

Running CMS-PDFT in *OpenMolcas*

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1. Introduction to CMS-PDFT

Compressed multi-state pair-density functional theory (CMS-PDFT) is a version of multi-state pair-density functional theory (MS-PDFT) that introduces state interactions into multiconfiguration pair-density functional theory (MC-PDFT).

2. Introduction to MS-PDFT

Although MC-PDFT can be used for both ground states and electronically excited states, it is a single-state method (although the SCF step used to obtain orbitals might be state-averaged, the final energies of the electronic states are calculated independently), and as such it does not have the correct topology at conical intersections. At and near conical intersections – or, more generally – whenever near degeneracy is present (and it is usually present for electronically excited states), one should use a multi-state (MS) approach. In such an approach, one sets up an effective Hamiltonian acting within a model space, which is a subspace spanned by selected CI roots. Final energies are then calculated as eigenvalues of the effective Hamiltonian.

The number of states in the model space is usually small (e.g., 2, 3, or a half dozen states). The CI method used in the first step may be the final stage of a state-averaged complete active space self-consistent-field (SA-CASSCF) calculation, the final stage of a state-averaged restricted active space self-consistent-field (SA-RASSCF) calculation, a complete active space configuration interaction (CASCI) calculation, or a restricted active space configuration interaction (RASCI) calculation. The CI states will be called reference states in what follows.

The MS-PDFT method is a method for including state interactions by MC-PDFT. An MS-PDFT method has four steps.

Step 1. Transform (i.e., rotate) the reference states into a set of intermediate states. The transformation matrix will be called the rotation matrix.

Step 2. Rotate the Hamiltonian matrix from the reference-state basis into the intermediate-state basis. The rotated Hamiltonian matrix is called the intermediate Hamiltonian matrix.

Step 3. Replace the diagonal elements of the intermediate Hamiltonian matrix with the MC-PDFT energies of the intermediate states. This gives the fully correlated effective Hamiltonian matrix, which is simply called the effective Hamiltonian matrix in the output.

Step 4. Diagonalize the fully correlated effective Hamiltonian matrix to obtain the MS-PDFT states and the energies.

Two special cases of MS-PFT are included in *OpenMolcas*, namely XMS-PDFT and CMS-PDFT. They differ only in the choice of intermediate states. This document describes CMS-

PDFT calculations in *OpenMolcas*. At present, analytic gradients are available for CMS-PDFT but not for XMS-PDFT.

3. Introduction to CMS-PDFT

The sum-over-states of the two-electron classical Coulomb energy is

$$Q = \sum_{K=1}^N \frac{1}{2} \sum_{pqrs} D_{pq}^{KK} D_{rs}^{KK} (pq|rs), \quad (1)$$

or

$$Q = \sum_{K=1}^N \frac{1}{2} \sum_{pqrs} D_{pq}^{KK} D_{rs}^{KK} g_{pqrs}, \quad (1a)$$

where N is the number of states in the model space, K is a state index, $p, q, r,$ and s are generic-orbital indices, D_{pq}^{KK} is the spinless reduced 1-particle density matrix for state K , and g_{pqrs} is a two-electron Coulomb integral given in Mulliken notation by $(pq|rs)$. In Mulliken notation, the indices p and q are for the first electron. and r and s are for the second electron; therefore we can rewrite Q as a sum of three terms, one with both electrons in inactive (i) orbitals, one with one electron in an inactive orbital and the other in an active (a) orbital, and the last one with both electrons in active orbitals:

$$Q = Q_{i-i} + Q_{i-a} + Q_{a-a} \quad (2)$$

$$Q_{i-i} = 2N \sum_{ij} g_{iijj}. \quad (3a)$$

$$Q_{i-a} = 2 \sum_{K=1}^N \sum_{itu} D_{tu}^{KK} g_{iitu}. \quad (3b)$$

$$Q_{a-a} = \frac{1}{2} \sum_{K=1}^N \sum_{tuvx} D_{tu}^{KK} D_{vx}^{KK} g_{tuvx}. \quad (3c)$$

where $t, u, v,$ and x are indices of active orbitals, and i and j are indices of inactive orbitals (which are orbitals that are doubly occupied in all configurations in all states).

In CMS-PDFT, the intermediate states maximize the sum-over-states of the two-electron classical Coulomb energy defined in eq 1 or eq 1a. According to eqs 2 and 3, maximizing the sum-over-states of two-electron classical Coulomb energy is equivalent to maximizing the trace of the active-active two-electron classical Coulomb energy in eq 3c, and the program actually maximizes Q_{a-a} .

The code for performing this kind of calculation is available on *OpenMolcas*, and the theory of CMS-PDFT is explained in the following reference:

“Compressed-State Multistate Pair-Density Functional Theory,” J. J. Bao, C. Zhou, Z, D. G. Truhlar. *J. Chem. Theory Comput.* **2020**, *16*, 7444-7452.
doi.org/10.1021/acs.jctc.0c00908

The theory of MS-PDFT and the details of XMS-PDFT method were given in the following earlier reference:

“Multi-State Pair-Density Functional Theory,” J. J. Bao, C. Zhou, Z, Varga, S. Kanchanakungwankul, L. Gagliardi and D. G. Truhlar. *2020. Faraday Discuss.*, **2020**, *224*, 348-272. doi.org/10.1039/D0FD00037J

4. Sample Input for CMS-PDFT

In *OpenMolcas*, a CMS-PDFT calculation requires two modules, in particular RASSCF and MCPDFT. The keywords that are added or extended for use in CMS-PDFT calculation are written in bold in the sample input below and are explained on comment lines in that input (comment lines begin with an asterisk).

Next is a complete input file to run a CMS-PDFT calculation for the lowest four singlet states of LiH on the z axis at an internuclear distance of 1.4 Å. For this calculation the reference states are obtained by SA(4)-CASSCF. Note that the first RASSCF module used in this sample is provided to compute the SA-CASSCF energies (these are not needed but may be desired for comparison to the CMS-PDFT results). In cases where the SA-CASSCF energies are not needed, only one RASSCF module (the one with the CMSI keyword) is needed.

```
&GATEWAY
  Coord=LiH.xyz
  Basis=aug-cc-pVQZ
  Group=XY Y
&SEWARD
&RASSCF
Spin=1
Symmetry=1
CIRoot= 4 4 1
Inactive=1 0 0 0
Ras2=5 1 0 1
Nactel=2 0 0
>>> COPY $CurrDir/LiH.RasOrb $Scratch/INPORB
*
* The following RASSCF module is for carrying out Steps 1 and 2.
&RASSCF
CIOOnly
Spin=1
Lumorb
Symmetry=1
CIRoot= 4 4 1
Inactive=1 0 0 0
Ras2=5 1 0 1
Nactel=2 0 0
CMSI
*The CMSI keyword is the keyword to generate CMS intermediate states and the Hamiltonian
* matrix for the intermediate states.
CMMA=40
*The CMMA keyword defines the maximum number of iterations to obtain the CMS
intermediate states. The default value is 100.

* The MCPDFT module accomplishes Steps 3 and 4.
```

```
&MCPDFT
KSDFT=T:PBE
MSPDft
```

*The MSPD keyword requires the program to construct the effective Hamiltonian matrix and to
*diagonalize it to obtain the MS-PDFT states and energies.

5. Sample Output for CMS-PDFT

Next we present some key information about the output file generated by the input file shown above.

5.1. SA-CASSCF energies

We first give the SA-CASSCF energies for the reference states and for the CMS intermediate states for readers who would like to reproduce this sample run.

For the reference states, the SA-CASSCF energies in hartrees are
-8.008456, -7.872778, -7.791271, -7.777081,
and for the intermediate states, they are
-7.992319, -7.785381, -7.799267, -7.872619.

5.2. RASSCF module output for CMS-PDFT

Here we present a part of the output from the RASSCF module, in which the CMSI keyword is used.

```
CMS INTERMEDIATE-STATE OPTIMIZATION
START MATRX      XMS INTERMEDIATE STATES
THRESHOLD       1.00E-08
MAX CYCLES      40
MIN CYCLES       5
```

```
=====
  Cycle      Q_a-a          Difference
-----
   1         2.71758261    4.0563E-002
   2         2.71758276    1.4646E-007
   3         2.71758276    1.8785E-013
   4         2.71758276   -3.9968E-015
   5         2.71758276    3.1086E-015
```

```
CONVERGENCE REACHED
```

```
=====
Do_Rotate.txt is found in scratch directory.
Following properties are for CMS intermediate states.
=====
```

The lines starting from CMS INTERMEDIATE-STATE OPTIMIZATION and ending with CONVERGENCE REACHED correspond to the process in which the program maximizes the sum over states of the active-active classical Coulomb energies (Q_{a-a}).

START MATRX is the guess matrix in the iterative process to find the CMS intermediate states. This is specified by the CMSS keyword, and the default value is XMS, which means the program will use the rotation matrix for XMS intermediate states as the initial guess. More details are provided in Section 5.4.

THRESHOLD is the threshold for convergence of the iterative process that maximizes Q_{a-a} , and it refers to the difference of Q_{a-a} from one cycle to the next. This is an input parameter provided by the CMTH keyword. If it is not given, the program uses a default value of 10^{-8} hartrees.

MAX CYCLES is the maximum number of cycles allowed in optimizing the CMS intermediate states. This is an input parameter provided by the CMMA keyword. If it is not given, the program uses the default of 100 cycles. Note that a cycle of the optimization is defined in the first paper mentioned in Section 3.

MIN CYCLES is the minimum number of cycles used in optimizing the CMS intermediate states. This is an input parameter provided by the CMMI keyword. If it is not given, the program uses the default value of 5 cycles.

The example given here uses the default value for MIN CYCLES, so the iterations stop after the 5th cycle, even though the change in Q_{a-a} was already below the threshold at an earlier stage.

The Difference column shows how much Q_{a-a} changes from the previous cycle.

The presence of the lines starting with Do_Rotate.txt and Following informs the user that the CMSI keyword is used, and that the rotation matrix is calculated and saved. The user is also informed that the file named Do_Rotate.txt has been located and that the rotated Hamiltonian matrix is saved.

5.3. MCPDFT module output for CMS-PDFT

Finally, we present the output from the MCPDFT module.

Note that the keyword MSPD stands for MS-PDFT, but there is more than one MS-PDFT method (two of them, XMS-PDFT and CMS-PDFT, are in *OpenMolcas*). The following three lines in the output state that the MCPDFT module is running a CMS-PDFT calculation.

```
=====
Keyword "MSPD" is used and file recording rotated Hamiltonian is found.
Switching calculation to Multi-State Pair-Density Functional Theory (MS-PDFT) calculation.
The MS-PDFT method is CMS-PDFT.
=====
```

Next, the program prints the information for the intermediate states in a similar way to the printing for MC-PDFT calculations. Below we show the printed information for an MS-PDFT calculation that is different from the information for an MC-PDFT calculation.

```
*****
**                               CMS-PDFT INTERMEDIATE STATE 01                               **
*****
...
Total MC-PDFT energy for intermediate state 1          -8.03001377
...
```

In MC-PDFT calculations, the header above the information for each state is

MC-PDFT RESULTS, STATE 01;

in CMS-PDFT calculations, the header is

CMS-PDFT INTERMEDIATE STATE 01.

In MC-PDFT calculations, the MC-PDFT energy is shown in the line that starts with

Total MC-PDFT energy for state;

in CMS-PDFT calculations, this line starts with

Total MC-PDFT energy for intermediate state.

After the information for intermediate states, the output shows the results for the final states as follows:

```
*****
                               CMS-PDFT FINAL RESULTS
*****
CMS-PDFT Effective Hamiltonian
-8.0300137706883206  0.0086805385940086  0.0402925741993991  0.0308581837959711
0.0086805385940086  -7.8095512031941876  0.0045013291543503  0.0238195047922836
0.0402925741993988  0.0045013291543508  -7.8244106577885955  -0.0141441112600727
0.0308581837959714  0.0238195047922833  -0.0141441112600727  -7.9002068202212827
CMS-PDFT Energies:
:: CMS-PDFT Root 1  Total energy:  -8.04515382
:: CMS-PDFT Root 2  Total energy:  -7.90064656
:: CMS-PDFT Root 3  Total energy:  -7.81671716
:: CMS-PDFT Root 4  Total energy:  -7.80166491
CMS-PDFT Eigenvectors:
Intermediate-state Basis
      Root 1      Root 2      Root 3      Root 4
-0.9569116447131962  -0.2262760767751129  0.1464903259044914  -0.1079806728444748
0.0093514356541431  0.2691048645053885  -0.2151869589381347  -0.9387170474928539
0.1886099476934316  -0.0695025288855445  0.9507392575654955  -0.2359884536018775
0.2205877206341591  -0.9335690159047241  -0.1683152436446677  -0.2268478097865361
Reference-state Basis
      Root 1      Root 2      Root 3      Root 4
-0.9998189322167506  0.0162642669204752  -0.0085033936473781  0.0050267980837990
0.0162065660002499  0.9998038740900903  0.0000268545768616  -0.0113824361082842
-0.0083862842938817  0.0003591971545575  0.9997234133989501  0.0219690217146399
```

```
-0.0053963168161035  -0.0112941557184064  0.0219268848052203  -0.9996812159554502
*****
```

The above part of the output does not exist for single-state MC-PDFT calculations. It contains three types of information: the fully correlated effective Hamiltonian matrix, the MS-PDFT energies that are eigenvalues of the effective Hamiltonian matrix, and the eigenvectors of the effective Hamiltonian matrix. The eigenvectors are expressed in terms of two sets of states, one is the set of intermediate states that maximize Q_{a-a} ; the other is the set of reference states, which are obtained in the SA-CASSCF, SA-RASSCF, CASCI, or RASCI calculations.

5.4. Guess Rotation Matrix

As of April 2, 2022, *OpenMolcas* supports reading a rotation matrix to start the iterative process that finds the CMS intermediate states. The rotation matrix has the same form as the rotation matrix stored in the file `Do_Rotate.txt`. Below we give a sample input that contains the keyword that reads the matrix and the information that is related to this keyword in the output file.

```
&GATEWAY
  Coord=LiH.xyz
  Basis=aug-cc-pVQZ
  Group=XY Y
&SEWARD
&RASSCF
Spin=1
Lumorb
Symmetry=1
CIRoot= 4 4 1
Inactive=1 0 0 0
Ras2=5 1 0 1
Nactel=2 0 0
CMSI
&RASSCF
LumOrb
nActEl=2 0 0
Inactive=1 0 0 0
Ras2=5 1 0 1
CIRoot=4 4 1
Symmetry=1
CMSI
CMSS=Do_Rotate.txt
```

Note that in this input file, the second RASSCF module contains a line `CMSS=Do_Rotate.txt`. This line means the program will read the rotation matrix named `Do_Rotate.txt` in the scratch directory. Note that this file is produced in the first RASSCF module and it stores the CMS intermediate-state rotation matrix. The information on finding the CMS intermediate states in the second RASSCF module in the output file is shown as follows,

```
CMS INTERMEDIATE-STATE OPTIMIZATION
START MATRX Do_Rotate.txt
```

```

THRESHOLD 1.00E-08
MAX CYCLES 100
MIN CYCLES 5

```

```

=====

```

Cycle	Q_a-a	Difference
1	2.71758276	-2.2204E-015
2	2.71758276	2.6645E-015
3	2.71758276	-3.5527E-015
4	2.71758276	2.2204E-015
5	2.71758276	0.0000E+000

```

-----
CONVERGENCE REACHED

```

Note that the line starting with START MATRX is Do_Rotate.txt instead of XMS INTERMEDIATE STATES because the keyword CMSS=Do_Rotate.txt is given. Because the iterations start with the one that already converges Q_{a-a} , Q_{a-a} is shown to be the same as the last one in Section 5.2.

6. CMS-PDFT compared to XMS-PDFT

An earlier method than CMS-PDFT¹ is called XMS-PDFT.² In XMS-PDFT, the intermediate states diagonalize the generalized Fock matrix as specified by Granovsky³ in the XMC-QDPT method. Both XMS-PDFT and CMS-PDFT are efficient methods. However, CMS-PDFT is more robust than XMS-PDFT, as discussed in the CMS-PDFT article.¹ Therefore we recommend using CMS-PDFT rather than XMS-PDFT.

References

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- 1 "Compressed-State Multi-State Pair-Density Functional Theory," J. J. Bao, C. Zhou, Z, D. G. Truhlar. *J. Chem. Theory Comput.* **2020**, *16*, 7444-7452.
 - 2 "Multi-State Pair-Density Functional Theory," J. J. Bao, C. Zhou, Z, Varga, S. Kanchanakungwankul, L. Gagliardi and D. G. Truhlar. *Faraday Discuss.*, **2020**, *224*, 348-272.
 - 3 "Extended Multi-Configuration Quasidegenerate Perturbation Theory: The New Approach to Multi-State Multi-Reference Perturbation Theory." Granovsky, A. A. *J. Chem. Phys.* **2011**, *134*, 214113.