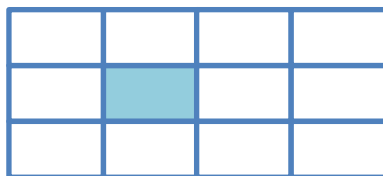# Computational Chemistry 2 – Chapter 2

Periodic boundary conditions and solid systems

Now we leave the DFT and start to look of quantum computations for periodic systems. This is natural setup for bulk materials where some unit cell is repeated to every direction. We can assume that the system is either infinite or very big.

Here the essential point is that the potential the electrons will see is periodic, V(r)= V(r+R) where R is the systems lattice vector. More precisely R = n_1A_1 + n_2A_2 + n_3A_3 and here the vectors A_1, A_2, A_3 will describe the unit cell.
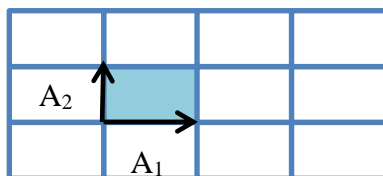
Now the energy is

$$E[\psi] = \langle\psi|G - V(r, R_I)|\psi\rangle = \langle\psi|G|\psi\rangle - \int d^3 r\, V(r, R_I)\rho(r)$$
$$H|\psi\rangle = \{G - V(r, R_I)\}|\psi\rangle = E|\psi\rangle$$

Where V is periodic and G do not depend on atomic positions. How this will affect the wave function. We can show that the wave function has form (Bloch theorem)

$$\psi(r + R) = e^{-ik.R}\psi(r)$$

Here k is so called inverse lattice vector. The proof is a bit complex, but let us define a translation operator T_R, $T_Rf(r)=f(r+R)$ in periodic system the T_R will commute with H

$$T_R \ H \ = \ T_R \ G \ - \ T_R \ V \ = \ G \ T_R \ - \ V \ T_R \ = \ H \ T_R$$

because G do not depend on positions and V(r) is periodic. Now

$$T_R \ (H|\psi\rangle) = H(T_R|\psi\rangle) = T_R \ E|\psi\rangle = E \ T_R|\psi\rangle ; \quad |\varphi\rangle = T_R|\psi\rangle \ \rightarrow \quad H|\varphi\rangle = E|\varphi\rangle$$

The wave function need to be also an eigen function of the translational operator. (Math: if two operators commute they will have same eigen functions.)

$$T_R \ |\psi\rangle = c(R)|\psi\rangle$$

$T_R T_{R'} \psi(r) = \psi(r+R+R') = c(R)c(R')\psi(r) = c(R+R')\psi(r)$, so the eigenvalue of the translational operator have a special property c(R)c(R')=c(R+R'). This is true only for an exponent function, so
c(R) = exp(-ik.R)

In principle k could be complex but the boundary conditions will force k to be real. k can be written using inverse lattice vectors B_n, k = $x_1 B_1$ + $x_2 B_2$ + $x_3 B_3$, and $B_i . A_j = 2\pi\delta_{ij}$ x's are real numbers. When the lattice vectors are known B's can be computed as: $B_1 = 2\pi$ $A_2 xA_3/\{A_1.(A_2 xA_3)\}$, $B_2 = 2\pi$ $A_3 xA_1/\{A_1.(A_2 xA_3)\}$, $B_3 = 2\pi$ $A_1 xA_2/\{A_1.(A_2 xA_3)\}$

So

$$\psi(r + R) = c(R)\psi(r) = e^{-ik.R}\psi(r) \qquad \text{(Bloch)}$$

This is an interesting result. In periodic system, the wave function will change only with a phase factor when moving with one lattice vector. This means that the electron density does not change,

$$\rho(r + R) = \sum_{n=1}^{N} [e^{-ik.R}\psi_{n,KS}(r)]^* e^{-ik.R}\psi_{n,KS}(r) = \sum_{n=1}^{N} [\psi_{n,KS}(r)]^* \psi_{n,KS}(r) = \rho(r)$$

Note that it is enough to know the density only in one unit cell. The discussion is completely valid for all quantum chemical methods.

Periodic (Born-von Karman) boundary conditions for the wave functions

Next let us look the **periodicity of the wave function**. We assume that the wf is periodic after (N_1, N_2, N_3)

$$\psi(r + N_1 A_1 + N_2 A_2 + N_3 A_3) = \psi(r)$$

Bloch theorem $\psi(r + R) = e^{-ik.R}\psi(r) = \psi(r)$ and exp(-ik.R)=1.
k.R = 2π(x₁N₁+x₂N₂+x₃N₃)= 2π*integer number. The periodicity is
fulfilled in every direction so x$_i$=m$_i$/N$_i$ (m is an integer). The
equation above gives a good way to understand the k-vector.

$$k = \left(\frac{m_x}{N_x}, \frac{m_y}{N_y}, \frac{m_z}{N_z}\right), m_i = 0, \dots N_i$$ k vector contain equally spaced point in
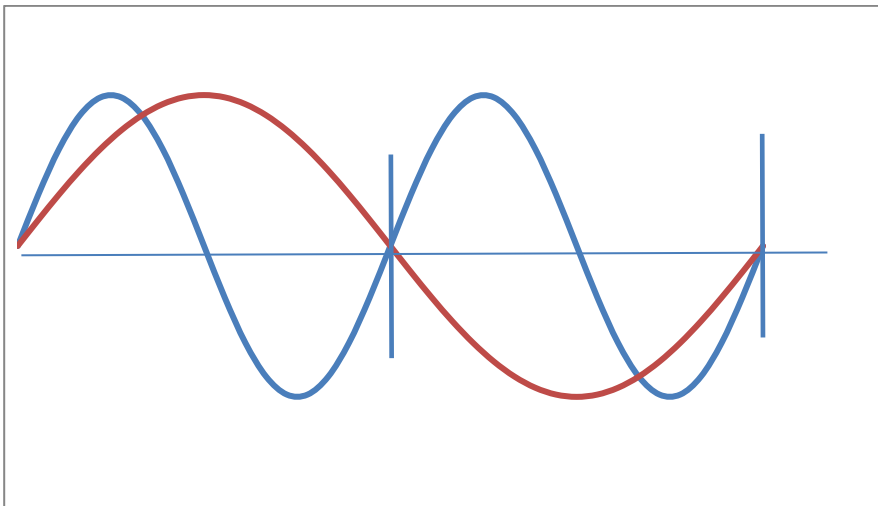
each direction.

This is not very useful for computing the wave function. We can
express the wf as a Fourier-series

$$\psi_k(r) \approx \sum_q^{Qmax} C_q e^{iq.r}$$

Here the wave vector q fits always to the box (N₁, N₂, N₃). We can also
expand the potential to Fourier-series. (In both cases the Qmax and
Kmax determinates the accuracy of the expansion.)

$$V(r) \approx \sum_K^{Kmax} V_K e^{iK.r}$$

Here K fit always exactly to the unit cell. Note that q has
periodicity of N$_i$A$_i$, and if N>1 q has longer wavelength.

Now we can compute all the components of the Schrödinger equation. First the kinetic energy:

$$-\nabla^2 \psi(r) = \sum_{q}^{Qmax} q^2 C_q e^{iq.r}$$

Now the Schrödinger equation can be written as (Note: in 1-particle or K-S formalism.)

$$\sum_{q}^{Qmax} e^{iq.r} \left\{ (q^2-E)C_q + \sum_{K} V_K C_{q-K} \right\} = 0$$

The Fourier vectors are linearly independent so the equation in brackets has to be =0

$$\left\{ (q^2-E)C_q + \sum_{K} V_K C_{q-K} \right\} = 0$$

A new variable **q=k+K'**, where k is always < min K. Remember K is a wave vector related to the unit cell.

$$\left\{ [(k+K')^2-E]C_{k+K'} + \sum_{K} V_K C_{k-K+K'} \right\} = 0$$

Still on more change of variable K-> K'-K

$$\left\{ [(k+K')^2-E]C_{k+K'} + \sum_{K} V_{K'-K} C_{k+K} \right\} = 0$$

Now the wave function can be written with C_{k-K} where k is < min K and K is the wave vector of the unit cell.

$$\psi_k(r) = \sum_{q}^{Qmax} C_q e^{iq.r} = \sum_{K}^{Kmax} C_{k+K} e^{i(k+K).r} = e^{ik.r} \sum_{K}^{Kmax} C_{k+K} e^{iK.r} = e^{ik.r} u_k(r)$$

Here the $u_k(r)$ is the part of wave function that has the periodicity of the unit cell. The only non-unit cell periodic part is the exp(-ik.r)

The density do not change but the kinetic energy will change. The impulse is

$$-i\nabla \psi_k(r) = -i\nabla \left(e^{ik.r} u_k(r) \right) = k e^{ik.r} u_k(r) - i e^{ik.r} \nabla u_k(r)$$

And the kinetic energy is

$$T\psi_k(r) = \tfrac{1}{2}(-i\nabla + k)^2 u_k(r) \qquad \text{(KIN)}$$

Finally, we can write the periodic Kohn-Sham equations

$$\left[\frac{1}{2}(-i\nabla + k)^2 + 2\int d^3 r_j \frac{\rho(r_j)}{|r_i - r_j|} - \sum_J \frac{Z_I e^2}{4\pi\varepsilon_0 |r_i - R_J|} + V_{xc}[\rho](r)\right] u_{k,n}^{KS}(r_i; R_I) = E u_{k,n}^{KS}(r_i; R_I),$$

$$\text{(DFT-P)}$$

$$\rho(r) = \sum_k \sum_n u_{n,k}^2(r)$$

So one need to solve wave functions $u_{k,n}(r)$ need to be solved with several k-points. Note that the density have the k-summation. It is important that the density and external potential are periodic. So it is enough to **solve the problem only in the unit cell**.

The only complicated term is the electrostatic potential

$$E_C = \frac{1}{2}\iint d^3 r d^3 r' \frac{\rho(r)\rho(r')}{|r - r'|} - \int d^3 r \sum_I \frac{\rho(r) Z_I}{|r - R_I|} + \frac{1}{2}\sum_{IJ} \frac{Z_I Z_J}{|R_I - R_J|}$$

First the **whole system need to be neutral** otherwise the electrostatic energy is infinite. This makes it difficult to study charged systems. Mathematically a constant charged background will be added to the system. This do not affect the atomic geometries and it usually have only a small affect to the density but the energies of differently charged system cannot be compared.

Note: periodic H-F is more complex and the computations need to be done carefully. Also the H-F computations are rather time consuming so the periodic hybrid-DFT calculations are much slower than pure DFT calculations. The computational speed can vary from one code to another.
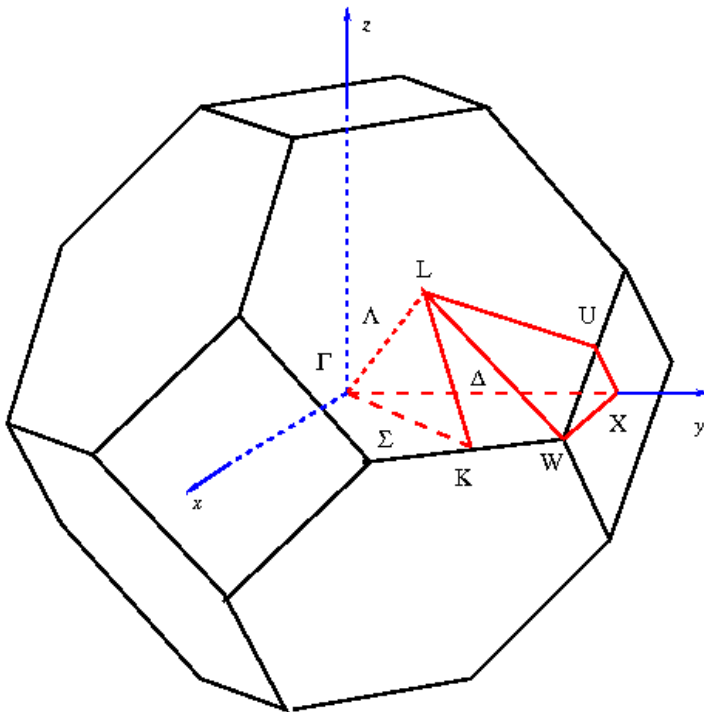
k-points

In above the non-periodicity is described with the k-vector and then exp(-ik.r) term. Let us next look more carefully the k-vectors. In equation (DFT-P) the wave function u(r) need to be solved with different k-vectors. Earlier we assumed that the wave functions are periodic in a large (N_x, N_y, N_z) box and this discretize the k-vectors.

$$k = \left(\frac{m_x}{N_x}, \frac{m_y}{N_y}, \frac{m_z}{N_z}\right), m_i = 0, \dots N_i$$

This means that it is enough to focus on certain k-points. Often the
high symmetry k-points have "names". The k=(0,0,0) (= Γ point) means
that the wave functions have the same symmetry as the unit cell. The
point k=(0.5,0,0) means that the wave function is periodic in x-
direction after two boxes and in y- and z-dictions the wf have the
unit cell symmetry. To get a good description of the system wave
functions need to be solved with several k-points. The number of k-
points depend strongly on the system. Insulators do not need much k-
points, semiconductors needs more and good description of a metal
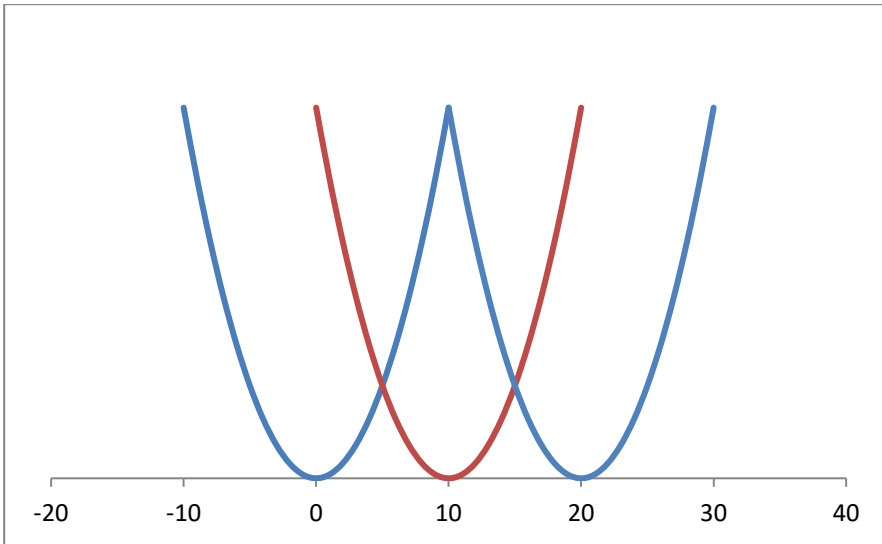require many k-points.

SPECIAL POINTS

First Brillouin zone of FCC lattice showing symmetry points (From: wikipedia, Electronic-band-
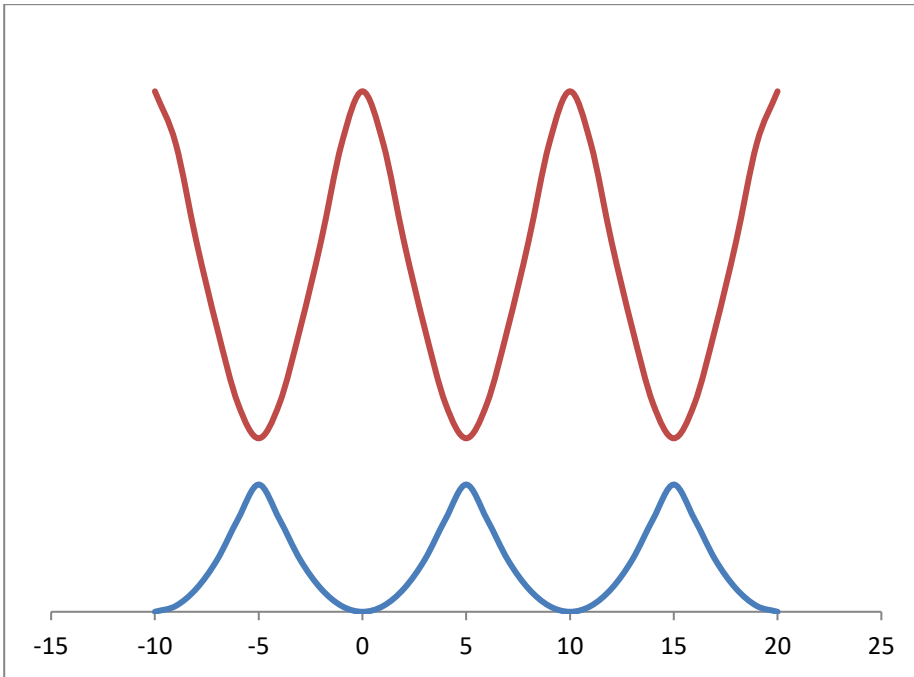structure)

If the external potential is weak V ≈ 0

$$\{[(k-K)^2 - E]C_{k-K} + \sum_{K'} V_{K'-K} C_{k-K'}\} = \{[(k-K)^2 - E]C_{k-K}\} = 0$$
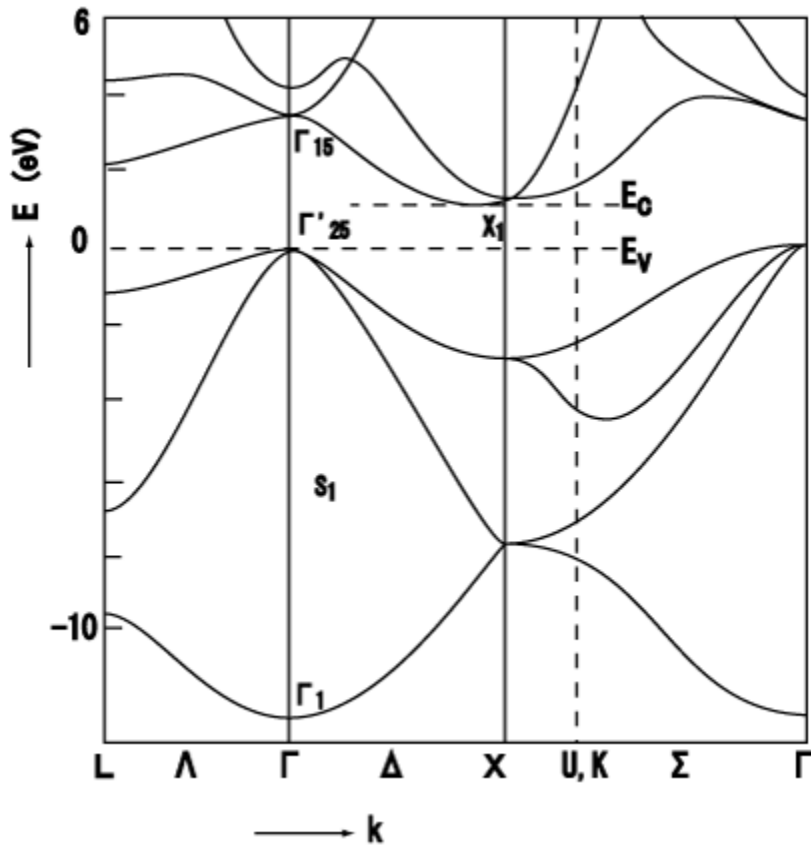
The energy is roughly parabolic in k. Note that the system is
periodic due to the unit cell k-vectors K.

There is always interactions in the system so the system will form **energy bands.** There is some times gaps between the bands.

This is one dimensional case. In general case the bands are 3-D.

Band structure of Silicon

The 3-D band structure is rather complex. We need to think how the electrons are distributed to the bands. Due to the spin there are two electrons in every band. The bands will be filled from below. The highest energy the electrons will have is the Fermi energy E_F. This is often the 0-point of the energy. Note that each k-points can have different number of k-points.

In silicon there is 4 (valence)electrons/atom, 1 s-electron and 3 p-ones. The lowest band is the s-band and the p-bands are higher. Often the p-band are degenerate (have the same energy). Compare the upper band in Γ, X, L and U points. In Si all the band are occupied with two electrons.

The band structure can also be measured.
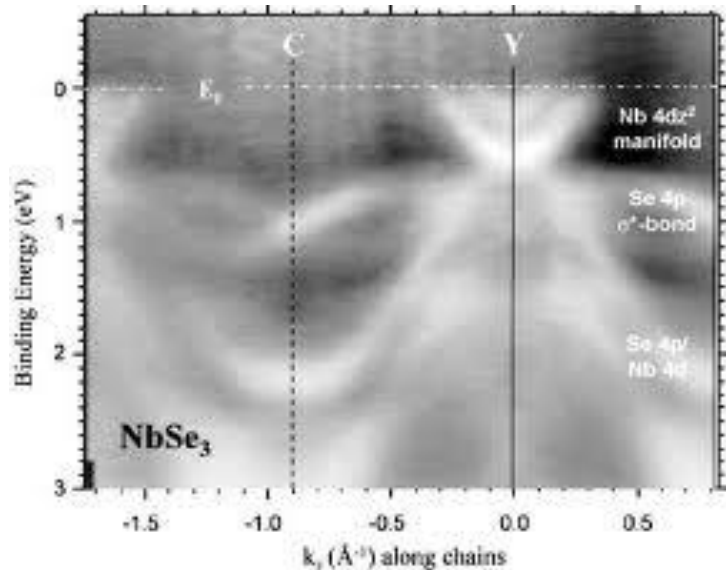
How the k-points should be choosen? There are several possibilities but the simple Monkhorst-Pack method where the k-points are equally spaced works well.

$$\vec{k} = \vec{b_1}\frac{n_1 + 1/2}{N_1} + \vec{b_2}\frac{n_2 + 1/2}{N_2} + \vec{b_3}\frac{n_3 + 1/2}{N_3}$$

If the computaional box is (roughly) cubic the N's are equal but is the box is elongated like Ax = 2Ay,Az then in x-direction it is enough to take half of the k-points (why?)

A rough rule is that there should be atleast 100 k-point/atom. Usually there is a lot of symmetry so not every point is needed to compute. There is always k=-k symmetry.

Computations

There are several periodic DFT based codes. In this course we use the GPAW programm.

```
from ase.structure import bulk
from gpaw import GPAW, FermiDirac
def groundstate(a, k):
    si = bulk('Si', 'diamond', a)
```

```
    si.calc = GPAW(kpts=(k, k, k),
                   xc='PBE',
                   gpts=(20, 20, 20),
                   occupations=FermiDirac(0.01),
                   txt='Si-PBE-%.3f-%d.txt' % (a, k))
    si.get_potential_energy()
    return si
```

Calculation for a lattice constant of 5.43 Å and a k-point sampling of 8*8*8 points:

```
si = groundstate(5.43, 8)
```

The band structure us rather easy to compute. The biggest mess is to
find the k-points. GPAW have ready routines to do such calculations.
We will look them in the excercises.


Bandstructure of Silicon
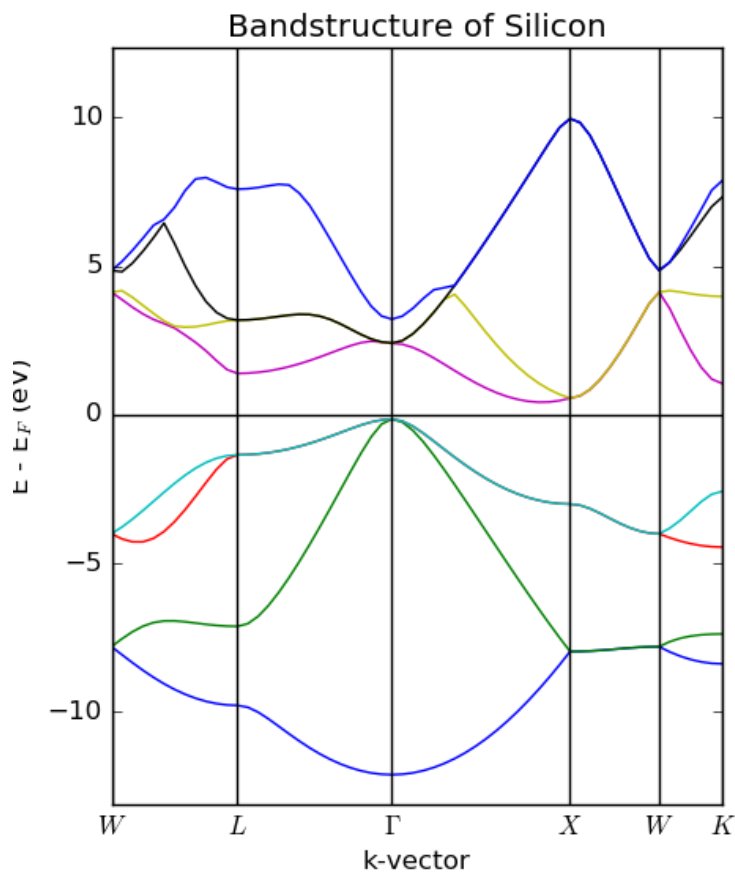
GPAW can use also hybrid functionals. The hybrid functionals usually gives better band structure but qualitatively the results are usually the same.

PBE and PBE0 bandstructure of Silicon
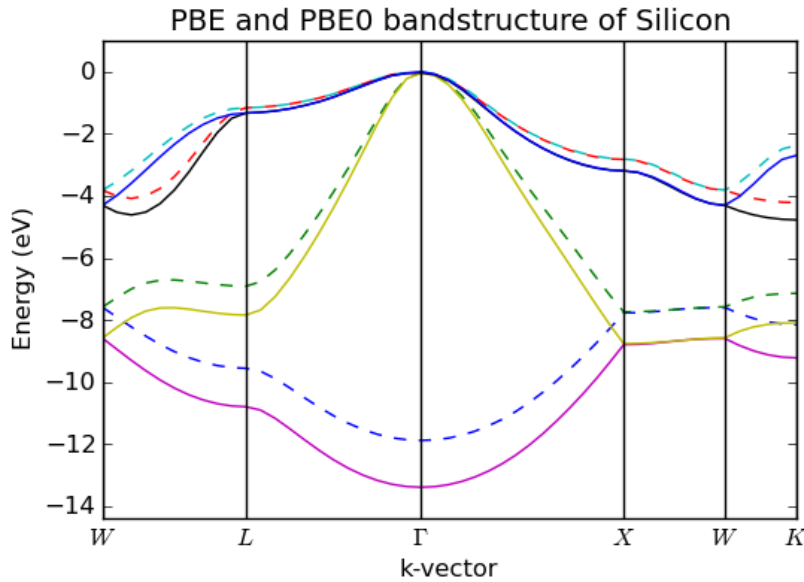
Si is a semiconductor but the band structure is also easy to compute for metals. Below is the band structure of Cu. Note that there is a band that crosses the Fermi energy = the system is a metal. The flat occupied bands comes from the d-electrons and parabolic band is the s-band. The s-band also crosses the Fermi energy. Cu have 11 valence electrons, 10 d-electrons and 1 s-electron. At Γ and L points all bands are occuped with 2 electrons! At W, X, and K points the s-band is empty. The d-bands are always occuped.

Bandstructure of Copper
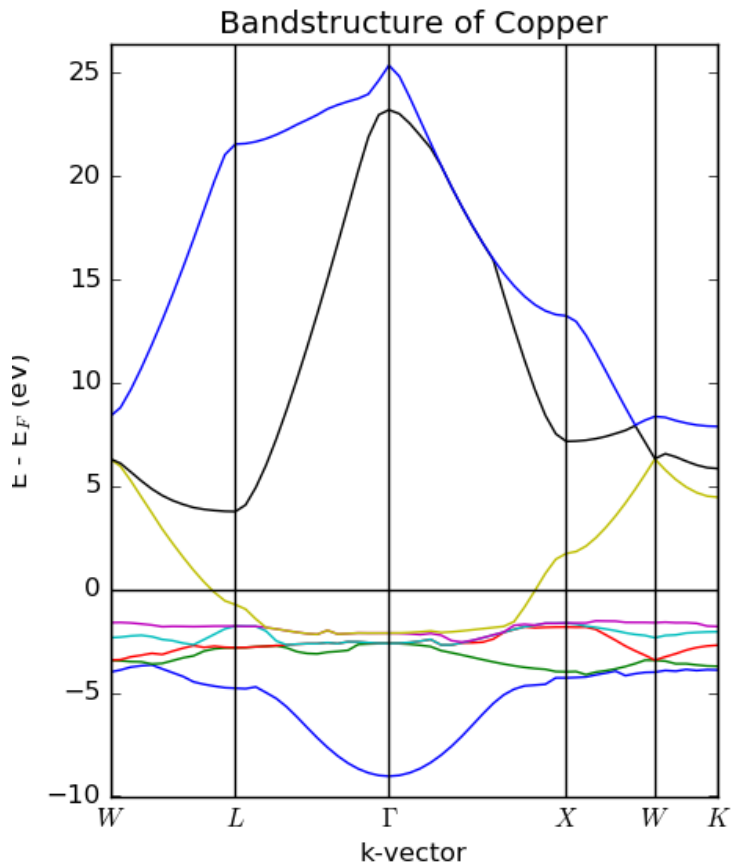
Last the insulators have large band gap. Below is the band structure of NaCl as an example. Note that the occupied bands are rather flat. The lowest is Cl's s-band and the next three are Cl's p-bands. There is no Na occupied band since the Na valence electron has moved to Cl.

Bandstructure of NaCl
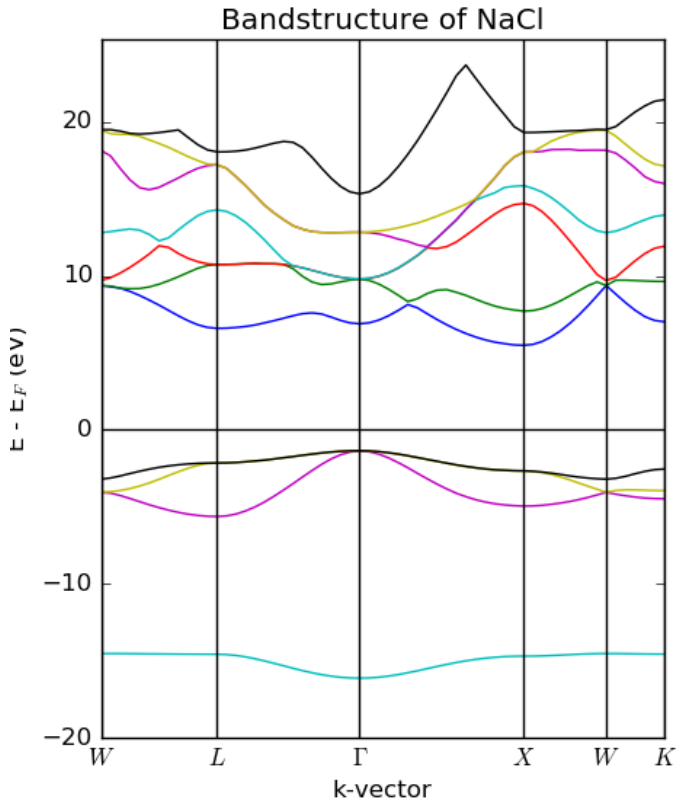
Basis functions

In principle, any basis function can be used in the periodic codes.
Historically the periodic codes used plane waves as basis, so the
wave functions were expressed with Fourier series (see equations
above)

$$\psi_k(r) = e^{ik.r} \sum_K^{Kmax} C_{k-K} e^{-iK.r} = e^{ik.r} u_k(r)$$

The plane waves is a good basis functions since they are periodic and
orthogonal to each other. As before the Kmax determine the accuracy
of the series. The orthogonality guarantees that always increasing
the Kmax the results will improve. The main problem with plane waves
is that a lot of them are needed if the wave functions have peaks.
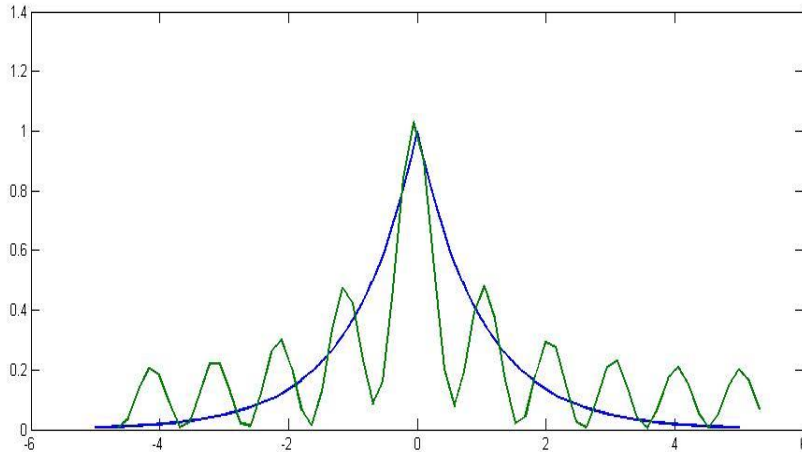This is the case near nucleas.

Figure: 1s function low resolution Fourier series.

The plane wave codes are disappearing. The GPAW used grids, CP2K uses Gaussians and plane waves. VASP uses plane waves. Gaussian (or any other local basis) can be written as:

$$\psi_k(r) = e^{ik.r} \sum_n C_{n,k}\, \zeta_n(r - R_I) = e^{ik.r} u_k(r)$$

Pseudopotentials

The Fourier series is inefficient when the function changes rapidly but this problem can be reduced if pseudopotentials are used. The pseudopotentials will replace the effect of the core electrons with an effective potential. Because the core electrons are very strongly bound to the nucleus and their wave functions are very localized they do not participate atoms chemical bonding, they can be leave out form the calculations. (They cannot be ignored since they e.g. screen the nuclear charge.) The pseudopotentials are unfortunately rather complex. They depend on the angular momentum, so s-type orbitals will see different potential than p-type.

The pseudopotentials will have several benefits: 1) They reduce the number of electrons needed to include to the system. Often it is enough to include only the valence electrons. 2) They smoothens the orbitals. This is very important for plane wave and grid basis.

The technical construction of pseudopotentials is rather complex. So we go through only the basic ideas. First, we define a cut-off radius after which the pseudopotential (and pseudo-orbital) match to the exact ones. Inside the cut-off a smooth pseudo-orbital is constructed. (Usually it is contain the same amount of charge as the

true orbital, so called norm-conserving pseudopotential.) From the smooth pseudo-orbital a pseudopotential is constructed.
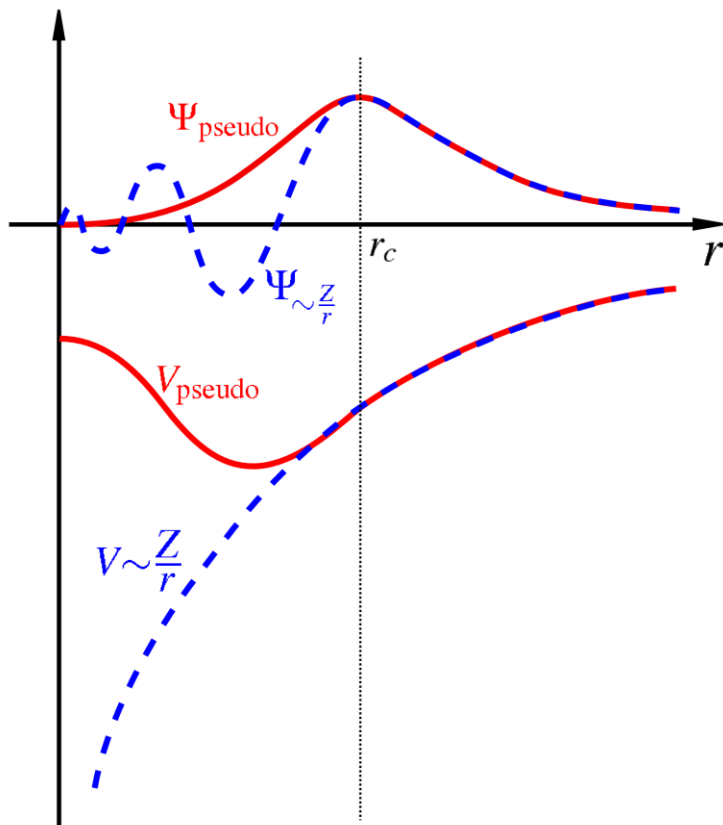
Near nucleus, the orbitals have oscillations that guarantee that they are orthogonal to the core orbitals. When this oscillation is removed we still need to keep the othogonality. This will force the pseudopotentials to be angular momentum dependent. Mathematically this will be done with projections

$$V_{NL}(r) = \sum_L V_L(r)|P_L\rangle\langle P_L|$$

here $|P_L\rangle$ is a projection function which have L-dependent symmetry(s-, p-, or d-symmetry), $P_L(r)$ can be written as $f_l(r)Y_{lm}(\theta,\varphi)$, and f(r)=0 when r > r_c.

$$\langle r|P_L\rangle\langle P_L|\psi\rangle = f_l(r)Y_{l,m}(\theta,\varphi) \int_0^{r_c} d^3r \; f_l(r)Y_{l,m}(\theta,\varphi)\psi(r)$$

These non-local pseudopotentials are computationally awkward but
modern codes, like GPAW, can handle them well. Also, the reliability
of the pseudopotentials is an important issue. There are challenging
cases like the alkali metals, which have only one valence electron.
Reasonable results can be obtained with one electron pseudopot but
also the lower core can be included to the pseudopot. This of course
increase the computational cost but if the system contain only few
alkali metals the more accurate pseudopot is better. Often for early
transition metals the lower core pseudopot can be better.

For plane waves and grid basis the smoothness of the pseudopot is
important. The norm-conserving pseudopotentials can be optimized for
the smoothness but they are not very smooth (Troulier-Martins
pseudopotentials). David Vanderbilt introduced so called 'ultra-soft'
pseudopotentials which are not norm-conserving. The missing charge
will be corrected with and extra term in the density.

$$\rho(r) = \sum_n |\psi_n(r)|^2 + \sum_{n,L} Q_L(r) \langle \psi_n | P_L \rangle \langle P_L | \psi_n \rangle$$

The Vanderbilt pseudopotentials has been used quite a lot, but now a
similar but more general PAW (Projected-Augmented-Wave) is much more
common. The GPAW program uses the PAW pseudopot. The PAW methods
allows also computation of all electron density. Also the PAW library
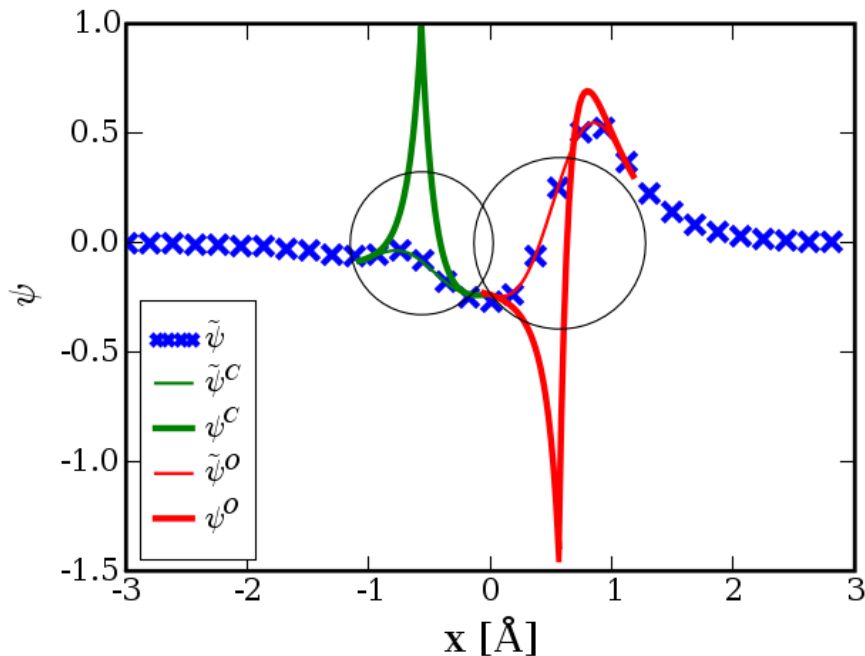covers almost all periodic table and the pseudopotentials are mostly
reliable.

Fig: CO molecules orbital. The blue crosses (and thin lines) are the smooth orbitals whereas the thick lines are the corrections to the orbitals.

The hard pseudopotentials are more convenient than ultra-soft or PAW pseudopotential is the softness is not required. This is the case if gauss functions are used for basis. Orca has some pseudopotentials and CP2K which uses mixed plane wave Gaussian basis uses it "own" GHT (Gödeker-Hutter-Teter) pseudopotentials.

Summary: the pseudopotentials are almost automatic and the user do not need to worry much of them.