Periodicity in real space and reciprocal space

- Example: honeycomb lattice

**Real space**

Lattice vectors $a_1, a_2, a_3$

Unit cell volume $\Omega$

Crystallographic basis consisting of two atoms

**Reciprocal (wave-vector) space**

Reciprocal-lattice vectors $b_1, b_2, b_3$, each perpendicular to a pair of lattice vectors

$$\vec{b}_i = \frac{2\pi}{\Omega} (\vec{a}_j \times \vec{a}_k)$$
From molecules to solids

- Electronic bands as limit of bonding and anti-bonding combinations of atomic orbitals

R. Hoffmann,

Bloch's theorem

- In an infinite periodic solid, the solutions of the Kohn-Sham equations must behave like
  \[ \psi_{j,k}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}} \psi_{j,k}(\mathbf{r}) \]
  under translations by a lattice vector
  \[ \mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \]
- Consequently, we can write
  \[ \psi_{j,k}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{j,k}(\mathbf{r}) \]
  with a lattice-periodic part \( u_{j,k}(\mathbf{r}) \).
- The index \( k \) is a vector in reciprocal space taken from the first Brillouin zone.
- The number of different \( k \)-indices equals the number of unit cells in a crystal.
Brillouin zones

- in two dimensions
  a) for a square lattice
  b) for a hexagonal lattice

- in three dimensions
  for a face-centered cubic (fcc) lattice

Band structure - schematic

The orbital energies are smooth functions of $k$

Example: chain of Pt-R$_4$ complexes

Brillouin zone sampling

- Charge densities (and other quantities) are represented by Brillouin-zone integrals

\[ n(r) = \sum_{j} \int_{\Omega_{BZ}} |\psi_{j,k}(r)|^2 \frac{d^3k}{\Omega_{BZ}} \]

- Integrand smooth (for non-metals): replace integral by sum over sampling points

\[ n(r) \approx \sum_{j} \sum_{n=1}^{\text{occ}} N_{kpt} w_n |\psi_{j,k_n}(r)|^2 \]


Fermi surfaces

In a metal, some (at least one) energy bands are only partially occupied by electrons. The Fermi energy \( \varepsilon_F \) defines the highest occupied state(s). Plotting the relation

\[ \varepsilon_j(k) = \varepsilon_F \]

in reciprocal space yields the Fermi surface(s).

The grid used in \( k \)-space must be sufficiently fine to accurately sample the Fermi surface.
Spin-resolved band structure for fcc iron

GW method (full)
LSDA (dashed)

Correct description of magnet properties requires dense k-space sampling!


---

How to treat metals in DFT

- Fermi distribution function $f_F$ enters Brillouin zone integral:

\[
    n(r) = \sum_j \int_{\Omega_{BZ}} f_F \left( \frac{\varepsilon_{j,k} - \varepsilon_F}{k_B T_{el}} \right) \left| \psi_{j,k}(r) \right|^2 \frac{d^3 k}{\Omega_{BZ}}
\]

- Simplest method: “smearing” of the Fermi function
  - artificially increased $k_B T^{el} \sim 0.2$ eV
  - Extrapolation of the total energy to $T^{el} = 0$

- Alternatives:

- Tetrahedron method
  - Fermi surface is approximated by a polyhedron consisting of small tetrahedra in each ‘plaquette’ [P. E. Blöchl et al., Phys. Rev. B 49, 16223 (1994)]
Density of states (DOS)

- Information about the single-particle contribution to the total energy

\[ \rho(\varepsilon) = \sum_i \int_{\Omega_{BZ}} \delta(\varepsilon - \varepsilon_{i,k}) \frac{d^3k}{\Omega_{BZ}} \approx \sum_i \sum_{n=1}^{N_{kpt}} \omega_n \delta(\varepsilon - \varepsilon_{i,k_n}) \]

- Projected density of states (PDOS)

\[ \rho_{I,l}(\varepsilon) = \sum_i \sum_{n=1}^{N_{kpt}} \omega_n \left( \int d^3r \varphi_{I,l}^{\ast}(r) \psi_{i,k_n}(r) \right) \delta(\varepsilon - \varepsilon_{i,k_n}) \]

\( \varphi_{I,l}(r) \) is the atomic orbital with angular momentum \( l \) at atom \( I \)

Recovery of the chemical interpretation in terms of orbitals

Qualitative analysis tool; ambiguities must be resolved by truncating the \( r \)-integral or by Löwdin orthogonalization of the \( \varphi_{I,l}(r) \)
Ferromagnetic half-metal: \( \text{Co}_2\text{MnSi} \)

Surfaces: geometric and electronic structure
atomic structure: relaxation and reconstruction

relaxation
- change of interlayer distances near the surface
- response of the surface atoms to an adsorbate

reconstruction
- change of the symmetry
- atomic rearrangement, formation of new bonds

Supercell approach to surfaces

Points to consider:
- Approach accounts for the lateral periodicity
- Sufficiently broad vacuum region to decouple the slabs
- Sufficient slab thickness to mimic semi-infinite crystal
- Semiconductors: saturate dangling bonds on the back surface
- Inequivalent surfaces: use dipole correction
- With some codes, slabs with inversion symmetry (for metals) are computationally more efficient
- Alternative: cluster model
Surface Brillouin zone

example: fcc crystal, (111) surface

Surface band structure of Cu(111)

Shockley surface state

Tamm surface state

(111)
Surface states (I)

approximation of the ‘nearly-free-electron’ metal

complex band structure

\[ \varepsilon(k) \]

gap

2 |\(V_G\)|

i\(\kappa\)

\[ \pi/a \]

\[ k_{\perp} \]

\[ \sim \exp[\lambda z] \]

\[ \exp[ i(k_{\perp} + i\kappa) z] \]

\[ \rightarrow \text{Shockley surface state} \]

Surface states (II)

In the tight-binding (localized orbital) picture, surface states may appear due to ‘dangling orbitals’ split off from the band edge

\[ \rightarrow \text{Tamm surface state} \]
**Co$_2$MnSi: spin-polarized surface state**

Spin-down components of d orbital of \textit{surface Mn} and \textit{subsurface Co}.

Surface states derived mainly from Co d$_{3r^2-z^2}$ in subsurface layer.

Orbital mixing of Co orbitals with Mn d$_{xz}$ d$_{yz}$ orbitals pushes Co states out of the gap.


---

**Dimerization at (001)-surface of group IV-elements**

Bulk-terminated atomic structure

Top view

Side view

Reconstruction

[001]

[1 1 0]

[1 1 0]
Stabilization of dimerized Si(100) surface

Jahn-Teller-like effect enhances the splitting of the surface state. [see, e.g., J. Dabrowski and M. Scheffler, Appl. Surf. Sci. 56-58, 15 (1992)]

Different reconstructions of group-IV (001)-surfaces

Surface reconstruction of Si(001)

A. Ramstad, G. Brocks, and P. J. Kelly,

top view of Si(001)

Thermodynamics of surfaces
surface free energy

definition:

\[ \gamma(n) = \text{free energy per unit area required to create a surface} \]

Depends on orientation of the plane in a crystal, and on temperature and pressure

Simple metal: potassium

DFT calculations at T=0 K:  

\[ \gamma A = E_{\text{slab}} - N_{\text{atom}} E_{\text{bulk}} \]
Quantum size effects: Al(110)

LDA, 20Ry plane wave cut-off, 16 k-points in IBZ


binary material: GaAs

- Gibbs free enthalpy \( G(p, T, N_{Ga}, N_{As}) \)
- Surface (free) energy
  \[ \gamma = \frac{G(p, T, N_{Ga}, N_{As}) - N_{Ga} \mu_{Ga} - N_{As} \mu_{As}}{A} \]
- equilibrium with bulk GaAs fixes one chemical potential: \( \mu_{Ga} + \mu_{As} = \mu_{GaAs} \)
- remaining variable (for instance, \( \mu_{As} \)) determined by gas pressure
- coexistence with elemental bulk phases sets bounds for \( \mu_{As}(p, T) \)

Ga crystal face

As crystal face
Surface relaxation: GaAs(001) \( \beta_2 \) (2x4)

LDA, 10 Ry plane-wave cut-off, 2 \( \times \) 4 \( k \)-points in full BZ

Slabs with \( n \) layers

\[
E_{\text{bulk}}(n) := \frac{[E_{\text{slab}}(n) - E_{\text{slab}}(n - 2)]}{N_{\text{at}}}
\]

Surface energy

\[
\gamma(n)A := E_{\text{slab}}(n) - (N_{\text{As}} + N_{\text{Ga}}) \quad E_{\text{bulk}}(n) - (N_{\text{As}} - N_{\text{Ga}})\mu_{\text{As}}(p, T)
\]

As\(_2\) pressure determines the stable structure

Under the conditions commonly used in molecular beam epitaxy, the \( \beta_2 \) surface reconstruction is stable.

Only at lower temperatures and higher As\(_2\) pressures, the \( c(4\times4) \) structure prevails (terminating As double layer).
The chemical physics of solid surfaces and interfaces is an active and exciting field of current research!