

DCDFTBMD

Divide-and-Conquer Density Functional Tight-Binding Molecular Dynamics

User Manual

Version 2.0

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Abstract

DCDFTBMD allows the users to perform quantum mechanical molecular dynamics (MD) simulation for large systems by using divide-and-conquer (DC) density functional tight-binding (DFTB) method. The scaling of DC-DFTB with respect to system size is close to linear. A high parallel efficiency has been achieved in the implementation with the hybrid of MPI and OpenMP. The program has functionalities not only for MD but also for geometry optimization, vibrational frequency calculation, and property evaluation.

DCDFTBMD website

General information about DCDFTBMD, including development background, program download, documentation, and publication can be found on the following website:

<http://www.chem.waseda.ac.jp/dcdftbmd/en/>

Improvements from old version

New features added to version 2.0

- Metadynamics simulation
- Geometry optimization with Quick-min or FIRE method
- LSQ method for accelerating SCC convergence
- Interruption and restarting numerical Hessian calculation
- Numerical gradient calculation
- Treating extended Slater-Koster parameters and f -electrons
- DFTB+U approach for SCC calculation
- Onsite correction for SCC calculation
- D3H5 correction for F element

Below is available for only MPI/OpenMP version:

- MPI-based Broyden charge mixing for reducing memory usage
- Better efficiency of orbitally resolved SCC calculation
- Spline interpolation algorithm for orbitally resolved SCC calculation

Default settings changed from version 1.0

- Threshold for scaling velocities in constant temperature MD simulation
Old: 100 K → New: 10000 K
- Step size for numerical differentiation of DFTB parameterized integrals to obtain first and second derivatives
Old: Fixed (0.01 atomic unit) → New: Adjustable parameter
- Step size for numerical differentiation of D3 gradient to obtain second derivatives
Old: Fixed (0.0001 atomic unit) → New: Adjustable parameter
- Reference Hubbard value to identify hydrogen in damped γ -function
Old: Fixed (0.4195 atomic unit) → New: Adjustable parameter

Below is changed for only serial and OpenMP versions:

- No use of disk I/O for storing some intermediate data

Bugs fixed from version 1.0

- DFTB3 atom resolved energy
- Zero charge guess for open-shell system

Below is fixed for only MPI/OpenMP version:

- Hubbard derivative parameter check in orbitally resolved SCC calculation

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1 Input for DCDFTBMD

To run the program **DCDFTBMD**, you need to prepare the input file and parameters (Slater-Koster files). The input file, which is named “**dftb.inp**” by default, mainly consists of 4 parts below:

- Keyword section: Information about the calculation ([section 1.1](#))
- Title section: Brief description of the calculation ([section 1.2](#))
- Parameter section: Specification of Slater-Koster parameters ([section 1.3](#))
- Geometry section: Specification of molecular coordinates ([section 1.4](#))

Each section is terminated with blank line (starting new line is indicated as ↵ in this document). For example, the input file looks like as follows in the case of SCC-DFTB single point energy calculation of water molecule:

```
SCC=TRUE_DC=FALSE.↵
```

Keyword section

```
↵
```

```
TITLE.↵
```

Title section

```
↵
```

```
2.↵
```

Parameter section

```
O_2.↵
```

```
oo.spl_oh.spl.↵
```

```
H_1.↵
```

```
ho.spl_hh.spl.↵
```

```
↵
```

```
3_0_1.↵
```

Geometry section

```
O _ 0.06275391_ 0.06275391_ 0.00000000.↵
```

```
H _ 1.01910555_-0.08185946_ 0.00000000.↵
```

```
H _-0.08185946_ 1.01910555_ 0.00000000.↵
```

```
↵
```

Additional input may be required after Geometry section if subsystems are specified manually in DC approach (see [section 1.4.3](#)). Note that blank area (represented as _ in this document) should be written with spaces (**DO NOT USE TABS!**).

1.1 Keyword section

1.1.1 General overview

```
SCC=TRUE_DC=FALSE.↓
```

SCC and DC keywords are turned on and off

The present example specifies two keywords in a single line. The same specification is possible by giving two separated lines as follows:

```
SCC=TRUE.↓
```

SCC keyword is turned on

```
DC=FALSE.↓
```

DC keyword is turned off

The following subsections account for the available keywords at present. Two keywords SCC and DC are activated if no keywords are given in the input. Other keywords can be turned on using the following forms:

```
keyword=TRUE.↓
```

The above specification employs the default value of options in curly bracket. Several keywords have options for controlling the calculation. The italic type in parenthesis stands for the data type of option. The options can be specified by the following forms:

```
keyword=(option1=value1_option2=value2...).↓
```

Setting option1 and option2 in a single line

```
keyword=(option1=value1).↓
```

Setting option1 and option 2

```
keyword=(option2=value2...).↓
```

in two separated lines

If option is written in red or blue character, that option is available in only serial and OpenMP or MPI/OpenMP version, respectively.

1.1.2 SCC

The keyword SCC sets whether a self-consistent charge (SCC) calculation is made or not. As already mentioned, the default is `SCC=TRUE`, namely the SCC-DFTB (DFTB2) [1] calculation is performed.

Basic settings

- `MAXITER` (*integer*) {200}
Maximum number of SCC cycles to reach convergence.
- `ENERGYCONV/ECONV` (*real*) {1.0e-09}
Convergence criteria for the energy change between two SCC cycles in Hartree unit.
- `DENSITYCONV/DCONV` (*real*) {1.0e-06}
Convergence criteria for the maximum difference in any charge density between two SCC cycles in atomic unit.

Charge mixing

- `MIXER` (*integer*) {1}
Charge mixing method to accelerate SCC convergence.
Note that modified Broyden mixing is used to solve coupled perturbed DFTB equation in analytical Hessian calculation.
 - 1: Modified Broyden [2]
 - 2: Simple mixing
 - 3: Modified Anderson [3]
 - 4: DIIS [4]
- `ALMIX` (*real*) {2.0e-01}
Charge mixing parameter used in charge mixing method.
The value should be larger than zero and less than one.
- `BROYITER/MAXBROYDEN` (*integer*) {70}
Maximum number of charge mixing using Broyden method.
- `NGEN` (*integer*) {4}
Number of iteration to start Anderson and DIIS charge mixing.
Simple mixing is used until reaching this value.

Initial charge guess

- READCHARGE (*method*) {NONE}
Enables to read initial charge information from file.
 - NONE constructs initial Mulliken population based on the number of valence electrons.
 - BINARY reads Mulliken population from the binary file "**chrgfile**". If this option is set but "**chrgfile**" is not found in the same directory as the one including the input file, this option will be turned off.
 - ASCII reads net atomic charges from the ASCII file "**charge.dat**" (see [section 1.5.2](#) for the format). If this option is set but "**charge.dat**" is not found in the same directory as the one including the input file, this option will be turned off.
- ZEROCHARGE (*logical*) {FALSE}
Enables to permanently set values of neutral atoms as initial charge guess in SCC calculation during geometry optimization and molecular dynamics. In the case of ZEROCHARGE=FALSE, the converged charge of previous geometry step is used as initial guess (better than zero charge guess).

Solver

- SOLVER (*integer*) {1}
Eigensolver for diagonalization of Hamiltonian matrix.
 - 1: DSYGVD
 - 2: DSYGV
- PSEUDODIAG/PDIAG (*logical*) {FALSE}
Enables to perform psuedodiagonalization using Jacobi rotations [5]. After reaching the SCC convergence with psuedodiagonalization, full diagonalization is performed to obtain final eigenvalues and eigenvectors.
- PDIAGTHRESH (*real*) {1.0e-02}
Threshold to activate psuedodiagonalization. Full diagonalization is performed to update reference eigenvalues until charge density difference becomes less than the specified value.
- PDIAGKAPPA (*real*) {4.0e-02}
Accuracy control parameter for psuedodiagonalization.

Third-order correction

- THIRDDIAG (*logical*) {FALSE}
Enables the use of third order corrections only for diagonal terms [6].
Hubbard derivatives need to be specified in Parameter section (see [section 1.3.2](#)).
- THIRDFULL (*logical*) {FALSE}
Enables the use of full third order corrections [7].
Hubbard derivatives need to be specified in Parameter section (see [section 1.3.2](#)).
The so-called DFTB3 model [7] requires damped γ -function for X–H pairs (DAMPXH=TRUE).

Modified γ -function

- DAMPXH (*logical*) {FALSE}
Enables the use of damped γ -function for X–H pairs [6–8].
- DAMPXHZETA (*real*) {4.0e+00}
Empirical parameter for the damped γ -function for X–H pairs.
- DAMPXHREFU (*real*) {4.195e–01}
Reference Hubbard value to identify hydrogen used in DAMPXH=TRUE.
- UDERIVGAUSS (*logical*) {FALSE}
Enables to add charge dependent Gaussian function to Hubbard derivative in on-site third-order correction (THIRDDIAG=TRUE) [9].
- UDERIVGAUSSD0 (*real*) {–9.0e–02}
Parameter of Gaussian function (height) used in UDERIVGAUSS=TRUE.
- UDERIVGAUSSG0 (*real*) {1.61e+01}
Parameter of Gaussian function (width) used in UDERIVGAUSS=TRUE.
- UDERIVGAUSSQ0 (*real*) {7.5e–01}
Parameter of Gaussian function (position of center) used in UDERIVGAUSS=TRUE.

- GAMMASPLINE (*logical*) {FALSE}
Enables to use cubic spline interpolation for exponentially decaying short-range part of γ -function.
See reference [\[10\]](#) for details.
For MPI/OpenMP version, this is incompatible with one of shell resolved calculation (RUNTYPE=SHELL0).
- GAMMASPLINEGRID (*real*) {4.0e-02}
Grid size of cubic spline interpolation for exponentially decaying short-range part of γ -function in atomic unit.

Open-shell and spin-polarization correction

- SPIN (*logical*) {FALSE}
Enables to perform collinear spin polarized calculation [\[11, 12\]](#).
Spin constants have to be stored in different file for each atom (see [sections 1.3.2](#) and [1.3.3](#)).
- SPINRELAX (*logical*) {FALSE}
Enables to relax total spin in spin-polarized calculation.
- NELECTHRESH (*real*) {1.0e-06}
Threshold for conservation of total number of electrons in SPINRELAX=TRUE.
- UNPAIREDELEC (*real*) {0.0e+00}
Number of unpaired electrons.
It is possible to set non-integer positive value.
Note that the specified spin multiplicity in Geometry section (see [section 1.4.1](#)) is discarded except for zero unpaired electrons.
- RESTRICT (*logical*) {FALSE}
Enables to use restricted approach in open-shell doublet calculation.
Default is unrestricted approach.

External field effect

- POINTCHARGE (*logical*) {FALSE}
Enables to include point charges.
Coordinates and charge value are set after atomic coordinates starting from the character "PC" (see [section 1.4.1](#)).

- NUMPC (*integer*) {0}
Number of point charges in system.
- EFIELD (*logical*) {FALSE}
Enables to include external static electric field.
This is available for only cluster models.
Static electric field vector is set after atomic coordinates starting from the character "EF" (see [section 1.4.1](#)).

DFTB+U correction

- PLUSU (*logical*) {FALSE}
Enables to add DFTB+U correction [13].
U–J parameters have to be stored in different file for each atom (see [sections 1.3.2](#) and [1.3.3](#)).
- PLUSUTYPE (*integer*) {1}
Method of DFTB+U correction.
 - 1: Fully localized limit (FLL)
 - 2: Pseudo self-interaction correction (pSIC)

Onsite correction

- ONSITE (*logical*) {FALSE}
Enables to add onsite correction [14].
Onsite parameters have to be stored in different file for each atom (see [sections 1.3.2](#) and [1.3.3](#)).
- STOREBLOCKPOP (*logical*) {TRUE}
Enables to store block population of last geometry step in memory for the improved initial guess in simulation with PLUSU=TRUE and ONSITE=TRUE.

Electronic property evaluation

- MAYER (*logical*) {FALSE}
Enables to perform Mayer bond order analysis [15].
- CM3 (*logical*) {FALSE}
Enables to perform CM3 charge analysis [16, 17].

- **ORBITALPOP/ORBPOP** (*logical*) {FALSE}
Enables to print Mulliken population of each orbital.
- **POLAR** (*logical*) {FALSE}
Enables to calculate dipole moment and static polarizability using external static electric field.
This is available for only cluster models.
- **POLEFSTR** (*real*) {2.0e-03}
Strength of external static electric field used in dipole moment and static polarizability calculation.

Additional options for only MPI/OpenMP version

- **RUNTYPE** (*method*) {ATOM}
Selects how to resolve DFTB calculations.
Note that serial and OpenMP versions employ atom resolved calculation.
 - **SHELLO**: Based on valence shells.
This is incompatible with third-order correction (THIRDFULL=TRUE and THIRDDIAG=TRUE).
 - **SHELL**: Based on valence shells.
This is incompatible with on-site third-order correction (THIRDDIAG=TRUE).
 - **ATOM**: Based on atoms.
This is incompatible with orbitally resolved SCC calculation (ORSCC=TRUE).
- **ORSCC** (*logical*) {FALSE}
Enables the use of orbitally resolved SCC calculation.
Different Hubbard parameters for different atomic angular momentum shells are used instead of the use of s-shell only.
The shell resolved calculation (RUNTYPE=SHELL) is mandatory.
The DFTB2 [12] and DFTB3 [18] methods can be extended with this treatment.
- **BROYPARALLEL** (*logical*) {FALSE}
Enables to reduce memory usage for Broyden method by using MPI communications.

- **MIXERSAVEMEMORY** (*logical*) {FALSE}
Enables to reduce memory usage for charge mixing methods.
This is implemented for atom resolved calculations (RUNTYPE=ATOM) and for closed-shell singlet calculations.
- **GSSAVEMEMORY** (*logical*) {FALSE}
Enables to reduce memory usage for computing exponentially decaying short-range part of γ -function of periodic system in GAMMASPLINE=TRUE.
- **GSDOMAIN** (*logical*) {FALSE}
Enables the use of cell-linked list (CLL) algorithm [19, 20] for computing exponentially decaying short-range part of γ -function in GAMMASPLINE=TRUE.
- **GSDOMAINBLOCKXYZ/GSDOMAINBLOCK** (*integer*) {5}
Block size in each of x -, y -, and z -directions used in GSDOMAIN=TRUE.
- **GSDOMAINBLOCKX** (*integer*) {5}
Block size in x -direction used in GSDOMAIN=TRUE.
- **GSDOMAINBLOCKY** (*integer*) {5}
Block size in y -direction used in GSDOMAIN=TRUE.
- **GSDOMAINBLOCKZ** (*integer*) {5}
Block size in z -direction used in GSDOMAIN=TRUE.
- **GSDOMAINNEIGHBOR** (*integer*) {1}
Number of linked neighbors referred to as adjacent cells in GSDOMAIN=TRUE.

1.1.3 NCC

The keyword NCC sets whether a non-SCC calculation (NCC-DFTB or DFTB1) [\[21, 22\]](#) is performed or not. NCC=TRUE is identical to set SCC=FALSE.

Solver

- SOLVER (*integer*) {1}
Eigensolver for diagonalization of Hamiltonian matrix.
 - 1: DSYGVD
 - 2: DSYGV

Open-shell

- RESTRICT (*logical*) {FALSE}
Enables to use restricted approach in open-shell doublet calculation.
Default is unrestricted approach.

Electronic property evaluation

- PRINTMULLIKEN (*logical*) {FALSE}
Enables to perform Mulliken population analysis.
This option is required for further analysis of NCC Mulliken population.
- MAYER (*logical*) {FALSE}
Enables to perform Mayer bond order analysis [\[15\]](#).
Mulliken population analysis (PRINTMULLIKEN=TRUE) is required.
- CM3 (*logical*) {FALSE}
Enables to perform CM3 charge analysis [\[16, 17\]](#).
Mulliken population analysis (PRINTMULLIKEN=TRUE) is required.
Note that the fitted parameters are taken from DFTB2.
- ORBITALPOP/ORBPOP (*logical*) {FALSE}
Enables to print Mulliken population of each orbital.
Mulliken population analysis (PRINTMULLIKEN=TRUE) is required.

1.1.4 DC

The keyword DC sets whether a divide-and-conquer approach [23, 24] is employed or not. This keyword is turned on without any specification as well as SCC keyword. DC=FALSE is necessary if DC-DFTB calculation is deactivated.

Basic settings

- BETA (*real*) {8.0e+02}
Inverse temperature parameter for the Fermi function in atomic unit.
- BUFRAD/BUFFERRADIUS (*real*) {5.0e+00}
Buffer radius to construct buffer region in Angstrom (Å) unit.
Atoms included in spheres centered at atoms in the central region are selected.
- SUBTYPE (*method*) {AUTO}
Method to construct central region.
 - ATOM defines one atom as each subsystem.
 - SPECIFY defines subsystems one by one for each atom (see [section 1.4.3](#)).
 - SYSTEM defines all atoms as one subsystem.
 - AUTO constructs subsystems automatically by dividing total system with the specified cubic or rectangular grid.
Default is 5.0 Å cubic box.
 - AUTOXH constructs subsystems similarly to SUBTYPE=AUTO without cutting covalent bonds involving hydrogen atom.
 - SEMIAUTO defines subsystems as the hybrid of AUTO and SPECIFY (see [section 1.4.3](#)).
 - SEMIAUTOXH constructs subsystems similarly to SUBTYPE=SEMIAUTO without cutting covalent bonds involving hydrogen atom.

Advanced options

- DELTARXYZ/DELTAR (*real*) {5.0e+00}
Grid length of cubic grid used in SUBTYPE=AUTO in Å unit.
- DELTARX (*real*) {5.0e+00}
Grid length of x-component used in SUBTYPE=AUTO in Å unit.

- DELTARY (*real*) {5.0e+00}
Grid length of y-component used in SUBTYPE=AUTO in Å unit.
- DELTARZ (*real*) {5.0e+00}
Grid length of z-component used in SUBTYPE=AUTO in Å unit.
- SUBXHSCALE (*real*) {1.1e+00}
Scaling factor for the sum of covalent radii [25] to judge the presence of covalent bonds involving hydrogen atom in SUBTYPE=AUTOXH and SUBTYPE=SEMIAUTOXH.
- TRANSCoord (*logical*) {TRUE}
Transformation of Cartesian coordinate in SUBTYPE=AUTO, SUBTYPE=SEMIAUTO, SUBTYPE=AUTOXH, and SUBTYPE=SEMIAUTOXH.
 - TRUE: Standard orientation is used.
 - FALSE: Input geometry is used as it is.
- NOFERMI (*logical*) {FALSE}
Common Fermi level is not determined during DC calculation.

Additional options for only MPI/OpenMP version

- FERMITYPE (*method*) {PARALLEL}
Algorithm to determine Fermi level.
See reference [26] for details.
 - PARALLEL: CRI (compute-reduce-interpolate) algorithm is used.
 - SERIAL: GSS (gather-sort-solve) algorithm is used.
- DOMAIN (*logical*) {FALSE}
Enables the use of CLL algorithm [19, 20] for accelerating assignment of subsystems to localization regions.
- DOMAINBLOCKXYZ/DOMAINBLOCK (*integer*) {5}
Block size in each of x-, y-, and z-directions used in DOMAIN=TRUE.
- DOMAINBLOCKX (*integer*) {5}
Block size in x-direction used in DOMAIN=TRUE.
- DOMAINBLOCKY (*integer*) {5}
Block size in y-direction used in DOMAIN=TRUE.

- **DOMAINBLOCKZ** (*integer*) {5}
Block size in z-direction used in DOMAIN=TRUE.
- **DOMAININDEXTYPE** (*method*) {ATOM}
Definition of particle for the index of linked list in DOMAIN=TRUE.
 - **SUBSYSTEM**: The index of subsystem will be given if all constituent atoms are located in the same domain.
 - **ATOM**: The index will be assigned to all atoms.
- **DOMAINNEIGHBOR** (*integer*) {1}
Number of linked neighbors referred to as adjacent cells in DOMAIN=TRUE.
- **SINGLEPREC** (*logical*) {FALSE}
Enables the use of single precision floating point number for distance calculations in assignment of subsystems to localization regions.
- **XHDOMAIN** (*logical*) {FALSE}
Enables the use of CLL algorithm [19, 20] for judging the presence of covalent bonds involving hydrogen atom in SUBTYPE=AUTOXH.
- **XHDOMAINBLOCKXYZ/XHDOMAINBLOCK** (*integer*) {5}
Block size in each of x-, y-, and z-directions used in XHDOMAIN=TRUE.
- **XHDOMAINBLOCKX** (*integer*) {5}
Block size in x-direction used in XHDOMAIN=TRUE.
- **XHDOMAINBLOCKY** (*integer*) {5}
Block size in y-direction used in XHDOMAIN=TRUE.
- **XHDOMAINBLOCKZ** (*integer*) {5}
Block size in z-direction used in XHDOMAIN=TRUE.
- **XHDOMAINNEIGHBOR** (*integer*) {1}
Number of linked neighbors referred to as adjacent cells in XHDOMAIN=TRUE.

1.1.5 DISP/DISPERSION

The keyword DISP/DISPERSION sets whether the noncovalent interaction (dispersion, hydrogen bond, and halogen bond) is empirically corrected or not.

Basic settings

- DISPTYPE (*integer*) {1}
Method of noncovalent interaction correction.
 - 1: Grimme's DFT-D2 [27]
 - 2: Slater-Kirkwood [28]
The required dispersion constants have to be stored in different file for each element (see [sections 1.3.2](#) and [1.3.3](#)).
 - 3: Lennard-Jones [29]
The default values of Lennard-Jones parameters are taken from values of UFF force field [30], while it is also possible to specify them manually in different file for each element (READUFF=TRUE).
 - 4: Grimme's DFT-D3 (zero-damping) [31]
 - 5: Grimme's DFT-D3(BJ) (Becke and Johnson damping) [31, 32]
 - 6: Řezáč's D3H4 [33]
Since this corrects hydrogen bonding interaction empirically, damped γ -function for X-H pairs may not be combined together (DAMPXH=FALSE in SCC keyword). See, for example, reference [34].
 - 7: DFT-ulg [35]
 - 8: dDMC [36]
 - 9: Řezáč's D3H5 [37]
Since H5 correction is designated to modify the original γ -function, namely DAMPXH=FALSE needs to be used in SCC keyword.
This is incompatible with non-SCC calculations (NCC=TRUE or SCC=FALSE).
 - 10: Kubillus's D3X [38]

Advanced options for Grimme's DFT-D2 (DISPTYPE=1)

- S6 (*real*) {1.0e+00}
Global scaling factor for Grimme's DFT-D2.

Advanced options for Slater-Kirkwood (DISPTYPE=2)

- UPDATESKPARAMS (*logical*) {FALSE}
Update Slater-Kirkwood dispersion parameters in each DFTB calculation. In the case of UPDATESKPARAMS=FALSE, dispersion parameters are kept fixed with those of initial geometry during the entire calculation.

Advanced options for Lennard-Jones (DISPTYPE=3)

- READUFF (*logical*) {FALSE}
Enables to specify Lennard-Jones parameters manually for Lennard-Jones dispersion (see [sections 1.3.2](#) and [1.3.3](#)).

Advanced options for Grimme's DFT-D3 (DISPTYPE=4, 5)

- ZEROS8 (*real*) {6.73e-01}
Global scaling factor for r^{-8} term of Grimme's DFT-D3.
- ZERORS6 (*real*) {1.235e+00}
Parameter for damping function of Grimme's DFT-D3.
- BJS8 (*real*) {5.883e-01}
Global scaling factor for r^{-8} term of Grimme's DFT-D3(BJ).
- BJA1 (*real*) {5.719e-01}
Parameter for Becke and Johnson damping of Grimme's DFT-D3(BJ).
- BJA2 (*real*) {3.6017e+00}
Parameter for Becke and Johnson damping of Grimme's DFT-D3(BJ).
- THREEBODY (*logical*) {FALSE}
Enables to Include three-body term for Grimme's DFT-D3 and DFT-D3(BJ).

Advanced options for Řezáč's D3H4 (DISPTYPE=6)

- D3H4S6 (*real*) {1.0e+00}
Parameter for Řezáč's D3H4 correction (D3 dispersion).
- D3H4RS6 (*real*) {1.215e+00}
Parameter for Řezáč's D3H4 correction (D3 dispersion).
- D3H4ALPHA (*real*) {3.0e+01}
Parameter for Řezáč's D3H4 correction (D3 dispersion).
- D3H4SHH (*real*) {3.0e−01}
Parameter for Řezáč's D3H4 correction (H–H repulsion).
- D3H4EHH (*real*) {1.431e+01}
Parameter for Řezáč's D3H4 correction (H–H repulsion).
- D3H4R0HH (*real*) {2.35e+00}
Parameter for Řezáč's D3H4 correction (H–H repulsion).
- D3H4CNN (*real*) {2.01e+00}
Parameter for Řezáč's D3H4 correction (H4 correction).
- D3H4CNO (*real*) {8.0e−01}
Parameter for Řezáč's D3H4 correction (H4 correction).
- D3H4CON (*real*) {2.58e+00}
Parameter for Řezáč's D3H4 correction (H4 correction).
- D3H4COO (*real*) {1.11e+00}
Parameter for Řezáč's D3H4 correction (H4 correction).
- D3H4CWAT (*real*) {1.32e+00}
Parameter for Řezáč's D3H4 correction (H4 correction).
- D3H4CSNHR3 (*real*) {2.33e+00}
Parameter for Řezáč's D3H4 correction (H4 correction).
- D3H4CSCOO (*real*) {1.22e+00}
Parameter for Řezáč's D3H4 correction (H4 correction).

Advanced options for DFT-ulg (DISPTYPE=7)

- ULGS (*real*) {7.012e-01}
Parameter for DFT-ulg.
Note that default value is adjusted to PBE functional.
- ULGB (*real*) {6.966e-01}
Parameter for DFT-ulg.
Note that default value is adjusted to PBE functional.

Advanced options for dDMC (DISPTYPE=8)

- DDMCA (*real*) {1.018e+00}
Parameter for dDMC.
- DDMCB0 (*real*) {1.857e+00}
Parameter for dDMC.
- DDMCS (*real*) {4.6e+01}
Parameter for dDMC.

Advanced options for Řezáč's D3H5 (DISPTYPE=9)

- D3H5S6 (*real*) {1.0e+00}
Parameter for Řezáč's D3H5 correction (D3 dispersion).
- D3H5S8 (*real*) {4.9e-01}
Parameter for Řezáč's D3H5 correction (D3 dispersion).
- D3H5RS6 (*real*) {1.25e+00}
Parameter for Řezáč's D3H5 correction (D3 dispersion).
- D3H5ALPHA (*real*) {2.961e+01}
Parameter for Řezáč's D3H5 correction (D3 dispersion).
- D3H5SHH (*real*) {3.0e-01}
Parameter for Řezáč's D3H5 correction (H-H repulsion).
- D3H5EHH (*real*) {1.431e+01}
Parameter for Řezáč's D3H5 correction (H-H repulsion).
- D3H5R0HH (*real*) {2.35e+01}
Parameter for Řezáč's D3H5 correction (H-H repulsion).

- D3H5SR (*real*) {7.14e-01}
Parameter for Řezáč's D3H5 correction (H5 correction).
- D3H5SW (*real*) {2.5e-01}
Parameter for Řezáč's D3H5 correction (H5 correction).
- D3H5KNH (*real*) {1.8e-01}
Parameter for Řezáč's D3H5 correction (H5 correction).
- D3H5KOH (*real*) {6.0e-02}
Parameter for Řezáč's D3H5 correction (H5 correction).
- D3H5KFH (*real*) {6.0e-02}
Parameter for Řezáč's D3H5 correction (H5 correction).
- D3H5KSH (*real*) {2.1e-01}
Parameter for Řezáč's D3H5 correction (H5 correction).

Advanced options for Kubillus's D3X (DISPTYPE=10)

- D3XS8 (*real*) {3.209e+00}
Parameter for Kubillus's D3X correction (D3 dispersion).
- D3XA1 (*real*) {7.46e-01}
Parameter for Kubillus's D3X correction (D3 dispersion).
- D3XA2 (*real*) {4.191e+00}
Parameter for Kubillus's D3X correction (D3 dispersion).
- D3XC1 (*real*) {7.761e+00}
Parameter for Kubillus's D3X correction (X correction).
- D3XC2 (*real*) {5.0e-02}
Parameter for Kubillus's D3X correction (X correction).
- D3XC3 (*real*) {4.518e+00}
Parameter for Kubillus's D3X correction (X correction).
- D3XDNCL (*real*) {1.526e+00}
Parameter for Kubillus's D3X correction (X correction).
- D3XDNBR (*real*) {1.349e+00}
Parameter for Kubillus's D3X correction (X correction).

- D3XDNI (*real*) {1.521e+00}
Parameter for Kubillus's D3X correction (X correction).
- D3XDOCL (*real*) {1.237e+00}
Parameter for Kubillus's D3X correction (X correction).
- D3XDOBR (*real*) {1.099e+00}
Parameter for Kubillus's D3X correction (X correction).
- D3XDOI (*real*) {1.313e+00}
Parameter for Kubillus's D3X correction (X correction).

Advanced options for frequency calculation

- D3STEPsize (*real*) {1.0e-04}
Step size for numerical differentiation of analytically calculated Grimme's DFT-D3 first derivatives (DISPTYPE=4-6, 9, 10) in harmonic vibrational frequency analysis (FREQTYPE=1 in FREQ/FREQUENCY keyword) in atomic unit.

Additional options for only MPI/OpenMP version

- H4IDOMAIN (*logical*) {FALSE}
Enables the use of CLL algorithm [19, 20] for index of hydrogen atoms for accelerating Řezáč's D3H4 calculation (H4 correction) in DISPTYPE=6.
- H4IDOMAINBLOCKXYZ/H4IDOMAINBLOCK (*integer*) {5}
Block size in each of x-, y-, and z-directions used in H4IDOMAIN=TRUE.
- H4IDOMAINBLOCKX (*integer*) {5}
Block size in x-direction used in H4IDOMAIN=TRUE.
- H4IDOMAINBLOCKY (*integer*) {5}
Block size in y-direction used in H4IDOMAIN=TRUE.
- H4IDOMAINBLOCKZ (*integer*) {5}
Block size in z-direction used in H4IDOMAIN=TRUE.
- H4IDOMAINNEIGHBOR (*integer*) {1}
Number of linked neighbors referred to as adjacent cells in H4IDOMAIN=TRUE.

- **H4VDOMAIN** (*logical*) {FALSE}
Enables the use of CLL algorithm [19, 20] for evaluation of atom valence for accelerating Řezáč's D3H4 calculation (H4 correction) in DISPTYPE=6.
- **H4VDOMAINBLOCKXYZ/H4VDOMAINBLOCK** (*integer*) {5}
Block size in each of *x*-, *y*-, and *z*-directions used in H4VDOMAIN=TRUE.
- **H4VDOMAINBLOCKX** (*integer*) {5}
Block size in *x*-direction used in H4VDOMAIN=TRUE.
- **H4VDOMAINBLOCKY** (*integer*) {5}
Block size in *y*-direction used in H4VDOMAIN=TRUE.
- **H4VDOMAINBLOCKZ** (*integer*) {5}
Block size in *z*-direction used in H4VDOMAIN=TRUE.
- **H4VDOMAINNEIGHBOR** (*integer*) {1}
Number of linked neighbors referred to as adjacent cells in H4VDOMAIN=TRUE.

1.1.6 PBC

The keyword PBC sets some parameters to control the calculation in periodic boundary condition. Note that the system is treated as periodic if three translation vectors are detected in Geometry section even if PBC=TRUE is not explicitly written (see [section 1.4.1](#)).

Basic settings

- STRESS (*logical*) {FALSE}
Enables to calculate stress tensors and lattice derivatives.
- COULOMBTYPE (*integer*) {1}
Method of Coulomb interaction calculation.
 - 1: Ewald summation
 - 2: Multipole expansion [\[39\]](#)
See reference [\[10\]](#) for details.
There are several limitations at present.
 - ✓ Stress tensor calculation is not supported (i.e. STRESS=FALSE).
 - ✓ Point charges should not be present (i.e. POINTCHARGE=FALSE in SCC keyword).
 - ✓ Atom resolved energies cannot be evaluated (i.e. PRINTATOME=FALSE in MISC keyword).
 - ✓ Shell resolved calculation in MPI/OpenMP version is not supported (i.e. RUNTYPE=ATOM in SCC keyword).
 - ✓ Only cubic unit cell has been tested.

Advanced options for Ewald summation (COULOMBTYPE=1)

- EWALDALPHA (*real*) {0.0e+00}
Fraction of Ewald summation between reciprocal and real space.
If value is larger than zero and smaller than one, manually specified value is used (in only single point calculation).
Otherwise, value is automatically determined (default and recommended).
- MAXGAMMA (*integer*) {7}
Maximum number of unit cell repetition for Ewald summation.

Advanced options for multipole expansion (COULOMBTYPE=2)

- FMMP (*integer*) {8}
Expansion order for multipole expansion.
- FMMN (*integer*) {3}
Number of aggregated units at each level of telescoping procedure in multipole expansion.
- FMMK (*integer*) {5}
Maximum number of level for multipole expansion.

Additional options for only MPI/OpenMP version

- EWALDSAVEMEMORY (*logical*) {FALSE}
Enables to reduce memory usage for computation of reciprocal space summation in Ewald summation.
Note that the computational cost is increased.
- EWALDMEMORYGB (*real*) {8.0e+00}
Maximum memory size for temporary arrays used in reciprocal space summation in Ewald summation in gigabyte (GB) unit.
If the estimated memory size for temporary arrays is larger than the specified value, the reduced memory usage approach is used in computations irrespective of EWALDSAVEMEMORY=FALSE.
- FMMSAVEMEMORY (*logical*) {FALSE}
Enables to reduce memory usage for computation of solid harmonics in multipole expansion.
Note that the computational cost is increased.

1.1.7 OPT/OPTIMIZE

The keyword OPT/OPTIMIZE sets whether the geometry optimization is performed or not.

Basic settings

- MAXITER (*integer*) {50}
Maximum number of optimization steps.
- GRADCONV/GCONV (*real*) {1.0e-04}
Convergence criteria for the maximum absolute value of force component in atomic unit.
- OPTTYPE (*integer*) {1}
Method for geometry optimization.
 - 1: Broyden-Fletcher-Goldfarb-Shanno (BFGS)
This uses covalent radius of atoms to construct initial Hessian matrix, which are taken from reference [\[25\]](#).
 - 2: Steepest descent
 - 3: Conjugate gradient
 - 4: Quick-min [\[40\]](#)
 - 5: Fast inertial relaxation engine (FIRE) [\[41\]](#)
- MAXMOVE (*real*) {3.0e-01}
Maximum movable size of atomic relaxation for OPTTYPE=2-5 in Å unit.
- PRINTCOORD (*logical*) {TRUE}
Enables to print molecular coordinate at each geometry step in the standard output file.
In the case of PRINTCOORD=FALSE, only the final molecular coordinate is printed in the standard output file.
- PRINTGRAD (*logical*) {TRUE}
Enables to print DFTB energy gradient at each geometry step in the standard output file.
In the case of PRINTGRAD=FALSE, maximum and root mean square forces are printed in the standard output file.

Constraint optimization

- **CONSTRAINT** (*logical*) {FALSE}
Enables to specify geometry constraints.
Constraint vector of x , y , z components is necessary for atoms to be constrained (see [section 1.4.2](#)).

Lattice optimization

- **LATTICEOPT** (*logical*) {FALSE}
Enables to optimize translation vectors.
It is not allowed to impose partial geometry constraints (CONSTRAINT=TRUE) and to set external point charges (POINTCHARGE=TRUE in SCC keyword).
Note that conjugate gradient optimizer is used when OPTTYPE=1 (BFGS).
- **EXTPRESSURE** (*real*) {0.0e+00}
External pressure during optimization of translation vectors in atomic unit.
If value is not zero, enthalpy ($E + pV$) of the system is additionally printed.
- **ISOSCALING** (*logical*) {FALSE}
Enables to scale translation vectors uniformly during optimization of translation vectors.
This is incompatible with FIXANGLE=TRUE.
- **FIXANGLE** (*logical*) {FALSE}
Enables to fix angles between translation vectors during optimization of translation vectors.
This is incompatible with ISOSCALING=TRUE.
- **FIXANGLE1** (*logical*) {FALSE}
Enables to fix length of first translation vector during optimization of translation vectors with FIXANGLE=TRUE.
- **FIXANGLE2** (*logical*) {FALSE}
Enables to fix length of second translation vector during optimization of translation vectors with FIXANGLE=TRUE.
- **FIXANGLE3** (*logical*) {FALSE}
Enables to fix length of third translation vector during optimization of translation vectors with FIXANGLE=TRUE.

- LATTICEONLY (*logical*) {FALSE}
Enables to fix atomic coordinates during optimization of translation vectors.
It is possible to apply the same option by putting a single asterisk (*) after z-coordinate for all atoms (see [section 1.4.2](#)).

Acceleration of SCC convergence

- LSMULLIKEN (*logical*) {FALSE}
Enables to predict better initial Mulliken charges using least squares fitting of geometric information to accelerate SCC convergence [42, 43]. This is not supported for block population used in DFTB+U correction (PLUSU=TRUE in SCC keyword) and onsite correction (ONSITE=TRUE in SCC keyword).
- LSGEN (*integer*) {5}
Maximum number of geometric steps to consider for least squares fitting in LSMULLIKEN=TRUE.
- LSFITGEOM (*logical*) {FALSE}
Enables to superimpose Cartesian coordinates of previous geometric steps on those of geometric step to be predicted in LSMULLIKEN=TRUE. This is available for only cluster models and unnecessary to be activated.

Advanced options for BFGS (OPTTYPE=1)

- BFGSSOLVER (*integer*) {1}
Eigensolver for diagonalization of Hessian matrix in BFGS method.
 - 1: DSYEVD
 - 2: DSYEV

Advanced options for steepest descent (OPTTYPE=2)

- STEPSIZE/STEPSTDC (*real*) {1.0e+02}
Step size along the forces for steepest descent method in atomic unit.

Advanced options for conjugate gradient (OPTTYPE=3)

- STEPCGRATOM (*real*) {1.0e-01}
Maximum step size of atom relaxation for conjugate gradient method in atomic unit.

- STEPCGRLATTICE (*real*) {1.0e-01}
Maximum step size of lattice relaxation for conjugate gradient method in atomic unit.

Advanced options for Quick-min (OPTTYPE=4)

- DELTATQMIN/DELTASTEPQMIN (*real*) {1.0e-15}
Time interval between two Quick-min steps in second (s) unit.

Advanced options for FIRE (OPTTYPE=5)

- DELTATFIRE/DELTASTEPFIRE (*real*) {1.0e-15}
Time interval between two FIRE steps in s unit.
- FIREMAXDELTA/FIREMAXDELTASTEP (*real*) {1.0e-14}
The largest time interval used in FIRE method in s unit.
- FIRENMIN (*integer*) {5}
Parameter for FIRE method.
- FIREFINC (*real*) {1.1e+00}
Parameter for FIRE method.
- FIREFDEC (*real*) {5.0e-01}
Parameter for FIRE method.
- FIREALPHASTART (*real*) {1.0e-01}
Parameter for FIRE method.
- FIREFALPHA (*real*) {9.9e-01}
Parameter for FIRE method.

1.1.8 FREQ/FREQUENCY

The keyword FREQ/FREQUENCY sets whether the harmonic vibrational frequency analysis is performed or not. If this keyword is turned on together with geometry optimization (`OPT=TRUE` or `OPTIMIZE=TRUE`), frequency calculation is carried out for the last optimization step of given structures. The frequency calculation is currently available for cluster models.

Basic settings

- `FREQTYPE` (*integer*) {1}
Method of Hessian matrix construction.
 - 1: Analytical second derivatives
This is not implemented for the following cases.
 - ✓ Open-shell system is calculated.
 - ✓ Point charges are included (`POINTCHARGE=TRUE` in SCC keyword).
 - ✓ Spline interpolation for exponentially decaying short-range part of γ -function is used (`GAMMASPLINE=TRUE` in SCC keyword).
 - ✓ DFTB+U correction is used (`PLUSU=TRUE` in SCC keyword).
 - ✓ Onsite correction is used (`ONSITE=TRUE` in SCC keyword).
 - ✓ Shell resolved calculation is chosen in MPI/OpenMP version (`RUNTYPE=SHELL`, `SHELL0` and `ORSCC=TRUE` in SCC keyword).
 - 2: Numerical second derivatives using first derivatives
- `STEPSIZE` (*real*) {1.0e-04}
Step size for numerical differentiation of first derivatives in `FREQTYPE=2` in atomic unit.
- `PRINTHESS` (*logical*) {FALSE}
Enables to print the lower triangle of Hessian matrix in the standard output file. Additionally, Hessian matrix information is stored in the binary file "**restart_hess**" for restarting purpose.
- `PRECFORMAT` (*logical*) {FALSE}
Enables to print high precision format for frequency eigenvectors.

- READHESS (*method*) {NONE}

Enables to read Hessian matrix information from file.

 - NONE calculates the Hessian matrix either analytically or numerically.
 - BINARY reads Hessian matrix information from the binary file "**restart_hess**".
 - ASCII reads Hessian matrix information from the ASCII file "**hess.dat**" (see [section 1.5.2](#) for the format).

Advanced options

- HESSSOLVER (*integer*) {1}

Eigensolver for diagonalization of Hessian matrix.

 - 1: DSYEVD
 - 2: DSYEV
- CPCONV (*real*) {1.0e-06}

Convergence criteria for coupled-perturbed DFTB equations for computation of analytical Hessian in SCC calculation in atomic unit.
- EFSTR (*real*) {2.0e-03}

Strength of external static electric field used in infrared (IR) and Raman intensities calculation in SCC calculation.
- PROJECTION (*logical*) {TRUE}

Projection out translational and rotational modes from normal coordinate analysis.

In the case of PROJECTION=FALSE, full Hessian matrix is diagonalized.
- READISOTOPE (*logical*) {FALSE}

Enables to specify arbitrary atomic mass (see [section 1.4.2](#) details).
- THERMOTEMP (*real*) {2.9815e+02}

Target temperature for thermochemical analysis in Kelvin (K) unit.
- THERMOPRES (*real*) {1.0e+00}

Target pressure for thermochemical analysis in standard atmosphere (atm) unit.
- THERMOSCALE (*real*) {1.0e+00}

Frequency scaling factor for thermochemical analysis.

- INTERRUPTCP (*logical*) {FALSE}
Enables to interrupt solving coupled-perturbed DFTB equations in computation of analytical Hessian in SCC calculation.
The partially constructed Hessian matrix is stored in the ASCII file "**hess.dat**" for restarting purpose.
- CPSTART (*integer*) {1}
Atom index to specify the beginning of partial Hessian matrix to be constructed in INTERRUPTCP=TRUE.
- CPEND (*integer*) {1}
Atom index to specify the end of partial Hessian matrix to be constructed in INTERRUPTCP=TRUE.
- INTERRUPTSEMINUM (*logical*) {FALSE}
Enables to interrupt performing numerical second derivatives calculation in FREQTYPE=2.
The partially constructed Hessian matrix is stored in the ASCII file "**hess.dat**" for restarting purpose.
- SEMINUMSTART (*integer*) {1}
Atom index to specify the beginning of partial Hessian matrix to be constructed in INTERRUPTSEMINUM=TRUE.
- SEMINUMEND (*integer*) {1}
Atom index to specify the end of partial Hessian matrix to be constructed in INTERRUPTSEMINUM=TRUE.

Additional options for only MPI/OpenMP version

- SAVEMEMORYANA (*logical*) {FALSE}
Enables to reduce memory usage for computation of analytical Hessian in SCC calculation.
Note that the computational cost is increased.

1.1.9 MD

The keyword MD sets whether the molecular dynamics (MD) using velocity Verlet integration scheme [\[44\]](#) is performed or not.

Basic settings

- NSTEP/MAXSTEP (*integer*) {10000}
Number of MD steps.
- DELTAT/DELTASTEP (*real*) {1.0e-15}
Time interval between two MD steps in s unit.
- PRINT (*integer*) {1}
Interval to write coordinate, velocity, and Mulliken atomic charges to the files **"traject"**, **"velocity"**, and **"mulliken"**, respectively.
- CHECKPOINT (*integer*) {100}
Interval to write the second restart file **"restart_chk"**.
- RESTART (*logical*) {FALSE}
Enables to read information for restarting MD from the binary file **"restart"**.
- READVELOCITY (*logical*) {FALSE}
Enables to read velocities for all atoms from the ASCII file.
 - TRUE: Read the file **"veloc.dat"** (see [section 1.5.2](#) for the format).
 - FALSE: No file to be read.

Constant energy ensemble

- NVE (*logical*) {TRUE}
Enables to run MD with NVE ensemble.
In the case of NVE=FALSE, NVT ensemble calculation is performed.
- INITTEMP (*real*) {2.9815e+02}
Target temperature of initial velocities in K unit.
Initial velocities are generated following the Maxwell-Boltzmann distribution.

Constant temperature ensemble

- **NVT** (*logical*) {FALSE}
Enables to run MD with NVT ensemble.
In the case of NVT=FALSE, NVE ensemble calculation is performed.
- **BATHTEMP/TEMPERATURE** (*real*) {2.9815e+02}
Target temperature of thermostat in K unit.
- **NVTTYPE** (*integer*) {3}
Method to control temperature for achieving constant temperature ensemble.
 - 1: Velocity scaling [\[45\]](#)
 - 2: Nosé-Hoover chain [\[46\]](#)
 - 3: Nosé-Hoover chain [\[46\]](#)
In comparison to NVTTYPE=2, NVTTYPE=3 allows to control some thermostat settings.
 - 4: Berendsen [\[47\]](#)
 - 5: Andersen [\[48\]](#)
- **ERRORTEMP** (*real*) {1.0e+04}
Threshold of temperature for scaling velocities in K unit.
If the absolute value of difference between the target temperature of thermostat and the MD temperature is greater than ERRORTEMP, the velocities are scaled so that the temperature becomes target value for NVT methods except for velocity scaling (NVTTYPE=2–5).
- **RMROTATION** (*logical*) {FALSE}
Removal of center of mass rotation in addition to translation.
This is available in only cluster model simulations.
- **RMSTEP** (*integer*) {10000}
Interval to remove center of mass translation (and rotation if RMROTATION=TRUE) for NVTTYPE=1–4.
- **CALCPRESSURE** (*logical*) {FALSE}
Enables to calculate virial pressure in constant energy or constant temperature ensemble.
This is available in only simulations of periodic system.

Advanced options for thermostat

- SCALESTEP (*integer*) {20}
Interval to scale velocities for velocity scaling method (NVTTYPE=1).
- NOSECLEAN (*logical*) {FALSE}
Enables to initialize internal parameters of Nosé-Hoover chain thermostat when MD is restarted.
- NBATH (*integer*) {3}
Number of particles for Nosé-Hoover chain thermostat (NVTTYPE=3).
- COUPLINGSTR (*real*) {1.5e+03}
Frequency of oscillation of the thermostat particles in cm^{-1} unit for Nosé-Hoover chain thermostat (NVTTYPE=3).
- TAUTEMP (*real*) {1.0e-13}
Time constant for Berendsen thermostat (NVTTYPE=4) in s unit.
- COLLISIONFREQ (*real*) {1.0e-02}
Random collision frequency for Andersen thermostat (NVTTYPE=5) in fs^{-1} unit (fs is femtosecond).
- MASSIVE (*logical*) {FALSE}
Method of scaling velocities for Andersen thermostat (NVTTYPE=5).
 - TRUE: All velocities are scaled simultaneously with the specified probability.
 - FALSE: Each atomic velocity is scaled individually with the specified probability.

Constant pressure ensemble

- NPH (*logical*) {FALSE}
Enables to run MD with NPH ensemble.
In the case of NPH=FALSE, NVE ensemble calculation is performed.
- NPT (*logical*) {FALSE}
Enables to run MD with NPT ensemble.
In the case of NPT=FALSE, NVE ensemble calculation is performed.

- **EXTPRESSURE** (*real*) {1.01325e+05}
Target pressure during constant pressure ensemble simulation in Pascal (Pa) unit.
- **NPHTYPE** (*integer*) {1}
Method to control pressure for achieving constant pressure ensemble.
 - 1: Berendsen [\[47\]](#)
- **NPTTYPE** (*integer*) {1}
Method to control pressure and temperature for achieving (isotropic) NPT ensemble.
 - 1: Hoover-Andersen [\[46\]](#)
- **ISOSCALING** (*logical*) {FALSE}
Enables to scale translation vectors uniformly during constant pressure ensemble simulation.
Default is anisotropic change of unit cell.

Advanced options for barostat

- **TAUPRESS** (*real*) {2.0e-12}
Time constant for Berendsen barostat (NPHTYPE=1) in s unit.
- **COUPLINGSTRLAT** (*real*) {1.5e+01}
Frequency of oscillation of the thermostat particles in cm^{-1} unit for Hoover-Andersen NPT ensemble (NPTTYPE=1).

Random number generation

- **RANDTYPE** (*integer*) {1}
Method to generate random numbers.
 - 1: Fortran intrinsic random number generator
Different platform may generate different random numbers using the same seed.
 - 2: Random number generator taken from reference [\[49\]](#).

- SEEDTYPE (*integer*) {1}
Method of random number generation for velocities.
 - 1: No specification (the same initial velocities may be reproduced on the same platform for the same given structure in Geometry section).
 - 2: Generation of random number from the current time.
 - 3: Specification of arbitrary random number using RANDOMSEED option.
- RANDOMSEED (*integer*) {0}
Seed to generate random number for initial velocities using SEEDTYPE=3.

Soft boundary potential

- SOFT/SOFTPOT (*logical*) {FALSE}
Enables to use soft potential.
- SOFTK (*real*) {1.5e+00}
Hardness of soft potential in kcal/(mol·Å²) unit.
- SOFTCENTERTYPE (*method*) {ATOM}
Method to specify center of soft potential.
 - ATOM defines one of atoms as center of soft potential.
 - SPECIFY manually sets the position of xyz coordinate.
 - COC is the abbreviation of "center of coordinate".
 - COM is the abbreviation of "center of mass".
- SOFTATOMNO (*integer*) {1}
Atom label to be the center of soft potential used in SOFTCENTERTYPE=ATOM.
- SOFTPOINTXYZ/SOFTPOINT (*real*) {0.0e+00}
Cartesian coordinate of the center of soft potential satisfying $x = y = z$ used in SOFTCENTERTYPE=SPECIFY in Å unit.
- SOFTPOINTX (*real*) {0.0e+00}
 x -component of the center of soft potential used in SOFTCENTERTYPE=SPECIFY in Å unit.

- SOFTPOINTY (*real*) {0.0e+00}
y-component of the center of soft potential used in SOFTCENTERTYPE=SPECIFY in Å unit.
- SOFTPOINTZ (*real*) {0.0e+00}
z-component of the center of soft potential used in SOFTCENTERTYPE=SPECIFY in Å unit.
- SOFTSHAPETYPE (*method*) {SPHERE}
Method to specify shape of soft potential.
 - SPHERE is sphere.
 - SQUARE is cubic or rectangular box.
 - ELLIPSOID is ellipsoid.
- SOFTRANGE (*real*) {1.0e+01}
Radius of soft potential used in SOFTSHAPETYPE=SPHERE in Å unit.
- SOFTSIDEXYZ/SOFTSIDE (*real*) {1.0e+01}
Grid length of cubic grid used in SOFTSHAPETYPE=SQUARE in Å unit.
- SOFTSIDE X (*real*) {1.0e+01}
Grid length of x-component used in SOFTSHAPETYPE=SQUARE in Å unit.
- SOFTSIDE Y (*real*) {1.0e+01}
Grid length of y-component used in SOFTSHAPETYPE=SQUARE in Å unit.
- SOFTSIDE Z (*real*) {1.0e+01}
Grid length of z-component used in SOFTSHAPETYPE=SQUARE in Å unit.
- SOFTSEMIAXISX (*real*) {1.0e+01}
Length of x-semi-principal axis used in SOFTSHAPETYPE=ELLIPSOID in Å unit.
- SOFTSEMIAXISY (*real*) {1.0e+01}
Length of y-semi-principal axis used in SOFTSHAPETYPE=ELLIPSOID in Å unit.

- SOFTSEMIAXISZ (*real*) {1.0e+01}
Length of z-semi-principal axis used in SOFTSHAPETYPE=ELLIPSOID in Å unit.

Constraint MD with RATTLE

- RATTLE (*method*) {NONE}
Constraint MD simulation using RATTLE algorithm [50] for bond lengths.
 - NONE corresponds to no constraints of bond lengths.
 - COVALENTXH fixes X–H covalent bonds as the sum of their covalent radii, which are taken from reference [25].
 - INITGEOMXH fixes X–H covalent bond distance as the value of initial structure.
 - SPECIFY sets any bond constraints using the file “**rattle.dat**” (see [section 1.5.2](#) for the format).
- RATTLEXH (*real*) {1.2e+00}
Threshold of X–H pair as the covalent bond in RATTLE=COVALENTXH and RATTLE=INITGEOMXH in Å unit.
- RATTLEITER (*integer*) {100}
Maximum number of cycles to satisfy RATTLE position and velocity constraints.
- RATTLECONV (*real*) {1.0e–06}
Convergence criteria for the RATTLE constraints in atomic unit.

Acceleration of SCC convergence

- LIMULLIKEN (*logical*) {FALSE}
Enables to predict better initial Mulliken charges using Lagrange interpolation to accelerate SCC convergence [43, 51].
This is not supported for block population used in DFTB+U correction (PLUSU=TRUE in SCC keyword) and onsite correction (ONSITE=TRUE in SCC keyword).
- LIDEGREE (*integer*) {0}
Degree of Lagrange polynomial in LIMULLIKEN=TRUE.
Default uses the previous converged charges for initial guess (conventional approach).

- LIMINDEG (*logical*) {FALSE}
Enables to obtain the appropriate degree of Lagrange polynomial within a range from 0 to the value set in LIDEGREE in LIMULLIKEN=TRUE. Degree which gives the smallest absolute error of the predicted charges from the converged values at N step is used at $N + 1$ step.
- LSMULLIKEN (*logical*) {FALSE}
Enables to predict better initial Mulliken charges using least squares fitting of geometric information to accelerate SCC convergence [42, 43]. This is not supported for block population used in DFTB+U correction (PLUSU=TRUE in SCC keyword) and onsite correction (ONSITE=TRUE in SCC keyword).
- LSGEN (*integer*) {5}
Maximum number of geometric steps to consider for least squares fitting in LSMULLIKEN=TRUE.
- LSFITGEOM (*logical*) {FALSE}
Enables to superimpose Cartesian coordinates of previous geometric steps on those of geometric step to be predicted in LSMULLIKEN=TRUE. This is available for only cluster models and unnecessary to be activated.

Annealing simulation

- ANNEAL (*logical*) {FALSE}
Enables to perform annealing simulation. Temperature scheduling is specified using the file "**anneal.dat**" up to 99 profiles (see [section 1.5.2](#) for the format).

Metadynamics

- METAD/METADYNAMICS (*logical*) {FALSE}
Enables to perform metadynamics simulation [52]. Information of collective variables (CVs) is specified using the file "**metacv.dat**" (see [section 1.5.2](#) for the format and the implemented CVs).
- METAMAXCV (*integer*) {10}
Maximum number of CVs used in metadynamics.
- METAFREQ (*integer*) {100}
Interval to deposit Gaussian bias potential during metadynamics.

- METAMAXGAUSS (*integer*) {10000}
Maximum number of Gaussian bias potentials to be deposited during metadynamics.
- METAHEIGHT (*real*) {4.0e-04}
Height of Gaussian to be deposited in Hartree unit.
- METARESTART (*logical*) {FALSE}
Enables to read history of Gaussian bias potential for restarting metadynamics from the binary file "**restart_meta**".
- METAREADBIAS (*logical*) {FALSE}
Enables to read history of Gaussian bias potential from the ASCII file.
 - TRUE: Read the file "**bias.dat**" (see [section 1.5.2](#) for the format).
 - FALSE: No file to be read.

Advanced options for metadynamics

- WTMETAD/WTMETADYNAMICS (*logical*) {FALSE}
Enables to perform well-tempered metadynamics simulation [\[53\]](#).
- WTMETABIASTEMP (*real*) {1.2e+03}
Bias temperature of well-tempered metadynamics in K unit.
- METAPBCMIC (*logical*) {TRUE}
Enables to apply minimum image convention to atom-pair distances for calculation of CVs in metadynamics of periodic system.
Note that minimum image convention is not used to calculate center of coordinate or center of mass and some CVs (see [section 1.5.2](#) for details).
- METAPRINTFES (*logical*) {TRUE}
Enables to write free energy surface to the file "**fes.dat**" every deposition of Gaussian bias potential.
Information of grid must be specified in "**metacv.dat**" (see [section 1.5.2](#) for details).
Note that scaling factor for the free energy surface is included in the case of well-tempered metadynamics [\[53\]](#).

- METAWALL (*logical*) {FALSE}
Enables to apply wall potential to constrain sampling range of CVs in metadynamics.
Information of wall potential must be specified in "**metacv.dat**" (see [section 1.5.2](#) for details).

1.1.10 MISC

The keyword MISC sets other miscellaneous options.

Additional analysis and property evaluation

- **PRINTFORCE/FORCE** (*logical*) {FALSE}
Enables to perform the force calculation after single point energy calculation.
If point charges are included (POINTCHARGE=TRUE in SCC keyword), forces of point charges are additionally printed.
If stress tensor calculation is performed (STRESS=TRUE in PBC keyword), stress tensor, lattice derivatives, volume and pressure are additionally printed.
- **PRINTRESOLVEDFORCE** (*logical*) {FALSE}
Enables to evaluate force contributions (electronic, repulsive, and dispersion term if included).
If stress tensor calculation is performed (STRESS=TRUE in PBC keyword), corresponding contributions of stress tensor are additionally evaluated.
Note that total forces are printed in the standard output while the respective contributions are printed in the detailed data file.
- **PRINTMO** (*logical*) {FALSE}
Enables to print eigenvectors.
Note that this option is available when the number of subsystem is equal to 1.
- **PRINTDENSITY** (*logical*) {FALSE}
Enables to print the lower triangle of density matrix in the standard output.
- **PRINTATOME** (*logical*) {FALSE}
Enables to evaluate atomic energy contributions (electronic, repulsive, and dispersion term if included).
Note that the respective contributions are printed in the detailed data file.

Global options

- **FORCETYPE** (*integer*) {1}
Method of gradient calculation.
 - 1: Analytical first derivatives.
 - 2: Numerical first derivatives using DFTB total energy.
- **FORCESTEPsize** (*real*) {1.0e-04}
Step size for numerical differentiation of DFTB total energy in FORCETYPE=2 in atomic unit.
- **HSSTEPsize** (*real*) {1.0e-02}
Step size for numerical differentiation of DFTB parametrized integrals in analytical first and second derivatives calculations in atomic unit.
- **WRITEDAT** (*method*) {APPEND}
Enables to control dumping of the detailed data file.
 - NONE never generates the data file.
 - APPEND opens the data file in the beginning of program run and writes the information of each DFTB calculation. The size of detailed data file may become huge if a large number of geometry steps is specified in geometry optimization or MD.
 - REPLACE opens/closes the data file at the beginning/end of DFTB calculation. Namely, in geometry optimization or MD, the data file contains the information of the last geometry step.
- **WRITECHRGFILE** (*logical*) {TRUE}
Enables to control dumping of the binary file "**chrgfile**" containing Mulliken charge information which is used in READCHARGE=BINARY in SCC keyword.
- **PRINTLAPTIME** (*logical*) {FALSE}
Enables to print wall clock time for DFTB computational steps.
Total wall clock time is additionally printed at the end of program run.
- **PRINTLOCALREGION** (*logical*) {FALSE}
Enables to print number of subsystems, atoms, and basis functions in localization regions in the standard output.
Note that the program terminates immediately without proceeding further DFTB computational steps.

- **PRINTHS** (*logical*) {FALSE}
Enables to print the lower triangle of non-perturbed Hamiltonian and overlap matrices in the standard output.
This option is available when the number of subsystem is equal to 1.
Note that the program terminates immediately without proceeding further DFTB computational steps.

Additional options for only serial and OpenMP versions

- **USESCRATCH** (*logical*) {FALSE}
Enables to use disk I/O for storing some intermediate data.
In the case of USESCRATCH=FALSE, all intermediate data are stored in memory.

1.2 Title section

TITLE ↵

Comment line

This is typically used for the comment of compound name, symmetry, electronic state, other relevant information, and so on. Each line should be less than 128 characters. All comments will be printed in the standard output file as it is (see [section 3.1](#)).

1.3 Parameter section

1.3.1 General overview

2↵	<i>Number of unique atom types</i>
O_2↵	<i>Atom symbol and its highest angular momentum for valence shells</i>
oo.spl_oh.spl↵	<i>Slater-Koster parameters: atom1–atom1 and atom1–atom2</i>
H_1↵	<i>Atom symbol and its highest angular momentum for valence shells</i>
ho.spl_hh.spl↵	<i>Slater-Koster parameters: atom2–atom1 and atom2–atom2</i>

This section starts from the line giving the number of atom types in the given structure. The present example is 2 since water molecule contains oxygen and hydrogen. Next, atom symbol and its maximum angular momentum are specified for the first atom type (*atom1*). The integer 1, 2, 3, 4 corresponds to the maximum angular momentum *s*, *p*, *d*, *f*, respectively. Then, the paths to Slater-Koster parameter files including the first atom types are specified in a single line. The order has to be consistent in the order of atom types specified in this section, namely *atom1* with *atom1*, *atom1* with *atom2* (the second atom type), *atom1* with *atom3* (the third atom type), ... These two lines are repeated until all atom types in the given structure are specified. Note that the present example assumes 4 Slater-Koster parameter files (**oo.spl**, **oh.spl**, **ho.spl**, **hh.spl**) are located in the same directory as the one containing the input file. When the prefix of current directory is explicitly included, this section looks like as follows.

```
2↵
O_2↵
./oo.spl_/oh.spl↵
H_1↵
./ho.spl_/hh.spl↵
```

For treating *f*-electrons, please ensure that relevant Slater-Koster files have the extended format.

1.3.2 Specification of additional constants

Several options request atom dependent constants which are not hard-coded or written in Slater-Koster files. Such constants are specified in two ways:

- Direct specification of employed values after the highest angular momentum for valence shells

This is necessary for Hubbard derivatives in third order corrections (THIRDFULL=TRUE or THIRDDIAG=TRUE in SCC keyword).

The Hubbard derivative should be specified after the maximum angular momentum.

In the case of orbitally resolved calculation (ORSCC=TRUE in SCC keyword) with MPI/OpenMP version, values of s -, p -, d -, and f -shells need to be provided separately.

```
O_2_-0.1575_
```

Atom resolved case (usual)

```
Cu_3_-0.20_-0.0575_-0.0575_
```

Orbitally resolved case (order is (f), d, p, s)

- Preparation of additional ASCII files

This is necessary for the following five options:

- Spin constants for spin polarized calculation (SPIN=TRUE in SCC keyword)
- U-J parameters for DFTB+U correction (PLUSU=TRUE in SCC keyword)
- Onsite parameters for onsite correction (ONSITE=TRUE in SCC keyword)
- Atomic polarizabilities, van der Waals radii, and effective charge for Slater-Kirkwood dispersion (DISPTYPE=2 in DISP/DISPERSION keyword)
- Lennard-Jones parameters for Lennard-Jones dispersion (DISPTYPE=3 and READUFF=TRUE in DISP/DISPERSION keyword)

The path of additional file should be specified after the maximum angular momentum (or Hubbard derivatives if they exist). In the case of specifying multiple files, the path of dispersion constants file should come first, followed by the path of spin constants file, subsequently the path of U-J parameter file, and finally the path of onsite parameter file.

Examples for oxygen atom are given below.

<code>O_2_o.wll_↓</code>	<i>Only spin constants file</i>
<code>O_2_o.dispsk_↓</code>	<i>Only dispersion constants file</i>
<code>O_2_o.uj_↓</code>	<i>Only U-J parameters file</i>
<code>O_2_o.oc_↓</code>	<i>Only onsite parameters file</i>
<code>O_2_o.dispsk_o.wll_↓</code>	<i>Both spin and dispersion constants files</i>
<code>O_2_o.dispsk_o.uj_↓</code>	<i>Both dispersion constants and U-J parameters files</i>
<code>O_2_o.dispsk_o.oc_↓</code>	<i>Both dispersion constants and onsite parameters files</i>
<code>O_2_o.wll_o.uj_↓</code>	<i>Both spin constants and U-J parameters files</i>
<code>O_2_o.wll_o.oc_↓</code>	<i>Both spin constants and onsite parameters files</i>
<code>O_2_o.uj_o.oc_↓</code>	<i>Both U-J parameters and onsite parameters files</i>
<code>O_2_o.dispsk_o.wll_o.uj_↓</code>	<i>Dispersion constants, spin constants and U-J parameters files</i>
<code>O_2_o.dispsk_o.wll_o.oc_↓</code>	<i>Dispersion constants, spin constants and onsite parameters files</i>
<code>O_2_o.dispsk_o.ud_o.oc_↓</code>	<i>Dispersion constants, U-J parameters and onsite parameters files</i>
<code>O_2_o.wll_o.ud_o.oc_↓</code>	<i>Spin constants, U-J parameters and onsite parameters files</i>
<code>O_2_o.dispsk_o.wll_o.ud_o.oc_↓</code>	<i>All dispersion constants, Spin constants, U-J parameters and onsite parameters files</i>

1.3.3 Format of ASCII files for additional constants

The ASCII files for specifying additional constants described in [section 1.3.2](#) have different format in each case. Here examples for carbon atom are shown.

Spin constants file

```
-0.031_↓  
-0.025_↓  
-0.025_↓  
-0.023_↓
```

The number of lines of spin constants file depends on the maximum angular momentum (1, 4, 9, 16 for *s*, *p*, *d*, *f*). Each line contains the atomic spin constant in atomic unit in the following order:

- *s*: *ss*
- *p*: *ss, sp, ps, pp*
- *d*: *ss, sp, sd, ps, pp, pd, ds, dp, dd*
- *f*: *ss, sp, sd, sf, ps, pp, pd, pf, ds, dp, dd, df, fs, fp, fd, ff*

For reference, PBE values for H, C, N, O, S, Fe, and Ni listed in DFTB+ manual [\[54\]](#) are stored into the file with suffix ".wll" in the slko directory.

U–J parameters file

```
0.178371875_1_↓  
0.178371875_1_↓
```

The number of lines of U–J parameters file depends on the maximum angular momentum (1, 2, 3, 4 for *s*, *p*, *d*, *f*). There should exist two columns in each line. The first column specifies the magnitude of effective on-site Coulomb interaction in atomic unit and the second column specifies the index of block for valence shells. For example, if *s*- and *p*-orbitals needs to be treated as separated block, the second column of second line will be changed from "1" to "2". Note that this file should be prepared with zero value for the first column even if no DFTB+U correction is applied for some atom types.

Onsite parameters file

```
0.00000_0.00000_␣
0.04973_0.10512_␣
0.04973_0.10512_␣
-0.01203_0.02643_␣
```

The number of lines of onsite parameters file depends on the maximum angular momentum (1, 4, 9, 16 for *s*, *p*, *d*, *f*). There should exist two columns in each line. The first and second columns specify the same and different spin parameters in atomic unit in the following order:

- *s*: *ss*
- *p*: *ss*, *sp*, *ps*, *pp*
- *d*: *ss*, *sp*, *sd*, *ps*, *pp*, *pd*, *ds*, *dp*, *dd*
- *f*: *ss*, *sp*, *sd*, *sf*, *ps*, *pp*, *pd*, *pf*, *ds*, *dp*, *dd*, *df*, *fs*, *fp*, *fd*, *ff*

For reference, PBE values for H, C, N, O, and S listed in reference [14] or in DFTB+ manual [54] are stored into the file with suffix ".oc" in the slko directory.

Slater-Kirkwood dispersion constants file

```
1.382_1.382_1.382_1.064_3.8_3.8_3.8_3.8_2.5_␣
```

There should exist nine columns in a single line. The first to fourth columns specify atomic polarizabilities in Å³ unit, the fifth to eighth columns specify van der Waals radii in Å unit, and the last column specifies effective charge. The values for atomic polarizabilities and van der Waals radii are given for zero, one, two, and three hydrogen neighbors. For reference, H, C, N, O, and S dispersion constants listed in DFTB+ manual [54] are stored into the file with suffix ".dispsk" in the slko directory.

Lennard-Jones dispersion parameters file

```
3.851_0.105_␣
```

There should exist two columns in a single line. The first column specifies non-bonded distance in Å unit and the second column specifies non-bonded energy in kcal/mol unit. For reference, H, C, N, O, S, Fe, and Ni Lennard-Jones parameters listed in reference [30] are stored into the file with suffix ".displj" in the slko directory.

1.4 Geometry section

1.4.1 General overview

```
3_0_1_
O _ 0.06275391_ 0.06275391_ 0.00000000_
H _ 1.01910555_-0.08185946_ 0.00000000_
H _-0.08185946_ 1.01910555_ 0.00000000_
```

*Number of atoms,
charge,
spin multiplicity
Cartesian coordinates
of atom label 1
Cartesian coordinates
of atom label 2
Cartesian coordinates
of atom label 3*

This section begins with the line giving three integers; number of atoms, charge, and spin multiplicity for the given structure. Then the position of atom is specified with Cartesian coordinates in Å unit with floating point number (**DO NOT USE INTEGERS!**).

If the given system is periodic, the unit cell can be specified by adding three translation vectors with label TV after the last Cartesian coordinates (TV should be an upper-case). The following example is for diamond crystal structure (primitive unit cell).

```
2_0_1_
C _ 0.00000000_ 0.00000000_ 0.00000000_
C _ 0.89169750_ 0.89169750_ 0.89169750_
TV_ 0.00000000_ 1.78339500_ 1.78339500_
TV_ 1.78339500_ 0.00000000_ 1.78339500_
TV_ 1.78339500_ 1.78339500_ 0.00000000_
```

If the external static electric field is included (EFIELD=TRUE in SCC keyword), the electric field vector can be specified by adding one line with label EF after the last Cartesian coordinates (EF should be an upper-case). The example of water molecule with electric field components of $x = 0.001$, $y = -0.001$, and $z = 0.000$ is given below.

```
3_0_1_␣  
O _ 0.06275391_ 0.06275391_ 0.00000000_␣  
H _ 1.01910555_-0.08185946_ 0.00000000_␣  
H _-0.08185946_ 1.01910555_ 0.00000000_␣  
EF_ 0.00100000_-0.00100000_ 0.00000000_␣
```

If the point charges are included (POINTCHARGE=TRUE in SCC keyword), the coordinates and charge value can be specified by adding lines with label PC after the last Cartesian coordinates (PC should be an upper-case). The example of water molecule with point charge of 1.0 positioned at $x = 5.0 \text{ \AA}$, $y = 5.0 \text{ \AA}$, and $z = 5.0 \text{ \AA}$ is given below.

```
3_0_1_␣  
O _ 0.06275391_ 0.06275391_ 0.00000000_␣  
H _ 1.01910555_-0.08185946_ 0.00000000_␣  
H _-0.08185946_ 1.01910555_ 0.00000000_␣  
PC_ 5.00000000_ 5.00000000_ 5.00000000_ 1.00000000_␣
```

1.4.2 Specification of additional information

Additional columns after Cartesian coordinates can be read when you would like to specify atoms to be moved or atomic masses to be changed to investigate the isotope effects of vibrational properties.

- Freeze the coordinate in geometry optimization or MD
If a single asterisk (*) is put, the position of atom will not be moved.
- Constraint geometry optimization (CONSTRAINT=TRUE in OPT/OPTIMIZE keyword)
Constraint vector of x, y, z components is either 0.0 (fixed) or 1.0 (moved). For example, the vector "0.0_0.0_1.0" will update only z component. The vector "0.0_0.0_0.0" is identical to put a single asterisk.
- Specification of different atomic masses in harmonic vibrational frequency analysis (READISOTOPE=TRUE in FREQ/FREQUENCY keyword)
The form "ISO=*value*" changes atomic mass from the default value in Slater-Koster parameter file to *value* (no space between ISO= and *value*). This specification should come later than the single asterisk or constraint vector when both options are activated.

Here is an example of the mixed specifications for water molecule.

```
3_0_1_
O _ 0.06275391_ 0.06275391_ 0.00000000_
H _ 1.01910555_-0.08185946_ 0.00000000_0.0_1.0_0.0_
H _-0.08185946_ 1.01910555_ 0.00000000_*_ISO=2.014102_
```

When the constraint geometry optimization is performed, the hydrogen with atom label 2 can be moved along only the y -axis and the coordinate of hydrogen with atom label 3 is never updated. If FREQ=(READISOTOPE=TRUE) is additionally specified, the atomic mass of hydrogen with atom label 3 is changed to 2.014102, namely the harmonic vibrational frequencies and corresponding thermochemical properties of HOD molecule will be obtained.

1.4.3 Manual construction of subsystems in DC-DFTB

This section supplements how to specify the subsystems using `SUBTYPE=SPECIFY` and `SUBTYPE=SEMIAUTO` options in DC keyword. After the blank line of Geometry section, the indices of subsystems for each atom are listed.

Here is an example of specification of 5 subsystems for the given structure containing 22 atoms in `SUBTYPE=SPECIFY`:

1_1_1_1_1_↓	<i>Index of subsystem for atom label 1, 2, 3, 4, 5</i>
2_2_2_2_↓	<i>Index of subsystem for atom label 6, 7, 8, 9</i>
3_3_3_3_↓	<i>Index of subsystem for atom label 10, 11, 12, 13</i>
4_4_4_4_↓	<i>Index of subsystem for atom label 14, 15, 16, 17</i>
5_5_5_5_5_↓	<i>Index of subsystem for atom label 18, 19, 20, 21, 22</i>

where atoms with label 1–5 belong to subsystem 1, atoms with label 6–9 belong to subsystem 2, atoms with label 10–13 belong to subsystem 3, and so on. It is not necessarily to use the same number of lines as the number of subsystems. The new line will be read until the total number of indices is equal to the number of atoms in the given structure.

In the case of `SUBTYPE=SEMIAUTO`, the integer “0” is used as an index for atoms to be assigned to subsystems automatically by using the grid box. The following is an example of system containing 22 atoms (using analogous format from the previous one for comparison):

1_1_1_1_1_↓	<i>Index of subsystem for atom label 1, 2, 3, 4, 5</i>
0_0_0_0_↓	<i>Index of subsystem for atom label 6, 7, 8, 9</i>
0_0_0_0_↓	<i>Index of subsystem for atom label 10, 11, 12, 13</i>
0_0_0_0_↓	<i>Index of subsystem for atom label 14, 15, 16, 17</i>
2_2_2_2_2_↓	<i>Index of subsystem for atom label 18, 19, 20, 21, 22</i>

where atoms with label 1–5 belong to subsystem 1, atoms with label 18–22 belong to subsystem 2, and atoms with label 6–17 are assigned to subsystems 3–X automatically (X depends on the given structure and size of grid box). If all indices are zero and positive integer, the option is identical to `SUBTYPE=AUTO` and `SUBTYPE=SPECIFY`, respectively.

1.5 Auxiliary input files

In addition to the main input file, Slater-Koster parameter files, and ASCII files for additional constants if any (see [section 1.3.3](#)), some auxiliary input files are necessary depending on computational setup. Each auxiliary input file has the specific filename and should be located in the same directory as the one containing the main input file. There are two types of auxiliary input files: (i) using binary file dumped in previous run of program and (ii) preparing ASCII file with specific format.

1.5.1 Binary format files

Binary format files serve to providing information for restarting purpose. See [section 3.3](#) or relevant options in the description for the contents of respective file. Note that the binary file should not be used with different versions (**DO NOT MIX: (i) OpenMP (serial) and MPI/OpenMP and (ii) version 1.0 and 2.0!**).

- **"chrgfile"**
This is required if `SCC=(READCHARGE=BINARY)` is specified.
Please make sure that the previous run of program specifies `SCC=TRUE` and `WRITECHRGFILE=TRUE` in MISC keyword.
- **"restart_hess"**
This is required if `FREQ=(RESTARTHESS=BINARY)` is specified.
Please make sure that the previous run of program specifies `PRINTHESS=TRUE` in FREQ/FREQUENCY keyword.
- **"restart"**
This is required if `MD=(RESTART=TRUE)` is specified.
Not only **"restart"** itself, **"restart_chk"** may be used after renaming.
- **"restart_meta"**
This is required if `MD=(METARESTART=TRUE)` is specified.
Not only **"restart_meta"** itself, **"restart_meta_chk"** may be used after renaming.
Please make sure that the previous and present run of program specifies `METAD=TRUE`, `METADYNAMICS=TRUE`, `WTMETAD=TRUE`, or `WTMETADYNAMICS=TRUE` in MD keyword.

1.5.2 ASCII format files

ASCII format files mainly serve to providing detailed information which depends on the given structure.

Reading initial charge in SCC calculation

- **"charge.dat"**

This is required if `SCC=(READCHARGE=ASCII)` is specified.

Please make sure that the previous run of program specifies `SCC=TRUE`.

Examples for water molecule are given below, where oxygen corresponds to atom label 1 and hydrogen corresponds to atom labels 2 and 3.

For serial and OpenMP versions, the first line of **"charge.dat"** is either **"ALLATOM"** or **"ATOMSPECIES"**.

➤ **ALLATOM** lists the net charge for every atom from the second line.

```
ALLATOM┆
```

```
-0.6┆
```

```
0.3┆
```

```
0.3┆
```

Mulliken population of O (atom label 1) is 6.6

Mulliken population of H (atom label 2) is 0.7

Mulliken population of H (atom label 3) is 0.7

➤ **ATOMSPECIES** lists the atom symbol and the net charge in the first and second columns from the second line until detecting blank line if any.

```
ATOMSPECIES┆
```

```
O_-0.6┆
```

```
H_ 0.3┆
```

Mulliken population of O (atom label 1) is 6.6

Mulliken population of H (atom labels 2 and 3) is 0.7

For MPI/OpenMP version, the first line of “**charge.dat**” is either “ALLSHELL” or “SHELLSPECIES”.

- **ALLSHELL** lists the net charge for every shell from the second line.

ALLSHELL┆	
0.2┆	<i>Mulliken population of s shell of O (atom label 1) is 1.8</i>
-0.8┆	<i>Mulliken population of p shell of O (atom label 1) is 4.8</i>
0.3┆	<i>Mulliken population of s shell of H (atom label 2) is 0.7</i>
0.3┆	<i>Mulliken population of s shell of H (atom label 3) is 0.7</i>

- **SHELLSPECIES** lists the atom symbol, subshell symbol (s/p/d/f), and the net charge in the first, second, and third columns from the second line until detecting blank line if any. If system is open-shell, alpha/beta spin symbol (a/b) is specified in the fourth column.

SHELLSPECIES┆	
O_s_ 0.2┆	<i>Mulliken population of s shell of O (atom label 1) is 1.8</i>
O_p_-0.8┆	<i>Mulliken population of p shell of O (atom label 1) is 4.8</i>
H_s_ 0.3┆	<i>Mulliken population of s shell of H (atom labels 2 and 3) is 0.7</i>

Reading Hessian matrix in frequency calculation

- “**hess.dat**”

This is required if `FREQ=(RESTARTHESS=ASCII)` is specified.

Please make sure that the previous run of program specifies `INTERRUPTCP=TRUE` or `INTERRUPTSEMINUM=TRUE` in `FREQTYPE=1` or `FREQTYPE=2` in `FREQ/FREQUENCY` keyword.

Each line consists of three columns: the first and second integers are used to specify the index of Hessian matrix and the third value is an element of Hessian matrix. It is enough for off-diagonal elements to set once in the file. Namely, the program assumes reading $3N(3N + 1)/2$ lines for the given structure containing N atoms.

1_1_-0.000171┆	<i>Hessian matrix element of (H)₁₁ is -0.000171</i>
2_1_ 0.000000┆	<i>Hessian matrix element of (H)₂₁ and (H)₁₂ is 0.000000</i>
3_1_ 0.000083┆	<i>Hessian matrix element of (H)₃₁ and (H)₁₃ is 0.000083</i>
...	

Reading initial velocity in MD simulation

- **"veloc.dat"**

This is required if MD=(READVELOCITY=TRUE) is specified.

Each line consists of three columns: x, y, z velocity components are given for each atom of the given structure in Geometry section in Å/fs unit. (**DO NOT INCLUDE ATOM SYMBOL!**)

0.00154193_ -0.00142221_ -0.00058536_	<i>Velocity components of atom label 1</i>
-0.02998618_ 0.02026292_ 0.00706185_	<i>Velocity components of atom label 2</i>
0.00549584_ 0.00232603_ 0.00223541_	<i>Velocity components of atom label 3</i>
...	

Manual construction of bond constraints in RATTLE

- **"rattle.dat"**

This is required if MD=(RATTLE=SPECIFY) is specified.

The first and second columns specify atom labels whose distance is fixed. The third column is an upper-case letter to determine how the specified bond distance is fixed. The program assumes no blank line until the end of file.

- C: Bond distance is fixed to the sum of covalent radii, which are taken from reference [25].
- I: Bond distance is fixed to the value of initial structure.
- S: Bond distance is fixed to the value specified in the fourth column in Å unit.

Note that the sum of covalent radii is used if no fourth column is set.

1_2_C_	<i>Bond distance of atom label 1 and 2 is the sum of covalent radii</i>
2_3_I_	<i>Bond distance of atom label 2 and 3 is the value of initial structure</i>
1_3_S_0.95_	<i>Bond distance of atom label 1 and 3 is 0.95 Å</i>

Setting temperature profile in annealing simulation

● **"anneal.dat"**

This is required if MD=(ANNEAL=TRUE) is specified.

The first column is an upper-case letter to determine how the temperature is varied and the second column specifies the number of MD steps that follows the corresponding profile. The third column is temperature value in K unit. The program assumes no blank line until the end of file.

- C: Temperature is set to constant value specified in the third column.
- L: Temperature varies linearly from the temperature of previous profile to the value specified in the third column.
- G: Temperature varies geometrically from the temperature of previous profile to the value specified in the third column.
- E: Temperature varies exponentially from the temperature of previous profile to the value specified in the third column.

The shape of exponential function is controlled by the value specified in the fourth column.

Note that the value of 5.0 is used if no fourth column is set.

- S: Temperature varies sigmoidally from the temperature of previous profile to the value specified in the third column.

The shape of sigmoid function is controlled by the value specified in the fourth column.

Note that the value of 3.0 is used if no fourth column is set.

C_ 1_ 300.0_	<i>The first step is set to 300 K</i>
L_1000_1000.0_	<i>INITTEMP option is updated with the specified value</i>
C_1000_1000.0_	<i>Next 1000 steps increase linearly from 300 to 1000 K</i>
C_1000_1000.0_	<i>Next 1000 steps keep the temperature 1000 K (equilibration)</i>
E_1000_ 500.0_3.0_	<i>Next 1000 steps decrease exponentially with decay factor of 3.0 from 1000 to 500 K</i>
C_1000_ 500.0_	<i>Next 1000 steps keep the temperature 500 K (equilibration)</i>
S_1000_ 300.0_2.0_	<i>Next 1000 steps decrease sigmoidally with gain factor of 2.0 from 500 to 300 K</i>

Setting CVs in metadynamics simulation

- **"metacv.dat"**

This is required if MD=(METAD=TRUE), MD=(METADYNAMICS=TRUE), MD=(WTMETAD=TRUE), or MD=(WTMETADYNAMICS=TRUE) is specified.

The first column of first row is the type of CVs, followed by the width of deposited Gaussian and the associated options. If free energy surface is written during the dynamics (METAPRINTFES=TRUE in MD keyword), the information of grid is additionally required. This is specified by adding three columns in the order of lower bound, upper bound, and grid spacing (unit is identical to that of Gaussian width). For some CVs, the integers to specify atom labels or species for a group of atoms are given in second and third rows.

If one needs to specify multiple CVs, the information of second and the subsequent CVs is added from the next line of the end of definition of preceding CVs.

The implemented CVs are listed with each example below, where total number of atoms in the system is assumed to be 10.

- ABSOLUTEPOSITION

The absolute position of an atom or a group of atoms.

For periodic system, minimum image convention is not applied even if METAPBCMIC=TRUE in MD keyword.

```
ABSOLUTEPOSITION_0.1_1_Z_LABELS_COC_
```

```
5_
```

The z-axis coordinate of atom label 5 is set to CV

where the second to sixth columns of the first row specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Number of atoms or species in a group
- ✓ 4th: Direction to be restricted (X/Y/Z)
- ✓ 5th: Method to define atoms
 - LABELS ... Atom labels
 - SPECIES ... Order of the listed elements in Parameter section
- ✓ 6th: Center of a group of atoms
 - COC ... Center of coordinate
 - COM ... Center of mass

➤ BONDDISTANCE

The distance between two atoms (*atom1–atom2*).

BONDDISTANCE_0.1_1_2_↓

Bond distance of atom label 1 and 2 is set to CV

where the second to fourth columns specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Label specifying *atom1*
- ✓ 4th: Label specifying *atom2*

➤ BONDANGLE

The angle defined by three atoms (*atom1–atom2–atom3*).

BONDANGLE_0.1_1_2_3_↓

Bond angle of atom label 1–2–3 is set to CV

where the second to fifth columns specify

- ✓ 2nd: Gaussian width in degree (deg) unit
- ✓ 3rd: Label specifying *atom1*
- ✓ 4th: Label specifying *atom2*
- ✓ 5th: Label specifying *atom3*

➤ BONDDIHEDRAL

The dihedral angle defined by four atoms (*atom1–atom2–atom3–atom4*).

BONDDIHEDRAL_0.1_1_2_3_4_↓

Bond dihedral of atom label 1–2–3–4 is set to CV

where the second to sixth columns specify

- ✓ 2nd: Gaussian width in deg unit
- ✓ 3rd: Label specifying *atom1*
- ✓ 4th: Label specifying *atom2*
- ✓ 5th: Label specifying *atom3*
- ✓ 6th: Label specifying *atom4*

➤ BONDDISTANCEDIFFERENCE

The difference between two bond distances in which each bond distance is calculated as the distance between two atoms as follows:

$$r_{atom1-atom2} - r_{atom3-atom4}$$

BONDDISTANCEDIFFERENCE_0.1_1_2_3_4_↓

Distance $r_{12} - r_{34}$ is set to
CV

where the second to sixth columns specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Label specifying *atom1*
- ✓ 4th: Label specifying *atom2*
- ✓ 5th: Label specifying *atom3*
- ✓ 6th: Label specifying *atom4*

➤ BONDDISTANCEADDITION

The summation over two bond distances in which each bond distance is calculated as the distance between two atoms as follows:

$$r_{atom1-atom2} + r_{atom3-atom4}$$

BONDDISTANCEADDITION_0.1_1_2_3_4_↓

Distance $r_{12} + r_{34}$ is set to
CV

where the second to sixth columns specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Label specifying *atom1*
- ✓ 4th: Label specifying *atom2*
- ✓ 5th: Label specifying *atom3*
- ✓ 6th: Label specifying *atom4*

➤ MINIMUMDISTANCE

The minimum value of atom pair distances r_{ij} given as follows:

$$\frac{\beta}{\ln \sum_{i \in \text{group1}}^{\text{atoms}} \sum_{j \in \text{group2}}^{\text{atoms}} \exp\left(\frac{\beta}{r_{ij}}\right)}$$

MINIMUMDISTANCE_0.1_3_2_500_LABELS_↓

1_2_3_↓

Group1 contains 3 atoms with labels 1, 2, and 3

4_5_↓

Group2 contains 2 atoms with labels 4 and 5

where the second to sixth columns of the first row specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Number of atoms or species in *group1*
- ✓ 4th: Number of atoms or species in *group2*
- ✓ 5th: Positive real parameter β to control smoothness
- ✓ 6th: Method to define atoms

LABELS ... Atom labels

SPECIES ... Order of the listed elements in Parameter section

➤ MEANDISTANCE

The mean distance between two groups of atoms given as follows:

$$\left[\frac{1}{N_{\text{group1}} N_{\text{group2}}} \sum_{i \in \text{group1}}^{\text{atoms}} \sum_{j \in \text{group2}}^{\text{atoms}} \left(\frac{1}{r_{ij}}\right)^n \right]^{-\frac{1}{n}}$$

MEANDISTANCE_0.1_3_2_6_LABELS_↓

1_2_3_↓

Group1 contains 3 atoms with labels 1, 2, and 3

4_5_↓

Group2 contains 2 atoms with labels 4 and 5

where the second to sixth columns of the first row specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Number of atoms or species in *group1*
- ✓ 4th: Number of atoms or species in *group2*
- ✓ 5th: Positive integer n to specify the power of inverse of distance
- ✓ 6th: Method to define atoms

LABELS ... Atom labels

SPECIES ... Order of the listed elements in Parameter section

➤ ATOMPOINTPLANEDISTANCE

The distance between the point defined by an atom position (*atom1*) and the plane defined by three atoms (*atom2*, *atom3*, and *atom4*). For periodic system, minimum image convention is not applied even if METAPBCMIC=TRUE in MD keyword.

ATOMPOINTPLANEDISTANCE_0.1_1_2_3_4_↓

Distance between atom label 1 and plane defined by atom labels 2, 3, and 4 is set to CV

where the second to sixth columns specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Label specifying *atom1* in the point
- ✓ 4th: Label specifying *atom2* in the plane
- ✓ 5th: Label specifying *atom3* in the plane
- ✓ 6th: Label specifying *atom4* in the plane

➤ ATOMPLANEPLANEANGLE

The angle between two planes in which each plane is defined by three atoms (*atom1*, *atom2*, *atom3* and *atom4*, *atom5*, *atom6*). For periodic system, minimum image convention is not applied even if METAPBCMIC=TRUE in MD keyword.

ATOMPLANEPLANEANGLE_0.1_1_2_3_4_5_6_↓

Angle between planes defined by atom labels 1, 2, 3 and 4, 5, 6 is set to CV

where the second to eighth columns specify

- ✓ 2nd: Gaussian width in deg unit
- ✓ 3rd: Label specifying *atom1* in the first plane
- ✓ 4th: Label specifying *atom2* in the first plane
- ✓ 5th: Label specifying *atom3* in the first plane
- ✓ 6th: Label specifying *atom4* in the second plane
- ✓ 7th: Label specifying *atom5* in the second plane
- ✓ 8th: Label specifying *atom6* in the second plane

➤ MIDPOINTDISTANCE

The distance between two points in which each point is calculated as either center of coordinate or center of mass of a group of atoms.

MIDPOINTDISTANCE_0.1_3_3_LABELS_COC_

1_2_3_

The first point is calculated using 3 atoms with labels 1, 2, and 3

4_5_6_

The second point is calculated using 3 atoms with labels 4, 5, and 6

where the second to sixth columns of the first row specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Number of atoms or species for the first point
- ✓ 4th: Number of atoms or species for the second point
- ✓ 5th: Method to define atoms
 - LABELS ... Atom labels
 - SPECIES ... Order of the listed elements in Parameter section
- ✓ 6th: Center of a group of atoms
 - COC ... Center of coordinate
 - COM ... Center of mass

➤ GYRATIONRADIUS

The radius of gyration of a group of atoms.

GYRATIONRADIUS_0.1_10_LABELS_COC_1

All 10 atoms are included
to calculate non-weighted
radius of gyration

where the second to fifth columns specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Number of atoms or species in a group
Note that no second line if total number of atoms is specified.
- ✓ 4th: Method to define atoms
LABELS ... Atom labels
SPECIES ... Order of the listed elements in Parameter section
- ✓ 5th: Center of a group of atoms
COC ... Center of coordinate, which calculates the non-weighted radius of gyration given by

$$\left[\frac{1}{N_{group1}} \sum_{i \in group1}^{atoms} (\mathbf{R}_i - \mathbf{R}_{COC})^2 \right]^{\frac{1}{2}},$$

where \mathbf{R} denotes a coordinate.

COM ... Center of mass, which calculates the mass-weighted radius of gyration given by

$$\left[\frac{1}{\sum_{i \in group1}^{atoms} m_i} \sum_{i \in group1}^{atoms} m_i (\mathbf{R}_i - \mathbf{R}_{COM})^2 \right]^{\frac{1}{2}},$$

where m is an atomic mass.

➤ INERTIAMOMENT

The moment of inertia of a group of atoms.

INERTIAMOMENT_0.1_10_LABELS_COC_1

All 10 atoms are included
to calculate non-weighted
moment of inertia

where the second to fifth columns specify

- ✓ 2nd: Gaussian width
- ✓ 3rd: Number of atoms or species in a group
Note that no second line if total number of atoms is specified.
- ✓ 4th: Method to define atoms
LABELS ... Atom labels
SPECIES ... Order of the listed elements in Parameter section
- ✓ 5th: Center of a group of atoms
COC ... Center of coordinate, which calculates the non-weighted moment of inertia given by

$$\sum_{i \in \text{group1}}^{\text{atoms}} (\mathbf{R}_i - \mathbf{R}_{\text{COC}})^2,$$

where \mathbf{R} denotes a coordinate. Note that Gaussian width is specified with \AA^2 unit.

COM ... Center of mass, which calculates the mass-weighted moment of inertia given by

$$\sum_{i \in \text{group1}}^{\text{atoms}} m_i (\mathbf{R}_i - \mathbf{R}_{\text{COM}})^2,$$

where m is an atomic mass. Note that Gaussian width is specified with $\text{AMU} \cdot \text{\AA}^2$ unit (AMU is atomic mass unit).

➤ RATIONALCOORDINATIONNUMBER

The coordination number between two groups of atoms using a rational function given as follows:

$$c \sum_{i \in \text{group1}}^{\text{atoms}} \sum_{j \in \text{group2}}^{\text{atoms}} \frac{1 - \left(\frac{r_{ij}}{r_0}\right)^n}{1 - \left(\frac{r_{ij}}{r_0}\right)^m}$$

RATIONALCOORDINATIONNUMBER_0.1_3_2_6_12_2.0_LABELS_AVERAGE_↓

1_2_3_↓

Group1 contains 3 atoms with labels 1, 2, and 3

4_5_↓

Group2 contains 2 atoms with labels 4 and 5

where the second to ninth columns of the first row specify

- ✓ 2nd: Gaussian width
Note that coordination number is unitless.
- ✓ 3rd: Number of atoms or species in *group1*
- ✓ 4th: Number of atoms or species in *group2*
- ✓ 5th: Positive integer n to specify the power appearing in numerator
- ✓ 6th: Positive integer m to specify the power appearing in denominator
- ✓ 7th: Reference distance r_0 in Å unit
- ✓ 8th: Method to define atoms
LABELS ... Atom labels
SPECIES ... Order of the listed elements in Parameter section
- ✓ 9th: Normalization factor c
SUM ... $c = 1$
AVERAGE ... $c = \frac{1}{N_{\text{group1}}}$

➤ FERMICOORDINATIONNUMBER

The coordination number between two groups of atoms using a Fermi function given as follows:

$$c \sum_{i \in \text{group1}}^{\text{atoms}} \sum_{j \in \text{group2}}^{\text{atoms}} \frac{1}{1 + \exp[\beta(r_{ij} - r_0)]}$$

FERMICOORDINATIONNUMBER_0.1_3_2_8.0_2.0_LABELS_AVERAGE_↓

1_2_3_↓

Group1 contains 3 atoms with labels 1, 2, and 3

4_5_↓

Group2 contains 2 atoms with labels 4 and 5

where the second to eighth columns of the first row specify

- ✓ 2nd: Gaussian width
Note that coordination number is unitless.
- ✓ 3rd: Number of atoms or species in *group1*
- ✓ 4th: Number of atoms or species in *group2*
- ✓ 5th: Positive real parameter β to control steepness of Fermi function
- ✓ 6th: Reference distance r_0 in Å unit
- ✓ 7th: Method to define atoms
LABELS ... Atom labels
SPECIES ... Order of the listed elements in Parameter section
- ✓ 8th: Normalization factor c
SUM ... $c = 1$
AVERAGE ... $c = \frac{1}{N_{\text{group1}}}$

➤ RMSD

The root mean square deviation (RMSD) of a group of atoms.

RMSD_0.1_10_LABELS_COC_FIT_ref.xyz.↓

RMSD with respect to the structure in ref.xyz is set to CV

where the second to seventh columns specify

- ✓ 2nd: Gaussian width in Å unit
- ✓ 3rd: Number of atoms or species in a group
Note that no second line if total number of atoms is specified.
- ✓ 4th: Method to define atoms
LABELS ... Atom labels
SPECIES ... Order of the listed elements in Parameter section
- ✓ 5th: Center of a group of atoms
COC ... Center of coordinate, which calculates the non-weighted RMSD given by

$$\left[\frac{1}{N_{group1}} \sum_{i \in group1}^{atoms} (\mathbf{R}_i - \mathbf{R}_i^{ref})^2 \right]^{\frac{1}{2}},$$

where \mathbf{R} denotes a coordinate.

COM ... Center of mass, which calculates the mass-weighted RMSD given by

$$\left[\frac{1}{\sum_{i \in group1}^{atoms} m_i} \sum_{i \in group1}^{atoms} m_i (\mathbf{R}_i - \mathbf{R}_i^{ref})^2 \right]^{\frac{1}{2}},$$

where m is an atomic mass.

- ✓ 6th: Method to compute RMSD
AS-IS ... Using Cartesian components without any transformation
FIT ... Superimposing present and reference coordinates by quaternion
This is available for only cluster models.
- ✓ 7th: Filename containing reference Cartesian coordinates
This is xyz format.

Reading bias potential in metadynamics simulation

- **"bias.dat"**

This is required if MD=(METAREADBIAS=TRUE) is specified.

Please make sure that the previous and present run of program specifies METAD=TRUE, METADYNAMICS=TRUE, WTMETAD=TRUE, or WTMETADYNAMICS=TRUE in MD keyword.

The format should be identical to the output file of metadynamics simulation, **"biaspot"**, which contains the history of Gaussian height, width, and value of CVs (see also [section 3.3.4](#)).

An example for CV of bond distance is given below.

```
GAUSSIAN_BIAS_POTENTIAL:_____1↵
***_AT_T=_____10.00_FSEC, _THIS_RUN'S_STEP_NO.=_____20↵
____Gaussian_height____=_____0.0040000000_a.u.↵
____Collective_variable_=_____1↵
____Coordinate_____ =_____1.6146539213_Angstrom↵
____Gaussian_width____=_____0.1000000000_Angstrom↵
...

```

The following remarks should be noted:

- Entry of Gaussian bias potential (first line) should not exceed the number specified in METAMAXGAUSS option.
- Information of simulation time and MD step (second line) is ignored when the program reads this file.
- Gaussian height (third line) is always constant (value specified in METAHEIGHT option) in standard metadynamics while it gradually decreases in well-tempered metadynamics.
- Collective variable, coordinate, and Gaussian width (fourth, fifth, sixth lines) are printed repeatedly if multiple CVs are specified in **"metacv.dat"**.

Setting wall potential in metadynamics simulation

This is required if MD=(METAWALL=TRUE) is specified.

The following even polynomial function can be imposed as wall potential:

$$\kappa(s_i - s_0)^n$$

The parameters are specified in “**metacv.dat**” together with direction of wall potential.

Here is an example of applying quadratic potential if the value of first CV is greater than 2.0 in two-dimensional metadynamics.

<Description of first CV>	See setting CVs in metadynamics simulation for details
<Description of second CV>	See setting CVs in metadynamics simulation for details
↵	One blank line to separate definitions of CVs and wall potentials
U_1_1.0_2.0_2_↵	Description of wall potential

where the first to fifth columns of the last line specify

- 1st: Direction of wall potential to be imposed
L ... Lower bound
U ... Upper bound
- 2nd: Index of CV i
- 3rd: Coefficient κ in kcal/(mol·Å²) unit
- 4th: Limit of CV value s_0
Note that the unit is identical to that of Gaussian width.
- 5th: Exponent n in positive even integer

If one needs to specify multiple wall potentials, the information of second and the subsequent wall potentials is added from the next line of the end of definition of preceding wall potentials.

2 Running DCDFTBMD

Once the input file “**dftb.inp**” is created, other requisites such as Slater-Koster parameters and auxiliary input files are needed to be placed in the appropriate directory. For example, in the case of SCC-DFTB single point energy calculation of water molecule shown in [section 1](#), 4 Slater-Koster parameter files (**oo.spl**, **oh.spl**, **ho.spl**, and **hh.spl**) must be placed in the same directory as the input file. The executable is used without any arguments.

Serial version	<installation path>/dftb_serial.00.x
OpenMP version	<installation path>/dftb_openmp.00.x
MPI/OpenMP version	mpirun -np_(number of processes) <installation path>/dftb_mpiomp.00.x

The header of input file may be specified arbitrarily by setting it as the first argument. The example of using “**file.inp**” is as follows.

Serial version	<installation path>/dftb_serial.00.x file
OpenMP version	<installation path>/dftb_openmp.00.x file
MPI/OpenMP version	mpirun -np_(number of processes) <installation path>/dftb_mpiomp.00.x file

For OpenMP parallelization, number of threads must be set before starting the calculation.

bash	export OMP_NUM_THREADS=(number of threads)
csh, tcsh	setenv OMP_NUM_THREADS_(number of threads)

If a large-scale calculation stops, one may need to increase the stack size.

bash	ulimit -s unlimited
	export OMP_STACKSIZE=(stack size value)
csh, tcsh	unlimit
	setenv OMP_STACKSIZE_(stack size value)

Note that the maximum number of basis sets in serial and OpenMP versions is limited to 16384.

3 Output of DCDFTBMD

If the calculation terminates normally, the standard output file and the detailed data file will be ordinarily appeared. By default (using “**dftb.inp**” as the input file), the corresponding filenames are “**dftb.out**” and “**dftb.dat**”, respectively. When the header of input file is specified arbitrarily (e.g. “**file.inp**” as described in [section 2](#)), the header of output and data files will be changed appropriately (e.g. “**file.out**” and “**file.dat**”). Here, the output files of serial and OpenMP versions for SCC-DFTB single point energy calculation of water molecule shown in [section 1](#) are briefly outlined. Those of MPI/OpenMP version are similar to serial and OpenMP versions although the format of detailed data file is slightly different for the information of subsystem and Mulliken population. In the following, symbols for representing new line (↵) and blank area () are omitted.

3.1 Standard output file

The standard output file begins with the header of program. The version number is varied depending on the released executables. After punching of start time, the comment line is printed as described in Title section (see [section 1.2](#)).

```

*****
DDDDDD   CCCCC   DDDDD   FFFFFFF TTTTTTTT BBBB BBB   MM   MM DDDDD
DDDDDDDD CCCCCCCC DDDDDDDD FFFFFFF TTTTTTTT BBB   BBB MMM   MMM DDDDDDD
DDD   DDD CCC   DDD   DDD FF   TTT   BBB   BBB MM   M M   MM DDD   DDD
DDD   DDD CCC   DDD   DDD FFFFF   TTT   BBBB BBB   MM   M   MM DDD   DDD
DDD   DDD CCC   DDD   DDD FFFFF   TTT   BBB   BBB MM   MM DDD   DDD
DDDDDDDD CCCCCCCC DDDDDDDD FF   TTT   BBB   BB MM   MM DDDDDDD
DDDDDD   CCCCC   DDDDD   FF   TTT   BBBB BBB   MM   MM DDDDD
VERSION 2.0 (Dec 2019)
*****
Execution of DCDFTBMD begun %a %b %d %H:%M:%S %Y
-----
TITLE
-----

```


Next, the path of Slater-Koster parameter files is printed, followed by the summary of calculation type.

```
2 kinds of elements will be used
  Pair of element 1 and element 1 : {path}/oo.spl
  Pair of element 1 and element 2 : {path}/oh.spl
  Pair of element 2 and element 1 : {path}/ho.spl
  Pair of element 2 and element 2 : {path}/hh.spl
```

```
SCC      = True
```

```
-----
```

```
Max cycle      = 200
Energy convergence = 1.0E-09
Density convergence = 1.0E-06
Charge mixing method = Broyden
  Broyden iteration = 70
Mixing parameter = 2.0E-01
Eigensolver    = DSYGVD
```

```
...
```

```
DC      = False
```

```
-----
```

```
DISP    = False
```

```
-----
```

```
PBC     = False
```

```
-----
```

```
OPT     = False
```

```
-----
```

```
FREQ    = False
```

```
-----
```

```
MD      = False
```

```
-----
```

```
MISC    = False
```

```
-----
```

Then, the system dependent quantities are printed.

```
Total number of basis set shells = 4
Number of basis functions      = 6
Number of electrons            = 8
Charge of system               = 0
Spin multiplicity              = 1
Number of occupied orbitals    = 4
Total number of atoms          = 3
```

Total number of atoms, charge, and spin multiplicity correspond to values specified in Geometry section (see [section 1.4.1](#)). The numbers of basis set shells, basis functions, and electrons are calculated for water molecule as follows:

- Number of basis set shells: $O(s) + O(p) + H(s) + H(s) = 4$
- Number of basis functions: $O(s) + O(p_x) + O(p_y) + O(p_z) + H(s) + H(s) = 6$
- Number of electrons: $O(s^2p^4) + H(s^1) + H(s^1) = 8$

Note that these quantities also depend on the used Slater-Koster parameter files and may be different from the chemical intuition considering minimal basis set and valence electrons.

Finally, the SCC-DFTB single point calculation starts in the present example.

```
*** Start single point energy calculation ***
*****

*** Start SCC-DFTB calculation ***
*****

Iter.  Total energy      Energy diff.    Density diff.   Fermi level
-----
  1    0.0726464067      0.0726464067   2.0000000000    0.0025000000
  2   -4.0712418245     -4.1438882313   0.0200187809    0.0025000000
  3   -4.0741988428     -0.0029570183   0.0590590622    0.3564583333
  4   -4.0779379555     -0.0037391127   0.0004103232    0.3525000000
  5   -4.0779381355     -0.0000001800   0.0000024570    0.3525000000
  6   -4.0779381355     0.0000000000    0.0000000001    0.3562500000

Final SCC-DFTB Energy = -4.0779381355 Eh after 6 iterations
Execution of DCDFBMD terminated normally %a %b %d %H:%M:%S %Y
```

Here, the SCC converged total energy is -4.0779381355 Hartree.

3.2 Detailed data file

The detailed data file contains the relevant properties of the given structure. The constructed subsystems and localization regions are initially printed. Since this calculation is `DC=FALSE`, all 3 atoms belong to subsystem 1.

```
SUBSYSTEM : 1
-----
  1    2    3
LOCALIZATION REGION : 1
-----
  1
```

If MPI/OpenMP version is used, this part looks concise excluding the case of `PRINTLOCALREGION=TRUE` in MISC keyword.

```
SUBSYSTEM
-----
  1    1    1
```

Next, the eigenvalues of the molecular orbitals in Hartree unit (first column) and the electron occupation number of that level (second column) are shown.

```
EIGENVALUES [Eh] AND OCCUPANCIES
-----
-0.8489865909    2.0000000000
-0.4143390336    2.0000000000
-0.3137537414    2.0000000000
-0.2591755518    2.0000000000
 0.3992760730    0.0000000000
 0.5583952222    0.0000000000
```

If PRINTMO=TRUE in MISC keyword, the eigenvectors are additionally printed. The occupied and virtual orbitals are distinguished with OCC. and VIRT., respectively.

EIGENVALUES [Eh], OCCUPANCIES, AND MO COEFFICIENTS

```
1   OCC.   -0.8489865909   2.0000000000
1   O   S   0  -0.8522740053
      P  -1   0.0017546133
      P   0   0.0000000000
      P   1   0.0017546133
2   H   S   0  -0.1530727458
3   H   S   0  -0.1530727458
2   OCC.   -0.4143390336   2.0000000000
1   O   S   0  -0.0000000000
      P  -1   0.4626963766
      P   0   0.0000000000
      P   1  -0.4626963766
2   H   S   0  -0.3908041098
3   H   S   0   0.3908041098
```

...

Then, the total Mulliken charge on the atom (second column) is shown together with the corresponding net charges (third column).

MULLIKEN POPULATIONS AND NET ATOMIC CHARGES

```
1   6.5926170634   -0.5926170634
2   0.7036914683   0.2963085317
3   0.7036914683   0.2963085317
```

If ORBITALPOP=TRUE in SCC or NCC keyword, the Mulliken charges on each atomic orbital are additionally printed.

MULLIKEN POPULATIONS AND NET ATOMIC CHARGES

```
-----  
1   O   6.5926170634  -0.5926170634  
    S  0  1.7342141199  
    P -1  1.4292014718  
    P  0  2.0000000000  
    P  1  1.4292014718  
2   H   0.7036914683   0.2963085317  
    S  0  0.7036914683  
3   H   0.7036914683   0.2963085317  
    S  0  0.7036914683
```

If MPI/OpenMP version is used, the shell resolved Mulliken population is printed.

MULLIKEN POPULATIONS

```
-----  
1.73421412   4.85840294   0.70369147   0.70369147
```

Then, the x , y , z dipole moment components and the norm using the Mulliken charges are shown in both atomic unit and Debye unit. This is not printed if periodic boundary condition is used.

DIPOLE MOMENT [a.u.]

```
-----  
      x           y           z  
0.4545263289   0.4545263289   0.0000000000
```

NORM : 0.6427972988

DIPOLE MOMENT [Debye]

```
-----  
      x           y           z  
1.1552906835   1.1552906835   0.0000000000
```

NORM : 1.6338277531

If MAYER=TRUE in SCC or NCC keyword, atomic valences (diagonal elements) and Mayer bond orders (off-diagonal elements) are shown with matrix representation.

ATOMIC VALENCIES AND MAYER BOND ORDERS

```
-----  
      1      2      3  
1  1.796085  0.898042  0.898042  
2  0.898042  0.912201  0.014159  
3  0.898042  0.014159  0.912201
```

If CM3=TRUE in SCC or NCC keyword, the CM3 net atomic charges and dipole moments are additionally printed.

CM3 NET ATOMIC CHARGES

```
-----  
1  -0.5833492665  
2   0.2916746332  
3   0.2916746332
```

CM3 DIPOLE MOMENT [a.u.]

```
-----  
      x      y      z  
0.4474181000  0.4474181000  0.0000000000
```

NORM : 0.6327447451

CM3 DIPOLE MOMENT [Debye]

```
-----  
      x      y      z  
1.1372233679  1.1372233679  0.0000000000
```

NORM : 1.6082767104

Finally, the different energy contributions to the total energy are shown in Hartree unit. If MPI/OpenMP version is used, PRINTATOME=TRUE in MISC keyword is necessary to obtain the corresponding information.

```
ENERGY CONTRIBUTION [Eh]
-----
ENERGY H0                = -4.1689461692
ENERGY SCC                =  0.0183616273
TOTAL ELECTRONIC ENERGY = -4.1505845420
REPULSIVE ENERGY        =  0.0726464065
TOTAL ENERGY            = -4.0779381355
```

If PRINTATOME=TRUE in MISC keyword, the atomic energy contributions to the total, electronic, and repulsive energies are additionally printed in Hartree unit.

```
ATOM RESOLVED ENERGY CONTRIBUTION [Eh]
-----
      TOTAL      ELECTRONIC      REPULSIVE
1    -3.3763986686   -3.4127218718    0.0363232032
2    -0.3507697335   -0.3689313351    0.0181616016
3    -0.3507697335   -0.3689313351    0.0181616016
```

3.3 Other output files

Additional output files will be generated depending on the type of calculations.

3.3.1 Output files in DFTB calculation

- **“chrgfile”**

This is generated if `SCC=TRUE` and `MISC=(WRITECHRGFILE=TRUE)`. The result of Mulliken population analysis is contained in binary format. The file may be used for setting initial charge in `READCHARGE=BINARY` in `SCC` keyword (see [section 1.5.1](#)).

Below may be found in serial and OpenMP versions.

- **“zacaz”, “zbcbz”, “zszz”**

These are generated if `MISC=(USESCRATCH=TRUE)`. The calculated orbital coefficients (**zacaz**, **zbcbz** for alpha and beta spins) and overlap matrix (**zszz**) of localization regions are contained in binary format. The files are temporary and thus not important to examine the results.

3.3.2 Output files in frequency calculation

- **"restart_hess"**

This is generated if `FREQ=(PRINTHESS=TRUE)`.

The calculated Hessian matrix elements are contained in binary format.

The file may be used for setting Hessian matrix in `RESTARTHESS=BINARY` in `FREQ/FREQUENCY` keyword (see [section 1.5.1](#)).

- **"hess.dat"**

This is generated if `FREQ=(INTERRUPTCP=TRUE)` or `FREQ=(INTERRUPTSEMINUM=TRUE)` in `FREQTYPE=1` or `FREQTYPE=2` in `FREQ/FREQUENCY` keyword.

The indices and calculated Hessian matrix elements are printed (see [section 1.5.2](#) for the format).

The file may be used for setting Hessian matrix in `RESTARTHESS=ASCII` in `FREQ/FREQUENCY` keyword (see [section 1.5.2](#)).

- **"dftb_vib.out"**

This is generated if `FREQ=TRUE`.

The information of harmonic vibrational frequency analysis is contained with Gaussian like format.

3.3.3 Output files in MD simulation

- **“restart”**

This is generated if MD=TRUE.
The information of last MD step is contained in binary format.
The file may be used for restarting purpose in RESTART=TRUE in MD keyword (see [section 1.5.1](#)).
- **“restart_chk”**

This is generated if MD=TRUE.
The information of last checkpoint step is contained in binary format.
The file may be used for restarting purpose in RESTART=TRUE in MD keyword after renaming to **“restart”** (see [section 1.5.1](#)).
- **“traject”**

This is generated if MD=TRUE.
Cartesian coordinates during MD simulation are printed in xyz format.
- **“velocity”**

This is generated if MD=TRUE.
Velocity components during MD simulation are printed in Å/fs unit in xyz format.
- **“mulliken”**

This is generated if MD=TRUE.
Mulliken net atomic charges during MD simulation are printed with the following format.

 - Serial and OpenMP versions
 - ✓ Line 1: Number of atoms (N_{atom})
 - ✓ Line 2: Comments (simulation time and MD step)
 - ✓ Line 3–($N_{\text{atom}} + 2$): Atom label (1st column), atom symbol (2nd column), and Mulliken net atomic charges (3rd column)
 - MPI/OpenMP version
 - ✓ Line 1: Number of shells (N_{shell} , 1st column) and N_{atom} (2nd column)
 - ✓ Line 2: Comments (simulation time and MD step)
 - ✓ Line 3–($N_{\text{shell}} + 2$): Atom label (1st column), atom symbol (2nd column), subshell symbol (3rd column), and Mulliken net charges for the shell (4th column)

3.3.4 Output files in metadynamics

Additional output files from MD simulation (see [section 3.3.3](#)) are listed.

- **“restart_meta”**

This is generated if MD=(METAD=TRUE), MD=(METADYNAMICS=TRUE), MD=(WTMETAD=TRUE), or MD=(WTMETADYNAMICS=TRUE).

The history of Gaussian bias potentials deposited during metadynamics is contained in binary format.

The file may be used for restarting purpose in METARESTART=TRUE in MD keyword (see [section 1.5.1](#)).

- **“restart_meta_chk”**

This is generated if MD=(METAD=TRUE), MD=(METADYNAMICS=TRUE), MD=(WTMETAD=TRUE), or MD=(WTMETADYNAMICS=TRUE).

The history of Gaussian bias potentials deposited during metadynamics at the last checkpoint step is contained in binary format.

The file may be used for restarting purpose in METARESTART=TRUE in MD keyword after renaming to **“restart_meta”** (see [section 1.5.1](#)).

- **“biaspot”**

This is generated if MD=(METAD=TRUE), MD=(METADYNAMICS=TRUE), MD=(WTMETAD=TRUE), or MD=(WTMETADYNAMICS=TRUE).

The history of Gaussian bias potentials deposited during metadynamics are printed (see [section 1.5.2](#) for the format).

The file may be used for restarting purpose in METAREADBIAS=TRUE in MD keyword after renaming to **“bias.dat”** (see [section 1.5.2](#)).

- **“fes.dat”**

This is generated if MD=(METAPRINTFES=TRUE).

The reconstructed free energy surface data are contained with the following format.

- 1st–(Number of CVs) columns: Grid point of CVs (unit is identical to that of Gaussian width)
- Last column: Free energy in Hartree unit

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