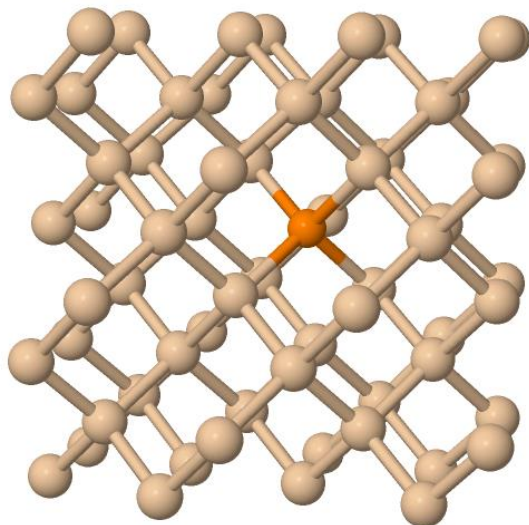


Computational Chemistry 2 – Chapter 3

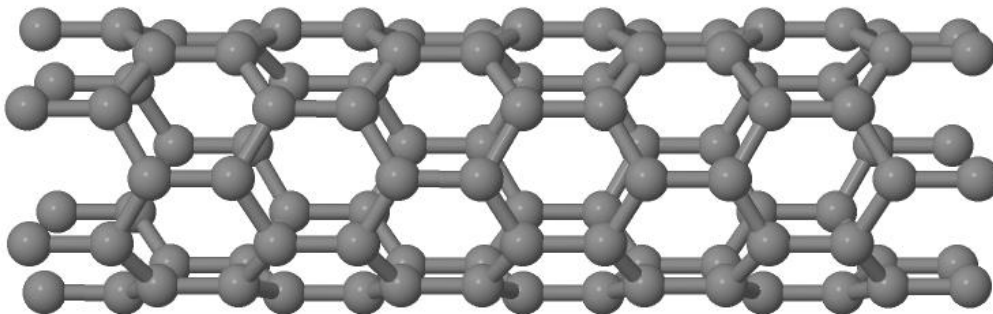
Solid systems

The most obvious application to periodic DFT is the modelling of the solid systems. We need to know the unit cell and atomic positions in it. Almost all solid materials can be modelled. The unit cell is usually small enough (excluding proteins and polymers). Also almost all elements in the periodic table can be modelled. The heaviest elements, like lanthanides and actinides, are difficult. The DFT/GGA models are not very good in the case of f-electrons. Note that the scalar relativistic effects are included to the pseudopotentials so the relativistic effect e.g. in gold (Au) can be handled.



Jmol

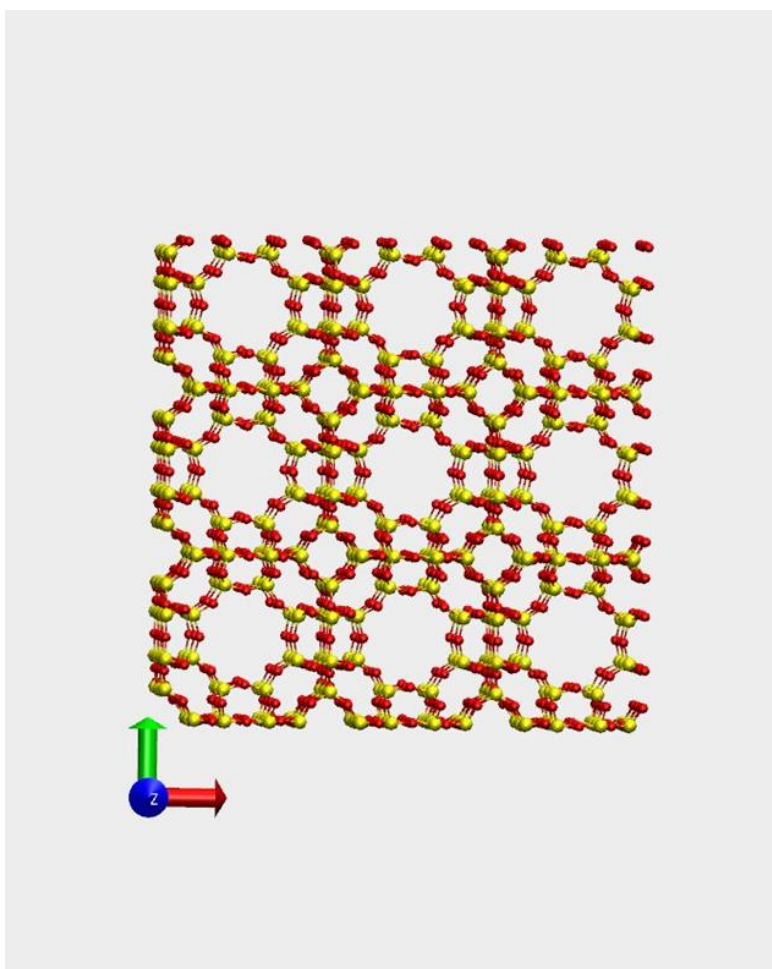
For most materials the good GGA/MGGA works well. The material can be metal, semiconductor or insulator. Also hydrogen bonded systems works quite well and even the weakly interacting materials can be modelled with dispersion corrected GGA's. Many of the new materials like carbon nanotubes or graphene can be modelled with DFT.



Jmol

Figure: (6,0) carbon nanotube

The largest system we have studied is Zeolite A with 3x3x3 unit cell. It has 1944 atoms, and **10368 (valence) electrons**. Note that the unit cell has 72 atoms.



Computational cell is usually larger than the unit cell.

It is very common to make the calculations with larger cell than the unit cells. From the point of view of the k-points the Brillouin zone is shrinking and k-points are more densely. If the computational cell is twice as large as the unit cell one can reduce the k-points in this direction to half and have the same sampling. This is not very effective way to improve the sampling since the computational scaling of the DFT calculations is $(N_{\text{at}})^3$ but it is linear in the k-points, N_{kp} . The increase of the computational cost is $\sim (N_{\text{at}})^2$.

The reason to use larger computational cell is always physical. We wanted to study some defect or phenomena that do not have the periodicity of the unit cell.

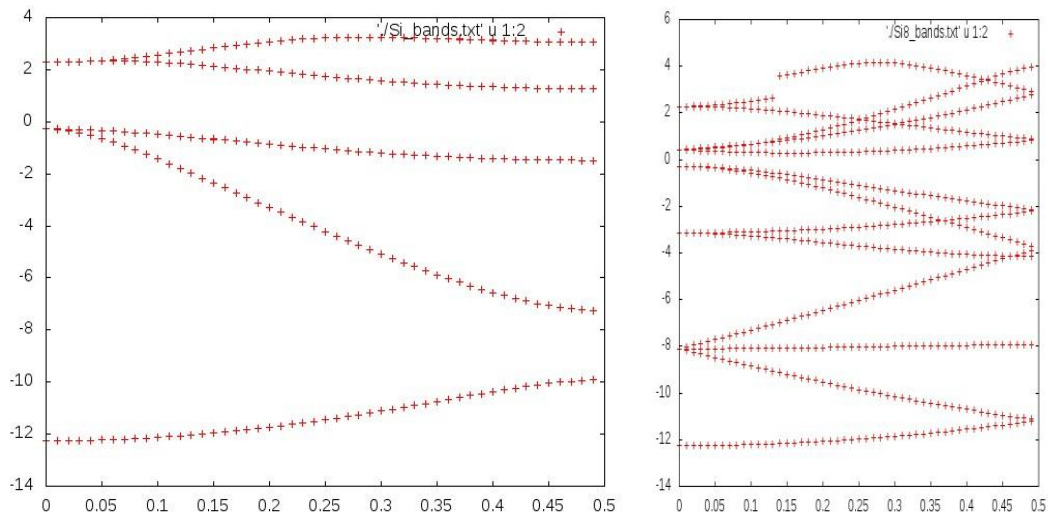
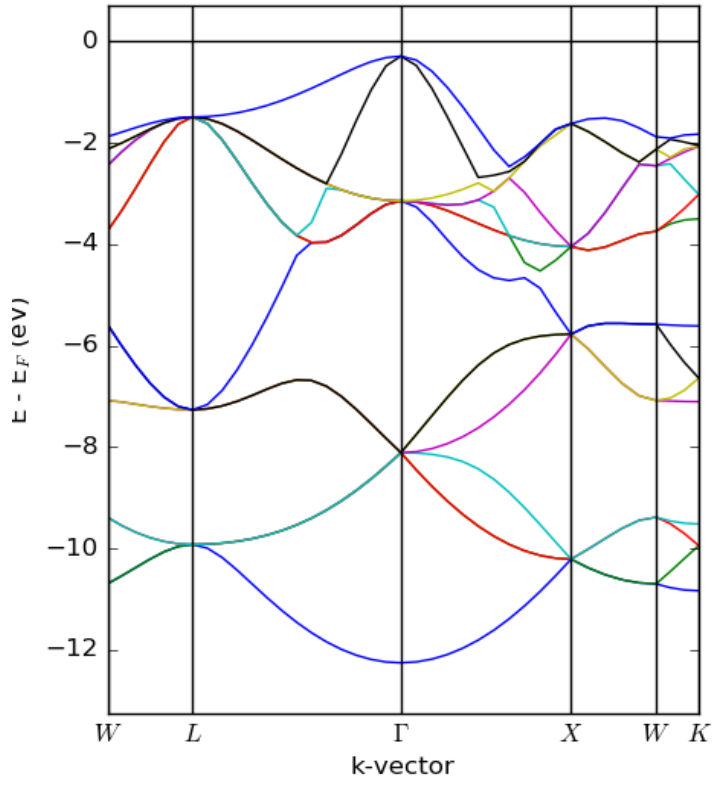
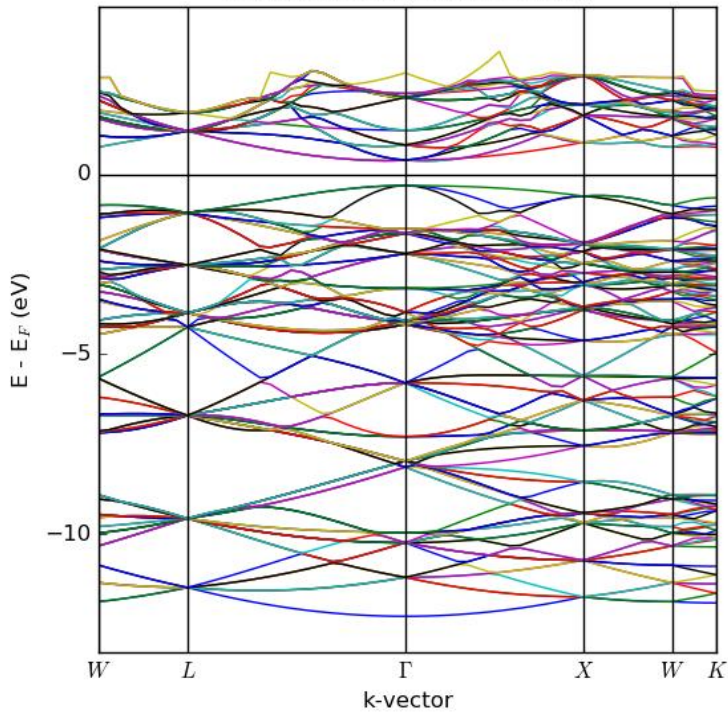


Figure: Si band structure in (1,0,0) direction at 2-atom cell (diamond structure) and 8-atom cell (cube). Also below a broader picture of the Si8 and Si64 band structures.

Bandstructure of 8 Silicon



Bandstructure of 64 Silicon

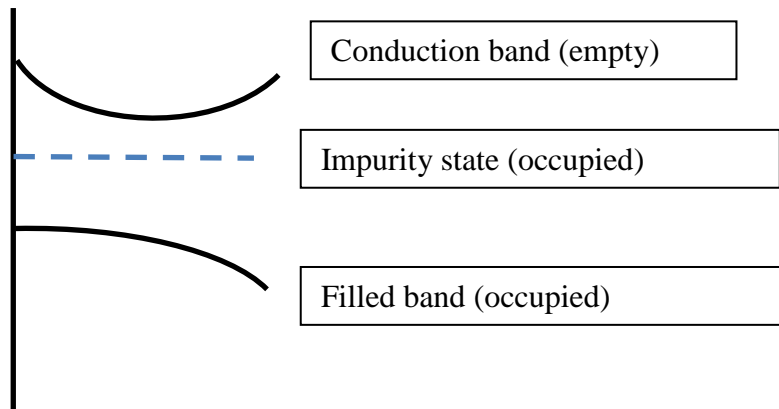


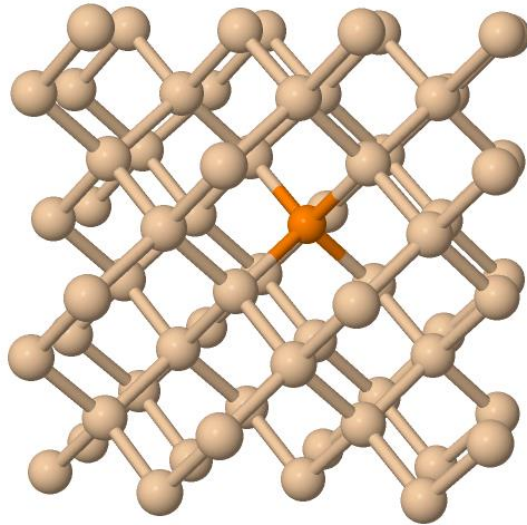
Point defects

Very often the materials defects like impurities are interesting. The simplest defects are point defects which are size of one atoms. The common point defects are vacancies (a missing atom), substitutional defects (a "wrong" atom in a lattice site) and interstitial atoms (an atom out of the lattice sites). Sometimes there can be two point defect near each other. Here we ignore these cases.

What a point defect will do to the electronic structure of the material? It cases so called impurity state (or band). This is very narrow band. In semiconductors the impurity band is often in the band gap but it can also be in the occupied band.

The former is interesting. The conductivity increases a lot if there is an impurity state near the conduction band. The conduction depend on the number of electrons in the conduction band and for ideal semiconductor at finite temperature it is proportional to $\exp(-E_{\text{gap}}/kT)$ but with the impurity it is proportional to $\exp(-(E_{\text{cond}} - E_{\text{imp}})/kT)$. The $E_{\text{cond}} - E_{\text{imp}}$ is much smaller than E_{gap} and due to the exponent the difference in conduction band occupancy is very large and thus the conductivity is larger. This is the key method to make n- or p-type silicon.

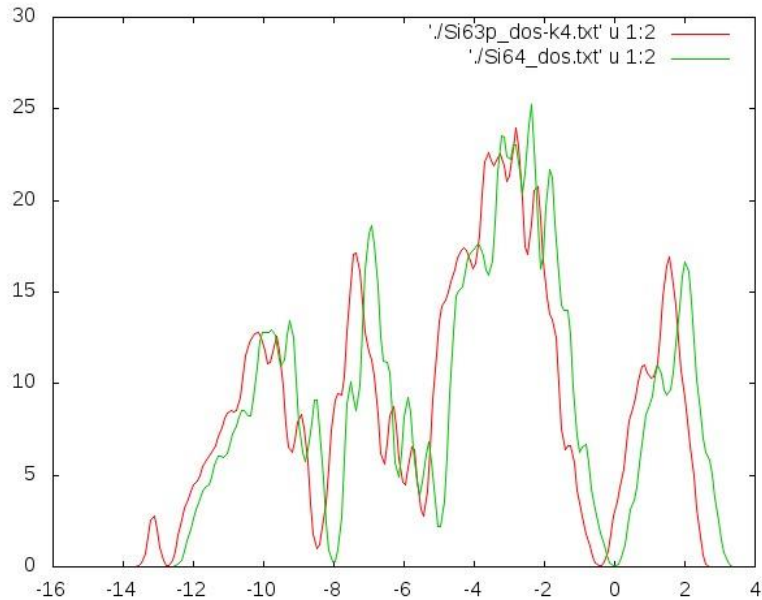




Jmol

Figure: P impurity in 64 atom Si lattice

The computations of point defects are quite a bit more time consuming than bulk materials but still doable in some hours (wihuri 12 cores). For Si the smallest reasonable systems is Si63X. The picture above shows Si63P system and below is the density of states of the same system. The impurity band is very close to the conduction band and it does not show in this DOS.



The point defect studies are rather easy if one knows the type of defect.

Density of states, DOS

The band structure is rather complex way to analyze the bands and much simpler quantity is the density of states (DOS). The normal DOS tells how many quantum states there are at given energy:

$$\rho(\varepsilon) = \sum_n \langle \varphi_n | \varphi_n \rangle \delta(\varepsilon - \varepsilon_n)$$

From the DOS one can see the energy gap and where the energy states are. The DOS is easy to compute.

```

from gpaw import *
from pylab import *

# Density of States
si, calc = restart('Si2.gpw')
e, dos = calc.get_dos(spin=0, npts=2001, width=0.4)
e_f = calc.get_fermi_level()
plot(e-e_f, dos)
axis([-15, 10, None, None])
ylabel('Si DOS')

```

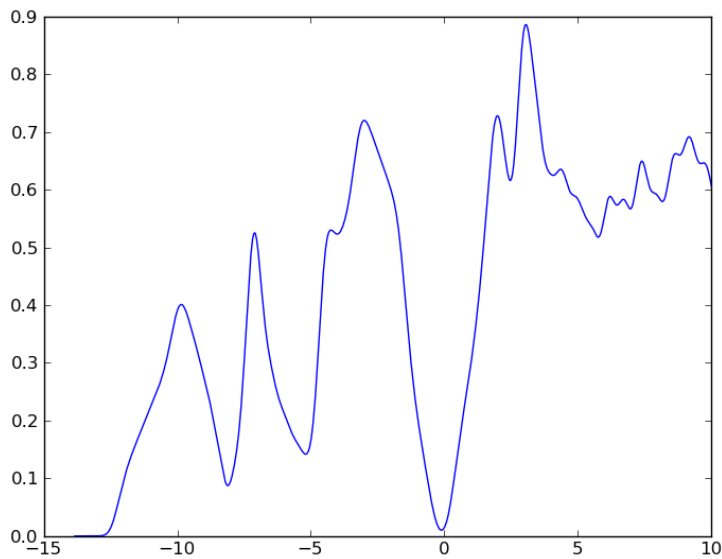


Figure: Bulk Si DOS (8x8x8 k-points)

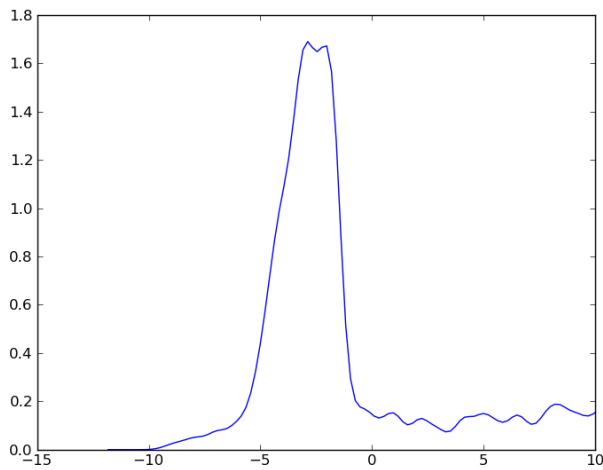


Figure: Cu DOS

From these figure one can see that Si is semiconductor and Cu is a metal. So called projected DOS is much more useful. In pDOS one can take an atomic (or atomic-like) state φ_m and project the orbitals to it. The most useful projection states are s-, p- or d-states.

$$\rho_m(\varepsilon) = \sum_n |\langle \varphi_m | \varphi_n \rangle|^2 \delta(\varepsilon - \varepsilon_n)$$

Below is a calculation of d-projection of Cu states.

```

from gpaw import *
from pylab import *

# Local Density of States
cu, calc = restart('Cu.gpw')
e, dos = calc.get_orbital_ldos(a=0, spin=0, angular='d', npts=2001, width=0.3)
e_f = calc.get_fermi_level()
plot(e-e_f, dos)
axis([-15, 10, None, None])
ylabel('d-DOS')

```

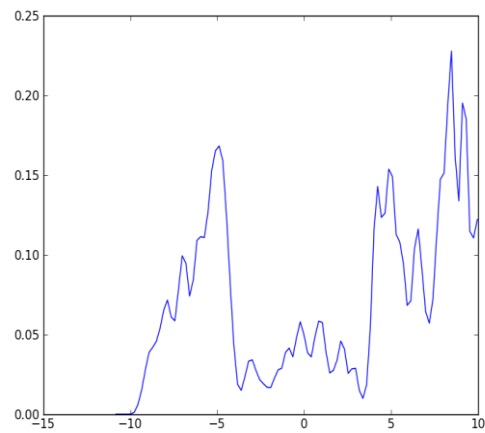
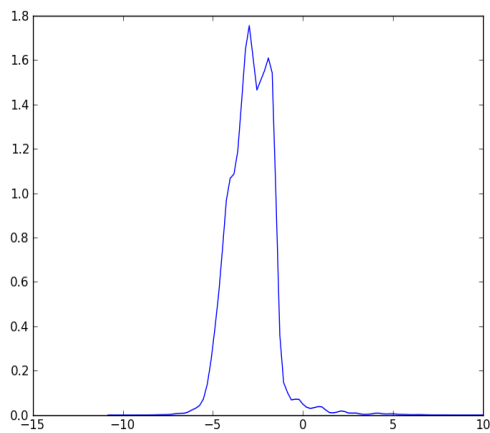
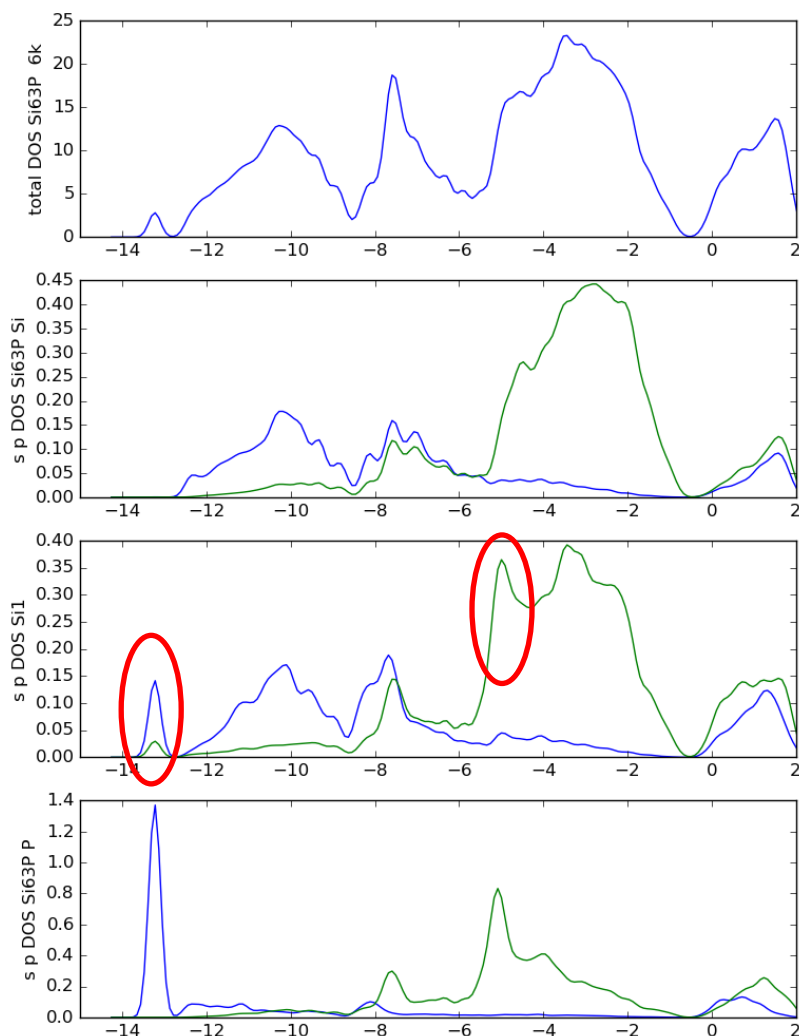


Figure: Cu projected DOS. On left, the d-states and on right s-states. Note the different scale. Compare these to the Cu total DOS. In Cu the conductivity is mostly due to the s-electrons.

The Si63P is also interesting. Below topmost figure is the total DOS. The two next ones are s- and p-projected Si pDOS. The first is from a Si atom far from the P defect and the second is from Si next to P (Si1). The last is the s- and p-projection of P. As one can see there is a state at E_F (energy =0). This has contribution of the P (and neighboring Si). Warning reading the DOS or pDOS is sometimes confusing but it will help to understand the **bulk** orbitals. The low energy peak in Si1 DOS is interesting. It is clearly where P has an s-state but Si has no states at this energy. Now an important fact: the dos sees bulk (or molecular) states NOT atomic states. This peak

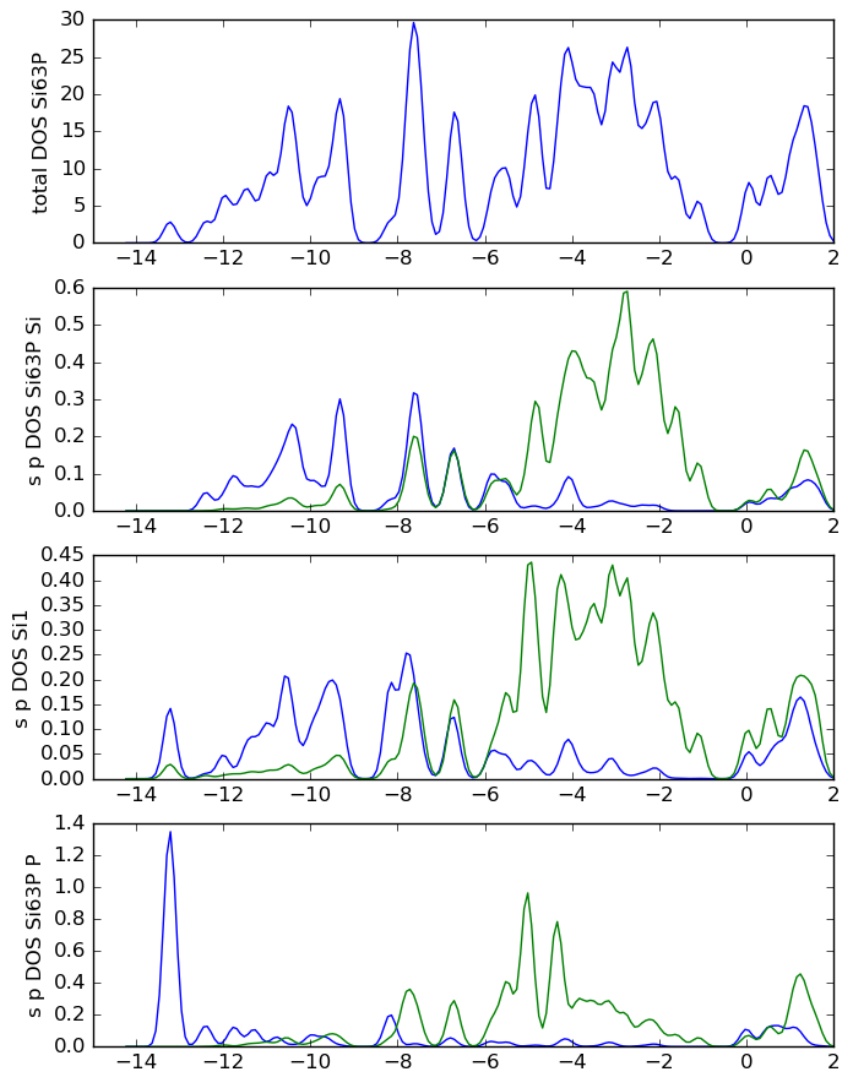
comes from P-Si bond: some Si s- and p-states make a bond between P's s-state. Similar bonding is also seen around -5 eV. There is stronger p-peaks at Si1 than Si. Similar p-peaks are also seen in P's DOS.

Note that the concentration of real point defects is very low, few ppm or so. Unit cell of 1 milj. atoms cannot be computed so a compromise of the computational cost and concentration has to be made. Unit cell of ca. 100 atoms is OK. Also the geometry of the system need to be optimized. The atoms near the defect will move from the ideal positions.



Note that the DOS figures can change quite a bit when different amount of k-points are used. Below are the same Si63P system with

2x2x2 k-points. With more k-points the dos is smoother (the figure above is with 6x6x6 k-points)



Magnetic materials

Some of the elements have permanent magnetic moment. The most well known is iron. One can solve the Kohn-Sham equations with spin. One need to solve the spin-up and spin-down states separately. This will lead to two "densities" $\rho_{\uparrow}(r)$ and $\rho_{\downarrow}(r)$, the total density is the sum of these. The E_{xc} now depend both the total density and the difference of the spin densities. $E_{xc}[\rho(r), \rho_{\uparrow}(r) - \rho_{\downarrow}(r)]$. For all xc-models there is the spin version, so the magnetic calculations are as easy as normal DFT calculations.

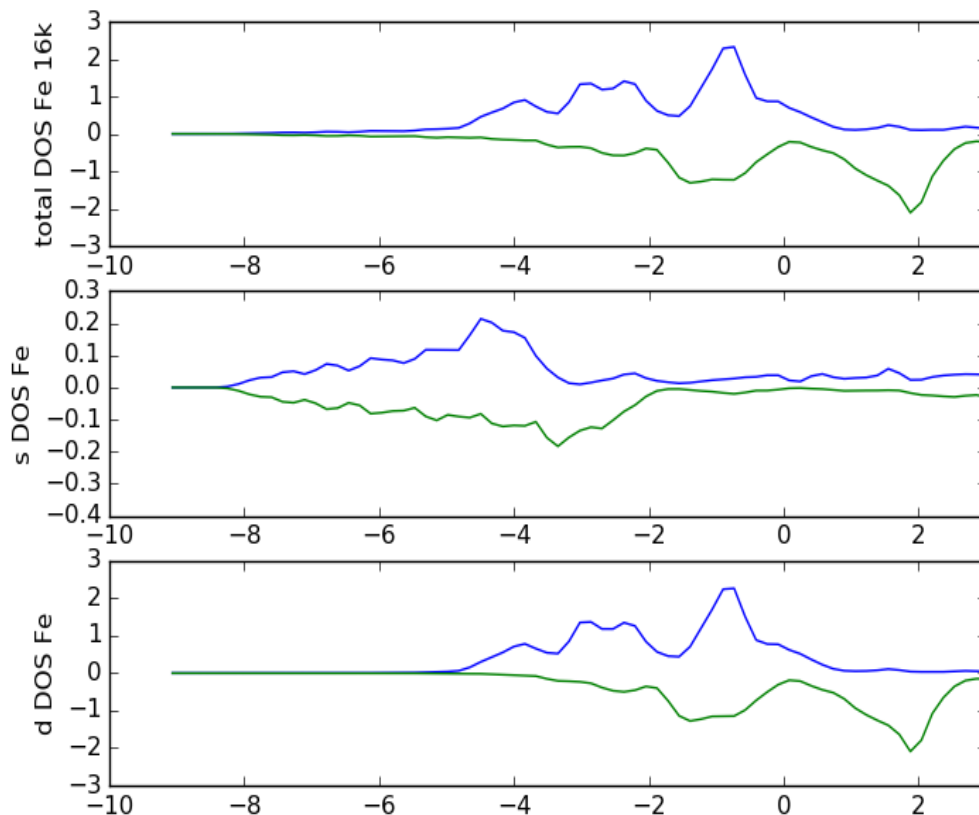
The py script is easy

```
Fe = bulk('Fe','bcc',a=2.87)
Fe.set_initial_magnetic_moments([2.2])

calc=(GPAW(h=hp, nbands=-10, xc='PBE',kpts=(k, k, k),
occupations=FermiDirac(FD),mixer=Mixer(beta=0.10, nmaxold=4, weight=90.0),
convergence={'eigenstates': 5.0e-5, 'density': 1.0e-4}, txt='Fe-mag.out'))

Fe.set_calculator(calc)
energy=Fe.get_potential_energy()
Fe.calc.write('Fe-mag-new.gpw')
```

One can then plot the pDOS for both spin states.



Bulk properties

Almost any quantity of the bulk material can be computed. Antti Karttunen will discuss of phonons and elastic properties. Naturally

the lattice constant need to be computed. The DFT/GGA lattice parameter is not the same as the experimental one and in computations the computed one should be used. The impurity energies and impurity-impurity energies can be computed. In addition, mixed systems can be studied. Especially interesting are the metal mixtures. In all cases the atoms are assumed to be roughly on ideal positions.

In the case of mixed metals the system size is rather large. Below is an example of 32 atoms FCC unit cell of 30 Cu and 2 Ag atoms. In figure a) the Ag atoms are next to each other and in b) a bit further. With these type of geometries one can estimate the Ag-Ag interaction in Cu. With this type of calculations a lot of properties of mixed metals systems can be studied but the calculations are a bit time consuming.

