

User's Manual

NTBM ver. 1.0

1. About NTBM

NTBM is a quantum-chemistry software for atomistic simulation of isolated molecules, nanostructures, and crystals. The interatomic interaction is described within the semi-empirical nonorthogonal tight-binding model. Currently, only four chemical elements (H, C, N, O) are available. Implementation of other elements (B, P, S) is in progress. To date, the following functionality is available: geometry optimizing, frequency and eigenmodes calculations, molecular dynamics (NVE and NVT ensembles), and hyperdynamics (accelerated molecular dynamics for long-time evolution analysis). Some tools for transition state search are also implemented.

NTBM is an open-source program. Anyone can use it as is or modify the code for any purpose. When using NTBM, the following references are mandatory:

NTBM parametrization:

M.M. Maslov, A.I. Podlivaev, K.P. Katin. Non-orthogonal tight-binding model with H-C-N-O parametrisation. Molecular Simulation. 2016. Vol. 42. P. 605-611. DOI: <https://doi.org/10.1080/08927022.2015.1044453>

2. Downloading and Installation

NTBM is available without any fee or registration at www.ntbm.info. There are two ways of downloading and using.

- Compilation from source files (any Fortran compiler is required).
 - Download archive NTBM_v1.rar from www.ntbm.info;
 - Extract all files into any folder;
 - Compile the source “main.f90” using any Fortran compiler (gfortran, ifort, etc.) to get an executable file.
- The use of the pre-compiled executable file.
 - Download the pre-compiled NTBM file NTBM_v1.exe suitable for your operating system, run it and enjoy.

3. Input and Output Files

To run NTBM, it is necessary to prepare the input file “input.inp”. The number and content of the output files are depended on the type of calculation. Detailed descriptions are presented below. Output files can be visualized within the ChemCraft (<http://www.chemcraftprog.com>),

Jmol (<http://jmol.sourceforge.net>), Vesta (<http://jp-minerals.org/vesta/en/>) or other visualization programs. We advise to install the visualizer before running NTBM.

4. Measuring Units

All physical quantities in NTBM program are measured in the following units: bond lengths and Cartesian atomic coordinates — in angstroms (Å), energies — in electron-volts (eV), forces — in electron-volts per angstrom (eV/Å), temperature — in Kelvins (K), time — in femtoseconds (fs). Frequencies are calculated in Hertz (Hz) and reversal centimeters (cm⁻¹).

5. Running NTBM: Geometry Optimization

The geometry optimization is realized within the steepest descent method. Atoms are moved in the direction of the acting forces. It is easy to regard or modify corresponding code presented in “relax.f90” file. The optimization command has the following notation:

```
$RUNTYPE
relax n N fmax step coord_type
$END
```

Here, the coordinates are outputted every n steps; N is the maximum number of outputs (so, maximum number of steps is equal to $n \cdot N$), $fmax$ (eV/Å) is the maximum acceptable value of the residual force; $step$ (Å²/eV) is the coefficient between acting force and atomic displacement ($step = 0.005$ is a suitable choice for the most cases); $coord_type$ is one of the strings: “cartesian” (for Cartesian coordinates) or “crystal” (for fractional coordinates).

5.1. Optimization of the periodic cell

If one wants to relax both atomic positions and lattice constants (translational vectors), please use “vc_relax_sym” or “vc_relax” instead of “relax”. “vc_relax_sym” provides the optimization with maintaining the symmetry of the crystal, whereas “vc_relax” provides more customized optimization of the translations vectors. In this case, one should add additional block “STRESS_RELAX”:

```
$STRESS_RELAX
eps_XX 1
eps_YY 1
eps_ZZ 0
```

```
eps_XY 1
eps_XZ 0
eps_YZ 0
$END
```

Where “1” means the relaxation along the corresponding stress, “0” means the absence of relaxation. Please, use six “1” for total cell relaxation:

```
$STRESS_RELAX
eps_XX 1
eps_YY 1
eps_ZZ 1
eps_XY 1
eps_XZ 1
eps_YZ 1
$END
```

Below one can see the simple example of the input file “input.inp” for geometry optimization:

input file (input.inp):

```
$RUNTYPE
relax 30 1000 0.01 0.005 cartesian
$END

$CELL_VECTORS
100.0  0.0  0.0    1-st vector of periodic cell (X1,Y1,Z1)
  0.0 100.0  0.0    2-nd vector of periodic cell (X2,Y2,Z2)
  0.0  0.0 100.0    3-rd vector of periodic cell (X3,Y3,Z3)
$END

$ATOMIC_COORDINATES
C 0 0 0
H -0.7 0.7 -0.
H -0.7 -0.5 -0.5
H -0.7 0.5 0.5
```

```
N 1 0 0
H 1.7 -0.5 -0.5
H 1.7 0.5 0.5
$END
```

5.2. Description of the input file “input.inp” for the geometry optimization:

Block RUNTYPE: Command «relax 30 1000 0.01 0.005 cartesian» means that the energy and atomic coordinates will be outputted to the “coord.xyz” file every 30 steps. The program will stop after 1000 outputs, or when all residual forces become smaller than 0.01 eV/\AA . The coefficient between atomic displacement and acting force is $0.005 \text{ \AA}^2/\text{eV}$. The keyword “cartesian” means that the coordinates in block \$ATOMIC_COORDINATES must be provided in the Cartesian form, not in fractional form.

Block CELL_VECTORS: This block provides three vectors that define the periodic cell. If the isolated non-periodic molecule is considered, one should set these vectors to be large enough to exclude the interaction of the system with the corresponding periodic images.

Block ATOMIC_COORDINATES: This block contains Cartesian atomic coordinates in the following format: atomic symbol (H, C, N, or O), x_coordinate, y_coordinate, z_coordinate (in Angstroms). In the example, we present the coordinates of methylamine CH_3NH_2 .

5.3. Description of the output file for the geometry optimization:

The output file “coord.xyz” contains several frames of gradually improved atomic coordinates. One can animate the optimization process using ChemCraft or Jmol. The last frame contains totally optimized atomic coordinates.

The output file “coord.cif” contains the final atomic coordinates in common *.cif format, which is suitable for crystals. One can open this file using VESTA (<http://jp-minerals.org/vesta/en/>) or any other visualization program.

6. Running NTBM: Frequencies Calculation

NTBM implements the calculation of the Hessian matrix, which contains the second derivatives of the system’s potential energy with respect to the atomic coordinates. For the system containing M atoms, dimension of the Hessian matrix is $3M \times 3M$. Eigenvalues and eigenvectors of this matrix correspond to vibrational frequencies and normal modes, respectively. One can regard or modify the source code for calculation of hessian (see file “hess.f90”) and for the output formation (see file “omega.f90”). The corresponding command has the following form:

```
$RUNTYPE
```

freq cartesian

\$END

As a rule, one should optimize atomic coordinates before the calculation of frequencies.

6.1. An example of input file “input.inp” for the frequency calculation:

input file (input.inp):

```
$RUNTYPE
freq cartesian
$END

$CELL_VECTORS
100.0  0.0  0.0    1-st vector of periodic cell (X1,Y1,Z1)
  0.0 100.0  0.0    2-nd vector of periodic cell (X2,Y2,Z2)
  0.0  0.0 100.0    3-rd vector of periodic cell (X3,Y3,Z3)
$END

$ATOMIC_COORDINATES
C  -0.10322781E+00  -0.41258670E-01  0.25387480E-02
H  -0.47318818E+00  0.99132986E+00  0.90209113E-01
H  -0.44528837E+00  -0.49408029E+00  -0.94013979E+00
H  -0.45401465E+00  -0.64399794E+00  0.86204343E+00
N   0.12902439E+01  -0.22010990E-02  -0.16401579E-01
H   0.18061238E+01  -0.72362175E+00  -0.50093024E+00
H   0.17793513E+01  0.71382989E+00  0.50268031E+00
$END
```

6.2. Description of the input file “input.inp” for the frequency calculation:

Block RUNTYPE: Command «freq» means that the Hessian matrix will be formed and corresponding frequencies and normal modes will be derived. The keyword “cartesian” means that the coordinates in block \$ATOMIC_COORDINATES must be provided in the Cartesian form, not in fractional form.

Block CELL_VECTORS: This block provides three vectors, which define the periodic cell. If the isolated non-periodic molecule is considered, it is necessary to set the vectors to be large enough to exclude the interaction of the system with the corresponding periodic images.

Block ATOMIC_COORDINATES: This block contains the geometry of the system in the following format: atomic symbol (H, C, N or O), x_coordinate, y_coordinate, z_coordinate (in Angstroms). The example presents the atomic coordinates of methylamine CH₃NH₂.

6.3. Description of the output file for frequency calculation

Output file «spec.dat» contains $3M$ (M is the number of atoms) frequencies sorted in the increasing order. Six lowest approximately zero frequencies correspond to the translational and rotational modes of the system as a whole. Every frequency is expressed in different units: eV/Å², Hz, cm⁻¹, eV. Output file “Hess.out” contains normal modes. One can open “Hess.out” using ChemCraft program to visualize them.

7. Running NTBM: NVT Molecular Dynamics

NTBM program implies the common molecular dynamics algorithm at a constant temperature. Equations of motions are integrated using the second-order velocity Verlet algorithm. Andersen’s thermostat (<https://doi.org/10.1063/1.439486>) provides a constant temperature. Two integer numbers should be inputted from the keyboard to set random seed. One can regard or modify corresponding source code in the source file “temp_Verlet.f90”. To run NVT molecular dynamics, please use the command

```
$RUNTYPE
md_nvt temp n N timestep
$END
```

Here *temp* is the temperature (in Kelvin); the coordinates are outputted every *n* steps; *N* is the maximum number of outputs (so, the maximum number of steps is equal to $n \cdot N$), *timestep* (in fs) is the time step in velocity Verlet algorithm. The value of *timestep* = 0.1 is suitable for most cases.

7.1. An example of the input file “input.inp” for NVT molecular dynamics:

input file (“input.inp”):

```
$RUNTYPE
md_nvt 300 10 100 0.1 cartesian
$END

$CELL_VECTORS
```

```

100.0  0.0  0.0    1-st vector of periodic cell (X1,Y1,Z1)
  0.0 100.0  0.0    2-nd vector of periodic cell (X2,Y2,Z2)
  0.0  0.0 100.0    3-rd vector of periodic cell (X3,Y3,Z3)
$END

$ATOMIC_COORDINATES
C   0.0  0.0  0.0
H  -0.5  1.0  0.0
H  -0.5 -0.6 -1.0
H  -0.5 -0.6  1.0
N   1.3  0.0  0.0
H   1.8 -0.6 -0.6
H   1.8  0.6  0.6
$END

```

7.2. Description of the input file “input.inp” for NVT molecular dynamics

Block RUNTYPE: Command «`md_nvt 300 10 100 0.1 cartesian`» means that the NVT molecular dynamics under constant temperature 300 K will be performed. Atomic coordinates will be outputted every 10 steps until the 100 outputs will be reached. Every time step corresponds to 0.1 fs. The keyword “cartesian” means that the atomic coordinates in block \$ATOMIC_COORDINATES must be provided in the Cartesian form, not in fractional form.

Block CELL_VECTORS: This block provides three vectors, which define the periodic cell. If the isolated non-periodic molecule is considered, it is necessary to set the vectors to be large enough to exclude the interaction of the system with the corresponding periodic images.

Block ATOMIC_COORDINATES: This block contains Cartesian atomic coordinates in the following format: atomic symbol (H, C, N, or O), x_coordinate, y_coordinate, z_coordinate (in Angstroms). In the example, we present the coordinates of methylamine CH_3NH_2 .

7.3. Description of the output file for NVT molecular dynamics

The output file “coord.xyz” contains several frames of the atomic coordinates corresponding to the system’s evolution in time. This file can be opened with ChemCraft or Jmol to animate the system’s evolution.

8. Running NTBM: NVE Molecular Dynamics

NTBM program implies the common molecular dynamics algorithm for the isolated system at a constant total energy of the system. Equations of motions are integrated using the second-order velocity Verlet algorithm. One can regard or modify the corresponding code in the source file “MD_Verlet.f90”. To run NVE molecular dynamics, please use the following script

```
$RUNTYPE
md_nve VEL temp n N timestep
$END
```

Where VEL should be one of the following strings: “zero” or “read_vel”. “zero” implies zero initial atomic velocities, whereas “read_vel” implies the velocities reading from the file “velocity.ini”. Further, *temp* is the temperature (in Kelvin); the coordinates are outputted every *n* steps; *N* is the maximum number of outputs (so, the maximum number of steps is equal to $n \cdot N$), *timestep* (in fs) is the time step in velocity Verlet algorithm. The value of *timestep* = 0.1 is suitable for most cases.

8.1. An example of the input file “input.inp” for NVE molecular dynamics:

input file (“input.inp”):

```
$RUNTYPE
md_nve zero 10 100 0.1 cartesian
$END

$CELL_VECTORS
100.0  0.0  0.0    1-st vector of periodic cell (X1,Y1,Z1)
  0.0 100.0  0.0    2-nd vector of periodic cell (X2,Y2,Z2)
  0.0  0.0 100.0    3-rd vector of periodic cell (X3,Y3,Z3)
$END

$ATOMIC_COORDINATES
C   0.0  0.0  0.0
H  -0.5  1.0  0.0
H  -0.5 -0.6 -1.0
H  -0.5 -0.6  1.0
N   1.3  0.0  0.0
```

```
H 1.8 -0.6 -0.6
H 1.8 0.6 0.6
$END
```

8.2. Description of the input file input.inp for NVE molecular dynamics:

Block RUNTYPE: Command «md_nve zero 10 100 0.1 cartesian» means that NVE molecular dynamics with zero initial atomic velocities will be performed. Atomic coordinates will be outputted every 10 steps until the 100 outputs will be reached. Every time step corresponds to 0.1 fs. The keyword “cartesian” means that the atomic coordinates in block \$ATOMIC_COORDINATES must be provided in the Cartesian form, not in fractional form.

Block CELL_VECTORS: This block provides three vectors, which define the periodic cell. If the isolated non-periodic molecule considered, it is necessary to set the vectors to be large enough to exclude the interaction of the system with the corresponding periodic images.

Block ATOMIC_COORDINATES: This block contains Cartesian atomic coordinates in the following format: atomic symbol (H, C, N, or O), x_coordinate, y_coordinate, z_coordinate (in Angstroms). In the example, we present the coordinates of methylamine CH₃NH₂.

8.3. Description of the output file for NVE molecular dynamics:

The output file “coord.xyz” contains several frames of atomic coordinates corresponding to the system’s evolution in time. This file can be opened using ChemCraft or Jmol to animate the system’s evolution. File “velocity.out” contains atomic velocities at the last step. One can use these data in order to restart the MD simulation.

9. Running NTBM: Hyperdynamics

Hyperdynamics is aimed at studying the evolution of a system for an extremely long time. The main purpose of this algorithm is to accelerate traditional molecular dynamics. Due to its multiscale architecture, this approach provides a long time scale simulation (up to several seconds or even more). One can regard or modify the corresponding code in the source file “NEW_hyperMD.f90”. Only NVT ensemble is available for hyperdynamics. To run hyperdynamics, please use the script:

```
$RUNTYPE
hyperMD temp n N timestep therm par_N par_M par_alpha cartesian
$END
```

where *temp* is the temperature (in Kelvin); the coordinates are outputted every *n* steps; *N* is the maximum number of outputs (so, maximum number of steps is equal to $n \cdot N$), *timestep* (in fs) is the time step in the velocity Verlet algorithm (*timestep* = 0.1 is suitable for the most cases), *therm* is the time needed for the initial thermalization (*therm* = 1000 is reasonable for most cases). Parameters *par_N*, *par_M*, and *par_alpha* are intrinsic dimensionless parameters of the algorithm. For the most cases, *par_N* = 10000; *par_M* = 100; *par_alpha* = 0.5 is a good choice. Higher values of *par_N* and *par_M* result in higher accuracy and lower performance.

9.1. An example of the input file “input.inp” for hyperdynamics

input file (“input.inp”):

```

$RUNTYPE
hyperMD 500 10 1000000 0.1 1000 10000 20 0.5 cartesian
$END

$CELL_VECTORS
100.0  0.0  0.0    1-st vector of periodic cell (X1,Y1,Z1)
  0.0 100.0  0.0    2-nd vector of periodic cell (X2,Y2,Z2)
  0.0  0.0 100.0    3-rd vector of periodic cell (X3,Y3,Z3)
$END

$ATOMIC_COORDINATES
C  0.0  0.0  0.0
H -0.5  1.0  0.0
H -0.5 -0.6 -1.0
H -0.5 -0.6  1.0
N  1.3  0.0  0.0
H  1.8 -0.6 -0.6
H  1.8  0.6  0.6
$END

```

9.2. Description of the input file “input.inp” for hyperdynamics

Block RUNTYPE: Command «hyperMD 500 10 1000000 0.1 2000 10000 20 0.5 cartesian» implies hyperdynamics at a constant temperature of 500 K. Atomic coordinates will be outputted every 10 steps until the 1000000 outputs will be reached. Every time step corresponds

to 0.1 fs. Initial thermalization is performed during 2000 steps. Intrinsic algorithm parameters par_N , par_M , and par_alpha are equal to 10000, 20, and 0.5, respectively. The keyword “cartesian” means that the atomic coordinates in block \$ATOMIC_COORDINATES must be provided in Cartesian form, not in fractional form.

Block CELL_VECTORS: This block provides three vectors, which define the periodic cell. If the isolated non-periodic molecule is considered, it is necessary to set the vectors to be large enough to exclude the interaction of the system with the corresponding periodic images.

Block ATOMIC_COORDINATES: This block contains Cartesian atomic coordinates in the following format: atomic symbol (H, C, N, or O), x_coordinate, y_coordinate, z_coordinate (in Angstroms). In the example, we present the coordinates of methylamine CH₃NH₂.

9.3. Description of the output file for hyperdynamics:

The output file “coord.xyz” contains several frames of the atomic coordinates corresponding to system’s evolution in time. This file can be opened using ChemCraft or Jmol to animate the system’s evolution.

10. Running NTBM: Local Optimization of the Transition States

Transition states can be located via Newton’s algorithm. Supposed geometry that is sufficiently close to the transition state is required. There are several methods to get this geometry; one of them is described in Section “Additional forces”. Optimized geometry of the transition state should be additionally checked via the frequency calculation (see section “Frequencies calculation”). To initiate the local transition state optimization, please use the script:

```
$RUNTYPE  
saddle n N fmax step cartesian  
$END
```

Here the coordinates are outputted every n steps; N is the maximum number of outputs (so, maximum number of steps is equal to $n \cdot N$), $fmax$ (eV/Å) is the maximum acceptable value of the residual force; $step$ (Å²/eV) is the coefficient between acting force and atomic displacement ($step = 0.005$ is a suitable choice for the most cases); $coord_type$ is one of the following strings: “cartesian” (for Cartesian coordinates) or “crystal” (for fractional coordinates).

10.1. An example of the input file “input.inp” for local transition state optimization

input file (“input.inp”):

```
$RUNTYPE
saddle 30 1000 0.01 0.005 cartesian
$END

$CELL_VECTORS
100.0  0.0  0.0    1-st vector of periodic cell (X1,Y1,Z1)
  0.0 100.0  0.0    2-nd vector of periodic cell (X2,Y2,Z2)
  0.0  0.0 100.0    3-rd vector of periodic cell (X3,Y3,Z3)
$END

$ATOMIC_COORDINATES
C  -0.26773498E+01  0.68637616E+00  0.0
C  -0.28064706E+01  -0.70117597E+00  0.0
C   0.45858485E+00  0.45440368E+00  0.0
C  -0.45858485E+00  -0.45440368E+00  0.0
C   0.28064706E+01  0.70117597E+00  0.0
C   0.26773498E+01  -0.68637616E+00  0.0
C  -0.14279934E+01  0.13488441E+01  0.0
C  -0.15293577E+01  -0.13838723E+01  0.0
C   0.15293577E+01  0.13838723E+01  0.0
C   0.14279934E+01  -0.13488441E+01  0.0
C  -0.11249566E+01  0.26973509E+01  0.0
C  -0.13609710E+01  -0.28110639E+01  0.0
C   0.13609710E+01  0.28110639E+01  0.0
C   0.11249566E+01  -0.26973509E+01  0.0
C   0.10858881E+00  0.34075371E+01  0.0
C  -0.10858881E+00  -0.34075371E+01  0.0
H   0.37631305E+01  0.12213400E+01  0.0
H   0.35820261E+01  -0.13088973E+01  0.0
H  -0.35820261E+01  0.13088973E+01  0.0
H  -0.37631305E+01  -0.12213400E+01  0.0
H   0.22544163E+01  0.34443038E+01  0.0
H   0.20086375E+01  -0.33650994E+01  0.0
H  -0.20086375E+01  0.33650994E+01  0.0
```

H	-0.22544163E+01	-0.34443038E+01	0.0
H	0.45471378E-01	0.45027934E+01	0.0
H	-0.45471379E-01	-0.45027934E+01	0.0
\$END			

10.2. Description of the input file “input.inp” for the transition state optimization

Block RUNTYPE: Command «saddle 30 100 0.01 0.005 cartesian» implies the transition state search. Atomic coordinates will be outputted every 30 steps until the 100 outputs will be reached or residual forces will become lower than 0.01 eV/Å. Atoms are moved in the direction of acting forces (along all the eigenmodes except the first) or in the reverse direction (along the first eigenmode); coefficient between displacement and corresponding force is 0.005 eV/Å². The keyword “cartesian” means that the atomic coordinates in block \$ATOMIC_COORDINATES must be provided in the Cartesian form, not in fractional form.

Block CELL_VECTORS: This block provides three vectors, which define the periodic cell. If the isolated non-periodic molecule is considered, it is necessary to set the vectors to be large enough to exclude the interaction of the system with the corresponding periodic images.

Block ATOMIC_COORDINATES: This block contains Cartesian atomic coordinates in the following format: atomic symbol (H, C, N, or O), x_coordinate, y_coordinate, z_coordinate (in Angstroms). In this example, we present the approximate coordinates of the transition state for Stone-Wales defect in pyrene molecule C₁₆H₁₀, which can be regarded as the smallest model of graphene.

10.3. Description of the output file for the transition state optimization

The output file “coord.xyz” contains several frames of atomic coordinates corresponding to the system’s evolution in time. This file can be opened using ChemCraft or Jmol to animate the system’s evolution. The last frame is usually the required transition state configuration. Additional checking of eigenmodes of this configuration is recommended, see Section “Frequencies calculation”.

11. Running NTBM: Additional Forces

NTBM provides a tuning of additional attraction or repulsive forces acting between the selected atoms. These forces can result in the formation/rupture of chemical bonds. So, one can get the approximated reaction path and the transition state as the highest energy configuration on the path. Approximated transition state should be further optimized, see Section “Local Optimization of the Transition States”.

To use this functional, one should add the following addition block to the control script:

```
$ADD_FORCES
nat1 nat2 force12 visc12
nat3 nat4 force34 visc34
nat5 nat6 force56 visc56
nat7 nat8 force78 visc78
$END
```

Here *nat1* and *nat2* are the numbers of interacted atoms (in accordance with the atomic order presented in the block \$ATOMIC_COORDINATES); *force12* is the additional force between them (positive and negative values correspond to repulsion and attraction, respectively); *visc12* is the effective “viscosity” of these two atoms (*visc12* = 0 corresponds to free atoms; *visc12* = 1 corresponds to fixed atoms; *visc12* = 0.5 means that the displacements for these two atoms are twice smaller than for others atoms). We recommend to set *visc12* in the range from 0.90 to 0.99; these values provide slow-moving of selected atoms and adiabatic fitting of the rest of the system. \$ADD_FORCES block may contain up to four strings.

11.1. An example of the input file “input.inp” for the geometry optimization with the additional forces

input file (“input.inp”):

```
$RUNTYPE
relax 10 300 0.0001 0.005 cartesian
$END

$CELL_VECTORS
100.0 0.0 0.0 1-st vector of periodic cell (X1,Y1,Z1)
0.0 100.0 0.0 2-nd vector of periodic cell (X2,Y2,Z2)
0.0 0.0 100.0 3-rd vector of periodic cell (X3,Y3,Z3)
$END

$ADD_FORCES
4 7 -7. 0.99
3 10 -7. 0.99
```

```

4 10 7. 0.
3 7 7. 0.
$END

$ATOMIC_COORDINATES
C -0.24897196E+01 0.68650325E+00 0.0
C -0.24897196E+01 -0.68650325E+00 0.0
C -0.13491731E-09 0.72423388E+00 0.0
C -0.52992788E-09 -0.72423388E+00 0.0
C 0.24897196E+01 0.68650325E+00 0.0
C 0.24897196E+01 -0.68650325E+00 0.0
C -0.12541300E+01 0.14552126E+01 0.0
C -0.12541300E+01 -0.14552126E+01 0.0
C 0.12541300E+01 0.14552126E+01 0.0
C 0.12541300E+01 -0.14552126E+01 0.0
C -0.12210239E+01 0.28813567E+01 0.0
C -0.12210239E+01 -0.28813567E+01 0.0
C 0.12210239E+01 0.28813567E+01 0.0
C 0.12210239E+01 -0.28813567E+01 0.0
C 0.13364343E-08 0.35716475E+01 0.0
C -0.85151715E-09 -0.35716475E+01 0.0
H 0.34375503E+01 0.12346721E+01 0.0
H 0.34375503E+01 -0.12346721E+01 0.0
H -0.34375503E+01 0.12346721E+01 0.0
H -0.34375503E+01 -0.12346721E+01 0.0
H 0.21605929E+01 0.34422177E+01 0.0
H 0.21605929E+01 -0.34422177E+01 0.0
H -0.21605929E+01 0.34422177E+01 0.0
H -0.21605929E+01 -0.34422177E+01 0.0
H 0.21238431E-08 0.46671085E+01 0.0
H -0.79685853E-09 -0.46671085E+01 0.0
$END

```

11.2. Description of the input file “input.inp” for geometry optimization with additional forces

Block RUNTYPE: Command «relax 10 300 0.0001 0.005 cartesian» means that the energy and atomic coordinates will be outputted to “coord.xyz” file every 10 steps. The program will stop after 300 outputs or when all residual forces become smaller than 0.0001 eV/Å. The coefficient between atomic displacement and acting force is 0.005 Å²/eV. The keyword “cartesian” means that the atomic coordinates in block \$ATOMIC_COORDINATES must be provided in the Cartesian form, not in fractional form.

Block CELL_VECTORS: This block provides three vectors, which define the periodic cell. If the isolated non-periodic molecule is considered, it is necessary to set the vectors to be large enough to exclude the interaction of the system with the corresponding periodic images.

Block ADD_FORCES: This block sets the addition forces between atoms with numbers 3, 4, 7, and 10. The value of these repulsive/attractive forces is 7 eV/Å. The “viscosity” of atoms 3, 4, 7, and 10 is 0.99; i.e., they move 100 times slower than the other atoms. An additional attraction in atomic pairs (4 and 7) and (3 and 10), as well as the additional repulsion in atomic pairs (4 and 10) and (3 and 7), results in Stone-Wales 5-7-7-5 defect in pyrene. So, one can get the approximated reaction path for the defect formation.

Block ATOMIC_COORDINATES: This block contains Cartesian atomic coordinates in the following format: atomic symbol (H, C, N, or O), x_coordinate, y_coordinate, z_coordinate (in Angstroms). In this example, we present the atomic coordinates of the pyrene molecule C₁₆H₁₀.

11.3. Description of the output file for the geometry optimization with additional forces

The output file “coord.xyz” contains several frames of the atomic coordinates along the reaction path. In Section 11.1, we investigate the formation of 5-7-7-5 Stone-Wales defect in pyrene (learn more about this defect: <http://dx.doi.org/10.1039/c6ra01762b>). To animate the defect formation path, one can open “coord.xyz” file with the help of ChemCraft or Jmol. The configuration with the highest energy is used as the initial geometry for the transition state search (see the previous section for details).

12. Support

The team of developers is strongly interested in the bugs fixing and further development of the NTBM program package. You can contact us via e-mail KPKatin@yandex.ru (Dr. Konstantin Katin), KSGrishakov@yahoo.com (Dr. Konstantin Grishakov), and Mike.Maslov@gmail.com (Dr. Mikhail Maslov) if you faced with any problems during the installation or using NTBM. We will be glad to provide rapid and detailed feedback. Any suggestions for improving the NTBM program package are fervently welcomed.