Sampling the Brillouin-zone:

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Overview

- introduction
- k-point meshes
- Smearing methods
- What to do in practice
For many properties (e.g.: density of states, charge density, matrix elements, response functions, ...) integrals \( I \) over the Brillouin-zone are necessary:

\[
I(\varepsilon) = \frac{1}{\Omega_{BZ}} \int_{BZ} F(\varepsilon) \delta(\varepsilon_{nk} - \varepsilon) d\mathbf{k}
\]

To evaluate computationally integrals \( \Rightarrow \) weighted sum over special \( k \)-points

\[
\frac{1}{\Omega_{BZ}} \int_{BZ} \Rightarrow \sum_{k} \omega_{k_i}
\]
**k-points meshes - The idea of special points**

Chadi, Cohen, PRB 8 (1973) 5747.

- function $f(k)$ with complete lattice symmetry
- introduce symmetrized plane-waves (SPW):

$$A_m(k) = \sum_{|\mathbf{R}|=C_m} e^{i\mathbf{k}\cdot\mathbf{R}}$$

sum over symmetry-equivalent $\mathbf{R}$

$$C_m \leq C_{m+1}$$

SPW $\Leftrightarrow$ ”shell” of lattice vectors

- develope $f(k)$ in Fourier-series (in SPW)

$$f(k) = f_0 + \sum_{m=1}^{\infty} f_mA_m(k)$$
• evaluate integral (=average) over Brillouin-zone

\[ \bar{f} = \frac{\Omega}{(2\pi)^3} \int_{\text{BZ}} f(k) dk \]

with: \[ \frac{\Omega}{(2\pi)^3} \int_{\text{BZ}} A_m(k) dk = 0 \quad m = 1, 2, \ldots \]

\[ \Rightarrow \bar{f} = f_0 \]

• taking \( n \) k-points with weighting factors \( \omega_k \) so that

\[ \sum_{i=1}^{n} \omega_{k_i} A_m(k_i) = 0 \quad m = 1, \ldots, N \]

\[ \Rightarrow \bar{f} = \text{weighted sum over k-points for variations of } f \text{ that can be described within the } \text{”shell” } \text{ corresponding to } C_N. \]
Monkhorst and Pack (1976):

Idea: equally spaced mesh in Brillouin-zone.

Construction-rule:

\[ \mathbf{k}_{prs} = u_p \mathbf{b}_1 + u_r \mathbf{b}_2 + u_s \mathbf{b}_3 \]

\[ u_r = \frac{2r + q_r - 1}{2q_r} \quad r = 1, 2, \ldots, q_r \]

\( \mathbf{b}_i \) reciprocal lattice-vectors

\( q_r \) determines number of k-points in r-direction
Example:

- quadratic 2-dimensional lattice
- \( q_1 = q_2 = 4 \Rightarrow 16 \) k-points
- only 3 inequivalent k-points (\( \Rightarrow \) IBZ)
  - \( 4 \times \mathbf{k}_1 = \left( \frac{1}{8}, \frac{1}{8} \right) \Rightarrow \omega_1 = \frac{1}{4} \)
  - \( 4 \times \mathbf{k}_2 = \left( \frac{3}{8}, \frac{3}{8} \right) \Rightarrow \omega_2 = \frac{1}{4} \)
  - \( 8 \times \mathbf{k}_3 = \left( \frac{3}{8}, \frac{1}{8} \right) \Rightarrow \omega_3 = \frac{1}{2} \)

\[
\frac{1}{\Omega_{\text{BZ}}} \int_{\text{BZ}} F(\mathbf{k}) d\mathbf{k} \Rightarrow \frac{1}{4} F(\mathbf{k}_1) + \frac{1}{4} F(\mathbf{k}_2) + \frac{1}{2} F(\mathbf{k}_3)
\]
Interpretation:
representation of function $F(k)$ on a discrete equally-spaced mesh

$$\sum_{n=0}^{N} a_n \cos(2\pi nk)$$

density of mesh $\Leftrightarrow$ more Fourier-components $\Rightarrow$ higher accuracy

Common meshes:
Two choices for the center of the mesh
- centered on $\Gamma$ ($\Rightarrow \Gamma$ belongs to mesh).
- centered around $\Gamma$. (can break symmetry !!)
Algorithm:

- calculate equally spaced-mesh
- shift the mesh if desired
- apply all symmetry operations of Bravais lattice to all k-points
- extract the irreducible k-points (≡ IBZ)
- calculate the proper weighting
**Smearing methods**

**Problem:** in metallic systems Brillouin-zone integrals over functions that are discontinuous at the Fermi-level.

⇒ high Fourier-components ⇒ dense grid is necessary.

**Solution:** replace step function by a smoother function.

**Example:** bandstructure energy

\[
\sum_{nk} \omega_k \varepsilon_{nk} \tilde{\Theta}(\varepsilon_{nk} - \mu)
\]

with: \(\tilde{\Theta}(x) = \begin{cases} 1 & x \leq 0 \\ 0 & x > 0 \end{cases} \)

\[\Rightarrow \sum_{nk} \omega_k \varepsilon_{nk} f \left( \frac{\varepsilon_{nk} - \mu}{\sigma} \right)\]

**necessary:** appropriate function \(f \Rightarrow f\) equivalent to partial occupancies.
**Fermi-Dirac function**

\[
f\left(\frac{\varepsilon_n k - \mu}{\sigma}\right) = \frac{1}{\exp\left(\frac{\varepsilon_n k - \mu}{\sigma}\right) + 1}
\]

**consequence:** energy is no longer variational with respect to the partial occupancies \(f\).

\[
(1) \quad F = E - \sum_n \sigma S(f_n)
\]

\[
(2) \quad S(f) = - [f \ln f + (1 - f) \ln (1 - f)]
\]

\[
(3) \quad \sigma = k_B T
\]

\(F\) free energy.

**new variational functional** - defined by (1).

\(S(f)\) entropy

of a system of non-interacting electrons at a finite temperature \(T\).

\(\sigma\) smearing parameter.

- can be interpreted as finite temperature via (3).

\(\Rightarrow\) calculations at finite temperature are possible (Mermin 1965)
Consistency:

(1) \[ F = E - \sum_n \sigma S(f_n) \]

(2) \[ S(f) = -[f \ln f + (1 - f) \ln (1 - f)] \]

(3) \[ \sigma = k_B T \]

(4) \[ \frac{\partial}{\partial f_n} \left[ F - \mu \left( \sum_n f_n - N \right) \right] = 0 \]

(1), (4) \[ \frac{\partial E}{\partial f_n} - \sigma \frac{\partial S}{\partial f_n} - \mu = 0 \]

(2) \[ \frac{\partial S}{\partial f} = -[\ln f + 1 - \ln(1 - f) - 1] = \ln \frac{1-f}{f} \]

(7) \[ \frac{\partial E}{\partial f_n} = \varepsilon_n \]

(5) - (7) \[ \varepsilon_n - \sigma \ln \frac{1-f_n}{f_n} - \mu = 0 \]

(8) \[ \exp \left[ \frac{\varepsilon_n - \mu}{\sigma} \right] = \frac{1}{f_n} + 1 \]

(9) \[ f_n = \frac{1}{\exp \left( \frac{\varepsilon_n - \mu}{\sigma} \right) + 1} \]
**Gaussian smearing**

broadening of energy-levels with Gaussian function.
⇒ \( f \) becomes an integral of the Gaussian function:

\[
 f \left( \frac{\varepsilon_{nk} - \mu}{\sigma} \right) = \frac{1}{2} \left[ 1 - \text{erf} \left( \frac{\varepsilon_{nk} - \mu}{\sigma} \right) \right]
\]

no analytical inversion of the error-function \( \text{erf} \) exists
⇒ entropy and free energy cannot be written in terms of \( f \).

\[
 S \left( \frac{\varepsilon - \mu}{\sigma} \right) = \frac{1}{2\sqrt{\pi}} \exp \left[ - \left( \frac{\varepsilon - \mu}{\sigma} \right)^2 \right]
\]

- \( \sigma \) has no physical interpretation.
- variational functional \( F(\sigma) \) differs from \( E(0) \).
- forces are calculated as derivatives of the variational quantity \( (F(\sigma)) \).
⇒ not necessarily equal to forces at \( E(0) \).
**Improvement:** extrapolation to $\sigma \to 0$.

\[
\begin{align*}
(1) \quad F(\sigma) &\approx E(0) + \gamma \sigma^2 \\
(2) \quad F(\sigma) &= E(\sigma) - \sigma S(\sigma) \\
(3) \quad S(\sigma) &= -\frac{\partial F(\sigma)}{\partial \sigma} \approx -2\gamma \sigma \\
(1) - (3) \Rightarrow (4) \quad E(\sigma) &\approx E(0) - \gamma \sigma^2 \\
(1), (4) \quad E(0) &\approx \hat{E}(\sigma) = \frac{1}{2} (F(\sigma) + E(\sigma))
\end{align*}
\]
**Method of Methfessel and Paxton (1989)**

**Idea:**

expansion of stepfunction in a complete set of orthogonal functions

\[ \Rightarrow \text{term of order } 0 = \text{integral over Gaussians} \]

\[ \Rightarrow \text{generalization of Gaussian broadening with functions of higher order.} \]
\[
f_0(x) = \frac{1}{2} (1 - \text{erf}(x))
\]
\[
f_N(x) = f_0(x) + \sum_{m=1}^{N} A_m H_{2m-1}(x) e^{-x^2}
\]
\[
S_N(x) = \frac{1}{2} A_N H_{2N}(x) e^{-x^2}
\]
with: \( A_n = \frac{(-1)^n}{n!4^n \sqrt{\pi}} \)

\( H_N \) : Hermite-polynomial of order \( N \)

advantages:

- deviation of \( F(\sigma) \) from \( E(0) \) only of order \( 2+N \) in \( \sigma \)
- extrapolation for \( \sigma \rightarrow 0 \) usually not necessary, but also possible:

\[
E(0) \approx \hat{E}(\sigma) = \frac{1}{N+2} \left((N+1)F(\sigma) + E(\sigma)\right)
\]
The significance of $N$ and $\sigma$

- MP of order $N$ leads to a negligible error, if $X(\varepsilon)$ is representable as a polynomial of degree $2N$ around $\varepsilon_F$.
- Linewidth $\sigma$ can be increased for higher order to obtain the same accuracy.
- "Entropy term" ($S = \sigma \sum_n S_N(f_n)$) describes deviation of $F(\sigma)$ from $E(\sigma)$.
  
  $\Rightarrow$ if $S < \text{few meV}$
  then $\hat{E}(\sigma) \approx F(\sigma) \approx E(\sigma) \approx E(0)$.

  $\Rightarrow$ forces correct within that limit.

- In practice: smearing of order $N=1$ or $2$ are sufficient
**Linear tetrahedron method**

**Idea:**

1. dividing up the Brillouin-zone into tetrahedra
2. Linear interpolation of the function to be integrated \( X_n \) within these tetrahedra
3. integration of the interpolated function \( \bar{X}_n \)
How to select mesh for tetrahedra

map out the IBZ

use special points
ad 2. interpolation

\[ \tilde{X}_n(k) = \sum_j c_j(k) X_n(k_j) \]

\( j \) ........... k-points
ad 3. k-space integration: simplification by Blöchl (1993)

remapping of the tetrahedra onto the k-points

\[ \omega_{nj} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d\mathbf{k} c_j(\mathbf{k}) f(\varepsilon_n(\mathbf{k})) \]

⇒ effective weights \( \omega_{nj} \) for k-points.

⇒ k-space summation:

\[ \sum_{nj} \omega_{nj} X_n(\mathbf{k}_j) \]
Drawbacks:

- tetrahedra can break the symmetry of the Bravais lattice
- at least 4 k-points are necessary
- Γ must be included
- linear interpolation under- or overestimates the real curve
Corrections by Blöchl (1993)

Idea:

- linear interpolation under- or overestimates the real curve
- for full-bands or insulators these errors cancel
- for metals: correction of quadratic errors is possible:

$$
\delta \omega_{kn} = \sum_T \frac{1}{40} D_T(\varepsilon_F) \sum_{j=1}^{4} (\varepsilon_{jn} - \varepsilon_{kn})
$$

- $j$ corners (k-point) of the tetrahedron $T$
- $D_T(\mu)$ DOS for the tetrahedron $T$ at $\varepsilon_F$. 

Result:

- best k-point convergence for energy
- forces:
  - with Blöchl corrections the new effective partial occupancies do not minimize the groundstate total energy
  - variation of occupancies $\omega_{nk}$ w.r.t. the ionic positions would be necessary
  - with US-PP and PAW practically impossible
Convergence tests (from P. Blöchl, O. Jepsen, O. K. Andersen, PRB 49, 16223 (1994).)
**What to do in practice**

**energy/DOS calculations:**
linear tetrahedron method with Blöchl corrections
   ISMEAR=-5

**calculation of forces:**
  - semiconductors: Gaussian smearing (ISMEAR=0; SIGMA=0.1)
  - metals: Methfessel-Paxton (N=1 or 2)
  - always: test for energy with LT+Blöchl-corr.

**in any case:**
careful checks for k-point convergence are necessary
The KPOINTS - file:

1> k-points for a metal
2> 0
3> Gamma point
4> 9 9 9
5> 0 0 0

1st line: comment

2nd line: 0 (⇒ automatic generation)

3rd line: Monkhorst or Gammapoint (centered)

4th line: mesh parameter

5th line: 0 0 0 (shift)
mesh parameter

- determine the number of intersections in each direction
- longer axes in real-space $\Leftrightarrow$ shorter axes in k-space

$\Rightarrow$ less intersections necessary for equally spaced mesh

Consequences:

- molecules, atoms (large supercells)
  $\Rightarrow (1 \times 1 \times 1)(\equiv \Gamma)$ is enough.

- surfaces (one long direction $\Rightarrow$ 2-D Brillouin-zone)
  $\Rightarrow (x \times y \times 1)$ for the direction corresponding to the long direction.

- ”typical” values (never trust them!): metals: $(9 \times 9 \times 9)/$atom
  semiconductors: $(4 \times 4 \times 4)/$atom
Example - real-space/ reciprocal cell

- doubling the cell in real space halves the reciprocal cell
  ⇒ zone boundary is folded back to Γ
- same sampling is achieved with halved mesh parameter
in certain cell geometries (e.g. hexagonal cells) even meshes break the symmetry

symmetrization results in non equally distributed k-points

Gamma point centered mesh preserves symmetry
Convergence tests

with respect to $\sigma$...

... and number of k-points in the IBZ