SUPPORTING INFORMATION

Electronic Structure of Methyl Radical Photodissociation

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Table of Contents

S1. Optimized Geometry for the Methyl Radical

The SA(7)-CASSCF(7,10) optimized geometry of the methyl radical is provided below. The molecule is planar, with an optimized C—H bond length of 1.091 Å, and three H—C—H bond angles of 120°. The Cartesian coordinates are given in XYZ format in Angstroms.

```
    4

C      0.00000000      0.00000000      0.00000000
H      1.09100000      0.00000000      0.00000000
H     -0.54550000      0.94483372      0.00000000
H     -0.54550000     -0.94483372      0.00000000
```

S2. Sample Input Files

1. Sample Input File for SA(7)-CASSCF(7,10) Geometry Optimization Calculation in *Molpro*

The following *Molpro* input file performs a geometry optimization using an SA-CASSCF calculation over seven electronic states using an active active space of 7 electrons in 10 orbitals. Molecular coordinates are read from the external file "`CH3.xyz`". The MG3S basis set is used in the calculation. Since the Molpro library does not include the MG3S basis set by default, the basis functions for the atoms involved (C and H) are explicitly defined within the input file.

```
***
memory,50,m
nosym,noorient,angstrom;

geometry = CH3.xyz

basis = {
!
! hydrogen              (5s,2p) -> [3s,2p]
s, H , 33.86500, 5.094790, 1.158790, 0.325840, 0.102741
c, 1.3, 0.0254938, 0.190373, 0.852161
c, 4.4, 1.000000
c, 5.5, 1.000000
p, H , 1.5000000, 0.3750000
c, 1.1, 1.0000000
c, 2.2, 1.0000000
!
! carbon                (12s,6p,2d) -> [5s,4p,2d]
s, C , 4563.240, 682.0240, 154.9730, 44.45530, 13.02900,
1.827730, 20.96420, 4.803310, 1.459330, 0.0438000, 0.1455850,
0.4834560
c, 1.6, 0.00196665, 0.0152306, 0.0761269, 0.2608010, 0.6164620,
0.2210060
c, 7.9, 0.114660, 0.919999, -0.00303068
c, 10.10, 1.0000000
c, 11.11, 1.000000
c, 12.12, 1.000000
p, C , 20.96420, 4.803310, 1.459330, 0.4834560, 0.1455850,
0.0438000
c, 1.3, 0.0402487, 0.237594, 0.815854
c, 4.4, 1.000000
c, 5.5, 1.000000
c, 6.6, 1.0000000
d, C , 1.2520000, 0.3130000
c, 1.1, 1.0000000
c, 2.2, 1.0000000
f, C , 0.8000000
c, 1.1, 1.0000000
```

```
}

{hf}

{multi
occ,11
closed,1
state,7
CPMCSCF,GRAD,1.1,record=5101.1}

FORCES
SAMC,5101.1

{optg}
```

2. Sample Input File for XMS-CASPT2 Single-Point Energy Calculation in *Molpro*

The following *Molpro* input file performs an XMS-CASPT2 calculation on the seven lowest electronic states of the methyl radical. Molecular coordinates are read from the external file "`CH3.xyz`". The MG3S basis set is explicitly defined within the input file. Permanent integral (`$Project.int`) and wavefunction (`$Project.wfu`) files are specified to ensure that each calculation can use information from the previous one.

```
***
memory,50,m
nosym,noorient,angstrom;
file,1,$Project.int
file,2,$Project.wfu
print,civector,basis,orbitals

geometry = CH3.xyz

basis={
!
! hydrogen              (5s,2p) -> [3s,2p]
s, H , 33.86500, 5.094790, 1.158790, 0.325840, 0.102741
c, 1.3, 0.0254938, 0.190373, 0.852161
c, 4.4, 1.000000
c, 5.5, 1.000000
p, H , 1.5000000, 0.3750000
c, 1.1, 1.0000000
c, 2.2, 1.0000000
!
! carbon                (12s,6p,2d,1f) -> [5s,4p,2d,1f]
s, C , 4563.240, 682.0240, 154.9730, 44.45530, 13.02900,
1.827730, 20.96420, 4.803310, 1.459330, 0.0438000, 0.1455850,
0.4834560
c, 1.6, 0.00196665, 0.0152306, 0.0761269, 0.2608010, 0.6164620,
0.2210060
c, 7.9, 0.114660, 0.919999, -0.00303068
c, 10.10, 1.0000000
c, 11.11, 1.000000
c, 12.12, 1.000000
p, C , 20.96420, 4.803310, 1.459330, 0.4834560, 0.1455850,
0.0438000
c, 1.3, 0.0402487, 0.237594, 0.815854
c, 4.4, 1.000000
c, 5.5, 1.000000
c, 6.6, 1.0000000
d, C , 1.2520000, 0.3130000
```

```
c, 1.1, 1.0000000
c, 2.2, 1.0000000
f, C , 0.8000000
c, 1.1, 1.0000000
}

{hf}

{multi,maxit=40,maxiti=400
occ,11
closed,1
wf,9,1,1
state,7
start,2140.2
orbital,2140.2}

{rs2,shift=0.3,g4,xms=1,mix=7
occ,11
closed,1
core,1
state,7}
```

3. Sample Input File for CMS-PDFT Single-Point Energy Calculation in *OpenMolcas*

The following *OpenMolcas* input file performs a CMS-PDFT calculation of the seven lowest electronic states of the methyl radical. Molecular coordinates are read from the external file "`CH3.xyz`". The calculation uses the MG3S basis set. In this case, the MG3S basis set file was added manually to the basis set library in *OpenMolcas*. The orbitals from the SA-CASSCF step are used for the subsequent CMS-PDFT calculation.

```
&GATEWAY
COOR = CH3.xyz
BASI = MG3S
GROU = C1

&SEWARD

&RASSCF
LumOrb
NACT = 7 0 0
INAC = 1
RAS2 = 10
CIRO = 7 7 1

>>> COPY $CurrDir/$Project.RasOrb $Scratch/INPORB

&RASSCF
LumOrb
NACT = 7 0 0
INAC = 1
RAS2 = 10
CIRO = 7 7 1
CMSI
CMMA = 200

&MCPDFT
KSDF = t:PBE
MSPD
```