# Density functional theory in solid state physics
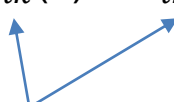
Lecture 9

Organization

- New discussion forum on StudOn for questions about the lecture

- Exam: I checked it with examination committee, examination through small projects is possible.

- Small project: one day to do calculations and write a short description of
  - theoretical background (method and approximations)
  - approach (convergence tests, choice of XC functional)
  - results (geometry, plots of bandstructures, or similar).

- Tell me if you don't like

- One way or another: Exam on September 14th.

- Exam application: I messed up, application over mein campus (not yet?) possible

- Tell me if you want to participate and I will enter everyone in mein campus by hand later

- Electronic groundstate: solution of Kohn-Sham Equation for fixed set of atomic positions and lattice parameters

- Combination of efficiency and accuracy through cutoff energy of planewave expansion, pseudopotentials and uniform *k*-point sampling of Brillouin zone.

- This gives us access to
    - Electron density
    - The electronic groundstate energy E_{KS}
    - The Fermi energy of the system
    - Single-particle orbitals and eigenvalues („bands")
    - The potentials acting on the electrons

- Global groundstate: Find atomic positions+lattice vectors, for which the total energy $E_{tot} = E_{KS} + E_{ion-ion}$ is minimized

- Accuracy is ensured through minimization of residual interatomic forces and cell stresses

- Iterative procedure:

Electronic structure from DFT
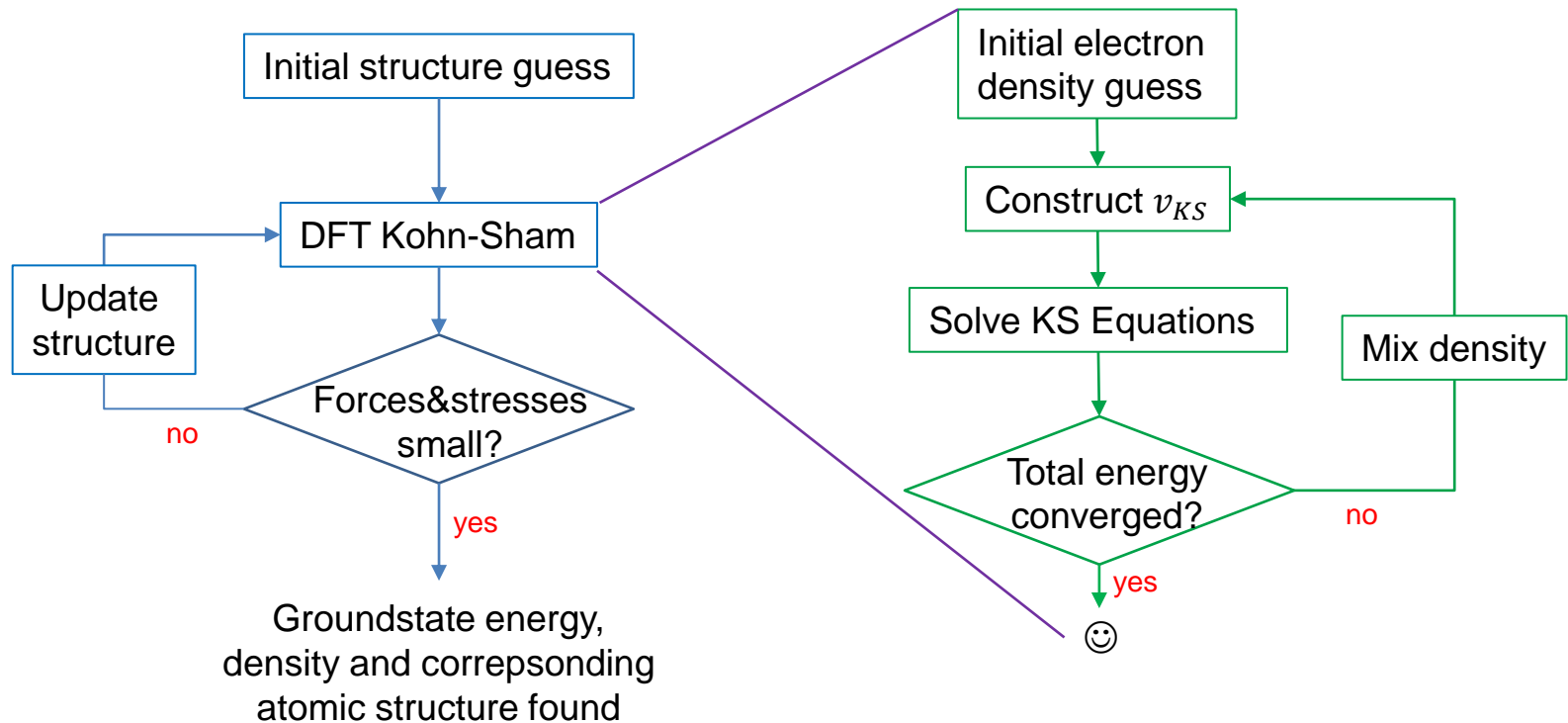
- Essentially all properties of interest are determined by the electronic structure of a system

- Finding groundstate through SCF procedure already gives us some insight into electronic structure without doing something special

$$\left(-\frac{1}{2}\nabla^2 + v(\vec{r}) + v_H(\vec{r}) + v_{XC}(\vec{r})\right)\varphi_{ik}(\vec{r}) = \varepsilon_{ik}\varphi_{ik}(\vec{r})$$

Single-particle orbitals and band energies on uniformd grid

- In principle can calculate density of states $\rho(E)$ from ε_{ik} obtained from SCF procedure

$$\rho(E) = \frac{1}{V_{BZ}}\sum_i \int_{BZ} \delta(\varepsilon_{ik} - E)dk \approx \frac{1}{N_k}\sum_{i,k} w_k \delta(\varepsilon_{ik} - E)$$
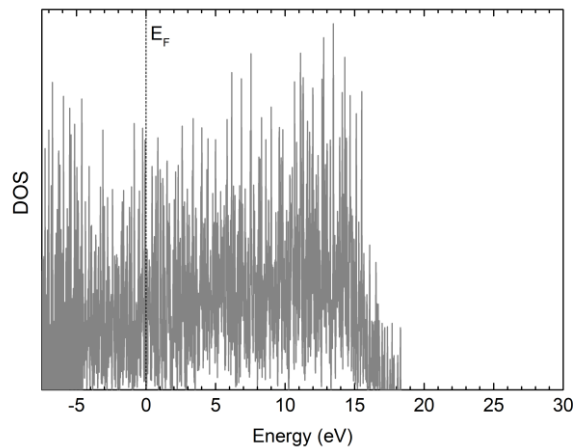
Weight of k-point k

Density-of-states from SCF

- Typically, obtain DOS through broadening of individual contributions from ε_{ik}
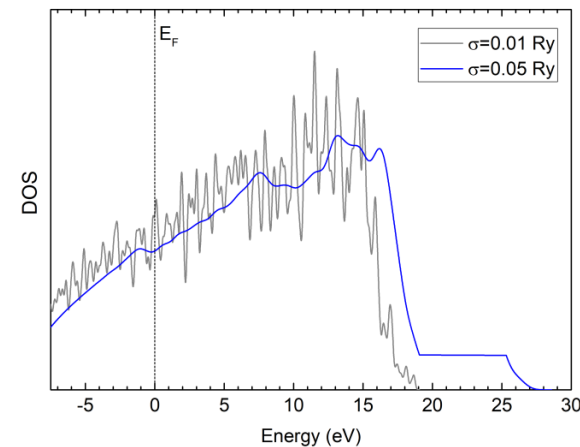
$$\rho(E) = \frac{1}{V_{BZ}} \sum_i \int_{BZ} \delta(\varepsilon_{ik} - E)dk \approx \frac{1}{N_k} \sum_{i,k} w_k \, g(\varepsilon_{ik} - E)$$

$$\text{peak shape function, } g(\varepsilon) = \begin{cases} A exp(-\frac{\varepsilon^2}{2\sigma}) & \text{(gaussian)} \\ A\frac{1}{1+\left(\frac{2\varepsilon}{\sigma}\right)^2} & \text{(lorentzian)} \end{cases}$$

- Example: Metallic Al, 14x14x14 k-point sampling

Introduce smearing

- DOS from peak broadening techniques depends on choice of smearing

- Peak broadening can be somewhat used to simulate temperature or scattering effects that affect experimentally measured DOS

- Alternative approach: We can use a better approximation to the integral in

$$\rho(E) = \frac{1}{V_{BZ}} \int_{BZ} \delta(\varepsilon_{ik} - E) dk$$

- Divide the space between discrete points into tetrahedra and use linear interpolation within the tetrahedra

Phys. Rev. B 89, 094515 (2014)

This can be performed analytically

$$\rightarrow \rho(E) = \sum_{j}^{N_{tetra}} \int_{Tetra\ j} \delta(\varepsilon_{ik} - E) dk$$

DOS from tetrahedra

- Interpolation allows for high-quality DOS without need for artificial peak broadening or extremely dense k-point samplings

- Example: Metallic Al, 14x14x14 k-point sampling
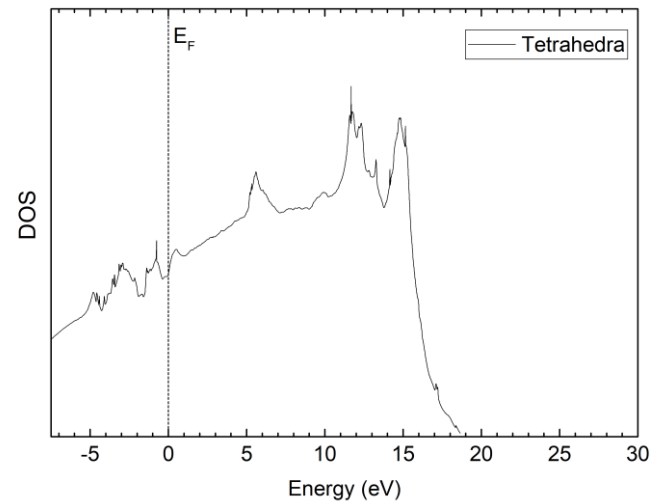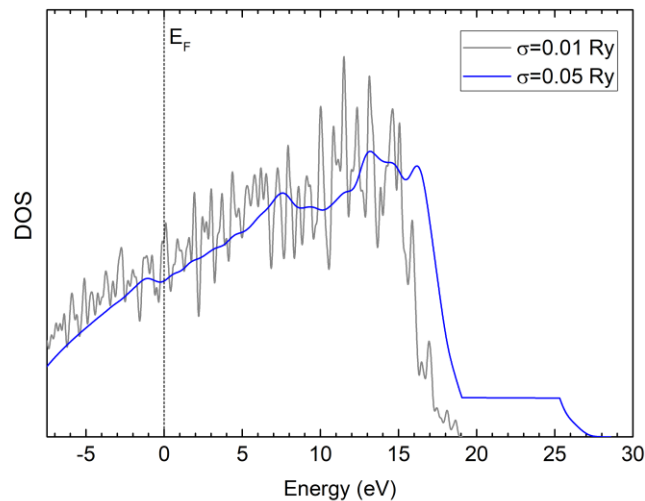
- Also: Same method can be used instead of occupation smearing to accelerate k-point sampling convergence in metals.

- Typically, faster k-point sampling convergence from tetrahedron method than from smearing (but smearing is easier to handle)

- Little disadvantage: Linear interpolation introduces systematic errors for purely concave or convex functions of k.

- Several correction schemes available:

  - <u>Blöchl</u>: Add correction term $\Delta I \equiv I^{quad} - I^{lin} \, \alpha \int_{\varepsilon_{ik} \leq E_F} \frac{\partial^2 A}{\partial k^2} dk$ to integral I to include information about curvature of to-be-integrated function A.   *Phys. Rev. B 49, 16223 (1994)*

  - <u>Optiminized tetrahedron method</u>: ‚*leveling* instead of *interpolating*‘, construct polynomial that approximates dispersion within tetrahedron, fit a linear function to the polynomial   *Phys. Rev. B 89, 094515 (2014)*


Linear interpolation
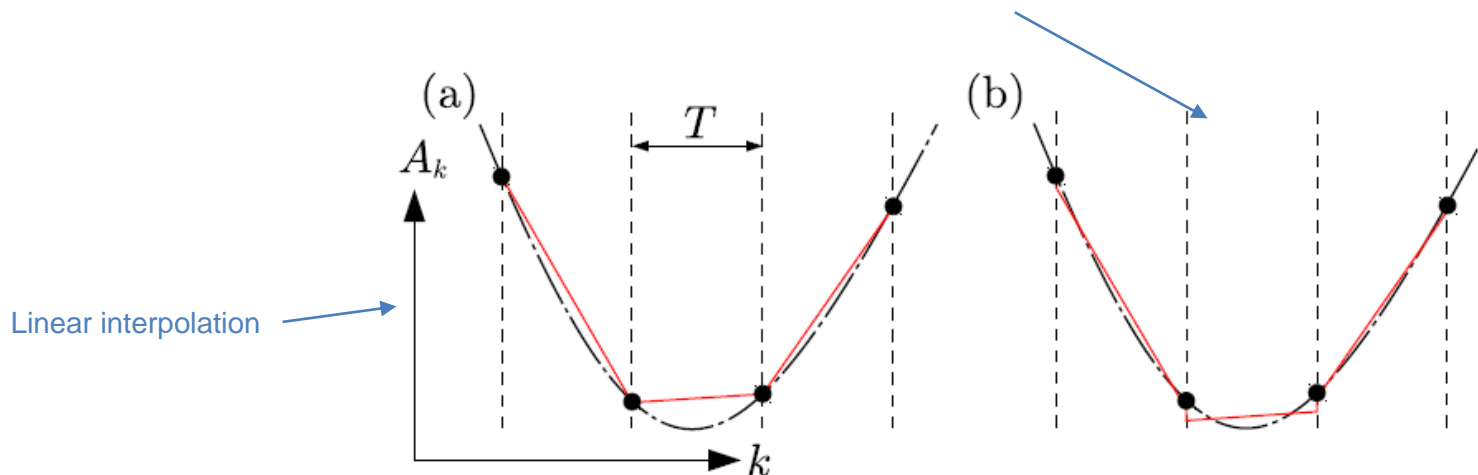
Fermi surface from DFT

- Also have access to k-resolved properties: e.g. Fermi surface

- Integral concept for the understanding of the electronic properties of metals, e.g. electronic transport

- From DFT, extract k-points for which an ε_{ik} lies within a certain energy window around the Fermi energy

- Example: Fermi surface of Cu

DFT
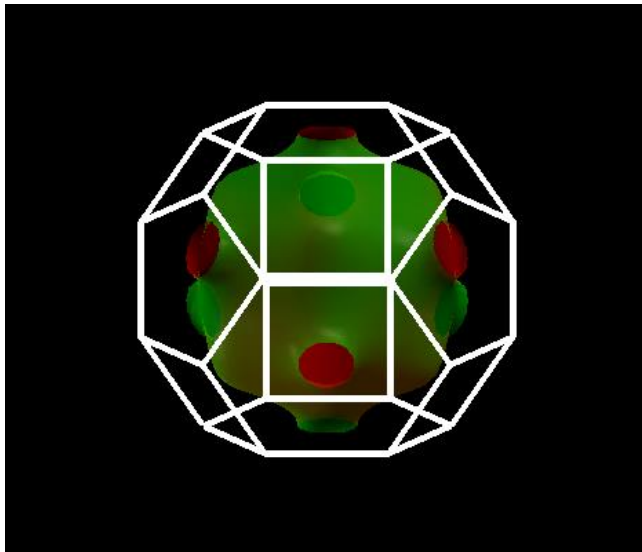
Experiment (2D-ACAR)
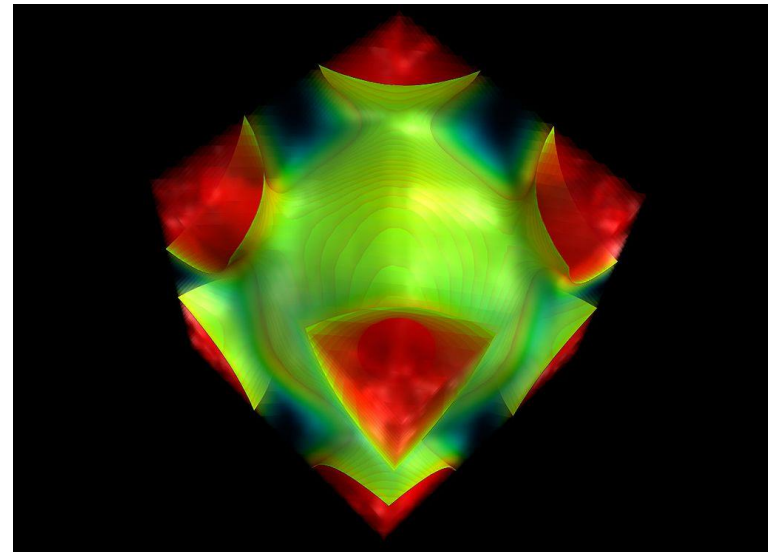
*J. Phys.: Conference Series. 443, 012092 (2013)*

- Also possible to derive information about the *character* of the states that contribute within a certain energy window

- Project wavefunctions of the electronic states onto atomic orbitals $\phi_{jm}(r)$

$$w_{ik}^{jm} = \langle \phi_{jm} | \varphi_{ik} \rangle$$

- <u>Partial/Projected density of states (PDOS)</u> corresponding to atomic orbital *j* of species *m*:

$$\rho_{jm}^{PDOS}(E) = \frac{1}{V_{BZ}} \sum_i \int_{BZ} w_{ik}^{jm} \delta(\varepsilon_{ik} - E) dk$$

- Example: bulk BN
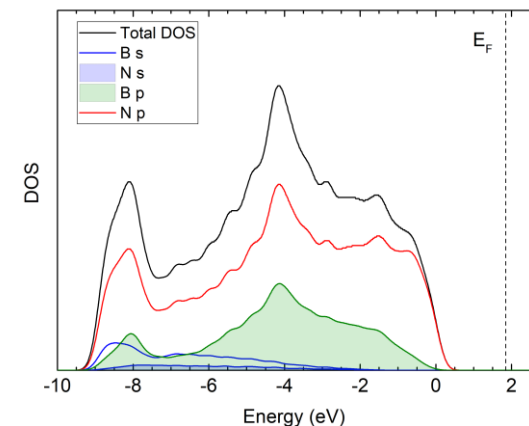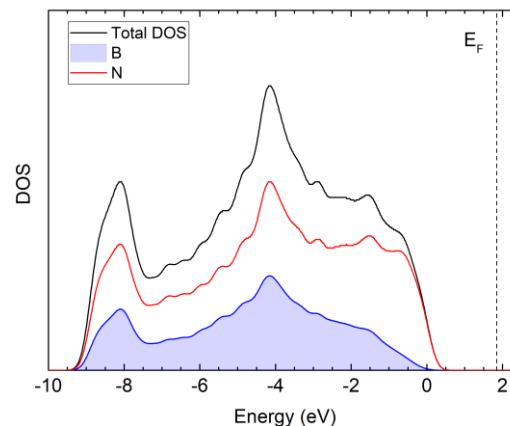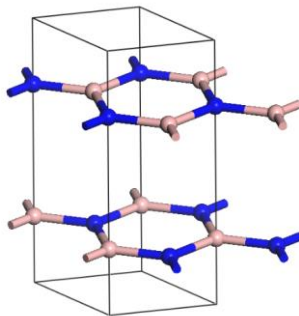
DOS from SCF results is inconvenient

- So far: use single-particle energies from SCF procedure for DOS calculations

- But: k-grid needed to get nice DOS is often denser than needed for converged ground state energy/density, especially for semiconductors or insulators
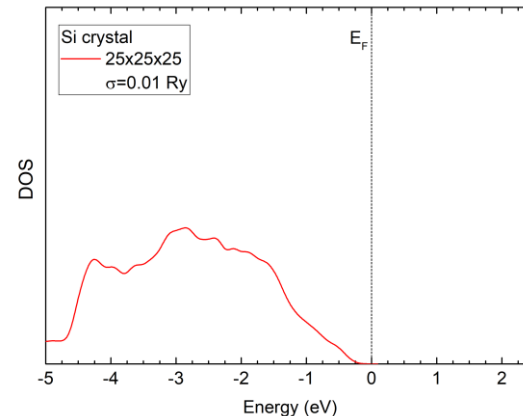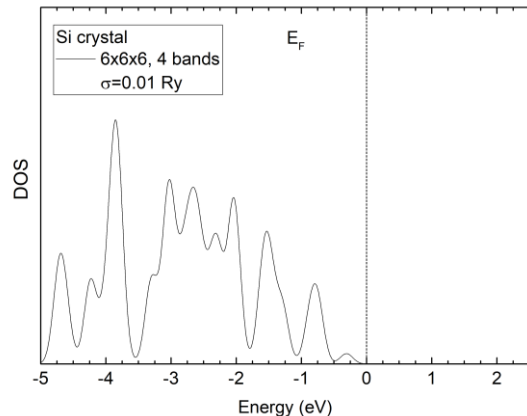
→ increased effort for doing SCF without meaninginful gain in groundstate accuracy

- Similarly: unoccupied bands not needed for the SCF procedure in semiconductors or insulators

→ no unoccupied DOS or increased effort for doing SCF

Non-selfconsistent calculations

- But: At the same time: potentials in KS-Hamiltonian is not *k*- or band index dependent

$$H_{KS} = -\frac{1}{2}\nabla^2 + v(r) + v_H[n(r)] + v_{XC}[n(r)]$$

- For DOS, we are only interested in single-particle energies (and maybe orbitals)

- Idea: If groundstate density known, we can solve the KS Eq. *non-selfconsistently* for a set of k-points of interest, keeping the electron density fixed

  → „band interpolation"

```
&control
    calculation = 'nscf'
    prefix='Cu',
    pseudo_dir = './',
    outdir='TMP_DIR/'
/
&system
    ibrav=0, nat= 1, ntyp= 1,ecutwfc =90.0, input_dft = 'pbesol',
    occupations='smearing', smearing='cold', degauss=0.01,
    nbnd=50
/
&electrons
    conv_thr =  1.0d-10
/
ATOMIC_SPECIES
 Cu  63.55  Cu.nc.UPF
ATOMIC_POSITIONS (crystal)
Cu      0.000000000   0.000000000   0.000000000
K_POINTS {automatic}
25 25 25 0 0 0
CELL_PARAMETERS (angstrom)
 -0.000000000   1.793927308   1.793927308
  1.793927308  -0.000000000   1.793927308
  1.793927308   1.793927308  -0.000000000
```

NSCF calculation scheme

Optimize geometry

SCF calculation
with sufficiently converged
parameters

Ground state
density $n(r)$

Choose dense k-point
sampling and states within
energy range of interest

Solve system

$$H_{KS}[n(r)]\varphi_{ik}(\vec{r}) = \varepsilon_{ik}\varphi_{ik}(\vec{r})$$

for each k-point of
interest, while keeping
$n(r)$ fixed

Do postprocessing etc.

Cost $\propto N_k$, similar to
one step with dense
k−point sampling and
number of bands

Si crystal
— 6x6x6, 4 bands
σ=0.01 Ry
DOS
E_F
-5 -4 -3 -2 -1 0 1 2 3 4 5
Energy (eV)

Si crystal
— 25x25x25, 30 bands
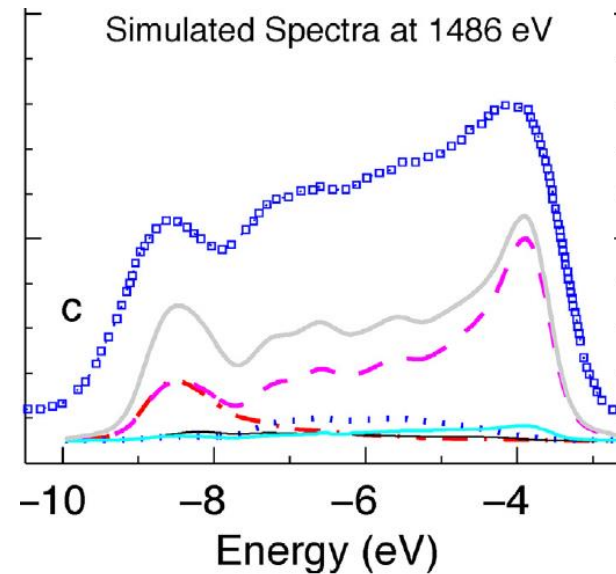σ=0.01 Ry
DOS
E_F
-5 -4 -3 -2 -1 0 1 2 3 4 5
Energy (eV)

- DFT usually gives a quite good description of the electronic dispersion and the DOS

- Example: In_2O_3 DFT vs XPS experiment
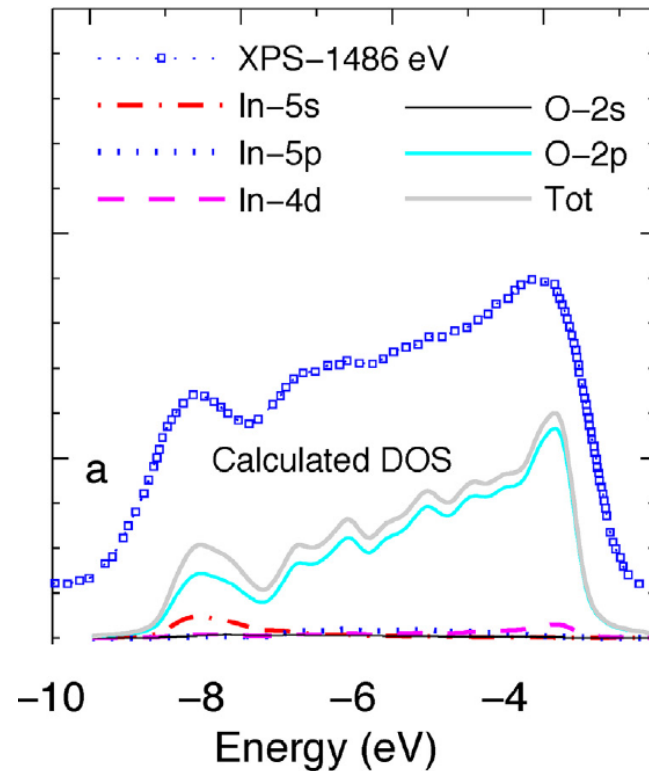
(can also improve descirption by considering energy-dependent scattering cross-sections)

*Journal of Electron Spectroscopy
and Related Phenomena 230, 1 (2019)*

- DOS plots are relatively straight-forward to get directly from SCF procedure, even if not very well resolved or convenient

- More difficult: electronic band structures along high-symmetry paths
  (and usually interested in bandstructures instead of DOS)

- Would need to extract points that lie on the high symmetry directions from uniform grid used in SCF calculations

- In the example on the left: a sampling of ~28x28 k-points in the depicted plane needed for 15 points along each on the path segments

- Easier: non-selfconsistent calculation
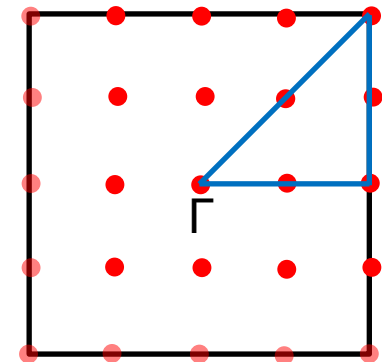
```
&control
    calculation = 'bands'
    restart_mode='from_scratch',
    prefix='Si',
    pseudo_dir = './',
    outdir='TMP_DIR/',
/
&system
    ibrav=0, nat= 2, ntyp= 1,
    ecutwfc =50.0, input_dft = 'pbe', nbnd=20
/
&electrons
    conv_thr =  1.0d-8
/
ATOMIC_SPECIES
 Si  14.0  Si.UPF
ATOMIC_POSITIONS (crystal)
Si       0.00 0.00 0.00
Si       0.25 0.25 0.25
K_POINTS (crystal_b)
    3
0.500  0.00  0.500  15
0.000  0.00  0.000  15
0.500  0.00  0.000   1
CELL_PARAMETERS (angstrom)
  -0.000000000   2.737747197   2.737747197
   2.737747197   2.737747197  -0.000000000
   2.737747197  -0.000000000   2.737747197
```

E_{gap}=0.61 eV

Energy (eV)

X (1/2,0,1/2)   Γ (0,0,0)   M (1/2,0,0)

g_2

g_3
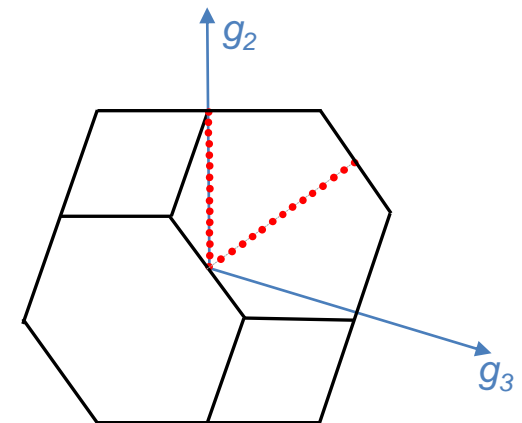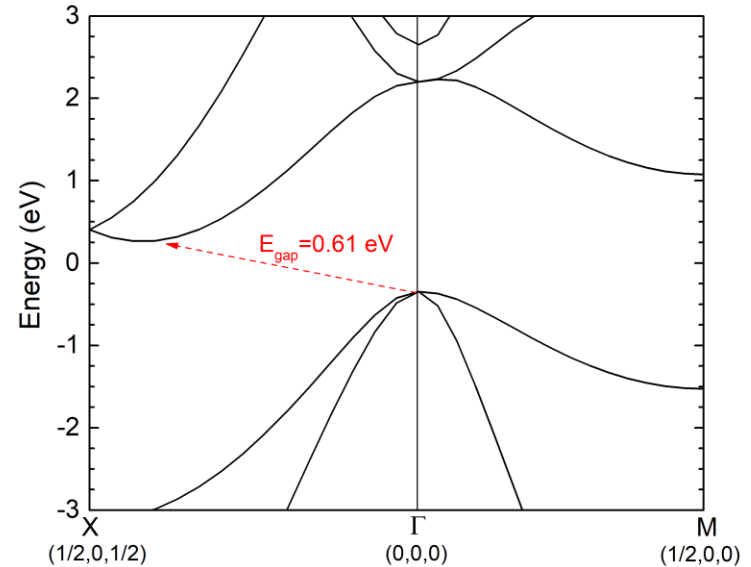
- Careful: technically mathematical artifacts, band gap underestimation from local XC functionals

- Rule-of-thumb: LDAs and GGAs underestimate E_{gap} by 50-100%

- Example: experimental Si band gap: E_{gap}=1.17 eV

- Electronic dispersion (usually) is qualitatively correct

- Access to bandstructure-related properties

  - Fermi velocity
    extract slope of energy dispersion near
    high-symmetry point of interest

  - Electron and hole effective masses
    fit parabola into conduction and
    valence band valleys
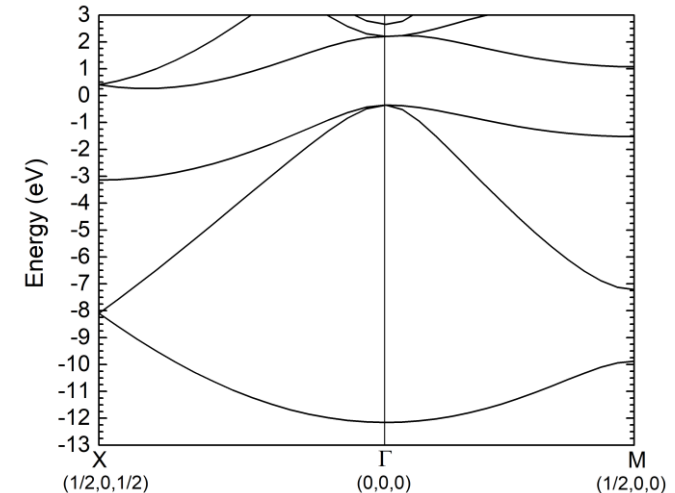
- Usually good correspondence to experiments, but DFT band widths usually ‚compressed'

- Example: Si valence band width: ~15 eV

- DFT bandstructures are often used for interpretation of experimental observations

- Similar to DOS: can also decompose bands into contributions from atomic orbitals („fat bands")

https://christoph-wolf.at/2018/07/24/from-fatbands-to-wannier-functions-of-silver/
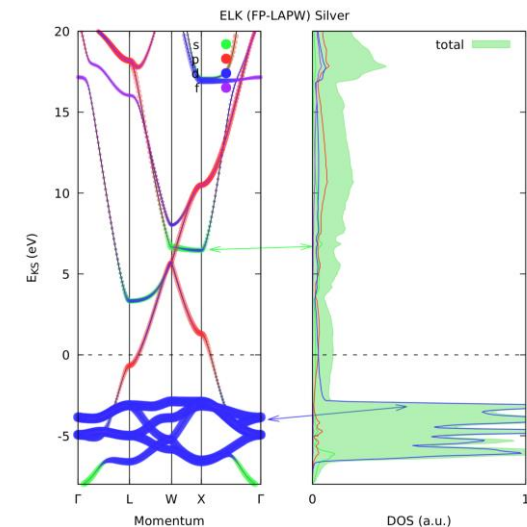
- Arguments before valid for local exchange-correlation functionals.

- Better agreement with experiments if we use hybrid functionals

- Several hybrid functionals implemented in QE: HSE03, HSE06, PBE0…
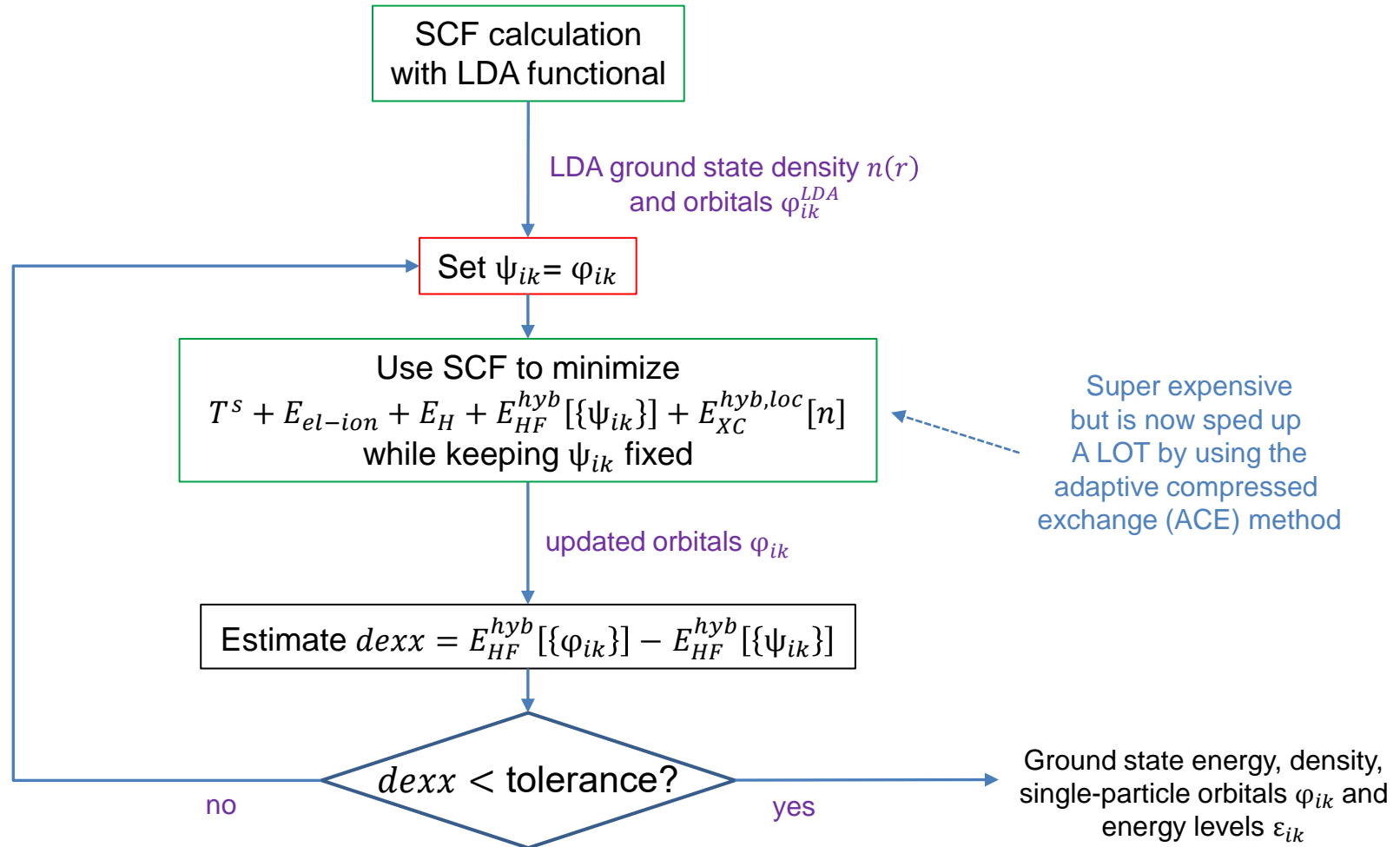
- For SCF calculations:

$$\frac{\delta}{\delta c_{ik}^*(\vec{G}')}\left(T^s + E_{el-ion} + E_H + E_{HF}^{hyb}[\{c_{ik}\}] + E_{XC}^{hyb,loc}[n]\right) = 0$$

$$E_{HF}^{hyb} = -\frac{2\pi}{V}\sum_{i,j,k,q}\sum_{\vec{G}} g(\vec{q},\omega)\frac{\left|C_{ikjq}(\vec{G})\right|^2}{\left|\vec{q}-\vec{k}+\vec{G}\right|^2}$$

with $C_{ikjq}(\vec{G}) = \sum_{\vec{G}'} c_{ik}^*(\vec{G}')c_{jq}(\vec{G}+\vec{G}')$

- Evaluation of E_{HF}^{hyb} requires summation over uniform grid of „q"-points in BZ.
  → makes hybrid functionals expensive

- For non-selfconsistent calculations, we need eigenvalue contribution $\frac{dE_{HF}^{hyb}}{dc_{ik}^*(\vec{G}')}$

- NSCF would thus require knowledge of occupied wavefunctions on q-point grid, in addition to electron density → not implemented (and difficult to do)

Hybrid functional calculation scheme

- How to do self-consistent hybrid functional calculations in Quantum Espresso?

SCF calculation
with LDA functional

LDA ground state density $n(r)$
and orbitals φ_{ik}^{LDA}

Set $\psi_{ik} = \varphi_{ik}$

Use SCF to minimize
$$T^s + E_{el-ion} + E_H + E_{HF}^{hyb}[\{\psi_{ik}\}] + E_{XC}^{hyb,loc}[n]$$
while keeping ψ_{ik} fixed

Super expensive
but is now sped up
A LOT by using the
adaptive compressed
exchange (ACE) method

updated orbitals φ_{ik}

Estimate $dexx = E_{HF}^{hyb}[\{\varphi_{ik}\}] - E_{HF}^{hyb}[\{\psi_{ik}\}]$

$dexx <$ tolerance?

no

yes

Ground state energy, density,
single-particle orbitals φ_{ik} and
energy levels ε_{ik}

- Why bother? This method is faster than if we do a SCF procedure with $E_{HF}^{hyb}[\{\varphi_{ik}\}]$

- How to get bandstructures and DOS from hybrid functionals?

- Goal: interpolate bandstructure through transformation of H into k-independent representation and back onto k-point on bandstructure path or dense grid

- One way to do this: Wannier functions w_n

$$\varphi_{nk}(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} w_n(\vec{r} - \vec{R}) \quad \rightarrow \quad w_{nR}(\vec{r}) = w_n(\vec{r} - \vec{R}) = \int_{BZ} e^{-i\vec{k}\cdot\vec{R}} \varphi_{nk}(\vec{r}) dk$$
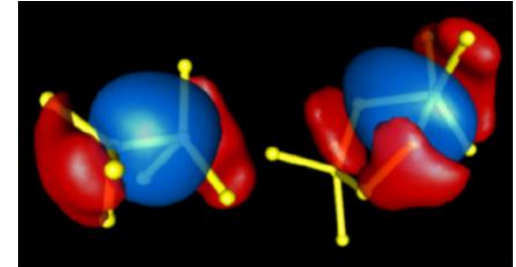
Similar to Fourier transformation

- Wannier function w_n contains the entire physical info of band n

Phys. Rev. Mod 84, 1419 (2012)

Wannier interpolation
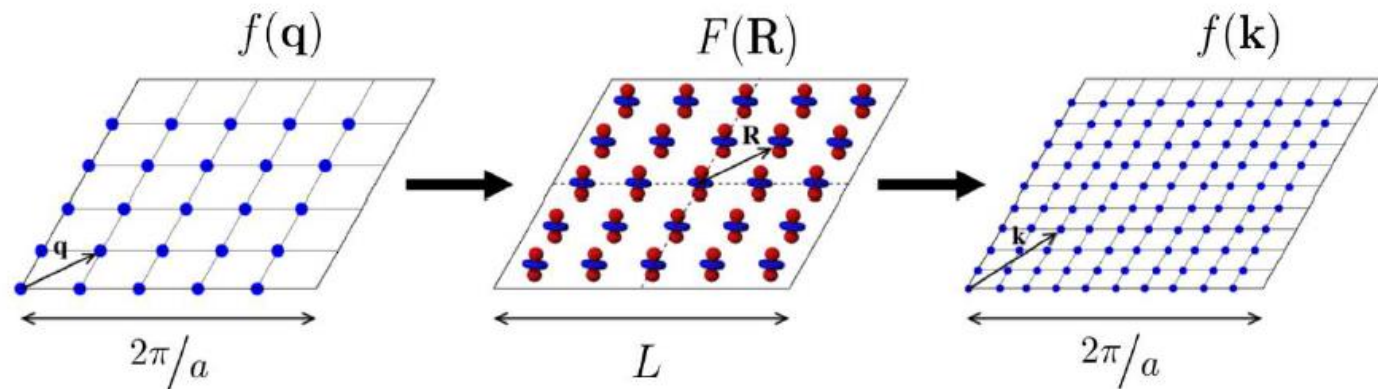
- Maximally localized wannier functions (MLWF): Wannier functions are as spatially localized as possible

- MLWF functions decay exponentially in insulators

Phys. Rev. Mod 84, 1419 (2012)

- We can recombine a set of *M* Bloch wavefunctions to form N functions $\varphi_{nk}^{(W)}$ such that

Unitary transformation

$$\varphi_{nk}^{(W)}(\vec{r}) = \sum_{m}^{M} U_{mn}^{(k)} \varphi_{mk}(\vec{r}) \qquad \rightarrow \qquad w_{nR}^{MLWF}(\vec{r}) = \int_{BZ} e^{-i\vec{k}\cdot\vec{R}} \varphi_{nk}^{(W)}(\vec{r}) dk$$

- $\varphi_{nk}^{(W)}$ are not necessarily eigenstates of the Kohn-Sham Hamiltonian $H(\vec{k})$

- We can use these to construct a *NxN* Hamiltonian matrix at each explicitly calculated $\vec{k}$:

$$H_{nm}^{(W)}(\vec{k}) = \left\langle \varphi_{nk}^{(W)} \middle| H(\vec{k}) \middle| \varphi_{mk}^{(W)} \right\rangle \quad \left(= \sum_{l} U_{ml}^{(k)} U_{nl}^{(k)} \varepsilon_{lk} \right)$$
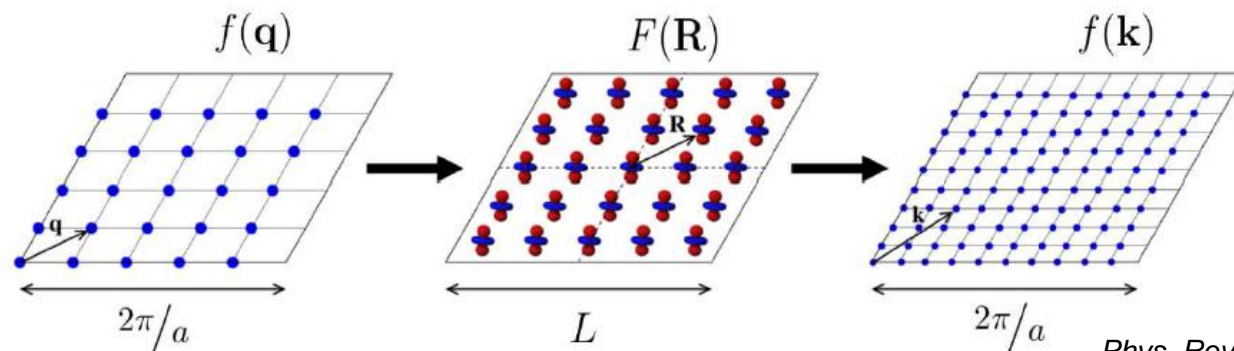
Wannier interpolation

- Now transform $H_{nm}^{(W)}(\vec{k})$ into Wannier basis

$$H_{nm,R}^{(MLWF)} = \langle w_{n0}^{MLWF}|H|w_{mR}^{MLWF}\rangle = \int_{BZ} e^{-i\vec{k}\cdot\vec{R}} H_{nm}^{(W)}(\vec{k})dk$$

- We can use this transformed Hamiltonian to interpolate band energies (and orbitals) at a k-point k', which we did not explicitly calculate from (g)KS procedure

$$H_{nm}^{(W)}(\vec{k}') = \sum_{\vec{R}} e^{i\vec{k}'\cdot\vec{R}} H_{nm,R}^{(MLWF)}$$

- Need band energies and orbitals on a full (i.e. non-reduced) uniform k-point grid as input (Exercise 1 of Exercise sheet 3)

Phys. Rev. Mod 84, 1419 (2012)

- Wannier interpolation is a powerfol tool

- Wannier functions in wide use in solid state physics simulations nowadays

  - Electron-phonon coupling

  - Transport properties

  - Modern theory of polarization, Berry phases

  - Molecular dynamics

  - Etc.