ReaxFF User Manual

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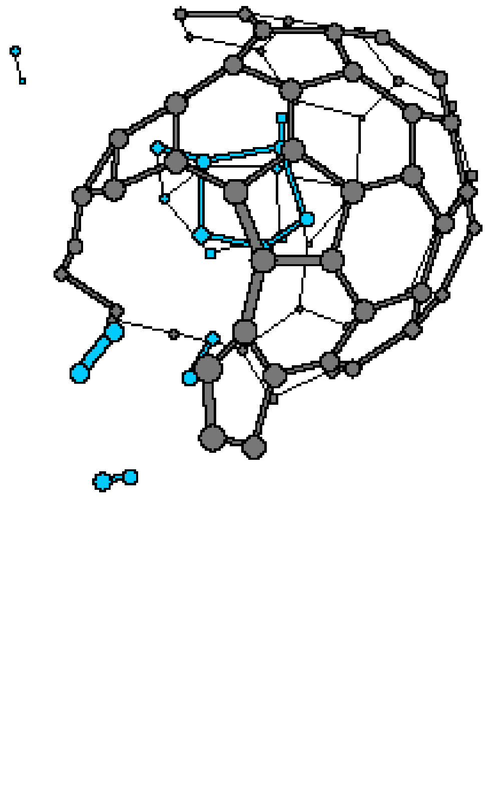


Contents

1. General overview

1.1 Concept. ReaxFF was developed to bridge the gap between quantum chemical (QC) and empirical force field (EFF) based computational chemical methods (Figure 1.1). Where QC methods are, in general, applicable to all chemical systems, regardless of connectivity, their computational expense makes them inapplicable for large (say, more than100 atoms) systems. Their computational expense also makes QC methods primarily applicable for single point or local energy minimization; high-temperature molecular dynamics (MD) simulations are generally too time-consuming.

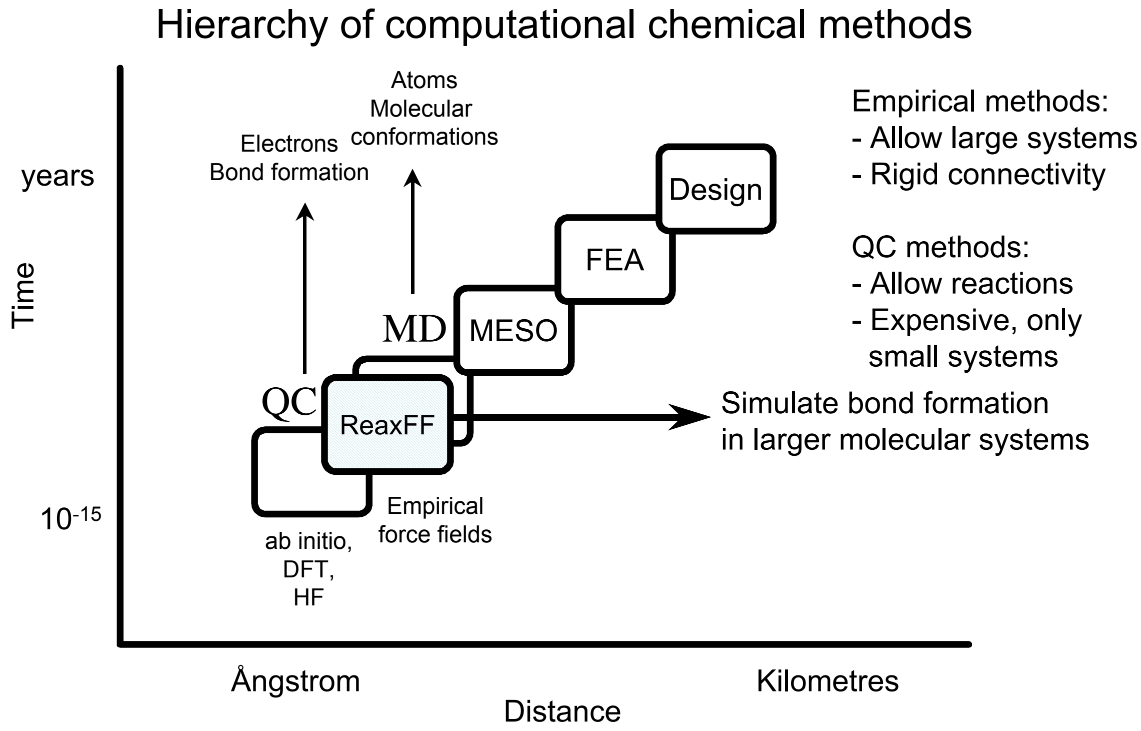


Figure 1.1: Position of ReaxFF in the computational chemical hierarchy.

EFF methods describe the relationship between energy and geometry with a set of relatively simple potential functions. In their most simple form, EFF methods describe molecular or condensed phase systems by simple harmonic equations that describe the stretching and compression of bonds and the bending of bond angles, usually augmented by van der Waals potential functions and Coulomb interactions to describe non-bonded interactions. Their relative simplicity allows EFF methods to be applied to much larger systems than QC systems (thousands of atoms on single processors; millions of atoms on multiprocessors). EFF methods have been very successful in describing physical interactions in and between molecules and condensed phase systems, and EFF methods haven been developed for a wide variety of chemical environments, including hydrocarbons [lit], proteins [lit] and many inorganic systems [lit]. However, EFF methods are mainly applicable for systems at or around their equilibrium configuration. Due to their empirical nature, EFF methods require that the parameters used in their potential functions are fitted against a suite of data, which can be gathered from experimental and/or from QC-sources (a.k.a. training set). The force field resulting from this fitting procedure can obviously be no more reliable than the data used in its training set. Furthermore, as the force field describes the system in an empirical rather than fundamental fashion, it should only be applied to systems similar to the ones present in the training set. As such, the quality and diversity of the training set define the transferability of the EFF method. With a few exceptions, current EFF methods are only trained for systems in which the bonds remain within about 75% of their equilibrium value. For this reason, these EFF methods cannot describe reactive systems, and in most cases the shape of the potential functions applied in these methods, like the aforementioned harmonic description of the bond length/bond energy relationship, would make it impossible to find parameter values that accurately describe bond energy towards the dissociation limit.

The concept of bond order/bond energy relation, as first formulated by Tersoff [lit], allows for the construction of EFF methods that can, in principle, handle connectivity changes. This concept was used by Brenner [lit] to construct the REBO-potential, an EFF method for hydrocarbon systems, allowing, for the first time, dynamical simulations of reactions in large (>>100 atoms) systems. Over the years, REBO has enjoyed widespread application, but its transferability is limited as it is based on a relatively small training set and because of its exclusion of all non-bonded interactions.

As with the Brenner potential, a bond order/bond energy relationship lies at the center of the ReaxFF-potential. Bond orders are obtained from interatomic distances (Figure 2) and are continually updated at every MD or energy minimization (MM) iteration, thus allowing for connectivity changes. These bond orders are incorporated in all valence terms (i.e. energy contributions dependent on connectivity, like valence angle and torsion angle energy) ensuring that energies and forces associated with these terms go to zero upon dissociation. Furthermore, ReaxFF describes non-bonded interactions between all atoms, irrespective of connectivity. Excessive short-range repulsive/attractive non-bonded interactions are circumvented by inclusion of a shielding term in the van der Waals and Coulomb interaction. For a more detailed description of the ReaxFF energy description see [lit].

ReaxFF aims to provide a transferable potential, applicable to a wide range of chemical environments. To ensure its transferability, the following general guidelines have been adopted in its development:

- No discontinuities in energy or forces, even during reactions.
- Each element is described by just one force field atom type. The ReaxFF metal oxide oxygen is described by the same parameters as the ReaxFF oxygen in organic molecules. ReaxFF does not have separate sp^2 and sp^3 atoms for carbon, the method determines the atoms hybridization from its chemical environment.
- No pre-definition of reactive sites is necessary using ReaxFF. Although it is possible to drive reactions using restraints (see Input files section) this is not required; given the right temperature and chemical environment reactions will happen automatically.

1.2 Features. At the moment of writing this manual, the ReaxFF-program supports the following features:

- NVT and NVE dynamics; limited NPT dynamics for molecular systems. Velocity and system volume scaling are performed using the Berendsen method [ref]. Velocity scaling can be performed on the entire system, on individual molecules or on individual atoms. Different temperature regimes can be applied to different parts of the system using the **tregime.in** file. This input file can also be used to increase and decrease system temperature during an MD-simulation and can be used to set op annealing runs.
- Steepest descent and conjugate gradient minimization methods.
- Numerical optimization of cell parameters. Default setting is for cubic optimization, but a/b/c parameters can be optimized separately. Also, c/a ratios can be varied separately (see sections on control and input geometry files).
- ReaxFF supports interatomic distance, angle, torsion angle and centre-of-mass restraints. These restraints can be used to drive reactions and can be defined in the **geo**-file (in .bgf-format). Sliding interatomic distance, angle and torsion restraints can be used in MD-simulations.
- ReaxFF can perform simulations on crystal unit cells, keeping track of bonds and valence angles between periodic images of atoms. Currently, this feature cannot be applied to systems requiring torsion angles across periodic boundaries (e.g. carbon crystals). None of the inorganic ReaxFF force fields developed to date have included torsion energy terms, and as such ReaxFF can do unit cell calculations for these systems. ReaxFF can also be used to create supercell structures (**fort.86**-output file).
- ReaxFF contains a force field optimization module. See input and output file sections for a further description.
- ReaxFF has been developed around the EEM charge derivation method [ref], allowing calculation of geometry dependent charge distributions. As default, ReaxFF equilibrates the charges over the entire systems, however, it can also equilibrate charges within each molecule or run with fixed charges (see **control**-file and **charges**-file in the input file section).
- ReaxFF generates. bgf, .geo, .xyz, .MOP, z-matrix (for molecules) and .pdf output files and can read .geo, .bgf, .xyz and z-matrix files. Trajectories are saved in .xyz-format, with optional velocities. Restart files are generated at user-specified intervals.

1.3 Performance. Calculation speed for ReaxFF greatly depends on the atom connectivity. Slowest calculation speed is obtained for high-density crystal systems requiring valence angle and torsion potentials (i.e. diamond). Table 1.1 shows the ReaxFF calculation speed for some benchmark systems. To date, the largest system ReaxFF has been applied for contained about 5000 atoms. Future developments in parallelizing the ReaxFF-code should greatly increase the feasible system size.

At low and medium temperatures (0-1500K) ReaxFF can run with time-steps of up to 0.5 femtoseconds and retain reasonable energy conservation. At higher temperatures smaller time-steps are required to retain energy conservation.

Table 1.1: Benchmark runs for some crystal and molecular systems. Simulations were performed on a single-processor Compaq XP1000-workstation. The Diamond crystal calculations involved valence and torsion angle energies, the Si(□) calculations did only involve valence angle energies.

System	#atoms	Time/MD simulation (s)
Diamond crystal (□=??)	64	0.5
Diamond crystal (□=??)	256	4
Si(□) crystal (□=??)	64	0.25
Si(□) crystal (□=??)	256	2
13 Methane molecules (□=??)	65	0.1
52 Methane molecules (□=??)	260	0.4

1.4 Current force fields. Table 1.2 shows for which systems ReaxFF has currently been parameterized and at which stage of development these parameters sets are. Note that there often exists a substantial overlap between the parameter sets mentioned in Table 1.2. for example, the ReaxFF^{RDX} parameter set contains the same carbon/hydrogen parameters as ReaxFF^{CH}, while the various metal oxide reactive force fields all share the same oxygen parameters, in accordance with the aforementioned ReaxFF philosophy of transferability.

Table 1.2: Currently available ReaxFF parameter set with quality denomination. * means that parameterization has only been performed for against a fairly limited training set, ** indicates that the parameters have been tested against a reasonably good training set but that further modifications and improvements are expected, *** indicates that these parameters have reached the application-stage.

Name	System	Quality	Reference
ReaxFF^{CH}	Hydrocarbons	***	[lit,lit]
ReaxFF^{CH}	All-carbon (buckyballs, nanotubes)	**	-
ReaxFF^{RDX}	Nitramines	***	[lit]
ReaxFF^{CONSH}	CONSH-systems, proteins	**	-
ReaxFF^{SiO}	Si/SiO$_2$ clusters and condensed phase	***	[lit]
ReaxFF^{AlO}	Al/AlO	***	-
ReaxFF^{SiN}	SiN clusters and condensed phase	*	-
ReaxFF^{ZrO}	Zr and ZrO$_2$ condensed phase	*	-
ReaxFF^{MoO}	Mo and Mo-oxides	**	-
ReaxFF^{Pt}	Pt bulk metal; Pt-C, Pt-H and Pt-O systems	*	-

Training sets for these force fields primarily, and for many systems exclusively, consist of QC data on clusters and condensed phases. Although some of these reactive potentials have been applied successfully neither of these parameter sets are considered final. Our approach is that during an application we will continuously scrutinize the ReaxFF results by checking against QC data (probably by performing targeted QC-simulations on representative small systems). When major discrepancies occur the QC data can be added to the appropriate training set and the parameters can be re-optimized.

By this continuous communication between QC and ReaxFF we should obtain increasingly reliable and transferable reactive force field descriptions.

2. Input Files

2.1 General. The ReaxFF input files can be divided into mandatory files, which are necessary for the program to run, and optional files, which are only needed for specific applications. Table 2.1 gives an overview of the input files.

Table 2.1: Overview of ReaxFF input files.

File name	Section	Short description
geo	Mandatory	system geometry
ffield	Mandatory	force field parameters
control	Mandatory	run control switches
exe	Mandatory	executable script
models.in	Optional	geometry file location
tregime.in	Optional	temperature regime definition
iopt	Optional	normal run/force field optimization toggle
charges	Optional	fixed charges
vels	Optional	restart-file
trainset.in	Force field optimization	training set definition
params	Force field optimization	optimizable force field parameters
koppel2	Force field optimization	links values force field parameters

2.2 Mandatory files.

geo-file. This file describes the system geometry. Currently, ReaxFF supports the .geo, .bgf, .xyz and z-matrix input formats (see examples below). By default, ReaxFF assumes **geo** contains a .geo or a z-matrix format; to use other formats the igeofor-switch in the **control**-file should be given a value of 1 for .bgf format and a value of 2 for .xyz-format. Future developments will be primarily centered around the .bgf-format and will move away from the .geo-format. As such, only a brief description of the .geo-format will be given in this manual.

All **geo**-input formats are format sensitive. Below follows a discussion of several examples of **geo**-input files.

Example 2.1: Non-periodic .bgf-input file.

```
BIOGRF 200
DESCRP  Ethane_radical.
REMARK Example
RUTYPE NORMAL RUN
# THIS LINE IS IGNORED
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM    1   C          39.53649  39.80304  39.57992   C   1 1  -0.2894
HETATM    2   H          39.96404  38.93497  39.07954   H   1 1   0.1031
HETATM    3   C          40.55862  40.34907  40.60075   C   1 1  -0.2330
HETATM    4   H          39.30695  40.55630  38.82721   H   1 1  0.1048
HETATM    5   H          38.62048  39.49467  40.08241   H   1 1  0.1048
HETATM    6   H          40.65314  39.88418  41.56157   H   1 1  0.1048
HETATM    7   H          41.36027  40.97776  40.26860   H   1 1  0.1048
FORMAT CONECT (a6,12i6)
CONECT    1    2    3    4    5
CONECT    2    1
CONECT    3    1    6    7
CONECT    4    1
CONECT    5    1
CONECT    6    3
CONECT    7    3
END
```

Example 2.1 shows a basic, non-periodic .bgf-input file. .bgf is a keyword-driven input format; each line starts with a keyword followed by information associated with that keyword. The .bgf-format is used by various molecular simulation software packages (i.e. Cerius2, Jaguar). As these programs should ignore lines starting with unrecognized keywords the .bgf-format should be easily portable between different applications. ReaxFF recognizes the following .bgf-keywords:

B IOGRF [VERSION NUMBER]: defines .bgf-version number. ReaxFF reads version number 200 (and will stop if other version numbers are provided).

DESCRP [NAME]: System description. This description can be used in **trainset.in** to define a force field training set.

REMARK: Remarks. Multiple REMARK lines are allowed.

RUTYPE [KEYWORD ;NUMBER]: Defines run parameters. If KEYWORD is NORMAL RUN (as in Example 2.1) ReaxFF uses the switches defined in the **control**-file. Alternatively, switches in the **control**-file can be overridden by the KEYWORD options listed in Table 2.2. This options is useful in force field optimizations as different MM-methods can be used for different training set geometries. If no RUTYPE-line is supplied, ReaxFF uses the **control**-file definitions

Table 2.2: RUTYPE keywords supported by ReaxFF.

KEYWORD	Description
NORMAL RUN	Use switches in control-file
MAXIT [NUMBER]	Stop MM-run after NUMBER iterations
ENDPO [NUMBER]	Stop MM-run when RMSG drops below NUMBER
MAXMOV [NUMBER]	Maximum atom movement (in 10^{-6} Å) during steepest descent MM minimization. With NUMBER=0 a conjugate gradient method is used.
SINGLE POINT	Stop MM-run after first point
DOUBLE PRECISION	Double MM maximum number of iterations and half RMSG end point criterion as defined in control-file
LOW PRECISION	Half MM maximum number of iterations as defined in control-file
CELL OPT [NUMBER]	Perform numerical cell optimization in MM. See control-file for options defined by NUMBER
NO CELL OPT	Do not perform numerical cell optimization

FORMAT [STRING]: Supplies format-information. ReaxFF ignores these FORMAT lines; they cannot be used to modify input formatting.

HETATM [ATOM INFO]: Defines atom type and atom position. In this order, the ATOM INFO consists of the atom number, the atom type, the x, y and z-coordinates of the atom in Å, the force field type (same as atom type for ReaxFF), two switches not used by ReaxFF and the atom partial charge. ReaxFF does not use these partial charges.

CONECT [ATOM NUMBER:CONNECTED ATOM NUMBERS]: Connection table. ReaxFF ignores these lines and calculates its own connections.

END: Last line of .bgf-input geometry.

Line starting with a # are ignored by ReaxFF and can be used to supply additional comment.

Example 2.2: Periodic .bgf-input geometry file.

```
XTLGRF 200
DESCRP fcc_1
REMARK Platinum fcc-structure
RUTYPE NORMAL RUN
CRYSTX     4.50640    4.50640    4.50640   90.00000   90.00000   90.00000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM     1    Pt            0.00000   0.00000   0.00000    Pt  1 1  0.00000
HETATM     2    Pt            2.25138   2.25138   0.00000    Pt  1 1  0.00000
HETATM     3    Pt            2.25138   0.00000   2.25138    Pt  1 1  0.00000
HETATM     4    Pt            0.00000   2.25138   2.25138    Pt  1 1  0.00000
FORMAT CONECT (a6,12i6)
END
```

Example 2.2 shows a periodic .bgf-input file. In principle, ReaxFF treats every system as periodic; in non-periodic systems it simply uses large values for the cell parameters (these values are defined by the axis1, axis2 and axis3-switches in the **control**-file). However, these **control**-file definitions are ignored if cell parameters are defined in the **geo**-file. Example 2.2 features the following keywords in addition to Example 2.1:

XTLGRF [VERSION NUMBER]: As BIOGRF-keyword, but tells ReaxFF that user-specified cell parameters are supplied with this geometry.

CRYSTX [A B C Alpha Beta Gamma]: Defines cell lengths (in Å) and cell angles (in degrees) for periodic system.

ReaxFF always uses Cartesian (not fractional) coordinates to define atom positions.

The .bgf-input format can also be used to define interatomic, valence angle, torsion angle and center-of-mass restraints used during MM or MD simulations. Such restraints can be used to drive reactions or to force conformational changes. Example 2.3 shows the

Example 2.3: .bgf-input file with restraints.

```
BIOGRF 200
DESCRP Hshift11
RUTYPE NORMAL RUN
FORMAT BOND RESTRAINT (15x,2i4,f8.4,f8.2,f8.5,f10.7)
#                        At1 At2  R12    Force1  Force2  dR12/dIteration(MD only)
BOND RESTRAINT    1   2  1.0900 7500.00 0.25000 0.0000000
FORMAT ANGLE RESTRAINT (16x,3i4,2f8.2,f8.4,f9.6)
#                          At1 At2 At3   Angle  Force1  Force2  dAngle/dIteration
(MD)
ANGLE RESTRAINT    1     2     3   120.00  250.00 1.00000  0.0000
FORMAT TORSION RESTRAINT (18x,4i4,2f8.2,f8.4,f9.6)
#                            At1 At2 At3 At4   Angle    Force1  Force2    dAngle/dIt
TORSION RESTRAINT    1     2     3    4     45.00     250.00  1.00000   0.0000
FORMAT MASCEN RESTRAINT FREE FORMAT
#                            x/y/z At1  At2   R      At3 At4  Force1  Force2
MASCEN RESTRAINT     x      1      3   1.50     4    7       50.00     0.25
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM    1   C            39.53692  39.80281  39.57996   C   1 1  0.00000
HETATM    2   H            39.96200  38.93424  39.07781   H   1 1  0.00000
HETATM    3   C            40.55717  40.34771  40.59881   C   1 1  0.00000
HETATM    4   H            39.30845  40.55556  38.82947   H   1 1  0.00000
HETATM    5   H            38.62310  39.49566  40.08262   H   1 1  0.00000
HETATM    6   H            40.65332  39.88631  41.56086   H   1 1  0.00000
HETATM    7   H            41.35903  40.97771  40.27048   H   1 1  0.00000
FORMAT CONECT (a6,12i6)
END
```

available restraint input options. The FORMAT lines give the required input format for these restraints. Example 2.3 features the following keywords:

BOND RESTRAINT [At1 At2 R12 Force1 Force2 dR12/dIteration]: Defines bond (i.e. interatomic) restraint between atoms At1 and At2. An additional force is added to the ReaxFF potential, aiming to keep the distance between At1 and At2 restraint at value R12. Force1 and Force2 are the force constants used for this additional force, which is defined in Equation 2.1:

$$E_{restraint}= Force1*\{1.0\text{-}\exp(Force2*(R_{ij}\text{-}R12)^2\} \qquad \textbf{Equation 2.1}$$

During MD-simulations the value of R12 will be modified by dR12/dIteration every iteration. By using this feature, ReaxFF can drive reactions during MD simulations. This option is not available during MM minimizations.

ANGLE RESTRAINT [At1 At2 At3 Angle Force1 Force2 dAngle/dIteration]: Defines angle restraint between atoms At1, At2 and At3. Any angle in the system can be restrained in this way, independent of connectivity. An additional force, similar to Equation 2.1, is added to the ReaxFF potential. As with the bond restraint, dAngle/dIteration can be used to drive angles during an MD simulation.

TORSION RESTRAINT [At1 At2 At3 At4 Angle Force1 Force2 dAngle/dIteration]: Defines torsion angle restraint between atoms At1, At2, At3 and At4. At this moment, this restraint can ONLY be used between connected atoms. In defining the torsion angle At2 should be smaller than At3. Force1 and Force2 define an additional force, similar to that described by Equation 1.2, that is added to the ReaxFF potential. dAngle/dIteration can be used to drive torsion angles during an MD simulation. Driving a torsion angle through 0^o or through 180 ^{o} might cause problems.

MASCEN RESTRAINT [x/y/z At1 At2 R At3 At4 Force1 Force2]: Defines center-of-mass restraints between atoms At1 to At2 and atoms At3 to At4 in either the x, y or z-direction. An additional force, similar to that described in Equation 2.1, is added to the ReaxFF potential, restraining the center-of-mass of atoms At1 to At2 at distance R in the x/y/z directions from the center-of-mass of atoms At3 to At4.

To facilitate building training sets with multiple geometries, ReaxFF can run multiple simulations from one **geo**-file. This is done by putting these geometries in one **geo**-file, separated by one empty line after each END-keyword. Alternatively, the **models.in**-file can be used to define the paths to these multiple **geo**-files.

When combining multiple geometries in one **geo**-file, ReaxFF can repeat simulations on the previous input geometry with modified cell volume. This is useful for obtaining equation of state information for condensed phase systems. Example 2.4 shows an .bgf-input file from which ReaxFF first runs a single point simulation on a Pt-fcc unit cell, followed by a simulation on the same structure in which the cell volume is reduced by 80% (and the atomic positions are rescaled accordingly). This is done using the VCHANGE keyword:

VCHANGE [NUMBER]: repeat the previous simulation with rescaled cell volume and atomic coordinates. The rescaling factor is NUMBER*100%. ReaxFF will automatically use the RUTYPE NO CELL OPT (Table 2.2) option for structure specified with VCHANGE.

As mentioned, future ReaxFF input file developments will primarily focus around the .bgf-format. Anticipated developments include:

- Making the .bgf-input format free.
- Making more **control**-file options available through .bgf-file input, thus allowing all run-input information to be supplied in only one input file.
- Allowing addition of force field training set information (charges, energies) to the .bgf-file. This information should be automatically picked up by ReaxFF and compared to ReaxFF output.

Example 2.4: Periodic .bgf-input geometry file followed by VCHANGE option.

```
XTLGRF 200
DESCRP fcc_1
REMARK Platinum fcc-structure
RUTYPE SINGLE POINT
CRYSTX     4.50640    4.50640    4.50640   90.00000   90.00000   90.00000
FORMAT ATOM   (a6,1x,i5,1x,a5,1x,a3,1x,a1,1x,a5,3f10.5,1x,a5,i3,i2,1x,f8.5)
HETATM     1    Pt            0.00000   0.00000   0.00000    Pt  1 1  0.00000
HETATM     2    Pt            2.25138   2.25138   0.00000    Pt  1 1  0.00000
HETATM     3    Pt            2.25138   0.00000   2.25138    Pt  1 1  0.00000
HETATM     4    Pt            0.00000   2.25138   2.25138    Pt  1 1  0.00000
FORMAT CONECT (a6,12i6)
END

XTLGRF 200
DESCRP fcc_2
REMARK Rerun fcc_1 at 80% volume
VCHANGE 0.80
END
```

As an alternative to the .bgf-input format, ReaxFF can also read .geo-, .xyz- and z-matrix formats. Example 2.5 shows an ReaxFF .geo input file. The first line of the .geo-format contains a control-character (C in Example 2.5) and the name of the structure. The next lines contain the atom number, atom type and the x,y and z-coordinates. By means of the control-character, the .geo-format provides most of the options available with the .bgf-format. As we are moving away from supporting the .geo-format we only summarize these options in Table 2.3; more information can be obtained from the author.

Example 2.5: .geo-input file.

```
C   Ethyl_radical
  1 C    0.39536921883140E+02  0.39802812097390E+02  0.39579964797377E+02
  2 H    0.39962000508882E+02  0.38934237894502E+02  0.39077807973956E+02
  3 C    0.40557168455097E+02  0.40347711311539E+02  0.40598809008712E+02
  4 H    0.39308447421804E+02  0.40555557250666E+02  0.38829468433362E+02
  5 H    0.38623101361336E+02  0.39495660102816E+02  0.40082615760111E+02
  6 H    0.40653318128573E+02  0.39886313307789E+02  0.41560863579234E+02
  7 H    0.41359032241168E+02  0.40977708035298E+02  0.40270480449231E+02
```

Table 2.3 Control character options available with .geo-format.

Control character	Effect
C	Normal run as defined in control-file
F	Use cell parameters (defined on lines 2+3 of .geo-format)
1	Single point
D	Double precision run
H	Low precision run
5	Use cell parameters; single point

Example 2.6: z-matrix input file.

```
I  Ethyl_radical
         1 C
      1  2 C                        1.08962
   1  2  3 C             42.38253   2.15999
2  3  1  4 H -119.14400 110.52474   1.08723
2  3  1  5 H  119.14417 110.52466   1.08723
5  1  3  6 H   38.20847 120.04903   1.07130
5  1  3  7 H -159.92026 120.04917   1.07130
```

Example 2.6 demonstrates the ReaxFF z-matrix input format. The ‘I’ on position 3 on the first line is required as a format-type identifier and is followed by the structure name. The following lines have the 4i3,1x,a2,3f10.5 format and contain at_l, at_k, at_j, at_i, atype, $tors_{ijkl}$, $angle_{ijk}$ and R_{ij}, where $tors_{ijkl}$ is the at_i-at_j-at_k-at_l torsion angle, $angle_{ijk}$ the at_i-at_j-at_k angle, R_{ij} the at_i-at_j interatomic distance and atype the atom type of at_i. By using internal instead of Cartesian coordinates, the z-matrix-input format facilitates building molecules. The z-matrix does not provide room to define cell parameters and, as such, can only be used in concert with the default cell parameters axis1, axis2 and axis3 from the **control**-file.

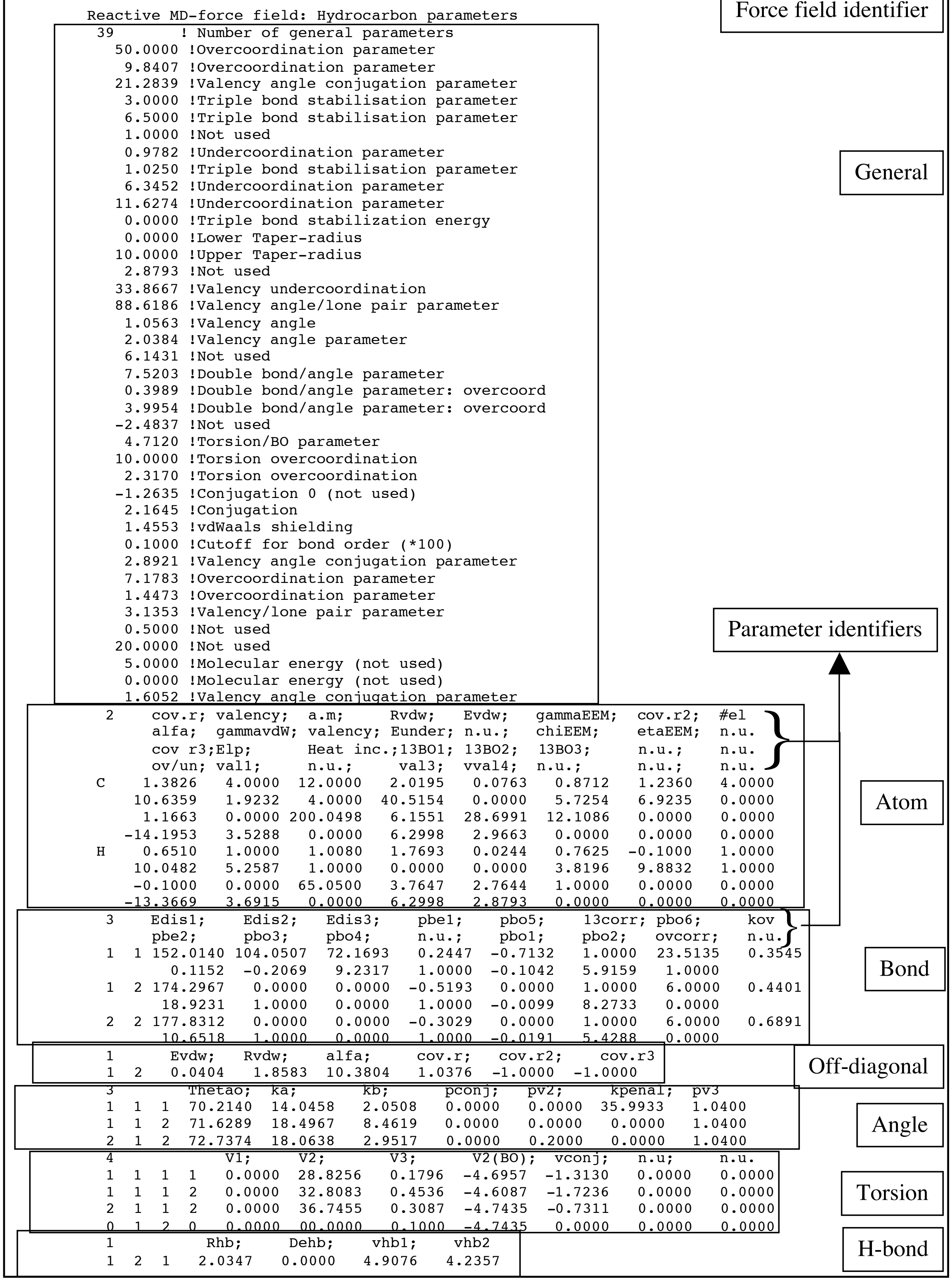
Example 2.7: .xyz-input file.

```
7
Ethyl_radical
C  39.53692  39.80281  39.57996
H  39.96200  38.93424  39.07781
C  40.55717  40.34771  40.59881
H  39.30845  40.55556  38.82947
H  38.62310  39.49566  40.08262
H  40.65332  39.88631  41.56086
H  41.35903  40.97771  40.27048
```

ReaxFF supports the .xyz-format in Example 2.7 because its simplicity facilitates communication with other simulation software and molecular viewers (e.g Icarus, Molden and Xmol). The first line of the .xyz-format contains the number of atoms, the second line the structure name. The other lines contain the type and x,y,z Cartesian coordinates for each of the atoms. The .xyz format cannot communicate cell parameters and, as such, can only be used with the default cell parameters axis1, axis2 and axis3 defined in the **control**-file.

ffield-file. The **ffield** input file contains the force field parameters. The first line of the **ffield**-input file contains a force field identifier (Example 2.8). Thereafter, the force field is divided into 7 sections, containing the general, atom, bond, off-diagonal, valence angle, torsion angle and hydrogen bond parameters. Below follows a description of the format and meaning of the force field parameters in each of these sections.

Example 2.8: **ffield**-input file.



```
Reactive MD-force field: Hydrocarbon parameters
 39       ! Number of general parameters
   50.0000 !Overcoordination parameter
    9.8407 !Overcoordination parameter
   21.2839 !Valency angle conjugation parameter
    3.0000 !Triple bond stabilisation parameter
    6.5000 !Triple bond stabilisation parameter
    1.0000 !Not used
    0.9782 !Undercoordination parameter
    1.0250 !Triple bond stabilisation parameter
    6.3452 !Undercoordination parameter
   11.6274 !Undercoordination parameter
    0.0000 !Triple bond stabilization energy
    0.0000 !Lower Taper-radius
   10.0000 !Upper Taper-radius
    2.8793 !Not used
   33.8667 !Valency undercoordination
   88.6186 !Valency angle/lone pair parameter
    1.0563 !Valency angle
    2.0384 !Valency angle parameter
    6.1431 !Not used
    7.5203 !Double bond/angle parameter
    0.3989 !Double bond/angle parameter: overcoord
    3.9954 !Double bond/angle parameter: overcoord
   -2.4837 !Not used
    4.7120 !Torsion/BO parameter
   10.0000 !Torsion overcoordination
    2.3170 !Torsion overcoordination
   -1.2635 !Conjugation 0 (not used)
    2.1645 !Conjugation
    1.4553 !vdWaals shielding
    0.1000 !Cutoff for bond order (*100)
    2.8921 !Valency angle conjugation parameter
    7.1783 !Overcoordination parameter
    1.4473 !Overcoordination parameter
    3.1353 !Valency/lone pair parameter
    0.5000 !Not used
   20.0000 !Not used
    5.0000 !Molecular energy (not used)
    0.0000 !Molecular energy (not used)
    1.6052 !Valency angle conjugation parameter
  2     cov.r; valency;  a.m;     Rvdw;   Evdw;   gammaEEM;  cov.r2;  #el
        alfa;  gammavdW; valency; Eunder; n.u.;   chiEEM;    etaEEM;  n.u.
        cov r3;Elp;      Heat inc.;13BO1; 13BO2;  13BO3;     n.u.;    n.u.
        ov/un; val1;     n.u.;     val3;  vval4;  n.u.;      n.u.;    n.u.
 C    1.3826   4.0000  12.0000   2.0195   0.0763   0.8712   1.2360   4.0000
     10.6359   1.9232   4.0000  40.5154   0.0000   5.7254   6.9235   0.0000
      1.1663   0.0000 200.0498   6.1551  28.6991  12.1086   0.0000   0.0000
    -14.1953   3.5288   0.0000   6.2998   2.9663   0.0000   0.0000   0.0000
 H    0.6510   1.0000   1.0080   1.7693   0.0244   0.7625  -0.1000   1.0000
     10.0482   5.2587   1.0000   0.0000   0.0000   3.8196   9.8832   1.0000
     -0.1000   0.0000  65.0500   3.7647   2.7644   1.0000   0.0000   0.0000
    -13.3669   3.6915   0.0000   6.2998   2.8793   0.0000   0.0000   0.0000
  3    Edis1;    Edis2;   Edis3;    pbe1;    pbo5;     13corr; pbo6;    kov
       pbe2;     pbo3;    pbo4;     n.u.;    pbo1;     pbo2;   ovcorr;  n.u.
  1  1 152.0140 104.0507  72.1693   0.2447  -0.7132   1.0000  23.5135   0.3545
         0.1152  -0.2069   9.2317   1.0000  -0.1042   5.9159   1.0000
  1  2 174.2967   0.0000   0.0000  -0.5193   0.0000   1.0000   6.0000   0.4401
        18.9231   1.0000   0.0000   1.0000  -0.0099   8.2733   0.0000
  2  2 177.8312   0.0000   0.0000  -0.3029   0.0000   1.0000   6.0000   0.6891
        10.6518   1.0000   0.0000   1.0000  -0.0191   5.4288   0.0000
  1      Evdw;   Rvdw;    alfa;     cov.r;   cov.r2;    cov.r3
  1  2   0.0404   1.8583  10.3804   1.0376  -1.0000  -1.0000
  3         Thetao;  ka;        kb;       pconj;   pv2;     kpenal;  pv3
  1  1  1  70.2140  14.0458   2.0508   0.0000   0.0000  35.9933   1.0400
  1  1  2  71.6289  18.4967   8.4619   0.0000   0.0000   0.0000   1.0400
  2  1  2  72.7374  18.0638   2.9517   0.0000   0.2000   0.0000   1.0400
  4             V1;      V2;        V3;      V2(BO);  vconj;   n.u;     n.u.
  1  1  1  1   0.0000  28.8256   0.1796  -4.6957  -1.3130   0.0000   0.0000
  1  1  1  2   0.0000  32.8083   0.4536  -4.6087  -1.7236   0.0000   0.0000
  2  1  1  2   0.0000  36.7455   0.3087  -4.7435  -0.7311   0.0000   0.0000
  0  1  2  0   0.0000  00.0000   0.1000  -4.7435   0.0000   0.0000   0.0000
  1            Rhb;     Dehb;    vhb1;    vhb2
  1  2  1   2.0347   0.0000   4.9076   4.2357
```

General parameters. The first section of the force field contains the general parameters, which affect all interactions regardless of atom type. The first line of this section contain the npar, the number of general parameters present in the force field file (format i3), followed by npar lines each containing a parameter value followed by a parameter identified. Of particular interest are the Upper Taper radius parameters, which describes the non-bonded cutoff radius, and the Cutoff for bond orders, which describes the bond order threshold, above which atoms are considered connected. Both these parameters have major impact on the ReaxFF calculation speed; decreasing the Upper Taper radius parameter or increasing the bond order cutoff parameter will can make ReaxFF run considerably faster. These parameters, however, have a major impact on the force description and can, as such, not be changed without re-parameterization of other parts of the force field.

Table 2.4: Description of the Carbon ('C') parameters in the **ffield**-file in Example 2.8. n.u. identifiers in the **ffield**-file signify 'not used'; these parameters are left out of the description in this table.

Parameter value	Identifier	Description
1.3826	cov.r	sigma bond covalent radius
4.0000	valency	Valency
12.0000	a.m.	Atomic mass
2.0195	Rvdw	van der Waals radius
0.0763	Evdw	van der Waals dissociation energy
0.8712	gammaEEM	EEM shielding
1.2360	cov. r2	pi bond covalent radius
4.0000	#el.	Number of valence electrons
10.6359	alfa	van der Waals parameter
1.9232	gammavdW	van der Waals shielding
4.0000	valency	valency for 1,3-BO correction
40.5154	Eunder	Undercoordination energy
5.7524	chiEEm	EEM electronegativity
6.9235	etaEEM	EEM hardness
1.1663	cov. r3	double pi bond covalent radius
0.0000	Elp	Lone pair energy
200.049	Heat inc.	Heat of formation increment
6.1551	13BO1	Bond order correction
28.6991	13BO2	Bond order correction
12.1086	13BO3	Bond order correction
-14.1953	ov/un	Over/undercoordination
3.5288	vval1	Valence angle energy
6.2998	vval2	Valence angle energy
2.9663	vval3	Valence angle energy

Atom parameters. The second section of the force field contains the atom parameters. The section starts with the number of atom types present in the force field, followed by four lines of parameter identifiers. Thereafter follow four lines for each atom, starting with a line containing the atom name an 8 parameter values (format 1x,a2,8f9.4) followed by three lines with 8 parameter values (format 3x, 8f9.4). Table 2.4 gives a short description of the meaning of each parameter for Carbon ('C' atom name) in the atom parameter section. If negative values are given to either of the three bond radii (sigma, pi and double pi) bond order contributions are ignored for that atom. In Example 2.8, only the sigma bond radius for H has a positive value (0.6510).

Table 2.5 Description of carbon-carbon bond parameters in the **ffield**-file in Example 2.8. n.u. identifiers in the **ffield**-file signify 'not used'; these parameters are left out of the description in this table.

Parameter value	Identifier	Description
152.0140	Edis1	Sigma-bond dissociation energy
104.0507	Edis2	Pi-bond dissociation energy
72.1693	Edis3	Double pi-bond dissociation energy
0.2447	pbe1	Bond energy
-0.7132	pbo5	Double pi bond order
1.000	13corr	1,3-Bond order correction
23.5135	pbo6	Double pi bond order
0.3545	kov	Overcoordination penalty
0.1152	pbe2	Bond energy
-0.2069	pbo3	Pi bond order
9.2317	pbo4	Pi bond order
-0.1042	pbo1	Sigma bond order
5.9159	pbo2	Sigma bond order
1.0000	ovcorr	Overcoordination BO correction

Bond parameters. The second section of the force field contains the bond parameters. This section starts with the number of bond types defined in the force field, followed by two lines of parameter identifiers. Then follow two lines for each bond type, the first of which (format 2i3,8f9.4) contains two atom type identifiers, followed by 8 parameter values. The atom type identifiers define the bond;'1 1', for example, describes the bond between atom #1 and atom #1 (the C-C bond in case of Example 2.8, as C is the first atom type defined in the Atom section). The second line (format 6x, 8f9.4) contains another 8 parameter values. ReaxFF will terminate if at *any* stage of the simulation a bond type is found that is not defined in the **ffield**-file. Table 2.5 gives a short description of the C-C bond parameters in the force field from Example 2.8.

Off-diagonal terms. This section allows for the definition of off-diagonal values for both bond order and van der Waals pair interactions. By default, ReaxFF calculates these terms from the combination rules and the atom parameters (i.e. the default C-H van der Waals radius is $(R_{vdW}[C]*R_{vdW}[H])^{0.5}$), but the off-diagonal section allows for the definition of different values. Any value given in the off-diagonal section overrules that obtained from the combination rules.

The off-diagonal section starts with the number of off-diagonal types defined in the force field, followed on the same line by parameter identifiers. Then follow one line each for each off-diagonal type (format 2i3,6f9.4), beginning with the type identifier ('1 2' in Example 2.8 defines the C-H off diagonal parameters) followed by six parameters. Table 2.6 gives a short description of the C-H off-diagonal parameters from Example 2.8.

Table 2.6 Description of C-H off diagonal parameters in the **ffield**-input file in Example 2.8. The negative values for cov.r2 and cov. r3 signify that pi and double pi bond orders are not calculated for C-H pairs.

Parameter value	Identifier	Short description
0.0404	Ediss	vdWaals dissociation energy
1.8583	Rvdw	vdWaals radius
10.3804	alfa	vdWaals parameter
1.0376	cov. r	sigma bond covalent radius
-1.0	cov. r2	pi bond covalent radius
-1.0	cov. r3	double pi bond covalent radius

Valence angle parameters. The fifth section in the **ffield**-file contains the valence angle parameters. This section starts with a line containing the number of valence angles defined in the force field, followed with the parameter identifiers. Thereafter follow one line for each valence angle type. Each of these lines (format 3i3,7f9.4) starts with the valence angle identifier (e.g. '1 1 1' in Example 2.8, which defines the C-C-C valence angle) followed by seven parameters. ReaxFF will ignore valence angles in the simulation that are not defined in the **ffield**-file. Table 2.7 gives a short description of the C-C-C valence angle parameters from Example 2.8.

Table 2.7 Description of C-C-C valence angle parameters in the **ffield**-input file in Example 2.8.

Parameter value	Identifier	Short description
70.2140	Thetao	180°-(equilibrium angle)[a]
14.0458	ka	1st force constant
2.0508	kb	2nd force constant
0.0000	pconj	Valence conjugation
0.0000	pv2	Undercoordination
35.9933	kpenal	Penalty energy
1.0400	pv3	Energy/bond order

[a]: This lead to an equilibrium angle of 109.7860° for the C-C-C sigma-bond angle.

Torsion angle parameters. The sixth section in the ffield-file contains the torsion angle parameters. This sections starts with a line containing the number of torsion angles defined in the force field and the parameter identifiers. Thereafter follows one line for each torsion angle type. Each of these lines (format 4i3,7f9.4) starts with the torsion angle identifier, followed by seven parameters. Two types of torsion angle parameters identifiers are available: (1) identification by only the central bond or (2) identification by all four atoms in the torsion angle. For example, the '1 1 1 1' identifier on the second line of the torsion angle section in Example 2.8 defines the C-C-C-C torsion angle parameters, while the '0 1 2 0' identifier defined all X-C-H-X torsion angles. The four-atom identifier overrules the central bond identifier, thus, it is possible to define all carbon-carbon torsion angles with '0 1 1 0' and define a special case for C-C-C-H torsion angles with '1 1 1 2'.

ReaxFF will ignore torsion angles not defined in the **ffield**-file. Table 2.8 gives a short description of the C-C-C-C torsion angle parameters from Example 2.8.

Table 2.8 Description of the C-C-C-C torsion angle parameters in the **ffield**-input file in Example 2.8. n.u. identifiers mean that this parameter field is currently not used.

Parameter value	Identifier	Short description
0.0000	V1	V1-torsion barrier
28.8256	V2	V2-torsion barrier
0.1796	V3	V3-torsion barrier
-4.6957	V2(BO)	V2/bond order
-1.3130	vconj	Torsion angle conjugation

Hydrogen bond parameters. The seventh section of the force field contains the hydrogen bond parameters. This section starts with a line containing the number of hydrogen bond types described in the force field and the parameter identifiers. Thereafter follows one line for each hydrogen bond type. This line (format 3i3,4f9.4) first defines the hydrogen bond type, followed by four parameter values. The identifier '1 2 1' in line 2 of the hydrogen bond section in Example 2.8 refers to the C-H - - C hydrogen bond. ReaxFF will ignore hydrogen bonds not defined in the **ffield**-input file. Table 2.9 gives a short description of the C-H - - C hydrogen bond parameters from Example 2.8.

Table 2.9 Description of the C-H - - C hydrogen bond parameters in the **ffield**-input file in Example 2.8.

Parameter value	Identifier	Short description
2.0347	Rhb	Hydrogen bond equilibrium distance
0.0000	Dehb	Hydrogen bond dissociation energy
4.9076	vhb1	Hydrogen bond/bond order
4.2357	vhb2	Hydrogen bond parameter

control-file. This file contains the run-control parameters for ReaxFF. Example 2.9 shows a **control**-file used for an NVT MD-simulation. Apart from the comment-lines (lines starting with a #) each line contains a number, a keyword and an optional keyword description. The **control**-file is format free and keywords can be arranged in any order. ReaxFF will re-check **control**-file during an MD-simulation of a force field optimization run, giving the user the option to modify a ongoing simulation. If a keyword is left out of the **control**-file ReaxFF will use a default value. Tables 2.10-2.13 describe the name, default value and function of the general, MD, MM and force field optimization keywords currently recognized by ReaxFF. This division in general, MD, MM and force field optimization parameters is used here for convenience only and bears no further significance.

Example 2.9. control-file for an NVT MD-simulation.

```
# General parameters
      0 imetho     0: Normal MD-run 1: Energy minimisation 2:MD-energy minimisation
      1 igeofo     0:xyz-input 1: Biograf input 2: xmol-input geometry
 80.000 axis1      a (for non-periodical systems)
 80.000 axis2      b (for non-periodical systems)
 80.000 axis3      c (for non-periodical systems)
 0.0010 cutof2     BO-cutoff for valency angles and torsion angles
  0.300 cutof3     BO-cutoff for bond order for graphs
      3 icharg     Charges. 1:EEM 2:- 3: Shielded EEM  4: Full system EEM 5: Fixed
      1 ichaen     Charges. 1:include charge energy 0: Do not include charge energy
     25 irecon     Frequency of reading control-file
# MD-parameters
      1 imdmet     MD-method. 1:Velocity Verlet+Berendsen 2:-;3:NVE 4: NPT
  0.500 tstep      MD-time step (fs)
0050.00 mdtemp     1st MD-temperature
      2 itdmet     0: T-damp atoms 1: - 2:System 3: Mols 4: Anderson
   25.0 tdamp1     1st Berendsen/Anderson temperature damping constant (fs)
0001000 nmdit      Number of MD-iterations
    005 iout1      Output to unit 71 and unit 73
   0050 iout2      Save coordinates
 000025 irten      Frequency of removal of rotational and translational energy
  00025 itrafr     Frequency of trarot-calls
      1 iout3      0: create moldyn.xxxx-files 1: do not create moldyn.xxxx-files
      1 iravel     1: Random initial velocities
 000500 iout6      Save velocity file
 02.50 range       Range for back-translation of atoms
```

Table 2.10. Name, default value and function of the general keywords in the **control**-file.

Name	Default	Function
imetho	0	0: MD-run; 1: MM-run; 2: MD-energy minimization
igeofo	0	0: .geo- or z-matrix input; 1: .bgf-input; 2: .xyz-input
axis1	200.0	a-cell parameter for non-periodic systems
axis2	200.0	b-cell parameter for non-periodic systems
axis3	200.0	c-cell parameter for non-periodic systems
cutof2	0.001	Bond order cutoff for valence and torsion angles
cutof3	0.300	Bond order cutoff for graphs and **fort.7**
icharg	3	Charge calculation. 1: EEM; 2 -; 3: Shielded EEM; 4: Full-system EEM; 5: fixed charges from charges-file
ichaen	1	0: Do not include charge energy; 1: include charge energy
iappen	0	1: Append **fort.7** and **fort.8**-connection tables 0: Overwrite
isurpr	0	0: Full output 1: Suppress some output; 2: Suppress most output and read in all geometries at once (for force field optimization)
icheck	0	0: Normal run; 1: Single point + 1st derivatives check;2: Single point
idebug	0	0: Normal run; 1: Output subroutine names in **fort.65**
ixmolo	0	0: Only x,y,z-coordinates in **xmolout**; 1: add velocities to **xmolout**

Table 2.11. Name, default value and function of the MD-related keywords in the **control**-file. Frequency refers to how often (in MD-iterations) a certain function is performed. Refer to the Output-section for more detail on output files.

Name	Default	Function
imdmet	3	MD-method. 1: NVT; 2: -; 3: NVE; 4: NPT
tstep	0.5	MD time step (fs)
mdtemp	298.0	MD temperature
itdmet	2	Systems used in temperature control method. 0: atoms; 1: -; 2: whole system; 3: molecules
tdamp1	2.5	Berendsen temperature damping constant (fs)
mdpres	0.0	MD pressure (GPa)
pdamp1	500.0	Berendsen pressure damping constant (fs)
inpt	0	0: Change all cell parameters in NPT; 1/2/3: fixed a/b/c
nmdit	1000	Number of MD-iterations
ichupd	1	Charge update frequency
iout1	5	Output frequency to **fort.71** and **fort.73**
iout2	50	Output frequency to **xmolout** and **moldyn.vel**
ivels	0	0: Use velocities from **vels** restart-file; 1: Zero initial velocities
iout3	0	0: create **moldyn.xxxx** .xyz-trajectory files; 1: Not.
iravel	0	0: Zero initial velocities; 1: Random initial velocities. Ignored if **vels**-restart file is present.
endmd	1.0	RMSG endpoint criterium for MD energy minimization
iout6	1000	Frequency of **molsav.xxxx** restart file creation
irten	25	Rotational and translational energy removal frequency
npreit	0	Number of MD-iterations in previous runs (for restarts)
range	2.50	Range for back-translation of atoms outside periodic box (Å)
irecon	25	Frequency of re-checking **control**-file

Table 2.12. Name, default value and function of the MM-related keywords in the **control**-file. Frequency refers to how often (in MM-iterations) a certain function is performed. Refer to the Output-section for more detail on output files.

Name	Default	Function
endmm	1.0	RMSG MM end point criterium
imaxmo	50	0: Conjugate gradient; >0: Maximum move (1/10^6 Å) in steepest descent
imaxit	50	Maximum number of MM iterations
iout4	50	Frequency of structure output in **xmolout**
iout5	0	1: remove **fort.57** and **fort.58**-files
icelop	0	0: No cell optimization 1: Numerical cell optimization
celopt	1.0005	Cell parameter optimization stepsize
icelo2	0	0: Cubic cell optimization; 1/2/3: only a/b/c; 4: c/a ratio

Table 2.13. Name, default value and function of the force field optimization related keywords in the control-file. For a more detailed discussion of these parameters see the Force field optimization input and output sections.

Name	Default	Function
parsca	1.0	Scale parameter step
parext	0.001	Parameter extrapolation
igeopt	1	0: Always use same start geometries; 1: Update start geometries
iincop	0	Heat increment optimization. 0: No; 1: Yes
accerr	2.50	Accepted increase error force field

exe-file. The **exe**-file contains the script that copies the input files to the right location, calls the ReaxFF-executable and, optionally, copies output files. The **exe**-script gets called from the UNIX command line. Example 2.10 shows the **exe**-script currently used by the author; users with a knowledge of UNIX scripting will probably want to personalize this file. Please note that the some of the input file names, like **geo** and **ffield**, used in this manual are defined in this script; the ReaxFF program only recognizes these input files as **fort.3** (**geo**) and **fort.4** (**ffield**). Other files (**control**, **models**.**in**, **trainset**.**in** and **tregime**.**in**) have their names hard coded in the ReaxFF source and need not to be moved by the **exe**-script to a fort.#-unit.

Example 2.10: **exe**-script used for running ReaxFF from the UNIX command line.

```
#
if (-f xmolout) rm xmolout
if (-f moldyn.vel) mv  moldyn.vel vels23
if (-f fort.58) cp fort.58 58s
if (-f fort.57) cp fort.57 57s
if (-f fort.71) cp fort.71 71s
if (-f fort.73) cp fort.73 73s
if (-f fort.13) cp fort.13 13s
if (-f fort.99) cp fort.99 99s
if (-f fort.7) cp fort.7 7s
if (-f fort.8) cp fort.8  8s
```

Save output files from previous run

```
touch fort.5a
touch moldyn.0a
touch molsav.0a
rm fort.*
rm moldyn.0*
rm molsav.0*
if  (-f control )  then
#
else
echo 'Missing control'
exit
endif
if  (-f geo )  then
cp geo fort.3
else
echo 'Missing geo'
exit
endif
if  (-f ffield )  then
cp ffield fort.4
else
echo 'Missing ffield'
exit
endif
```

Check presence mandatory files; stop if not present.
Copy **geo** to **fort.3** and **ffield** to **fort.4**

```
if  (-f ranfile )  then
cp ranfile fort.35
else
echo 'Created ranfile in unit 35'
echo '234535.1' > fort.35
endif
if (-f iopt ) then
cp iopt fort.20
else
echo 'Created iopt in unit 20; assume normal run'
echo '  0   0: Normal run   1: Force field optimization' > fort.20
endif
```

Create default **ranfile** and **iopt** if not provided.
If provided, copy these files to units 35 and 20.

```
touch fort.9
if (-f params) cp params fort.21
if (-f koppel2) cp koppel2 fort.23
if (-f charges) cp charges fort.26
if (-f vels) cp vels moldyn.vel
```

Copy optional files to their units.

```
reac > run.log
exit
```

→ Call executable; redirect output to run.log

2.3 Optional files.

models.in-file. As an alternative to running ReaxFF using a **geo**-file containing one or more input geometries, the **models.in**-file can be used to communicate the location of input geometry files to ReaxFF. This has the advantage that these geometry files can be organized in directories. Example 2.11 demonstrates the use of the models.in-file.

Example 2.11**. models.in** input file.

```
#Location           Keyword for trainset.in
../Pt/Pt_fcc1.bgf   fcc_1
../Pt/Pt_fcc2.bgf   fcc_2
../Pt/Pt_fcc3.bgf   fcc_3
END
```

Lines commencing with a #, as line 1 in Example 2.11, are ignored by ReaxFF. Lines 2-5 define the path to three separate input files, which will be run in consecutive order. **models.in** also allows the user to attach a keyword to these input geometries, which can be used by **trainset.in** in a force field optimization procedure. This is the same as the identifier in the DESCRP-field of the .bgf-input format. The keyword defined in the **models.in**-file overrides that defined in the DESCRP-field. The END-command is optional and indicates to ReaxFF that the final geometry has been reached.

tregime.in-file. This file can be used to define temperature regimes during an NVT of NPT MD-simulation. Example 2.12 demonstrates the format used in this file.

Example 2.12. **tregime.in** input file .

```
#Start #Zones At1 At2  Tset1 Tdamp2 dT1/dIt At3  At4  Tset2 Tdamp2 dT2/dIt
0       2      1   20  200.0 50.0    0.05    21   40   10.0  1.0     0.00
10000   2      1   20  700.0 50.0    0.00    21   40   10.0  1.0     0.00
20000   2      1   20  700.0 50.0   -0.10    21   40   10.0  1.0     0.00
```

This example splits the system into 2 zones (#Zones), atoms 1-20 (At1-At2) and atoms 21-40 (At3-At4). Atoms 1-20 get heated up at a rate of 0.05K/iteration during the first 10,000 MD-iterations, taking their temperature from 200.0 to 700.0 K. During the second stage (iteration 10,000-20,000; line 3) atoms 1-20 remain constant at 700K after which they get cooled down at a rate of 0.10K/iteration during the last stage (iteration 20,000-end). Meanwhile, atoms 21-40 are kept at a temperature of 10.0K during the entire simulation. In principle, unlimited amounts of temperature zones and temperature stages can be defined in this way, thus allowing for intricate annealing simulations.

iopt-file. As the force field optimization routines are written as a shell around the rest of the ReaxFF program, the **control**-file cannot be used to switch between a normal and a force field optimization run. For this reason, the **iopt**-file, which gets copied by the **exe**-script to **fort.20**, gets read by this outside shell. The **iopt**-file only contains 1 integer, format i3. If a value of 0 is given a normal run is performed, while a 1 results in a force field optimization run. Officially, this file in mandatory, but the **exe**-script (Example 2.10) will create a default **fort.20** with a value of 0 if this file is not present in the directory from which it is invoked.

charges-file. When a value of 5 is given for icharge keyword in the **control**-file (Table 2.10) ReaxFF will run with fixed charges, which it will read in from the **charges**-input file. Example 2.13 demonstrates the format of this file.

Example 2.13. **charges**-file for a system containing 5 methane (molecule 1 to 5) and 5 water molecules (molecule 6 to 10).

```
   2              ! Number of molecule types (format i4)
   1   5   6  10  ! Molecule type definition (format 20i4)
Methane           ! Molecule 1 identifier
   5              ! Number of atoms in molecule 1
   1   -0.4800    ! Atom number; charge (format (i4,f10.6) )
   2    0.1200
   3    0.1200
   4    0.1200
   5    0.1200
Water             ! Molecule 2 identifier
   3              !  Number of atoms in molecule 2
   1   -0.8200    ! Atom number; charge
   2    0.4100
   3    0.4100
```

The **charges**-file input format facilitates defining fixed charges for systems containing multiple copies of the same molecule. With a bit of editing, this file can be straightforwardly generated from the ReaxFF partial charges output in **fort.56**. Running with fixed instead of geometry-dependent charges will make ReaxFF run faster and may help at the initial stages of equilibration, as the flexible charges may make a unequilibrated system unstable. However, in many cases partial charge distributions will be greatly modified by reactions. For that reason, running a reactive simulation with fixed charges might lead to unrealistic results.

The **charges**-file gets copied to **fort.26** by the **exe**-script, from which it is accessed by ReaxFF.

vels-file. The **vels**-file contains the atom positions, velocities and accelerations and can be used to restart an MD-simulation. During an MD-simulation ReaxFF will, at intervals defined by **control**-keywords iout2 and iout6 (Table 2.11), generate **moldyn.vel** and **molsav.xxxx** restart files. **moldyn.vel** contains the most recent system information. By copying one of these restart files to **vels** and re-running the **exe**-script ReaxFF will continue the MD-simulation. The geometry in **vels** will override any geometry given in the **geo**-file. The **geo**-file is still required, however, and ReaxFF will check whether the **geo** and the **vels**-file contain the same number of atoms. Example 2.14 demonstrates the format of the **vels**-file.

The **vels**-file gets (somewhat confusingly) copied to **moldyn.vel** by the **exe**-script. ReaxFF reads this **moldyn.vel**-file and subsequently overwrites it, at MD-iteration intervals defined by the iout2-keyword (Table 2.11) in the **control**-file, with the latest coordinates, velocities and accelerations.

Example 2.14: **vels**-restart file generated from an MD-simulation on an ethyl radical. The previous acceleration data is outdated and is of no influence to the ReaxFF-run.

```
Lattice parameters:
   80.00000000    80.00000000    80.00000000
   90.00000000    90.00000000    90.00000000
  7 Atom coordinates (Angstrom):
  0.392027787892917E+02  0.400902383055691E+02  0.396569719222545E+02   C
  0.408076194536754E+02  0.407017914536647E+02  0.409641189620557E+02   H
  0.406156358473423E+02  0.399085739070730E+02  0.402446784332288E+02   C
  0.389320157142440E+02  0.409742263417328E+02  0.391261065022365E+02   H
  0.384743625215192E+02  0.392966529997087E+02  0.397356676283833E+02   H
  0.413546771765171E+02  0.399886339278518E+02  0.394389532581619E+02   H
  0.407016447482017E+02  0.389398236842467E+02  0.407560383741949E+02   H
 Atom velocities (Angstrom/s):
 -0.639976248783438E+12  0.451200007339684E+11 -0.216754312886992E+12
 -0.703141792567835E+11  0.421377644135005E+13  0.824472191800807E+13
  0.447898432906652E+12 -0.105077751499844E+13 -0.658290512224369E+11
  0.195067105934229E+13  0.289176812368303E+13 -0.140045800761676E+14
  0.476126532155786E+13 -0.152785617001799E+13  0.169491694508477E+14
  0.456467329116016E+13  0.118352257917078E+14 -0.396100285863348E+12
 -0.891965482760371E+13 -0.544080092166964E+13 -0.742912333885548E+13
 Atom accelerations (Angstrom/s**2):
 -0.810436027147472E+27 -0.981147717871880E+27 -0.313616213868668E+27
  0.116753745428499E+29  0.109570643908876E+29  0.135954922986376E+29
 -0.244853315374905E+27 -0.599286401168541E+27 -0.831858387309253E+27
  0.105361267406127E+28  0.134697085751095E+28 -0.115819691864393E+27
  0.208416152961380E+28  0.364332842399750E+28 -0.673228416751219E+27
 -0.149559883359616E+28 -0.125042567119739E+28  0.468080992010752E+28
 -0.754581549567212E+27  0.411775389213967E+28 -0.385065171515426E+28
 Previous atom accelerations:
  0.000000000000000E+00  0.000000000000000E+00  0.000000000000000E+00
  0.000000000000000E+00  0.000000000000000E+00  0.000000000000000E+00
  0.000000000000000E+00  0.000000000000000E+00  0.000000000000000E+00
  0.000000000000000E+00  0.000000000000000E+00  0.000000000000000E+00
  0.000000000000000E+00  0.000000000000000E+00  0.000000000000000E+00
  0.000000000000000E+00  0.000000000000000E+00  0.000000000000000E+00
  0.000000000000000E+00  0.000000000000000E+00  0.000000000000000E+00
 MD-temperature (K):
  0.550040311117348E+02
```

2.3 Force field optimization files.

trainset.in-file. This file allows the user to generate a training set or cost function, which can be used to optimize the force field parameters. **trainset.in** uses the identifiers defined in the DESCRP-field in the geo-file (.bgf-format) or in the models.in file to compare force field derived geometries and energy differences to literature or QC-values. **trainset.in** is format-free, although it does require that fields are space-separated. Also, the -, + and / symbols have special meaning in the **trainset.in**-file and should not be used in identifiers. Example 2.15 demonstrates how this file can be used to set up a cost function. The **trainset.in**-file is divided into 5 sections, each of which communicates a particular data type to ReaxFF. Each of these sections starts with a keyword (CHARGE, HEATFO, GEOMETRY, CELL PARAMETER and ENERGY) followed by data lines and ending by a END [keyword] line. In the CHARGE, HEATFO, GEOMETRY and CELL PARAMETER sections the data lines start with the structure identifier, followed by the weight of the data point. This is followed by a type identifier (the atom number for the CHARGE section, the bond/valence angle/torsion angle definition for the GEOMETRY section and a/b /c/alpha/beta/gamma for the CELL PARAMETER section) and, finally, the literature/QC value with which the ReaxFF-data is to be compared. The HEATFO section, which compares ReaxFF heat of formation data to literature data, does not require a type identifier. If an identifier is not provided in the GEOMETRY section ReaxFF is going to compare the ReaxFF RMSG of the forces.

Example 2.15: **trainset.in**-file with CHARGE, HEATFO, GEOMETRY, CELL PARAMETER and ENERGY sections. Lines commencing with a # are ignored by ReaxFF.

```
CHARGE
#Iden Weight Atom  Lit
chexane 0.1    1   -0.15
ENDCHARGE
HEATFO
#Iden   Weight Lit
methane  2.00 -17.80                    !Heat of formation
chexane  2.00
ENDHEATFO
GEOMETRY
#Iden   Weight At1 At2 At3 At4 Lit
chexane  0.01   1  2           1.54     !bond
chexane  1.00   1  2  3        111.0    !valence angle
chexane  1.00   1  2  3  4     56.0     !torsion angle
chexane  1.00                  0.01     !RMSG
ENDGEOMETRY
CELL PARAMETERS
#Iden       Weight Type Lit
chex_cryst  0.01    a  11.20
END CELL PARAMETERS
ENERGY
#Weigh op1 Ide1  n1 op2 Ide2    n2    Lit
#alfa vs. beta vs. gamma cleavage in butylbenzene
 1.5   +  butbenz/1 -  butbenz_a/1   -90.00
 1.5   +  butbenz/1 -  butbenz_b/1   -71.00
 1.5   +  butbenz/1 -  butbenz_c/1   -78.00
#cyclohexane heat of vaporization
 1.0   + chex_cryst/16 – chexane/1  -11.83
ENDENERGY
```

In the ENERGY section **trainset.in** allows comparison of ReaxFF energy differences between structures to literature/QC data. In this case each data line starts with the weight of the data point, followed by up to five operator/identifier/divider parts and finishes with the literature/QC value. The operator is either '+' or '-' ('+' is the default). The energy associated with the identifier is divided by the divider, allowing comparison of condensed phase structures to monomers, as exemplified in the last data line of the ENERGY section in which the ReaxFF heat of vaporization for cyclohexane is compared to a value of –11.83 kcal/mol by dividing the energy of a crystal by its number of monomers (16) and subtracting the energy of the gas molecule. The '/' character in the ENERGY section data lines is optional.

After running ReaxFF on the structures associated with the keywords in **trainset.in** the program will automatically compare the ReaxFF-data with the literature/QC data provided in the training set and produce **fort.13** and **fort.99** output file (see Output section).

BUGS:

- Literature/QC values of zero (0.00) cannot be used and will cause unpredictable results. This can be avoided by comparing with a very small value (i.e. 0.0001) instead.

- Structure identifiers should always refer to only one structure; if the same structure identifier is used twice ReaxFF will get confused when that identifier is mentioned in the ENERGY section. As of yet, ReaxFF does not stop or give a warning of this, so users should make certain that they use unique identifiers.

params-file. The **params**-file tells ReaxFF which force field parameters are to be incorporated in the force field optimization scheme. Example 2.16 demonstrates the format of the **params**-file.

Example 2.16: **params**-file, describing the parameters used in the force field optimization procedure.

```
 1  1  1   0.100  75.000  25.000  !1st general parameter
 1  2  1   0.010  10.000   9.00   !2nd general parameter
 2  1  1   0.001   1.600   1.350  !2nd section,1st type,1st parameter
 2  2  1   0.001   0.700   0.600  !2nd section,2nd type,1st parameter
 2  2  5   0.010   0.020   0.030  !2nd section,2nd type,5th parameter
 6  3  4   0.050  -3.000  -5.000  !6th section,3rd type,4th parameter
```

Each line (format 3i3,3f8.4) starts with three integers defining the force field parameter. The first of these integer defines the force field section (general, atom, bond, off-diagonal, valence angle, torsion angle, hydrogen bond; see Example 2.8), the second the type and the third the parameter. For example, the last line of **params** in Example 2.16 identifies parameter '6 3 4', which is the 4th parameter of the H-C-C-H (2-1-1-2) torsion angle for the **ffield**-file of Example 2.8. The value following these three integers defines the interval within which the parameter value is to be searched during the force field optimization procedure. This value is followed by the maximum and minimum allowed for that particular force field parameter.

As such, the last line of Example 2.16 instructs ReaxFF to perform a parameter search for the 4th parameter of the H-C-C-H torsion angle. This torsion angle parameter starts at a value of –4.7435 (Example 2.8); ReaxFF is going to increase and decrease its value by a factor 0.050, recalculate the cost function, and determine an optimal value based on a fit to the training set, using a parabolic extrapolation constrained by a maximum value of –3.000 and a minimum value of –5.000.

ReaxFF simply starts at the first line of **params** and works its way down, until it reaches the end of the file after which it terminates. For each parameter the constrained parabolic extrapolation procedure described previously is followed. For each parameter thus optimized information is written to **fort.79** regarding the results from the parabolic extrapolation. The parext-keyword in the **control**-file regulates how far outside the search interval ReaxFF is allowed to extrapolate, while the parsca-keyword can be used to decrease and increase the search interval (as the **control**-file is read continuously this can be useful to modify long-running force field optimizations).

The **params**-file gets copied to **fort.21** by the **exe**-script, from which it is accessed by ReaxFF.

koppel2-file. The **koppel2**-file allows the user to establish links between different force field parameters during the force field optimization procedure. Example 2.17 demonstrates the format of the **koppel2**-file.

Example 2.17: **koppel2**-file, used for linking force field parameter values.

```
5  1  7  5      !Parameter identifier; Nr. of links
5  2  7
5  3  7
5  4  7         !Parameters linked to parameter 5  1  7
5  5  7
5  6  7
```

The **koppel2**-file starts with a parameter identifier, which is formulated similar as in the **params**-file (‘5 1 7’ in Example 2.17 indicating section 5 (valence angles), type 1, parameter 7 {1.0400 for the **ffield**-file in Example 2.8}). Thereafter follows how many other force field parameters are to retain the same value as parameter ‘5 1 7’. The subsequent lines in **koppel2** define these other parameters, after which another link can be defined. The **koppel2**-file requires a 4i3-format.

The **koppel2**-file gets copied to **fort.23** by the **exe**-script, from which it is accessed by ReaxFF.

3. Output Files

3.1 General. Table 3.1 categorizes and gives a short description of the ReaxFF output files.

Table 3.1: ReaxFF output files.

Name	Related to	Description
NAME.bgf[a]	all runs	Output geometry in .bgf-format
NAME.geo	all runs	Output geometry in .geo-format
output.pdf	MM/MD runs	Output geometry in .pdf-format
output.MOP	MM/MD runs	Output z-matrix in MOPAC format
xmolout	all runs	Trajectory in .xyz-format
moldyn.vel	MD runs	restart file (see vels-file)
molsav.####[b]	MD runs	restart file, controlled by iout6[c]
moldyn.####	MD runs	trajectories, controlled by iout2[c]
fort.7	all runs	Connection table using cutof3 bond order cutoff[c]
fort.8	all runs	Connection table+charges
fort.13	FF optimization	Total error force field
fort.24	FF optimization	Values for heat increments (iincop=1)
fort.40	all runs	Forces (icheck>0[c])
fort.41-fort.50	all runs	Partial forces (icheck>0[c])
fort.56	MM/MD runs	ReaxFF charge distribution
fort.57	MM-runs	Energy minimization report
fort.58	MM-runs	Partial energy contribution report
fort.59	MD-runs	NPT: pressure report
fort.65	all runs	idebug=1[c]: subroutine names
fort.71	MD-runs	Energy/temperature/pressure report
fort.73	MD-runs	Partial energy contribution report
fort.74	all runs	Heat of formation+volume
fort.76	all restraint runs	Restraint report
fort.79	FF-optimization	Parabolic extrapolation report (see params-file)
fort.83	FF-optimization	Force field files from FF-optimization
fort.90	MM/MD runs	.bgf-output
fort.91	MM/MD runs	z-matrix output
fort.98	MM/MD runs	.geo-output
fort.99	FF-optimization	Detailed cost-function report

[a]: NAME=identifier in DESCRP field. [b]: #### is number of iterations/iout6. [c]: see **control**-file section.

Some of these output files are fairly straightforward or are, format-wise, the same as files discussed in the Input-files section. The sections below give a more elaborate description for the output-files that do not fall into either of these two categories.

3.2 MM/MD output files.

xmolout-file. The **xmolout**-file contains the trajectory from the MD-run or the MM-minimization. It is the generally the most useful file for interaction with molecular viewing programs. Programs like Icarus, Xmol, Molden and Jmol can directly read in **xmolout** and can provide graphical animations. In MD-runs, the frequency of structure output to **xmolout** is controlled by the **control**-file keyword iout2; a frame is saved every iout2 MD-iterations. In a similar way, iout4 controls the frame output frequency during MM simulations. **xmolout** always gets appended (i.e. never overwritten) during ReaxFF-simulations. The **exe**-script (see Example 2.10) can remove **xmolout**-files from the run directory; if this is not done the **xmolout**-output is appended. When ReaxFF is run on multiple geometries (either by putting them in one **geo**-input file or using the **models.in**-file **xmolout** will contain output for all these geometries. Example 3.1 demonstrates the format of the **xmolout**-file.

Example 3.1: **xmolout**-file, containing 3 frames from an MD-simulation on an ethyl radical.

```
7                                 !Number of atoms
Ethyl_radical                     !Structure identifier
C   39.19924  40.08333  39.66585 !Atom type;x/y/z
H   40.88239  40.79608  40.81249 !(format a2,3f10.5)
C   40.61413  39.91227  40.24250
H   38.86032  41.06389  39.38266
H   38.59716  39.25081  39.41763
H   41.33155  39.78117  39.45850
H   40.65892  39.04746  40.86980
   7
Ethyl_radical
C   39.20278  40.09024  39.65697
H   40.80762  40.70179  40.96412
C   40.61564  39.90857  40.24468
H   38.93202  40.97423  39.12611
H   38.47436  39.29665  39.73567
H   41.35468  39.98863  39.43895
H   40.70164  38.93982  40.75604
   7
Ethyl_radical
C   39.20278  40.09024  39.65697
H   40.80762  40.70179  40.96412
C   40.61564  39.90857  40.24468
H   38.93202  40.97423  39.12611
H   38.47436  39.29665  39.73567
H   41.35468  39.98863  39.43895
H   40.70164  38.93982  40.75604
```

If the ixmolo control-switch has a value of 1 additional velocity and molecule number output is generated in the **xmolout**-file.

fort.7/fort.8-files. These files contain the ReaxFF-generated connection table and charge distribution. **fort.8** contains information on all bonds, **fort.7** contains only the bonds with a bond order greater then **control**-file keyword cutof2. These files get updated with the same frequency as the **xmolout**-file; every iout2 iterations during MD-simulations or every iout4 iterations during an MM-run. Example 3.2 demonstrates the format of these files.

Example 3.2: **fort.7**-connection table for an ethyl radical.

```
7 Ethyl_radical
  1  1  2  3  4  5  0  1  0.985  1.024  0.986  0.986  0.000  3.981  0.000 -0.289
  2  2  1  0  0  0  0  1  0.985  0.000  0.000  0.000  0.000  0.985  0.000  0.103
  3  1  1  6  7  0  0  1  1.024  0.987  0.987  0.000  0.000  2.999  0.000 -0.233
  4  2  1  0  0  0  0  1  0.986  0.000  0.000  0.000  0.000  0.986  0.000  0.105
  5  2  1  0  0  0  0  1  0.986  0.000  0.000  0.000  0.000  0.986  0.000  0.105
  6  2  3  0  0  0  0  1  0.987  0.000  0.000  0.000  0.000  0.987  0.000  0.105
  7  2  3  0  0  0  0  1  0.987  0.000  0.000  0.000  0.000  0.987  0.000  0.105
```

The first line of the **fort.7** and **fort.8**-files contain the number of atoms and the structure identifier. After that follows a line for each atom, starting with the atom number and the atom type number (as defined in the **ffield**-file). Then follow a number of integers, indicating the connectivity of this atom. The last integer gives the molecule number. Then follow the bond orders for each bond defined by the connectivity, followed by the sum of the bond orders, the number of lone pairs and finally the partial charge.

Normally, **fort.7** and **fort.8** get overwritten by the most recent information. Setting control-file keyword iappen to 1, though, causes output to these files to get appended.

fort.57-file. This file contains a report from the MM-energy minimization. - Example 3.3 demonstrates the format of this file.

Example 3.3: **fort.57**-output file generated from an MM conjugate gradient minimization (RMSG endpoint criterion 0.500) on an ethyl radical.

```
Ethyl_radical
 Iter.       Epot            Max.move     Factor      RMSG       nfc
   0     -664.0048203101    0.000000    0.500000    4.969706     0
   1     -664.0170216413   15.795587    0.089117    3.360058     0
   2     -664.0394728751    9.339616    0.135649    6.279516     0
   3     -664.0765683298    0.001387    1.957694    3.047916     0
   4     -664.0956555161    0.000342    3.000000    2.270724     0
   5     -664.1009627083    0.001933    0.585262    1.026026     0
   6     -664.1025221864    0.000851    1.000000    0.465193     0
```

Of main interest in the **fort.57** file are the columns related to the potential energy (Epot, in kcal/mol) and the RMSG of the forces on the structure (RMSG). The other columns show data related to the conjugate gradient minimizer performance. When

RMSG drops below the value of **control**-file keyword endmm the MM run terminates. Alternatively, the run terminates when the maximum number of iterations (**control**-file keyword maxit) has been reached.

fort.58-file. This file contains a partial energy report from the MM-energy minimization. -Example 3.4 demonstrates the format of this file.

Example 3.4: **fort.58**-output file generated from the same MM-run as used for Example 3.3.

```
 Ethyl_radical
  Iter.  Eatom   Elopa     Ebond     Emol   Eval   Ecoa   Ehb    Etor   Econj   Evdw      Ecoul
     0  -6.922  0.000   -907.050  0.000  0.237  0.000  0.000  4.715  -0.508  257.018   -22.970
     1  -6.741  0.000   -907.442  0.000  0.244  0.000  0.000  4.801  -0.512  257.123   -22.966
     2  -6.559  0.000   -908.118  0.000  0.242  0.000  0.000  4.876  -0.516  257.524   -22.965
     3  -6.196  0.000   -909.827  0.000  0.233  0.000  0.000  5.013  -0.523  258.720   -22.972
     4  -6.283  0.000   -910.220  0.000  0.230  0.000  0.000  4.954  -0.521  259.253   -22.985
     5  -6.305  0.000   -910.733  0.000  0.234  0.000  0.000  4.924  -0.520  259.819   -22.996
     6  -6.340  0.000   -911.121  0.000  0.234  0.000  0.000  4.896  -0.519  260.277   -23.006
```

Energy contributions reported in **fort.58** include over+undercoordination energy (Eatom), lone-pair energy (Elopa), bond energy (Ebond), molecular energy (Emol; not used in current force fields), valence angle energy (Eval), valence angle conjugation energy (Ecoa), hydrogen bond energy (Ehb), torsion angle energy (Etors), van der Waals energy (Evdw) and Coulomb energy (Ecoul). Currently, it does not contain the energy required for generating the charges (Echarge, see **fort.73**-output file) which means that the sum of the partial energies in **fort.58** does not add up to the potential energy in **fort.57**.

fort.71-file. This file contains the energy, temperature and pressure information from an MD-simulation. Example 3.5 demonstrates the format of this file.

Example 3.5: **fort.71**-output file generated from a 45-iteration MD simulation.

```
Iter.  Nmol  Epot    Ekin    Etot    T(K)  Eaver(b) Eaver(tot) Taver  Tmax  Pres  sdev1  sdev2 Tset  Tstep RMSG
    5  1  1  -663.7   0.8  -662.9   38.3  -663.8   -663.8   41.3   46.0  0.0   0.1    0.1  50.0  0.5  22.2
   10  1  1  -663.9   0.9  -663.0   42.4  -663.8   -663.8   42.2   44.5  0.0   0.0    0.0  50.0  0.5  28.7
   15  1  1  -663.8   0.9  -662.9   43.9  -663.8   -663.8   42.5   43.9  0.0   0.0    0.0  50.0  0.5  18.9
   20  1  1  -663.9   1.0  -662.9   49.9  -663.9   -663.8   48.6   49.9  0.0   0.0    0.0  50.0  0.5   7.4
   25  1  1  -663.7   0.8  -662.9   37.1  -663.7   -663.8   40.5   45.4  0.0   0.1    0.0  50.0  0.5  25.0
   30  1  1  -663.8   0.5  -663.3   24.6  -663.8   -663.8   21.5   25.6  0.0   0.1    0.0  50.0  0.5  31.1
   35  1  1  -663.8   0.5  -663.3   25.0  -663.8   -663.8   25.4   27.0  0.0   0.0    0.0  50.0  0.5  15.0
   40  1  1  -663.7   0.5  -663.2   25.3  -663.7   -663.8   24.3   25.4  0.0   0.0    0.0  50.0  0.5  13.1
   45  1  1  -663.7   0.6  -663.2   26.9  -663.7   -663.8   24.9   26.9  0.0   0.0    0.0  50.0  0.5  30.0
```

control-file keyword iout1 regulates the output-frequency to **fort.71** (5 in case of Example 3.5). The **fort.71**-file has 16 columns, which contain the following information:

Column header Information

- Iter: Number of MD-iterations.

- Nmol: Number of molecules; number of molecules using **control**-file keyword cutof2 as bond order criterion (comparable with information in **fort.8** and **fort.7**).

- Epot: Total potential energy.

- Ekin: Total kinetic energy.
- Etot: Epot+Ekin.
- T(K): MD-temperature.
- Eaver(b): Block average potential energy over the last iout1-iterations.
- Eaver(tot): Average potential energy over entire run.
- Taver: Average temperature over the last iout1 iterations.
- Tmax: Maximum temperature in the last iout1 iterations.
- Pres: MD-pressure (in MPa) based on intermolecular interactions (cannot yet be used to evaluate pressures in condensed phase materials).
- sdev1: Standard deviation in potential energy over last iout1 iterations.
- sdev2: Standard deviation in average potential energy over entire run.
- Tset: Set temperature.
- Tstep: MD time step (on fs).
- RMSG: Root mean square of forces. In an MD-energy minimization run (**control**-file keyword imetho=2) ReaxFF will terminate if the RMSG drops below the value of **control**-file keyword endmd.

fort.73-file. This file contains the partial energy contribution information from an MD-run. Example 3.6 demonstrates the format of this file.

Example 3.6: **fort.73-**output file generated from the same MD-simulation as that used for Example 3.5.

```
Iter.   Ebond    Eatom    Elp     Emol    Eval    Ecoa    Ehbo    Etors   Econj   Evdw    Ecoul   Echarge
    5  -905.00   -7.39   0.00    0.00    0.30    0.00    0.00    4.57   -0.49   255.78  -22.93   11.45
   10  -913.27   -6.45   0.00    0.00    0.34    0.00    0.00    4.87   -0.51   262.72  -23.33   11.76
   15  -915.74   -5.42   0.00    0.00    0.20    0.00    0.00    5.38   -0.53   263.86  -23.29   11.74
   20  -910.80   -5.68   0.00    0.00    0.23    0.00    0.00    5.42   -0.53   258.94  -23.05   11.54
   25  -907.76   -6.64   0.00    0.00    0.44    0.00    0.00    4.97   -0.51   257.35  -23.13   11.60
   30  -910.68   -6.80   0.00    0.00    0.37    0.00    0.00    4.74   -0.51   260.62  -23.32   11.76
   35  -914.36   -6.12   0.00    0.00    0.37    0.00    0.00    4.95   -0.53   263.46  -23.23   11.68
   40  -910.62   -6.00   0.00    0.00    0.47    0.00    0.00    5.17   -0.53   259.26  -22.80   11.34
   45  -906.77   -6.74   0.00    0.00    0.31    0.00    0.00    4.98   -0.51   256.49  -22.88   11.40
```

The output-frequency to **fort.73** is regulated by **control**-file keyword iout1 (5 in case of Example 3.6). **fort.73** contains all energy contributions, including bond energy (Ebond), over+undercoordination energy (Eatom), lone-pair energy (Elp), molecular energy (Emol; not use in recent force fields), valence angle energy (Eval), angle conjugation energy (Ecoa), hydrogen bond energy (Ehbo), torsion angle energy (Etors), van der Waals energy (Evdw), Coulomb energy (Ecoul) and charge polarization energy (Echarge). The sum of these terms should be the same as the number in the Epot-column in **fort.71**.

3.3 Force field optimization output files.

fort.13-file. This file contains the total error of the force field, calculated from the cost function defined in **trainset.in**. Example 3.7 shows the output to **fort.13** that could get generated in conjunction with the **params**-input file from Example 2.16 and the **ffield**-input file from Example 2.8.

Example 3.7: **fort.13**-output file generated using the **ffield**-, **params-** and **trainset.in**-input files from Examples 2.15, 2.16 and 2.18. See also the **fort.79**-example in the next section.

```
91.5209        !Total FF error using 45.00 for parameter 1  1  1
91.5893        !Total FF error using 55.00 for parameter 1  1  1
91.6449        !Total FF error using 50.00 for parameter 1  1  1
91.5209        !Total FF error using optimized value for parameter 1  1  1 (see fort.79)
91.6038        !Total FF error using 9.7423 for parameter 1  2  1
91.4330        !Total FF error using 9.9391 for parameter 1  2  1
91.5175        !Total FF error using 9.8407 for parameter 1  2  1
91.3896        !Total FF error using optimized value for parameter 1  2  1 (see fort.79)
```

As Example 2.8 demonstrates, for each parameter named in **params** four separate ReaxFF runs are performed on the input geometries associated with the training set, creating four entries in **fort.13**. In the first two of these runs the parameter value is decreased and increased according to the search interval defined in the **params**-file. The third run is performed with the unmodified force field. The total force field errors (see **fort.99** for a discussion on how this total error is determined) from these 3 runs are subsequently entered in a parabolic extrapolation procedure (see **fort.79** for a detailed discussion of this procedure) from which an optimal value for that parameter is calculated. The fourth run is performed with this optimal value, after which the next parameter in the **params**-file is tackled.

fort.79-file. This file contains the report from the parabolic extrapolation procedure used by ReaxFF to optimize the force field parameters. Example 2.9 demonstrates the format of this file. This example is linked to the discussion of the **fort.13**-file in the previous section. In the first section of the **fort.79**-example, concerning the 1 1 1-parameter, the parabolic search identifies a hill parabol (a<0). This means that extrapolation is not possible, so ReaxFF simply sticks with the best of the three parameter values. In the second section, concerning the 1 2 1-parameter, it identifies 7.4 as the optimal parameter value, but as this lies outside the parext extrapolation limit it chooses 8.6 instead as the new parameter value.

After calculating the total force field error for three parameter values ReaxFF tries to draw a parabol (ax^2+bx+c) through these three points. If a>0 than ReaxFF will use extrapolation (within the limits set by the parext **control**-file parameter) or interpolation to find the optimum parameter value.

Example 2.9: **fort.79**-output generated using the **ffield**-, **params**-and **trainset.in**-input files from Examples 2,15, 2.16 and 2.18. See also the **fort.13**-example in the previous section.

```
Values used for parameter  1  1  1
   0.4500000000E+02    0.5500000000E+02    0.5000000000E+02
Differences found
   0.9152086304E+02    0.9158925608E+02    0.9164489675E+02
Parabol: a=   -0.3593487269E-02  b=    0.3661880309E+00  c=    0.8231921337E+02
Minimum of the parabol    0.5095162492E+02
Difference belonging to minimum of parabol    0.9164814892E+02
New parameter value    0.4500000000E+02
Difference belonging to new parameter value    0.9152086100E+02

Values used for parameter  1  2  1
   0.9742293000E+01    0.9939107000E+01    0.9840700000E+01
Differences found
   0.9160380360E+02    0.9143296226E+02    0.9151752206E+02
Parabol: a=    0.8889634892E-01  b=   -0.2617639062E+01  c=    0.1086682558E+03
Minimum of the parabol    0.1472298410E+02
Difference belonging to minimum of parabol    0.8939852465E+02
New parameter value    0.9988802535E+01
Difference belonging to new parameter value    0.9139091180E+02
```

This one-parameter search procedure has the advantage of being robust. Furthermore, it is relatively straightforward to retrace one or more steps if the force field optimization has gone astray (for example, if a parameter reaches a physically unrealistic value). More sophisticated multiparameter search methods may be more economical, but do run the risk of finding themselves trapped in the strong ReaxFF inter-parameter correlations.

fort.99-file. This file contains a detailed report of the ReaxFF reproduction of the data in the training set (as defined in the **trainset.in**-file). Example 3.10 demonstrates the format of the **fort.99**-file. This example was generated from the trainset.in-file from Example 2.15.

Example 3.10: **fort.99**-output file as generated using the **trainset.in-file** from Example 2.15. For cross-reference see the **fort.13** and **fort.79**-examples (Example 3.8 and 3.9).

```
                                          FField value QM/Lit value  Weight     Error   Total error
methane           Heat of formation:          -17.8000    -17.8000    2.0000    0.0000     0.0000
chexane           Charge atom:   1             -0.1604     -0.1500    0.1000    0.0109     0.0109
 Heat of formation:                           -29.4900    -29.4900    2.0000    0.0000     0.0109
 Bond distance:  1   2                          1.5586      1.5400    0.0100    3.4571     3.4679
 Bond distance:  1   7                          1.1696      1.1000    0.0200   12.1227    15.5906
 Bond distance:  1   8                          1.1713      1.1000    0.0200   12.7203    28.3109
 Valence angle:  1   2   3                    110.8117    111.0000    1.0000    0.0354    28.3463
 Valence angle:  7   1   8                    104.3207    107.0000    1.0000    7.1788    35.5251
chex_cryst        a:                           11.8448     11.2000    0.4000    2.5987    38.1238

Energy +butbenz/  1 -butbenz_a/  1                -96.6941    -90.0000    1.5000   19.9158    58.0396
Energy +butbenz/  1 -butbenz_b/  1                -63.4751    -71.0000    1.5000   25.1663    83.2060
Energy +butbenz/  1 -butbenz_c/  1                -77.1805    -78.0000    1.5000    0.2985    83.5045
```

The force field error, i.e. the deviation between the ReaxFF and QC/Literature values, is calculated by Equation 3.1:

$$\text{Error}^{\text{ReaxFF}}=\{[v^{\text{ReaxFF}}-v^{\text{QC/Lit}}]/\text{weight}\}^2 \qquad \text{Equation (3.1)}$$

The sum of these errors, at the bottom of the last column in **fort.99**, is the value used in **fort.13** and **fort.79** to optimize the force field.

4. Potential functions

This section gives an overview of the potential functions used in the ReaxFF reactive force fields. As ReaxFF descriptions are being developed for new chemical systems these potential functions are subject to modifications; as such, this section can only supply a snapshot of the current situation. Using the force field example given in Example 2.8 and Tables 2.4-2.9 this section will also indicate which parameters operate in which potential functions.

Equation 4.1 describes the system energy description currently used in ReaxFF.

$$E_{system} = E_{bond} + E_{atom} + E_{lp} + E_{angle} + E_{co,angle} + E_{hb} + E_{tors} + E_{co,tors} + E_{Coulomb} + E_{vdWaals} + E_{ch\arg e}$$