User’s guide of FSindo

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Contents of Sample Files

Sample files are found in sindo-4.0/doc/FSindo/sample_FSindo

1.water/
VSCF, VCI[3]-(8), VMP2-(4), VQDPT2-(4)

2.ethylene/
VCI[3]-(6), VMP2-(4), VQDPT2-(4)

3.water-hexamer/
nc-VCI[3]-(6), nc-VQDPT2-(4)

3.water-hexamer_oc/
oc-VSCF, oc-VCI[3]-(6), oc-VQDPT2-(4)

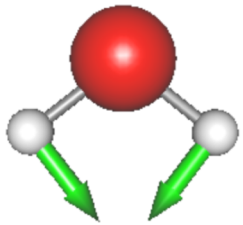
How to run SINDO

```
$ sindo < xxx.inp > xxx.out
```

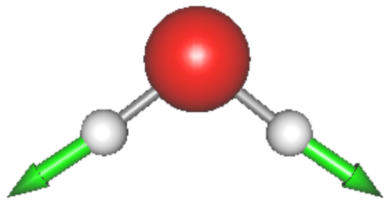
1. Water

- h2o.minfo

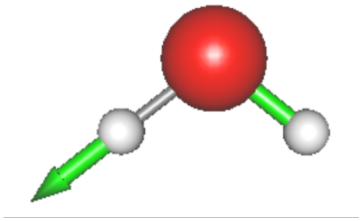
  Includes the equilibrium geometry, harmonic frequencies, and vibrational displacement vectors. They can be visualized by JSindo.



Q1
HOH bending



Q2
Sym. OH stretching



Q3
Asym. OH stretching

- *.pot

  Includes the information of grid potential.

eq.	q0.pot
1MR	q1.pot, q2.pot, q3.pot
2MR	q2q1.pot, q3q1.pot, q3q2.pot
3MR	q3q2q1.pot

```
 B3LYP/cc-pVDZ (11)
# Number of grids and data
    11      1
#   q2              Energy
   -28.05499848     6.7066429978e-02
   -21.28549000     4.3536327557e-02
   -15.49364050     2.5681778470e-02
   -10.14497826     1.2204347140e-02
    -5.02301699     3.3101913787e-03
    -0.00000000     0.0000000000e+00
     5.02301699     4.1200574795e-03
    10.14497826     1.8799126027e-02
    15.49364050     4.9578584037e-02
    21.28549000     1.0751025106e-01
    28.05499848     2.2150954913e-01
q2.pot (END)
```

- vscf.inp

```
#--- [  INPUT PARAMETER  ]
&mol minfofile='h2o.minfo' /     input minfo file
&sys maxmem=10 /                 max memory in MB

#--- [  VIB  ]
&vib  MR=3  vmaxAll=10  vscf=.t. /
```

- MR : Mode coupling order of the PES
- vmaxAll : Max num of quanta of HO basis sets for all modes.
- vscf : true invokes VSCF.

```
#--- [ TARGET STATES ]
&states  fund=.t. /      Targets all fundamental levels.

#--- [  VSCF  ]
&vscf  Maxitr=20  Ethresh=1.D-03 /
```

- Maxitr : Max iteration for VSCF
- Ethresh : Threshold of convergence in cm^{-1}.

- log/vscf.out

```
>> BASIS FUNCTIONS
   MODE :         1         2         3
   MAXV :        10        10        10
   FREQ :   1659.40  3752.61  3853.49
```

Setting of HO basis sets. Frequencies are taken from the minfo file.

```
>> POTENTIAL

  [  OPTIONS  ]

    MR        =       3
    MCS_CUTOFF = 0.10E-03
    MCS_GRID  = -.10E+01
    POTDIR    = ./


    1MR-PEF

    o GRID PEF

      MODE=   1, GRID=  11    B3LYP/cc-pVDZ (11)
      MODE=   2, GRID=  11    B3LYP/cc-pVDZ (11)
      MODE=   3, GRID=  11    B3LYP/cc-pVDZ (11)


    2MR-PEF

    o GRID PEF

      MODE=   2   1, GRID=  11  11    B3LYP/cc-pVDZ (11)
      MODE=   3   1, GRID=  11  11    B3LYP/cc-pVDZ (11)
      MODE=   3   2, GRID=  11  11    B3LYP/cc-pVDZ (11)


    3MR-PEF

    o GRID PEF

      MODE=   3   2   1, GRID=  11  11  11    B3LYP/cc-pVDZ (11)
```

1MR

2MR

3MR

```
>> STATE 000:   ZERO-POINT STATE

    o INITIAL GUESS FROM (CONTRACTED) HARMONIC OSCILLATOR

-- (ITERATION) -------- (EOLD) -------- (ENEW) ----- (DELTA E) --
             1         4687.67         4589.42      -0.983D+02
             2         4589.42         4586.72      -0.270D+01
             3         4586.72         4586.64      -0.809D-01
             4         4586.64         4586.64      -0.254D-02
             5         4586.64         4586.64      -0.800D-04
-------------------------------------------------------------------
    E(VSCF)=     4586.63552176
```

VSCF iteration

Zero-point Energy

```
>> VIRTUAL VSCF ENERGIES

   o VSCF STATES          TOTAL ENERGY          E-E0
     1_1                  6184.36878830         1597.73326654
     2_1                  8220.27988057         3633.64435881
     3_1                  8388.85466071         3802.21913894
```

It's a good practice to check if the PES is specified in the way you intended.

Virtual VSCF energies for the fundamental levels.

- vci.inp

```
#--- [  VIB  ]
&vib  MR=3  vmaxAll=10  vscf=.t. vci=.t. /
```

vscf = .t. and vci = .t. invokes VSCF/VCI.

```
#--- [  VCI  ]
&vci  nstate=20  nCUP=3  maxSum=8 /
```

- nstate : Number of states to obtain.
- nCUP : Max number of modes to excite.
- maxSum : Max sum of quantum numbers to excite.

* nCUP=3 and maxSum=8 means VCI[3]-(8).

- log/vci.out

```
>> VCI OPTIONS

   o VCI SPACE SELECTION
     - MAX NUM. OF MODES TO EXCITE :          3
     - MAX SUM OF QUANTUM NUM.     :          8
     - MAX EXCITATION OF EACH MODE :    8  8  8

   o VCI DIMENSION   :        165
   o NUM_OF_STATES   :         20
```

VCI[3]-(8)

Dimension of VCI matrix

```
  > STATE 00000: ZERO-POINT STATE

      E(VCI)   =     4567.81121

      COEFF.  WEIGHT      CONFIG.
      0.999   0.998         0_0
      0.039   0.001         2_1    3_2

  > STATE 00001:   1_1

      E(VCI)   =     6158.00730
      E(VCI)-E0=     1590.19608

      COEFF.  WEIGHT      CONFIG.
     -0.998   0.996         1_1
     -0.038   0.001         1_1    2_1    3_2
```

Zero-point energy

CI coeff.

1st excitation of the 1st mode

Total energy and excitation energy

CI coeff.

- vmp2.inp

```
#--- [  VIB  ]
&vib  MR=3  vmaxAll=10  vscf=.t. vpt=.t. /

#--- [  VPT  ]
&vpt  maxSum=4 /
```

vscf = .t. and vpt = .t. invokes VMP2.

- maxSum : Max sum of quantum numbers to excite.
  * maxSum=4 means VMP2-(4).

- log/vmp2.out

```
>> VPT OPTIONS

   o VPT WITH ZERO-POINT VSCF REFERENCE (VMP)
     READ VSCF WFN   : vscf-000.wfn

   o VPT LEVEL:
     NCUP    =   3
     MAXSUM  =   4

   o THRESH_ENE :   0.100E-03
```

VMP2-(4)

```
 o STATE 000:   ZERO-POINT STATE

        --- Q-SPACE COMPONENTS---
            1-MODE :        0
            2-MODE :       18
            3-MODE :        4
             TOTAL :       22
        ------------------------

        E(0th)     =    4509.75410
        E(1st)     =      76.88145
        E(2nd)     =     -18.89655

        E(VMP1)    =    4586.63555
        E(VMP2)    =    4567.73900
```

1st and 2nd order energy

```
 o STATE 001:   1_1

        --- Q-SPACE COMPONENTS---
            1-MODE :       13
            2-MODE :       24
            3-MODE :        7
             TOTAL :       44
        ------------------------

        E(0th)     =    6107.48744
        E(1st)     =      76.87803
        E(2nd)     =     -24.52433

        E(VMP1)    =    6184.36547
        E(VMP2)    =    6159.84114

        E(VMP1)-E0 =    1597.72993
        E(VMP2)-E0 =    1592.10214
```

1st excitation of the 1st mode

1st and 2nd order energy

1st and 2nd order excitation energy

- vqdpt2.inp

```
#--- [  VIB  ]
&vib  MR=3  vmaxAll=10  vscf=.t. vqdpt=.t. /
                              vscf = .t. and vqdpt = .t. invokes VQDPT2.

&states
fund=.t.     All fundamental levels.
nstate=3
target_state(2,1)=2
target_state(2,2)=1
target_state(3,2)=1
target_state(3,3)=2
/

#--- [  VPT  ]
&vqdpt  nGen=3 maxSum=4 /
```

- nGen : Max number of iteration for generating the P space.
- maxSum : Max sum of quantum numbers to excite.

add (020), (011), (002)

- log/vqdpt2.out

```
>> VQDPT OPTIONS

   o VQDPT WITH ZERO-POINT VSCF REFERENCE
     READ VSCF WFN   : vscf-000.wfn

   o P-SPACE CONSTRUCTION
     NGEN =     3
     THRESH_P0   = 0.50E+03
     THRESH_P1   = 0.10E+00
     THRESH_P2   = 0.50E-01
     THRESH_P3   = 0.90E+00
     P SET       =         0

   o Q-SPACE CONSTRUCTION
     NCUP    =     3
     MAXSUM =     4
```

Parameters for the P space.

Parameters for the Q space.

```
 o STATE 000:    ZERO-POINT STATE

        --- Q-SPACE COMPONENTS---
            1-MODE :         0
            2-MODE :        18
            3-MODE :         4
             TOTAL :        22
        -------------------------

        E(0th)     =     4509.75410
        E(1st)     =       76.88145
        E(2nd)     =      -18.89655

        E(VMP1)    =     4586.63555
        E(VMP2)    =     4567.73900
```

1st and 2nd order correction

1st and 2nd order energy

```
 o GROUP 002:   2_1

    --- P-SPACE COMPONENTS ---------------------------------------
 *     1)   2_1
       2)   1_2
    -------------------------------------------------------------
                                          * IS THE TARGET STATE

   o Q-SPACE COMPONENTS:          66

     (CLOCK) ----> LAST STEP: USER     0.00, SYSTEM     0.00 SECS   <----

   > STATE 001:   1_2

      E(VQDPT2)   =     7714.41978
      E(VQDPT2)-E0=     3146.68078

      COEFF.  WEIGHT      CONFIG.

      -0.987   0.975        1_2
      -0.159   0.025        2_1

   > STATE 002:   2_1

      E(VQDPT2)   =     8149.29727
      E(VQDPT2)-E0=     3581.55827

      COEFF.  WEIGHT      CONFIG.

      -0.987   0.975        2_1
       0.159   0.025        1_2


     (CLOCK) ----> LAST STEP: USER     0.00, SYSTEM     0.00 SECS   <----
```

P space components.

VCI-like output for the P space.

Quiz

Find the fundamental frequencies of H_2O from the output files, and fill in a table below.

	Harm	VCI[3]-(8)	VMP2-(4)	VQDPT2-(4)	Exp.
1					1595
2					3652
3					3756

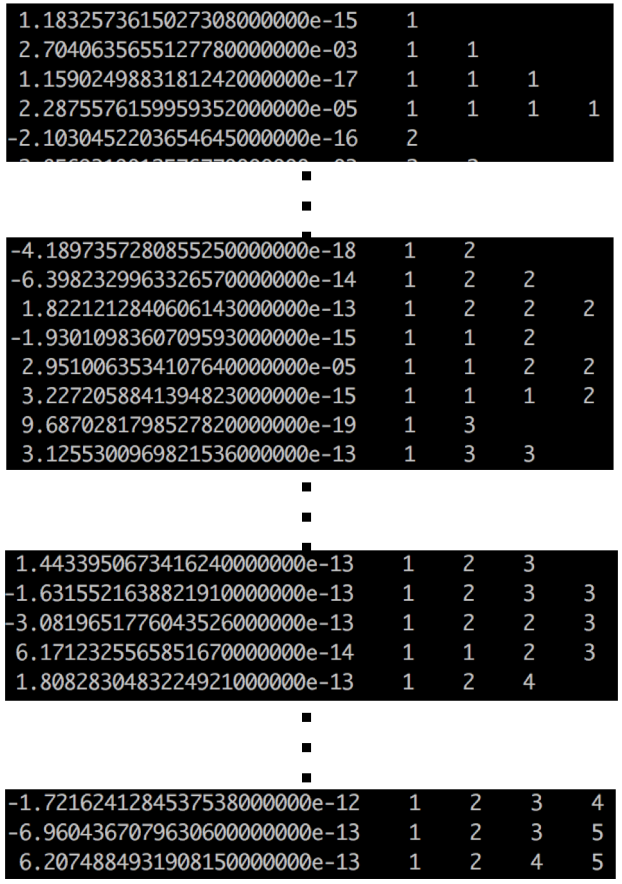
2. Ethylene

- eq-mp2dz.minfo

  Includes the equilibrium geometry, harmonic frequencies, and vibrational displacement vectors. They can be visualized by JSindo.

- prop_no_1.mop

  Includes the information of QFF



one-body terms:

ci, cii, ciii, ciiii

two-body terms:

cij, cijj, cijjj, ciij, ciijj, ciiij

three-body terms:

cijk, cijkk, cijjk, ciijk

four-body terms: cijkl

- vci.inp, vmp2.inp, vqdpt2.inp
  - Input for QFF

```
#--- [  MRPES ]
&mrpes mopFile='prop_no_1.mop' mcs_cutoff=-1.0D-03 /
```

    - mopFile : Name of a QFF file.
    - mcs_cutoff : Cut-off threshold for coupling terms based on MCS.

  - Input for VCI, VMP2, VQDPT2 is the same as in the case of water.
  - Output for QFF

```
>> POTENTIAL

   [  OPTIONS  ]

      MR         =         3
      MCS_CUTOFF = -.10E-02
      MCS_GRID   = -.10E+01
      POTDIR     = ./
      MOPFILE    = prop_no_1.mop
```

```
1MR-PEF
o QFF   MP2/cc-pVDZ

  MODE=   1
  MODE=   2
  MODE=   3
  MODE=   4
  MODE=   5
  MODE=   6
  MODE=   7
  MODE=   8
  MODE=   9
  MODE=  10
  MODE=  11
  MODE=  12
```

1MR

```
2MR-PEF
o QFF   MP2/cc-pVDZ

  NUMBER OF TERMS=      66

3MR-PEF
o QFF   MP2/cc-pVDZ

  NUMBER OF TERMS=     220
```

2MR

3MR

Quiz

Find the fundamental frequencies of C_2H_4 from the output files, and fill in a table below.

	Harm	VCI[3]-(8)	VMP2-(4)	VQDPT2-(4)	Exp.
1					826
2					940
3					949
4					1026
5					1222
6					1344
7					1442
8					1625
					1662
9					2989
10					3022
11					3083
12					3105

3. Water Hexamer

- h2o_6-mp2dz.minfo

  Includes the equilibrium geometry, harmonic frequencies, and vibrational displacement vectors. They can be visualized by JSindo. In this example, we only treat internal vibration of water molecules (i.e., OH stretching and HOH bending modes) neglecting intermolecular modes. We set modes 31 – 40 to active, and others to inactive.

- prop_no_1.mop

  Includes the information of QFF. This is 4MR-QFF for all 48 modes. (In fact, it is costly to get this QFF.)

- ocvscf.inp

```
#--- [  VIB  ]
&vib  MR=4  ocvscf=.t.  vscf=.f. vci=.f. vpt=.f.
                    ocvscf = .t. invokes oc-VSCF.

    vmaxAll = -1     Make all modes inactive.
    vmax(31) = 10
    vmax(32) = 10    } Make 31-48 active.
    …
    vmax(48) = 10
/

#--- [  OCVSCF  ]
&ocvscf mopfile='prop_no_1.mop' /
```

- mopFile : Name of a QFF file.

  * For oc-VSCF, QFF needs to be full 4MR-QFF.

- log/ocvscf.out


```
o TRANSFORMATION MATRIX WRITTEN TO : [ u1.dat ]
o FORCE CONSTANTS WRITTEN TO       : [ prop_no_1.mop_ocvscf ]
o NEW COORDINATES WRITTEN TO       : [ h2o_6-mp2dz_ocvscf.minfo ]
```

These files are used in subsequent VSCF calculations.

- ncvci.inp, ncvqdpt2.inp

  VCI and VQDPT2 calculations based on normal coordinates.
  They read h2o_6-mp2dz.minfo and prop_no_1.mop.

- ocvci.inp, ocvqdpt2.inp

  VCI and VQDPT2 calculations based on optimized coordinates.
  The read h2o_6-mp2dz_ocvscf.minfo and prop_no_1.mop_ocvscf.

Quiz

Visualize the normal and optimized coordinates of water hexamer, and discuss on their differences.

List of all Options

&mol

Character(80) :: minfoFile

The name of the .minfo file, in which the information of molecule is written.

Integer :: Nat

The number of atoms

Real(8), dimension(Nat) :: Mass

The mass of each atoms (in atomic mass unit)

Real(8), dimension(3,Nat) :: x

The reference (equilibrium) geometry (in Angstrom)

Real(8), dimension(Nfree) :: omega

The frequencies for the HO basis sets (in cm−1)

Real(8), dimension(Nat*3,Nfree) :: L

The vibrational displacement vectors

[Note] 'minfoFile' is mutually exclusive from others.

&sys

Integer(8) :: Maxmem

Maximum size of memory (MB)

&mrpes

Integer :: MR
    Mode representation (MR=1-4)
Real(8) :: mcs_cutoff
    Cutoff of QFF based on MCS in cm-1 (default = 1.d-04)
Logical :: au
    The grid data in atomic unit (default = true)
Character(80) :: mopFile
    The name of the mop file.

&vib

Integer :: Nfree
    Number of degrees of freedom (default = 3Nat - 6)
Integer :: MR
    Mode representation (MR=1-4)
Integer, dimension(Nfree) :: vmax
    Number of basis functions for each mode (default=10)
Integer :: vmaxALL
    Number of basis functions for all modes (default=10)
Integer :: vmax base
    same as vmaxALL
Logical :: vscf, ocvscf, vci, vpt, vqdpt
    invoke vscf/ocvscf/vci/vpt/vqdpt
Logical :: prpt
    invoke property calculation
Logical :: readBasis
    read the basis functions from cho.basis

&states

Integer :: Nstate

Number of states to calculate

Integer, dimension(Nfree,Nstate) :: target state

Labels of the target states

Logical :: fund

Compute fundamentals

&vscf

Logical :: state specific

State specific VSCF if true (default = .false.)

Logical :: restart

Restart from vscf xxx.wfn (default = .false.)

Integer :: Maxitr

Maximum number of iteration (default = 10)

Real(8) :: Ethresh

Threshold of convergence (default = 1e-03 cm−1)

&ocvscf

Integer :: maxOptIter

Maximum number of iteration (default = 30)

Real(8) :: ethresh

Threshold of the energy (default = 1e-06 cm−1)

Real(8) :: gthresh

Threshold of the gradient (default = 1e-06 cm−1 rad−1)

Integer :: pfit

Order of the Fourier fitting (default = 2)

Character(80) :: mopFile

The name of the mopfile

Character(80) :: u1File

The name of the file to write the transformation matrix (default = u1.dat)

Integer :: icff

Switch on CFF when icff = 1 and QFF when icff = 0 (default = 0)

Integer :: iscreen

Switch off/on pair selection when iscreen=0/1 (default = 1)

Real(8) :: eta12thresh

Threshold value for the pair screening (default = 500 cm−1)

&vci

Integer :: Nstate
    Number of states to calculate
Integer :: nCI
    Max CI dimension (cutoff based on the energy)
Integer(Nfree) :: maxEx
    Max quantum number to excite for each mode
Integer :: maxExALL
    Max quantum number to excite for all the modes
Integer :: maxSum
    Max sum of quantum number
Integer :: nCUP
    Max number of modes to excite
Logical :: geomAv
    If true, calculate vibrationally averaged geometry
Logical :: dump
    If true, dump the vci wavefunction to vci-w.wfn
Real(8) :: printWeight
    Print the configuration with the weight larger than this threshold
Logical :: readCIbasis
    If true, read CI basis from vci-w.wfn
Logical :: dumpHmat
    If true, write the VCI hamiltonian matrix
Logical :: noDiag
    If true, the diagonalization is skipped

&vpt

Integer :: maxSum
    Max sum of quantum number to excite (default = -1)
Integer :: maxEx
    Max quantum number to excite (default = -1)
Integer :: nCUP
    Max number of modes to excite (default = MR)
Real(8) :: thresh ene
    Threshold energy to avoid divergence (default=1e-04 Hartree)
Logical :: dump
    Dump the information to vmp-w.wfn

&vqdpt

Integer :: nGen
    The generation of P space (default=3)
Real(8) :: thresh p0
    E0 pruning (default=500 cm−1)
Real(8) :: thresh p1
    VPT based pruning (default=0.1)
Real(8) :: thresh p2
    VCI pruning (default=0.05)
Real(8) :: thresh p3
    VCI pruning (default=0.9)
Integer :: pset
    Combine the p-space generated from several target states
    =0 when the target states have an overlap (default)
    =1 when the p-space components have an overlap

Integer :: maxSum
Max sum of quantum number to excite (default = -1)
Integer :: nCUP
Max number of modes to excite (default = MR)
Integer :: pqSum
P/Q interaction scheme
> 0 prune the interaction when λpq > maxSum (default)
< 0 full interaction
Integer :: vqdpt2 loop
=0 loop over q, then p, p' (default)
=1 loop over p, then p', q
Real(8) :: thresh ene
Threshold energy to avoid divergence (default=1e-04 Hartree)
Real(8) :: printWeight
Print the configuration with the weight larger than this threshold (default=0.001)
Logical :: dump
Dump the information to vqdpt-w.wfn (default=true)

&prpt

Logical :: vscfprpt, vciprpt, vptprpt, vqdptprpt
Invoke property calculation for vscf, vci, vpt, vqpdt wavefuncion
Integer :: MR
Mode representation (default = 3)
Character :: extn(*)
The extension of the property files
Integer :: matrix(*)
= 0 calculate only the average
> 0 calculate the matrix
Logical :: infrared
If true, calculate the IR intensity.

&prptvci

Integer :: Nstate

The number of states

&IRspectrum

Real(8) :: minOmega, maxOmega

Min/Max value of the spectrum (default = 100 - 4000 cm−1)

Real(8) :: delOmega

Interval of the data (default = 1 cm−1)

Real(8) :: fwhm

Full-width half maximum of the Lorentz function for convolutions (default = 20 cm−1)

Real(8) :: cutoff

Cutoff of the band (default = -1 km mol−1)