are given and explained in the following. Please be aware that the two subdirectories need to exist before SHARC can be started.

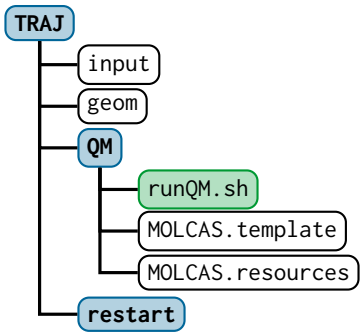


Figure S7: Input files for a SHARC dynamics simulation of a single, independent trajectory.

Input File

The SHARC input file ("`input`") contains the dynamics settings and names of additional input files (geometry, velocity, coefficients). An example is given below:

```
geomfile "geom"
veloc random 0.1

nstates 4 0 3
state 3 mch
coeff auto

ezero -94.41294549
```

```
tmax 25.000000
stepsize 0.5

surf sharc
coupling overlap
decoherence_scheme edc

grad_select
eselect 0.1
select_directly
```

The meaning of these keywords is: The geometry is read from file `geom`. The nuclear velocities are picked at random, with 0.1 eV kinetic energy per atom. Four singlet states and three triplet states will be included in the simulation (0 is the number of doublet states). The initial state is the third state (the S_2). The initial coefficients will be set automatically (the initial state will have a coefficient of 1.0, the remaining states a coefficient of zero). The diagonal elements of the Hamiltonian will be shifted by $-94.412\,945\,49\,E_\mathrm{h}$. The simulation will run for 25 fs with a 0.5 fs timestep. The SHARC formalism will be used (propagation on the diagonalized states). Nonadiabatic interactions are described with wave function overlaps. SHARC will select which gradients to compute at each time step, with a selection threshold of 0.1 eV. SHARC will select these gradients directly, without doing two quantum chemistry calculations per time step.

Geometry File

The geometry file "`geom`" contains the chemical symbols, atomic charge, x, y and z coordinates and the relative atomic masses.

```
C 6.0 +0.00000000 +0.00000000 +0.00000000 12.00000000
N 7.0 +0.00000000 +0.00000000 +2.45664494 14.00307401
H 1.0 +1.78220520 +0.00000000 -1.02895628 1.00782504
H 1.0 +1.78220520 +0.00000000 +3.55174167 1.00782504
H 1.0 -1.78220520 +0.00000000 +3.55174167 1.00782504
H 1.0 -1.78220520 +0.00000000 -1.02895628 1.00782504
```

QM Run Script

At each timestep, SHARC writes the current geometry and different keywords to the file `QM/QM.in` and then calls `runQM.sh`. After this call is finished, SHARC reads the results of the quantum chemistry calculation from `QM.out`.

In most of the cases, in `runQM.sh` simply one of the SHARC-interfaces is called:

```
cd QM
$SHARC/SHARC_MOLCAS.py QM.in >> QM.log 2>> QM.err
```

The interface will do all work necessary to produce the desired file `QM.out`.

Template File

The interface needs as additional input file giving the settings for the electronic structure calculation. The file is called "`MOLCAS.template`". It employs a simple keyword-argument structure and looks like:

```
basis cc-pVDZ
nactel 6
ras2 4
inactive 5
```

```
roots 4 0 3
method casscf
no-douglas-kroll
```

Resource File

The interface additionally needs some paths (e.g., to the OpenMolcas installation) and resource settings, both of which are read from the file "`MOLCAS.resources`".

```
molcas $MOLCAS
scratchdir $TMPDIR/
savedir ../restart/

memory 1000
ncpu 1
```

Running SHARC

With the input files prepared, the trajectory can then be started by simply executing:

```
$SHARC/sharc.x input
```

Output

SHARC produces four output files, `output.log`, `output.lis`, `output.dat` and `output.xyz`. The file `output.log` contains mainly a listing of the chosen options and the resulting dynamics settings. At higher print levels, the log file contains also information per timestep. `output.lis` contains a table with one line per timestep, giving active states, energies and expectation values. `output.dat` contains a list of all important matrices and vectors at each timestep. This information can be extracted with `data_extractor.x` to yield plottable table files. `output.xyz` contains the geometries of all timesteps, allowing visualization of the trajectory with the appropriate software (e.g., Molden).

Light–Matter Interaction

```
&GATEWAY
Title = CuCl4(-2)
Coord = 5
 CuCl4
 Cu                 0.00000000    0.00000000    0.00000000
 Cl                 2.23300000    0.00000000    0.00000000
 Cl                -2.23300000    0.00000000    0.00000000
 Cl                 0.00000000    2.26800000   -0.00000000
 Cl                 0.00000000   -2.26800000   -0.00000000
Group = NoSym
Basis = ANO-RCC-VTZP.
AngMom = 0.00 0.00 0.00
RICD

&SEWARD

&SCF
uhf; charge = -2; zspin = 1
End of input

&RASSCF
```

```
charge = -2
spin = 2
LUMORB
symmetry = 1
inactive
 46
nactel
7 0 0
ras1
0
ras2
4
ras3
0
End of input

&RASSCF
charge = -2
spin = 2
FileOrb = $Project.RasOrb
symmetry = 1
ALTER
1
1 1 46
SUPSYM
1
1 1
inactive
 45
nactel
9 1 0
ras1
1
ras2
4
ras3
0
CIROOT
5 5
1 2 3 4 5
1 0 0 0 0
End of input

>>> copy $Project.JobIph JOB001

&RASSI
Dipr = 1.0D-10
TMos
```

```
&GATEWAY
Title = CuCl4(-2)
Coord = 5
 CuCl4
 Cu                 0.00000000    0.00000000    0.00000000
 Cl                 2.23300000    0.00000000    0.00000000
 Cl                -2.23300000    0.00000000    0.00000000
 Cl                 0.00000000    2.26800000   -0.00000000
 Cl                 0.00000000   -2.26800000   -0.00000000
Group = NoSym
Basis = ANO-RCC-VTZP.
RICD

&SEWARD

&SCF
uhf; charge = -2; zspin = 1
End of input

&RASSCF
charge = -2
```

```
spin = 2
LUMORB
symmetry = 1
inactive
 46
nactel
7 0 0
ras1
0
ras2
4
ras3
0
End of input

&RASSCF
charge = -2
spin = 2
FileOrb = $Project.RasOrb
symmetry = 1
ALTER
1
1 1 46
SUPSYM
1
1 1
inactive
 45
nactel
9 1 0
ras1
1
ras2
4
ras3
0
CIROOT
5 5
1 2 3 4 5
1 0 0 0 0
End of input

>>> copy $Project.JobIph JOB001

&RASSI
NrOfJobIphs = 1
All
Dipr = 1.0D-14
SpinOrbit
KVec = 37
1.0 0.0 0.0
0.996194698 0.087155742 0.0
0.984807753 0.173648177 0.0
0.965925826 0.258819045 0.0
0.939692620 0.342020143 0.0
0.906307787 0.422618261 0.0
0.866025403 0.500000000 0.0
0.819152044 0.573576436 0.0
0.766044443 0.642787609 0.0
0.707106781 0.707106781 0.0
0.642787609 0.766044443 0.0
0.573576436 0.819152044 0.0
0.500000000 0.866025403 0.0
0.422618261 0.906307787 0.0
0.342020143 0.939692620 0.0
0.258819045 0.965925826 0.0
0.173648177 0.984807753 0.0
0.087155742 0.996194698 0.0
0.0 1.0 0.0
-0.087155742 0.996194698 0.0
```

```
-0.173648177 0.984807753 0.0
-0.258819045 0.965925826 0.0
-0.342020143 0.939692620 0.0
-0.422618261 0.906307787 0.0
-0.500000000 0.866025403 0.0
-0.573576436 0.819152044 0.0
-0.642787609 0.766044443 0.0
-0.707106781 0.707106781 0.0
-0.766044443 0.642787609 0.0
-0.819152044 0.573576436 0.0
-0.866025403 0.500000000 0.0
-0.906307787 0.422618261 0.0
-0.939692620 0.342020143 0.0
-0.965925826 0.258819045 0.0
-0.984807753 0.173648177 0.0
-0.996194698 0.087155742 0.0
-1.0 0.0 0.0
```

Multiconfigurational Dyson Orbitals in RASSI

```
* A small calculation of photo-electron spectroscopy (PES)
* of H2O -> H2O-

* ----- Initialize the calculation

&GATEWAY
Coord
3

O1   0.000000   0.000000   0.000000 Angstrom
H2   0.000000   0.756650  -0.588880 Angstrom
H3   0.000000  -0.756650  -0.588880 Angstrom
BASIS
ANO-RCC-MB
Group
nosym

&SEWARD

&SCF

* ----- Calculate 2 PES initial states for singlet H2O

>> COPY $Project.ScfOrb INPORB

&RASSCF
LUMORB
Spin
1
nActEl
6 0 0
Inactive
2
Ras1
0
Ras2
5
Ras3
0
CIRO
2 2 1

>> COPY $Project.JobIph S.JobIph

* ----- Calculate 3 PES final states for doublet H2O-

>> COPY $Project.RasOrb INPORB
```

```
&RASSCF
LUMORB
Spin
2
nActEl
5 0 0
Inactive
2
Ras1
0
Ras2
5
Ras3
0
CIRO
3 3 1

>> COPY $Project.JobIph D.JobIph

* ----- Calculate state interactions

>> COPY S.JobIph JOB001
>> COPY D.JobIph JOB002

&RASSI
SpinOrbit

* - Enable calculation of Dyson amplitudes
* - (Without DYSExport the spin-orbit amplitudes would be approximated
* - directly from the spin-fee Dyson amplitudes without explicit
* - construction of the spin-orbit Dyson orbitals, for all included
* - spin-orbit states)

DYSOn

* - Enable exportation of Dyson orbitals to molden format for the first
* - 2 spin-free and first 1 spin-orbit states as PES initial states
* - (A full calculation of spin-orbit amplitudes is performed, but only
* - for the PES initial states given below)
* - Dyson orbitals are contained in:
* - $Project.dys.molden.SF.<initialstate>
* - $Project.dys.molden.SO.<initialstate>.Re
* - $Project.dys.molden.SO.<initialstate>.Im

DYSExport
2 1
```

Orbital Properties

Printing Orbital Second Moment $\langle r^2 \rangle$ for All Orbitals to Identify Rydberg Orbitals

We take a *trans*-1,3-butadiene molecule as an example. First, generate at least one orbital file, such as the CASSCF natural orbitals (`$Project.RasOrb`, `$Project.RasOrb.1`, `$Project.RasOrb.2`, ...):

```
&GATEWAY
 Symmetry = XY XYZ
 Basis set
  C.aug-cc-pVTZ....
  C1 1.740343 0.616556 0.0000000 /Angstrom
  C2 0.397343 0.616556 0.0000000 /Angstrom
 End of Basis
 Basis Set
```

```
  H.cc-pVTZ....
  H3 -0.126346 1.577069 0.000000 /Angstrom
  H4 2.279054 1.568725 0.000000 /Angstrom
  H5 2.279054 -0.335614 0.000000 /Angstrom
 End of Basis

&SEWARD
 NoDeleted
 Grid input
  Grid = Ultrafine
 End of grid input

&SCF

&RASSCF
 CIRoot = 3 3 1
 nActEl = 4 0 0
 Inactive = 7 0 0 6
 Frozen = 0 0 0 0
 RAS2 = 0 4 4 0
 Deleted = 0 0 0 0
 Symmetry = 4
 Spin = 1
 Charge = 0

>> COPY $Project.RasOrb.1 $CurrDir/Orb.1
>> COPY $Project.RasOrb.2 $CurrDir/Orb.2
```

Then, to print the orbital $\langle r^2 \rangle$ for individual natural orbitals of each of the first two states, `$Project.RasOrb.1` and `$Project.RasOrb.2`, use the following input:

```
>> export MOLCAS_PRINT = VERBOSE

&GATEWAY
 Symmetry = XY XYZ
 Basis set
  C.aug-cc-pVTZ....
  C1 1.740343 0.616556 0.0000000 /Angstrom
  C2 0.397343 0.616556 0.0000000 /Angstrom
 End of Basis
 Basis Set
  H.cc-pVTZ....
  H3 -0.126346 1.577069 0.000000 /Angstrom
  H4 2.279054 1.568725 0.000000 /Angstrom
  H5 2.279054 -0.335614 0.000000 /Angstrom
 End of Basis

>> COPY $CurrDir/Orb.1 INPORB

&SEWARD
 NoDeleted
 Grid input
  Grid = Ultrafine
 End of grid input
 Vectors
 OrbCon
 OrbAll

>> COPY $CurrDir/Orb.2 INPORB

&SEWARD
 NoDeleted
 Grid input
  Grid = Ultrafine
 End of grid input
 Vectors
 OrbCon
 OrbAll
```

Then, the magnitude of orbital $\langle r^2 \rangle$ and its components (especially its $\langle z^2 \rangle$ component

because the molecule is on the xy plane) printed in the output indicates how diffuse an orbital is.

Binatural Orbitals

Generation of binatural orbitals for a transition between two anion states of pentadienyldithiol (PDDT).

```
&GATEWAY
  Coord = 15
    Pentadienyldithiol
    H    -4.84571108   0.32877242   0.00000000
    S    -3.95804045   1.33861182   0.00000000
    H    -2.65472176  -0.74484138   0.00000000
    C    -2.48336436   0.31635830   0.00000000
    C    -1.25747677   0.83346283   0.00000000
    H    -1.14108339   1.90451723   0.00000000
    C     0.00000000   0.00000000   0.00000000
    H     0.00000000  -0.65023754   0.86937108
    H     0.00000000  -0.65023754  -0.86937108
    H     1.14108339   1.90451723   0.00000000
    C     1.25747677   0.83346283   0.00000000
    C     2.48336436   0.31635830   0.00000000
    H     2.65472176  -0.74484138   0.00000000
    S     3.95804045   1.33861182   0.00000000
    H     4.84571108   0.32877242   0.00000000
  Group = Z
  Basis = ANO-RCC-VDZP

&SEWARD

&RASSCF
  File = PDDT.RasOrb
  NActEl   =  9
  Inact    = 26  5
  RAS2     =  4  4
  Symmetry =  1
  Spin     =  2
  CIRoot   =  2  2  1
>> COPY $Project.JobIph JOB001

&RASSCF
  File = PDDT.RasOrb
  NActEl   =  9
  Inact    = 26  5
  RAS2     =  4  4
  Symmetry =  2
  Spin     =  2
  CIRoot   =  2  2  1
>> COPY $Project.JobIph JOB002

&RASSI
  NrOfJobIph = 2 all
  BiNatural  = 1
    2  1
```

The WFA Module

```
&GATEWAY
Coord = 4

  C1      0.000000000      0.000000000      0.592249000
  O3      0.000000000      0.000000000     -0.595374000
```

```
  H5      0.000000000      0.924901000      1.170727000
  H7      0.000000000     -0.924901000      1.170727000
Group = xy
Title = Molcas-SP
Basis = STO-3G

&SEWARD

&SCF

&WFA
H5file = $Project.scf.h5

&RASSCF
Spin   = 1
NActEl = 6,0,0
Inact  = 4 1
RAS2   = 2 3
CIRoot = 2,2,1
Thrs   = 1.0e-10 1.0e-6 1.0e-6

>> SAVE $Project.JobIph JOB001

>> SAVE $Project.rasscf.h5 singlet.h5

&RASSCF
Spin   = 3
NActEl = 6,0,0
Inact  = 4 1
RAS2   = 2 3
CIRoot = 2,2,1
Thrs   = 1.0e-10 1.0e-6 1.0e-6

>> SAVE $Project.JobIph JOB002

&WFA
H5file = $Project.rasscf.h5
Mulliken

>> SAVE $Project.rasscf.h5 triplet.h5

&RASSI
NrOfJobIphs
2 2 2
1 2
1 2
TRD1

&WFA
H5file = $Project.rassi.h5
RefSt = 2
```

Example of FDET Calculation

We will briefly describe the OpenMolcas input for a FDET calculation aiming at reproducing the effect of the presence of a nearby water molecule on the excitation energies of Br_2. Following the flow-chart of fig. S8, we see that the input requires the definition of the full $A + B$ system in GATEWAY. Note the necessity of keywords such as `NOMOVE` and `GROUP`, as well as the appropriate usage of the `BSSE` keyword that defines the system for which the density will be generated in the subsequent SCF calculation. In this example, a PBE density is produced for the subsystem B and stored with additional information on the file `AUXRFIL`. In the second call to GATEWAY, the role of A and B with respect to the keyword `BSSE` is exchanged, as we are now going to compute CAS-CI

wavefunctions for A embedded in B. Note the use of the keyword `FAKE` in SEWARD to avoid recomputing Cholesky vectors for the AO basis. The first RASSCF run in the input generates $\rho_A^{\mathrm{ref}}(\boldsymbol{r})$ (ground-state CAS-CI) for the subsequent linearized FDET calculation. The latter will be automatically activated by the presence of the file `PRERFIL` that stores information about $\rho_A^{\mathrm{ref}}(\boldsymbol{r})$. FDET is introduced in the second RASSCF run with the keyword `OFEM`, that stands for orbital-free embedding potential. This keyword requires a string with two arguments, representing the functional for $T_s^{\mathrm{nad}}[\rho_A, \rho_B]$ and $E_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A, \rho_B]$, respectively, separated by a slash. In the present input, `LDTF/PBE` indicates that the Thomas–Fermi functional is used for $T_s^{\mathrm{nad}}[\rho_A, \rho_B]$, whereas PBE is chosen for $E_{\mathrm{xc}}^{\mathrm{nad}}[\rho_A, \rho_B]$. Finally, the CASPT2 run with `OFEM` uses also the keyword `GHOST` in order to eliminate from the first-order interacting space any excitation to orbitals localized onto the subsystem B. The threshold value chosen of 0.1 includes in the correlation treatment any orbital with a Mulliken-type population higher than 10 % on subsystem A.

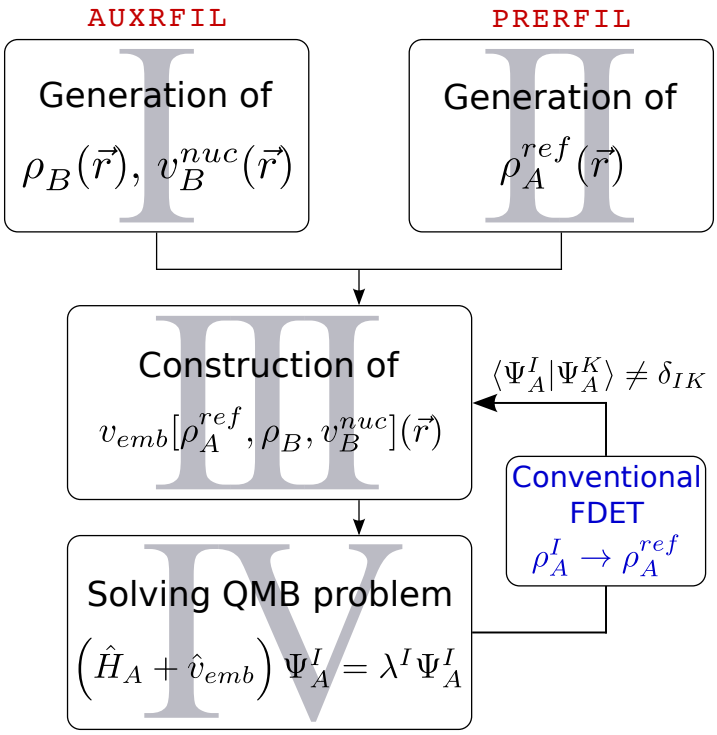


Figure S8: Flow-chart of the computational building blocks for a typical FDET calculation in OpenMolcas. The iterative update of $\rho_A^{\mathrm{ref}}(\boldsymbol{r})$ is not needed when using linearized FDET.[S12] Furthermore, it should be noted that for a given electronic state I of the embedded subsystem A, the corresponding eigenvalue λ^I of the embedded Hamiltonian does not represent the value for the energy functional that is minimized in FDET, as a consequence of the inhomogeneity of the nonadditive kinetic and exchange–correlation functionals.[S13,S14]

```
&GATEWAY
  Title = (Emb. Species)---H2O, Subsystem B
  Coord = Br2.xyz
  Coord = H2O.xyz
  BSSE = 1
  Basis = aug-cc-pVDZ
  NoMove
  Group = NoSym
  RICD
```

```
&SEWARD

>>> COPY $Project.GssOrb INPORB

&SCF
  Title = HF for H2O subsystem
  Charge = 0

>>> COPY $Project.RunFile AUXRFIL

&GATEWAY
  Title = Emb. Species---(H2O), Subsystem A
  Coord = Br2.xyz
  Coord = H2O.xyz
  BSSE = 2
  Basis = aug-cc-pVDZ
  NoMove
  Group = NoSym
  RICD

&SEWARD
  Fake RICD

**********************************
* First CAS-CI run (isol + bfs)  *
**********************************

&RASSCF
  Title = Isolated CASCI Sub A
  NActEl = 14 0 0
  Charge = 0
  Spin = 1
  RAS2 = 8
  CIOnly
  CIRoot = 6 6
    1 2 3 4 5 6
    1 0 0 0 0 0
  OrbListing = Nothing

*******************************
* Embedded CAS-CI-PT2         *
*******************************

>>> COPY $Project.RunFile PRERFIL

&RASSCF
  Title = CASCI Subsystem A
  FileOrb = $Project.RasOrb
  NActEl = 14 0 0
  Spin = 1
  CIOnly
  CIRoot = 6 6
    1 2 3 4 5 6
    1 1 1 1 1 1
  OFEmbedding = LDTF/PBE
  OrbListing = Nothing

&CASPT2
  Multistate = 6  1 2 3 4 5 6
  OFEmbedding
  Ghost = 0.1
```

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