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.

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!)
4. How large is the bandgap?
5. What can you tell about the semi-conductor properties of silicon from looking at its band structure plot?
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?
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?