

# Keywords of deMonNano

## MOLECULES

Keyword to defines MOLECULES. After this line, there is one line per molecule with the unit number and the molecule type like : 1 WAT except if MOLTYPE is used (see below). This keyword should appear in the input file at the very end. The running directory should contain a file named MOLECULES with for each molecule type a line like WAT NAT=3 (3 letters for the molecule name and the number of atoms). The NAT next lines are standard atom name plus xyz inputs (C 0.071715 0.071715 0.000000).

MOLTYPE=

all units are of the same type of molecule defined after MOLTYPE=

## PARAM

The path to the DFTB parameters folder will be written on the next line. If this keyword is not present, you should have a SLAKO or SCC-SLAKO file in your running directory

PTYPE=

specifies the parameter : absent for non SCC, MAT or BIO for SCC

## CHARGE

This keyword specifies the charge of the system. for instance : CHARGE 3

## GEOMETRY

This keyword It specifies the molecular geometry and should be placed at the end of the input file. It is followed by the molecular geometry

BOHR

Coordinates or bond distances are given in atomic units

ANGST

Coordinates or bond distances are given in Angstrom. (This is the default

CARTE

The molecular structure is given in Cartesian coordinates. This is the default.

## MULTIPLICITY

This keyword specifies the multiplicity of the system, integer following MULTIPLICITY 3

## OPTIMIZATION

This keyword controls the geometry optimization

MAX=

Maximum number of optimisation steps. The default is 100

TOL=

Optimization convergence criterion for the energy. Default is  $3 \times 10^{-4}$  Hartree.

GRADTOL=

Optimization convergence criterion for the gradients. Default is  $3 \times 10^{-6}$  Hartree.

STEP=

Maximum step size in optimization. Default is 0.3 Bohr

CGRAD

Uses the conjugate gradient method. This is the default.

SDC=

Uses the steepest descent method for geometry optimisation with specified multiplier of the gradient. The default is 0.1

SDC

Uses the steepest descent method for geometry optimisation

OUT=

Interval to output structure during optimisation

## MONTECARLO

Perform Monte Carlo simulation

MAX=

Indicates the number of steps after "="

SEED=

indicates value of the SEED if Monte Carlo simulation is intended

NDBG=

Type NDBG=ON to print a lot of MC information

WALL=

Refuses any displacement leading to structure not entering in a sphere of radius specified after '='. Defaults is 1000 a0. It only makes sense for a finite size system.

## **MCTEMP**

Additional information about for Monte Carlo simulation. Should appear after the MONTEC keyword.

TMC=

Temperature for MC simulation (no parallel tempering)

NTEMP=

Number of temperatures, defines a parallel tempering MONTE CARLO scheme

LIST

The set of temperatures is readen from a list. After the MCTEMP line are the NTEMP lines. Each line contain : the trajectory number, the temperature, the initial center of mass displacement step, the initial quaternion displacement step

GEOM

The set of temperatures follows a geometric pattern

LINEAR

The set of temperatures follows a linear pattern

TEMPMIN=

The smallest temperature

TEMPMAX=

The largest temperature

X=

inital displacement for smallest temperature

Q=

initial displacement for lowest temperature quaternion displacement

RESCALE=

Frequency to rescale displacement steps

SWAP=

Kind of swap, it can be NO (no exchange), SE(exchange only between successive temperatures, AE (all exchange-exchange MC, ie possible between all temperatures, this is all exchange)

SMOD=

number of steps without trying any swap

SPERCENT=

probability to try a swap each "SWAP" step

SDBG

print some information (mostly to debug)

OUT=

frequency for output

## **PATHS**

perform paths over the PES, only works with quaternion approach. A deMon.pth.inp file contain the points defined with CHKPTS NAME=PT1 followed by a line per subsystem defined with quaternions (see quaternions keyword for this general input) like for instance : " 1 0.0 0.0 0.0 1.0 0.0 0.0 0.0"

NMOL=  
number of subsystems  
NPTS=  
number of points  
NPTS=  
number of paths

## **FREQUENCY**

This keyword activates frequency analysis.

VIB=  
Scaling factor for the numerical step size

## **DIPOLE**

This keyword activates the calculation of molecular electrostatic moments.

OUTFILE  
writes the dipole in an output file

## **MDYNAMICS**

This keyword activates the Born-Oppenheimer molecular dynamic (BOMD) simulation

ZERO  
Start a trajectory with initial velocities of the nuclei set to zero. This is the default.

RANDOM=  
Start a trajectory using random initial velocities, which have no net momentum or angular momentum and give the requested temperature specified after =.

RAN  
Start a trajectory using random initial velocities, which have no net momentum or angular momentum and give the initial temperature of MDTEMP keyword.

READ

Start a new MD trajectory. Velocities of the nuclei are given in Cartesian form in the input file, immediately following the MDYNAMICS keyword.

**RESET**

This option resets all averages and the MD step of the trajectory. It only makes sense with the RESTART option, otherwise it has no effect.

**WALL=**

This option imposes a spherical potential around the system during an MD simulation. It only makes sense for a finite size system. The radius of the wall has to be provided in angstrom. The definition of the wall is  $ENER*(r-WALL)**EXP$ . WARNING: the wall is centered at the c.o.m. of the system which has to be in (0,0,0). The calculation will stop if not `KEEPCOM=.true.` or if `OUT_PBC=.true.`

**ENER=**

the ENER parameter in the definition of the wall. Value is in Hartree

**EXP=**

the EXP parameter in the definition of the wall.

## QUATERNION

Keyword allowing input with quaternions. After this line, there is one line per molecule that should look like : 1 1.0 0.0 .0 1.0 0.0 0.0 0.0 (unit number, coordinates of center of mass, 4 quaternions numbers) This should be associated with the MOLECULE keyword.

**NMOL=**

number of molecules

**RIGID**

molecules are treated as rigid bodies (this only holds for Monte Carlo exploration)

**ALLATOMS**

molecules are not treated as rigid except for the input file

**RANDOM**

Quaternions will be created randomly

## MDSTEPS

This keyword controls the steps of the molecular dynamic (MD) simulation

**MAX=**

Maximum number of MD steps. The default is 1.

**OUT=**

Step interval to update the deMon.mol file. The default is 10.

**SOUT=**

Step interval to update the deMon.out file. The default is 1.

TSIM=

Maximum MD run time in ps.

## **MDTEMP**

Desired MD temperature in Kelvin. The default is 300.

## **TIMESTEP**

This keyword specifies the time step of the molecular dynamic (MD) simulation in fs

## **MDBATH**

This keyword specifies the temperature bath used in the molecular dynamic (MD) simulation.

SCAL

The velocities are scaled in order to control the temperature. This option is only meaningful for very large systems or for the first equilibration steps of a trajectory.

BERE

Berendsen thermostat is applied to the system as a whole.

LOCA

Berendsen thermostat is applied individually to each atom

NOSE

The Nose-Hoover chain thermostat is applied

VAL=

if (thermostat = SCALING) : number of steps between velocity resets / if (thermostat = BERENDSEN or LOCAL) = Thermostat time constant in picoseconds[ps]. Default is = 0.5 ps.

NTHER=

Specifies the size of the chain used in the Nose-Hoover thermostat (i.e. the number of thermostats). The default value is NTHER = 4.

FREQTH=

Specifies the frequency of the Nose-Hoover thermostat. The default value is FREQTH = 100 cm<sup>-1</sup>.

NONE

No temperature bath. This is the default

## CONSERVE

The keywords requests imposition of constraints on some or all mechanical constants of the overall motion of the system.

NONE

Do not impose constraints. This is the default, except for MDYNAMICS RANDOM.

ALL

Equivalent to COM, ANG and MOM. This is the default for MDYNAMICS RANDOM

COM

Reset position of the centre of mass of the system to (0,0,0) on each MD step.

ANG

Reset overall angular momentum of the system to zero on each MD step. This constraint makes no sense, and is ignored, for periodic calculations

MOM

Reset overall momentum of motion of the system to zero on each MD step.

## MDCONSTRAINTS

This keyword imposes atomic constraints during a molecular dynamics simulation (read pdf manual)

## METADYNAMICS

Perform a metadynamics calculation in combination with molecular dynamics.

PLUMED1

Perform a metadynamics simulation using PLUMED 1.2. The input file for the MetaD parameters has to be plumed.dat. Please cite: M. Bonomi, D. Branduardi, G. Bussi, C. Camilloni, D. Provasi, P. Raiteri, D. Donadio, F. Marinelli, F. Pietrucci, R.A. Broglia and M. Parrinello, PLUMED: a portable plugin for free energy calculations with molecular dynamics, *Comp. Phys. Comm.* C180, 1961 (2009)

## DFTB

Perform a DFTB calculation

SCC

The self-consistent charge variant of DFTB. The default is non-SCC.

MEMOSCC

use previous atomic charges to restart the SCC process at a new geometry. This keyword automatically set SCC calculation (even without SCC keyword)

TOL=

The SCC convergence criterion in electron charges. The default is 1.0E-8.

MAX=

Maximum number of SCC cycles. The default is 100

MIX=

Mixing value for simple and Broyden mixing. The default is 0.2. This value is independent from the DFT mixing value

SIMPLE

Simple mixing instead of Broyden convergence acceleration is performed for SCC. This is per default switched off

L-DEP

Angular momentum resolved SCC. Here, the self-consistent charge procedure is applied to Mulliken shell charges rather than to Mulliken atomic charges. By default, this option is deactivated.

FERMI=

As FERMI, but with used-specified Fermi temperature (in K) following the keyword.

FERMI

The electron occupation follows a Fermi distribution

DISP=

London dispersion with a damping function. By default this option is switched off. DISP=1 Zhechkov et al., JCTC 2005 DISP=2 : Rapacioli et al., JCP, 2009

DISP

Equivalent to DISP=1. By default this option is switched off.

## **PRINT**

This keyword controls optional printing.

MOE

Print molecular orbital energies and occupations

MOS=

Print molecular orbital energies, occupations and coefficients.

DE2

Print Hessian matrix.

DEBUG

Generate debug output



## CARPAR

Activates a Car-Parrinello Molecular Dynamics simulation. This option is only available for DFTB. By default, this option is off.

FOM=

Fictitious orbital mass for Car-Parrinello DFTB (in atomic units).

LGTOLE=

The requested tolerance to ensure orthonormality of the orbitals using a Lagrange multiplier. The default is  $10^{-10}$  in atomic units.

BO

The Car-Parrinello approach is used to reach the Born Oppenheimer surface at each point

DELMO=

Multiplier for MO energy gradient for the MO optimisation using the Car-Parrinello approach in conjunction with the steepest descent technique (requires CARPAR BO). The default is 0.1.

MOMD=

Same as the MOMD keyword, but specifying the friction parameter. The default is  $10^{-2}$ .

MOMD

Requests a molecular dynamics-like optimisation of the molecular orbitals: A Car-Parrinello MD is carried out. Whenever gradient and velocity of an orbital have opposite signs an additional friction term is added to the equations of motion.

## MOLECULES

Keyword to defines MOLECULES. After this line, there is one line per molecule with the unit number and the molecule type like : 1 WAT except if MOLTYPE is used (see below). This keyword should appear in the input file at the very end. The running directory should contain a file named MOLECULES with for each molecule type a line like WAT NAT=3 (3 letters for the molecule name and the number of atoms). The NAT next lines are standard atom name plus xyz inputs (C 0.071715 0.071715 0.000000).

MOLTYPE=

all units are of the same type of molecule defined after MOLTYPE=

## PARAM

The path to the DFTB parameters folder will be written on the next line. If this keyword is not present, you should have a SLAKO or SCC-SLAKO file in your running directory

PTYPE=

specifies the parameter : absent for non SCC, MAT or BIO for SCC

## CUTSYS

Separate the system in subsystems (not necessary if MOLECULES keyword is used)

NMOL=

number of subsystems

NATMOL=

number of atoms per subsystem (all molecules have the same number of atoms)

RIGID

In the case of Monte Carlo exploration, these subsystems will be treated as rigid

ALLATOMS

The subsystems will never be treated as rigid

RANDOM

Random quaternions will be associated to these subsystems

## CHARGE

This keyword specifies the charge of the system. for instance : CHARGE 3

## GEOMETRY

This keyword It specifies the molecular geometry and should be placed at the end of the input file. It is followed by the molecular geometry

BOHR

Coordinates or bond distances are given in atomic units

ANGST

Coordinates or bond distances are given in Angstrom. (This is the default

CARTE

The molecular structure is given in Cartesian coordinates. This is the default.

MIXED

The first atoms of the molecular structure are defined by Cartesian coordinates and the following ones are defined by a Z-Matrix.

ZMATR

The molecular structure is defined by a Z-Matrix

## MULTIPLICITY

This keyword specifies the multiplicity of the system, integer following MULTIPLICITY 3

## OPTIMIZATION

This keyword controls the geometry optimization

MAX=

Maximum number of optimisation steps. The default is 100

TOL=

Optimization convergence criterion for the energy. Default is  $3 \times 10^{-4}$  Hartree.

GRADTOL=

Optimization convergence criterion for the gradients. Default is  $3 \times 10^{-6}$  Hartree.

STEP=

Maximum step size in optimization. Default is 0.3 Bohr

CGRAD

Uses the conjugate gradient method. This is the default.

SDC=

Uses the steepest descent method for geometry optimisation with specified multiplier of the gradient. The default is 0.1

SDC

Uses the steepest descent method for geometry optimisation

NUCFRIC=

Perform optimisation via MD with additional friction term with a user-defined multiplier to the dissipative term.

NUCFRIC

Perform geometry optimisation via MD with additional friction term for degrees of freedom where velocity and gradient have opposite sign. The multiplier of the dissipative term is by default 0.6

OUT=

Interval to output structure during optimisation

## MONTECARLO

Perform Monte Carlo simulation

MAX=

Indicates the number of steps after "="

SEED=

indicates value of the SEED if Monte Carlo simulation is intended

NDBG=

Type NDBG=ON to print a lot of MC information

WALL=

Refuses any displacement leading to structure not entering in a sphere of radius specified after '='. Defaults is 1000 a0. It only makes sense for a finite size system.

BASINHOP

Perform basin hopping simulation

## MCTEMP

Additional information about for Monte Carlo simulation. Should appear after the MONTEC keyword.

TMC=

Temperature for MC simulation (no parallel tempering)

NTEMP=

Number of temperatures, defines a parallel tempering MONTE CARLO scheme

LIST

The set of temperatures is readen from a list. After the MCTEMP line are the NTEMP lines. Each line contain : the trajectory number, the temperature, the initial center of mass displacement step, the initial quaternion displacement step

GEOM

The set of temperatures follows a geometric pattern

LINEAR

The set of temperatures follows a linear pattern

TEMPMIN=

The smallest temperature

TEMPMAX=

The largest temperature

X=

inital displacement for smallest temperature

Q=

initial displacement for lowest temperature quaternion displacement

XMIN=

inital displacement for the smallest temperature (not compatible with NTEMP=1 and LIST keyword)

XMAX=

initial displacement for largest temperature (not compatible with NTEMP=1 and LIST keyword)

QMIN=

initial displacement for the lowest temperature quaternion displacement  
(not compatible with NTEMP=1 and LIST keyword)

QMAX=

initial displacement for the largest temperature quaternion displacement  
(not compatible with NTEMP=1 and LIST keyword)

RESCALE=

Frequency to rescale displacement steps

SWAP=

Kind of swap, it can be NO (no exchange), SE(exchange only between successive temperatures, AE (all exchange-exchange MC, ie possible between all temperatures, this is all exchange)

SMOD=

number of steps without trying any swap

SPERCENT=

probability to try a swap each "SWAP" step

SDBG

print some information (mostly to debug)

OUT=

frequency for output

## MCSTATS

Monte Carlo statistics options

DOS

compute densities of states

## PATHS

perform paths over the PES, only works with quaternion approach. A deMon.pth.inp file contain the points defined with CHKPTS NAME=PT1 followed by a line per subsystem defined with quaternions (see quaternions keyword for this general input) like for instance : " 1 0.0 0.0 0.0 1.0 0.0 0.0 0.0"

NMOL=

number of subsystems

NPTS=

number of points

NPTH=

number of paths

## FREQUENCY

This keyword activates frequency analysis.

VIB=

Scaling factor for the numerical step size

## DIPOLE

This keyword activates the calculation of molecular electrostatic moments.

OUTFILE

writes the dipole in an output file

DIPBIN

Dipole file is a binary file

## MDYNAMICS

This keyword activates the Born-Oppenheimer molecular dynamic (BOMD) simulation

RESTA

Restart previous molecular dynamics simulation using information of de-Mon.qmd file

ZERO

Start a trajectory with initial velocities of the nuclei set to zero. This is the default.

RANDOM=

Start a trajectory using random initial velocities, which have no net momentum or angular momentum and give the requested temperature specified after =.

RAN

Start a trajectory using random initial velocities, which have no net momentum or angular momentum and give the initial temperature of MDTEMP keyword.

READ

Start a new MD trajectory. Velocities of the nuclei are given in Cartesian form in the input file, immediately following the MDYNAMICS keyword.

RESET

This option resets all averages and the MD step of the trajectory. It only makes sense with the RESTART option, otherwise it has no effect.

WALL=

This option imposes a spherical potential around the system during an MD simulation. It only makes sense for a finite size system. The radius of

the wall has to be provided in angstrom. The definition of the wall is  
ENER\*(r-WALL)\*\*EXP. WARNING: the wall is centered at the c.o.m.  
of the system which has to be in (0,0,0). The calculation will stop if not  
KEEPCOM=.true. or if OUT\_PBC=.true.

ENER=

the ENER parameter in the definition of the wall. Value is in Hartree

EXP=

the EXP parameter in the definition of the wall.

## QUATERNION

Keyword allowing input with quaternions. After this line, there is one line per molecule that should look like : 1 1.0 0.0 .0 1.0 0.0 0.0 0.0 (unit number, coordinates of center of mass, 4 quaternions numbers) This should be associated with the MOLECULE keyword.

NMOL=

number of molecules

RIGID

molecules are treated as rigid bodies (this only holds for Monte Carlo exploration)

ALLATOMS

molecules are not treated as rigid except for the input file

RANDOM

Quaternions will be created randomly

## MDSTEPS

This keyword controls the steps of the molecular dynamic (MD) simulation

MAX=

Maximum number of MD steps. The default is 1.

OUT=

Step interval to update the deMon.mol file. The default is 10.

SOUT=

Step interval to update the deMon.out file. The default is 1.

MDRST=

Step interval to update the deMon.qmd file. The default is 1.

TSIM=

Maximum MD run time in ps.

## **MDTEMP**

Desired MD temperature in Kelvin. The default is 300.

## **TIMESTEP**

This keyword specifies the time step of the molecular dynamic (MD) simulation in fs

## **MDBATH**

This keyword specifies the temperature bath used in the molecular dynamic (MD) simulation.

### **SCAL**

The velocities are scaled in order to control the temperature. This option is only meaningful for very large systems or for the first equilibration steps of a trajectory.

### **BERE**

Berendsen thermostat is applied to the system as a whole.

### **LOCA**

Berendsen thermostat is applied individually to each atom

### **NOSE**

The Nose-Hoover chain thermostat is applied

### **VAL=**

if (thermostat = SCALING) : number of steps between velocity resets / if (thermostat = BERENDSEN or LOCAL) = Thermostat time constant in picoseconds[ps]. Default is = 0.5 ps.

### **NTHER=**

Specifies the size of the chain used in the Nose-Hoover thermostat (i.e. the number of thermostats). The default value is NTHER = 4.

### **TTHER=**

Specifies the desired temperature. The default value is TTHER = 500 K.

### **FREQTH=**

Specifies the frequency of the Nose-Hoover thermostat. The default value is FREQTH = 100 cm<sup>-1</sup>.

### **NONE**

No temperature bath. This is the default



## CONSERVE

The keywords requests imposition of constraints on some or all mechanical constants of the overall motion of the system.

NONE

Do not impose constraints. This is the default, except for MDYNAMICS RANDOM.

ALL

Equivalent to COM, ANG and MOM. This is the default for MDYNAMICS RANDOM

COM

Reset position of the centre of mass of the system to (0,0,0) on each MD step.

ANG

Reset overall angular momentum of the system to zero on each MD step. This constraint makes no sense, and is ignored, for periodic calculations

MOM

Reset overall momentum of motion of the system to zero on each MD step.

## MDCONSTRAINTS

This keyword imposes atomic constraints during a molecular dynamics simulation (read pdf manual)

## BONDPARAM

BOND PARAMETER FOR DFTB CM3 or DFTB WMUL depending on the DFTB oprions. The next lines define the parameters like O H 0.32 (to define the OH bond) be careful the order of atoms is important (one definition per bon type pair).

## MDPRESSURE

Activates constant-pressure molecular dynamics

P=

External pressure in MPa. The default is 0.1

TAU=

Berendsen Coupling constant in ps. The default is 1.0

COMP=

Compressibility of the system in 1/MPa. The default is set to be reasonable for water.

## METADYNAMICS

Perform a metadynamics calculation in combination with molecular dynamics.

### PLUMED1

Perform a metadynamics simulation using PLUMED 1.2. The input file for the MetaD parameters has to be `plumed.dat`. Please cite: M. Bonomi, D. Branduardi, G. Bussi, C. Camilloni, D. Provasi, P. Raiteri, D. Donadio, F. Marinelli, F. Pietrucci, R.A. Broglia and M. Parrinello, PLUMED: a portable plugin for free energy calculations with molecular dynamics, *Comp. Phys. Comm.* C180, 1961 (2009)

### PLUMED2

Perform a metadynamics simulation using PLUMED 2.XX. The input file for the MetaD parameters has to be `plumed.inpt`. Please cite: Tribello, Bonomi, Branduardi, Camilloni and Bussi *Comput. Phys. Commun.*, DOI:10.1016/j.cpc.2013.09.018 (2013)

## PARATEMP

Perform a parallel-tempering molecular dynamics simulation. **WARNING:** to use this approach, the code has to be compiled using OpenMPI and the preprocessing option `-DMPI`. **WARNING:** in the actual implementation, one mpi process can handle only one replica.

### TMINIMUM=

Minimum temperature of the MPDT algorithm

### TMAXIMUM=

Maximum temperature of the MPDT algorithm

### NUMREP=

Number of replicas in the MPDT algorithm

### NBREQ=

Number of points to indicate as equilibration after an MDPT exchange in the `deMon.out` file. These points are indicated by a 1.0 in the last column of the file.

### EXSTEP=

Number of MD STEPS between MDPT exchanges

### SHORT

If activated, this option avoids to write the average properties along the MDPT run in the `deMon.out` files

### LINEAR

Linear distribution of temperatures between TMINIMUM and TMAXIMUM. The default is an exponential distribution.

## VISUALIZATION

This keyword activates the interface to the visualization programs MOLDEN and MOLEKEL

### MOLDE

The MOLDEN interface is activated. The MOLDEN input is written to the file deMon.mol. This is the default

### MOLEK

The MOLEKEL interface is activated. The MOLEKEL input is written to the file deMon.mkl.

### FULL

A full MOLDEN or MOLEKEL input is written. This is the default if the option MOLDEN or MOLEKEL is set.

## DFTB

Perform a DFTB calculation

### SCC

The self-consistent charge variant of DFTB. The default is non-SCC.

### MEMOSCC

use previous atomic charges to restart the SCC process at a new geometry. This keyword automatically set SCC calculation (even without SCC keyword)

### TOL=

The SCC convergence criterion in electron charges. The default is 1.0E-8.

### DIAG=

User-specified diagonalisation routine for the generalised Eigen value systems. The method is specified after the '='. Legal options are DSYGVD, DSYGV, DSYGVR, SOM.

### ETOL=

Requested energy tolerance for iterative solvers of the total energy (used for CPBO, see CARPAR section)

### MAX=

Maximum number of SCC cycles. The default is 100

### MIX=

Mixing value for simple and Broyden mixing. The default is 0.2. This value is independent from the DFT mixing value

### SIMPLE

Simple mixing instead of Broyden convergence acceleration is performed for SCC. This is per default switched off

### L-DEP

Angular momentum resolved SCC. Here, the self-consistent charge procedure is applied to Mulliken shell charges rather than to Mulliken atomic charges. By default, this option is deactivated.

FERMI=

As FERMI, but with user-specified Fermi temperature (in K) following the keyword.

FERMI

The electron occupation follows a Fermi distribution

THIRD

Third order DFTB; The running directory should contain a file named 3ord\_param for 3rd order derivatives parameters, each line being like H -0.1857, recommended to be used with GCOR (reference Gauss et al. JCTC, 011, 7, 931)

GCOR=

Correction for gamma function for short range; value for Zeta provided after GCOR= (reference Gauss et al. JCTC, 011, 7, 931)

DISP=

London dispersion with a damping function. By default this option is switched off. DISP=1 Zhechkov et al., JCTC 2005 DISP=2 : Rapacioli et al., JCP, 2009

DISP

Equivalent to DISP=1. By default this option is switched off.

CONST=

Perform charge constrained DFTB calculation, the number after "=" specifies the subsystem on which the charge is localised

CONST

Perform charge constrained DFTB calculation.

NMOL=

Specifies the number of subsystems for constrained or CI-DFTB calculation

CI

Perform DFTB+CI calculation (to be used with CONST and SIZECI keywords). By default diagonal terms are computed with the overlaps between SLATER determinants (not using the HOMO approximation).

NOSLAT

Compute CI matrices assuming that only the HOMO orbitals are involved instead of computing matrix elements with Slater determinants.

SIZECI=

Specifies the size of the CI matrix for DFTB-CI calculation.

LEV\_S=

Use level-shift for the SCC convergency

CM3POT

Use CM3 charges instead of Mulliken charge for all the system. CM3 parameter defined by BONDPARAM keyword

WMUL

Weight the Mulliken distribution, the weights are fixed by parameters defined byu BONDPARAM keyword

EPSMUL

Weight the Mulliken distribution, the weight is  $\text{epsii}/(\text{epsii}+\text{epsjj})$

LRESP

Perform a TDDFTB calculation (Linear response)

## PRINT

This keyword controls optional printing.

MOE

Print molecular orbital energies and occupations

MOS=

Print molecular orbital energies, occupations and coefficients.

DE2

Print Hessian matrix.

DEBUG

Generate debug output

## CARPAR

Activates a Car-Parrinello Molecular Dynamics simulation. This option is only available for DFTB. By default, this option is off.

FOM=

Fictitious orbital mass for Car-Parrinello DFTB (in atomic units).

LGTOLE=

The requested tolerance to ensure orthonormality of the orbitals using a Lagrange multiplier. The default is  $10^{-10}$  in atomic units.

BO

The Car-Parrinello approach is used to reach the Born Oppenheimer surface at each point

DELMO=

Multiplier for MO energy gradient for the MO optimisation using the Car-Parrinello approach in conjunction with the steepest descent technique (requires CARPAR BO). The default is 0.1.

MOMD=

Same as the MOMD keyword, but specifying the friction parameter. The default is  $10 \times 10^{-2}$ .

MOMD

Requests a molecular dynamics-like optimisation of the molecular orbitals: A Car-Parrinello MD is carried out. Whenever gradient and velocity of an orbital have opposite signs an additional friction term is added to the equations of motion.

## **BAND**

BAND STRUCTURE CALCULATION

NK1=

Number of kpoints in 1st vector

NK2=

Number of kpoints in 2st vector

NK3=

Number of kpoints in 3st vector

## **MOLECULES**

Keyword to defines MOLECULES. After this line, there is one line per molecule with the unit number and the molecule type like : 1 WAT except if MOLTYPE is used (see below). This keyword should appear in the input file at the very end. The running directory should contain a file named MOLECULES with for each molecule type a line like WAT NAT=3 (3 letters for the molecule name and the number of atoms). The NAT next lines are standard atom name plus xyz inputs (C 0.071715 0.071715 0.000000).

MOLTYPE=

all units are of the same type of molecule defined after MOLTYPE=

## **PARAM**

The path to the DFTB parameters folder will be written on the next line. If this keyword is not present, you should have a SLAKO or SCC-SLAKO file in your running directory

PTYPE=

specifies the parameter : absent for non SCC, MAT or BIO for SCC

## **CUTSYS**

Separate the system in subsystems (not necessary if MOLECULES keyword is used)

NMOL=

number of subsystems

NATMOL=

number of atoms per subsystem (all molecules have the same number of atoms)

RIGID

In the case of Monte Carlo exploration, these subsystems will be treated as rigid

ALLATOMS

The subsystems will never be treated as rigid

RANDOM

Random quaternions will be associated to these subsystems

## CHARGE

This keyword specifies the charge of the system. for instance : CHARGE 3

## GEOMETRY

This keyword It specifies the molecular geometry and should be placed at the end of the input file. It is followed by the molecular geometry

BOHR

Coordinates or bond distances are given in atomic units

ANGST

Coordinates or bond distances are given in Angstrom. (This is the default

CARTE

The molecular structure is given in Cartesian coordinates. This is the default.

MIXED

The first atoms of the molecular structure are defined by Cartesian coordinates and the following ones are defined by a Z-Matrix.

ZMATR

The molecular structure is defined by a Z-Matrix

## MULTIPLICITY

This keyword specifies the multiplicity of the system, integer following MULTIPLICITY 3

## OPTIMIZATION

This keyword controls the geometry optimization

MAX=

Maximum number of optimisation steps. The default is 100

TOL=

Optimization convergence criterion for the energy. Default is 3  
10E-4 Hartree.

GRADTOL=

Optimization convergence criterion for the gradients. Default is 3 10E-6  
Hartree.

STEP=

Maximum step size in optimization. Default is 0.3 Bohr

CGRAD

Uses the conjugate gradient method. This is the default.

SDC=

Uses the steepest descent method for geometry optimisation with specified  
multiplier of the gradient. The default is 0.1

SDC

Uses the steepest descent method for geometry optimisation

NUCFRIC=

Perform optimisation via MD with additional friction term with a user-  
defined multiplier to the dissipative term.

NUCFRIC

Perform geometry optimisation via MD with additional friction term for  
degrees of freedom where velocity and gradient have opposite sign. The  
multiplier of the dissipative term is by default 0.6

OUT=

Interval to output structure during optimisation

## MONTECARLO

Perform Monte Carlo simulation

MAX=

Indicates the number of steps after "="

SEED=

indicates value of the SEED if Monte Carlo simulation is intended

NDBG=

Type NDBG=ON to print a lot of MC information



WALL=

Refuses any displacement leading to structure not entering in a sphere of radius specified after '='. Defaults is 1000 a0. It only makes sense for a finite size system.

BASINHOP

Perform basin hopping simulation

## MCTEMP

Additional information about for Monte Carlo simulation. Should appear after the MONTEC keyword.

TMC=

Temperature for MC simulation (no parallel tempering)

NTEMP=

Number of temperatures, defines a parallel tempering MONTE CARLO scheme

LIST

The set of temperatures is readen from a list. After the MCTEMP line are the NTEMP lines. Each line contain : the trajectory number, the temperature, the initial center of mass displacement step, the initial quaternion displacement step

GEOM

The set of temperatures follows a geometric pattern

LINEAR

The set of temperatures follows a linear pattern

TEMPMIN=

The smallest temperature

TEMPMAX=

The largest temperature

X=

inital displacement for smallest temperature

Q=

initial displacement for lowest temperature quaternion displacement

XMIN=

inital displacement for the smallest temperature (not compatible with NTEMP=1 and LIST keyword)

XMAX=

initial displacement for largest temperature (not compatible with NTEMP=1 and LIST keyword)

QMIN=

initial displacement for the lowest temperature quaternion displacement  
(not compatible with NTEMP=1 and LIST keyword)

QMAX=

initial displacement for the largest temperature quaternion displacement  
(not compatible with NTEMP=1 and LIST keyword)

RESCALE=

Frequency to rescale displacement steps

SWAP=

Kind of swap, it can be NO (no exchange), SE(exchange only between successive temperatures, AE (all exchange-exchange MC, ie possible between all temperatures, this is all exchange)

SMOD=

number of steps without trying any swap

SPERCENT=

probability to try a swap each "SWAP" step

SDBG

print some information (mostly to debug)

OUT=

frequency for output

## MCSTATS

Monte Carlo statistics options

DOS

compute densities of states

## PATHS

perform paths over the PES, only works with quaternion approach. A deMon.pth.inp file contain the points defined with CHKPTS NAME=PT1 followed by a line per subsystem defined with quaternions (see quaternions keyword for this general input) like for instance : " 1 0.0 0.0 0.0 1.0 0.0 0.0 0.0"

NMOL=

number of subsystems

NPTS=

number of points

NPTH=

number of paths

## FREQUENCY

This keyword activates frequency analysis.

VIB=

Scaling factor for the numerical step size

## DIPOLE

This keyword activates the calculation of molecular electrostatic moments.

OUTFILE

writes the dipole in an output file

QCM3

Dipole is computed with CM3 charges

QMULL

Dipole is computed with Mulliken charges

QALL

Dipole with CM3 and Mulliken charges are printed

DIPBIN

Dipole file is a binary file

## MDYNAMICS

This keyword activates the Born-Oppenheimer molecular dynamic (BOMD) simulation

RESTA

Restart previous molecular dynamics simulation using information of deMon.qmd file

ZERO

Start a trajectory with initial velocities of the nuclei set to zero. This is the default.

RANDOM=

Start a trajectory using random initial velocities, which have no net momentum or angular momentum and give the requested temperature specified after =.

RAN

Start a trajectory using random initial velocities, which have no net momentum or angular momentum and give the initial temperature of MDTEMP keyword.

READ

Start a new MD trajectory. Velocities of the nuclei are given in Cartesian form in the input file, immediately following the MDYNAMICS keyword.

## RESET

This option resets all averages and the MD step of the trajectory. It only makes sense with the RESTART option, otherwise it has no effect.

## WALL=

This option imposes a spherical potential around the system during an MD simulation. It only makes sense for a finite size system. The radius of the wall has to be provided in angstrom. The definition of the wall is  $ENER*(r-WALL)**EXP$ . WARNING: the wall is centered at the c.o.m. of the system which has to be in (0,0,0). The calculation will stop if not `KEEPCOM=.true.` or if `OUT_PBC=.true.`

## ENER=

the ENER parameter in the definition of the wall. Value is in Hartree

## EXP=

the EXP parameter in the definition of the wall.

## QUATERNION

Keyword allowing input with quaternions. After this line, there is one line per molecule that should look like : 1 1.0 0.0 .0 1.0 0.0 0.0 0.0 (unit number, coordinates of center of mass, 4 quaternions numbers) This should be associated with the MOLECULE keyword.

## NMOL=

number of molecules

## RIGID

molecules are treated as rigid bodies (this only holds for Monte Carlo exploration)

## ALLATOMS

molecules are not treated as rigid except for the input file

## RANDOM

Quaternions will be created randomly

## MDSTEPS

This keyword controls the steps of the molecular dynamic (MD) simulation

## MAX=

Maximum number of MD steps. The default is 1.

## OUT=

Step interval to update the deMon.mol file. The default is 10.

## SOUT=

Step interval to update the deMon.out file. The default is 1.

## MDRST=

Step interval to update the deMon.qmd file. The default is 1.

TSIM=

Maximum MD run time in ps.

## **MDTEMP**

Desired MD temperature in Kelvin. The default is 300.

## **TIMESTEP**

This keyword specifies the time step of the molecular dynamic (MD) simulation in fs

## **MDBATH**

This keyword specifies the temperature bath used in the molecular dynamic (MD) simulation.

SCAL

The velocities are scaled in order to control the temperature. This option is only meaningful for very large systems or for the first equilibration steps of a trajectory.

BERE

Berendsen thermostat is applied to the system as a whole.

LOCA

Berendsen thermostat is applied individually to each atom

NOSE

The Nose-Hoover chain thermostat is applied

VAL=

if (thermostat = SCALING) : number of steps between velocity resets / if (thermostat = BERENDSEN or LOCAL) = Thermostat time constant in picoseconds[ps]. Default is = 0.5 ps.

NTHER=

Specifies the size of the chain used in the Nose-Hoover thermostat (i.e. the number of thermostats). The default value is NTHER = 4.

TTHER=

Specifies the desired temperature. The default value is TTHER = 500 K.

FREQTH=

Specifies the frequency of the Nose-Hoover thermostat. The default value is FREQTH = 100 cm<sup>-1</sup>.

NONE

No temperature bath. This is the default

## CONSERVE

The keywords requests imposition of constraints on some or all mechanical constants of the overall motion of the system.

NONE

Do not impose constraints. This is the default, except for MDYNAMICS RANDOM.

ALL

Equivalent to COM, ANG and MOM. This is the default for MDYNAMICS RANDOM

COM

Reset position of the centre of mass of the system to (0,0,0) on each MD step.

ANG

Reset overall angular momentum of the system to zero on each MD step. This constraint makes no sense, and is ignored, for periodic calculations

MOM

Reset overall momentum of motion of the system to zero on each MD step.

## MDCONSTRAINTS

This keyword imposes atomic constraints during a molecular dynamics simulation (read pdf manual)

## BONDPARAM

BOND PARAMETER FOR DFTB CM3 or DFTB WMUL depending on the DFTB oprions. The next lines define the parameters like O H 0.32 (to define the OH bond) be careful the order of atoms is important (one definition per bon type pair).

## MDPRESSURE

Activates constant-pressure molecular dynamics

P=

External pressure in MPa. The default is 0.1

TAU=

Berendsen Coupling constant in ps. The default is 1.0

COMP=

Compressibility of the system in 1/MPa. The default is set to be reasonable for water.

## METADYNAMICS

Perform a metadynamics calculation in combination with molecular dynamics.

### PLUMED1

Perform a metadynamics simulation using PLUMED 1.2. The input file for the MetaD parameters has to be `plumed.dat`. Please cite: M. Bonomi, D. Branduardi, G. Bussi, C. Camilloni, D. Provasi, P. Raiteri, D. Donadio, F. Marinelli, F. Pietrucci, R.A. Broglia and M. Parrinello, PLUMED: a portable plugin for free energy calculations with molecular dynamics, *Comp. Phys. Comm.* C180, 1961 (2009)

### PLUMED2

Perform a metadynamics simulation using PLUMED 2.XX. The input file for the MetaD parameters has to be `plumed.inpt`. Please cite: Tribello, Bonomi, Branduardi, Camilloni and Bussi *Comput. Phys. Commun.*, DOI:10.1016/j.cpc.2013.09.018 (2013)

## PARATEMP

Perform a parallel-tempering molecular dynamics simulation. **WARNING:** to use this approach, the code has to be compiled using OpenMPI and the preprocessing option `-DMPI`. **WARNING:** in the actual implementation, one mpi process can handle only one replica.

### TMINIMUM=

Minimum temperature of the MPDT algorithm

### TMAXIMUM=

Maximum temperature of the MPDT algorithm

### NUMREP=

Number of replicas in the MPDT algorithm

### NBREQ=

Number of points to indicate as equilibration after an MDPT exchange in the `deMon.out` file. These points are indicated by a 1.0 in the last column of the file.

### EXSTEP=

Number of MD STEPS between MDPT exchanges

### SHORT

If activated, this option avoids to write the average properties along the MDPT run in the `deMon.out` files

### LINEAR

Linear distribution of temperatures between TMINIMUM and TMAXIMUM. The default is an exponential distribution.

## VISUALIZATION

This keyword activates the interface to the visualization programs MOLDEN and MOLEKEL

### MOLDE

The MOLDEN interface is activated. The MOLDEN input is written to the file deMon.mol. This is the default

### MOLEK

The MOLEKEL interface is activated. The MOLEKEL input is written to the file deMon.mkl.

### FULL

A full MOLDEN or MOLEKEL input is written. This is the default if the option MOLDEN or MOLEKEL is set.

## DFTB

Perform a DFTB calculation

### SCC

The self-consistent charge variant of DFTB. The default is non-SCC.

### MEMOSCC

use previous atomic charges to restart the SCC process at a new geometry. This keyword automatically set SCC calculation (even without SCC keyword)

### TOL=

The SCC convergence criterion in electron charges. The default is 1.0E-8.

### DIAG=

User-specified diagonalisation routine for the generalised Eigen value systems. The method is specified after the '='. Legal options are DSYGVD, DSYGV, DSYGVR, SOM.

### ETOL=

Requested energy tolerance for iterative solvers of the total energy (used for CPBO, see CARPAR section)

### MAX=

Maximum number of SCC cycles. The default is 100

### MIX=

Mixing value for simple and Broyden mixing. The default is 0.2. This value is independent from the DFT mixing value

### SIMPLE

Simple mixing instead of Broyden convergence acceleration is performed for SCC. This is per default switched off

### L-DEP



Angular momentum resolved SCC. Here, the self-consistent charge procedure is applied to Mulliken shell charges rather than to Mulliken atomic charges. By default, this option is deactivated.

FERMI=

As FERMI, but with user-specified Fermi temperature (in K) following the keyword.

FERMI

The electron occupation follows a Fermi distribution

THIRD

Third order DFTB; The running directory should contain a file named 3ord\_param for 3rd order derivatives parameters, each line being like H -0.1857, recommended to be used with GCOR (reference Gauss et al. JCTC, 011, 7, 931)

GCOR=

Correction for gamma function for short range; value for Zeta provided after GCOR= (reference Gauss et al. JCTC, 011, 7, 931)

DISP=

London dispersion with a damping function. By default this option is switched off. DISP=1 Zhechkov et al., JCTC 2005 DISP=2 : Rapacioli et al., JCP, 2009

DISP

Equivalent to DISP=1. By default this option is switched off.

CONST=

Perform charge constrained DFTB calculation, the number after "=" specifies the subsystem on which the charge is localised

CONST

Perform charge constrained DFTB calculation.

NMOL=

Specifies the number of subsystems for constrained or CI-DFTB calculation

CI

Perform DFTB+CI calculation (to be used with CONST and SIZECI keywords). By default diagonal terms are computed with the overlaps between SLATER determinants (not using the HOMO approximation).

NOSLAT

Compute CI matrices assuming that only the HOMO orbitals are involved instead of computing matrix elements with Slater determinants.

SIZECI=

Specifies the size of the CI matrix for DFTB-CI calculation.

LEV\_S=

Use level-shift for the SCC convergency

CM3POT

Use CM3 charges instead of Mulliken charge for all the system. CM3 parameter defined by BONDPARAM keyword

WMUL

Weight the Mulliken distribution, the weights are fixed by parameters defined byu BONDPARAM keyword

DWEIGHT

Weight the Mulliken distribution, the weights are obtained from the density matrix  $P_{ii}/(P_{ii}+P_{jj})$

EPSMUL

Weight the Mulliken distribution, the weight is  $\text{eps}_{ii}/(\text{eps}_{ii}+\text{eps}_{jj})$

LRESP

Perform a TDDFTB calculation (Linear response)

## **PRINT**

This keyword controls optional printing.

MDEXTRA

Print insanely detailed MD output

ATOMMAP

Print atom ordering maps

MOE

Print molecular orbital energies and occupations

MOS=

Print molecular orbital energies, occupations and coefficients.

DE2

Print Hessian matrix.

OPT

Generate full optimization output

RAM

Print RAM allocation table.

PBC

Print periodic boundary conditions information

MD

Print detailed MD output

DEBUG

Generate debug output

## CARPAR

Activates a Car-Parrinello Molecular Dynamics simulation. This option is only available for DFTB. By default, this option is off.

FOM=

Fictitious orbital mass for Car-Parrinello DFTB (in atomic units).

LGTOLE=

The requested tolerance to ensure orthonormality of the orbitals using a Lagrange multiplier. The default is  $10^{-10}$  in atomic units.

BO

The Car-Parrinello approach is used to reach the Born Oppenheimer surface at each point

DELMO=

Multiplier for MO energy gradient for the MO optimisation using the Car-Parrinello approach in conjunction with the steepest descent technique (requires CARPAR BO). The default is 0.1.

MOMD=

Same as the MOMD keyword, but specifying the friction parameter. The default is  $10^{-2}$ .

MOMD

Requests a molecular dynamics-like optimisation of the molecular orbitals: A Car-Parrinello MD is carried out. Whenever gradient and velocity of an orbital have opposite signs an additional friction term is added to the equations of motion.

LGPROP

propagate lagrangian coefficients

## BAND

BAND STRUCTURE CALCULATION

NK1=

Number of kpoints in 1st vector

NK2=

Number of kpoints in 2st vector

NK3=

Number of kpoints in 3st vector