1 Band structure of the free electron gas

The model of the free electron gas (non-interacting electrons) is quite often used to show trends for specific physical quantities in solids. It can be regarded as kind of an analogon to the Hydrogen atom in basic quantum theory, because a lot of complex formulae simplify to very easy expressions e. g. for band structure (dispersion relation), density of states ($D(E) \sim \sqrt{E}$), dielectric function (Lindhard theory) or heat capacity (Sommerfeld model).

In this exercise, we want to take a look at the band structure. You should already be familiar with the resulting plot! What happens when you vary the parameter `nvalence`?

```
from ase.build import bulk
from ase.calculators.test import FreeElectrons
import matplotlib.pyplot as plt
import matplotlib as mpl
mpl.rcParams.update({"lines.linewidth": 4, "font.size": 32})

# create fictive simple cubic material
c = bulk("Si", "sc", 5.43)
# treat material as FEG with sampling along the x-direction
c.calc = FreeElectrons(nvalence=3, kpts={"path": "XGX", "npoints": 200})
c.get_potential_energy()
# plot band structure
bs = c.calc.band_structure()
bs.plot(emax=16, filename="egas.png")  # emax = ylim w.r.t. Fermi energy
# set a larger plot range -> show more bands
plt.ylim([0, 12])
plt.show()
```

Note@admin: The bands are by default all colored green. By replacing `kwargs=dict(color=color)` with `kwargs=dict()` in file `ase/spectrum/band_structure.py` - class `BandStructurePlot`, you can have them colored individually.

Solution:

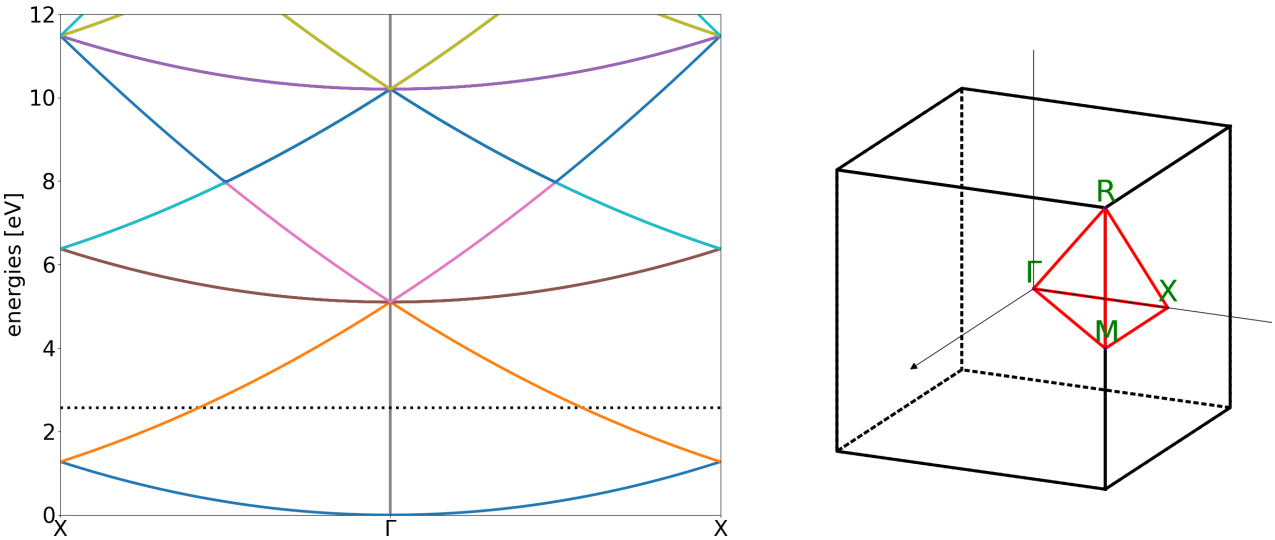

Figure 1: Bandstructure of the free electron gas in three dimensions for a simple cubic lattice as calculated with ASE. The Fermi energy E_F (horizontal dashed black line) shifts upwards with the number of valence electrons. For detailed explanation on how to interpret these bands, see section “Reduced Zone Scheme” in [1, §8.1.5].

2 Band structure of your system

1. Now, try to calculate the band structure for your system along a reasonable path in momentum space. Use 200 sampling points spread over the entire path. Don't forget to set the calculator from electron gas back to GPAW for the ground state calculation!
   https://en.wikipedia.org/wiki/Brillouin_zone

```python
# find special points in Brillouin zone
from ase.dft.kpoints import special_paths, sc_special_points
from ase.build import bulk
from gpaw import GPAW

import matplotlib.pyplot as plt
import matplotlib as mpl
mpl.rcParams.update({"lines.linewidth": 4, "font.size": 32})

# find high symmetry k-point path in 1st Brillouin zone of fcc cell
print(special_paths["fcc"])
for special_point, coordinates in sc_special_points["fcc"].items():
    print(f"{special_point} : {coordinates}")

# STUDENT: create bulk silicon in diamond structure, perform GS
# calculation and save density with si.calc.write('si.gpw')

# restart from saved density but instead of running SCF iterations
# calculate eigenvalues along the kpt path to create band structure
si = bulk("Si", "fcc", 5.43)
si.calc = GPAW("si.gpw").fixed_density(
    nbands=16,  # need more for metals or magnetic systems
    symmetry="off",  # calc all k-points, not only IBZ
    kpts={"path": "LGXU,KG", "npoints": 200},  # 200 pts total
    txt="gpaw.log"
)
print("Fermi Energy:", si.calc.get_fermi_level().round(3))

# compute eigenvalues, set E_F = 0 and plot band structure
bs = si.calc.band_structure().subtract_reference()
bs.plot(filename="si.png", show=False, emax=16)
plt.ylim([-12.5, 10])
plt.show()
```

2. Compare your result with the picture on Wikipedia:
   https://de.wikipedia.org/wiki/Bandstruktur#/media/File:Band_structure_Si_schematic.svg

3. How large is the Fermi energy E_F? What is the physical meaning of its value?
   (Find the corresponding member function of the GPAW calculator class!)
   Solution:
   The Fermi energy is about 5.375 eV. Use `si.calc.get_fermi_level()`.
   Note, that this absolute value has no further physical meaning. This is why electronic structure codes tend to return bandstructure energy data relative to the Fermi energy, i. e. they plot $(E(\boldsymbol{k}) - E_\mathrm{F})$ instead of $E(\boldsymbol{k})$ on the y-axis.

4. How large is the bandgap?
   Solution:

```
from ase.dft.bandgap import GapInfo, bandgap
# full description as reported by GPAW output
ibz_kpts = si.calc.get_ibz_k_points()
print(GapInfo.fromcalc(si.calc).description(ibz_kpoints=ibz_kpts))
# or for less text simply use
bandgap(si.calc,direct=False)
```

   $E_\mathrm{G}^\mathrm{id} = 0.472$ eV is an indirect band gap starting at the Gamma point (0,0,0) and ending somewhere near the X point. By contrast, $E_\mathrm{G}^\mathrm{d} = 2.530$ from $\Gamma \to \Gamma$ is the direct gap.

   Note, that these bandgaps are far off the "real" ones. This is a perfect example for DFT not being able to reproduce absolute energies very well - at least not in the simple fashion we followed in this exercise. On top of that, the true band gap is in fact a quasiparticle property that involves not only ground state but also excited state energies. However, our DFT bandstructure covers all important symmetries and intersections qualitatively correct. For quantitatively good results, one had to employ more advanced approaches like usage of hybrid functionals, extensions like DFT+U or even entirely different theories like GW.

5. What can you tell about the semi-conductor properties of silicon from looking at its band structure plot?
   Solution:
   The energy gap, i. e. the minimal distance between the lowest states above and the highest states below the Fermi energy cannot be overcome without an additional change in the wave vector. In other words: the maximum of the valence band and the minimum of the conduction band are not located at the same $\boldsymbol{k}$-point. Hence, Silicon is an indirect semi-conductor.

6. Repeat the calculation with values 0,2,4,5,8,-1 for the paramter `nbands`. What does the program tell you? How can you determine the minimum number of bands you have to use?
   Solution:
   There are 4 bands below the Fermi energy. This matches the number of valence electrons in the silicon system (diamond configuration) divided by 2 (2x Si atom with 4 VE each = 8 VE):
   Si: [Ne] + $\underset{3s^2}{\uparrow\downarrow}$ $\underset{3p^2}{\uparrow\ \uparrow\ -\ -}$
   GPAW's default value for `nbands` is 4 + 1.2 times the number of occupied bands. For a system where all spins pair, you would need at least as many bands as half the number of valence electrons. In case of diamond-silicon, this is 8/2 = 4. In case of spin-polarized calculations with a total magnetic moment greater than zero, there are even more bands necessary. In fact, it is usually a good idea to set `nbands` to a rather high number, especially for metals!
   https://wiki.fysik.dtu.dk/gpaw/documentation/basic.html#number-of-electronic-bands

7. Have a look again at the part of the band structure below the Fermi energy, where all states/bands are fully occupied. Can you possibly assign orbital labels like "s" or "p" to these lower bands?
   Solution:
   There is no simple way of telling if a band is a p-band or s-band, simply because neither is true in general. By calculating the so-called projected (or partial) density of states (w. r. t. to certain atomic orbitals) illustrates this effect well as shown in Fig. 3. A very good answer to this question can also be found here: https://physics.stackexchange.com/questions/278844/why-do-p-orbitals-correspond-to-the-valence-band-in-semiconductors

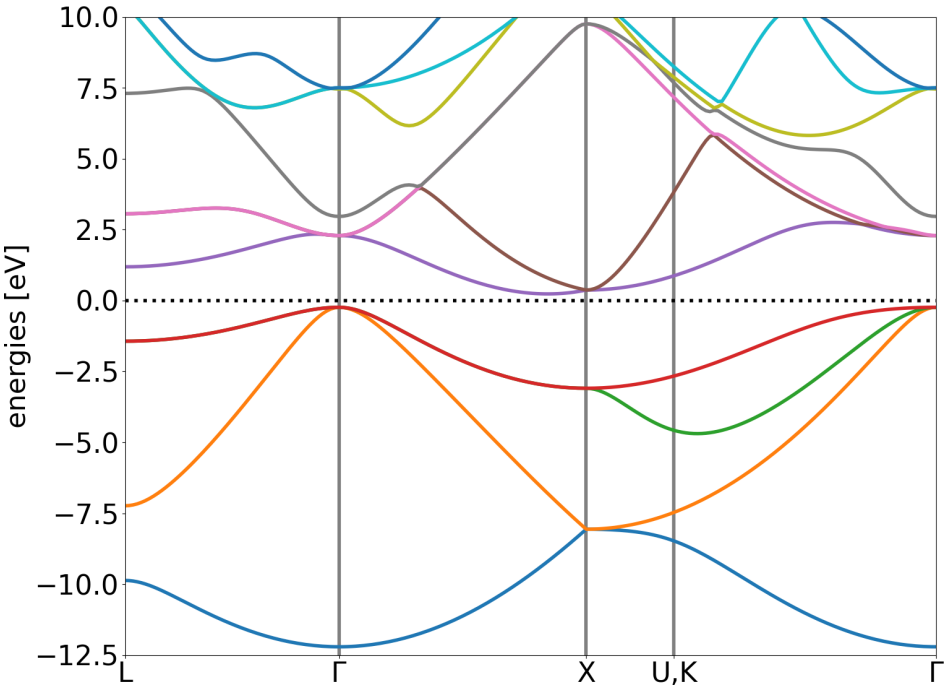

Figure 2: Bandstructure of silicon as calculated with GPAW. Energies are given relative to the Fermi energy. Although the band gap is too narrow, all important features have been reproduced qualitatively correct.

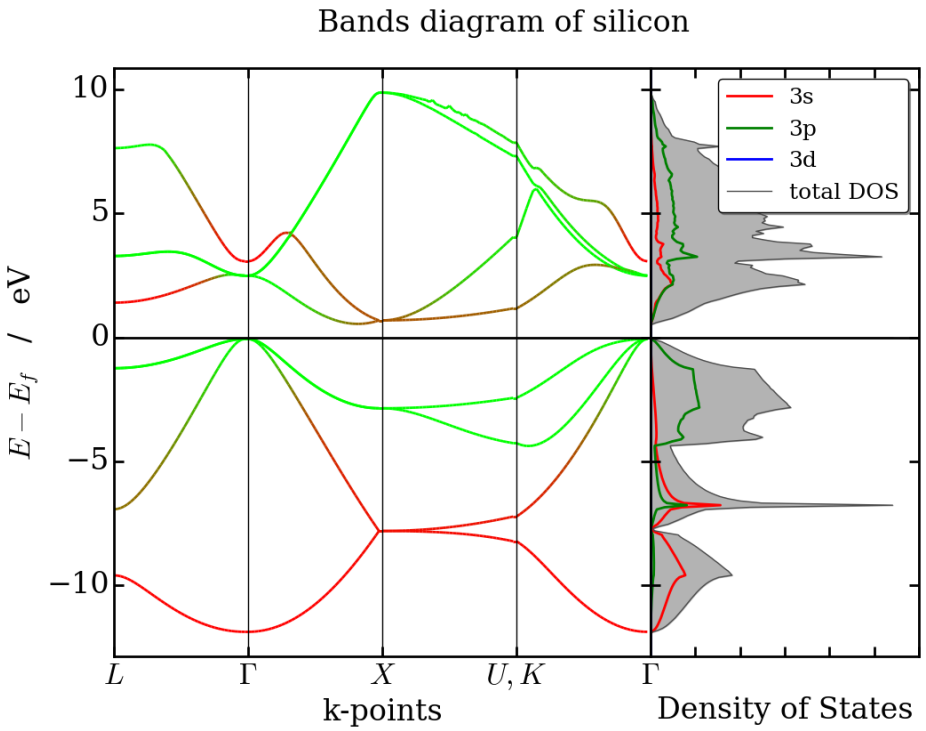

Figure 3: Bandstructure of silicon colored according to projected density of states on 3s and 3p atom orbitals. Provided by G.S. Vallverdu under MIT license: https://github.com/gVallverdu/bandstructureplots/blob/master/Si_bands/bands_Si.png.

References

[1] Rudolf Gross and Achim Marx. *Festkörperphysik*. 2., aktualisierte Auflage. Berlin ; Boston: De Gruyter, 2014. ISBN: 978-3-11-035869-8.