www.newtonx.org

NEWTON-X
a package for Newtonian dynamics close to the crossing seam

Documentation based on NEWTON-X version 2.2 build 07 (release 2019-01-10)

1 Table of contents

2 About NEWTON-X

2.1 General Information

NEWTON-X[1, 2] is a general-purpose program for molecular dynamics in the electronic excited states, including nonadiabatic effects via surface hopping.

NEWTON-X modular development allows it to be easily linked to any quantum chemistry package that can provide energy gradients and (optionally) nonadiabatic coupling vectors. NEWTON-X does not require pre-computed global potential energy surfaces, as it is based on the on-the-fly computation of electronic properties during dynamics propagation.

In the current version, NEWTON-X can simulate nonadiabatic dynamics using COLUMBUS,[3] TURBOMOLE,[4] GAUSSIAN,[5] GAMESS,[6] BAGEL,[7] and DFTB+[8] program packages, as well as with several built-in analytical models. Dynamics using hybrid gradients (including QM/MM approach) is available for combinations between TINKER[9] and one of the following programs COLUMBUS, TURBOMOLE, DFTB+, BAGEL, and analytical models. Other third-party programs providing energies and nonadiabatic couplings can be easily integrated to work with NEWTON-X as well.

For programs and methods that do not count on nonadiabatic couplings, NEWTON-X can be used to dynamically compute the coupling, through a numerical approach[10] implemented in two different ways.

In addition to dynamics, NEWTON-X can also be used to generate initial conditions and to simulate absorption, emission, and photoelectron spectra using the nuclear ensemble approach.[11]

NEWTON-X code is distributed free of charge for non-commercial and non-profit uses. You may use the program freely and adapt the code to your needs. Please, if you have any enhancements, share them with us. You are, however, not allowed to re-distribute code or binaries in parts or total. Anyone intending to use NEWTON-X must contact us.

NEWTON-X *is shipped to the user "as is." There is no guarantee that it will work as described. Usage is at your own risk; there is no liability taken for any damage or loss of data and/or money.* If you experience problems, please tell the developers supplying the version number. They are always grateful for any hint but bear in mind that there is no kind of official support for NEWTON-X.

2.2 Contact Information

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The program, this documentation, and tutorials can be downloaded from:
www.newtonx.org

Support can be obtained through the discussion forum at:
groups.google.com/d/forum/newtonx

2.3 What is new in this version

NEWTON-X version 2.2 is a minor update to version 2.1. The main modifications are:

- DFTB+/NEWTON-X interface
- Importance sampling algorithm
- Spin-Boson Hamiltonian built-in model.

NEWTON-X version 2.1 is a minor update to version 2.0. The main modifications are:

- BAGEL/NEWTON-X interface

NEWTON-X version 2.0 is a major update to version 1.4. The main modifications are:

- Photoelectron spectra.[12]
- Tully 1D models.[13]
- OD Scheme[14] for calculations of couplings with TURBOMOLE and GAUSSIAN 09 interfaces.
- (U)TDDFT, (U)TDA, and (U)CIS with GAUSSIAN 09.
- Many codes were rewritten for improved performance.

3 Mixed quantum-classical dynamics simulations

Mixed quantum-classical approaches[15, 16] are the most employed class of methods to perform excited-state molecular dynamics simulations accounting for nonadiabatic effects. In these approaches, which include the surface hopping and the mean field Ehrenfest methods, the nuclear time evolution is treated classically, while the time evolution of the population of each electronic state is dealt with separately.

In surface hopping,[17] the time evolution of the population is obtained in two steps: first, nonadiabatic transition probability between each pair of states is computed, and a stochastic algorithm is applied to decide in which state the classical trajectory is propagated in the next time step. Second, statistics over a large set of independently computed trajectories allows getting the fraction of trajectories (occupation) in each state as a function of time. The main hypothesis underlying the surface hopping approach is that the *occupation* and the quantum *population* of each electronic state are the same if an infinite number of trajectories are computed.[13] The method is reviewed in Ref.[18].

There are several proposed ways to evaluate the nonadiabatic transition probabilities, since simple methods, which just assume that the probability is the unity if the energy gap between the states is smaller than some threshold, to more sophisticated approaches, which take into account the variation of wavefunction coefficients[19] or compute the Landau-Zener transition probability.[20] One of the most reliable procedures to calculate the nonadiabatic transition probability for surface hopping simulations is the Tully's fewest switches algorithm.[13] In this approach, the time-dependent Schroedinger equation (TDSE) is integrated simultaneously with the classical trajectory.[21] To cope with the lack of non-local information introduced by the independent-trajectories approach, non-local terms in the TDSE are neglected, and the nuclear wavefunction is supposed to be entirely localized at the classical position determined by Newton's equation. The integration of this semi-classical version of the TDSE gives the adiabatic populations of the electronic states, which are then used to compute the probability using the fewest switches formula.

The integration of the TDSE depends on nonadiabatic coupling terms connecting different states. If adiabatic representation is used to expand the molecular wavefunction, nonadiabatic coupling vectors should be computed. Alternatively, if the diabatic representation is used, non-diagonal Hamiltonian matrix elements should be calculated. Either way, the computation of the nonadiabatic coupling terms are the bottleneck for nonadiabatic dynamics approaches. These terms are not usually available for most of the quantum chemical methods, and when they are, their computational cost increases with the square of the number of electronic states.[22] These difficulties have motivated the search for approximated hopping algorithms as those mentioned above, and on the other hand, the computation of coupling terms based on wave function overlaps.

A consequence of the hyper-localization of the nuclear wavefunction in mixed quantum-classical approaches is that non-diagonal terms in the density matrix do not vanish with time as they should do. In surface-hopping, this lack of decoherence results in an excessive number of hopping events from lower to upper states, which disturbs the evolution of the populations. Decoherence can be recovered by applying an *ad hoc* correction to the adiabatic population every time step, which forces the non-diagonal terms in the density matrix to damp to zero within a certain time constant.[23]

When a hopping between two states takes place, it usually does through a finite energy gap. To keep the total energy constant in the subsequent trajectory, it is necessary to correct the kinetic energy, for example, by rescaling the momentum or by adding more momentum at the direction of the nonadiabatic coupling vector.[3] It may also happen that the stochastic algorithm attempts to hop from a lower to an upper state in a region where there is not enough energy to do so. Such cases have usually been treated

by forbidding the hopping occurrence.[21] The momentum can be kept or reversed afterward. Another possibility is to take the time uncertainty principle to search for a geometry nearby where the hopping is allowed.[24]

Because of the stochastic nature of the fewest-switches surface-hopping approach, trajectories starting with the same initial conditions gives rise to different time development. Moreover, the initial conditions should reflect the initial phase space distribution. Therefore, the averages that define the state occupation should in principle be performed over this double ensemble of trajectories starting at different points of the phase space, several times in each one. Because of computational limitations, this procedure is usually reduced to a single ensemble of trajectories starting in different points of the phase space only once in each one.

The initial condition ensemble can be generated in a diversity of ways.[25] For instance, the simulation of an instantaneously excited wave packet into the Franck-Condon region may be done by selecting geometries and velocities from dynamics in the grounds state. Alternatively, each nuclear degree of freedom can be treated within the harmonic approximation, and a Wigner distribution can be built.

Most of the methods and algorithms mentioned in this introduction are implemented in the NEWTON-X program.

4 Developers and Contributors

The NEWTON-X program has been developed in a multi-institutional collaboration, involving researchers from several countries.

People working in the general NEWTON-X development are:

Mario Barbatti	Aix-Marseille University	France
Hans Lischka	Tianjin University	China
Matthias Ruckenbauer	University of Vienna	Austria
Felix Plasser	Loughborough University	UK
Rachel Crespo-Otero	Queen Mary University	UK

Many other people have contributed in the past or are still contributing to development of specific algorithms in NEWTON-X. They are:

Surface hopping routines and initial condition distributions

Giovanni Granucci	University of Pisa	Italy
Maurizio Persico	University of Pisa	Italy

HST DD nonadiabatic couplings

Jiri Pittner	J. Heyrovsky Institute	Czech Republic

OD nonadiabatic couplings

Ilya G. Ryabinkin	University of Toronto Scarborough	Canada
Jayashree Nagesh	University of Toronto	Canada
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NEWTON-X/GAMESS interface

Aaron West	Iowa State University	USA
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NEWTON-X/DFTB+ interface

Ljiljana Stojanovic	Queen Mary University	UK
Thomas Niehaus	University of Lyon	France

NEWTON-X/BAGEL interface

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Toru Shiozaki	Northwestern University	USA

Importance sampling and fragment analysis

Fábris Kossoski	Aix-Marseille University	France

Contributions from the following colleagues are also acknowledged:
Mirjana Eckert-Maksić, Xing Gao, Miquel Huix-Rotllant, Sergio A. Losilla Fernández, Vladimir Lukeš, Thomas Niehaus, Iakov Polyak, Bernhard Sellner, Peter Szalay, Atila Tajti, Mario Vazdar, Markus Weihs, Oliver Weingart, Gunther Zechmann, and Tomas Zeleny.

5 How to reference NEWTON-X

Please, cite NEWTON-X as:

- Barbatti, M.; Ruckenbauer, M.; Plasser, F.; Pittner, J.; Granucci, G.; Persico, M.; Lischka, H., NEWTON-X: A Surface-Hopping Program for Nonadiabatic Molecular Dynamics. *WIREs: Comp. Mol. Sci.* **2014,** *4*, 26-33.

- Barbatti, M.; Granucci, G.; Ruckenbauer, M.; Plasser, F.; Crespo-Otero, R.; Pittner, J.; Persico, M.; Lischka, H., NEWTON-X: A package for Newtonian dynamics close to the crossing seam. Version 2, **2016**, www.newtonx.org.

References to specific methods, algorithms and third-party programs used in NEWTON-X are given along this documentation. For a summary, see Chapter 7.

6 Quick start

6.1 NEWTON-X Tutorial

NEWTON-X tutorials with step-by-step procedures for several examples are available at www.newtonx.org.

6.2 The NXINP tool

Most of the NEWTON-X inputs are prepared with nxinp program. To execute nxinp, type:
`$NX/nxinp`

The first screen should looks like:

```
============================================================
                          NEWTON-X
        Newtonian dynamics close to the crossing seam
                       www.newtonx.org
============================================================

               MAIN MENU


        1. GENERATE INITIAL CONDITIONS


        2. SET BASIC INPUT


        3. SET GENERAL OPTIONS


        4. SET NONADIABATIC DYNAMICS


        5. GENERATE TRAJECTORIES AND SPECTRUM


        6. SET STATISTICAL ANALYSIS


        7. EXIT

Select one option (1-7):_
```

The next sections will guide you through each one of these options. By now, it is enough to note that nxinp is self-explaining. When you select one of the options, say, option 2 (Set basic input), you are asked about a series of parameters. A sequence of input may be, for example:

```
============================================================
                          NEWTON-X
        Newtonian dynamics close to the crossing seam
                      www.newtonx.org
============================================================

                     SET BASIC OPTIONS


nat:  Number of atoms.
There is no value attributed to nat
Enter the value of nat  : 12
Setting nat = 12

nstat:  Number of states.
The current value of nstat  is: 2
Enter the new value of nstat  : 3
Setting nstat = 3

nstatdyn:  Initial state (1 - ground state).
The current value of nstatdyn  is: 2
Enter the new value of nstatdyn  :
Setting nstatdyn = 2

dt:  Time step for the classical equations.
The current value of dt (fs) is: 0.5
Enter the new value of dt (fs) : 0.1
Setting dt = _
```

Each parameter contains a short description and, most of the time, an attributed default value. To use the default values, just press <ENTER>. More information about each parameter can be found in this documentation.

6.3 Initial conditions generation

Input

1- Prepare geom file with equilibrium geometry. Use xyz2nx to create geom from xyz files.
2- Prepare force.out file with the harmonic frequencies using, for example, TURBOLOME.
3- Run nxinp program. Select option `1. GENERATE INITIAL CONDITIONS`. nxinp will help you choose the input parameters to control the initial condition generation. Exit nxinp.

Run

```
$NX/initcond.pl > initcond.log
```

Output

final_output: Initial conditions.
initcond.log: Log file.

Further options

Optionally, you can control the number of excitation quanta in each vibrational modes by providing a file qvector (see Chapter 10) together with the other input files.

It is also possible to pick points from previous dynamics calculations or to generate random velocities to be used as initial conditions.

6.4 Dynamics Input

6.4.1 Adiabatic dynamics (dynamics on one surface)

Input

1- Create a directory called JOB_AD containing a set of input files for geometry optimization (1 step) with the chosen electronic structure program.

2- Run nxinp program. First, select option `2. SET BASIC INPUT`. nxinp will help you select the input parameters to control the dynamics. After that, select option `3. SET GENERAL OPTIONS` if you want to change some more technical parameter. Exit nxinp.

Hint
Check control.dyn file. If the keyword "thres" is defined there, be sure that its value is 0 (`thres = 0`).

6.4.2 Nonadiabatic dynamics (Surface hopping)

Input

1- Create a directory called JOB_NAD containing an input for nonadiabatic coupling (single point) with the chosen electronic structure program.

2- Run nxinp program (`$NX/nxinp`). First, select option `2. SET BASIC INPUT`. nxinp will help you select the input parameters to control the dynamics. After that, select option `3. SET GENERAL OPTIONS` if you want to change some more technical parameter. Optionally, select option `4. SET NONADIABATIC DYNAMICS` to change the nonadiabatic-dynamics options. Exit nxinp.

Hint
Check control.dyn file. If the keyword "thres" is defined there, be sure that its value is 100 (`thres = 100`).

6.4.3 Mixed adiabatic and nonadiabatic dynamics

Input

1- Create a directory called JOB_AD containing a set of input files for geometry optimization (1 step) with the chosen electronic structure program.

2- Create a directory called JOB_NAD containing an input for nonadiabatic coupling (single point).

3- Run nxinp program (`$NX/nxinp`). First, select option `2. SET BASIC INPUT`. nxinp will help you select the input parameters to control the dynamics. Optionally, select option `3. SET GENERAL OPTIONS` if you want to change some more technical parameter. Optionally, select option `4. SET NONADIABATIC DYNAMICS` to change the nonadiabatic-dynamics options. Exit nxinp.

Hint

Check control.dyn file. The keyword “thres” must be defined there. Its value is the energy difference threshold (eV) bellow to which the nonadiabatic dynamics starts. *This option is not fully tested.*

6.5 Creating the trajectory inputs

Input

1- Copy final_output file created after the initial conditions generation, section 6.3, into the same directory containing all files and directories created in the dynamics input, section 6.4.

2- If the jobs will run in a batch system, also copy the submission script file to that directory. In $NX/../batch you may find several examples of submission scripts.

3- Run nxinp program (`$NX/nxinp`). Select option `5. GENERATE TRAJECTORIES AND SPECTRUM`. nxinp will help you to select the input parameters to control the trajectory inputs generation. At the end of the input selection, NEWTON-X will automatically generate the trajectory directories. This process can take some few minutes.

Output

The trajectories inputs were written to `TRAJECTORIES/TRAJn`, where `n` is the trajectory number.

6.6 Running the dynamics

1- Go to each `TRAJECTORIES/TRAJn` (see section 6.5) and run
`$NX/moldyn.pl > moldyn.log &`
or, if is this the case, submit the job to the batch system.

2- Alternatively, go to `TRAJECTORIES` and run
`$NX/submit.pl`
It will allow you to automatically submit several sequential jobs to the batch system.

6.7 Where are the results?

1- During or after the dynamics, go to directory `TRAJECTORIES/TRAJn/RESULTS` and run:
`$NX/plot` to generate "energy x time" graph with GNUPLOT.
`molden dyn.mld` to see motion with MOLDEN or any visualization package (xyz format).
`$NX/arrow` to generate a MOLDEN file for a specific time step, containing the velocity and, in the case of dynamics with COLUMBUS, also molecular orbitals and nonadiabatic coupling vectors.

2- dyn.out file contains details about the geometry, velocity, energy and wave function (adiabatic coefficients) along the trajectory. tprob contains information about the hopping probability at each time step. en.dat contains information about the energy of each state. sh.out contains further information about the TDSE integration.

3- In `TRAJECTORIES/TRAJn`, the standard output (moldyn.log) contains the log information of the job and information about states, gradients and nonadiabatic couplings. The standard output is also written to `RESULTS/nx.log`.

4- In `TRAJECTORIES/TRAJn/DEBUG`, runnx.error contains occasional error messages. log.conv contains the information about convergence of ab initio calculations.

5- `TRAJECTORIES/TRAJn/INFO_RESTART` contains a complete set of files to restart the dynamics from the last time step that run.

6.8 Overview of the file structure

6.8.1 Dynamics simulations

The basic structure of directories and files during the dynamics simulations is shown in Figure 1.

In the case of hybrid calculations (QM/MM) the structure is very similar. The main difference is that in this case the JOB_AD and JOB_NAD directories have a substructure specifying the several jobs. The inset in Figure 1 shows an example of this substructure for a QM/MM job with COLUMBUS and TINKER.

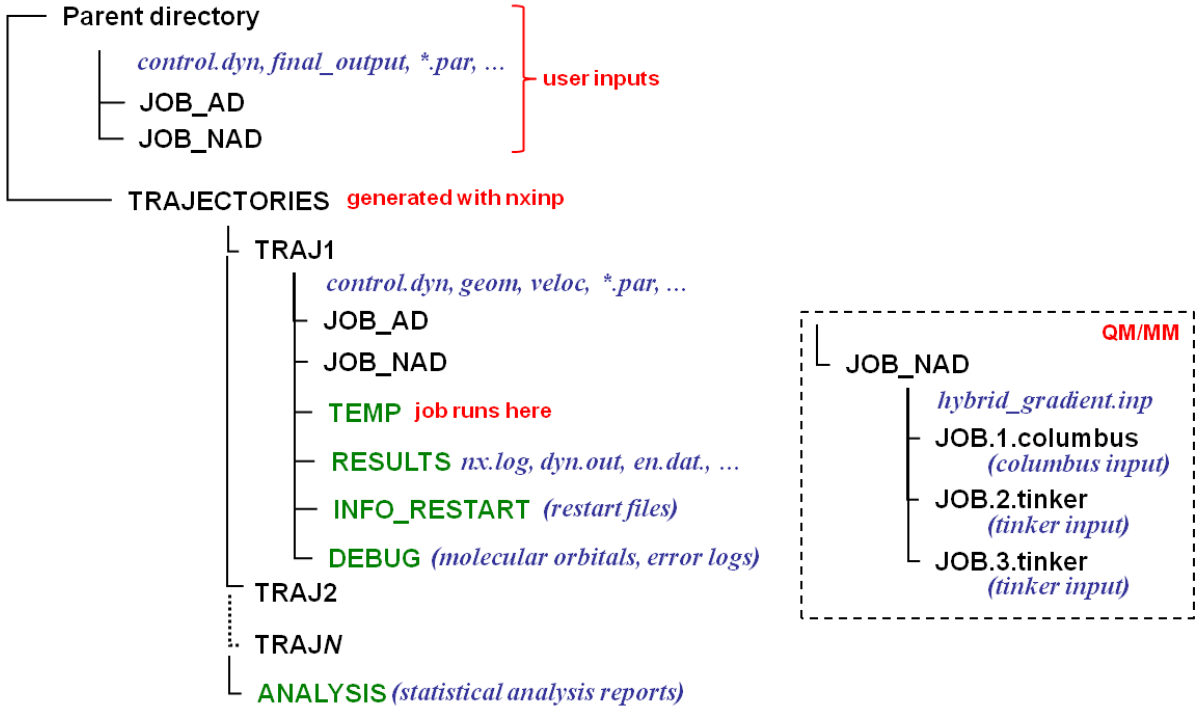

Figure 1 Basic structure of files and directories for a dynamics simulation. The inset shows an example for QM/MM simulations.

7 Capabilities

7.1 General features and references

Features	Options
NEWTON-X [1, 2]	
Dynamics	On-the-fly dynamics with the velocity-Verlet algorithm [26, 27]
	Mixed quantum-classical (nonadiabatic) dynamics [15]
	Fewest switches surface hopping (FSSH) [13]
	Dynamics with nonadiabatic coupling vectors
	Dynamics with overlap-based nonadiabatic couplings (Hammes-Schiffer/Tully approach) [10]
	Determinant derivative (DD) approach for MRCI and TDDFT [22]
	DD approach for ADC and CC2 [28]
	Orbital derivative (OD) approach [14, 29]
	FSSH with local diabatization [30, 31]
	Simplified decay of mixing (SDM) decoherence corrections [23]
	Lagrangian extrapolation of orbitals [32]
	Damped dynamics (kinetic energy always null)
	Andersen thermostat [33, 34]
	Hybrid dynamics (QM/MM) [35]
Interfaces	COLUMBUS (MCSCF,MRCI) [36, 37]
	Interface COLUMBUS/NEWTON-X [38]
	TURBOMOLE [4]
	Interface TURBOMOLE/NEWTON-X for TDDFT [39]
	Interface TURBOMOLE/NEWTON-X for CC2, ADC(2) [28]
	DFTB (DFTB)[40]
	DFTB+ (TD-DFTB)[8]
	Interface DFTB+/ NEWTON-X [41]
	TINKER[9]
	QM/MM dynamics in NEWTON-X [35]
	GAUSSIAN (CASSCF, (U)TD-DFT(TDA), (U)CIS) [5]
	Interface GAUSSIAN/NEWTON-X [28]
	DFT-MRCI [42]
	GAMESS (MCSCF, CCSD(T), MP2) [6]
	Interface GAMESS/ NEWTON-X [43]
	BAGEL (CASSCF, CASPT2) [7]
	Interface BAGEL/ NEWTON-X [44]
Built-in models	Tully 1D models [13]
	1D Double arch [45]
	1D Nikitin Hamiltonian [46]
	2D Conical intersection [21]
	Spin-Boson Hamiltonian [47]
Initial conditions	Wigner distribution
	Quantum and classical harmonic oscillator distributions
	Hermite function with arbitrary Gaussian component
	Pick points from previous dynamics
	Random velocity generation[48]
Spectrum simulation	Photoabsorption cross-section and photoemission spectra[11]
	Steady and time-resolved photoionization spectra[49]

	Transformation between spectra results from sampling to target probability distributions functions with the importance sampling technique[50]
File management	Friendly input via nxinp facility Automatic management of files and directories in multiple trajectories
Output and analysis	Statistical analysis of results (internal coordinates and forces, energies, wave function properties), with the possibility to compute the observables for distinct target and sampling distributions.[50] Normal Mode Analysis, Essential Dynamics Analysis[51, 52] Recomputation of internal coordinates On-the-fly graphical outputs (MOLDEN, GNUPLOT)

7.2 Overview of the available interfaces

Program	Version	Method	Initial conditions / Spectrum			Dynamics				
			Normal modes reading	Absorp./ emission spectrum	Photo-electron spectrum	Adiabatic	Nonadiabatic (surface hopping)			
							NAC	CIO	OD	LD
COLUMBUS	5.9	MRCI MCSCF	■	■		■	■	■		■
	7	MRCI MCSCF	■	■		■	■	■		■
TURBOMOLE		TDDFT TDA	■	■		■		■	■	■
		CC2 ADC(2)	■	■		■		■	■	■
DFTB		DFTB	■	■		■				
DFTB+	1.3.0	TD-DFTB	■	■		■		■	■	■
GAUSSIAN	03/09	CASSCF	■			■	■			
	09	(U)TDDFT (TDA) (U)CIS	■	■	■	■		■	■	■
TINKER		MM				■				
DFT-MRCI		DFT-MRCI		■						
GAMESS		MCSCF	■	■		■	■			
		CCSD(T) MP2	■	■		■				
BAGEL		CASPT2 CASSCF	■	■		■	■			■
MOLDEN		-	■							
ANALYTICAL		Built-in User-defined				■	■			

■ Available feature

NAC – Based on nonadiabatic coupling vectors.
CIO – Based on wave function overlaps.
OD – OD method.
LD – Based on local diabatization.

8 How to get NEWTON-X

NEWTON-X code is distributed free of charge for non-commercial and non-profit uses. To request a copy, visit www.newtonx.org.

The third-party quantum chemistry and visualization programs are not distributed with NEWTON-X. They should be directly obtained from the respective distributors and owners.

9 How to install NEWTON-X

9.1 Binary distribution

Binary files for Linux-compiled NEWTON-X are distributed together with the source code. As the first option, we strongly recommend using this version. In this case:

1) uncompress the distribution file
```
tar -zxf nx-<version>.tgz
```
or, alternatively,
```
gunzip nx-<version>.tgz
tar -xf nx-<version>.tar
```

2) Then, set the shell-variable `$NX` to `<install-path>/bin`
For c-shell users, this is done by:
```
setenv NX <install-path>/bin
```

For bash-shell users, this is done by:
```
export NX=<install-path>/bin
```

3) Install the CIOVERLAP-OD program as explained in the README.install file.

9.2 To install NEWTON-X you need

We strongly recommend that you use the binary files that we provide. However, if for any reason you wish to compile the program yourself, follow the instructions in the README.install file, which can be found in the NEWTON-X distribution.

9.3 To run NEWTON-X you need

- At least one of the interfaced third-party programs (COLUMBUS, TURBOMOLE, DFTB, TINKER, GAUSSIAN, GAMESS, BAGEL). Alternatively, you can also run NEWTON-X with one of the built-in Hamiltonian models. See Chapter 7 of this documentation for an updated list of available interfaces.

For full functionality, you also need:
- GNUPLOT (www.gnuplot.info).
- Some molecular visualization program able to read xyz files (e.g., MOLDEN or VMD).

9.4 Setup of third-party programs

NEWTON-X works using third-party programs, such as COLUMBUS, TURBOMOLE, GAUSSIAN, and others. These programs should be separately obtained from their distributors and installed according to their specific instructions.

Depending on the job, NEWTON-X assumes that a series of variables are defined in the system. They are:

Program	Variable	Example of the file pointed by each variable

COLUMBUS	$COLUMBUS	`ls $COLUMBUS > ... runc ...`
DFTB	$DFTB	`ls $DFTB > ... dftb ....`
DFTB+	$DFTBP	`ls $DFTBPLUS > dftb+`
	$DP_TOOLS	`ls $DP_TOOLS > ... xyz2gen ...`
GAUSSIAN 03	$g03root	`ls $g03root/g03 > ... g03 ...`
GAUSSIAN 09[1]	$g09root	`ls $g09root/g09 > ... g09 ...`
DFT-MRCI	$DFTCI	`ls $DFTCI > ... mrci ...`
	$KSCIHOME	`ls $KSCIHOME > ... dftparam.s.bhlyp ...`
GAMESS	$GAMESS	`ls $GAMESS > ... rungms ...`
TURBOMOLE[2]	$TURBODIR	`ls $TURBODIR > ... scripts bin ...`
	$PATH	`echo $PATH > ... :$TURBODIR/bin/x86_64-unknown-linux-gnu:$TURBODIR/scripts: ...`
TINKER[3]	$PATH	`echo $PATH > ...:/usr/bin/tinker-bin-linux:...`
BAGEL	$BAGEL	

[1] In the case of GAUSSIAN 09, the GAUSSIAN profile must be sourced before executing NEWTON-X. Example (C-shell): source $g09root/g09/bsd/g09.login

[2] For TURBOMOLE, directories containing the executables (e.g., $TURBODIR/bin/x86_64-unknown-linux-gnu) and scripts (e.g., $TURBODIR/scripts) must be in the standard path.

[3] For TINKER, directories containing the executables (e.g., /usr/bin/tinker-bin-linux) must be in the standard path.

9.5 Verification of installation

To test the installation, create a directory to execute the tests. Move into it and select the tests that you want to perform by running

```
$NX/inp-testnx.pl
```

It will return a list of all available tests. You can select particular tests or all of them. It will create a file called test.inp containing a space-separated list with the number of the tests that should run.

Then, run the program

```
$NX/test-nx.pl > test-nx.log &
```

This program will run the selected tests. If test.inp is not present, all tests are selected by default. The tests are a series of quick pre-build examples. It will check whether they have normal termination or not, and it will compare the results to those of standard files. Check the results in test-nx.log.

Tests invoking GAMESS may need special adjustments for each system. When such tests are requested, inp-testnx.pl additionally asks a few questions about GAMESS environment (executable number, scratch directory, and execution script name). This information is written to games.par file, which is used by the jobs running under test-nx.pl command.

10 Initial conditions generation

INITCOND is a set of programs developed to generate initial conditions for the molecular dynamics and spectrum simulation.

It is possible to generate initial conditions by sampling the data according to harmonic oscillator distributions (classical and quantum). It is also possible to pick at random points from a previous dynamics calculation performed with NEWTON-X or to generate random velocities for some specific geometry.

For NACT = 1, 2 or 3 the initial conditions are based on normal modes. The normal modes themselves should be generated in a separate run and given as input to NEWTON-X. NEWTON-X can read the normal modes directly from the output files of several third-party programs (see IPROG below). Despite the initial format, the normal modes are internally transformed into mass-weighted normal modes **L**. For NACT = 1 or 2, for each normal mode, an amplitude Q_n and momentum $\dot{Q}_n$ are randomly selected from a harmonic oscillator distribution. The Cartesian coordinates and velocities of all atoms are then determined from the normal coordinates by the inverse transformation.[52] If NACT = 3, only Q_n is randomly selected, while $\left|\dot{Q}_n\right|$ is scaled as to give the harmonic oscillator energy. For NACT = 2, if the vibrational numbers are zero, the distribution matches the Wigner distribution for the quantum harmonic oscillator [53, 54]. For higher vibrational quantum numbers, the distribution for each normal mode is

$$\left|\psi_{N_n}\left(Q_n\right)\right|^2 \left|\xi_{Nn}\left(P_n\right)\right|^2 \quad (1)$$

where $\psi_{N_n}\left(Q_n\right)$ and $\xi_n\left(P_n\right)$ are respectively the harmonic oscillator wavefunctions in the coordinate and momentum spaces. These are Hermite functions, given by the product of a Gaussian and a Hermite polynomial of degree *n*. One can also sample according to a Hermite function whose Gaussian exponent and center are provided by the user.

If NACT = 4, random points are picked from a previously performed dynamics. If NACT = 5, random velocities are generated for a fixed velocity according to the algorithm described in Ref. [48]. If NACT = 6, single point electronic structure calculations are performed for a previously computed set of initial conditions.

10.1 How to execute INITICOND

Run

```
$NX/initcond.pl > initcond.log
```

10.2 Input parameters

File: initqp_input
Namelist: DAT

Parameter	Default	Description	Dependencies
NACT	= [2]	1 - Each normal mode contains an energy in the initial state, according to the vibrational quantum number, and the distribution of coordinates and momenta is that of a classical harmonic oscillator.	

		2 - The distribution of coordinates and momenta is that of a quantum mechanical harmonic oscillator in the specified vibrational state. The sample of the coordinates and momenta is uncorrelated. In the ground vibrational state, this distribution matches the Wigner distribution for the harmonic oscillator. The sampling can also be performed with a Hermite function with an arbitrary Gaussian component. 3 - The distribution of coordinates and momenta is that of a quantum mechanical harmonic oscillator in the specified vibrational state. Only coordinates are sampled. For each normal mode, the momenta are scaled to the coordinates up to the have the correct harmonic vibrational energy. The sampling can also be performed with a Hermite function with an arbitrary Gaussian component. 4 - NPOINTS points are picked up from some previously run dynamics simulations. 5 - Gaussian-distributed random velocities are generated for some specific geometry. (Not valid for photoionization.) 6 - Single point electronic structure calculations for a previously computed set of initial conditions.	
NUMAT	= []	number of atoms	NACT ≤ 5
NPOINTS	= [1]	number of initial conditions generated	NACT ≤ 5
FILE_GEOM	= [geom]	file containing the equilibrium geometry of the molecule in NEWTON-X format. (See section 15.6 for conversion tools)	NACT ≤ 3 or NACT = 5
IPROG	= [4]	Read vibrational modes from: 1 - GAMESS 2 - TURBOMOLE 3 - COLUMBUS 4 - GAUSSIAN 5 - MOLDEN 6 - DFTB 7 - ACES2 8 - BAGEL 9 - DFTB+	NACT ≤ 3
NM_FLAG	= [1]	If normal modes should be read from a MOLDEN file, then the type of normal mode should be given. 1 - Cartesian normal modes ($amu^{-1/2}$) 2 - Normalized Cartesian normal modes 3 - Mass weighted normal modes	IPROG = 5
FILE_NMODES	= []	file containing the normal coordinates and the vibrational frequencies (in cm^{-1}). Normally it is an output file from some quantum chemistry program (see option IPROG).	NACT ≤ 3

ANH_F	= [1.0]	Multiply all frequencies by ANH_F. Useful to add anharmonic effects. If importance sampling is to be used (run_IS=1 in mkd.inp), the default must not be modified.	NACT ≤ 3
TEMP	= [0]	Temperature (K). For NACT = 2 or 3: Wigner sampling is broadened by a factor $\tanh(\hbar\omega / 2k_BT)$.[55] For NACT = 5: If TEMP = 0 (default), this option generates random velocities corresponding to kinetic energy Ekin (microcanonical ensemble). If TEMP > 0, canonical ensemble of random velocities is generated with mean kinetic energy EKIN and standard deviation $\sigma = k_BT(3N/2)^{1/2}$. In any case, translational and rotational velocities are zero.	NACT 2, 3, or 5
CHK_E	= [0]	0 - Do not check the energies. (Also use this value for photoelectron spectra.) 1 - Check the energies between states NIS and NFS. For ground state dynamics, set CHK_E = 0. For NACT = 4, CHK_E flags whether energies should be read or not from the dynamics dataset.	NACT ≤ 4
NIS	= [1]	Initial state (Ground state = 1).	NACT = 6 and ICF_FLG = N or CHK_E = 1
NFS	= [2]	Final state. (Information for all states between NIS and NFS are stored.)	NACT = 6 and ICF_FLG = N or CHK_E = 1
ADDRESS	= []	Path to the set of previous trajectories from which the initial conditions must be picked. The default address [/home/old_dyn/TRAJECTORIES] certainly should be changed.	NACT = 4
TRAJI	= [1]	Initial trajectory to be read.	NACT = 4
TRAJF	= [10]	Final trajectory to be read.	NACT = 4
N_PICK	= [-1]	Method to pick up points: -1 - pick random points from trajectories. n (integer) - pick time step n from trajectories.	NACT = 4
TI	= [0]	Start to pick points only after time TI (fs) of each trajectory.	N_PICK = -1
TF	= [-1]	Do not pick points after time TF (fs) of each trajectory. Diagnostic.pl (see section 15.5) is always called in this kind of run. The time suggested in its output (diag.log) is used if it is smaller than TF. If TF = -1, always use the time suggested in diag.log file.	N_PICK = -1

REORDER	= [1]	Sort the points according to the trajectory number and time step. 0 - Do not sort. 1 -Sort.	N_PICK = -1
ETOT_DEV	= [0.5]	Allowed variation in the total energy (eV).	N_PICK = -1
POP_DEV	= [0.1]	Allowed variation in the norm of the adiabatic population.	N_PICK = -1
NIS	= [1]	Initial state (Ground state = 1).	NACT = 6 or CHK_E = 1
NFS	= [2]	Final state. (Information for all states between NIS and NFS are stored.)	NACT = 6 or CHK_E = 1
KVERT	= [1]	0 - Use the provided EVERT. 1 - Use EVERT of the equilibrium geometry that is calculated in the first step of the program.	NACT ≤ 3 and CHK_E = 1
EVERT	= [5.0]	Required vertical energy (eV).	NACT ≤ 3 and CHK_E = 1 and KVERT = 0
DE	= [100]	Allowed variation around EVERT is +/-DE/2 (eV). The large default value implies do not apply any restriction.	NACT ≤ 3 and CHK_E = 1
CMP_E	= [0]	0 - Read energies from dynamics output 1 - Compute energies.	NACT = 4 and CHK_E = 1
ICS_FLG	= []	Are these initial conditions for ionization cross sections? (y/n)	NACT or NACT = 6
PROG	= [6.5]	Program to compute vertical excitation energies: 1 - COLUMBUS 2.0 - TURBOMOLE CC2 2.1 - TURBOMOLE TDDFT 2.2 - TURBOMOLE ADC2 6.5 - GAUSSIAN 09 8.0 - DFTB legacy 8.1 - DFTB+ legacy 8.5 - DFTB+ new interface 9 - DFT-MRCI 10 - GAMESS MCSCF 12 - BAGEL 20 - HYBRID ENERGY	ICS_FLG = N and [(NACT ≤ 3 and CHK_E = 1) or (CMP_E = 1) or (NACT = 6)]
PROG	= [6.5]	Program to compute vertical excitation energies: 6.5 - GAUSSIAN 09	(ICS_FLG = Y)
EKIN	= [0]	Kinetic energy (eV).	NACT = 5
NIS_MOL	= [1]	Initial state of the N-electron system (Ground state = 1). Use nis_mol = 1 within Koopmans approximation.	ICF_FLG = Y and NACT ≤ 3
NFS_CAT	= [1]	Maximum electronic state of the (N-1)-electron system (Ground state = 1).	ICF_FLG = Y and NACT ≠ 4
IP_TYPE	= [2]	Method to calculate the ionization potentials (IPs). 1 - IP = -E[MO] (Koopmans approximation)	ICF_FLG = Y and NACT ≠ 4

		2 - IP = E[N] - E[N-1] 3 - IP computed with the Outer Valence Green's Function (OVGF) method	
DO_TYPE	= [1]	Method to calculate the Dyson orbitals (DOs). 1 - MO (Koopmans approximation) 2 - DOs computed accurately	ICF_FLG = Y and NACT ≠ 4
EQ_GEOM	= []	Do you want to use only the equilibrium geometry? (y/n)	ICF_FLG = Y and NACT ≤ 3
ISEED	= [-1]	Random number seed 0 Use standard value for the random number seed. -1 Use random seed. Any integer > 0 is used as the seed itself. Use ISEED = -1 if the job will be split (see section 15.7).	NACT ≤ 5
LVPRT	= [1]	1 - Standard print level. 2 - Debug print level.	

Example of initqp_input file:

```
&DAT
 nact=        2,
 numat=       2,
 npoints=     20,
 file_geom=   hf.geom,
 file_nmodes=hf.nmodes,
 file_out=    qvector,
 evert=       5.0,
 de=          0.25,
 kvert=       1,
 chk_e=       1,
 prog =       1.0,
 iprog =      2.0,
 nis =        1,
 nfs =        2,
&END
```

Note about DFTB and DFTB+ calls: Until NEWTON-X version 2.0, the DFTB job was invoked through PROG = 5 and DFTB+ though PROG = 8. With the development of the new DFTB+ interface in version 2.1, these keywords were changed. DFTB is now called through PROG = 8.0, the old DFTB+ interface is called through PROG = 8.1, and the new DFTB+ interface through PROG = 8.5. The DFTB and the old DFTB+ interfaces are kept only for legacy and will be discontinued in the future.

File : columbus.par
Optional file containing information for COLUMBUS jobs.

Parameter	Default	Description
MEM	[200]	COLUMBUS core memory in Mwords (1 GB = 134 Mwords). For COLUMBUS 7, MEM is internally converted to GB.

File : turbomole.par
Optional file containing information for TURBOMOLE jobs.

Parameter	Default	Description

PARALLEL	[1]	Number of cores to use for parallel Turbomole (SMP only, no MPI!) [Deprecated]

Turbomole parallel environment should be set independently of NEWTON-X, in the way it is done for conventional Turbomole jobs. In this case, parallel keyword does not need to be set in turbomole.par.

In the past, this set up used to be done via parallel keyword in turbomole.par. In this case, SMP parallelized version of Turbomole executables (dscf_smp and ricc2_smp) were chosen by specifying parallel keyword. This option, which sets the environment variable $OMP_NUM_THREADS internally during NEWTON-X execution, should be avoided.

File : dftb.par
Optional file containing information for DFTB jobs for PROG = 8.0.

Parameter	Default	Description
DFTB_EXEC	= [dftb]	Name of the DFTB executable file. $DFTB variable must be defined in the system. NEWTON-X will run $DFTB/<dftb_exec>.

File : dftb+.par
Optional file containing information for DFTB+ jobs for PROG = 8.1 or 8.5.

Parameter	Default	Description
DFTBP_EXEC	= [dftb+]	Name of the DFTB+ executable file. $DFTBP variable must be defined in the system. NEWTON-X will run $DFTBP/<dftb_exec>.
DFTBP_KSF	= [$DFTB/sk/3ob-3-1]	Path to the directory with the Slater Koster files.

File : dftci.par
Optional file containing information for DFT-MRCI jobs.

Parameter	Default	Description
maxiter	= [6]	Maximum number of MRCI cycles.

File: gamess.par
Optional file containing information for GAMESS jobs.

Parameter	Default	Description
VERNO	= [00]	Version number of GAMESS executable.
NCPUS	= 1	Number of computer processes to be run.
RUN_GAMESS	= [rungms]	Name of GAMESS execution script.
SCR	= [1]	GAMESS scratch directory: 0: Use default GAMESS options as defined in RUN_GAMESS script. 1: Create SCR directory inside TEMP directory of NEWTON-X.

File : do.par
Optional file containing information for Dyson orbitals computation.

Parameter	Default	Description
NJOBS_DYSON	= [1]	Number of DOs to be computed at the same time.
EPS_CISCFFS	= [1E-2]	Threshold of the electronic expansion coefficients.

EPS_OVERLAP	= [1E-1]	Threshold of the Slater Determinant overlaps. (For writing purposes only.)

10.3 What you need to execute

- initqp_input with the set of parameters. (It can be generated with nxinp tool.)

10.3.1 Additional files and directories

If NACT ≤ 3:

- file with the equilibrium geometry (see FILE_GEOM keyword). Hint: the program tm2nx converts the coord file (TURBOMOLE format) to the NEWTON-X format.

- file with the vibrational modes (see FILE_NMODES keyword). **Warning 1:** The atom order in FILE_NMODES and FILE_GEOM must be the same. **Warning 2:** The orientation of the normal mode coordinates in FILE_NMODES orientation must be consistent with the orientation of the optimized geometry in FILE_GEOM.

- file with the vibrational quantum numbers (qvector). The default is the ground state (0 quantum in each mode). If you want to change these default values, write a list of quanta in each mode. Example of qvector:

```
0 0 0 0 0
0 0 0 0 0
0 1
```

  This example puts one quantum at the highest frequency mode of a system with 12 modes (6 atoms). Keep the format with 5 columns of integers. The order of the modes is the same as in FILE_NMODE. If qvector does not exist, the program assumes 0 for all modes. To set -0.5 for a mode makes this mode contribute with 0 to the initial energy.

- optional file (samp_dist) with the user-specified Gaussian parameters (see Section 10.3.5).

- JOB_AD directory containing input files for excited-state single point calculation with a third-party quantum chemistry program (only if CHK_E=1).

- save_file, optional file (see section 10.3.4).

If NACT = 4:

- The TRAJn directories of some dynamics calculations previously performed.

If NACT = 5:

- Geometry file with the initial geometry in NEWTON-X format.

If NACT = 6:

- A previously computed set of initial conditions in the NEWTON-X format renamed final_output.old.

- JOB_AD directory containing input files for excited-state single point calculation with a third-party quantum chemistry program.

- save_file, optional file (see section 10.3.4).

For photoelectron spectrum (ICS_FLG = Y):

- JOB_N directory containing input files for single point calculation for the N-electron system with a third-party quantum chemistry program.
- JOB_N-1 directory containing input files for single point calculation for the N-electron system with a third-party quantum chemistry program.

10.3.2 The JOB_AD directory

The JOB_AD directory contains input files for excited-state single point calculation with a third-party quantum chemistry program.

For the cases that this directory is needed, set the oscillator strength to be calculated by the quantum chemistry program. This setting will give you the possibility of generating UV spectra as well as to use the transition probability to select the initial conditions.

Specifically for COLUMBUS calculations (PROG = 1.0): Input files must be prepared for a single point MCSCF or CI calculation in C_1 point group (no symmetry).

For Gaussian 09 (PROG = 6.5): Prepare input files for a single point vertical excitation at the TDDFT level. The input file must be called gaussian.com, and the geometry must be given in Cartesian coordinates. The check point file named gaussian.chk containing the initial molecular orbitals may be provided as well. A suitable example of gaussian.com content is:

```
%chk=gaussian
%mem=2000MB
# B3LYP/6-31G(d) TD=NStates=2 NoSymm

methaniminium

1 1
N    0.000000   0.000000    0.637342
C    0.000000   0.000000   -0.703614
H   -0.648747   0.572349    1.177883
H    0.648745  -0.572350    1.177883
H    0.618844   0.701080   -1.278050
H   -0.618844  -0.701080   -1.278049
```

Note that the geometry is given in Angstroms in this version of NEWTON-X. Up to NEWTON-X 1.3, the keyword Unit=AU was mandatory. To avoid troubles with differences between input and standard orientations in Gaussian, it is highly recommended to use NoSymm keyword in the Gaussian.com as well as in the computation of the normal modes (FILE_NMODES).

In addition to gaussian.com, JOB_AD must also contain a file named basis with information about the basis set. In this example, basis will have a single line with:

```
6-31G(d)
```

See Section 12.1.5.8 for more information on how to write the basis file.

NEWTON-X executes GAUSSIAN 09 by invoking the command:

```
g09 < gaussian.com
```

It is assumed that the user sources the g09 profile before running NEWTON-X.

For DFTB calculations (PROG = 8.0; former PROG = 5 in NEWTON-X 2.0 and earlier): Input files must be prepared for excited-state spectrum calculation using code 10. The DFTB input parameter and geometry files must be named dftb.in and in.gen, respectively.

For DFTB+ calculations with the old interface (PROG = 8.1; former PROG = 8 in NEWTON-X 2.0 and earlier): Input files must be prepared for a DFTB calculation yielding energy and gradient. The DFTB input parameter and geometry files must be named dftb.in and in.gen, respectively. At present, only QM/MM ground state dynamics (no TD) is available with this program.

The variables $DFTBP (pointing to the directory with the DFTB+ executable) and $DP_TOOLS (pointing to the directory containing the DFTB+ tool xyz2gen) must be defined. The number of CPU cores can be set with $OMP_NUM_THREADS variable. Additionally, it is necessary to compile the MODES program provided with the DFTB+ package for diagonalization of the Hessian matrix.

For DFTB+ calculations with the new interface (PROG = 8.5): Prepare DFTB+ input for excited-state TD-DFTB calculation. The DFTB+ input must be named dftb_in.hsd and should be within JOB_AD directory.

The variables $DFTBP (pointing to the directory with the DFTB+ executable) and $DP_TOOLS (pointing to the directory containing the DFTB+ tool xyz2gen) must be defined. The number of CPU cores can be set with $OMP_NUM_THREADS variable.

For DFT-MRCI calculations (PROG = 9.0): JOB_AD should contain a complete set of input files for TURBOMOLE DFT calculation, including the auxiliary basis set, and the specific input file for the DFT-MRCI program. The DFT-MRCI input file must be named mrci.inp and should be set to the total number of excited states.

10.3.3 The JOB_N and JOB_N-1 directories

For photoelectron spectrum simulations, these JOB_N and JOB_N-1 should be provided in place of JOB_AD. They should contain templates for the N and N-1 electron systems, involving the states of interests.

For TDDFT with Gaussian 09, each of these directories must contain two files named gaussian.com and basis. gaussian.com should contain the input template. For example, in the case of photoionization from the ground state, gaussian.com in JOB_N may look like:

```
%chk=gaussian
%rwf=gaussian
%nproc=4
%mem=5000mb
#p CAM-B3LYP/aug-cc-pVDZ gfinput NoSymm

Ground state at CAM-B3LYP/aug-cc-pVDZ level

0   1
N      0.741641    0.815030    0.000057
N     -0.112197   -1.223606   -0.000099
…
```

Corresponding to a DFT calculation. IN JOB_N-1, gaussian.com may look like:

```
%chk=gaussian
%rwf=gaussian
%nproc=4
%mem=5000mb
#p TD(NStates=20) CAM-B3LYP/aug-cc-pVDZ NoSymm
```

```
First 20 states at CAM-B3LYP/aug-cc-pVDZ level

1   2
N       0.741641     0.815030     0.000057
N      -0.112197    -1.223606    -0.000099
…
```

The file basis should contain the basis set description (and the basis set must be the same for N and N-1). In this example, basis should simply have a single line with:

```
aug-cc-pVDZ
```

See Section 12.1.5.8 for more information on how to write the basis file.

10.3.4 Save files option

When electronic structure calculations are performed during the initial condition generation (NACT ≤ 3 with CHK_E = 1 or NACT = 6), it is possible to give a list of files or directories that should be saved for every initial condition. This is simply done by creating a file name save_file and including a list of file names to be saved. save_file must contain only one file name per line. For instance, you may want to save the molecular orbitals (mos file) and the scf log file (dscf.out) resulting from the TURBOMOLE calculations for each initial condition. In this case, the following save_file should be given together with the other input files:

Example of save_file file:

```
dscf.out
mos
```

The required files are tar-compressed and written to the DEBUG directory renamed as ic<card>-filename.tgz, where <card> is the number of the initial condition as given in the final_output file. In the example above, DEBUG will contain:

```
ic0-dscf.out.tgz
ic0-mos.tgz
ic1-dscf.out.tgz
ic1-mos.tgz
ic2-dscf.out.tgz
ic2-mos.tgz
…
ic0-<NPOINTS>.out.tgz
ic0-<NPOINTS>.tgz
```

The routine that saves the files runs right after the execution of the third-party program, before the cleanup of the execution directory.

If the file that should be saved is inside a directory, the relative path must be provided. For instance, if we want to save the MCSCF log file of COLUMBUS jobs (mcscfsm.sp), save_file should contain "LISTINGS/mcscfsm.sp". The full LISTINGS directory will be saved is save_file contains "LISTINGS".

10.3.5 samp_dist file

This optional file contains the Gaussian parameters (exponent and center) of the Hermite functions from which coordinates and momenta are sampled. The default is an unmodified Gaussian function, with a 1.0 exponent and a 0.0 shift. If the file exists, the program is expected to read exponent and shift for the position, and then exponent and shift for momentum. For each normal mode, this set of parameters must

be given in a separate line, and that must follow the same order as defined in FILE_NMODES. Within each line, reading is free format. One example of the samp_dist file could be:

```
1.0  0.0  1.0  0.5
0.8  0.0  0.8  -0.4
```

Here, the coordinate for the first normal mode follows the default Gaussian distribution, while the momentum is sampled according to a Gaussian displaced by 0.5 units. Meanwhile, both coordinate and momentum of the second normal mode are sampled by a Gaussian with a 0.8 exponent, where the center of the later is displaced by -0.4 units.

10.4 Output

The initial conditions are written to the final_output file. When NACT=2 or NACT=3, the parameters that define the sampling distribution are written to the samp_param file, while the actual arguments for each sampled point are written to the samp_points file. These serve as input files for the importance sampling program. In the samp_points file, the first column corresponds to coordinate and the second to momentum. An inner loop over normal modes and an outer loop over the number of points define the order of the points. The data from spectrum simulation are written to the cross-section.dat, spectrum.dat and spectrum-hist.dat files.

Initial condition for multiple states are written to final_output.[initial-state].[final-state]. Thus, for example, final_output.1.3 contains initial conditions for transitions from state 1 (ground state) to state 3. The final_output file is the same as final_output.[NIS].[NFS].

DEBUG directory contains the error log information (runnx.error) and files that should be saved when save_file file is provided (see section 10.3.4).

In the case of photoelectron simulations, the output data will be written to file ip.dat and to directories GEOMETRIES and MO_DYSON.

ip.dat contains the IPs for every nuclear geometry generated and electronic state of the cation considered.

GEOMETRIES directory contains a set of files with the nuclear geometry of all corresponding initial conditions in NEWTON-X format.

MO_DYSON contains a set of compressed files with names of the form `dyson_mo_ic.nis.nfs.gz`, where `ic` is number of the initial condition, `nis` is the electronic state of the N-electron molecule (before the ionization) and `nfs` is the state of the (N–1)-electron molecule after the ionization. Each of these files contains the corresponding DO in both the atomic and molecular orbital basis sets. After uncompressing (gunzip), they look like this:

```
   0.95661948383739         0.95661948801718
151                      Linear Combination of Molecular Orbitals
 0.02479467089699         0.00000000000000        0.00001739644645
-0.06220374938866        -0.00000000000000       -0.00010166649522
-0.10326132366492         0.00000000000000        0.00003001393284
  …
```

In the first column, the DO is represented in the atomic basis set: the first element is the norm of the DO (0.9566, in this case), the second element is the size of the basis set (N_{bf}), and the remaining N_{bf} elements are the atomic orbital coefficients. In columns two and three, the DO is represented as a linear combination of α (column 2) and β (column 3) molecular orbitals. The first element of column 2 is the norm of the DO computed in the molecular basis set, written for testing purposes only.

10.5 Running in several computers

It is possible to split the spectrum and initial condition generation job to run in different computers and merge them again afterward. See section 15.7 for general instructions.

Do not forget to set ISEED = -1 when the jobs are split.

11 Trajectory-input generation, initial conditions for multiple states, and spectra

11.1 INPUT FOR SPECTRUM AND TRAJECTORIES

The section "5. GENERATE TRAJECTORIES AND SPECTRUM" of nxinp input program allows multiple different tasks, which can be selected in the sub menu:

```
============================================================
                          NEWTON-X
          Newtonian dynamics close to the crossing seam
                       www.newtonx.org
============================================================

                GENERATE TRAJECTORIES AND SPECTRUM


type:  What do you want to do?
       1 - Generate absorption or emission spectrum
       2 - Generate photoelectron spectrum
       3 - Select initial conditions for multiple initial states
       4 - Generate trajectories
       5 - Return to main menu
The current value of type  is: 4
Enter the new value of type  :
```

After selecting one of these options, you will be asked a series of question about the specificities of your job. In the end, the file mkd.inp will be generated, and the program makedir.pl will be automatically running if you see the message:

```
Processing data: This may take some minutes. Please, wait...
```

If you want, after leaving nxinp, makedir.pl can be executed again by running:

```
$NX/makedir.pl > makedir.log
```

In the case of the photoelectron spectrum, instead of running makedir.pl, you should run:

```
$NX/ixsec.pl > ixsec.log
```

The options in these two programs may be changed by setting the following keywords in mkd.inp.

Name: mkd.inp

Parameter	Default	Description
TYPE	= [4]	1 - Generate absorption or emission spectrum 2 - Generate photoelectron spectrum 3 - Select initial conditions for multiple initial states 4 - Generate trajectories

NIS	= [1]	Initial state. 1 is the ground state. (Spectrum simulation.)
NFS	= [2]	Array of final states (space separated, e.g., 2 3 4). If not only spectrum, but trajectories input is required as well, only one final state is allowed. For photoelectron spectrum, NFS is the maximum electronic stat of the N-1 electron system.
SCREEN	= [0]	Energy restriction: 0 - don't apply any restriction 1 - use the original energy restriction written in the final_output files 2 - apply new energy restriction
E_CENTER	= [0.0]	Center of the energy restriction (Only if SCREEN = 2) x - value of the center of restriction (eV) ref n - use the vertical excitation of final_output.nis.n file
E_VAR	= [0.5]	Width of the energy restriction. (eV) (Only if SCREEN = 2)
OS_CONDON	= [-1]	Oscillator strength: -1 - try to read from final_output file x - oscillator strength is always x (Condon approximation)
PROB_KIND	= [F]	Probabilities in the spectrum generation will be computed according to A – Einstein-coefficients A (spontaneous emission) B – Einstein-coefficients B (induced absorption or induced emission) E – Fluorescence (radiative decay rate) F – Absorption (photoabsorption cross-section) I – Ionization (photoionization cross-section)
NORM	= [local]	Normalization of the Einstein's coefficients: local - Use energy-restricted data set global - Use complete data set
SEED	= [0]	Seed for the random number generation 0 - a default random number seed is used 1 - a randomized seed is used Any other positive integer is used itself as the random number seed.
L_SHAPE	= [lorentz]	Line shape: gauss – Normalized Gaussian function lorentz – Normalized Lorentzian function
DELTA	= [0.05]	Phenomenological broadening of the line shape (in eV). The default Δ corresponds to a small broadening, equivalent to 0.5 nm.
TEMP	= [0]	Temperature correction for the spectrum (in K). Beware that this is a (usually very small) correction regarding the population of electronically excited states. In order to account for the (much more important) temperature effect on the nuclear degrees of freedom, the importance sampling technique should be used (see Section 15.8).
NREF	= [1]	Refraction index
EPS	= [0.005]	Distance between consecutive points in the spectrum using the Gaussian method. (in eV)
KAPPA	= [3]	κ (integer) is used to define the range of the spectrum between $\Delta E_{min}-\kappa.\Delta$ and $\Delta E_{max}-\kappa.\Delta$.

ICS_COMP	= [1]	Compute photoelectron spectra using: 1 - Dyson orbital norm approach 2 – Cross section approach (requires ezDyson)
ICS_KIND	= [2]	Type of experiment to be simulated: 1 - Ep (photon energy) ranging from Ep_min to Ep_max 2 - Ep fixed and Ek (kinetic energy) ranging from Ek_min to Ek_max
ICS_PROC	= [2]	Vibrational modulation of the kinetic energy distribution using: 1 – constant vibrational broadening (CVB, recommended for time-resolved spectrum) 2 – peaked vibrational broadening (PVB, recommended for steady spectrum)
EZDYSON_PATH	=[]	Path to ezDyson executable.
E_POINTS	=[]	Number of kinetic energy points (ICS_PROC = 1) or photoenergy points (ICS_KIND = 2) to be considered.
L_MAX	= [6]	Maximum angular momentum of the ejected electron.
EP_MIN	= [5]	Minimum value of the photoenergy (eV).
EP_MAX	= [2]	Maximum value of the photoenergy (eV).
EPHOTON	= [10]	Photoenergy (eV).
EKMIN	= []	Minimum photoelectron kinetic energy (eV). Recommended values: 0.00 for ICS_COMP = 1 0.01 for ICS_COMP = 2
EQ_GEOM	= [n]	Type of photoelectron spectrum: Y – compute for equilibrium geometry only (geom.0). N - Compute for all geometries.
TITLE	= [nx]	Title. Useful if the job runs in batch.
SUBFILE	= [pmold]	If the job run in batch, SUBFILE is the name of the submission script.
BATCHDEF	= [-N]	Definition of the batch system. Default is SGE, but NEWTON-X attempts to read it from SUBFILE and change it when some suitable value is found.
RUN_IS	= [0]	0 - Target and sampling probability density functions are the same. 1 - Compute observables for a target probability density function different from the sampling one.

11.2 Absorption and emission spectra

NEWTON-X computes the spectrum with the nuclear ensemble approach[38, 56] by assigning to each initial condition a line shape function g with the height P and a width representing some phenomenological broadening (Δ) and plotting the sum (S) of these line shape functions as a function of the transition energy E, i.e.,

$$S(E) = \sum_{n=1}^{Npoints} P_n(\Delta E_n) g\left(E - \Delta E_n\right). \quad (2)$$

E (eV) and $S(E)$ (arbitrary unities) are written to spectrum.dat file. The line shape options are the Gaussian function

$$g_{Gauss}\left(E-\Delta E_{il},\delta\right)=\left(\frac{2}{\pi}\right)^{1/2}\frac{\hbar}{\delta}\exp\left(\frac{-2\left(E-\Delta E_{il}\right)^2}{\delta^2}\right) \quad (3)$$

or the Lorentzian function

$$g_{Lorentz}\left(E-\Delta E_{il},\delta\right)=\frac{\hbar\delta}{(2\pi)}\left[\left(E-\Delta E_{il}\right)^2+\left(\delta/2\right)^2\right]^{-1}. \quad (4)$$

The intensity of each line *P* can be taken as the Einstein coefficient *A* and *B* or the oscillator strength *f*. Absolute values for the Einstein's coefficients [57] can be obtained from the log information written in makedir.log. First, note that the Einstein's coefficients are given by

$A=C_A f\Delta E^2$,

$B=C_B A\Delta E^{-3}$,

with $C_A=2\pi e^2/\left(h\varepsilon_0 mc^3\right)$ and $C_B=c^3h^2/8\pi$. As usual, *e*, *h*, *m*, *c* and ε_0 are, respectively, fundamental charge, Planck's constant, electron mass, speed of light, and free-space permittivity. Therefore, to compute the absolute values of the Einstein's coefficients, first check the units of vertical excitation energy in final_output file. If they are in eV, then multiply coefficients *A* by 0.43392×10^8 or *B* by 0.11445×10^{15}. If they are in hartree, then multiply coefficients *A* by 0.32130×10^{11} or *B* by 0.56800×10^{10}. The final units of *A* will be s^{-1} and of *B* will be $m^3s^{-2}J^{-1}$.

Note that the algorithm assumes the same degeneracy factor for both states ($g_i = g_f$) and refraction index $n = 1$. When spectrum involving multiple states is selected by attributing several values to the NFS array, final_output.nis.isf files (ISF is each value in NFS array) for each transition must be present.

The file spectrum.dat is composed of two columns:
E (eV) *S* (arbitrary units)

When the intensity is selected to be *f* (PROB_KIND = F), the photoabsorption cross section is written to the file cross-section.dat. The cross section is given by[56]

$$\sigma\left(E\right)=\frac{\pi e^2\gamma}{2mc\varepsilon_0 n}\sum_{l\neq i}^{N_{fs}}\left[\frac{1}{N_p^l}\sum_{k}^{N_p^l}f_{il}\left(\mathbf{R}_k\right)g\left(E-\Delta E_{il}\left(\mathbf{R}_k\right),\delta\right)\right] \quad (5)$$

where the internal sum runs over each of the NPOINTS initial coordinate $\mathbf{R}_k$ and the external sum runs over the several states (NFS). The factor γ is given by[58]

$\gamma=1-\exp\left(-E/k_BT\right)$.

In order to compare the simulations to the experiments it useful to remind that photoabsorption cross sections (cm^2) and molar extinction coefficients (ε in $M^{-1}cm^{-1}$) can be interconverted by the relation[59]

$\sigma=10^3\ln(10)\frac{\varepsilon}{N_A}$,

where N_A is the Avogadro's number.

The error in the cross section due to the statistical sampling can be estimated by

$$\delta\sigma\left(E\right)=\frac{\pi e^2\hbar\gamma}{2mc\varepsilon_0 n}\sum_{l\neq i}^{N_{fs}}\frac{1}{N_p^{1/2}\left(N_p-1\right)^{1/2}}\left[\sum_{k}^{N_p}\left(f_{il}\left(\mathbf{R}_k\right)g_L\left(E-\Delta E_{il}\left(\mathbf{R}_k\right),\delta\right)-\left\langle s_l\right\rangle\right)^2\right]^{1/2},$$

where

$$\left\langle s_l\right\rangle=\frac{1}{N_p}\sum_{k'}^{N_p}\Delta E_{0l}\left(\mathbf{R}_{k'}\right)f_{il}\left(\mathbf{R}_{k'}\right)g_L\left(E-\Delta E_{il}\left(\mathbf{R}_{k'}\right),\delta\right),$$

The file cross-section.dat is composed of four columns:
E (eV) λ (nm) σ (Å^2.molecule^{-1}) $\delta\sigma$ (Å^2.molecule^{-1})

11.3 Photoelectron spectra

For TYPE = 2, the photoelectron spectrum is computed with the nuclear ensemble approach according to[49]

$$\Gamma(E,E_k) = E\sum_F \frac{1}{N_p}\sum_{l=1}^{N_p}\sigma_{IF}\left(E,E_k,\mathbf{R}_l\right) w\left[E_k;E-\Delta V_{IF}(\mathbf{R}_l)\right], \tag{6}$$

where σ_{IF} denotes the photoelectron cross section as a function of the nuclear coordinates **R**. *w* is a function modulating the electron kinetic energy distribution. In this equation, E_k is the ejected electron kinetic energy, *E* is the photoenergy, and ΔV_{IF} is the ionization potential. For ICS_PROC = 1, it is given by a rectangular function

$$w_r\left[E_k,E_2-\Delta V_{IF}\right]=\begin{cases}\left(E_2-\Delta V_{IF}\right)^{-1} & \text{for } E_k \le E_2-\Delta V_{IF},\\ 0 & \text{for } E_k > E_2-\Delta V_{IF}.\end{cases} \tag{7}$$

When Eq. (7) is used we call it the constant vibrational broadening (CVB) model.

For ICS_PROC = 2, the kinetic energy modulation is done by a peaked function, which for L_SHAPE = GAUSS is

$$w_s\left[E_k,E-\Delta V_{IF},\delta\right]=\frac{1}{(2\pi)^{1/2}(\delta/2)}\exp\left(\frac{-\left(E_k-\left(E-\Delta V_{IF}\right)\right)^2}{2(\delta/2)^2}\right), \tag{8}$$

while for L_SHAPE = LORENTZ it is

$$w_s\left[E_k,E-\Delta V_{IF},\delta\right]=\frac{1}{\pi(\delta/2)}\frac{(\delta/2)^2}{\left(E_k-\left(E-\Delta V_{IF}\right)\right)^2+(\delta/2)^2}. \tag{9}$$

In both cases, δ (defined by keyword DELTA) is an arbitrary parameter determining the line width. It should be much smaller than the bandwidth to not interfere with the results, usually $\delta \ll 1$ eV is enough to satisfy this requirement. When either Eq. (8) or (9) is used, we call it the peaked vibrational broadening (PVB) model.

For ICS_COMP = 1, the photoelectron cross section is approximated to

$$\sigma_{IF} \approx C\left\|\psi_{IF}^d\right\|^2, \tag{10}$$

where *C* is an arbitrary constant and $\left\|\psi_{IF}^d\right\|$ is the norm of the Dyson orbital. In this case, the spectrum simplified (with relative height) to

$$\sigma_k(E) \propto E\sum_{IF}\frac{1}{N_p}\sum_{l=1}^{N_p} g_I\left\|\psi_{0F}^d\right\|^2 w. \tag{11}$$

where g_I accounts for the spin degeneracy of state *I*. This is called the DO norm approach.

For ICS_COMP = 2, the cross section is computed as

$$\sigma_k(E) = \sum_{IF}\frac{1}{N_p}\sum_{l=1}^{N_p}\left\|\psi_{IF}^d\right\|^2\sigma_R\, w, \tag{12}$$

where σ_R is the spherically averaged total cross section for a fixed geometry. This is called the cross-section approach. The cross sections for fixed geometries are computed by EZDYSON:

$$\sigma_R = \frac{\pi}{3}\frac{m_e g_I}{\varepsilon_0 c\hbar^3}kE\left|\langle F_k\,|\,\mu\,|\,\bar{\psi}_{IF}^d\rangle_{\mathbf{r}_N}\right|^2. \tag{13}$$

In this case, an ezdyson.xml file should be provided together with the other input files, to serve as a template for NEWTON-X. In this file, set the attribute NORM to 1, as the Dyson norms are already accounted for in NEWTON-X. For instance:

```
<DMO norm="1.000000"    transition="…
```

IP, electron momentum, geometry, l_max, and Dyson orbital coefficients are adjusted automatically by NEWTON-X during the run. All other keywords (as charge_of_ionized_core, n_points, spin_degeneracy, etc.) must be adequately set in the template.

Note that for a photoelectron spectrum run, in addition to mkd.inp and the optional ezdyson.xml, one should also provide an ip.dat file containing the IP information for each state and ensemble point, a MO_DYSON directory containing the Dyson orbitals, and a GEOMETRIES directory containing all geometries. See the tutorial for detailed information on these files and directories.

The photoelectron spectrum run can be split between several machines using

```
$NX/split_intesities.pl
```

The results can be merged with

```
$NX/merge_intensities.pl
```

11.4 Initial conditions for multiple states

In Chapter 10, it was explained how to generate initial conditions for starting the dynamics in a single excited state. That procedure may be generalized to create initial conditions for multiple adiabatic states, weighting each one according to their oscillator strength.

Having the final_output.[nis].[nfs] files in the same directory, run nxinp and select option

```
2 - Select initial conditions for multiple initial states
```

The energy restriction may be changed or not. After running makedir.pl, a new directory called `SELECTED_INITIAL_CONDITIONS` is created. Inside this directory, there are new final_output.[nis].[nfs] files containing initial conditions for each nfs state. These files can be individually used to start the dynamics in each nfs state. When run_IS is set to 1, the files samp_param.[nis].[nfs] and samp_points.[nis].[nfs] will also be created, which should then be copied as samp_param and samp_points when generating the trajectories.

Suppose you want to generate initial conditions to start the dynamics simultaneously from S_2 and S_1 states. `SELECTED_INITIAL_CONDITIONS` directory should contain the files final_output.1.2 and final_output.1.3. The number of initial conditions in each one reflects the dipole transition probability from S_0 into these two states. If, for example, if S_1 state has $\pi\pi^*$ character and S_2 state has $n\pi^*$ character, the number of points in final_output.1.2 will be substantially larger than in final_output.1.3. When the dynamics is performed, the number of trajectories starting in S_1 and S_2 states should reflect this proportion.

11.5 Managing several trajectories

For managing several trajectories, it is useful to use the script makedir.pl. makedir.pl reads final_output file generated by the initial condition generation procedure and writes a new NEWTON-X input directory for each initial condition accepted.

After preparing the inputs using nxinp tool, be sure that you have in the same directory:

- final_output (always)
- control.dyn (always)
- JOB_AD (if necessary for the specific job)

- JOB_NAD (if necessary for the specific job)
- jiri.inp (if necessary for the specific job)
- sh.inp (if necessary for the specific job)
- wf.inp (if necessary for the specific job)
- <third-party program>.par (if necessary for the specific job)
- therm.inp (if necessary for the specific job)
- freeze.inp (if necessary for the specific job)
- therm.freeze (if necessary for the specific job)
- boundaries.inp (if necessary for the specific job)
- mkd.inp (optional)
- pmold (if available, see below)

Run

```
$NX/makedir.pl > makedir.log
```

If TYPE = 3, makedir.pl will create the directories TRAJECTORIES/TRAJi, where i is the number of the accepted condition.

11.6 About energy restrictions

If energy restrictions are applied (SCREEN = 2) or spectrum generation is chosen (TYPE = 1), vertical excitation energy (ΔE) and the oscillator strength (f) are collected from each initial condition in final_output.nis.isf or final_output files (where isf is each value in nfs array). For each initial condition within E_CENTER ± E_VAR, the quantity f, $A = f.\Delta E^2$ or $B = A.\Delta E^{-3}$ proportional to the oscillator strength or Einstein's coefficients is computed according to PROB_KIND keyword. The normalization may be done by the maximum A or B values within the window restriction (NORM = local) or within the complete set of values (NORM = global). The relative "transition probability" $P = f/f_{max}$, A/A_{max} or $P = B/B_{max}$ is compared to a random number in order to select whether the initial condition will be accepted or not.

12 Dynamics inputs

12.1 What is necessary to run the jobs

For the input you need the following files:

Always:
control.dyn - with parameters to control de dynamics.
geom - with the initial geometry.
veloc - with the initial velocity.

Depending on the settings in control.dyn:
jiri.inp - with parameters to control nonadiabatic dynamics.
sh.inp - with parameters to control nonadiabatic dynamics.
<third-party>.par - with third-party program options.
therm.inp - with thermostat options.
freeze.inp - with frozen atoms information.
therm.freeze - with atoms not affected by thermostat.
boundaries.inp - with boundary condition options.
NX_analysis - with instructions for a customized analysis of the results.
stopsign.inp - with instructions to terminate the simulations.

You also need the input files for the program that will calculate the energies, gradients, and nonadiabatic couplings.

JOB_AD - directory containing input files for adiabatic calculation. Energy and gradient for one state.

JOB_NAD - directory containing input files for nonadiabatic calculations. Energy, gradient and nonadiabatic coupling.

For adiabatic dynamics or nonadiabatic dynamics using time-derivative couplings[22], only JOB_AD is necessary.

For mixed, non- and adiabatic dynamics (using the THRES keyword), both JOB_AD and JOB_NAD are necessary.

For nonadiabatic dynamics using nonadiabatic coupling vectors, only JOB_NAD is necessary.

12.1.1 control.dyn

File control.dyn should contain the main parameters for the dynamics:

File: control.dyn
Namelist: input

Parameter	Default	Description
NAT	= [3]	Number of atoms.
NSTAT	= [2]	Number of states (dynamics will be performed on the highest one). NSTAT ≥ NSTATDYN.
NSTATDYN	= [nstat]	Initial state.

NDAMP	= [0]	0 : normal dynamics. 1 : velocity is dumped to zero at each time step.
KT	= [1]	Print output at each KT steps.
DT	= [0.5]	Time step (fs).
T	= [0.0]	Initial time (fs).
TMAX	= [10.0]	Maximum time (fs).
NINTC	= [3*Nat-6]	Number of internal coordinates to read from the ab initio program. Change default if the system is linear or has redundant coordinates.
MEM	= [200]	Core memory for the ab initio program (Mwords). (Relevant if PROG = 1)
KILLSTAT	= [1]	Finish dynamics if after a hopping the system remains more than timekill fs on state KILLSTAT.
TIMEKILL	= [0]	See KILLSTAT. 0 : deactivate KILLSTAT and TIMEKILL
PROG	= [1]	Program to compute energies, gradients and nonadiabatic coupling vectors (if available): 0 : Analytical model (see section "Using analytical models") 1 : COLUMBUS 2.0 : TURBOMOLE RI-CC2 / ADC(2) 2.1 : TURBOMOLE TDDFT 6 : GAUSSIAN 7 : TINKER 8.0 : DFTB (Legacy; round state) 8.1 : DFTB+ (Legacy; QM/MM ground state) 8.5 : DFTB+ (New interface; TD-DFTB nonadiabatic dynamics) 10.0 : GAMESS 10.1 : GAMESS ADIABATIC 12.0 : BAGEL (Nonadiabatic) 12.1 : BAGEL (Arbitrary adiabatic method) 20 : Hybrid jobs
THRES	= [0 for PROG = 2.*x* and 5] = [100 for PROG = 0, 1 and 6]	Energy-difference threshold to initiate nonadiabatic dynamics (eV).
LVPRT	= [1]	Amount of output to print and output files to keep: 0 : Minimal level 1 : Normal level 2 : Debug level (huge amount of data) 5 : Read geometries from geom.list (see Section 12.1.14)
ETOT_JUMP	= [0.5]	Kill trajectory if total energy deviate more than ETOT_JUMP eV in one time step.
ETOT_DRIFT	= [0.5]	Kill trajectory if total energy deviate more than ETOT_DRIFT (eV) in comparison to the value in t = 0.
NXRESTART	= [0]	Restart options: 0: new job.

1: restart job using the content of INFO_RESTART directory. See details in Section 12.4.

[default values] written in inp.f90.

Example 1:

```
&input
Nat    = 6         ! Number of atoms
nstat = 3          ! Number of states
nstatdyn = 3       ! Initial state
dt     = 0.5       ! Time step (fs)
tmax   = 200.0     ! Total time (fs)
prog   = 2.1       ! Dynamics with TURBOMOLE (TDDFT).
/&end              ! Do not forget &input and /&end.
```

Example 2: Ethylene S_1-state dynamics, calculating S_0, S_1 and S_2 energies. Time step of 0.1 fs during 200 fs and output printed at each 2 fs. 100,000,000 words of memory. If potential energy difference between two consecutive states drops below 2.0 eV, start nonadiabatic dynamics. Finish dynamics if after a hop to S_0, the system remains more than 10 fs on this state. Get energies, gradients and nonadiabatic couplings with COLUMBUS.

```
&input
Nat    = 6
nstat = 3
nstatdyn = 2
kt     = 20
dt     = 0.10
tmax   = 200.0
mem    = 100
thres = 2.0
killstat = 1
timekill = 10.0
/&end
```

Do not forget "&input" and "/&end".

Note about DFTB and DFTB+ calls: Until NEWTON-X version 2.0, the DFTB job was invoked through PROG = 5 and DFTB+ though PROG = 8. With the development of the new DFTB+ interface in version 2.1, these keywords were changed. DFTB is now called through PROG = 8.0, the old DFTB+ interface is called through PROG = 8.1, and the new DFTB+ interface through PROG = 8.5. The DFTB and the old DFTB+ interfaces are kept only for legacy and will be discontinued in the future.

12.1.2 Geometry

The geometry input is (free format, au):

Name: geom

```
Symbol_1    Z_1    x_1    y_1    z_1    M_1
Symbol_2    Z_2    x_2    y_2    z_2    M_2
:
Symbol_nat  Z_nat  x_nat  y_nat  z_nat  M_nat
```

where Z is the nuclear charge, x,y, and z are the Cartesian coordinates, and M, the atomic masses.

Example:

```
C       6.   -1.27572383    0.00000000    0.00000000   12.00000000
C       6.    1.27572383    0.00000000    0.00000000   12.00000000
H       1.   -2.34867651    0.00000000   -1.75798067    1.00782504
H       1.   -2.34867651    0.00000000    1.75798067    1.00782504
H       1.    2.34867651    0.00000000   -1.75798067    1.00782504
H       1.    2.34867651    0.00000000    1.75798067    1.00782504
```

12.1.3 Velocity

The velocity input is (free format, au):

Name: veloc

```
vx_1   vy_1    vz_1
vx_2   vy_2    vz_2
:
vx_nat vy_nat  vz_nat
```

Example:

```
 3.226196727134333E-004 -7.803939823701649E-004  3.501212063660452E-004
 8.831202616257374E-005  1.103339279899924E-003 -7.468292758584672E-004
-1.994896289256706E-004  4.345679802152278E-004 -6.123248174920957E-004
-3.735660908785368E-003  2.225120145326573E-003  1.414904777249870E-003
-2.272632671568894E-003 -2.177375422081543E-003  3.098061686476041E-003
-6.469986389583130E-004  1.402416374342127E-004  2.362055042392439E-003
```

12.1.4 Freezing atoms

Cartesian coordinates of specific atoms can be kept frozen along the dynamics. For that, a list of atoms should be given in a file called freeze.inp. This file should be given together with the other input files. The atoms in the list are identified by its positions in the geom file and the list is blank separated.

Example of freeze.inp:

```
1 3
```

(Cartesian coordinate of atoms one and three in geom file will not change during the dynamics.)

If a file freeze.inp is present in the input, the atoms defined there will also not be affected by the thermostat.

The velocity of the atoms to be kept frozen should be set to zero in the veloc file (section 12.1.3). If the velocity of the frozen atoms is not initially set to zero, the program will stop with an error message.

Be aware that this algorithm may introduce spurious rotations and translation in the molecule depending on how the initial velocities of the remaining atoms were generated.

12.1.5 Specific input for quantum-chemistry electronic-structure calculations

Please, refer to the documentation of each particular program to see details on their inputs. Here, we present a brief summary of the main option that should be selected for some frequent jobs.

12.1.5.1 WHICH ELECTRONIC METHOD TO USE

Nonadiabatic dynamics will always demand a compromise between quality and computational costs. In principle, the description of state crossing regions should be described by a multireference method like

MRCI. However, often this is not affordable. In many cases (but not always), single references cases like TDDFT or ADC(2) have proven to give an adequate description of the nonadiabatic problem. You may keep the following thumb rules in mind when deciding which method to use in the simulation:

- Crossings between excited states at TDDFT and ADC(2) levels are in general well described if the ground state DFT is still single reference.
- Crossings between excited states will cause convergence problems at CC2 level.
- The description of crossings between the first excited state and the ground state is not reliable at TDDFT, CC2 or ADC(2) levels.

12.1.5.2 USING ANALYTICAL MODELS

Analytical models for potential energies, gradients and nonadiabatic coupling vectors can be used in the molecular dynamics.

The analytical model is supposed to be a program in any language that reads molecular geometry from geom and velocities (if needed) from veloc, and writes the potential energies to epot, gradients to grad and grad.all, and nonadiabatic coupling vectors to nad_vectors. The format of each one of these files is described in the section 16.3. If the analytical model requires additional files besides the executable file (for example, parameter inputs) they must be put in JOB_NAD directory. During the dynamics, the content of this directory is copied to the same location as the other NEWTON-X input files.

NEWTON-X provides several built-in analytical models, including the three Tully's 1D models,[13] the 2D conical intersection model by Ferreti et al.,[21] and the Spin-Boson Hamiltonian.[47]

Users can also provide their own models. The specific location of the program to be called can be set via analyt.par. The options are given below.

Name: analyt.par

Parameter	Default	Description
ANMOD	[analytical.model]	File name of the executable containing the analytical model. There are two built-in options: analytical.model - 2D conical-intersection analytical model by Ferretti et al.[21] tully_models.pl - 1D models by Tully.[13] sbh.pl – Spin-Boson Hamiltonian.[47]
PATH	[$NX]	Absolute path to ANMOD file. The default PATH = $NX is adequate for the built-in models.
For ANMOD = tully_models.pl		
TULLY_MOD	[1]	Specific model: 1 – Simple avoided crossing 2 – Dual avoided crossing 3 – Extended coupling with reflexion

Example of analyt.par file:

```
anmod = my_model.x
path = /home/model/
```

The parameters of the built-in models can be set via JOB_NAD directory. The options are given below.

12.1.5.3 BUILT-IN MODEL: 2D CONICAL INTERSECTION

This conical intersection model is described in Ref. [21]. It is called by setting ANMOD = analytical.model and providing its parameters in a file named con_int.dat located within JOB_NAD.

ANMOD = analytical.model
Name: JOB_NAD/con_int.dat
namelist DAT

Parameter	Default	Description
α	= [3.0]	See Ref. [21]
β	= [1.5]	
K_x	= [0.02]	
K_y	= [0.10]	
Δ	= [0.01]	
X_1	= [4.0]	
X_2	= [3.0]	
X_3	= [3.0]	
γ	= [0.04]	

Example of con_int.dat

```
&DAT
  alpha=3.0
  beta=1.5
  kx=0.02
  ky=0.10,
  delta=0.01
  x1=4.0
  x2=3.0
  x3=3.0
  gamma=0.04
&END
```

12.1.5.4 BUILT-IN MODEL: 1D COLLECTION

A collection of 1D models can be simulated with ANMOD = tully_models.pl. It includes the three models used by Tully to test the FSSH algorithm in Ref. [13], the Double-Arch model by Subotnik and Shenvi,[45] and the Nikitin Hamiltonian (Eq. 7 of Ref.[46]). Their parameters in a file named constants.dat within JOB_NAD. 1D Marcus problem (conventional and inverted regions) can be simulated using the Spin-Boson Hamiltonian described in Section 12.1.5.5.

ANMOD = tully_models.pl
Name: JOB_NAD/constants.dat

Model	Parameters				
Simple avoided crossing[13]	A	B	C	D	
tully_mod = 1	0.01	1.6	0.005	1.0	
Dual avoided crossing[13]	A	B	C	D	E0
tully_mod = 2	0.10	0.28	0.015	0.06	0.05
Extended coupling with reflection[13]	A	B	C		
tully_mod = 3	6E-4	0.1	0.9		
Double arch[45]	A	B	C	Z	
tully_mod = 4	6E-4	0.1	0.9	0.4	

Nikitin Hamiltonian	A	B	theta (π/n)	alpha	DE
tully_mod = 5	0.05	0.1	12	2	0.01

Example of constants.dat

```
A=0.01
B=1.6
C=0.005
D=1.0
```

The atomic masses must be set directly in the geom file. In the case of Tully's models, the original work used 2000 m_e. In geom, it corresponds to 1.09716 amu.

Example of geom file for Tully's models starting at x = -10 a_0.

```
H  1.0  -10.000 0.000 0.000 1.09716
```

The implementation of the 1D collection models in the tully_models.pl program is made in a very modular way, which allows straightforward implementation of other 1D models. Given the diabatic potential energy functions V_{11} and V_{22} and the coupling function V_{12}, the relevant adiabatic quantities are:

1) Energies

$$E_{1,2} = \frac{1}{2}\left(V_{11}+V_{22}\right) \pm \left(\frac{1}{4}\left(V_{22}-V_{11}\right)^2 + V_{12}^2\right)^{1/2}. \tag{14}$$

2) Energy gradients

$$G_{1,2}(x) = \frac{1}{2}\left(\frac{dV_{11}}{dx}+\frac{dV_{22}}{dx}\right) \pm \left(\frac{1}{2}\left(V_{22}-V_{11}\right)\left(\frac{dV_{22}}{dx}-\frac{dV_{11}}{dx}\right)+2V_{12}\frac{dV_{12}}{dx}\right)\left(\frac{1}{4}\left(V_{22}-V_{11}\right)^2+V_{12}^2\right)^{-1/2}, \tag{15}$$
$$G_{1,2}(y) = G_{1,2}(z) = 0.$$

3) Nonadiabatic coupling vector

$$F_{12}(x) = \frac{1}{1+\left(\frac{2V_{12}}{V_{22}-V_{11}}\right)^2}\left(\frac{1}{\left(V_{22}-V_{11}\right)}\frac{dV_{12}}{dx} - \frac{V_{12}}{\left(V_{22}-V_{11}\right)^2}\left(\frac{dV_{22}}{dx}-\frac{dV_{11}}{dx}\right)\right), \tag{16}$$
$$F_{12}(y) = F_{12}(z) = 0.$$

To implement a new 1D model, it is enough to modify tully_models.pl to provide the new V_{11}, V_{22}, and V_{12}, as well as the respective derivative functions.

12.1.5.5 BUILT-IN MODEL: SPIN-BOSON HAMILTONIAN

Surface hopping with the spin-boson Hamiltonian (SBH) is discussed in Refs.[60-63]. The implementation in NEWTON-X is done through the Perl program sbh.pl in adiabatic representation. The sbh.pl program reads geometries from geom file and dynamics parameters from control.dyn. Then, it computes energies

$$E_i = \frac{1}{2}\sum_{j=1}^{N} M_j\omega_j^2 R_j^2 + (-1)^i\left[\eta^2+v_0^2\right]^{1/2} \quad (i=1,2), \tag{17}$$

where

$$\eta = \left(\sum_{j=1}^{N} g_j R_j + \varepsilon_0\right). \tag{18}$$

gradients

$$\frac{\partial E_i}{\partial Q_k} = M_k \omega_k^2 R_k + (-1)^i \, g_k \left[\frac{\eta}{\left[\eta^2 + v_0^2\right]^{1/2}} \right] \quad (k = 1 \cdots N), \tag{19}$$

and nonadiabatic couplings

$$F_{12}^k = -F_{21}^k = -\frac{1}{2} g_k \left[\frac{v_0}{\eta^2 + v_0^2} \right]. \tag{20}$$

These quantities are written to the standard NEWTON-X files (etot, grad, grad.all, and nad_vectors).

The coupling to the bath is done in terms of the spectral density model

$$J(\omega) = \frac{\pi}{2} \sum_{j=1}^{N} \frac{c_j^2}{M_j \omega_j} \delta(\omega - \omega_j). \tag{21}$$

where $c_j = 2 g_j / q_0$.

Typical choices for the spectral density are the Debye

$$J_D(\omega) = \frac{E_r}{2} \frac{\omega \omega_c}{\omega^2 + \omega_c^2}, \tag{22}$$

where E_r is the bath reorganization energy and ω_c is the characteristic frequency; and the Ohmic model

$$J_O(\omega) = \frac{1}{2} \pi \hbar \xi \omega e^{-\omega/\omega_c}, \tag{23}$$

where ξ is the Kondo parameter.

In the Debye case, discretization can be done according to[64]

$$\begin{aligned} g_j &= \left[\frac{M_j E_r}{\pi N} \tan^{-1}\left(\frac{\omega_{\max}}{\omega_c} \right) \right]^{1/2} \omega_j, \\ \omega_j &= \tan\left(\frac{j}{N} \tan^{-1}\left(\frac{\omega_{\max}}{\omega_c} \right) \right) \omega_c. \end{aligned} \tag{24}$$

In the Ohmic case, discretization is given by[65]

$$\begin{aligned} g_j &= \left(\xi \hbar \omega_0 M_j \right)^{1/2} \omega_j, \\ \omega_j &= -\omega_c \ln\left(1 - j \frac{\omega_0}{\omega_c} \right), \end{aligned} \tag{25}$$

where

$$\omega_0 = \frac{\omega_c}{N} \left(1 - e^{-\omega_{\max}/\omega_c} \right). \tag{26}$$

The sbh.pl program can be accessed through ANMOD = sbh.pl. The parameters for the SBH model are written in two files, sbh.par and user_sd_sbh.inp. Both should be given in JOB_NAD directory. The parameters and keywords in sbh.par are defined below.

ANMOD = sbh.pl
Name: JOB_NAD/sbh.par

Parameter	Keyword	Value	Observations
Active state	nstatdyn	integer	Only if control.d is not present
ε_0	e0	real (cm^{-1})	
v_0	v0	real (cm^{-1})	
N	N	integer	

Type of spectral density	Jw	debye ohmic user	Jw = user for dynamics. For Jw = user, user_sd_sbh.inp must be provided.
ω_c	wc	real (cm^{-1})	
ω_{max}	wmax	real (cm^{-1})	
ξ	xi	real (dimensionless)	Only for Jw = ohmic
E_r	Er	real (cm^{-1})	Only for Jw = debye

Example of sbh.par:

```
e0 = 12000
v0 = 800
N = 2
Jw = user
```

The user_sd_sbh.par file, required if Jw = user, should contain an unformatted list of ω_k (cm^{-1}) and g_k (hartree/bohr), one pair per line, for the N oscillators. Example of user_sd_sbh.par for N = 2 (Nat = 2 in control.dyn):

```
138.2378        0.012
203.879         0.000
```

In this example, the first oscillator has ω_1 = 138 cm^{-1} and g_1 = 0.012 hartree/a_0; the second oscillator has ω_2 = 203 cm^{-1} and g_1 = 0.000 hartree/a_0.

Geometry and velocity in NEWTON-X should be given in geom and veloc, as usual. The main difference is that each oscillator is treated as a new atom and only the x column is populated (y and z should be given as zeros). Example of geom:

```
 C     1.0    2.76111090    0.00000000    0.00000000    5.55160000
 C     1.0    0.10000000    0.00000000    0.00000000    5.93720000
```

and of veloc:

```
 0.0020 0.000 0.000
-0.0001 0.000 0.000
```

In the example above, M_1 = 5.5516 amu starts at R_1 = 2.76 a_0 with velocity 0.002 au, while M_2 = 5.9372 amu starts at R_2 = 0.1 a_0 with velocity -0.0001 au. Atomic symbols and atomic numbers are not read and may be given arbitrary values.

12.1.5.6 COLUMBUS

COLUMBUS 5.9

Adiabatic dynamics: JOB_AD directory

Prepare a set of input files for a Columbus job (geometry optimization, one iteration, NROOT option). For MCSCF jobs, prepare input for CI gradient, but set "Maximum excitation level" to 0 in the CIDRT input. It is also possible to use MCSCF gradients, but in this case, only single state dynamics are allowed (NSTAT = 1).

Nonadiabatic dynamics using nonadiabatic coupling vectors: JOB_NAD directory

Prepare input files for a single-point nonadiabatic coupling calculation.

Nonadiabatic dynamics using time-derivative couplings: JOB_AD directory

Prepare a set of input files for a Columbus job (geometry optimization, one iteration, NROOT option). For MCSCF jobs, prepare input for CI gradient, but set "Maximum excitation level" to 0 in the CIDRT input.

COLUMBUS 7.0

Adiabatic and nonadiabatic (using coupling vectors or time-derivative couplings) dynamics are directly available at the SA-MCSCF and MR-CI levels. All inputs can be performed using the "nonadiabatic coupling" option in COLUMBUS, and only the necessary terms are computed for each case. Optionally, adiabatic and time-derivative MR-CI dynamics may still be performed through "geometry optimization." Please set version=7.0 when using COLUMBUS 7.0.

Parameters to control COLUMBUS jobs

Name: columbus.par

Parameter	Default	Description
VERSION	= [5.9]	COLUMBUS version
MEM	= [200]	Core memory for COLUMBUS (Mwords). The same as MEM in control.dyn, but with priority over it. (1 GB = 134 Mwords). For COLUMBUS 7, MEM is automatically converted into GB.
CIRESTART	= [0]	0: do not use previous CI vector 1: use previous CI vector
MOCOEF	= [4]	0: use the same mocoef file in all time steps 1: use the mocoef file from the previous time step k: Lagrangian extrapolation of molecular orbitals at order k-1 (k ≤ 11) (see Section 12.1.11)
PRT_MO	= [20]	Save mocoef file to DEBUG file every PRT_MO timesteps. (Only if mocoef = 1.)
IVMODE	= [8]	Initial CI-vector generation mode. See COLUMBUS docs (ciudg program) for a list of options. CIRESTART keyword has priority over IVMODE keyword.
CITOL	=["1E-4"]	Tolerance for MR-CI calculations
REDUCE_TOL	= [1]	0: keep rtolci and rtolbk in ciudgin as CITOL for all states. 1: use CITOL only to NSTATDYN. For all other states use 1E-3. 2: use CITOL only to NSTATDYN. Use 1E-3 for states coupled to NSTATDYN according to transmomin Columbus file. For all other states use 1E-1. Note that energies computed with 1E-1 are not reliable estimates. Although they are written to the output files, they do not have significance.
MC_CONV	= [0]	If mcscf calculation do not converge: 0: warn and continue 1: kill trajectory
CI_CONV	= [0]	If CI calculation does not converge: 0: warn and continue 1: kill trajectory
QUAD_CONV	= [60]	Set value of NCOUPL in mcscfin
MULL_POP	= [0]	1: print out the Mulliken populations from the COLUMBUS calculation to nx.log

12.1.5.7 TURBOMOLE

Adiabatic dynamics: JOB_AD directory

Prepare a set of input files for a TURBOMOLE job at TDDFT or CC2 level without symmetry and copy them to JOB_AD directory.

The initial geometry (TURBOMOLE coord file), the number of states (TURBOMOLE control file), and the state for which the gradient should be computed (TURBOMOLE control file) are automatically set by NEWTON-X during the program execution, overwriting the options in JOB_AD.

For TDDFT dynamics, TURBOMOLE control file is automatically changed to have:

```
$soes all NSTAT-1
$exopt NSTATDYN-1
```

For RI-CC2 or ADC(2) dynamics, TURBOMOLE control file is automatically changed to have:

```
$excitations
  irrep=a nexc=NSTAT-1
  exgrad states=(a NSTATDYN-1)
```

If TURBOMOLE auxbasis file is provided in JOB_AD, NEWTON-X assumes that the resolution-of-identity (RI) should be used. For CC2 or ADC(2) dynamics, auxbasis must always be provided, and the `ricc2` program is invoked every time step. For DFT dynamics, the presence of auxbasis file is optional. If it is provided, `ridft` program is invoked, otherwise `dscf` program is invoked.

The NEWTON-X input for CC2 and ADC(2) dynamics are exactly the same. The only difference is in the TURBOMOLE control file within JOB_AD directory, which should be adequate to the desired method. During the execution, NEWTON-X search for ADC(2) keyword in the TURBOMOLE control file. If it is not found, the CC2 ground state energy is used. If it is found, MP2 ground state energy is used.

If you want to perform only adiabatic dynamics, set THRES = 0 (default in control.dyn file) to avoid that NEWTON-X starts the nonadiabatic dynamics calculations.

The TURBOMOLE mos file is not updated during the dynamics.

Nonadiabatic dynamics: JOB_AD directory

Prepare the TURBOMOLE input files as explained in the previous item. The nonadiabatic dynamics options are described in section 12.1.7.

Set THRES = 100 in control.dyn file.

Parameters to control TURBOMOLE jobs

Name: turbomole.par

Parameter	Default	Description
PARALLEL	= [1]	Number of cores to use for parallel Turbomole (smp, no mpi!) [Deprecated]
For ADC(2) and CC2 jobs:		
MULTIPLICITY	[1]	Multiplicity of the excited states given as one of the irrep options in control file of Turbomole. It is possible, for instance, to have a singlet closed-shell ground state and triplet (MULTIPLICITY=3) excited states.
NPRE	[NSTAT-1]	Number of roots used in preoptimization steps given as one of the irrep options in control file of Turbomole.

NSTART	[NPRE]	Number of start vectors generated or read from file given as one of the irrep options in control file of Turbomole.

During ADC(2) and CC2 jobs, NEWTON-X rewrites the control file of Turbomole. In particular, the irrep line in $excitations is given as:

```
irrep=a  multiplicity=<MULTIPLICITY> nexc=<NSTAT-1> npre=<NPRE> nstart=<NPRE>
```

The xgrad line, controlling for which state the gradient should be computed, is written as:

```
exgrad states=(a{3} <NSTATDYN-1>)
```

for MULTIPLICITY = 3. For all other cases, it is given by:

```
exgrad states=(a <NSTATDYN-1>)
```

Turbomole parallel environment should be set independently of NEWTON-X, in the way it is done for conventional Turbomole jobs. In this case, parallel keyword does not need to be set in turbomole.par.

In the past, this set up used to be done via parallel keyword in turbomole.par. In this case, SMP parallelized version of Turbomole executables (dscf_smp, grad_smp, egrad_smp and ricc2_smp) were chosen by specifying parallel keyword. This option, which sets the environment variable $OMP_NUM_THREADS internally during NEWTON-X execution, should be avoided.

Inputs for old versions of NEWTON-X

For NEWTON-X versions prior the 1.0.8, additional input files should be provided for TDDFT simulations if NSTATDYN = 1 and NSTAT > NSTATDYN. In this case, the following files are required in JOB_AD directory:
control.opt - TURBOMOLE control file for ground state gradient (GRAD) calculation.
control.sp - TURBOMOLE control file for excited state single point (ESCF) calculation.
For excited state gradient calculations (NSTATDYN > 1), no additional files are needed.

12.1.5.8 GAUSSIAN

CASSCF level

Surface-hopping nonadiabatic dynamics between the ground and the first excited state can be performed at CASSCF level with GAUSSIAN 03 or 09.

Content of JOB_NAD directory

Prepare input files for a single point conical intersection calculation at CASSCF level. The input file must be called gaussian.com and the geometry must be given in Cartesian coordinates. The check point file named gaussian.chk containing the initial molecular orbitals must be provided as well. A suitable example of gaussian.com content is:

```
%chk=gaussian
%mem=20000000
#P OPT=(Conical,MaxCycle=1) CAS(4,3) IOp(5/7=200) Guess=read 3-21G Nosymm

methaniminium

1 1
N    0.000000  0.000000   0.637342
C    0.000000  0.000000  -0.703614
H   -0.648747  0.572349   1.177883
H    0.648745 -0.572350   1.177883
H    0.618844  0.701080  -1.278050
H   -0.618844 -0.701080  -1.278049
```

Note that OPT=(Conical,MaxCycle=1), Nosymm and Guess=read keywords and options should be given exactly as in this example. IOp(5/7=MaxIt) controls the maximum number of iterations in the CASSCF calculation.

Parameters to control GAUSSIAN jobs

Name: gau.par (g03.par in previous NX versions)

Parameter	Default	Description
G_VERS	= [09]	Gaussian version 03: Gaussian 03 09: Gaussian 09
MOCOEF	= [1]	0: use the initial molecular orbitals in all time steps 1: use the check point file from the previous time step as the source of molecular orbitals
PRT_MO	= [20]	Save gaussian.chk file to DEBUG file every PRT_MO timesteps. (Only if mocoef = 1.)

NEWTON-X executes GAUSSIAN by invoking the command:

```
.  $gXroot/gX/bsd/gX.profile;$gXroot/gX/gX gaussian.com
```

where X is the value of G_VARS. If this path is not adequate for your system, you can change it in $NX/run-g03.pl program.

(U)TDDFT, (U)TDA, and (U)CIS level

Surface-hopping nonadiabatic dynamics with an arbitrary number of states can be performed at TDDFT level with GAUSSIAN 09.

Content of the JOB_AD directory

Prepare input files for a single point calculation at TDDFT, TDA, or CIS level. The input file must be called gaussian.com and an optional check point file named gaussian.chk. These calculations can be also performed for open shell systems using cioverlap open shell version (See description below). In the case of open shell systems, the program detects the multiplicity and performs an unrestricted calculation by default, unless the $KIND_G09 is set to 1 in g09.par.

For nonadiabatic dynamics, NEWTON-X calls rwfdump program of Gaussian. **$g09root/g09/bsd/g09.login should be sourced either in the user profile or in the submission script before running the job**.

To run a calculation in parallel, the number of processors has to be specified with the keyword %nproc in the GAUSSIAN input. It also has to be specified in the submission script.

In file *gaussian.com*, the DFT functional, basis set and TD, CIS, or TDA keyword with the proper options should be specified. **The user should not use the keywords Guess=Read and TD(Read)** in the input file. These options must be defined in g09.par file (see below). NEWTON-X adds NoSymm keyword automatically to avoid any problems due to differences between input and standard orientations.

The basis set may be directly given in the route or defined through GEN keyword. **For nonadiabatic dynamics, the basis set must also be provided in an additional file called *basis***. Different ways of defining the basis sets are illustrated in the next examples.

- Example 1: The simplest case. The same basis set is used for all atoms, and it is defined in the GAUSSIAN library.

Example of the content of *gaussian.com* file:

```
%chk=gaussian
%rwf=gaussian
%mem=200mw
#TD(Nstates=3,Root=2) 3-21G BHandHLYP nosymm

test bs1

0   1
  Si        -0.010544          0.010835          0.808752
   C         0.015819         -0.050721         -0.931069
   H         0.009875          1.149573          1.543340
   H         0.172225         -1.176299          1.509994
   H         0.071356          1.042598         -1.452426
   H        -0.149187         -0.712162         -1.664254
```

Example of *basis* file:

```
3-21G
```

In this example, there is a redundancy in the basis set definition, which appears in *gaussian.com* and in *basis*. You should carefully check whether both files contain the same definitions.

- Example 2: Basis set is not defined in the GAUSSIAN library. Then you have to use the GEN keyword in gaussian.com and provide the basis set. In addition, you have to copy the basis set to the *basis* file.

Example of GAUSSIAN input:

```
%chk=gaussian
%rwf=gaussian
%mem=200mw
#TD(Nstates=3,Root=2) GEN BHandHLYP nosymm

test bs1

0   1
   Si        -0.010544          0.010835          0.808752
    C         0.015819         -0.050721         -0.931069
    H         0.009875          1.149573          1.543340
    H         0.172225         -1.176299          1.509994
    H         0.071356          1.042598         -1.452426
    H        -0.149187         -0.712162         -1.664254

H     0
S   2   1.00
      5.4471780              0.1562850
      0.8245470              0.9046910
S   1   1.00
      0.1831920              1.0000000
****
C     0
S   3   1.00
    172.2560000              0.0617669
```

```
     25.9109000              0.3587940
      5.5333500              0.7007130
SP   2   1.00
      3.6649800             -0.3958970              0.2364600
      0.7705450              1.2158400              0.8606190
SP   1   1.00
      0.1958570              1.0000000              1.0000000
****
Si     0
S   3   1.00
    910.6550000              0.0660823
    137.3360000              0.3862290
     29.7601000              0.6723800
SP   3   1.00
     36.6716000             -0.1045110              0.1133550
      8.3172900              0.1074100              0.4575780
      2.2164500              0.9514460              0.6074270
SP   2   1.00
      1.0791300             -0.3761080              0.0671030
      0.3024220              1.2516500              0.9568830
SP   1   1.00
      0.0933392              1.0000000              1.0000000
****
```

Content of *basis* file:

```
  H     0
S   2   1.00
      5.4471780              0.1562850
      0.8245470              0.9046910
S   1   1.00
      0.1831920              1.0000000
****
C     0
S   3   1.00
    172.2560000              0.0617669
     25.9109000              0.3587940
      5.5333500              0.7007130
SP   2   1.00
      3.6649800             -0.3958970              0.2364600
      0.7705450              1.2158400              0.8606190
SP   1   1.00
      0.1958570              1.0000000              1.0000000
****
Si     0
S   3   1.00
    910.6550000              0.0660823
    137.3360000              0.3862290
     29.7601000              0.6723800
SP   3   1.00
     36.6716000             -0.1045110              0.1133550
      8.3172900              0.1074100              0.4575780
      2.2164500              0.9514460              0.6074270
SP   2   1.00
      1.0791300             -0.3761080              0.0671030
      0.3024220              1.2516500              0.9568830
SP   1   1.00
      0.0933392              1.0000000              1.0000000
```

In this case, the basis set defined in *basis* will be used in the dynamics even if *gaussian.com* has a different definition.

- Example 3: Different basis sets for different atoms. GEN keyword is also needed in this case.

Example of GAUSSIAN input:

```
%chk=gaussian
%rwf=gaussian
%mem=200mw
#TD(Nstates=3,Root=2) GEN BHandHLYP nosymm

test bs1

0   1
   Si        -0.010544         0.010835          0.808752
    C         0.015819        -0.050721         -0.931069
    H         0.009875         1.149573          1.543340
    H         0.172225        -1.176299          1.509994
    H         0.071356         1.042598         -1.452426
    H        -0.149187        -0.712162         -1.664254
```

Content of *basis* file:

```
1 0
6-31G(d)
****
2 0
6-31G(d)
****
3 0
3-21G
****
4 0
3-21G
****
5 0
6-31G
****
6 0
6-31G
```

In this case, the basis set defined in *basis* will be used in the dynamics even if *gaussian.com* has a different definition.

Parameters to control GAUSSIAN jobs

Name: g09.par

Parameter	Default	Description
MOCOEF	= [0]	0: compute the initial guess at every time step. 1: use the check point file from the previous time step as the source of molecular orbitals. 2: use the initial molecular orbitals in all time steps.
TD_ST	= [0]	0: compute the excited states without previous reference. 1: read the states from the checkpoint file, the checkpoint file is controlled by MOCOEF (1 or 2). We don't recommend using this option in nonadiabatic dynamics calculations.

PRT_MO	= [20]	Save gaussian.chk file to DEBUG file every PRT_MO timesteps.
LD_THR	= [14]	N: Controls the linear dependency threshold (10^{-N}) in G09 calculations.
KIND_G09	= [0]	0: Closed shell (default for singlets, spin multiplicity (M)=1) 1: Open shell (default M≠1). To run an unrestricted calculation for M=1, KIND_G09=1 has to be specified in g09.par. In these cases, the user needs to be aware that unless the initial wave function is properly defined (for example using guess=mix, check G09 manual), the program normally converges to the closed shell solution).

NEWTON-X executes GAUSSIAN 09 by invoking the command:

```
.  $g09root/g09/bsd/g09.profile;$g09root/g09/g09 gaussian.com
```

If this path is not adequate for your system, you can change it in $NX/run-g09.pl program.

12.1.5.9 TINKER

Adiabatic ground-state dynamics with forcefield-gradients and –energies can be performed with TINKER.

Content of the JOB_AD-directory

An TINKER-XYZ file called tinkin.xyz and the corresponding keyword-file tinkin.key have to be present. The file tinkin.key has to state at least the name of the parameter file ('parameters <filename>') and 'digits 12'.
The command executed by NEWTON-X is

```
testgrad tinkin.xyz -k tinkin.key y n n
```

If the TINKER-executables are not in the $PATH, testgrad.x can also be provided as binary in the JOB_AD directory.

12.1.5.10 DFTB+ (PROG = 8.5)

Nonadiabatic dynamics can be performed using the time-dependent density functional theory tight binding (DFTB) method.[66] The interface uses the methods implemented in the DFTB+ code,[8] including the non-self-consistent charge (non-SCC)[67, 68] and SCC-DFTB (DFTB2 and DFTB3)[69] for the electronic ground state. Electronic excitations can be calculated with linear-response (LR) TD-DFTB.[66] The treatment of dispersion interactions (+D) is possible in the DFTB+ code via Lennard-Jones potentials,[70] with the Slater-Kirkwood polarizable atomic model,[71] and on the level of the DFT-D3 method.[72] The interface is described in Ref.[41]. QM/MM is still not available.

Input for surface hopping dynamics: JOB_AD directory

Prepare DFTB+ input for excited-state TD-DFTB calculation. The DFTB+ input must be named dftb_in.hsd and should be within JOB_AD directory.

The variables $DFTBP (pointing to the directory with the DFTB+ executable) and $DP_TOOLS (pointing to the directory containing the DFTB+ tool xyz2gen) must be defined. The number of CPU cores can be set with $OMP_NUM_THREADS variable.

Parameters to control the DFTB+ jobs

Name: dftb+.par

Parameter	Default	Description
DFTBP_EXEC	[dftb+]	Name of the DFTB+ executable file. $DFTBP variable must be defined in the system. NEWTON-X will run $DFTBP/<dftbp_exec>.
DFTBP_SKF	[$DFTBP/sk/3ob-3-1]	Path to the directory containing the Slater-Koster files.

12.1.5.11 LEGACY: DFTB+ (PROG = 8.1)

An NEWTON-X/DFTB+ interface for ground state dynamics with QM/MM is available in former versions of NEWTON-X. This version is still available and can be accessed via PROG = 8.1 in control.dyn (see Section 12.1.1).
This interface is based on an outdated version of DFTB program, and it will not be updated anymore. Users should use the new DFTB+ interface (Section 12.1.5.10).

Input for ground-state dynamics: JOB_AD directory

Prepare DFTB+ input for conjugated-gradient ground-state calculation (code 4 in the DFTB program). The DFTB+ input and geometry information must be called dftb.in and in.gen, respectively.

Parameters to control the DFTB+ jobs

Name: dftb+.par

Parameter	Default	Description
DFTBP_EXEC	[dftb+]	Name of the DFTB+ executable file. $DFTBP variable must be defined in the system. NEWTON-X will run $DFTBP/<dftbp_exec>.

12.1.5.12 LEGACY: DFTB (PROG = 8.0)

Adiabatic dynamics in the ground and excited states can be performed using the time-dependent density functional theory tight binding (TD-DFTB) method. Information about the program can be obtained at www.dftb.org.

This interface is based on an outdated version of DFTB program, and it will not be updated anymore. Users should use the new DFTB+ interface (Section 12.1.5.10).

Input for ground state dynamics: JOB_AD directory

Prepare DFTB input for conjugated-gradient ground-state calculation (code 4 in the DFTB program). The DFTB input and geometry information must be called dftb.in and in.gen, respectively.

Input for excited-state dynamics: JOB_AD directory

Prepare TD-DFTB input for conjugated-gradient excited-state calculation (code 4 in the DFTB program). The DFTB input and geometry information must be called dftb.in and in.gen, respectively.

Parameters to control the DFTB jobs

Name: dftb.par

Parameter	Default	Description
DFTB_EXEC	[dftb]	Name of the DFTB executable file. $DFTB variable must be defined in the system. NEWTON-X will run $DFTB/<dftb_exec>.

OTHER_STATE	[1]	It is possible to perform dynamics on one surface, and at the same time to keep track of the properties of other states (energies and oscillator strengths). In this case, however, DFTB must run twice per time step, which makes the calculation more expensive. 0 - Do not monitor other states 1 - Monitor other states
MULT	[S]	Multiplicity of the states. Only states with the same multiplicity are allowed. S - singlet T - triplet

12.1.5.13 GAMESS

Adiabatic dynamics: JOB_AD directory

Prepare a gradient input file for a GAMESS job at some adiabatic level (e.g., CCSD(T) or MP2) without symmetry and copy the file to the JOB_AD directory. The input file should be labeled either gamessinput_original.inp (without the $DATA group) or nx_gamess.inp (with the $DATA group). Either way, starting coordinates for the run always get taken from the NEWTON-X geom file.

The initial geometry, the number of states, and the state for which the gradient should be computed are automatically set by NEWTON-X during the program execution. Please ensure the iroot variable (in $det or similar group) in nx_gamess.inp is the same as nstatdyn in control.dyn file.

If you want to perform only adiabatic dynamics, set THRES = 0 in control.dyn file to avoid nonadiabatic dynamics calculations.

Analytic gradients are available for state-averaged runs and are activated with wtsok=.t. in the $det group (and no NUMGRD=.t. in $contrl).

GAMESS input examples exist in $NX/test-nx.

Nonadiabatic dynamics using nonadiabatic coupling vectors: JOB_NAD directory

NA couplings are available at the SA-MCSCF level.

Specific NA coupling selection schemes are also available through the jiri.inp file with napick=.t. in $cpconv. All NA couplings can be calculated with napick=.f. in $cpconv along with appropriate input to jiri.inp.

Prepare input files for a single-point nonadiabatic coupling calculation.
Prepare either:
1)
gamessinput_original.inp: runtyp=nacme without $DATA and $VEC
gamessinput_original.vec: $VEC group
2)
nx_gamess.inp: runtyp=nacme with $DATA and $VEC

Parameters to control GAMESS jobs

Name: gamess.par

Parameter	Default	Description

VERNO	= [00]	Version number of GAMESS executable.
NCPUS	= 1	Number of computer processes to be run.
RUN_GAMESS	= [rungms]	Name of GAMESS execution script.
SCR	= [0]	GAMESS scratch directory: 0: Use default GAMESS options as defined in RUN_GAMESS script. 1: Create SCR directory inside TEMP directory of NEWTON-X.
MOCOEF	= [1]	0: use the initial molecular orbitals in all time steps 1: use the mocoef file from the previous time step k: Lagrangian extrapolation of molecular orbitals at order k-1 ($k \leq 11$) (see Section 12.1.10)

12.1.5.14 HYBRID GRADIENTS (QM/MM)

The hybrid gradients module allows adiabatic and nonadiabatic dynamics with combinations of programs (COLUMBUS, TINKER, TURBOMOLE, and Analytical Model). The current implementation is described in Ref.[35].

General explanations of hybrid calculations

Energies and gradients for subsets of atoms are treated with different programs, and the partial gradients are then joint into a resulting total (hence 'hybrid') energy and gradient. For that purpose, the set of atoms of the whole system is split into disjoint regions. These regions need not to follow physical reasoning (they often will, but the can also pick, e.g. single atoms out of molecules), but are logical entities for the definition of the single partial calculations.

The whole calculation is split into jobs. Each of these jobs can treat one or more regions of atoms, and the partial result are multiplied by a user-defined factor before being added to the total. One region can be treated by multiple jobs and to care about 'double counting' of atoms is left to the user completely.

For COLUMBUS and TURBOMOLE there is the possibility to include regions only as point charges and not as atoms with basis-set. A hybrid setup (which is done in the JOB_AD or JOB_NAD directory) consists of some general information about the hybrid setup ('control' parameters), the definition of the atoms, some of their properties and membership to the regions and the definition of the partial jobs, which regions they are concerned with and how they shall be put together to the overall result. The main input file is named hybrid_gradients.inp.

The nonadiabatic couplings, oscillator strengths, and other nonadditive properties are given by only one job. It is possible to restrict the hybrid NAD-vectors to some regions. The NAD-vector components on all atoms not belonging to these regions are replaced by Zeros in this case. Also for back hoppings only the kinetic energy of these nad-regions is regarded as available energy.

For the treatment of bonded interaction between two regions link atoms can be inserted in bond connecting them. The gradient- and nonadiabatic coupling vector elements of these link atoms will be distributed to the two atoms between which it has been inserted. To avoid over-polarization effects, the point charges near the link atom can be set to zero and, so as to retain the overall charge, re-distributed to a set of other atoms. The job, where the link atom is inserted is (suggestively) called ‘QM_JOB’ regardless of the method really used in this job. Similarly is the naming of ‘QM_ATOM’ and ‘MM_ATOM.’

Format of the hybrid_gradients.inp file

Each section begins with $<name> and ends with $end, where <name> can be 'control', 'job' or 'atoms'. Parameters for sections '$control' and '$job' are set in key=value pairs. All key=value pairs have to be separated with blanks.

Name: hybrid_gradient.inp

Section	Keyword	Description
$control	NATOMS	number of atoms (optional)
	PROPERTIES	ID of the job, that gives the properties (oscillator strength, nonadiabatic couplings, optional)
	NADREGIONS	array of regions to which the hybrid nad-vector shall be restricted
$job	ID	unique numeric (integer) identification for the job
	PROGRAM	name of the program to be used for this job *(Columbus, Tinker, Turbomole)*
	REGIONS	array of regions, that shall be treated by this job *(comma separated)*
	FACTOR	pre-factor with that the result of this job enters the total result (energy, gradients)
	POINTCHARGES	array of regions, that shall be treated as point-charges *(for Columbus and Turbomole, comma separated, optional)*
$atoms	(For each atom give in one single line and in this order:)	
	<name>	Label for an atom (compulsory). Can be anything without blanks, comma and similar. The type of atom is recognized from the nuclear charge.
	<nuclear charge>	Nuclear charge.
	<x,y,z coords>	Cartesian coordinate (Bohr).
	<pointcharge>	Effective point charge for this atom. If this atom is not treated as point charge, this can be left to 0.0000.
	<mass>	Atomic mass for this atom (amu).
	<region>	The region in which this atom is.
link	QM_JOB	ID of the job where the link atom shall be inserted.
	QM_ATOM	number (=position in input) of the atom connected to the link atom at the QM-side.
	MM_ATOM	number (=position in input) of the atom connected to the link atom at the MM side.
	RATIO	ratio of distances QMat→LINKat/QMat→MMat.
	ZERO	comma separated list of atoms for which the point charge shall be set to 0.000 in the QM_JOB.

SCATTER	comma separated list of atoms to which the accumulated charge of the ZERO-atoms shall be distributed.

The section $atoms is an extension of the NEWTON-X geom. with the two additional columns, <pointcharge> and <region>.

Each atom has to be in **exactly one** region.

All values in section $atoms have to be separated with blanks.
Every section has to be ended with $end. No section (except '$jobs') is allowed to appear twice.
There are no further formatting rules to the file.

Example of hybrid_gradient.inp file:

```
$job ID = 1  regions = 1,2  program = columbus  pointcharges = 2  factor = 1 $end
$job ID = 2  regions = 1,2  program = tinker  factor = 1 $end
$job ID = 3  regions = 1  program = tinker  factor = -1 $end
$control  properties = 1  nadregions = 1 natoms = 9 $end
$atoms
         C   6.0    -0.58698100    -0.10086826     0.12744020    12.00000000   0.0000   1
         O   8.0     1.68492145     0.00195156     0.55748655    15.99491464   0.0000   1
         N   7.0    -1.73272850    -2.27661770    -0.35180374    14.00307401   0.0000   1
         H   1.0    -1.76941972     1.58570542     0.11857328     1.00782504   0.0000   1
         H   1.0    -3.64014444    -2.31932440    -0.70744017     1.00782504   0.0000   1
         H   1.0    -0.69532029    -3.86742067    -0.35771869     1.00782504   0.0000   1
        OW   8.0    -6.90020375    -2.40598424    -1.31691242    15.99491464  -0.8340   2
        HW   1.0    -7.75621060    -2.20340156    -2.90625351     1.00782504   0.4170   2
        HW   1.0    -8.26652850    -2.54571452    -0.12804111     1.00782504   0.4170   2
$end
```

This example is explained in details in the NEWTON-X tutorial.

Example including link atoms (some lines not displayed):

```
# 2-butene with cyclohexane rings attached to the sides
# Z2-scheme is used for point charges,i.e. first and second
#    neighbour to the link atom have zero charges and the
#    their charge is distributed to their next-neighbours on the MM side

$job ID=1 regions=1,2,3 program=turbomole turbo_method=TDDFT pointcharges=2,3  factor=1 $end
$job ID = 2  regions = 1,2,3  program = tinker  factor = 1 $end
$job ID = 3  regions = 1  program = tinker  factor = -1 $end
$link qm_job=1 qm_atom=1 mm_atom=11 ratio=0.713 zero=11,12,13,14 scatter=15,16,17 $end
$link qm_job=1 qm_atom=4 mm_atom=34 ratio=0.713 zero=34,35,36,37 scatter=38,39,40 $end
$control  properties = 1 nadregions=1 natoms = 56 $end

$atoms
    C   6.0     1.44087838     0.85091533    -3.47469613    12.00000000   0.0000   1 #atom 1
                                                                        # linked to atom 11
    C   6.0     1.23567680    -0.48733580    -6.00452731    12.00000000   0.0000   1
    C   6.0     2.80448775    -2.25355699    -6.92713507    12.00000000   0.0000   1
    C   6.0     5.12903987    -3.34336584    -5.64481794    12.00000000   0.0000   1 #atom 4
                                                                        # linked to atom 34
    H   1.0     1.17513186     2.91664300    -3.78035178     1.00782504   0.0000   1
    H   1.0     3.36724819     0.62483228    -2.66873550     1.00782504   0.0000   1
    H   1.0    -0.40125500     0.07262218    -7.17351567     1.00782504   0.0000   1
    H   1.0     2.39776578    -3.02448967    -8.82452971     1.00782504   0.0000   1
    H   1.0     4.98819669    -5.44423296    -5.69313068     1.00782504   0.0000   1
```

```
    H   1.0     5.18046121    -2.82088113    -3.61093594     1.00782504   0.0000   1
   CT   6.0    -0.52739233    -0.13060275    -1.57905516    12.00000000  -0.1200   2 #atom 11
   HC   1.0    -0.25927609    -2.20323737    -1.33315643     1.00782504   0.0600   2
   HC   1.0    -2.45999068     0.14865342    -2.36823880     1.00782504   0.0600   2
   CT   6.0    -0.33457412     1.20138205     0.99721226    12.00000000  -0.1200   2
   HC   1.0     1.56440222     0.83732631     1.83045298     1.00782504   0.0600   2
   HC   1.0    -0.45614398     3.28079700     0.68304340     1.00782504   0.0600   2
    :    :       :     :        :     :        :     :        :     :      :  :# lines omitted
   CT   6.0    -2.23690095     2.08870485     5.28849685    12.00000000  -0.1200   2
   HC   1.0    -0.32070164     1.91506358     6.14394752     1.00782504   0.0600   2
   HC   1.0    -2.48154867     4.11306830     4.76133507     1.00782504   0.0600   2
   CT   6.0     7.60087913    -2.51304285    -6.92702736    12.00000000  -0.1200   3 #atom34
   HC   1.0     9.21362621    -3.51540650    -6.01449183     1.00782504   0.0600   3
   HC   1.0     7.56925645    -3.13134234    -8.93790950     1.00782504   0.0600   3
   CT   6.0     8.05428868     0.35505686    -6.77227957    12.00000000  -0.1200   3
   HC   1.0     7.92399962     0.94155983    -4.75349648     1.00782504   0.0600   3
   HC   1.0     6.51305828     1.36826754    -7.78612331     1.00782504   0.0600   3
   CT   6.0    10.63311478     1.21580066    -7.83079266    12.00000000  -0.1200   3
   HC   1.0    12.15373961     0.13167423    -6.84744154     1.00782504   0.0600   3
    :    :       :     :        :     :        :     :        :     :      :  :# lines omitted
$end
```

Generating and updating the remaining input files

After having written hybrid_gradient.inp file, the complete set of input files can be created by run

```
$NX/hybrid_read_onefile.pl
```

Subdirectories for the different jobs will be created as well. Appropriate geom files for each job are provided in these subdirectories. Set up the third-party single jobs inputs in the subdirectories in the same way as for normal NEWTON-X dynamics. If you chose to include some atoms as point-charges to a COLUMBUS- or TURBOMOLE-job you have to set the jobs up appropriately. Refer to the documentations of the programs for information on how to do that (hybrid_read_onefile.pl will provide some useful files containing most of the things that have to be done extra to a normal setup).

In the subdirectories for partial hybrid jobs to be computed with COLUMBUS including point-charges, two files 'potential.xyz' and 'elpotin' are provided. Do not delete these files!

In the subdirectories for partial hybrid jobs to be computed with TURBOMOLE including point-charges two files ‘pointcharges’ and ‘control-additions’ are provided. Do not delete the pointcharges-file. The contents of the file ‘control-additions’ have to be inserted in the control-file at an appropriate position after setting up the TURBOMOLE calculation.

If any change is done to hybrid_gradient.inp, hybrid_read_onefile.pl should be run again to update the remaining files.

12.1.6 Thermostat control

Thermal-equilibration may be obtained during the dynamics by using a thermostat [34]. In the current NEWTON-X version, the Andersen thermostat is available [33]. The parameters of the thermostat may be adjusted by using nxinp tool, in the input section “Set General Options”. The options are given below.

Name: therm.inp
namelist therm

Parameter	Default	Description
KTHERM	= [1]	Thermostat type:

		0 - No thermostat. 1 - Andersen [33].
TEMP	= [300]	Temperature (K).
KTS	= [1]	Turn the thermostat on at time step KTS. (KTS ≥ 1, integer)
LTS	= [-1]	Turn the thermostat off at time step LTS. (LTS > KTS, integer) -1 - Do not turn it off.
NSTHERM	= [1]	If the system is in the excited state: 0 - turn the thermostat off. 1 - apply the thermostat.
GAMMA	= [0.2]	Collision frequency (fs^{-1}).
RADIUS	= [10.0]	Collision radius (bohr). (Only in Andersen-Lowe thermostat.)
ISEED	= [1]	Random number seed for the thermostat. 0 - default seed value. 1 - generate random seed. > 1 - use this value (integer) as the seed.
LVP	= [1]	Print level. (In any case, relevant information is written to NEWTON-X log.) 1 - Do not print thermostat log file. 2 - Print minimum thermostat log file. 3 - Print debug-level thermostat log file.

Example of therm.inp file:

```
&therm
  ktherm = 1
  kts = 1
  lts = -1
  nstherm = 1
  temp = 300
  gamma = 0.6
  iseed = 0
  lvp = 3
&end
```

You can choose a subset of atoms that will not be affected by the thermostat. For that, a list of atoms should be given in a file called therm.freeze. This file should be given together with the other input files. The atoms in the list are identified by its positions in the geom file, and the list is blank-separated.

Example of therm.freeze:

```
1 3
```

(Atoms one and three in geom file will not be affected by the thermostat.)

If a file freeze.inp is present in the input, the atoms defined there will also not be affected by the thermostat (see section 12.1.4).

12.1.7 Nonadiabatic dynamics control

The nonadiabatic dynamics is controlled by two input files, sh.inp and jiri.inp.

SH is a stand-alone module for surface-hopping. It reads nuclear velocities and nonadiabatic couplings and gives as output the electronic wavefunction expansion coefficients on the adiabatic set of states. Switch from one adiabatic PES to another is ruled by the Tully's fewest switches algorithm [13].

The parameters for nonadiabatic dynamics can be set via nxinp tool, at the input option "Set nonadiabatic dynamics". The options are given below.

Name: sh.inp
namelist shinp

Parameter	Default	Description
VDOTH	= [0]	Dynamics with nonadiabatic coupling vectors or with time-derivative couplings (DD or OD models [10, 22]). -1 – Local-diabatization method.[30] 0 - Compute nonadiabatic coupling vectors. 1 - Compute time-derivative couplings.[22] The default is reset to 1 for methods without nonadiabatic coupling vectors (ADC(2), TDDFT, etc.). OD or DD is chosen with CPROG keyword.
SEED	= [1]	0 a default random-number seed is used. 1 a randomized seed is used >1 random number seed
INTEGRATOR	= [5]	selects the integrator of the TDSE: 0 - a "home-made" integrator, see Ref. [21]. 1 - standard 4th order Runge-Kutta. 2 - Adams Moulton predictor-corrector, 5th order. 3 - Adams Moulton predictor-corrector, 6th order. 4 - Unitary propagator. 5 - Butcher, 5th order.[73] 6 – Unitary propagator for Local-Diabatization method. Good choices are usually 3, 4, and 5. For vdoth = -1 (local diabatization) integrator must be 6.
PHASE	= [1]	Integrate the phase along the trajectory (only for debug purposes): 0 - No. Phase is always zero. 1 - Yes.
NOHOP	= [0]	Force the hopping at a certain time step. 0 - The trans. prob. are computed, and hopping is allowed (normal surface hopping). -1 - Hopping is not allowed at any time. n - Hopping is forced at (and only at) timestep n (n = positive integer).
FORCESURF	= [1]	Force the hopping to the surface FORCESURF (ground state = 1).
NRELAX	= [0]	number of cycles after a surface hopping, in which other hopping is forbidden.
MS	= [20]	number of subtime-steps for integration of the time-dependent Schroedinger equations is dt/ms, where dt is the time-step of the classical trajectory defined in control.dyn file. In the ms-1 substeps between t and t+dt, the nonadiabatic coupling vector and the velocity vector is obtained by linear interpolation. The potential energy is interpolated with a cubic polynomial. 0 - Do not interpolate. 1 - Time-step will be divided by one. The results are the same as using ms = 0, but now the interpolation programs are called. For vdoth = -1 (local diabatization), ms must be 0.
GETPHASE	= [1]	0 use phase provided by the overlap of CI vectors.

1 use phase provided by the scalar product between h(t) and h(t-dt). Usually, this is the best choice for multistate dynamics.

TULLY = [1] Fewest-switches algorithm:
0 - Tully [13].
1 - Hammes-Schiffer and Tully [10].
For Local Diabatization (VDOTH = -1), the fewest switches probability formula is given by Eqs. 17-19 of Ref.[30].

DECAY = [0.1] Apply the decoherence correction to the time-dependent coefficients C_K of state K [23]. The value of DECAY is assumed by the variable α in the equations:

$$C_K^{'} = C_K \exp\left(-\Delta t / \tau_{KM}\right) \quad \forall K \neq M ,$$

$$C_M^{'} = C_M \left[\frac{1 - \sum_{K \neq M} \left| C_K^{'} \right|}{\left| C_M \right|^2} \right]^{1/2} ,$$

$$\tau_{KM} = \frac{\hbar}{\left| E_K - E_M \right|} \left(1 + \frac{\alpha}{E_{kin}} \right) ,$$

where M is the current state and E_{kin} is the nuclear kinetic energy. α (DECAY) must be given in atomic units (Hartree). The recommended value is α = 0.1 Hartree. -1 means normal calculation (without correction). After integrating the TDSE to obtain the coefficients $\boldsymbol{C}$ and using the fewest-switches to determine the current state M, the equations above are used to obtain the coefficients $\boldsymbol{C}'$. The $\boldsymbol{C}'$ are then used to continue the time evolution of the electronic wave function.

PROBMIN = [0] Do not hop if probability is smaller than PROBMIN.

MOM = [1] After a frustrated hopping:
-1 - Invert momentum direction.
1 - Keep momentum direction.

ADJMOM = [0] After a hopping, adjust momentum:
-1 - along the momentum direction.
0 - along the nonadiabatic coupling vector **h**.
90 - along the gradient difference vector **g**.
For any value larger or equal to 0, ADJMOM is assumed to be an angle α in degrees, which defines the unitary vector

$$\hat{\varepsilon} = \sin(\alpha) \frac{\mathbf{g}}{\|\mathbf{g}\|} + \cos(\alpha) \frac{\mathbf{h}}{\|\mathbf{h}\|}$$

The momentum is adjusted in the direction of $\hat{\varepsilon}$.
Note: Until NEWTON-X version 0.10a, the definition of ADJMOM and the default value were different. Check old input files before running.
The default is reset to -1 if VDOTH = 1.

POPDEV = [0.05] Kill trajectory if total adiabatic population deviate more than POPDEV from the unity.

Example of sh.inp file:

```
&shinp
  seed=0,
  integrator=4,
  nrelax=0,
  ms=10,
  getphase=1,
&end
```

The following keywords in jiri.inp file allow additional control over the nonadiabatic coupling calculations by restricting which states should be included in the calculations. In combination with THRES defined in control.dyn, it is possible to substantially reduce the computational costs by excluding couplings that should not contribute to the hopping probabilities[22]. The default (THRES = 0, KROSS = 1, CASCADE = 0, CURRENT = 1, NEVER_STATE = 0, INCLUDE_STATE = 0) implies that all possible coupling vectors between the current and the other states will be computed. When time derivative couplings are used (VDOTH = 1), the default of NEVER_STATE = 1, meaning that nonadiabatic coupling with the ground state is not computed. When OD approach is used to compute couplings (CPROG = 2 in jiri.inp), these keywords are ignored. In this case, all couplings between excited states are computed, and couplings between an excited state and the ground state are neglected.

Internally, the restrictions implied by these keywords are independently applied to the complete list of $N_C = N_{stat}(N_{stat}-1)/2$ possible coupling vectors, and the result is a restricted list of couplings. This information is written every timestep to the file transmomin. Thus, the list of coupling vectors that should be computed is dynamically updated along the simulation. If a transmomin file is given with the input in JOB_NAD, it will be replaced by the new one already in step 0.

Name: jiri.inp
Namelist: jirinp

Parameter	Default	Description
KROSS	= [1]	0 - do not calculate nonadiabatic couplings between non-consecutive states. For example, between S_0 and S_2. 1 - calculate nonadiabatic couplings between non-consecutive states.
CASCADE	= [0]	Compute nonadiabatic couplings only for states below the current state and state: 0 - above and below (e.g., in S_2 get S_2-S_1 and S_2-S_3) 1 - only below (e.g., in S_2 get S_2-S_1 but not S_2-S_3)
CURRENT	= [1]	Compute nonadiabatic couplings only for pairs of states including the current state.
NEVER_STATE	= [0]	Array of states for which the nonadiabatic coupling vectors should never be computed. E.g., if never_state=1,2: don't compute couplings with S_0 or S_1 (1 – ground state). The array must be comma separated. The maximum number of states in the array is 10. The default (0) means do not exclude any state. The default is 1 when VDOTH = 1.
INCLUDE_PAIR	= [0]	Define the pairs of states for which the nonadiabatic coupling vector for the following pairs should always be computed when the current state is one of the states in the pair. E.g., include_pair=1,2,1,3: when the molecule is in S_0, always compute couplings S_0-S_1 and S_0-S_2 (1 – ground state). The array must be comma separated. The maximum number of pairs is 5.
E_CI	= [0.2]	Check the energy difference between every pair of states and report it when this difference drops below the e_ci threshold (in eV). The information is written to RESULTS/report.CI and it is useful to locate conical intersections.

If VDOTH ≠ 0 in sh.inp:

CI_CONS	= [1]	0 - Compute all determinant overlap terms. 1 - Neglect determinant overlap terms when the hank is too high or when the determinants are orthogonal.
CIO_OPTIONS	COLUMBUS: =[“-t 5e-4 -e 2 -i”] TURBOMOLE: CC2, ADC(2): =[“-s transmomin -a -t 5e-4 -e -1”] TURBOMOLE: TDDFT: =[“-s transmomin -a -t 5e-4 -e -1”] GAUSSIAN: TDDFT: =[“-s transmomin -a -t 5e-4 -e -1”] DFTB+: =[“-s transmomin -a -t 5e-3 -e -1”]	Options to the cioverlap program (given in quotation marks). See detailed description in section 16.6.
CISC_OPTIONS	COLUMBUS: =[“”] TURBOMOLE: CC2, ADC(2): =[“”] TURBOMOLE: TDDFT: =[“-o”] GAUSSIAN: TDDFT: =[“-o”] DFTB+: =[“-o”]	Options to the cis_casida program (given in quotation marks). See detailed description in section 16.6. For TDDFT and TD-DFTB wavefunctions: • cisc_options = "": use **(X+Y)** without orthonormalizing • cisc_options = "-c": use **F** without orthonormalizing • cisc_options = "-o": use **(X+Y)** and orthonormalize it (recommended) • cisc_options = "-c -o": use **F** and orthonormalize it
NCORE	= [0]	Number of core orbitals that should be ignored in the CIS Casida procedure (using the -i option of the cis_casida executable).
NDISC	= [0]	Number of virtual orbitals that should be ignored in the CIS Casida procedure (using the -I option of the cis_casida executable).
CPROG	= [1]	Method to compute the approximate couplings: 1- Approximate derivative couplings using the Hammes-Schiffer and Tully approach with DD approach. (section 12.1.8) [10] 2- Approximate derivative couplings OD method (See description in section 12.1.9)
COPTDA	= [1]	Linear response vectors used in the evaluation of NAD 0- |X> 1- |X+Y>
BLASTHREAD	= [1]	Number of CPU cores used by BLAS in CIOVERLAP programs. 1- Serial execution. > 1 - Parallel execution. Beware of this option: cioverlap program may freeze for large number of cores.

Example of jiri.inp file:

```
&jirinp
 kross    = 0
 cascade  = 1
/&end
```

Do not forget "&jirinp" and "/&end".

There are eight possible combinations of the keywords KROSS, CASCADE and CURRENT. Each one corresponds to a different model. The models are called: two-state (TS), three-state (3S), horizontal coupling (HC), lower diagonal (LD), partial coupling (PC), neighbor coupling (NC), lower triangular, and complete coupling (CC).[22] In the Table below, the keyword combination for each of these models is given, as well as the number N_c of coupling vectors computed in each time step. An example of which coupling vectors are actually computed in the case of dynamics with N_{stat} = 5 states with the molecule instantaneously in $N_{statdyn}$ = 3 state is also shown in the Table. The bold line shows the default option.

kross	cascade	current	Model	N_c	Example: NSTAT=5,NSTATDYN=3									
					21	31	32	41	42	43	51	52	53	54
0	1	1	TS	1			x							
0	0	1	3S	2			x			x				
1	1	1	HC	$N_{statdyn}-1$		x	x							
0	1	0	LD	$N_{statdyn}-1$	x		x							
1	**0**	**1**	**PC**	**$N_{stat}-1$**		**x**	**x**			**x**			**x**	
0	0	0	NC	$N_{stat}-1$	x		x			x				x
1	1	0	LT	$N_{statdyn}(N_{statdyn}-1)/2$	x	x	x							
1	0	0	CC	$N_{stat}(N_{stat}-1)/2$	x	x	x	x	x	x	x	x	x	x

In addition to these eight models, other combination can be built by using the keywords NEVER_STATE, INCLUDE_PAIR, and THRES (in control.dyn). For example, the following jiri.inp:

```
&jirinp
 kross    = 0
 cascade  = 1
 current  = 1
 include_pair = 1,2
/&end
```

will result in a modified TS model for which the coupling vector from state 1 (ground) to state 2 is computer whenever the molecule is in state 1.

12.1.8 Time-derivative couplings with DD approach

Dynamics using time-derivative couplings to compute the nonadiabatic surface hopping probabilities can be performed with COLUMBUS (MCSCF, MRCI), TURBOMOLE (TDDFT, TDA, CC2, ADC(2)), GAUSSIAN ((U)TDA,(U)TDDFT,(U)CIS), and DFTB+ (TD-DFTB). The method was proposed by Hammes-Schiffer and Tully,[10] who showed that time-derivative couplings could be computed from wavefunction overlaps. The current implementation based on the determinant derivative (DD) approach for MRCI and TDDFT is described in Ref.[22]. For ADC and CC2, it is described in Ref. [28]. For TD-DFTB, Ref. [41].

For all available single reference methods, the DD approach can be used not only to compute couplings between excited states but also between an excited state and the ground state. Nevertheless, because these methods cannot adequately describe the multireference character of the electronic wavefunction near intersections with the ground state, these latter coupling values may not be reliable.

12.1.9 Time-derivative couplings with OD approach

Overlap-based time-derivative couplings can also be computed using the orbital derivative (OD) approach proposed in Ref.[14]. The method is available in the TURBOMOLE (TDA, ADC(2), CC2), Gaussian (TDA, TDDFT, and CIS), and DFTB+ (TD-DFTB) interfaces. This method replaces the evaluation of the derivatives of the Slater determinants for the evaluation of the time derivative of the

molecular orbitals, reducing the computational cost. This is specified in the jiri.inp with CPROG=2. The current implementation[29] only allows calculating the couplings between excited states.

12.1.10 Wave function coefficients

The real and imaginary parts of the coefficients of the time-dependent Schroedinger equation are automatically updated to the file wfrun during the dynamics. The default is to start the dynamics with 1.0 at the initial state and 0.0 for all other states. It is possible to change this default by just including wf.inp as an additional input file, with the format:

```
Re(C_1) Im(C_1)
Re(C_2) Im(C_2)
...
Re(C_NSTATDYN) Im(C_NSTATDYN)
...
Re(C_NSTAT)    Im(C_NSTAT)
```

For example, the default for a two-state dynamics (S_0 and S_1), starting in S_1 is:

```
0.0 0.0
1.0 0.0
```

One possibility to start with 20% at S_2 and 80% in S_1 is:

```
0.894427191  0.0
0.447213596  0.0
```

12.1.11 Propagation of molecular orbitals

The keyword MOCOEF, appearing in some of the <third-party>.par files, controls how the molecular orbital coefficients are transferred from one step to the following. The original (time step n = 0) coefficients may be used, or the coefficients from step n may be given as guess for step n+1 (COLUMBUS, GAUSSIAN, AND GAMESS).

A set of k molecular orbital coefficients computed between steps n-k and n can also be extrapolated to create the guess for step n+1 (COLUMBUS AND GAMESS). This is done by means of Lagrangian Extrapolation of Molecular Orbitals (LEMO) algorithm described in Ref. [32]. Briefly, the molecular orbital coefficient guess ($\mathbf{c}_{guess}$) for step n+1 is given in terms of the previously converged coefficients ($\mathbf{c}_{conv}$) by

$$c^{n+1}_{guess,i,j} = \sum_{l=0}^{k-1} L_{k-1,l} c^{n-l}_{conv,i,j}, \quad \left(1 \le i \le n_{bas},\ 1 \le j \le n_{bas}\right), \tag{27}$$

where **L** is the set of Lagrangian coefficients for polynomial interpolation and n_{bas} is the number of basis functions.

The treatment of orbital rotations in the version of LEMO algorithm implemented in NEWTON-X differs from the one proposed in Ref. [32]. In NEWTON-X, the overlap factor

$$S_i^{n,n-k} = \frac{\sum_{j=1}^{n_{bas}} c^{n}_{conv,i,j} c^{n-k}_{conv,i,j}}{\sum_{j=1}^{n_{bas}} \left(c^{n}_{conv,i,j}\right)^2}, \quad \left(1 \le i \le n_{mo}\right) \tag{28}$$

is computed for a sub-set of n_{mo} orbitals, usually the occupied ones. If $S_i^{n,n-k} < S_{min}$, then the orbital i is not extrapolated and it is given by

$$c^{n+1}_{guess,i,j} = c^{n}_{conv,i,j}. \tag{29}$$

In the current version, n_{bas} and n_{mo} are automatically set by NEWTON-X reading the COLUMBUS input files. S_{min} is set to 0.7.

For a given extrapolation order *k*-1, *k* sets of molecular orbital coefficients are necessary. At the beginning of the dynamics, while the step number is still smaller than *k*, the LEMO algorithm is executed at lower extrapolation order, using the molecular orbital sets available.

12.1.12 Boundaries

The system can be included in rigid boundaries (at the moment, only spherical). If the file 'boundaries.inp' is present in the treatment of boundaries is activated.

In the spherical boundary, if any molecule attempts to move outwards, it undergoes an elastic collision, and their radial velocity is inverted.

Name: boundaries.inp

Parameter	Description
INSPHERE	Include system in a rigid sphere. At the second line give the radius and Cartesian coordinates for the center of the sphere in Bohr. rr.r xx.x yy.y zz.z

12.1.13 Stop conditions

It is possible to define quite arbitrary set of conditions that when satisfied will cause the end of the simulations. This is done through a series of conditions connected by logic operators written to stopsign.inp file.

Each condition X (integer) with operator Y (and, or) is defined by four keywords.

Name: stopsign.inp

Parameter	Description
%comm_Y[X]	Single line Perl command to collect information to be checked.
%text_Y[X]	Description of the command.
%oprt_Y[X]	Any of: `==, !=, eq, ne, <, <=, >, >=` (Perl operators)
%thrs_Y[X]	Threshold or value to be tested.

No defaults are available. An arbitrary number of conditions can be set.

Using the information from stopsign.inp, NEWTON-X automatically writes a Perl program called ss-script.pl. ss-script.pl is run every timestep, checks the conditions and writes the values for each one to ss-Y-X file. Then, it reads these values and if the conditions to stop are satisfied (considering all AND and OR operations), it writes the instruction "%STOP" to ss-result file. moldyn.pl checks the contents of ss-result every time step. If it finds %STOP, the trajectory simulation is ended.

Example: Stop trajectory if the energy gap between the ground state and the first excited state is smaller than 0.2 eV.

In this case, only one condition should be checked. The stopsign.inp may look like:

```
%comm_and[1] %= open(IN,"epot");$e0=<IN>;$e1=<IN>;$de=($e1-$e0)*27.21138386;
open(OUT,">ss-and-1");print OUT $de;close(OUT);close(IN); # %comm_and[1] must be
%text_and[1] %= "E1-E0 (eV)"                                given in a single line!
%oprt_and[1] %= <=
%thrs_and[1] %= 0.2
```

%comm_and[1] is a single line instruction in Perl to read the values of the ground state ($e0) and excited state ($e1) energies from epot file, to compute the difference and convert it to eV ($de) and to print this value to ss-and-1 file.

The condition to be satisfied is:

```
%text_and[1]   %oprt_and[1] %thrs_and[1]
"E1-E0 (eV)"       <=            0.2
```

12.1.14 Repeating dynamics calculations

It is possible to use a precomputed sequence of geometries (for instance, from another dynamics simulation) as an input for NEWTON-X (version 2.2 build 06 and above).

If LEVLPRT = 5 in control.dyn, then Newton-X will not integrate the classical equations for the nuclei and it will take the geometries from a geom.list input file. geom.list should contain a sequence of geometries in conventional xyz format (Angstrom).

A sequence of velocities can also be provided in the input file veloc.list. The velocities in veloc.list should be atomic units (same format as in veloc file) and with a blank line separating each time step. If veloc.list is not present, NEWTON-X estimate the velocity from the difference between two consecutive geometries divided by the time step.

Such jobs may not conserve energy. Therefore, ETOT_JUMP and ETOT_DRIFT in control.dyn should be set to large values (100, for instance).

12.2 How to execute NEWTON-X

Having all input files at the same directory, type:

```
$NX/moldyn.pl > moldyn.log &
```

where $NX is the variable containing the path to the NEWTON-X files.

12.3 Output files

The output files are written to RESULTS directory.

1) The main output with a survey of the dynamics is written to dyn.out.

2) nx.log contains information about gradients, nonadiabatic coupling vectors and state configurations along the trajectory.

3) File dyn.mld contains a sequence of cartesian coordinates in conventional XYZ format with the dynamics history. It can be read by most of graphic programs such as MOLDEN, MOLEKEL or VMD.

4) File intec contains the internal coordinates for each time step.

5) File en.dat contains the potential energy (au) of each state for each time step (fs) in the following order: Time, Epot(S0), Epot(S1), ..., Epot(nstat), Epot(nstatdyn), suitable to produce Energy x time graphs.

6) At each time step, the random number, the cycle and the transition probabilities (in this order) are written to tprob. Hopping events are marked with 20 in the pace of the actual random number. The file tprobbyfs gives similar information but in fs^{-1} units.

7) At each time step, the populations, the wave function normalization and the product **v**.**h** are written to sh.out.

8) File properties contains oscillator strengths and transition dipole moments for each time step (when available).

9) File report_CI contains informs the trajectory point with energy gaps smaller than E_CI. Useful to locate conical intersections.

10) At every hopping the geometry and velocity are written out as hopp_geom.<surf1>.<surf2>.<time> and hopp_veloc.<surf1>.<surf2>.<time>

In DEBUG directory:

11) File log.conv (DEBUG directory) gives information about the convergence of the ab initio calculations during the dynamics.

12) Dynamics using COLUMBUS program keeps the molecular orbital coefficients for each time step t in the respective subdirectory DEBUG/COL.t.

13) Error messages are written to runnx.error file.

14) With lvprt ≥ 2, lots of debug data are written to this directory.

In INFO_RESTART directory:

15) At each time step the INFO_RESTART directory is updated with all necessary information to restart the trajectory if it is necessary. Specific information about the restart status can be found in INFO_RESTART/restart.inf.

12.4 Restarting the job

To restart trajectories:

1) Replace the original control.dyn by the modified control.dyn written to the INFO_RESTART directory. (It may be necessary to set a new value for TMAX in this file.)

2) Run the job again in the usual way.

When control.dyn contains NXRESTART = 1, NEWTON-X uses the files contained in INFO_RESTART directory as new inputs input files. INFO_RESTART/control.dyn, however, is not used and should be copied to the input directory as indicated in point 1) above. If any keyword should be changed in the restarted job, this must be done in the INFO_RESTART files (except in the case of control.dyn).

With NXRESTART = 1, the contents of DEBUG, RESULTS and INFO_RESTART directories are not deleted, and NEWTON-X produces a continuous output with the previous and the restarted job together. In the case of jobs running in a batch system, be sure of copying these directories to the node machine together with the other input files.

The content of INFO_RESTART directory can also be used to restart an independent job, without reference to the previous one. In this case, use NXRESTART = 0 or simply delete this keyword in control.dyn.

It is advisable to back up the trajectory before restarting it.

12.5 Customized analysis

If an executable file NX_analysis is present, it will be executed after every time step. This option requires some familiarity with the NEWTON-X file structure, but it gives the possibility of performing specific customized tasks without having to modify the source code. An example NX_analysis file could look like this:

```
#!/bin/bash
echo "Performing custom analysis"
/mypath/analysis1.x >> ../RESULTS/ana1.log
/mypath/analysis2.x JOBEX_1.columbus/WORK/ciudgls* >> ../RESULTS/ana2.log
```

This set of instructions in the example will run the programs analysis1.x and analysis2.x provided by the user and then write the results to ana1.log and ana2.log, respectively. Note that NX_analysis is executed inside TEMP (see Figure 1). Therefore, the RESULTS directory is reached by ../RESULTS.

13 Statistical analysis

ANALYSIS is a set of programs developed to analyze the results of the molecular dynamics simulation performed with NEWTON-X.

The program evaluates the mean value and the standard deviation over several trajectories for several properties. The result is given in function of time.

The input for statistical analysis can be done using nxinp, option

```
6. SET STATISTICAL ANALYSIS
```

Then a sequence of submenus gives a series of options which are discussed below. The input and the analysis execution should be done in the directory containing the TRAJi results.

13.1 What is needed to run

1. The ANALYSIS program reads the results written into the TRAJi/RESULTS directories, where i is the number of each trajectory. This structure of directories is automatically generated by the program makedir.pl (see section 6.5).

2. File prop.inp should contain the main parameters for the analysis:

Parameter	Default	Description
ITRJ	= [1]	initial trajectory to be analyzed.
JTRJ	= [10]	final trajectory to be analyzed.
TMIN	= [0]	initial time for the analysis (fs).
TMAX	= [100]	final time for the analysis (fs).
DT	= [0.5]	time step (fs) with which outputs are written. If, for example, dynamics run with DT = 0.5 fs and KT = 3 in control.dyn, the outputs were written every DT*KT = 1.5 fs. Therefore, the time step for analysis should be DT = 1.5. If TRAJ(ITRJ)/control.dyn is found, DT and KT are read from this file and default is DT*KT, otherwise default is 0.5 fs.
PROPTYPE	= [1]	Kind of properties to be analyzed. 1. Energy. 2. Wave function. 3. Internal coordinates. 4. Internal forces (only for PROG = 1 in NEWTON-X (COLUMBUS dynamics)). 5. Velocity autocorrelations function. 6. Nuclear configurations and fragments.
RUN_IS	= [0]	0. Target and sampling probability density functions are the same. 1. Compute observables for a target probability density function different from the sampling one.
The next keywords are needed only if PROPTYPE = 1-4 or 6:		
NSTAT	= [2]	Number of states to be analyzed.
The next keywords are needed only if PROPTYPE = 2:		

COMPLETE_DATA	= [0]	Complete data for broken trajectories. 0. Do not complete data. Other positive value. If the last time in the trajectory is larger than COMPLETE_DATA, repeat the last set of data until TMAX. Neglect trajectories whose last time is smaller than COMPLETE_DATA.

The next keywords are needed only if PROPTYPE = 3 or 4:

NIC	= [1]	Number of internal coordinates to be analyzed. (Maximum = 100)
ICLIST	= [1]	Array with the number of internal coordinates to be analyzed. Example: if the stretch corresponds coordinate 1 and the torsion to 12, and one wants to analyze both, ICILIST =1,12 and nic = 2.
BMAT	= [0]	0. Get the internal coordinates from the output files. (Only for PROG = 1 in NEWTON-X (COLUMBUS dynamics)) 1. Run cart2int.x program from COLUMBUS to get the internal coordinates. In this case, an intcfl file with the definition of the internal coordinates is required. A standard cart2intin input file will be automatically generated unless the user provides one.
NAT	= [2]	Number of atoms (relevant only if BMAT = 1).

The next keywords are needed only if PROPTYPE = 6:

INT_STAT	= [0]	Would you like to distinguish the electronic states of the nuclear configurations and dissociation channels? 0 - No 1 - Yes

---

Example of prop.inp file:

```
&collect
  itrj     = 1,
  jtrj     = 20,
  tmin     = 0.0,
  tmax     = 50.0,
  dt       = 0.5,
  proptype = 1,
  nstat    = 2,
  nic      = 3,
  iclist   = 8,9,12,
  bmat     = 0,
&end
```

Do not forget "&collect" and "&end".

13.2 How to execute ANALYSIS

Got to directory TRAJECTORIES and execute

```
$NX/diagnostic.pl
```

The execution of diagnostic.pl before running the analysis program is optional but recommendable.

Run nxinp to create the input file (see section 13.1).

Having prop.inp and diag.log (optional output of diagnostic.pl) in the TRAJECTORIES directory, execute

```
$NX/analysis.pl >analysis.log &
```

If run_IS = 1, the samp_points, samp_param and targ_param files are expected. The former two were generated when the TRAJECTORIES directory was created. Information about the importance sampling calculation will be printed in the importance_sampling.log file.

If PROPTYPE = 3 and BMAT = 1, this directory must also contain an intcfl file, with the definitions of the internal coordinates (see section 13.1). See COLUMBUS documentation to get specific information about intcfl.

If you change PROPTYPE and run analysis.pl again, the previous results will not be deleted.

13.3 Output files

All output files are written to ANALYSIS directory.

1) prop.proptype (proptype = 1..6) contains the history of the dynamics in the format:

```
Trajectory  Time    Prop(1)    Prop(2)    ...    Prop(nprop)
----------  ----    ------     ------            ------
  itrj      tmin      ...        ...      ...      ...
  itrj       ...      ...        ...      ...      ...
  itrj      tmax      ...        ...      ...      ...
  itrj+1    tmin      ...        ...      ...      ...
  ...        ...      ...        ...      ...      ...
  jtrj      tmax      ...        ...      ...      ...
```

where Prop(i) is each one of the properties analyzed.

2) Order of the properties in prop.proptype files:

```
Prop Traj Time Prop(1) Prop(2) Prop(3) Prop(4) Prop(5)        Prop
type                                                          (nprop)
---- ---- ---- ------- ------- ------- ------- -------   ...  ------
  1    n    t    Epot    Etot    Ekin    E0      E1       ...  E_nstat
  2    n    t    PS      CS      PS.CS   A0      A1       ...  A_nstat
  3    n    t    C_1     C_2     ...                           C_nic
  4    n    t    F_1     F_2     ...                           F_nic
  5    n    t    VAF
  6    n    t    conf
```

where:
n - number of trajectory
t - time (fs)
Epot - current potential energy (atomic unit)
Etot - total energy (atomic unit)
Ekin - kinetic energy (atomic unit)
E0 - ground state potential energy (atomic unit)
E1 - first excited state potential energy (atomic unit)
PS - previous surface
CS - current surface
PS.CS - real number formed by PS and CS. Useful to monitoring the hoppings. Examples:
2.2 = previous surface 2, current surface 2 (no hopping)
1.3 = previous surface 1, current surface 3 (1 -> 3 hopping)
1 = ground state.
A0 - Adiabatic population of the ground state.
A1 - Adiabatic population of the first excited state.

The adiabatic population is computed from the real and imaginary part of the electronic wave function (ψ) given in dyn.out. For state *j*, it is:

$$A_j = \mathrm{Re}\left(\psi_j\right)^2 + \mathrm{Im}\left(\psi_j\right)^2. \tag{30}$$

C_i - internal coordinate i (Angstrom, rad).
F_i - internal force for coordinate i.
VAF - Velocity autocorrelation function for trajectory *n* defined as

$$VAF(t,t_0) = \frac{S_n(t,t_0)}{S_n(0,t_0)},$$
$$S_n(t,t_0) = \frac{1}{N_{at}} \sum_{i=1}^{N_{at}} \mathbf{v}_{i,n}(t_0) \cdot \mathbf{v}_{i,n}(t_0 + t), \tag{31}$$

where $\mathbf{v}_{i,n}$ is the velocity vector for atom *i*.
conf - index of the nuclear configuration (see fragments.log file).

3) Order of the properties in mean_value.proptype files:

```
Prop Time N Prop(1) Prop(2) Prop(3) Prop(4) Prop(5) Prop(6) Prop(7)      Prop
type                                                                     (nprop)
---- ---- - ------- ------- ------- ------- ------- ------- ------- ... ------
  1    t   k <Epot>  D(Epot) <Etot>  D(Etot) <Ekin>  D(Ekin) <E0>    ...    D
                                                                         (Enstat)
  2    t   k  f_0    <A0>    D(A0)   f_1     <A1>    D(A1)    <A2>    ...    D
                                                                         (Anstat)
  3    t   k  <C_1>  D(C_1)  <C_2>   D(C_2)   ...                            D
                                                                         (C_nic)
  4    t   k  <F_1>  D(F_1)   F_2>   D(F_2)   ...                            D
                                                                         (F_nic)
  5    t   k  c*t    <VAF>   D(VAF)

  6    t   k  conf 1 conf 2  conf 3  ...                                 conf nconf
```

where:
k - number of points used in the computation of the mean value and of the standard deviation.
f_i - relative amount of trajectories in the state i.
<P> - mean value of P over k trajectories.
D(P) - Standard deviation of P. The standard deviation is computed as the square root of the bias-corrected variance:

$$S[P(t)] = \left[\frac{1}{k-1} \sum_{i=1}^{k} \left(P(t,i) - \langle P(t) \rangle \right)^2 \right]^{1/2}. \tag{32}$$

c - speed of light in cm/fs.
conf_i - relative amount of trajectories in the configuration i.

4) When proptype = 3 and bmat =1, file intec_new is added to each TRAJi/RESULTS directory. With proptype = 3 you may experience discontinuities of π and/or 2π of the torsion as a function of time. You can use smoothangle.pl (in your NEWTON-X-directory) to correct this, but read the documentation first. There are some caveats!

5) When proptype = 6, information about the nuclear configurations and dissociation channels is presented in the fragments.log file.

6) The prop.proptype files contain the histories of all trajectories sequentially. You can use splithist.pl (in your NEWTON-X-directory) to split this into single files for all trajectories. You get a set of files named prop.proptype.trajnr.

7) With the tool collectjumps.pl (in you NEWTON-X-directory) you can collect some information about hopping events.

14 Normal Mode and Essential Dynamics Analysis

The idea of the Normal Mode Analysis (NMA) is to describe the molecular motion in terms of its normal mode displacements. Another approach for analyzing dynamics motions is called Essential Dynamics. [51] It is a principal component analysis of the geometric displacements intended to find important motions in the dynamics. This is performed by diagonalizing the covariance matrix. The eigenvectors give the modes of interest; the corresponding eigenvalues represent the variance of these modes.

The NMA package in NEWTON-X [52] was developed to perform normal mode analysis, essential dynamics and other related tasks using the output structure of the program. It is driven by the program `nma.pl` which allows for several options. The main option *nma* performs the normal mode analysis. Before that, superposition can be carried out with option *align*. As reference, it is possible to take an equilibrium structure or the average structure over all trajectories, created with option *av_struc*. Essential dynamics can be carried out with option *ess_dyn* (after optional superposition). The output from *ess_dyn* has the form of a normal mode collection and can be used as an alternative input for *nma*.

14.1 Normal mode analysis

First, a reference structure is subtracted from the coordinate vector. This difference vector is multiplied with the inverse of the normal mode matrix for the coordinate transformation. Several averages are printed out and optionally plots are created.

Go to TRAJECTORIES directory and run:

```
$NX/nma.pl nma
```

14.1.1 Input parameters

The input is contained in nma.inp which has to be in the folder from which the script is executed. The normal mode matrix is read in from a Molden input file.

File: nma.inp

Parameter	Description
REF_STRUC_FILE	File with a reference structure (either an equilibrium structure or the average structure created with av_struc.py).
REF_STRUC_TYPE	File type of this file (xyz, tmol, ...).
VIBRATION_FILE	MOLDEN input file that contains the normal modes.
FIRST_TRAJ	Index of the first trajectory
LAST_TRAJ	Index of the last trajectory
DT	Length of time step (fs)
NUM_STEPS	Maximum number of analyzed time steps.

ABS_LIST	List of normal modes for which the absolute value is taken because of symmetry. The numbering is according to the Molden input file. Without this setting, all non-totally symmetric modes should average out to 0.
NEG_LIST	List of normal modes where the negative value is taken in **total_std.txt** and **cross_av_std.txt**. This is only for convenience when viewing the results.
ANA_INTS	For which time intervals the averaging is carried out.
PLOT	Plots are automatically created. For this the matplotlib/pylab package has to be installed.
DESCR	Name of the subdirectory into which results are written.

Example of nma.inp file:

```
# input for nma.py
ref_struc_file = '../coord'
ref_struc_type = 'tmol'
vibration_file = '../molden.input'
first_traj = 1
last_traj = 50
dt = .5
num_steps = 201
abs_list = [7,8,9,11,12,15,16,17,19,20,22,26,28,29,30,32,33,36,37]
neg_list = abs_list
ana_ints = [[0,101],[101,201],[0,201]]
plot = True
descr = ''
```

14.1.2 Text Output

Output text files are space separated tables and can be read into a plotting program. All values are in Angstrom.

- Trajectory specific information in each **RESULTS** directory
  - **nma_<descr>.txt** contains the direct transformation of the coordinates for one trajectory. After plotting, the time evolution of each coordinate can be observed.
  - **nma_<descr>_av.txt** and **nma_<descr>_std.txt** contain average and standard deviation of the trajectory in the analyzed time intervals
- Several averages are put into the **NMA/<descr>** folder:
  - **mean_against_time.txt**, **std_against_time.txt** - For every timestep the average and standard deviation over all trajectories. These files show the coherent motions.
  - **total_std.txt** - Total standard deviation over all time steps and trajectories, one number per time interval analyzed. It is representative of the total (random and coherent) activity of a normal mode. For a harmonic motion, the standard deviation is directly related to the amplitude.
  - **cross_av_std.txt** - Standard deviation of the average trajectory. Through the first averaging random motions are cancelled out and only coherent activity is seen.

14.1.3 Graphical Output

Graphics output for averages and for single trajectories can be created if the matplotlib/pylab package is installed.

- Average (created if plot=True in the input file or with '**python nma.py plot**'>)
  - bar graphs in **NMA/<descr>/bar_graphs**

    representing the standard deviation shown in **total_std.txt** and **cross_av_std.txt**.

  - in **NMA/<descr>/time_plots** the time evolution of the normal modes with cross-trajectory-standard-deviation is seen.
- Plots for single trajectories can be drawn by specifying the trajectory index, e.g. '**nma.py plot 1 2 3**' or '**nma.py plot all**', if specific modes are supposed to be plotted into one figure: '**nma.py plot 1 2 3 modes 22 25 27**'. The figures are put into each trajectory's **RESULTS** directory.

14.2 Trajectory alignment

Use this option for aligning a set of trajectories using a least-square fit. Aligning will cancel out the rotational and translational normal mode but leave the other results basically unchanged. Fitting can be a problem when structures are strongly changing, for more information see Ref. [74].

Go to TRAJECTORIES directory and run:

```
$NX/nma.pl align <first_traj> <last_traj>
```

<first_traj> and <last_traj> are, respectively, the numbers of the initial and final trajectories in the set of interest.

14.2.1 Input parameters

File: align.inp

Parameter	Description
REF_STRUC_FILE	File with a reference structure (either an equilibrium structure or the average structure created with av_struc.py).
REF_STRUC_TYPE	File type of this file.
OUT_DIR	Output directory.

Example of align.inp

```
# input for align.sh
ref_struc_file = '../../opt_vib/coord'
ref_struc_type = 'tmol'
out_dir='Aligned_Trajs'
```

14.3 Average Structure

Creates the average structure of a set of trajectories.

Go to TRAJECTORIES directory and run:

```
$NX/nma.pl av_struc
```

14.3.1 Input parameters

File: av_struc.inp

Parameter	Description
FIRST_TRAJ	Index of the first trajectory

LAST_TRAJ	Index of the last trajectory
NUM_STEPS	Maximum number of time steps in a trajectory

Example of av_struc.inp:

```
# input for av_struc.py
first_traj = 1
last_traj = 50
num_steps = 601
```

14.4 Essential Dynamics

Finds the most active linear motions through Principal Component Analysis (diagonalization of the covariance matrix) [51].

Go to TRAJECTORIES directory and run:

```
$NX/nma.pl ess_dyn
```

14.4.1 Input parameters

File: ess_dyn.inp

Parameter	Description
REF_STRUC_FILE	File with a reference structure (it is only used for reading in the atom types)
REF_STRUC_TYPE	File type of this file.
FIRST_TRAJ	Index of the first trajectory
LAST_TRAJ	Index of the last trajectory
NUM_STEPS	Number of analyzed time steps. This has to be at least as large as the maximum number of time steps in any trajectory.
ANA_INTS	For which time intervals the averaging is carried out.
DESCR	Name of the subdirectory into which results are written.

Example of ess_dyn.inp:

```
# input for ess_dyn.py
ref_struc_file = '../../opt_vib/coord'
ref_struc_type = 'tmol'
first_traj = 1
last_traj = 10
num_steps = 2001
ana_ints = [[0,501],[501,2001],[0,2001]]
descr = ''
```

The output consists of MOLDEN vibration files for the analyzed time intervals. **total_cov** contains the results with the total covariance over all trajectories and time steps. **cross_av** shows the essential dynamics of the average trajectory.

For time-dependent results, the output from this script can be further analyzed with *nma* option.

14.5 Python subroutine libraries

These libraries are the basis for the provided scripts and could be used for other programming tasks. For more information, look at the documentation included in the python files (either in the source code or with the python 'help(...)' command).

- **chk_dep.py** : check whether necessary packages are installed
- **traj_manip.py**: operations for manipulation of trajectories
- **struc_linalg.py**: package for performing linear algebra operations on structures
- **plotting.py**: plotting routines
- **superposition.py**: superposition of molecules with a quaternion fit
- **vib_molden.py**: code for parsing a MOLDEN vibration file
- **file_handler.py**: basic file operations

14.6 Required packages to run NMA analysis

To run the NMA programs, the packages below should be installed in the system. All of them may be found as part of the UNIX distribution (and should be quickly installed with e.g. '**yum install <package>**') or they can be downloaded from the URLs specified.

- NUMPY Python package (numpy.scipy.org)
- OPENBABEL-PYTHON package (openbabel.org/wiki/Python)
- PYTHON-MATPLOTLIB package (optional for plotting, matplotlib.sourceforge.net)

15 Tools

15.1 Plotting energy x time

From RESULTS directory, call
`$NX/plot`

The program plot produces a simple gnuplot graph for dynamics by reading en.dat.

The potential energies (atomic units) for all states are plotted in function of time (fs) with lines. For nonadiabatic dynamics, the current potential energy is also plotted, but with points.

To plot the energy difference (eV) between two states along time (fs), call
`$NX/plotdiff <option1=[arg1] option2=[arg2] …>`

The options are

Option	Argument	Description
FILE	filename	Writes the graph to 'filename' on the disk instead of displaying it on the screen. png format is used
TITLE	'Plot title'	Specifies the title of the plot. The default is a combination of the trajectory name and the states, i.e., TRAJn: E(state 1)-E(state 2) where n is the number of the trajectory.
NSTAT1	state number	Takes an integer value state number that specifies state number 1. If not given as a parameter, the user will be prompted to enter a value interactively.
NSTAT2	state number	Takes an integer value state number that specifies state number 2. If not given as a parameter, the user will be prompted to enter a value interactively.

To plot the potential energy (atomic units) of several trajectories at once versus time (fs), go to TRAJECTORIES directory and call
`$NX/plotall`

15.2 Plotting velocities and molecular orbitals

From RESULTS directory, call
`$NX/arrow`

The program arrow produces a MOLDEN output file for a certain time step defined by the user. The velocity and nonadiabatic coupling vectors (if available) at this time step are written as a normal mode and can be visualized with MOLDEN compatible programs. For COLUMBUS dynamics is also possible to visualize the molecular orbitals.

The program reads the information from dyn.out, moldyn.log and JOB_(N)AD and multiplies the velocities components by 100.

The output is the file arrow.mld.

15.3 Smoothangle

Analyzing the torsional mode may give discontinuities of π and/or 2π of the torsion as a function of time. This should be fixed with this script. It is simply looking for change of more than π/2 and then correcting this assuming that only jumps of pi, 3π/2 or 2π occur.

Beware! Of course, the script cannot know which columns are angles and which are not. It will try to correct *all* values that vary more than π/2 from line to line (what can be a problem if you have timesteps bigger than 1.5!). If you expect one value to do so, then don't use this script. This is going to be changed in future versions.

Usage:
1) Prepare the prop.3 file with $NX/analysis.pl
2) run

```
$NX/smoothangle.pl
```

The original prop.3 file will be saved as prop.3.old and the new prop.3 file contains the smoothed data.

15.4 Collectjumps

Collects information about surface hops (max 2 states for the moment).

Usage:

1) prepare file collectjumps.inp with parameters in lines. Possible parameters are:

Parameter	Default	Description
NTRAJ	= [100]	Number of trajectories to analyze
NFIRST	= [1]	First trajectory to analyze
MAXTIME	= [500]	Maximum time, that can occur
ENERGY		Print out energies to jumps
GEOMETRY		Print out selected columns from prop.3
GCOLS		Columns to read from prop.3.j in everyday counting (starting with 1); comma separated list
GLABELS		Labels for geometry columns (comma separated and in the same order as GCOLS)

There is not much checking whether your input is sensible, so you are responsible for this alone. You can write whatever else you want as long as lines beginning with one of the keywords and then a '=' sign is followed by a fit argument lines beginning with anything else will be ignored - write a novel if you feel like it.

2) prepare prop.i.j - files with splithist.pl
prop.2.j files are mandatory (they contain info about hops)
rop.1.j and prop.3.j are needed if you want info from there

3) run

```
$NX/collectjumps.pl
```

Output files are:

jump_collection.csv -> comma separated values with info
jump_collection.txt -> rather statistical information

15.5 Diagnostic

The script diagnostic.pl goes through the TRAJi directories and collects information about error termination and problems with conservation of energy and adiabatic population. A diagnostic of the trajectories is written to diag.log, including up to which time step the information in each trajectory is reliable.

The file diag.log can read by the analysis program (see Chapter 13) and by the initial condition generation program in some cases (see Section 6.3).

To run diagnostic.pl, go to TRAJECTORIES directory and execute:
`$NX/diagnostic.pl`

In the beginning of the execution, diagnostic.pl will ask some few questions about path, number of trajectories and time. This same information may be directly provided by means of diag.inp file. The parameters in diag.inp are defined below.

Name: diag.inp

Parameter	Default	Description
AD	= [current path]	Path to the trajectories.
ITRAJ	= [1]	Initial trajectory to be checked.
FTRAJ	= [no default]	Final trajectory to be checked.
TMIN	= [0.0]	Initial time (fs). It must be common to all trajectories.
ETOT_DEV	= [0.5]	Allowed variation in the total energy (eV).
POP_DEV	= [0.1]	Allowed variation in the norm of the adiabatic population.

Example of diag.inp file:

```
ad = /home/my_system/TRAJECTORIES
itraj = 1
ftraj = 10
tmin = 100
```

15.6 Conversion tools

Convert geometry files:

Program	From	To	Usage	Input file	Output file
nx2tm	NX/COLUMBUS	TURBOMOLE	`$NX/nx2tm`	geom	coord
nx2xyz	NX/COLUMBUS	XYZ	`$NX/nx2xyz`	geom	geom..xyz
nx2dftb	NX/COLUMBUS	DFTB	`$NX/nx2dftb`	geom	in.gen
tm2nx	TURBOMOLE	NX/COLUMBUS	`$NX/tm2nx`	coord	geom
xyz2nx	XYZ	NX/COLUMBUS	`$NX/xyz2nx < <file>`	<file>	geom.
dftb2nx	DFTB	NX/COLUMBUS	`$NX/dftb2nx`	in.gen	geom.
finaloutput2dynmld.pl	NX	XYZ	`$NX/ finaloutput2dynmld.pl`	final_output	dyn.mld
xyz2zmat	XYZ	ZMAT	`$NX/xyz2zmat`	geom..xyz	geom..zmat

nx2gamess.f90	NX/COLUMBUS	GAMESS $DATA	$NX/nx2gamess	geom	Gamessgeom
nx2bagel.f90	NX	BAGEL	$NX/nx2bagel	geom	bagel-geom

The script do_nx2molden can be used to convert Dyson orbitals from the format used in NEWTON-X into Molden format. As for input, you need to provide the Dyson orbital within the MO_DYSON directory, the corresponding geometry within the GEOMETRIES directory, and a file name molden_basis with the basis set in Molden format.

15.7 Split and merge initial conditions

To split the spectrum and initial condition generation jobs into several jobs to run in several computers, just prepare the input explained in Chapter 10. Use ISEED = -1 in initqp_input file, otherwise, all jobs will generate the same set of initial conditions. Then run

```
$NX/split_initcond.pl
```

This program will ask a few simple questions (like in how many jobs the parent job should be split), then it will create a directory called `INITIAL_CONDITIONS`, and inside it will create a sequence of subdirectories called `I1`, `I2`, ..., each one containing a complete set of input files.

Copy each subdirectory to a different computer and run the jobs normally.

Script submit_ic.pl can be adapted to make a batch submission to your system.

Per default a calculation for the equilibrium geometry is performed in every `I*` directory to compute the reference energy, which is written to a file `epot0`. If you provide this file before the calculation, the initial calculation is skipped. To do this, you can run the calculation in `I1` first and copy `I1/TEMP/epot0` to the other directories.

To merge the jobs, after the calculations, copy the directories `I1`, `I2`, ... back to `INITIAL_CONDITIONS` directory and from inside this directory run

```
$NX/merge_initcond.pl
```

This program will ask the number of jobs to be merged, and it will create a new directory called `I_merged` with merged results. The file map is also created, which tells how the indexes of the final_output files map into the indexes of the initial condition generation.

In the same way, the computation of the photoelectron spectrum with ixsec.pl may be split between several computers. For that, after having the Dyson orbitals and doing the input for spectrum, run

```
$NX/split_intensities.pl
```

Subdirectories named `I1`, `I2`, ..., are then created within a new directory named called `INTENSITIES`. After running each job, they can be merged with:

```
$NX/merge_intensities.pl
```

15.8 Importance sampling

The importance sampling (IS) program allows for the transformation of results obtained from a given sampling probability distribution function (PDF) to any desired target PDF. The sampling PDF must be generated with a quantum-based distribution (NACT=2 or NACT=3). Any type of spectra calculation

implemented in NEWTON-X can be combined with the IS technique, which is done by setting the flag run_IS to 1 in the mkd.inp file. For dynamics simulations, the flag run_IS must be set to 1 in both the generations of trajectories (mkd.inp file) and when executing the analysis tool (prop.inp file).

When the IS code is called, three input files are expected: samp_points, samp_param and targ_param, the first two being created when the initial conditions are generated and require no further modification. The targ_param file contains the parameters that define the target PDF, and it has the same structure as the samp_param file, which can thus serve as a model. The following flags define the distribution parameters: temp, freq, vib, dist, occ, which are all optional and do not need to be presented in any specific order. After each flag, the associated variable(s) are expected, as follows:

- temp: temperature (K). The default is the sampling temperature.
- freq: normal modes frequencies (cm^{-1}). The default is the set of sampling frequencies.
- vib: vibrational quantum numbers. The default is the same as for the sampling PDF.
- dist: Gaussian parameters. The default is the standard 1.0 exponent and 0.0 shift. The format is the same as in the samp_dist file.
- occ: vibrational occupation numbers. This allows for fractional occupation numbers, thus being a generalization of the integer quanta provided with the vib flag. If the flag is provided, then the values assigned with vib are ignored. After the occ flag, the next line should have the maximum vibrational level for which the occupation numbers are given. Then comes the list of occupation numbers, with one normal mode per line. If this flag is not present, then the file temp_occ is generated, which contains the set of occupation numbers for the provided temperature. In this case, the printing stops when the sum of occupation numbers for the lowest frequency is converged to within a fraction of 10^{-4}.

To correctly obtain the desired target PDF, it is important to understand the underlying hierarchy of the above parameters and how they combine among themselves. The following points should be kept in mind:

- freq is always considered. The sampling PDF must have been generated with anh_f = 1 (the default value).
- When occ is provided, then both vib and temp are ignored.
- The dist parameters applies to all vibrational levels (as defined by either vib or occ).
- For non-default dist parameters, temp is ignored. This is mode specific as well as coordinate/momentum specific.
- When vib is provided, then temp is ignored, unless the quantum number equals 0. This is mode specific.
- Therefore, temp is considered only when both dist and vib assume their default values.

Within the makedir.pl script, the IS program computes the IS weights, which are written to the IS_weight file (same format as samp_points). Also, the log file importance_sampling.log is created, which contains information on whether the parameters were correctly read, how sampling and target PDF are represented, and some further information regarding the sample size.

The importance sampling program can also be called directly with:

```
$NX/importance_sampling > importance_sampling.log
```

If the IS_weight already exists, then the weights are not recomputed. If a new calculation is to be performed, the IS_weight file must be deleted before.

16 Technical details

16.1 Templates and interfaces to new programs

NEWTON-X is written in such a way that is easy to interface it with any quantum chemistry package that can provide gradients and other properties necessary for the dynamics. Directory source/template contains some templates to guide the interfacing.

First, it is necessary to have a conversion tool to transform NEWTON-X geometries to the third-party program format. nx2prog.f90 template will help with this.

Second, it is necessary to tell NEWTON-X how to call the new program and how to read and write the properties generated by it. For this purpose, runprog.pl template helps to program this part.

Third, the usage of the new program in the initial condition and absorption spectrum generation, demands a set of instructions of how to call the program and extract energies and oscillator strengths. The template runprog-initcond.pl helps to implement this task.

Besides these specific programs, some intervention in the common code is also required. Normally, only the files moldyn.pl (main NEWTON-X driver), lib/colib_perl.pm (NEWTON-X libraries), and nxinp (input tool) need some changes, which may be identified by comparing the references to previously interfaced programs.

Currently, the following interfaces are defined or reserved for future implementation:

- For initial-conditions/spectrum normal-modes reading:

IPROG	Program
1	GAMESS
2	TURBOMOLE
3	COLUMBUS
4	GAUSSIAN
5	MOLDEN
6	DFTB
7	ACES2
8	BAGEL
9	DFTB+

- For initial-conditions/spectrum energy-transition checking:

PROG	Program	Method
1	COLUMBUS	
2.0	TURBOMOLE	CC2
2.1	TURBOMOLE	TDDFT
2.2	TURBOMOLE	ADC2
6.5	GAUSSIAN 09	
8.0	DFTB	TD-DFTB
8.1	DFTB+ (legacy)	DFTB/MM
8.5	DFTB+ (new interface)	TD-DFTB
9	DFT-MRCI	
10	GAMESS	MCSCF
12	BAGEL	
20	HYBRID ENERGY	

- For dynamics:

PROG	Range	Program	Subkey	Method

0	0.00 ≤ PROG < 0.95	Built-in models		
		User models		
1	0.95 ≤ PROG < 1.95	COLUMBUS		
2	1.95 ≤ PROG < 2.95	TURBOMOLE		
			2.0:	RI-CC2 /ADC(2)
			2.1:	TDDFT
3	2.95 ≤ PROG < 3.95	ACES2/CFOUR		
4	3.95 ≤ PROG < 4.95	MOPAC		
6	5.95 ≤ PROG < 6.45	GAUSSIAN		CASSCF
	6.45 ≤ PROG < 6.95	GAUSSIAN 09		CASSCF/TDDFT
7	6.95 ≤ PROG < 7.95	TINKER		
8	7.95 ≤ PROG < 8.05	DFTB	8.0:	Legacy: old interface
8	8.05 ≤ PROG < 8.15	DFTB+	8.1:	Legacy: old interface
	8.45 ≤ PROG < 8.95	DFTB+	8.5:	New interface
9	8.95 ≤ PROG < 9.95	DFT/MRCI		
10	9.95 ≤ PROG < 10.95	GAMESS	10.0	MCSCF
			10.1	Other methods
12	11.95 ≤ PROG < 12.95	BAGEL	12.0	CASSCF/CASPT2
			12.1	Other methods
20	19.95 ≤ PROG < 20.95	Hybrid jobs		

If you want to contribute to the official version of NEWTON-X, by building a new interface, please, contact us before to reserve a key.

16.2 Conversion factors

Physical and mathematical constants, parameters and conversion factors are defined in source/modulus/units_mod.f90 and source/lib/colib_perl.pm and used throughout NEWTON-X. Some of them are:

Quantity	Atomic units	Other used units
Energy	1 (hartree)	27.21138386 eV
Mass	1 (electron mass)	1/1822.888515 amu
Time	1	$24.188843265\times10^{-3}$ fs
Length	1 (bohr)	1/0.52917720859 Å

16.3 Format of internal files

NEWTON-X is built to be mostly application independent. This means that as soon the third-party program calculates some property, this property is written in a standard format that NEWTON-X can read without knowing which program really produced it. Note that, although NEWTON-X reads free format, it is essential to keep the predefined ordering. The following standards are currently defined:

Geometry
During the calculations, the geometry will be updated and written with full double precision Format: free, au.
Name: geom

```
Symbol_1   Atomic_number_1    x_1    y_1    z_1    mass_1
Symbol_2   Atomic_number_2    x_2    y_2    z_2    mass_2
.
.
Symbol_Nat Atomic_number_Nat  x_Nat  y_Nat  z_Nat  mass_Nat
```

Velocity
Format: free, au
Name: veloc

```
vx_1    vy_1     vz_1
vx_2    vy_2     vz_2
:
vx_nat vy_nat   vz_nat
```

Gradient
Format: free, au
Name: grad

```
gx_1    gy_1     gz_1
gx_2    gy_2     gz_2
:
gx_nat gy_nat   gz_nat
```

Potential energy
Format: free, au
Name: epot

```
Epot_1
Epot_2
:
Epot_nstat
```

Nonadiabatic coupling vectors
Name: nad_vectors
Format: free, au

```
V(1,2)1,x     V(1,2)1,y     V(1,2)1,z
V(1,2)2,x     V(1,2)2,y     V(1,2)2,z
  :
V(1,2)Nat,x      ...
  :
V(1,3)1,x        ...
  :
V(NS-1,NS)Nat,x ...        V(NS-1,NS)Nat,z
```

where NS = NSTAT.

The order follow the lines of the triangular matrix:

```
          1      2      3     4      ..    NS-1    NS
1
2       1,2
3       1,3    2,3
4       1,4    2,4    3,4
:       ..
NS-1    ..
NS      1,NS   2,NS   3,NS   4,NS   .. NS-1,NS
```

Final order:

```
1,2
1,3
2,3
1,4
2,4
 :
NS-1,NS
```

Wave function
Name: wfrun (during the calculations) and wf.inp (input)
Format: free

```
A1_real            A1_imag
:                  :
A_nstat_real       A_nstat_imag
```

Oscillator strength
Oscillator strengths and transition dipole moments are not written in a standard format to be read *posteriori* by NEWTON-X. These properties are read directly from the quantum chemistry program outputs by the routine osc_strength in library lib/colib_perl.pm.

State configuration
NEWTON-X still does not have a standard defined to write the state configuration (e.g., coefficients of the main configurations of the CI vector). For each program, this information is only grepped and written to the standard output at each time step.

16.4 Normal modes

In the initial condition generation, NEWTON-X might need to read the normal modes generated by a third-party program. This is done according to the following scheme:

IPROG	NM_FLAG	Program	Input	Unit
1	1	GAMESS	l_c	$(amu)^{-1/2}$
2	2	TURBOMOLE	l_{nc}	1
3	3	COLUMBUS	l_{mw}	1
4	2	GAUSSIAN	l_{nc}	1
5	*x*	MOLDEN	*nm_flag*	-
6	1	DFTB	l_c	$(amu)^{-1/2}$
7	3	ACES2	l_{mw}	1
8	2	BAGEL	l_{nc}	1
9	2	DFTB+	l_{nc}	1

In this Table:
l_c - Cartesian normal modes
l_{nc} - $l_c\,\mu^{1/2}$ normalized Cartesian normal mode
l_{mw} - mass-weighted normal mode
μ - reduced mass
amu - g/mol, atomic mass unity

Thus, when IPROG is set to 1 (read GAMESS output), NEWTON-X assumes that the normal modes are given as Cartesian normal modes in $(amu)^{-1/2}$, and the NM_FLAG is internally set to 1. If IPROG = 5 (read MOLDEN file), NM_FLAG must be given as an input as well because any kind of normal modes may be written to this type of file.

16.5 Output files of the SH program

In the RESULTS directory:

1) sh.out
log file

2) tprob

transition probabilities:
`random number | current step| trans_prob_1 | ... | trans_prob_nstat`
Values for a specific time step are printed only when at least one of the trans_prob values is larger than 10^{-7}.

In the TEMP directory:

3) wfrun (overwritten)
current value of the electronic wave function coefficients

4) popev_info
direct access working file

5) veloc and control.d
updated in the case of surface hopping

6) irk
hopping state in the last step
0 - normal, 1 - hopping, 2 - frustrated hopping

7) sh.log
Log information

16.6 CIOVERLAP documentation

(Documentation based on the original manual written by Jiri Pittner, September 01, 2010.)

Executables involved:
cioverlap
cis_casida
cis_slatergen
civeccompare
civecconsolidate
readsifs
mcpc.x, cipc.x

The functionality, input options and input files of these programs are explained in the following sub-sections. The CIOVERLAP set of programs is a stand-alone package developed by Jiri Pittner to compute the overlap of two CI wavefunctions.

The options and input files necessary to run the CIOVERLAP program during the dynamics run are internally created and updated by NEWTON-X. The command line options of the core program (CIOVERLAP) can be controlled by the user through the keyword CIO_OPTIONS and CISC_OPTIONS in jiri.inp file (see section 12.1.7). These options are described below, in section 16.6.1.

16.6.1 CIOVERLAP program

Core program to compute overlap of two CI wave functions

Command line options:	***Description:***
-s screening_mask_file	name of file with transmomin format, tells cioverlap which overlap matrix elements are needed and the Slater det. prescreening is based on this info

-a	align phases of "new" w.f. in rows (bras); use file "phases.old" to patch phases of wavefunctions from the previous step
-b	align phases of "new" w.f. in columns (kets); use file "phases.old" to patch phases of wavefunctions from the previous step
-o	use file "phases.old" to patch phases of wavefunctions from the previous step
-t screeningthr	double; threshold for the Slater determinant prescreening procedure
-e excitrank	integer; excitation rank for the Slater determinant prescreening procedure determinant pairs which are mutually more than excitrank-excited will be omitted. For TDDFT the value -1 suppresses this screening and unnecessary generation of excitlistfile
-i inactive	integer; number of orbitals which are never excited from generally, it is >= ncore. This parameter influences only efficiency of the computation if omitted or lower than correct value is given; incorrectly high value will cause an erroneous result
-A activerange_from activerange_to	[type] integer; default value 0 calculates overlap in the basis of Slater determinants (standard input described below) value 1 calculates overlap in the basis of FULL CI GUGA wave functions (standard input is different)

Standard input:	***Description***
nbas	integer; total number of basis functions, includes core and discarded ones
ncore	integer; number of frozen core orbitals into ncore count only such core orbitals which are not included in slaterfile
ndisc	integer; number of discarded virtual orbitals
nelec	integer; total number of electrons
Sraw	square matrix of dimension 2*number of AOs; obtained as AO overlap matrix of "doubled molecule" combining the bra's and ket's geometry
braLCAO	LCAO matrix of bra, in AO,MO order
ketLCAO	LCAO matrix of ket, in AO,MO order

External files:	***Description:***
slaterfile	input, binary file of signed 16-bit integers contains a list of the Slater determinants forming the N-electron basis alpha spinorbitals with +, beta with – sign ncore orbitals are not included in these determinants generated by cipc.x, mcpc.x, cis_slatergen, or civecconsolidate also output if sorting to lexical order has been requested (presently inactive)
slaterpermfile	output, permutation of slater determinants. if sorting to lexical order has been requested presently inactive
eivectors1	input, binary file with two 32-bit integers followed by doubles dimensions and content of the matrix of bra CI wave functions
eivectors2	input, binary file with two 32-bit integers followed by doubles dimensions and content of the matrix of ket CI wave functions

phases.old	input, binary file of doubles phases by which "old" eigenvectors were scaled what is old and new depends on option -a/-b
Phases	output, binary file of doubles phases by which "new" eigenvectors should be scaled to align phases what is old and new depends on option -a/-b
Excitlistfile	input/output, binary file of integers auxiliary file for the screening by excitation rank (-e) if not existent/empty it will be created otherwise it will be read

Execution example:

```
(echo $nbas $ncore $ndisc $nelec; cat SMAT $BASEDIR/tmp.old/WORK/lcao lcao) |
cioverlap -s transmomin -b -t 1e-5 -e 2
```

16.6.2 CIS_CASIDA

Auxiliary program to generate CIS-like wavefunction coefficients from response functions.

Command line options:	***Description:***
-o	orthonormalize the wave functions
-c	In TDDFT, use **F** instead of **(X+Y)** to build the wave function. Note that the resulting wavefunction will not necessarily be orthonormal unless -o is used simultaneously.
-i inactive_occ	integer; neglect all excitations from the number of lowest orbitals in the TDDFT response function
-I inactive_virt	integer; neglect all excitations to the number of highest orbitals in the TDDFT response function

Standard input:	***Description:***
ncore	integer; number of frozen core orbitals which were not active in TDDFT
nocc	integer; number of occupied orbitals which were active in TDDFT, including those to be later excluded by -i option
nvirt	integer; number of virtual orbitals which were active in TDDFT, including those to be later excluded by -I option
orbener	integer size + vector of doubles, size ncore+nocc+nvirt KS orbital energies
energies	integer size + vector of doubles ground and excited state energies
tddft_coefs	vector of matrices response function coefficients for all excited states

External files:	***Description:***
casidawf	output, binary file with the wave function suitable as eigenvectors input for cioverlap

Execution example:

```
(echo $ncore $nocc $nvirt; cat orbener energies tddft_coefs)|cis_casida
```

16.6.3 CIS_SLATERGEN

Auxiliary program to generate CIS-like Slater determinant basis for TDDFT runs.

Command line options:	*Description:*
-i inactive_occ	integer; neglect all excitations from the number of lowest orbitals in the TDDFT response function must be the same as in cis_casida
-I inactive_virt	integer; neglect all excitations to the number of highest orbitals in the TDDFT response function must be same as in cis_casida

Standard input:	*Description:*
All must be same as for cis_casida	
ncore	integer; number of frozen core orbitals which were not active in TDDFT
nocc	integer; number of occupied orbitals which were active in TDDFT, including those to be later excluded by -i option
nvirt	integer; number of virtual orbitals which were active in TDDFT, including those to be later excluded by -I option

External files:	**Description:**
slaterfile	output, binary file of signed 16-bit integers file with Slater determinant basis suitable as input to cioverlap

Execution example:

```
echo $ncore $nocc $nvirt |cis_casida
```

16.6.4 CIVECCOMPARE

Debugging tool to compare CI wave functions from different sources.

This program is normally not used in the overlap calculation; it can be used to compare e.g. CASSCF and FCI wave functions or CI wave functions computed by different programs.

Command line options:	*Description:*
-f	flip spins in w.f. 1
-g	flip spins in w.f. 2
eivectors1	input file name
slaterfile1	input file name
eivectors2	input file name
slaterfile2	input file name

Standard input:	*Description:*
freeze1	integer; number of electrons to be frozen from w.f.1 before comparison
freeze2	integer; number of electrons to be frozen from w.f.2 before comparison
nelec	integer; number of active electrons, must be same for w.f. 1 and 2 after the freezing threshold double; threshold to consider difference in CI coefficients significant

External files:	*Description:*
only files named on the command line (see above)	

Execution example:

```
echo 14 0 3 .00001 |\
/home/pittner/cioverlap-1.0/civeccompare -f \
/home/pittner/cipc/COL.0.50/WORK/eivectors1 \
/home/pittner/cipc/COL.0.50/WORK/slaterfile  \
/home/pittner/mcpc/COL.0.50/WORK/eivectors1 \
/home/pittner/mcpc/COL.0.50/WORK/slaterfile
```

16.6.5 CIVECCONSOLIDATE

Auxiliary program to simplify "raw" CI wave functions obtained from cipc.x or mcpc.x.

Since cipc.x and mcpc.x, in general, generate (up to a permutation of spinorbitals) identical Slater determinants repeatedly from different GUGA spin adapted functions, this program shortens the CI wave function expansion by sorting and merging them to a unique order. Omitting its execution should only decrease efficiency, but might also slightly affect the result if the prescreening is involved.

Command line options:	***Description:***
eivector_original	input file name
slaterfile_original	input file name
eivector	output file name
slaterfile	output file name
consolidatefile	input/output - data for the consolidation transformation, created if not existing yet

Standard input:	***Description:***
nelec	integer; number of electrons
orbnumshift	integer; shift orbital numbers by subtracting this during processing

Execution example:

```
echo $nelec 0 |civecconsolidate eivectors2.org slaterfile.org eivectors2 slaterfile
consolidatefile
```

16.6.6 READSIFS

Auxiliary program to read Columbus integral files. It converts Columbus integral files in SIFS format to a form suitable for cioverlap.

Command line options:	***Description:***
-1	process only one-electron integrals
aoints	aoints file name

External files:	***Description:***
aoints, aoints2	input, SIFS integral files
aoints1S	output, binary files with integer dimensions followed by double precision contents of individual matrices (symmetric in packed storage)

Execution example:

```
dalton.x
```

```
readsifs -1 aoints >readsifsls
bin2smatrix aoints1S >SRAW
```

(In NX cio_end is employed instead of bin2smatrix to convert the overlap matrix for formatted input to cioverlap.)

16.6.7 CIPC.X, MCPC.X

Programs borrowed from COLUMBUS to generate slaterfile and eigenvectors file for cioverlap. See appropriate sections of Columbus manual or run them and follow the interactive menu. Columbus has to be compiled with the "-assume byterecl" option, as shown in the machine configuration file "linux64.ifc.byterecl".

17 Links to third-party programs

COLUMBUS:
www.univie.ac.at/columbus

TURBOMOLE:
www.turbomole.com

DFTB and DFTB+:
www.dftb.org_ENREF_1

GAUSSIAN:
www.gaussian.com

TINKER:
dasher.wustl.edu/tinker

GAMESS:
www.msg.ameslab.gov/gamess

BAGEL:
nubakery.org

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