Running XMS-PDFT or MS-PDFT with a User-Supplied Rotation Matrix in *OpenMolcas*

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1. Introduction to MS-PDFT and XMS-PDFT

Extended Multi-State Pair-Density Functional Theory (XMS-PDFT) is a version of multi-state pair-density functional theory (MS-PDFT). The code for performing this kind of calculation is currently being uploaded to *OpenMolcas,* and the theory is explained 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

As mentioned above, XMS-PDFT is one possible version of MS-PDFT. As discussed in the above reference, MS-PDFT depends on rotation of the energy eigenstates to a basis of intermediate states. Sections 2-4 of this document discuss usage of the XMS choice of these intermediate states, as explained in Section 2. For this choice, the program generates the rotation matrix. Section 5 of this document explains how to run a calculation with a user-supplied rotation matrix that is generated beforehand by the user.

2. Methodology of XMS-PDFT

A brief explanation of XMS-PDFT is as follows:

Step 1. We first obtain a set of reference wave functions by state-averaged complete active space self-consistent-field (SA-CASSCF), state-averaged restricted active space self-consistent-field (SA-RASSCF), complete active space configuration interaction (CASCI), or restricted active space configuration interaction (RASCI). Then we rotate these states by an orthogonal transformation into intermediate states, where the intermediate states are specified by the method proposed by Granovsky[1] for extended multi-configuration quasi-degenerate perturbation theory XMC-QDPT, and they will be called XMS intermediate states. (The XMS intermediate states are also used in calculations by extended multi-state complete active space second-order perturbation theory (XMS-CASPT2)).

Step 2. The Hamiltonian matrix is then transformed into the basis of XMS intermediate states.

Step 3. We replace the diagonal elements of the rotated Hamiltonian matrix by the MC-PDFT energies of the XMS intermediate states. This yields an effective Hamiltonian matrix whose diagonal elements are the MC-PDFT energies of the XMS intermediate states, and whose off-diagonal elements are the same as at the end of step 2.

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[1] A. A. Granovsky, Extended multi-configuration quasi-degenerate perturbation theory: the new approach to multi-state multi-reference perturbation theory, *J. Chem. Phys.*, 2011, **134**, 214113.

Step 4. We diagonalize the effective Hamiltonian matrix to get the XMS-PDFT energies and XMS-PDFT states.

3. Sample Input for XMS-PDFT

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

Next is a complete input file to run an XMS-PDFT calculation for the ground and first excited singlet states of LiF at an internuclear distance of 2.6 Å.

```
* The following part generates initial orbitals for an SA-CASSCF calculation
&Gateway
Coord
2
Angstrom
Li  0.0  0.0  0.8
F   0.0  0.0 -0.8
Group=XY Y
Basis=STO-3G
&Seward
&SCF
* End of initial-orbital generation

&Gateway
Coord
2
Angstrom
Li  0.0  0.0  1.3
F   0.0  0.0 -1.3
Group=XY Y
Basis=STO-3G

&Seward

* The following two &RASSSCF modules are for carrying out Steps 1 and 2.
&RASSCF
Spin=1
Symmetry=1
CIRoot= 2 2 1
Inactive=2 0 0 0
Ras2=4 1 0 1
Nactel=8 0 0
XMSI
```

* The MCPDFT module accomplishes Steps 3 and 4.
&MCPDFT
KSDFT=TPBE
NoGrad
MSPDft
* MSPD is a new keyword that does multi-state PDFT calculations.

4. Sample Output for XMS-PDFT

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

4.1. RASSCF module output for XMS-PDFT

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

```
==============================================================
    Do_Rotate.txt is found in scratch directory.
    Following properties are for XMS intermediate states.
==============================================================
```
The presence of both of these lines informs the user that the XMSI 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.

4.2. MCPDFT module output for XMS-PDFT

Finally, we present the output from MCPDFT module. Note that H0_Rotate.txt is necessary for an MS-PDFT calculation to run. This is also why we create the H0_Rotate.txt file in the RASSCF module.

Note that the keyword MSPD stands for MS-PDFT (multi-state pair density functional theory), which refers to more than one method. *OpenMolcas* contains two MS-PDFT methods, namely extended MS-PDFT (XMS-PDFT) and compressed MS-PDFT (CMS-PDFT).

The following three lines in the output state that the MCPDFT module is running an MS-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 XMS-PDFT.
```

==

The word XMS-PDFT in the third line comes from the last line of Do_Rotate.txt. In the RASSCF module with the XMSI keyword, the module first prints the Do_Rotate.txt file with the line, which is after the rotation matrix, saying XMS-PDFT. Then still in this module, the H0_Rotate.txt file is created with its last line copying the information from the line that is after the rotation matrix in Do_Rotate.txt, namely XMS-PDFT. In the MCPDFT module where the MSPD keyword is used, the information, namely XMS-PDFT, in the line after the Hamiltonian matrix in the H0_Rotate.txt file will be used in the third line after "method is".

The part where the module prints ground-state MC-PDFT energies and energy contributions starts with "XMS-PDFT INTERMEDIATE STATE 01" for MS-PDFT calculations (instead of "MC-PDFT RESULTS, STATE 01", which is written for state-specific MC-PDFT calculations). INTERMEDIATE STATE means that the energy contributions are not for the final XMS-PDFT states.

The effective Hamiltonian and MS-PDFT (in this case, XMS-PDFT) results are printed in the following form:

```
*********************************************************
                 XMS-PDFT FINAL RESULTS
*********************************************************
   XMS-PDFT Effective Hamiltonian
 -105.5291101616690099     0.0345985805430900
    0.0345985805430900   -105.4785548063528893

   XMS-PDFT Energies:
  ::   XMS-PDFT Root  1   Total energy:   -105.54668132
  ::   XMS-PDFT Root  2   Total energy:   -105.46098365

   XMS-PDFT Eigenvectors:
         Root 1                Root 2
 -0.8916072059865702   -0.4528096622564738
  0.4528096622564738   -0.8916072059865702
     *********************************************************
```

This part does not exist for single-state MC-PDFT calculations. It contains three types of information, the effective Hamiltonian matrix, the XMS-PDFT energies (which are the eigenvalues of the effective Hamiltonian matrix), and the XMS-PDFT eigenvectors.

5. MS-PDFT with a User-Supplied Rotation Matrix

The output information discussed in Section 4.1 is presented on two separate lines because the XMSI keyword contains the function of the ROST keyword. The ROST keyword is used to rotate the MCSCF states in the RASSCF module with a file that saves a rotation matrix and that is named Do_Rotate.txt. The ROST keyword allows one to use an external rotation matrix to obtain rotated states. The XMSI keyword calculates the rotation matrix, and then lets the subroutine that is activated by the ROST keyword to calculate the rotated states and the rotated Hamiltonians. The

possibility of using an external rotation matrix is useful because MS-PDFT is a category of methods (of which XMS-PDFT is just one choice), and other methods in the MS-PDFT category use other intermediate states. The rotation matrix of a specific method that is used to generate its intermediate states can be obtained with the RASSCF module by using an externally generated rotation matrix with the ROST keyword in the RASSCF module. If the Do_Rotate.txt file does not have any information after the rotation matrix, the RASSCF module will put an unknown method in the line after the Hamiltonian matrix in the H0_Rotate.txt file. As a result, the MS-PDFT method is unknown to the program, and the third line of the following information is modified as follows:

> 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 calculations are based on a user-supplied rotation matrix.

Similarly, one will see MS-PDFT FINAL RESULTS instead of XMS-PDFT FINAL RESULTS, MS-PDFT energies instead of XMS-PDFT energies, and so on.