MANUAL
for DFTBopt

Version 1.0

Van Quan Vuong

March 11, 2019

Contents

Chapter 1

An Introduction to DFTB Parameterization

1.1 DFTB

Expansion from DFT

$$
\begin{aligned}
E[\rho^0(r)+\Delta\rho(r)] = & \sum_i^{occ}\langle\psi_i|H^0|\psi_i\rangle \Big\} E^{BS} \\
& -\frac{1}{2}\int\int\frac{\rho^0(r')\rho^0(r)}{|r-r'|}dr'dr - \int v^{xc}[\rho^0(r)]\rho^0(r)dr \Big\} \approx \frac{1}{2}\sum_{a,b}V_{ab}^{rep}(R_{ab}) = E^{rep} \\
& +E^{xc}[\rho^0(r)] + E^{NN} \\
& +\frac{1}{2}\int\int\left(\frac{1}{|r-r'|}+\frac{\delta^2E^{xc}[\rho(r)]}{\delta\rho(r')\delta\rho(r)}\Big|_{\rho^0(r')\rho^0(r)}\right)\Delta\rho(r')\Delta\rho(r)dr'dr \Big\} E^{2nd} \\
& +\frac{1}{6}\int\int\int\left(\frac{\delta^3E^{xc}[\rho(r)]}{\delta\rho(r'')\delta\rho(r')\delta\rho(r)}\Big|_{\rho^0(r'')\rho^0(r')\rho^0(r)}\right) \Big\} E^{3rd} \\
& \Delta\rho(r'')\Delta\rho(r')\Delta\rho(r)dr''dr'dr \\
& +\ldots.
\end{aligned}
\tag{1.1}
$$

None Consistent-Charge (NCC)-DFTB

$$
E^{NCC-DFTB} = \sum_i^{occ}\langle\psi_i|H^0|\psi_i\rangle + E^{rep}. \tag{1.2}
$$

Eigenvalue problem:

$$
\sum_\nu^{AO} c_{\nu i}(H^0_{\mu\nu} - \varepsilon_i S_{\mu\nu}) = 0. \tag{1.3}
$$

Hamiltonian matrix elements, $H^0_{\mu\nu}$:

$$
H^0_{\mu\nu} = \begin{cases} \left\langle\phi_\mu\right| -\frac{1}{2}\nabla^2 + V[\rho^0_a+\rho^0_b]\left|\phi_\nu\right\rangle & \text{if } a\neq b \\ \varepsilon^{\text{free atom}} & \text{if } a=b, \mu=\nu \\ 0 & \text{if } a=b, \mu\neq\nu. \end{cases} \tag{1.4}
$$

Self-Consistent-Charge (SCC)-DFTB

$$E^{SCC-DFTB} = \sum_{i}^{occ} \langle \psi_i | H^0 | \psi_i \rangle + E^{rep} + \frac{1}{2} \sum_{a,b} \gamma_{ab}(R_{ab}) \Delta q_a \Delta q_b. \tag{1.5}$$

Eigenvalue problem:

$$\sum_{\nu}^{AO} c_{\nu i}(H_{\mu\nu} - \varepsilon_i S\mu\nu) = 0, \tag{1.6}$$

Hamiltonian, $H_{\mu\nu}$:

$$H_{\mu\nu} = H^0_{\mu\nu} + \frac{1}{2} S_{\mu\nu} \sum_c (\gamma_{ac} + \gamma_{bc}) \Delta q_c. \tag{1.7}$$

Mulliken charge, Δq :

$$\Delta q_a = \frac{1}{2} \sum_i n_i \sum_{\mu \in a} \sum_{\nu} (c_{\mu i} c_{\nu i} S_{\mu\nu} + c_{\nu i} c_{\mu i} S_{\nu\mu}) - q^0_a, \tag{1.8}$$

Δq_c depends on MO coefficients $\Rightarrow$ must be solved iteratively.

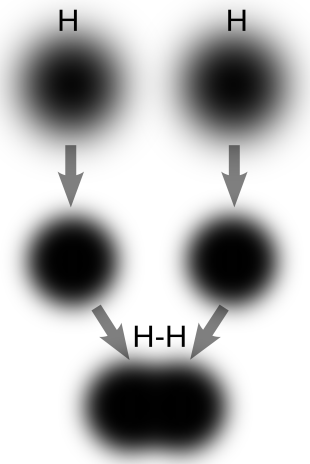
1.2 Electronic Parameters

- Minimal basis set:

  Pure atomic orbitals (AOs) are too diffuse

- Electron density ρ^o:

  ρ is more compressed in molecule



$$\Rightarrow \left[-\frac{1}{2}\nabla^2 + v^{eff}[\rho^{atom}] + \left(\frac{r}{r_o} \right)^2 \right] \phi_\mu = \varepsilon_\mu \phi_\mu \tag{1.9}$$

Free variables:

Minimal AO basis set $\Rightarrow r_o^{wf}$

Electron density $\rho^o \Rightarrow r_o^{dens}$

1.3 Repulsive Potentials

Repulsive Potentials E^{rep}: sum of two-center repulsions,

$$E^{rep} = \frac{1}{2}\sum_{A,B} V_{AB}(|\mathbf{R}_A - \mathbf{R}_B|), \tag{1.10}$$

Where,

$$V_{AB}(R_{AB}) = \begin{cases} e^{-a_1 * R_{AB} + a_2} + a_3, & R_{AB} < R_{AB,0}, \\ \sum_{i=0}^{4} a_{AB,n,i}(R_{AB} - R_{AB,n})^i, & R_{AB,n} \leq R_{AB} < R_{AB,n+1}; 4 \leq n \leq 6 \\ 0, & R_{AB,cut-off} \leq R_{AB}, \end{cases} \tag{1.11}$$

Free variables: $R_{AB,n}$ and $a_{AB,n,i}$.

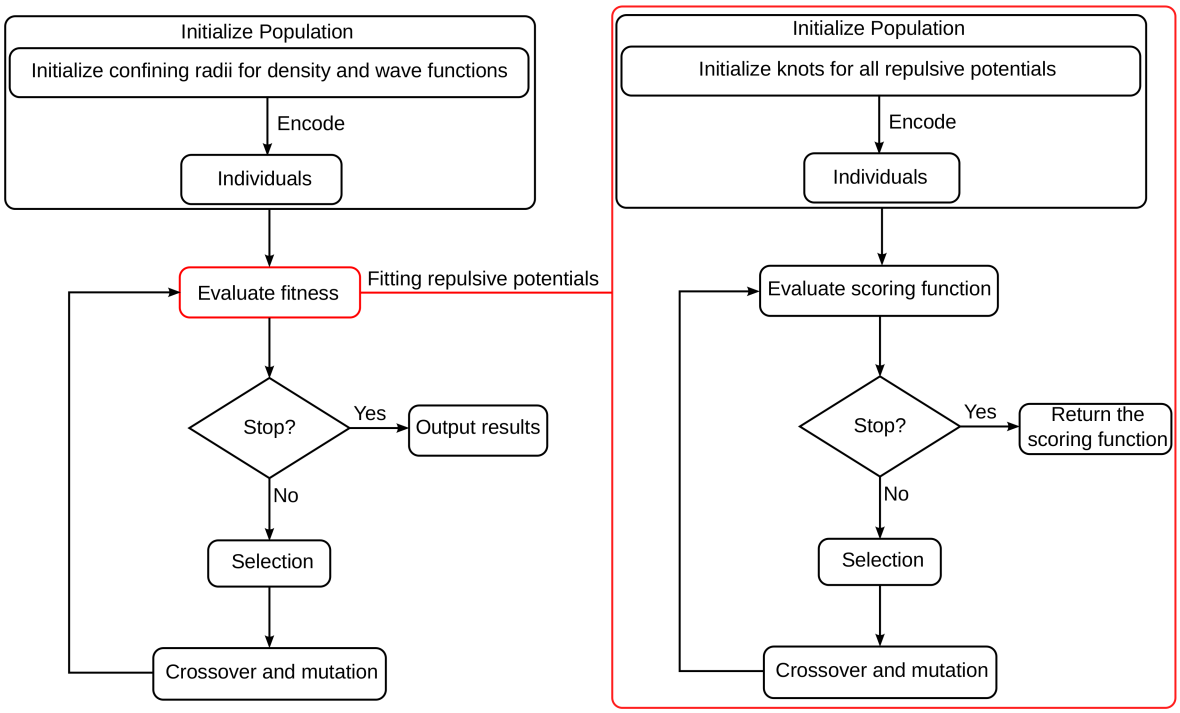
1.4 Scoring Function

$$\begin{aligned} f^{score} = & \sum_{i \in equi} W_{at,i} \left| E^{ref}_{at,i} - E^{DFTB}_{at,i} \right| + \sum_{i \in bar} W_{bar,i} \left| E^{ref}_{bar,i} - E^{DFTB}_{bar,i} \right| \\ & + \sum_{i \in equi} W_{f,i} \sum_{j \in 3N_i} \left| F^{DFTB}_{i,j} \right| + \sum_{i \in pert} W_{f,i} \sum_{j \in 3N_i} \left| F^{ref}_{i,j} - F^{DFTB}_{i,j} \right|, \end{aligned} \tag{1.12}$$

$W_{at,i}, W_{bar,i}, W_{f,i}$: Weight factors

E_{at}: Atomization energies
E_{bar}: Proton transfer barriers
N: Number of atoms
F: Forces

1.5 Genetic Algorithm



Chapter 2

Overview and Installation of DFTBopt

2.1 Overview

DFTBopt[2] is a package to automatically optimize electronic, repulsive, and dispersion parameters for Density-Functional based Tight-Binding (DFTB) method. The package includes two main programs: (1) **repopt** for optimization of only repulsive potentials and (2) **erepopt** for optimization of all DFTB parameters. **erepopt** uses **repopt** for the repulsive potentials fitting. Currently, **repopt** is stable released version 1.0. On the other hand, **erepopt** is still in the beta-development version. In addition, the package also provide some tools to analyze or evaluate new DFTB parameters.

Most of the codes were written in C++. The code required two libraries: **galib247** and **eigen3**. A part of the repulsive fitting (**repopt**) uses some piece of code from a semi-automatic erepfit program originally developed by Michael Gaus.[1] This manual was prepared using same style of DFTB+ manual, making it looks similar to DFTB+ manual. ◡̈◡̈◡̈

2.2 Installation

To get the code:

git clone https://github.com/v2quan89/dftbopt.git

or download compressed file

wget https://github.com/v2quan89/DFTBopt.tar.gz

Note, both links may not work at this moment. You can send an email to **v2quan89@gmail.com** if the links do not work. Then, extract DFTBopt.tar.gz using

tar -xzvf DFTBopt.tar.gz

Change to directory **DFTBopt** and type "**./install.sh**". Currently, **DFTBopt** was tested for two compilers: GNU(g++) and INTEL(icpc).

You can choose the compiler by setting **$CXX="g++"** or **$CXX="icpc"** in the **"install.sh"** file. To compile **"erepopt"**, a MPI library is also required. The **install.sh** script will try to get all the required library and compile the code. You might have to adjust some flags in the **makefile**.

After the compilation, if you use **bash**, you can add following command to you ".bashrc" or run it before using DFTBopt,

source path-to-DFTBopt-directory/dftbopt_on.bash

Chapter 3

Manual for REPOPT

"**repopt**" is a program to optimize DFTB repulsive potentials. To run the program, type:

```
repopt rep.inp
```

where **repopt** is program name and **rep.inp** is name of the input file. The input file is organized in "block" sections. Each section begins with "**$blockname:**" and end with "**$end:**". '#' is the comment character. Everything after '#' will be skipped.

3.1 Required Inputs

The general "block" format of required sections is showed as following

```
$blockname:
  keyword_1                    value_1
  ...                          ...
  keyword_n                    value_n
$end
```

Following input block must be presented in all kind of running job.

3.1.1 $system:

Keyword	Type	Range	Default
dftb_version	string		dftb+
idecompose	integer	1:7	6
ilmsfit	integer	1:4	4
nreplicate	integer	$\geq$1	1

dftb_version Executable dftb-program

idecompose Select decomposition method from EIGEN library:

1 => ldlt
2 => partialPivLu
3 => fullPivLu
4 => householderQr

5 => colPivHouseholderQr
6 => fullPivHouseholderQr
7 => completeOrthogonalDecomposition
Please check the website for more information.

ilmsfit Select regression method from EIGEN library:
1 => householderQr
2 => colPivHouseholderQr
3 => fullPivHouseholderQr
4 => bdcSvd
Please check the website for more information.

nreplicate Number of the fitting will be replicated. **nreplicate** should be 1. Larger than 1 only for testing purpose to measure the effect of decomposition and regression methods on the computing time.

Example:

```
$system:
   dftb_version          dftb+
   idecompose            6
   ilmsfit               4
   nreplicate            1
$end:
```

3.1.2 $genetic_algorithm:

Keyword	Type	Range	Default
ga	bool	0|1	1
runtest	bool	0|1	0
score_type	integer	1|2|4	2
read_spline	bool	0|1	1
popsizemax	integer	$\geq$1	1000
preserved_num	integer	$\geq$0	100
destroy_num	integer	$\geq$0	10
popsizemin	integer	$\geq$1	2
ngen	integer	$\geq$0	1000
pmut	integer	0.0:1.0	0.02
pcross	integer	0.0:1.0	0.90
grid_update	bool	0|1	0

ga switch on or off genetic algorithm

runtest switch on or off testing job

score_type set scoring function to:
1 => sum of absolute deviation
2 => sum of squared deviation

4 => sum of quartic deviation

read_spline how "grid" input file would be used:
0 => only read the cutoff and count the number of knots from "grid" input file
1 => use all knots in the "grid" input file as initial guess

popsizemax set the initial and maximum population size for GA.

preserved_num set the number of best individuals would be kept from "n-1" to "n" generation.

destroy_num set the number individuals be removed every generation. If greater than 0, the population size will be reduced generation by generation.

popsizemin set the final and minimum population size for GA. **popsizemin** is used only if **destroy_num**$\geq$1.

ngen set the number of generation for GA.

pmut set the mutation probability for GA.

pcross set the crossover probability for GA.

grid_update How "grid" input file would be updated:
0 => leave the "grid" input file untouched.
1 => the "grid" input file is updated at the end of the GA optimization using the best found knots.

Example:

```
$genetic_algorithm:
  ga                    1
  runtest               0
  score_type            2
  read_spline           1
  popsizemax            1000
  preserved_num         100
  destroy_num           10
  popsizemin            2
  ngen                  1000
  pmut                  0.02
  pcross                0.90
  grid_update           0
$end:
```

3.2 Optional Inputs

The general "block" format of required sections is showed as following

$blockname:			
entry_name_1	option_1_1	...	option_1_m
...	...	...	...
entry_name_n	option_n_1	...	option_n_m
$end			

Following input blocks in optional, depending on the desired job.

3.2.1 $element_types:

String	Real(a.u.)
element_name_1	atomic_energy_1
...	...
element_name_n	atomic_energy_n

element_name name of fitting element, must be two lower case letters characters long. The underscore character '_' is added if element name has only one character.

atomic_energy Atomic energy in a.u. for the corresponding fitting element.

Note: if **element_name** is provided, **atomic_energy** must be provided also. **atomic_energy** (can be calculated by DFT) is needed to fit atomization energy. If **element_name** is not listed, the **atomic_energy** will be optimized. You can interpret the meaning of **atomic_energy** as: If **atomic_energy** is provided, the absolute atomization energy will be fitted (by fitting atomization energy). If **atomic_energy** is optimized (not provided), the relative atomization energy (reaction energy) will be fitted (by fitting atomization energy).

Example:

$element_types:	
h_	-0.256789
c_	-0.456789
$end:	

3.2.2 $repulsive_potentials:

string	Real(Å)	string	Real(Å)	integer	integer	0|1
name_1	min_r	knot-vector	min_step	spline order	smooth	negative?
...	...	...	...	...	...	...
name_n	min_r	knot-vector	min_step	spline order	smooth	negative?

name name of fitting potential

min_r limit the small knot. The small knot must larger than or equal to shortest bond length min(R_{bond}) - min_r

knot-vector name of the file containing division points in the format (in Å):

knot_1

...

knot_n

cutoff

The number of knot will be counted from the not-vector

min_step set the smallest difference between knot

spline order the order of spline function to be used (currently only support 4th order)

smooth smoothing level of that potential

0 => constrain on potential energy
1 => constrain on the first derivative of energy
2 => constrain on the second derivative of energy
3 => constrain on the third derivative of energy

negative? and allowance the potential to be attractive or not.

0 => repulsive potential energy must be always positive 1 => repulsive potential energy can be negative

Example:

```
$repulsive_potentials:
  h_h_    0.2    grids/hh.grdx    0.05    4    2    0
  c_h_    0.3    grids/ch.grdx    0.05    4    2    1
  c_c_    0.3    grids/cc.grdx    0.30    4    2    1
$end
```

3.2.3 $compounds:

string	Real(kcal/mol)	string	Real	string	0|string	integer
structure1	E^{at}	eweight	fweight	dftbinp	forceinput	placeholder
...	...	...	...	...	...	...
structuren	E^{at}	eweight	fweight	dftbinp	forceinput	placeholder

list of filenames for geometries of the fitting molecular.

name file name for geometry, the files need to be in xyz-format

E^{at} reference atomization energy of the molecule. The atomization energy is defined as:

$$E^{at} = -E^{tot} + \sum_{i=1}^{N_{atom}} E_i^{atom}$$

eweight weights for energy equations

fweight weights for force equations

dftbinp input-file to run a single point energy and force calculation using the dftb

forceinput for an equilibrium structure, should be a "0", otherwise a reference force file can be specified which is formatted as (in a.u.):

Ref_Force-Atom_1_X Ref_Force-Atom_1_Y Ref_Force-Atom_1_Z
...
Ref_Force-Atom_n_X Ref_Force-Atom_n_Y Ref_Force-Atom_n_Z

placeholder for developement only, must be '0' for now

Example:

$compounds:						
path/h2.xyz	109.9	1	1	path/dftb_inp1.hsd	0	0
path/ch4.xyz	420.1	1	1	path/dftb_inp2.hsd	0	0
path/h3cch3.xyz	712.0	1	1	path/dftb_inp2.hsd	0	0
path/h2_d0.1.xyz	000.0	0	1	path/dftb_inp2.hsd	path/hh_d0.1.frc	0
$end						

3.2.4 $definition_reactions:

For specifying reaction equations

string	string	string
abbreviation	filename	dftbinp
...	...	...
abbreviation	filename	dftbinp

abbreviation abbrev name for a geometry

filename file name for the geometry, the files need to be in xyz-format

dftbinp input-file to run a single point energy calculation using the DFTB

Example:

$definition_reactions:		
h2	path/h2.xyz	path/dftb_inp1.hsd
ch4	path/ch4.xyz	path/dftb_inp2.hsd
h3cch3	path/h3cch3.xyz	path/dftb_inp2.hsd
$end		

3.2.5 $reactions:

integer	string		integer	string	string	Real(kcal/mol)	Real
coeff	abbreviation	...	coeff	abbreviation	->	reactionenergy	reaweight
...	...	...	...	...	->	...	...
coeff	abbreviation	...	coeff	abbreviation	->	reactionenergy	reaweight

coeff reaction coefficient
if positive => reactant
if negative => product

abbreviation defined in the $definition_reactions: block

reactionenergy reaction energy

reaweight weight for reaction energy equations

Example:

```
$reactions:
  +1          h3cch3      +1      h2      -2      ch4      ->      -18.33      1.0
$end
```

3.3 Output

The output of a successful **repopt** contains:

scoring function scoring function as a function of generation

input interpreted input, a list of all distances appearing within the reference geometries sorted by atom type pair.

technical information a list of number of fitting equation, number of free variables...

summary of fitting summary of the MSE, MUE, and RMS

residual in detail residuals for each equation predicted by the fitted parameters in comparison to the reference are listed.

fitted atomic energies fitted atomic energies if they are optimized

repulsive potentials the repulsive potentials are given in a format of the "Spline" format.

If there is no error, **repopt** ends with a statement "repopt normal termination". Any warnings concerning the fit will appear after **#ga end!**.

3.4 Tips

Chapter 4

Manual for EREPOPT

"**erepopt**" is a program to optimize all DFTB parameters simultaneously. To run the program, type:

```
erepopt erep.inp
```

where **erepopt** is program name and **erep.inp** is name of the input file. The input file is organized in "block" sections. Each section begins with "**$blockname:**" and end with "**$end:**". '#' is the comment character. Everything after '#' will be skipped.

4.1 Input

4.1.1 $system:

Keyword	Type	Range	Default
nthreads	integer	≥ 1	1
dftbversion	string		dftb+
skgen	string		skgen
onecent	string		hfatom_spin
twocent	string		sktwocnt_lr
gasrepfit	string		repopt
power	integer	≥ 2	2
dgrid	Real	≥ 0.0	0.1
ngrid	integer	≥ 1	120
grids	string		grids
rep.in	string		rep4e.in
libdir	string		libskf4e
scratchfolder	string		/dev/shm
skfclean	bool	0|1	0
outfile	string		gaserepfit.log
popinitialfile	string		pop.initial.dat
popfinalfile	string		pop.final.dat

Example:

$system:	
nthreads	1
dftbversion	dftb+
skgen	skgen
onecent	hfatom_spin
twocent	sktwocnt_lr
gasrepfit	repopt
power	2
dgrid	0.1
ngrid	120
grids	grids
rep.in	rep4e.in
libdir	libskf4e
scratchfolder	/dev/shm
skfclean	0
outfile	gaserepfit.log
popinitialfile	pop.initial.dat
popfinalfile	pop.final.dat
$end	

4.1.2 $genetic_algorithm:

Keyword	Type	Range	Default
ga	bool	0|1	1
runtest	bool	0|1	0
fit_type	integer	1|2|4	2
popsize	integer	$\geq$1	1000
preserved_num	integer	$\geq$0	100
ngen	integer	$\geq$0	1000
pmut	integer	0.0:1.0	0.02
pcross	integer	0.0:1.0	0.90
readr	bool	0|1	1
restart	bool	0|1	1

Example:

$genetic_algorithm:	
ga	1
runtest	0
fit_type	0
popsize	32
preserved_num	3
ngen	30
pmut	0.05
pcross	0.9
readr	1
restart	0
$end:	

4.1.3 $element_type:

Example:

```
$element_types:
  H          11    0    2.9 2.9 2.9    1    2.9 2.9 2.9    1
  O          111   1    2.7 2.8 2.9    1    2.7 2.8 2.9    1    2.7 2.8 2.9    1
  N          111   1    3.0 3.2 3.4    1    3.0 3.2 3.4    1    3.0 3.2 3.4    1
  C          111   1    3.6 3.8 4.0    1    3.6 3.8 4.0    1    3.6 3.8 4.0    1
$end
```

4.1.4 $d3:

Example:

```
$d3:
  s6          1.00 1.00 1.00          2
  s8          1.40 1.40 1.40          1
  a1          0.48 0.48 0.48          2
  a2          4.70 4.70 4.70          1
$end:
```

4.1.5 $vorbes:

Example:

```
$vorbes:
  N          2S          -0.83 -0.82 -0.81          3
$end:
```

4.2 Output

4.3 Tips

Chapter 5

Utility Tools

In the following section, some utility tools will be explained. These tools were originally developed by Michael Gaus and were later modified by the author.

5.1 Convert repopt-output to skf-files

The bash-scripts **rep2XabSpl** and **xabSpl2spl** are available in the "utils" directory as well as the C++ program **ord2abSpl** which is called by the **xabSpl2spl** script.

rep2XabSpl Usage: **rep2XabSpl repout-output-file**
The **rep2XabSpl** extracts the Spline of repulsive potentials from the output-file and writes it in separate files. The ending of the files are XabSpl.

xabSpl2spl Usage: **xabSpl2spl XabSpl-file skf-electronic-file 1**
The **xabSpl2spl** script combines one XabSpl file with skf-electronic-file into the final skf-file.

ord2abSpl called by the **xabSpl2spl**

For a short description of all options run **rep2XabSpl** or **xabSpl2spl** without any arguments.

Example

```
# doing the rep fitting
repopt rep.in > rep.out

# extract Spline for H-H
rep2XabSpl rep.out
mv h_h_.4abSpl hh.4abSpl

# create the final skf-files
xabSpl2spl hh.4abSpl hh_elec.skf 1
```

Under **utils** folder, a script named **combine.sh** can do all jobs at once.

5.2 Plot Repulsive Potentials

SplineAnsch is a script to plot repulsive potentials and its derivatives. The script requires gnuplot and gv ghostscript interpreter.

Usage

one skf file: SplineAnsch -a r_{min}:r_{max} file1.skf

two skf file: SplineAnsch -a r_{min}:r_{max} -v file1.skf file2.skf

Note: any files in the XabSpl or spl format can be also be used. You can find all options by running SplineAnsch without arguments.

Example

```
# to plot new cc.skf zoom in on a range of 2.0-5.0 (a.u.).
SplineAnsch -a 2.0:5.0 cc.skf

# to compare the new cc.skf with cc.skf from mio set.
SplineAnsch -a 2.0:5.0 -v cc_mio.spl cc.4abSpl
```

Chapter 6

Tutorials

For **repopt**, there are two examples rep1.in and rep2.in under the **examples** folder. It is straight forward to run these examples:

```
# cd to the examples folder and type
repopt rep1.in >& rep1.out
repopt rep2.in >& rep2.out
```

For **erepopt**, the exmamples are under construction.

Bibliography

[1] Michael Gaus, Chien-Pin Chou, Henryk Witek, and Marcus Elstner. Automatized Parametrization of SCC-DFTB Repulsive Potentials: Application to Hydrocarbons. *J. Phys. Chem. A*, 113(43):11866–11881, 2009. 7

[2] Van Quan Vuong, Jissy Akkarapattiakal Kuriappan, Maximilian Kubillus, Julian J. Kranz, Thilo Mast, Thomas A Niehaus, Stephan Irle, and Marcus Elstner. Parametrization and Benchmark of Long-Range Corrected DFTB2 for Organic Molecules. *J. Chem. Theory Comput.*, 14(1):115–125, 2018. 7