

Calculating band structures and density of states with DFTB+

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Abstract

This document demonstrates on the example of GaAs how the band structure and the density of states (DOS) of periodic systems (wires, surfaces, solids) can be obtained using DFTB+.

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1 Introduction

The calculation of the band structure for a periodic system consists of two steps. First, the charges in the system must be calculated using a converged k-point sampling. Then, keeping the obtained charges fixed, the one-electron levels must be calculated for k-points chosen along specific lines for which the band structure should be determined in the Brillouin-zone.

The current tutorial uses GaAs as example. You can download the input files and the scripts used in this tutorial from the overview page about the howtos. The input file for DFTB+ must be named `dftb_in.hsd`, so you have to rename the file `dftb_in.charge.hsd` to run DFTB+ for creating the charges, or rename `dftb_in.band.hsd` to calculate the band structure.

Please note, that the quality of the band structure you obtain depends very much on the parametrisation you use. Most parametrisations were made without paying attention to a correct conduction band structure. Additionally, they are usually done using a minimal basis, which in many

cases makes it impossible to obtain a correct conduction band (e.g. silicon with sp-basis results in a direct-gap semiconductor). Therefore, make sure, that the parametrisation you use is capable of describing the regions of the band structure which you are interested in.

This tutorial uses the GaAs parameters from the hyb-0-1 parametrisation set to calculate the band structure of GaAs. The parameters for GaAs were tuned to obtain a sensible description of the GaAs surface. No attention was paid to the band structure. Consequently, the gap obtained with that parametrisation is far too large. The shape of the band edges, however, is qualitatively right.

The tutorial assumes, that you downloaded the parametrisation set hyb-0-1 and extracted it into the directory, where the input for DFTB+ is located. (The parameters are not part of the tgz-archive containing the input files for the tutorial.)

2 Creating the proper density

In order to calculate a band structure in Density Functional Theory, at first the ground-state density for the given system must be obtained. In the DFTB picture that corresponds to obtaining self-consistent charges on the atoms. The charges must be convergent with respect to two quantities: Tolerance of the SCC cycle and quality of the k-point sampling to give the correct results. In the current tutorial, the SCC tolerance is set to $1e-5$. For the k-point sampling the $8 \times 8 \times 8$ Monkhorst-Pack set is used. Both quantities ensure good convergence in the charges for this case.

The input `dftb_in.hsd` for GaAs is as follows:

```
Geometry = {
  Periodic = Yes
  LatticeVectors [Angstrom] = {
    2.80 2.80 0.00
    2.80 0.00 2.80
    0.00 2.80 2.80
  }
  TypeNames = { "Ga" "As" }
  TypesAndCoordinates [relative] = {
    1 0.00 0.00 0.00
    2 0.25 0.25 0.25
  }
}

Hamiltonian = DFTB {
  SCC = Yes
  SCCTolerance = 1e-5
  MaxAngularMomentum = {
    Ga = "d"; As = "d"
  }
  SlaterKosterFiles = Type2FileNames {
```

```

Prefix = "./hyb-0-1/"
Separator = "-"
Suffix = ".skf"
}
KPointsAndWeights = SupercellFolding {
  8 0 0
  0 8 0
  0 0 8
  0.5 0.5 0.5
}
}

```

A few notes about the input:

- The position of the atoms is specified in relative coordinates (in the coordinate system spanned by the lattice vectors):

```

TypesAndCoordinates [relative] = {
  1 0.00 0.00 0.00
  2 0.25 0.25 0.25
}

```

- The SupercellFolding method is used to specify the k-points. If only the diagonal elements are specified and the shift vectors are set to 0.5 for even numbers in the diagonal (or 0.0 for odd ones), the resulting k-point set corresponds to the appropriate Monkhorst-Pack k-point scheme. (See the manual of DFTB+ for more details.)
- The convergency with the current parameters can be checked by choosing stronger SCC tolerance criteria (e.g. $SCCTolerance = 1e-8$) or a higher order Monkhorst-Pack mesh (e.g. $10 \times 10 \times 10$). The total energy does not change considerably in any of the two cases, so that the used parameters can be considered to yield convergent charges.

The calculation with dftb+ and the input above completes successfully after a few iterations. The file charges.bin is created (as well a several others), which contains the orbital population (charges) from the last iteration as a binary file.

3 Plotting the density of states

Using the eigenvalues obtained from the run containing the charges, the density of states can be visualized by smearing the eigenvalues with Gaussians. This can be done using the dosplot script, which can be downloaded from the web site (it is part of the tgz archive of this tutorial). As a first step the data in the output file band.out should be converted to raw data. You do that with band2dat script by issuing:

```
band2dat -N band.out band.dat
```

After successful execution, the file `band.dat` contains the raw data. (The option `-N` instructs the script not to include an enumeration of the K-points as first column of the raw data.)

Then, the following `dosplot` input should be created:

```
[gauss]

coefficient = 0.2
exponent = 20.0

[data]

nr_kpoints = 256
kweights = 1.000000

eigenvalues = << band.dat
eigval_order = k_major
```

The first block specifies the parameters of the Gaussian functions

$$f(x) = C \exp(-\alpha(x - x_0))$$

where C is the coefficient and α is the exponent. These parameters strongly influence the resulting DOS. Setting the exponent too small, the DOS will be smeared too much and lose details. Setting the exponent too high yields a "spiky" DOS. The optimal values depend on the system you are calculating, so that one should adjust them accordingly.

The `[data]` block defines the nr. of k-points and their weights. If the weights of the K-points is equal, only one value must be specified. Otherwise, the weight for all K-points must be specified individually. Please note, that continuation lines must be marked by a space or a tab at the beginning of that line.

The `eigenvalues` option specifies the eigenvalues. In the example above, they are read in from the external file `band.dat`. The values in the file must be arranged either in `band_major` order (each line contains the values for a given band in all K-points) or in `k_major` order (each line contains the values of all bands in a given K-point). The `band.dat` file contains the eigenvalues in `k_major` order.

After storing the input in a file (e.g. `dosplot.in`) the `dosplot` program should be invoked as

```
dosplot dosplot.in > dos.dat
```

The resulting output (`dos.dat`) can be plotted by any scientific visualisation tool (e.g. `gnuplot`, `xmgrace` etc.). For GaAs Figure 1 shows the result.

4 Calculating the band structure

Once the orbital population (charges) for the system had been obtained, the band structure can be calculated at any chosen k-points. The following input calculates the GaAs band structure along the line $L-\Gamma-X$.

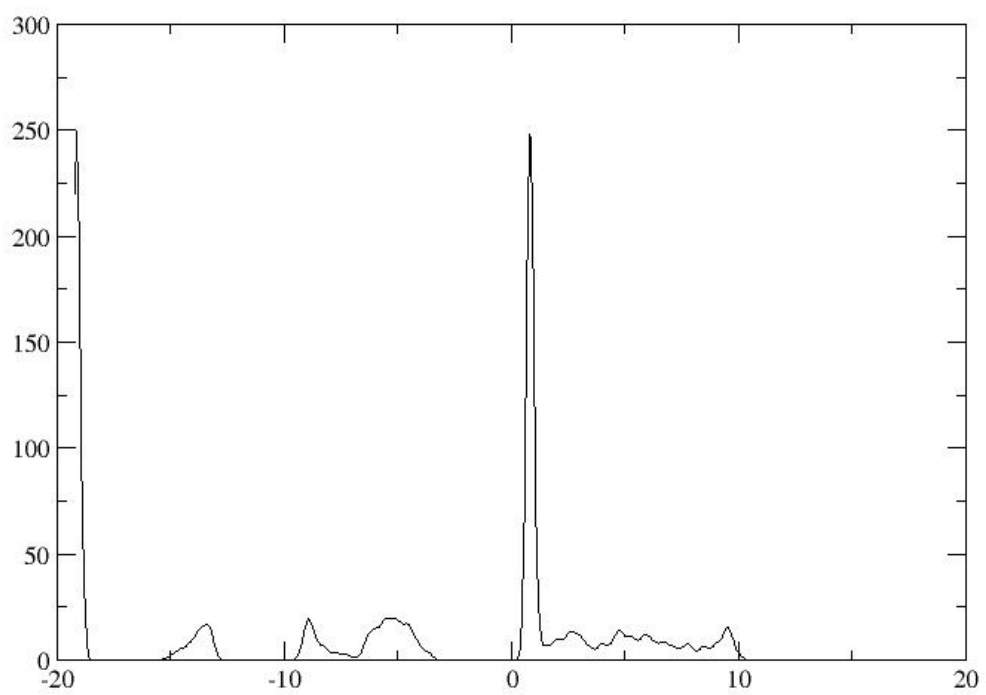


Figure 1: Density of states for GaAs with DFTB+ using the parametrization set hyb-0-1.

```

Geometry = {
  Periodic = Yes
  LatticeVectors [Angstrom] = {
    2.80 2.80 0.00
    2.80 0.00 2.80
    0.00 2.80 2.80
  }
  TypeNames = { "Ga" "As" }
  TypesAndCoordinates [relative] = {
    1 0.00 0.00 0.00
    2 0.25 0.25 0.25
  }
}

Driver = {}

Hamiltonian = DFTB {
  SCC = Yes
  SCCTolerance = 1e-5
  MaxSCCIterations = 1
  Mixer = Broyden {}
  MaxAngularMomentum = {
    Ga = "d"; As = "d"
  }
  SlaterKosterFiles = Type2FileNames {
    Prefix = "./hyb-0-1/"
    Separator = "-"
    Suffix = ".skf"
  }
  KPointsAndWeights = KLines {
    1 0.5 0.0 0.0 # L (11-1)
    20 0.0 0.0 0.0 # Gamma (000)
    20 0.5 0.5 0.0 # X (100)
  }
  ReadInitialCharges = Yes
}

Options = {
  RestartFrequency = 0
}

```

Some notes on the input:

- The geometry must be exact the same as the previous calculation where the charges were obtained.
- The Driver option must to be set to the empty value, since geometry optimisation during band structure calculation does not make any sense.

- The number of maximal SCC cycles had been set to 1:

```
MaxSCCIterations = 1
```

This is essential in order to prevent DFTB+ from making SCC cycles that may change the charges.

- The DFTB block contains the

```
ReadInitialCharges = Yes
```

option, which advises DFTB+ to read in the charges from the file charges.bin and use those to initialise the SCC loop. The charges.bin file should be the one containing the converged charges for the current structure (produced by the previous DFTB+ run).

- The K-points are specified using the KLines directive:

```
KPointsAndWeights = KLines {
  1  0.5  0.0  0.0  # L (11-1)
  20 0.0  0.0  0.0  # Gamma (000)
  20 0.5  0.5  0.0  # X (100)
}
```

Every line specifies a line segment. The first column gives the number of K-points along the line segment between (but excluding) the end of the previous line segment and the K-point specified in the next three columns (which is the end point of the current line segment). The specified number of K-points is evenly distributed along the line, the last K-point coincides with the end point of the segment. The coordinates of the K-points are relative coordinates (given in the coordinate system spawned by the reciprocal lattice vectors of the periodic structures). The starting point of the first line segment is the Γ point.

The example above calculates first the line segment between the Γ point and the L-point using only one K-point. The starting point of a line segment is always excluded and the last K-point along it always coincides with the specified end point, therefore, the line

```
1  0.5  0.0  0.0  # L (11-1)
```

instructs DFTB+ to do a single K-point calculation for the L point. Then 20 K-points are calculated along the L- Γ line (the last one being the Γ point itself). Finally additional 20 K-points are calculated along the Γ -X line. All together 41 K-points will be calculated, whereby the 1st one corresponds to L, the 21st to Γ and the 41st to X.

- The Options block contains

```
RestartFrequency = 0
```

This prevents DFTB+ from writing restart information to the disc and thus from overwriting the charges.bin file (with the converged charges) with meaningless charges obtained during the band structure calculation.

Running DFTB+ with the input above, the eigenlevel spectrum is calculated at the required k-points. The results are written to the file `detailed.out` and in more readable format to `band.out`. You can again use the script `band2dat` to extract the data from it, which can be then directly plotted by some data visualisation tool (like `xmgrace`):

```
band2dat band.out bandstruct.dat
```

If you import the data file `bandstruct.dat` into `xmgrace` as `NXY` set, you should obtain a band structure similar to Fig. 2.

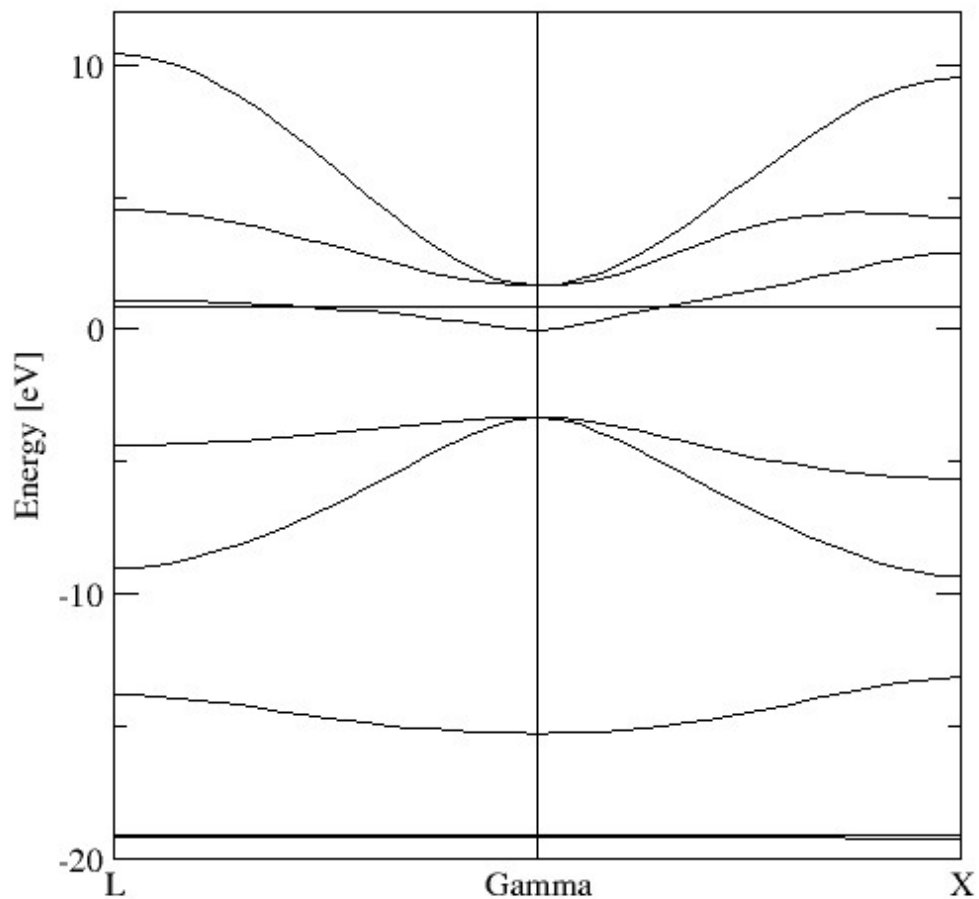


Figure 2: Band structure of GaAs calculated with DFTB+ along the $L-\Gamma-X$ line using the parametrisation `hyb-0-1`.