

Running CMS-PDFT in *OpenMolcas*

Jie J. Bao and Donald G. Truhlar

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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), which 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 MC-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*.

3. Introduction to CMS-PDFT

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

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

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 two-electron classical Coulomb energy defined in eq 1. 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 program actually maximizes Q_{a-a} .

The code for performing this kind of calculation is currently being uploaded to *OpenMolcas*, and the theory of CMS-PDFT is explained in the following reference:

“Electrostatically-Driven Multi-State Pair-Density Functional Theory,” J. J. Bao, C. Zhou, Z. D. G. Truhlar. *Journal of Chemical Theory and Computation*, to be published.

The theory of MS-PDFT was first introduced in the following reference:

“Multi-State Pair-Density Functional Theory,” J. J. Bao, C. Zhou, Z. Varga, S. Kanchanakungwankul, L. Gagliardi and D. G. Truhlar. 2020. *Faraday Discussions*, online as of May 7, 2020 as Accepted Manuscript at 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 at an internuclear distance of 1.4 Å. For this calculation the reference states are obtained by SA(4)-CASSCF.

```
&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 CMSI 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=TPBE
  NoGrad
  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 our results.

For the reference states, the SA-CASSCF energies in a.u. are -8.008460, -7.872783, -7.791272, -7.777087, respectively, and those for the rotated states are -7.992319, -7.785377, -7.799274, -7.872632.

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 STATES OPTIMIZATION
  THRESHOLD 1.00E-06
  MAX CYCLES  40
  MIN CYCLES   5
=====
  Cycle      Q_a-a          Difference
-----
    1      2.71757636    4.0546E-002
    2      2.71757650    1.4478E-007
    3      2.71757650    1.8208E-013
    4      2.71757650   -4.4409E-016
    5      2.71757650    1.3323E-015
CONVERGENCE REACHED
=====
=====
Do_Rotate.txt is found in scratch directory.
Following properties are for CMS intermediate states.
=====

```

The lines starting from CMS INTERMEDIATE STATES 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}).

THRESHOLD is the threshold for Q_{a-a} to converge from one cycle to another. This is an input parameter provided by the CMTH keyword. If it is not given, the program uses the default value of 10^{-6} 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 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 MCPDFT module.

Note that the keyword MSPD stands for MS-PDFT, but there is more than one MS-PDFT method (two of them, XMS-PDT 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.
```

The effective Hamiltonian CMS-PDFT results are printed in the following form:

```
*****
CMS-PDFT FINAL RESULTS
*****
```

CMS-PDFT Effective Hamiltonian

-8.0300129787611905	0.0087064043213068	0.0402907984794167	0.0308633927056217
0.0087064043213069	-7.8095470613609148	0.0044879379207994	0.0238059281048484
0.0402907984794168	0.0044879379207992	-7.8244197213714761	-0.0141519873713839
0.0308633927056214	0.0238059281048482	-0.0141519873713837	-7.9002221508168589

CMS-PDFT Energies:

```
:: CMS-PDFT Root 1 Total energy: -8.04515695
:: CMS-PDFT Root 2 Total energy: -7.90065433
:: CMS-PDFT Root 3 Total energy: -7.81672094
:: CMS-PDFT Root 4 Total energy: -7.80166969
```

CMS-PDFT Eigenvectors:

Root 1	Root 2	Root 3	Root 4
-0.9569000512912461	-0.2262995425224389	0.1465269269955501	-0.1079845755568174
0.0094749127487594	0.2689948469372592	-0.2146006282795126	-0.9388815520030430
0.1886138087716894	-0.0695435428469522	0.9508896537756030	-0.2353665080920494
0.2206294382167769	-0.9335919799482154	-0.1681823306705948	-0.2268113084013380

This 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.

6. CMS-PDFT compared to XMS-PDFT

An earlier method than CMS-PDFT is called XMS-PDFT. In XMS-PDFT, the intermediate states diagonalize the generalized Fock matrix. Both XMS-PDFT and CMS-PDFT are efficient methods. However, CMS-PDFT is more robust than XMS-PDFT, as we have pointed out in the first reference mentioned in Section 3. So we recommend using CMS-PDFT rather than XMS-PDFT.