Transition State Tools for ReaxFF

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Chapter 1

Transition State Tools for ReaxFF

1.1 List of abbreviations

CG	Conjugate Gradient
FIRE	Fast Inertial Relaxation Engine
L-BFGS	Limited-memory Broyen-Fletcher-Goldfarb-Shanno
NEB	Nudged Elastic Band
NEB	Nudged Elastic Band
NEB-TR	Nudged Elastic Band method with the removal of translational and rotational degrees of freedom
QM	Quick-Min
SD	Steepest Descents

1.2 General

Table 1.1: Overview of the existing control tags for the transition state tools.

Control tag	Value	Description
imetho	0	Normal MD-run (Default)
	1	Energy minimisation
	2	MD-minimisation
	3	Vibrational analysis
	4	Quasi-Newton optimisation
	5	**Transition State Tools for ReaxFF**
runNeb	0	Nudged Elastic Band calculation (Default)
	1	Energy minimisation (Available optimiser: FIRE, CG, L-BFGS, QM, SD)
	2	Energy minimisation and subsequent frequency analysis
	3	Frequency analysis
	4	Dimer search
	5	Lanczos method

1.3 Nudged Elastic Band

For the execution of a Nudged Elastic Band (NEB) calculation, the text files control, geo, and ffield are required. Depending on the selected control tag *imgInt*, the geo file must contain the endpoints and the respective N intermediate images (*imgInt*=0, *imgNeb*=N), the initial and final structure (*imgInt*=1 or *imgInt*=4) or the endpoints and one intermediate image (*imgInt*=2 or *ImgInt*=5). If the optimisation of the endpoints is activated before the NEB calculation, the energy minimisation criteria *optEmi*, *endEmi*, and *maxEmi* (see Table 1.3) are applied.

Table 1.2: Overview of the existing control tags for the NEB module of the transition state tools.

Control tag	**Value**	**Description**
imgNeb	*int*	Number of NEB images between initial and final state (Default: 0)
imgInt	0	No image interpolation (all images must be included in the geo) (Default)
	1	Linear interpolation of the images between the two end points (geo file must hold two structures)
	2	Linear interpolation of the images between the initial, transition, and final state (geo file must hold three structures)
	4	Plain output of the linear image interpolation between the two endpoints into the fort.90 file (without an NEB calculation)
	5	Plain output of the linear image interpolation between initial, transiton and final state into the fort.90 file (without an NEB calculation)
imgNeb	*int*	Number of NEB images between initial and final state (Default: 0)
imgInt	0 — 1	Use the climbing image algorithm for the NEB calculation: 0 - Off (default), 1 - On
dnudge	0	Disable double nudging during the NEB calculation (Default)
	1	Enable modified double nudging during the NEB calculation (smoothly turns off the double nudging as the NEB converges)
	2	Enable double nudging during the NEB calculation (original approach by Trygubenko and Wales [1])
redRTr	0 — 1	Use the NEB-TR algorithm for the NEB calculation: 0 - Off (Default), 1 - On
maxNeb	*int*	Number of maximal NEB steps (Default: 5000)
spring	*real*	Spring constant between the images in $\mathrm{kcal\,mol^{-1}\,\AA^{-2}}$ (Default: $5.0\,\mathrm{kcal\,mol^{-1}\,\AA^{-2}}$)
optNeb	*int*	Set the optimiser for the NEB calculation: 1 - CG, 2 - FIRE (Default), 3 - L-BFGS, 4 - QM, 5 - SD
opeNeb	0 — 1	Optimise the endpoints before the NEB calculation: 0 - Off, 1 - On
endNeb	*real*	Convergence criterion for the NEB calculation in $\mathrm{kcal\,mol^{-1}\,\AA^{-1}}$ (Default: $1.0\,\mathrm{kcal\,mol^{-1}\,\AA^{-1}}$)

1.4 Structure optimisation

Table 1.3: Overview of the structure optimisation control tags within the transition state tools for ReaxFF.

Control tag	Value	Description
optEmi	*int*	Set the optimiser for the energy minimisation: 1 - CG, 2 - FIRE (Default), 3 - L-BFGS, 4 - QM, 5 - SD
endEmi	*real*	Convergence criterion for the energy minimisation in $\mathrm{kcal\,mol^{-1}\,Å^{-1}}$ (Default: $1.0\,\mathrm{kcal\,mol^{-1}\,Å^{-1}}$)
maxEmi	*int*	Maximal energy minimisation steps (Default: 5000)
convcr	0 — 1	Satisfaction of the convergence criterion is based on 0 - $\mathbf{F}_{\mathrm{total}}^{1/2}$, 1 - $\mathbf{F}_{\mathrm{max,atom}}$ (Default)
itraj	0 — 1	Output of the optimisation trajectory: 0 - Off (Default), 1 - On
frtraj	*int*	Frequency of the optimisation trajectory output (Default: 1)

Within the transition state tools for ReaxFF, it can be specified whether the atom's respective coordinate(s) are allowed to change during the structural optimisation. To this end, the keyword CONSTRAINTS has to be added to the header of the geo file:

CONSTRAINTS [At1 At2 flagX flagY flagZ]

All atoms with indices between At1 and At2 are optimised according to the specified flags. Setting flag values of 0 or 1 disables or allows the optimisation of the specified atoms along the respective spatial directions. Setting all flags to 0 is equivalent to the use of the FIXATOMS keyword. All non-specified atoms are assumed to be free of optimisation constraints (all flags are set to 1).

```
1  XTLGRF 200
2  DESCRP Al100
3  REMARK Al100_with_Au_constraint
4  FIXATOMS 1 8
5  CONSTRAINTS 13 13 0 0 1
6  CRYSTX      5.72756     5.72756    13.75000    90.00000    90.00000    90.00000
7  FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
8  HETATM     1 Al                    0.00000    0.00000    4.00000     Al  0 0   0.00000
9  HETATM     2 Al                    2.86378    0.00000    4.00000     Al  0 0   0.00000
10 HETATM     3 Al                    0.00000    2.86378    4.00000     Al  0 0   0.00000
11 HETATM     4 Al                    2.86378    2.86378    4.00000     Al  0 0   0.00000
12 HETATM     5 Al                    1.43189    1.43189    6.02500     Al  0 0   0.00000
13 HETATM     6 Al                    4.29567    1.43189    6.02500     Al  0 0   0.00000
14 HETATM     7 Al                    1.43189    4.29567    6.02500     Al  0 0   0.00000
15 HETATM     8 Al                    4.29567    4.29567    6.02500     Al  0 0   0.00000
16 HETATM     9 Al                    0.00000    0.00000    8.05000     Al  0 0   0.00000
17 HETATM    10 Al                    2.86378    0.00000    8.05000     Al  0 0   0.00000
18 HETATM    11 Al                    0.00000    2.86378    8.05000     Al  0 0   0.00000
19 HETATM    12 Al                    2.86378    2.86378    8.05000     Al  0 0   0.00000
20 HETATM    13 Au                    1.43189    1.43189    9.75000     Au  0 0   0.00000
21 END
```

Listing 1.1: Example for using the CONSTRAINTS keyword. Due to the FIX-

ATOMS keyword, the atoms 1 to 8 are kept in their bulk position. The gold atom (atom index 13) will only be relaxed in the z-direction.

1.5 Optimiser settings

Table 1.4: Overview of the control tags for the respective force-based optimisers of the transition state tools.

Control tag	Value	Description
maxmov	*real*	Maximum allowed step size for translation (Default: 0.2)
fdsOpt	*real*	Finite difference step size (CG, L-BFGS(line)) (Default: 0.005)
dtOpt	*real*	Finite difference step size (FIRE, QM) (Default: 0.005)
memOpt	*int*	Number of memorised steps for the construction of the inverse Hessian matrix (L-BFGS) (Default: 20)
aicOpt	0 — 1	Initial inverse curvature is determined automatically (L-BFGS): 0 - Off, 1 - On (Default)
ivcOpt	*real*	Initial inverse curvature for the construction of the inverse Hessian matrix (L-BFGS) (Default: 0.01)
damOpt	*real*	Damping Parameter to control the variation of the step size (L-BFGS) (Default: 1.1)
flmOpt	0 — 1	L-BFGS approach to determine the new atomic positions: 0 - L-BFGS(Hess) (Default), 1 - L-BFGS(Line)
mdtOpt	*real*	Define the maximum allowed dynamic time step (Default: 1.0)
idtOpt	*real*	Factor to increase the dynamic time step (FIRE) (Default: 1.1)
ddtOpt	*real*	Factor to decrease the dynamic time step (FIRE) (Default: 0.5)
falOpt	*real*	Parameter to adjust the velocity damping (FIRE) (Default: 0.1)
dalOpt	*real*	Factor to decrease α (FIRE) (Default: 0.99)
fnmOpt	*int*	Minimum number of steps before modifying α and the dynamical time step (FIRE) (Default: 5)
qmfOpt	0 — 1	Force the velocity in the direction of the force (FIRE): 0 - Off (Default), 1 - On
salOpt	*real*	Factor to control the step size (SD) (Default: 0.01)

1.6 Frequency analysis

Table 1.5: Overview of the control tags for the vibrational analysis module of the transition state tools for ReaxFF.

Control tag	Value	Description
ifrMet	*int*	Method to perform the vibration analysis: 0 - finite difference method [2] (Default), 1 - modified approach by Frederiksen *et al.* [3]
infree	0	Single displacement per atom and cartesian coordinate (backwards)
	1	Single displacement per atom and cartesian coordinate (forward)
	2	Central difference displacements per atom and cartesian coordinate (Default)
	4	Four displacements per atom and cartesian coordinate
freAll	0	The vibration modes are calculated according to the FREQANALYSIS keyword in the geo file
	1	Calculate the vibrational modes for all non-fixed atoms (specified via the FIXATOMS keyword)
	2	Calculate the vibrational modes for all atoms (Default)
ifrMet	*real*	Magnitude of atom displacements in Å (for $freAll \neq 0$) (Default: in 0.01 Å)

The calculation of the vibration modes can be controlled via the FREQANALYSIS keyword in the header of the geo file:

FREQANALYSIS [At1 At2 disX disY disZ]

The frequency analysis is carried out for all atoms in the range of At1 and At2 using disX, disY, and disZ as displacement values (in Å) in the respective spatial directions.

```
XTLGRF 200
DESCRP Al100
REMARK frequency_analysis
FIXATOMS 1 8
FREQANALYSIS 13 13 0.05 0.05 0.05
CRYSTX      5.72756     5.72756    13.75000    90.00000    90.00000    90.00000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM      1 Al                   0.00000    0.00000    4.00000     Al  0 0   0.00000
HETATM      2 Al                   2.86378    0.00000    4.00000     Al  0 0   0.00000
HETATM      3 Al                   0.00000    2.86378    4.00000     Al  0 0   0.00000
HETATM      4 Al                   2.86378    2.86378    4.00000     Al  0 0   0.00000
HETATM      5 Al                   1.43189    1.43189    6.02500     Al  0 0   0.00000
HETATM      6 Al                   4.29567    1.43189    6.02500     Al  0 0   0.00000
HETATM      7 Al                   1.43189    4.29567    6.02500     Al  0 0   0.00000
HETATM      8 Al                   4.29567    4.29567    6.02500     Al  0 0   0.00000
HETATM      9 Al                   0.00000    0.00000    8.05000     Al  0 0   0.00000
HETATM     10 Al                   2.86378    0.00000    8.05000     Al  0 0   0.00000
HETATM     11 Al                   0.00000    2.86378    8.05000     Al  0 0   0.00000
HETATM     12 Al                   2.86378    2.86378    8.05000     Al  0 0   0.00000
HETATM     13 Au                   1.43189    1.43189    9.75000     Au  0 0   0.00000
END
```

Listing 1.2: Example for using the FREQANALYSIS keyword. Here, the vibration modes are calculated for the Au adatom (atom index 13) using an atomic displacement of 0.05 Å, respectively.

1.7 Dimer search and Lanczos method

In order to perform a saddle point search (Dimer search and Lanczos method), the text files geo, control and ffield are required. Also, the initial lowest modes are needed at the beginning of a saddle point search. If the control tag *iSMode*=0 is set, the $3N$ initial directions along the dimer for the N atoms are taken from the modes.in file. The line sequence corresponds to the atom order from the geo file. The three columns correspond to the atoms' initial direction along the respective coordinate. Also, the geo file has to provide the initial structure for the saddle point search).

```
XTLGRF 200
DESCRP image_004
REMARK image_004
FIXATOMS      1      8
CRYSTX      5.76999     5.76999    26.12000    90.00000    90.00000    90.00000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM      1 Au                   1.44250    1.44250   10.00000     Au  0 0   0.00000
HETATM      2 Au                   4.32749    1.44250   10.00000     Au  0 0   0.00000
HETATM      3 Au                   1.44250    4.32749   10.00000     Au  0 0   0.00000
HETATM      4 Au                   4.32749    4.32749   10.00000     Au  0 0   0.00000
HETATM      5 Au                   0.00000    0.00000   12.04000     Au  0 0   0.00000
HETATM      6 Au                   2.88500    0.00000   12.04000     Au  0 0   0.00000
HETATM      7 Au                   0.00000    2.88500   12.04000     Au  0 0   0.00000
HETATM      8 Au                   2.88500    2.88500   12.04000     Au  0 0   0.00000
HETATM      9 Au                   1.41837    1.44250   14.16715     Au  0 0   0.00000
HETATM     10 Au                   4.32155    1.44250   14.16585     Au  0 0   0.00000
HETATM     11 Au                   1.42036    4.32749   14.16875     Au  0 0   0.00000
HETATM     12 Au                   4.31938    4.32749   14.16674     Au  0 0   0.00000
HETATM     13 Au                   5.72280    5.76232   16.34443     Au  0 0   0.00000
HETATM     14 Au                   2.85003    0.00860   16.26047     Au  0 0   0.00000
HETATM     15 Au                   5.72280    2.89267   16.34443     Au  0 0   0.00000
HETATM     16 Au                   2.85003    2.87640   16.26047     Au  0 0   0.00000
HETATM     17 Au                   3.20078    4.32750   18.55147     Au  0 0   0.00000
END
```

Listing 1.3: The geo file contains the initial structure for the saddle point search, whereby the atom sequence has to match the line entries from the modes.in file.

To restart a calculation, the resulting newmodes.out file from the previous run can be used as the new modes.in file.
Alternatively, the entries of the modes.in file can be generated automatically by

```
 0.000000          0.000000          0.000000
 0.000000          0.000000          0.000000
 0.000000          0.000000          0.000000
 0.000000          0.000000          0.000000
 0.000000          0.000000          0.000000
 0.000000          0.000000          0.000000
 0.000000          0.000000          0.000000
 0.000000          0.000000          0.000000
 0.052585          0.000000         -0.002857
 0.038785          0.000000          0.001094
 0.051217          0.000000         -0.004286
 0.040670          0.000000          0.001824
 0.143408          0.008420         -0.039971
 0.106233         -0.006748          0.027843
 0.143408         -0.008420         -0.039971
 0.106233          0.006748          0.027843
-0.959900          0.000000          0.036505
```

Listing 1.4: The modes.in file contains an Nx3 matrix with the initial directions along the dimer in the respective spatial directions for the N atoms of the system.

setting iSMode=1. Here, a target structure must be provided as a second entry in the geo file.

```
XTLGRF 200
DESCRP Initial_structure
REMARK Saddle point search
FIXATOMS      1      8
CRYSTX      5.76999     5.76999    26.12000    90.00000    90.00000    90.00000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM      1 Au                    1.44250    1.44250   10.00000     Au  0 0   0.00000
HETATM      2 Au                    4.32749    1.44250   10.00000     Au  0 0   0.00000
HETATM      3 Au                    1.44250    4.32749   10.00000     Au  0 0   0.00000
HETATM      4 Au                    4.32749    4.32749   10.00000     Au  0 0   0.00000
HETATM      5 Au                    0.00000    0.00000   12.04000     Au  0 0   0.00000
HETATM      6 Au                    2.88500    0.00000   12.04000     Au  0 0   0.00000
HETATM      7 Au                    0.00000    2.88500   12.04000     Au  0 0   0.00000
HETATM      8 Au                    2.88500    2.88500   12.04000     Au  0 0   0.00000
HETATM      9 Au                    1.41837    1.44250   14.16715     Au  0 0   0.00000
HETATM     10 Au                    4.32155    1.44250   14.16585     Au  0 0   0.00000
HETATM     11 Au                    1.42036    4.32749   14.16875     Au  0 0   0.00000
HETATM     12 Au                    4.31938    4.32749   14.16674     Au  0 0   0.00000
HETATM     13 Au                    5.72280    5.76232   16.34443     Au  0 0   0.00000
HETATM     14 Au                    2.85003    0.00860   16.26047     Au  0 0   0.00000
HETATM     15 Au                    5.72280    2.89267   16.34443     Au  0 0   0.00000
HETATM     16 Au                    2.85003    2.87640   16.26047     Au  0 0   0.00000
HETATM     17 Au                    3.20078    4.32750   18.55147     Au  0 0   0.00000
END

XTLGRF 200
DESCRP Target_structure
REMARK Automatic modes.in generation
FIXATOMS      1      8
CRYSTX      5.76999     5.76999    26.12000    90.00000    90.00000    90.00000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM      1 Au                    1.44250    1.44250   10.00000     Au  0 0   0.00000
HETATM      2 Au                    4.32749    1.44250   10.00000     Au  0 0   0.00000
HETATM      3 Au                    1.44250    4.32749   10.00000     Au  0 0   0.00000
HETATM      4 Au                    4.32749    4.32749   10.00000     Au  0 0   0.00000
HETATM      5 Au                    0.00000    0.00000   12.04000     Au  0 0   0.00000
HETATM      6 Au                    2.88500    0.00000   12.04000     Au  0 0   0.00000
HETATM      7 Au                    0.00000    2.88500   12.04000     Au  0 0   0.00000
HETATM      8 Au                    2.88500    2.88500   12.04000     Au  0 0   0.00000
HETATM      9 Au                    1.43567    1.44250   14.16621     Au  0 0   0.00000
HETATM     10 Au                    4.33431    1.44250   14.16621     Au  0 0   0.00000
HETATM     11 Au                    1.43721    4.32749   14.16734     Au  0 0   0.00000
HETATM     12 Au                    4.33276    4.32749   14.16734     Au  0 0   0.00000
HETATM     13 Au                    5.76998    5.76509   16.33128     Au  0 0   0.00000
HETATM     14 Au                    2.88498    0.00638   16.26963     Au  0 0   0.00000
HETATM     15 Au                    5.76998    2.88990   16.33128     Au  0 0   0.00000
HETATM     16 Au                    2.88498    2.87862   16.26963     Au  0 0   0.00000
HETATM     17 Au                    2.88498    4.32750   18.56348     Au  0 0   0.00000
END
```

Listing 1.5: The geo file has to contain the initial structure for the saddle point search and the target structure as an additional entry for the automatic generation of the modes.in file.

In the absence of a target structure and modes.in, the initial lowest modes may be generated randomly ($iSMode$=2). However, this increases the chance of failure in the saddle point search or results in unexpected behaviour.

Table 1.6: Overview of the saddle point search control tags within the transition state tools for ReaxFF.

Control tag	Value	Description
optSad	*int*	Set the optimiser for the saddle point search: 1 - CG (Default, recommended), 2 - FIRE, 3 - L-BFGS, 4 - QM, 5 - SD
endSad	*real*	Convergence criterion for the saddle point search in $\mathrm{kcal\,mol^{-1}\,Å^{-1}}$ (Default: $1.0\,\mathrm{kcal\,mol^{-1}\,Å^{-1}}$)
maxSad	*int*	Maximal saddle point search steps (Default: 5000)
iSMode	0	Read initial lowest modes from modes.in file (Default)
	1	Generate initial lowest modes from input structures
	2	Create random initial lowest modes (not recommended)
disSad	0 — 1	Perform an initial displacement before starting the saddle point search: 0 - Off (Default), 1 - On
disFac	*real*	Scaling factor for initial displacement (Default: 0.01)
intSad	0 — 1	Interpolate the initial structure for the saddle point search from two given end point structures: 0 - Off (Default), 1 - On
DRoMax	*int*	Set the maximum number of rotational steps per translational step (Dimer search) (Default: 1)
DdrSep	*real*	Seperation of the dimers in Å (Dimer search) (Default: 0.001 Å)
DFNMin	*real*	Threshold for the rotational force in $\mathrm{kcal\,mol^{-1}\,Å^{-1}}$ below which the dimer is not rotated (Dimer search) (Default: $0.23\,\mathrm{kcal\,mol^{-1}\,Å^{-1}}$)
DFNMax	*real*	Threshold for the rotational force in $\mathrm{kcal\,mol^{-1}\,Å^{-1}}$ below which dimer rotation stops. At least one rotation iteration is carried out if the rotational force ranges between DFNMin and DFNMax. (Dimer search) (Default: $2.3\,\mathrm{kcal\,mol^{-1}\,Å^{-1}}$)
lanTol	*real*	Tolerance for eigenvalue convergence (Lanczos) (Default: 0.01)
lanSdr	*real*	Finite difference step length in Å (Lanczos) (Default: 0.001 Å)
lanSnl	*int*	Maximum size of Lanczos matrix (Lanczos) (Default: 20)
lanQLc	*real*	Convergence criteria for QL algorithm (Lanczos) (Default: 10^{-30})
lanQLs	*real*	Implicit shift in QL-routine (Lanczos) (Default: 0.0001)

Bibliography

[1] S. A. Trygubenko, D. J. Wales, *The Journal of Chemical Physics* **2004**, *120*, 2082–2094.

[2] A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dułak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, E. D. Hermes, P. C. Jennings, P. B. Jensen, J. Kermode, J. R. Kitchin, E. L. Kolsbjerg, J. Kubal, K. Kaasbjerg, S. Lysgaard, J. B. Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Peterson, C. Rostgaard, J. Schiøtz, O. Schütt, M. Strange, K. S. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng, K. W. Jacobsen, *Journal of Physics: Condensed Matter* **2017**, *29*, 273002.

[3] T. Frederiksen, M. Paulsson, M. Brandbyge, A.-P. Jauho, *Phys. Rev. B* **2007**, *75*, 205413.