Sampling the Brillouin-zone:

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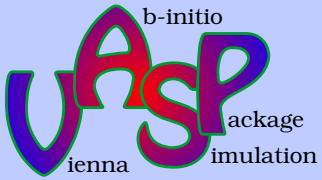


Overview

- introduction
- k-point meshes
- Smearing methods
- What to do in practice

Introduction

For many properties

(e.g.: density of states, charge density, matrix elements, response functions, ...)

integrals (I) over the Brillouin-zone are necessary:

$$I(\varepsilon) = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} F(\varepsilon)\delta(\varepsilon_{n\mathbf{k}} - \varepsilon) d\mathbf{k}$$

To evaluate computationally

integrals $\Rightarrow$ weighted sum over special k-points

$$\frac{1}{\Omega_{\mathrm{BZ}}} \int_{\mathrm{BZ}} \quad \Rightarrow \quad \sum_{\mathbf{k}} \omega_{\mathbf{k}_i}$$

k-points meshes - The idea of special points

Chadi, Cohen, PRB 8 (1973) 5747.

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

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

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

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

SPW $\Leftrightarrow$ "shell" of lattice vectors

- develope $f(\mathbf{k})$ in Fourier-series (in SPW)

$$f(\mathbf{k}) = f_0 + \sum_{m=1}^{\infty} f_m A_m(\mathbf{k})$$

- evaluate integral (=average) over Brillouin-zone

$$\bar{f} = \frac{\Omega}{(2\pi)^3} \int_{\mathrm{BZ}} f(\mathbf{k}) d\mathbf{k}$$

$$\text{with:} \frac{\Omega}{(2\pi)^3} \int_{\mathrm{BZ}} A_m(\mathbf{k}) d\mathbf{k} = 0 \qquad m = 1, 2, \ldots$$

$$\Rightarrow \bar{f} = f_0$$

- taking n k-points with weighting factors $\omega_{\mathbf{k}}$ so that

$$\sum_{i=1}^{n} \omega_{\mathbf{k}_i} A_m(\mathbf{k}_i) = 0 \qquad m = 1, \ldots, N$$

$\Rightarrow \bar{f}$ = weighted sum over k-points for variations of f that can be described within the "shell" corresponding to C_N.

Monkhorst and Pack (1976):

Idea: equally spaced mesh in Brillouin-zone.

Construction-rule:

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

$$u_r = \frac{2r - q_r - 1}{2q_r} \qquad r = 1, 2, \ldots, q_r$$

$\mathbf{b}_i$ reciprocal lattice-vectors

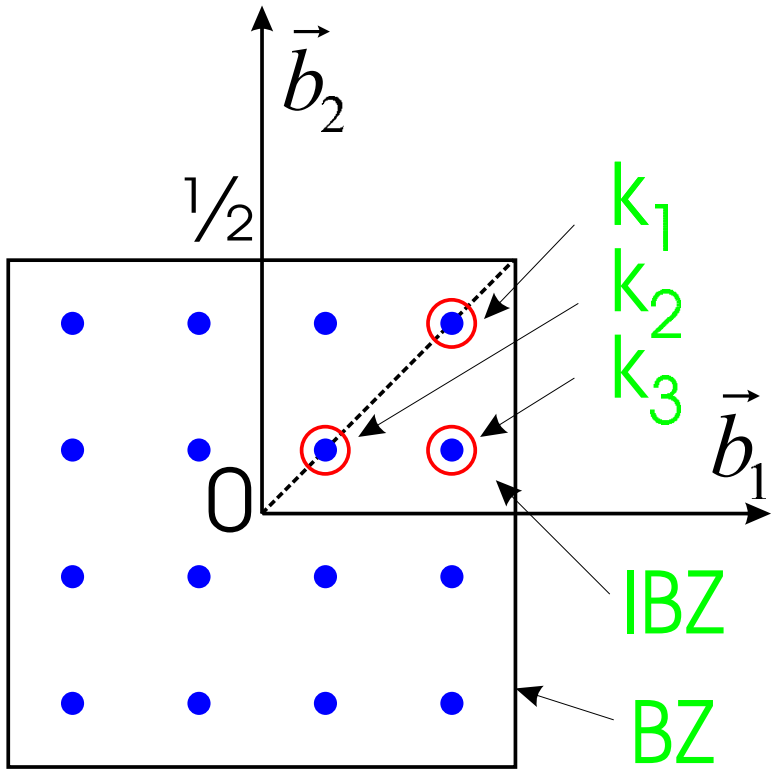
q_r determines number of k-points in r-direction

Example:

- quadratic 2-dimensional lattice
- $q_1 = q_2 = 4 \Rightarrow$ 16 k-points

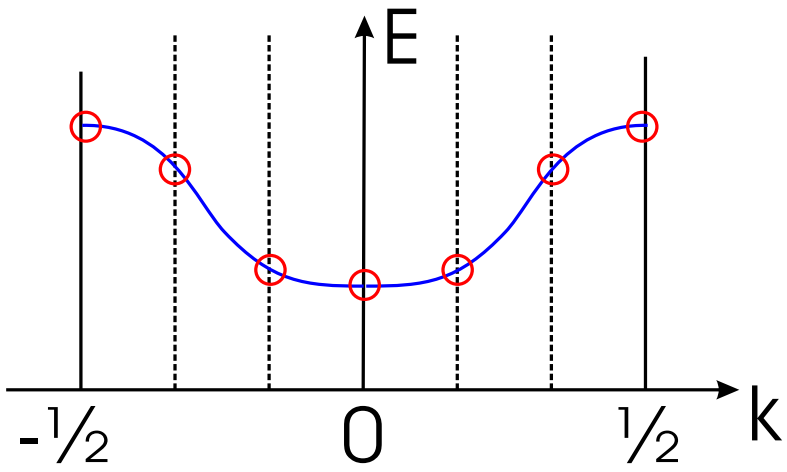
- only 3 inequivalent k-points ($\Rightarrow$ IBZ)
  - $4 \times \mathbf{k}_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$
  - $4 \times \mathbf{k}_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$
  - $8 \times \mathbf{k}_3 = (\frac{3}{8}, \frac{1}{8}) \Rightarrow \omega_3 = \frac{1}{2}$

$$\frac{1}{\Omega_{\mathrm{BZ}}} \int_{BZ} F(\mathbf{k}) d\mathbf{k} \Rightarrow \frac{1}{4} F(\mathbf{k}_1) + \frac{1}{4} F(\mathbf{k}_2) + \frac{1}{2} F(\mathbf{k}_3)$$



Interpretation:

representation of function $F(\mathbf{k})$ on a discrete equally-spaced mesh



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

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

Common meshes :

Two choices for the center of the mesh

- centered on Γ ($\Rightarrow$ Γ belongs to mesh).
- centered around Γ. (can break symmetry !!)

Algorithm:

- calculate equally spaced-mesh
- shift the mesh if desired
- apply all symmetry operations of Bravaislattice to all k-points
- extract the irreducible k-points ($\equiv$ IBZ)
- calculate the proper weighting

Smearing methods

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

$\Rightarrow$ high Fourier-components $\Rightarrow$ dense grid is necessary.

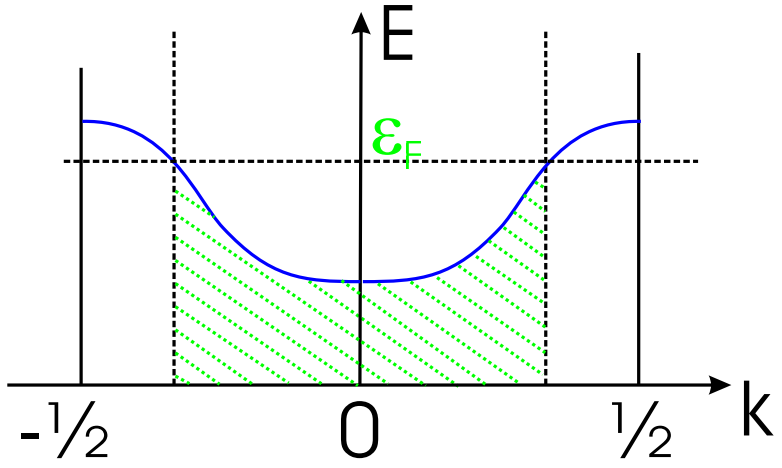
Solution: replace step function by a smoother function.

Example: bandstructure energy

$$\sum_{n\mathbf{k}} \omega_{\mathbf{k}} \varepsilon_{n\mathbf{k}} \bar{\Theta}(\varepsilon_{n\mathbf{k}} - \mu)$$

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

$$\Rightarrow \sum_{n\mathbf{k}} \omega_{\mathbf{k}} \varepsilon_{n\mathbf{k}} f\left(\frac{\varepsilon_{n\mathbf{k}} - \mu}{\sigma}\right)$$



necessary: appropriate function $f \Rightarrow f$ equivalent to partial occupancies.

Fermi-Dirac function

$$f\left(\frac{\varepsilon_{n\mathbf{k}}-\mu}{\sigma}\right)=\frac{1}{\exp\left(\frac{\varepsilon_{n\mathbf{k}}-\mu}{\sigma}\right)+1}$$

consequence: energy is no longer variational with respect to the partial occupacies f.

$$(1) \qquad F = E - \sum_n \sigma S(f_n)$$

$$(2) \qquad S(f) = -\left[f\ln f + (1-f)\ln(1-f)\right]$$

$$(3) \qquad \sigma = k_B T$$

F *free energy.*

new variational functional - defined by (1).

$S(f)$ *entropy*

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

σ *smearing parameter.*

can be interpreted as finite temperature via (3).

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

Consistency:

$$
\begin{aligned}
(1) \quad & F = E - \sum_n \sigma S(f_n) \\
(2) \quad & S(f) = -\left[f \ln f + (1-f)\ln(1-f)\right] \\
(3) \quad & \sigma = k_B T \\
(4) \quad & \frac{\partial}{\partial f_n}\left[F - \mu\left(\sum_n f_n - N\right)\right] = 0 \\
(1),(4) \rightarrow (5) \quad & \frac{\partial E}{\partial f_n} - \sigma \frac{\partial S}{\partial f_n} - \mu = 0 \\
(2) \rightarrow (6) \quad & \frac{\partial S}{\partial f} = -\left[\ln f + 1 - \ln(1-f) - 1\right] = \ln \frac{1-f}{f} \\
(7) \quad & \frac{\partial E}{\partial f_n} = \varepsilon_n \\
(5) - (7) \rightarrow (8) \quad & \varepsilon_n - \sigma \ln \frac{1-f_n}{f_n} - \mu = 0 \\
(8) \rightarrow (9) \quad & \exp\left[\frac{\varepsilon_n - \mu}{\sigma}\right] = \frac{1}{f_n} + 1 \\
(9) \rightarrow \quad & f_n = \frac{1}{\exp\left(\frac{\varepsilon_{n\mathbf{k}} - \mu}{\sigma}\right) + 1}
\end{aligned}
$$

Gaussian smearing

broadening of energy-levels with Gaussian function.

$\Rightarrow f$ becomes an integral of the Gaussian function:

$$f\left(\frac{\varepsilon_{n\mathbf{k}}-\mu}{\sigma}\right)=\frac{1}{2}\left[1-\mathrm{erf}\left(\frac{\varepsilon_{n\mathbf{k}}-\mu}{\sigma}\right)\right]$$

no analytical inversion of the error-function erf exists

$\Rightarrow$ entropy and free energy cannot be written in terms of f.

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

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

Improvement: extrapolation to $\sigma \to 0$.

$$
\begin{aligned}
& (1) \quad F(\sigma) \approx E(0) + \gamma\sigma^2 \\
& (2) \quad F(\sigma) = E(\sigma) - \sigma S(\sigma) \\
& (3) \quad S(\sigma) = -\frac{\partial F(\sigma)}{\partial \sigma} \approx -2\gamma\sigma \\
(1)-(3) \to (4) \quad & E(\sigma) \approx E(0) - \gamma\sigma^2 \\
(1),(4) \quad & E(0) \approx \hat{E}(\sigma) = \tfrac{1}{2}\left(F(\sigma) + E(\sigma)\right)
\end{aligned}
$$

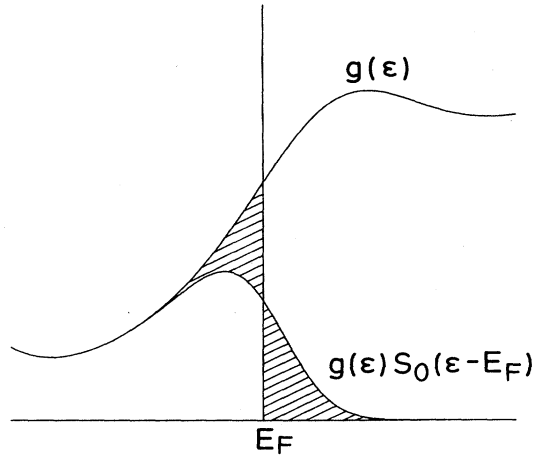
Method of Methfessel and Paxton (1989)

Idea:

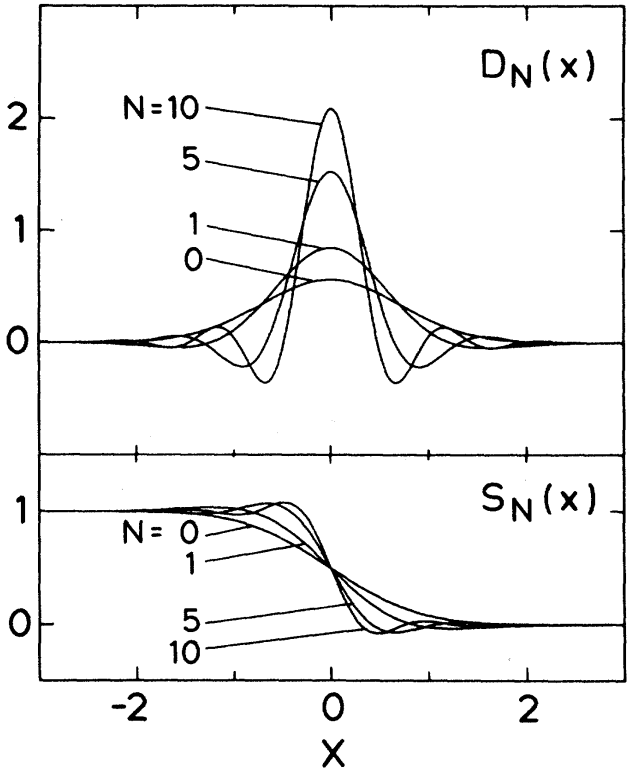
expansion of stepfunction in a complete set of orthogonal functions

$\Rightarrow$ term of order 0 = integral over Gaussians

$\Rightarrow$ generalization of Gaussian broadening with functions of higher order.



$$
\begin{aligned}
f_0(x) &= \tfrac{1}{2}\left(1-\mathrm{erf}(x)\right) \\
f_N(x) &= f_0(x) + \sum_{m=1}^{N} A_m H_{2m-1}(x) e^{-x^2} \\
S_N(x) &= \tfrac{1}{2} A_N H_{2N}(x) e^{-x^2} \\
\text{with:}\quad A_n &= \frac{(-1)^n}{n!\,4^n\sqrt{\pi}} \\
H_N: &\quad \text{Hermite-polynomial of order } N
\end{aligned}
$$



advantages:

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

$$
E(0) \approx \hat{E}(\sigma) = \frac{1}{N+2}\left((N+1)F(\sigma) + E(\sigma)\right)
$$

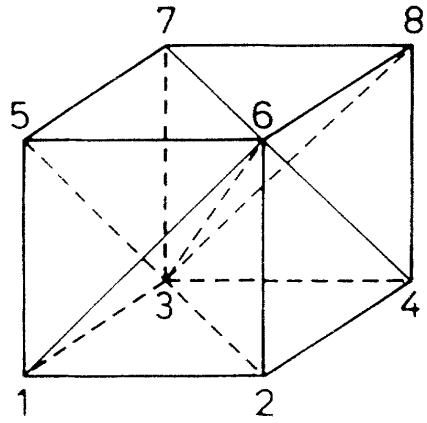
The significance of N and σ

- MP of order N leads to a negligible error, if $X(\varepsilon)$ is representable as a polynomial of degree $2N$ around ε_F.
- linewidth σ can be increased for higher order to obtain the same accuracy
- "entropy term" ($\mathbf{S} = \sigma \sum_n S_N(f_n)$) describes deviation of $F(\sigma)$ from $E(\sigma)$.

  $\Rightarrow$ if $\mathbf{S}<$ few meV
  then $\hat{E}(\sigma) \approx F(\sigma) \approx E(\sigma) \approx E(0)$.

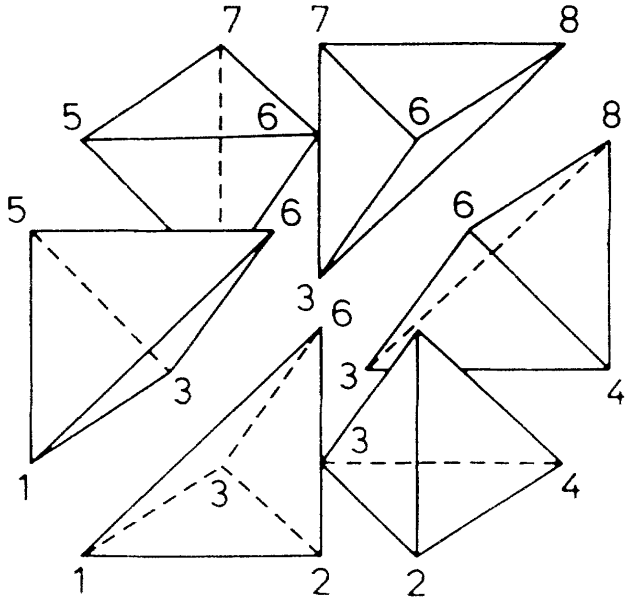
  $\Rightarrow$ forces correct within that limit.
- in practice: smearings of order N=1 or 2 are sufficient

Linear tetrahedron method



Idea:

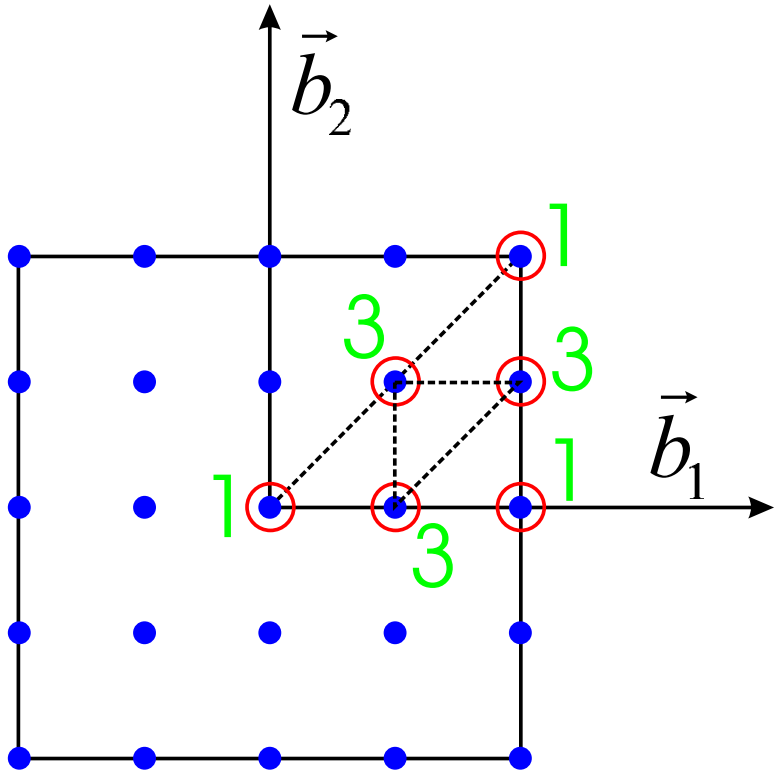
1. dividing up the Brillouin-zone into tetrahedra
2. Linear interpolation of the function to be integrated X_n within these tetrahedra
3. integration of the interpolated function $\bar{X}_n$



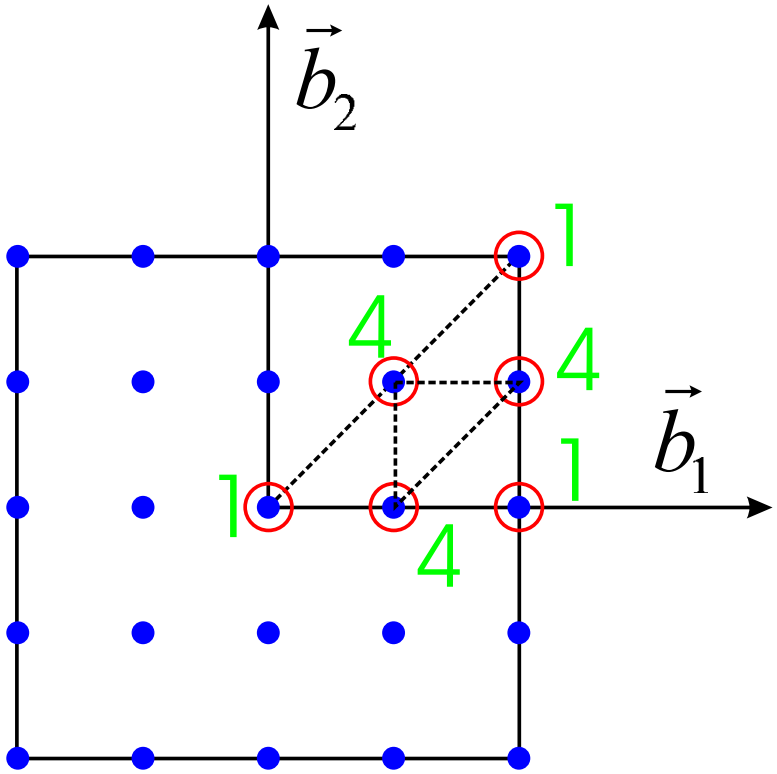
ad 1.

How to select mesh for tetrahedra

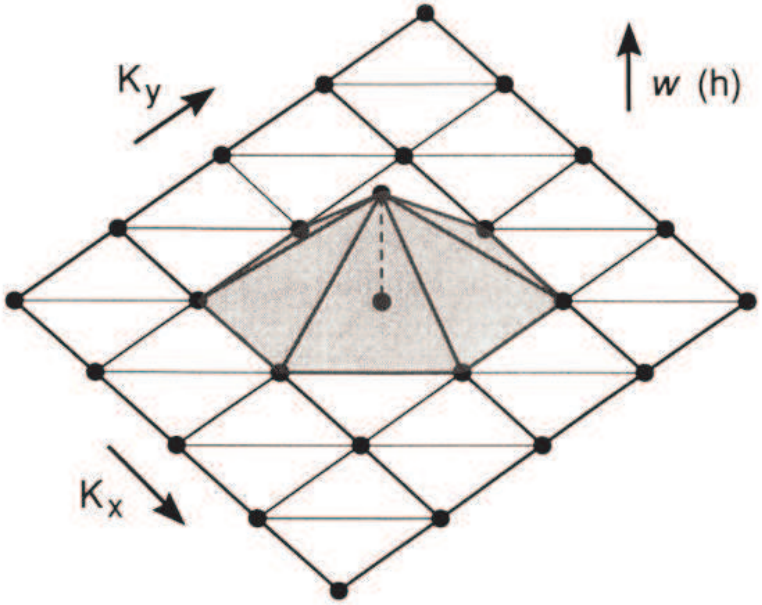
map out the IBZ



use special points



ad 2. interpolation



$$\bar{X}_n(\mathbf{k}) = \sum_j c_j(\mathbf{k}) X_n(\mathbf{k}_j)$$

j ..... k-points

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

remapping of the tetrahedra onto the k-points

$$\omega_{nj} = \frac{1}{\Omega_{\mathrm{BZ}}} \int_{\Omega_{\mathrm{BZ}}} d\mathbf{k} c_j(\mathbf{k}) f\left(\varepsilon_n(\mathbf{k})\right)$$

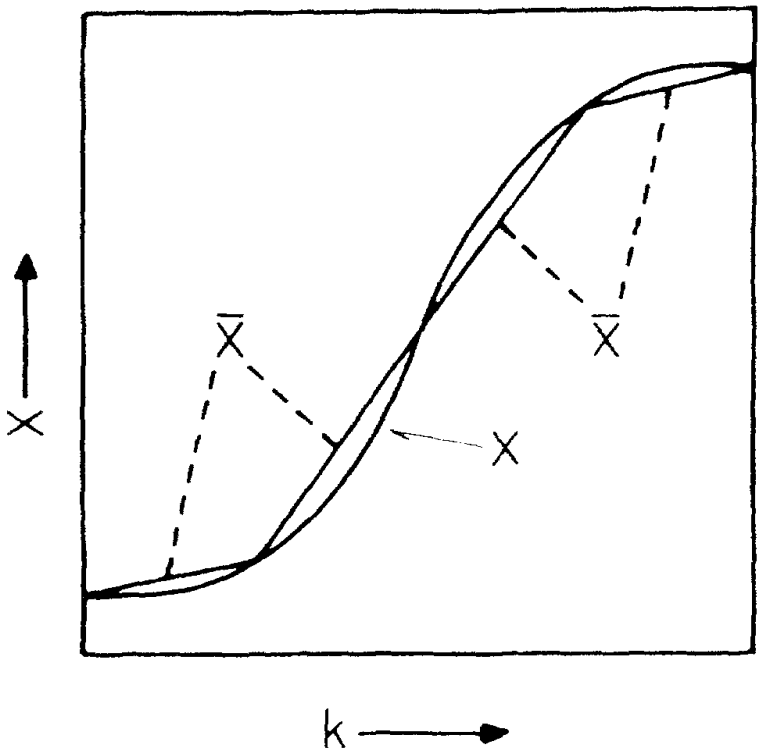
$\Rightarrow$ effective weights ω_{nj} for k-points.

$\Rightarrow$ k-space summation:

$$\sum_{nj} \omega_{nj} X_n(\mathbf{k}_j)$$

Drawbacks:

- tetrahedra can break the symmetry of the Bravaislattice
- 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:

$$\delta\omega_{\mathbf{k}n} = \sum_{\mathrm{T}} \frac{1}{40} D_{\mathrm{T}}(\varepsilon_{\mathrm{F}}) \sum_{j=1}^{4} (\varepsilon_{jn} - \varepsilon_{\mathbf{k}n})$$

j	corners (k-point) of the tetrahedron T
$D_{\mathrm{T}}(\mu)$	DOS for the tetrahedron T at ε_{F}.

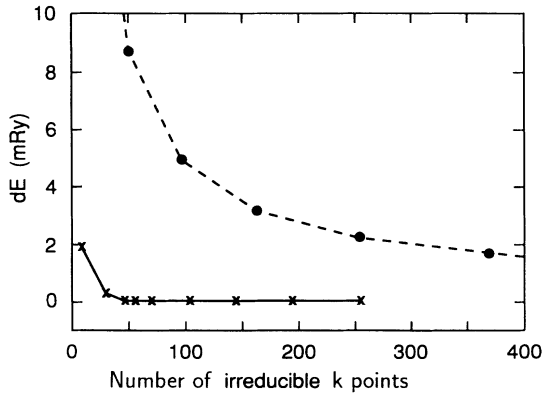
Result:

- 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 $\omega_{n\mathbf{k}}$ w.r.t. the ionic positions would be necessary
  - with US-PP and PAW practically impossible

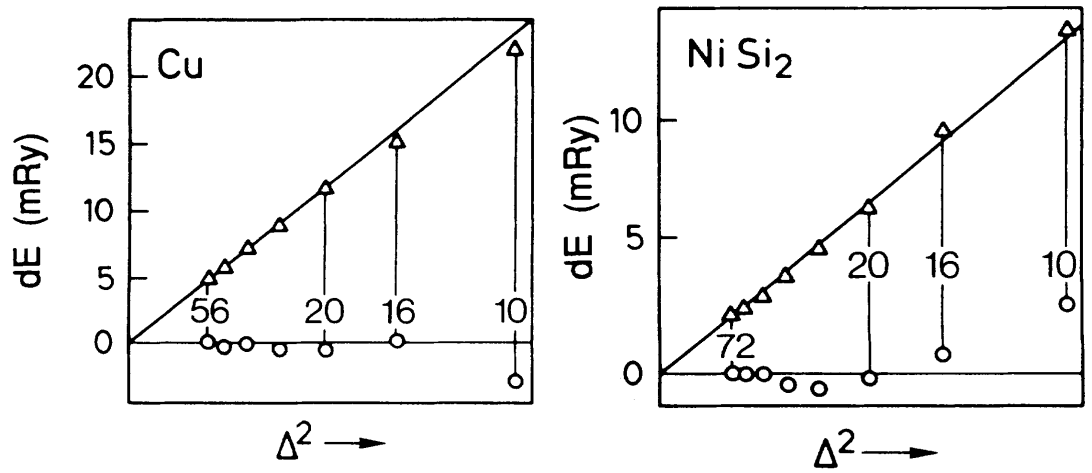
Convergence tests

(from P.Blöchl, O. Jepsen, O.K. Andersen, PRB **49**,16223 (1994).)

bandstructure energy of silicon:
conventional LT -method vs.
LT+Blöchl corrections



bandstructure energy vs. k-point spacing Δ:



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 ($\Rightarrow$ automatic generation)

3rd line: *M*onkhorst or *G*ammapoint (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

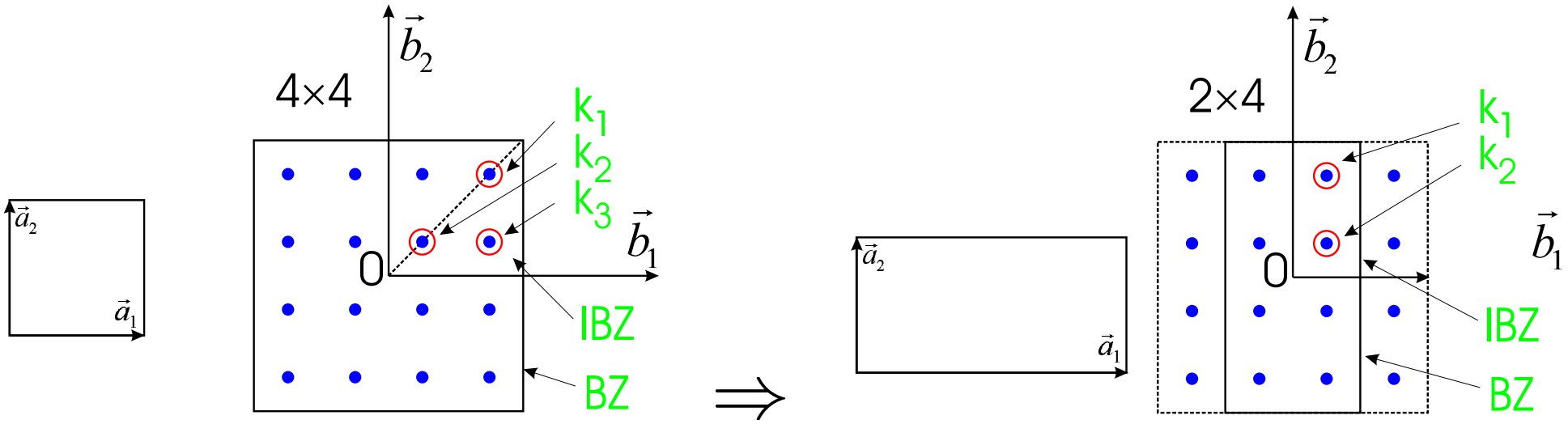
  $\Rightarrow$ less intersections necessary for equally spaced mesh

  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!):

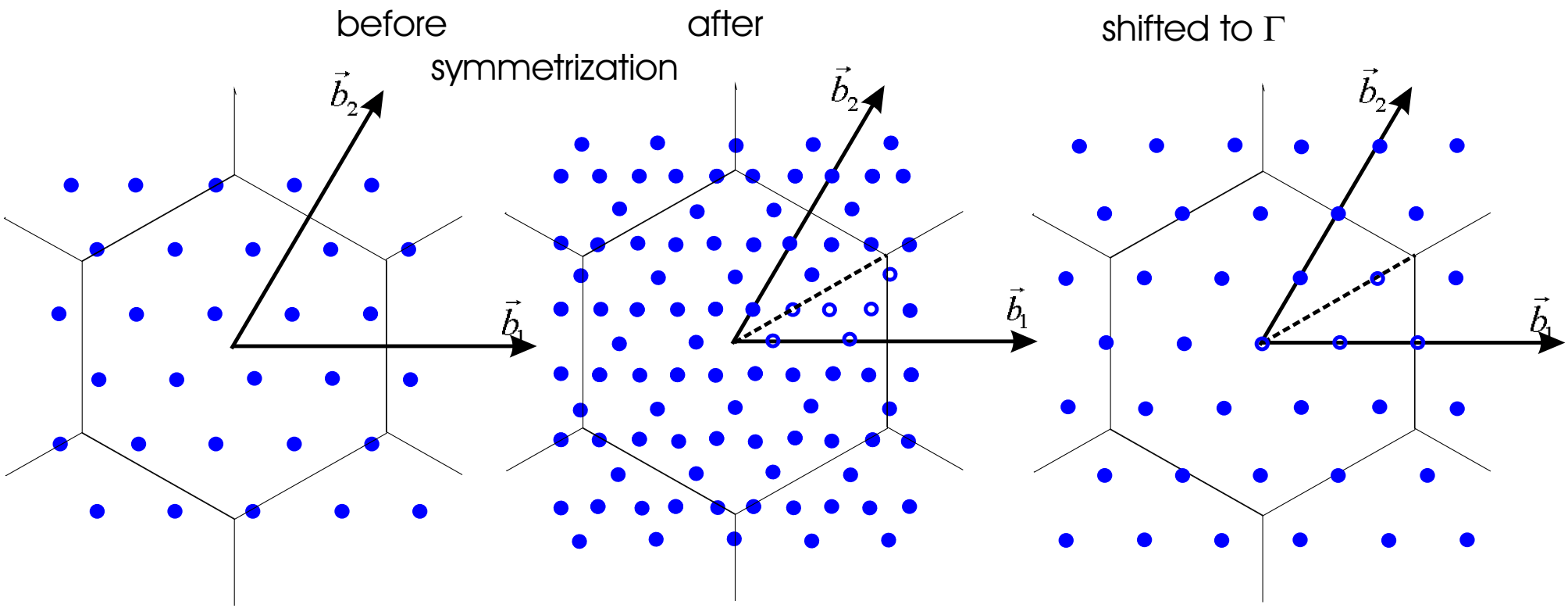
metals:	$(9 \times 9 \times 9)$/atom
semiconductors:	$(4 \times 4 \times 4)$/atom

Example - real-space/ reciprocal cell



- doubling the cell in real space halves the reciprocal cell
  $\Rightarrow$ zone boundary is folded back to Γ
- same sampling is achieved with halved mesh parameter

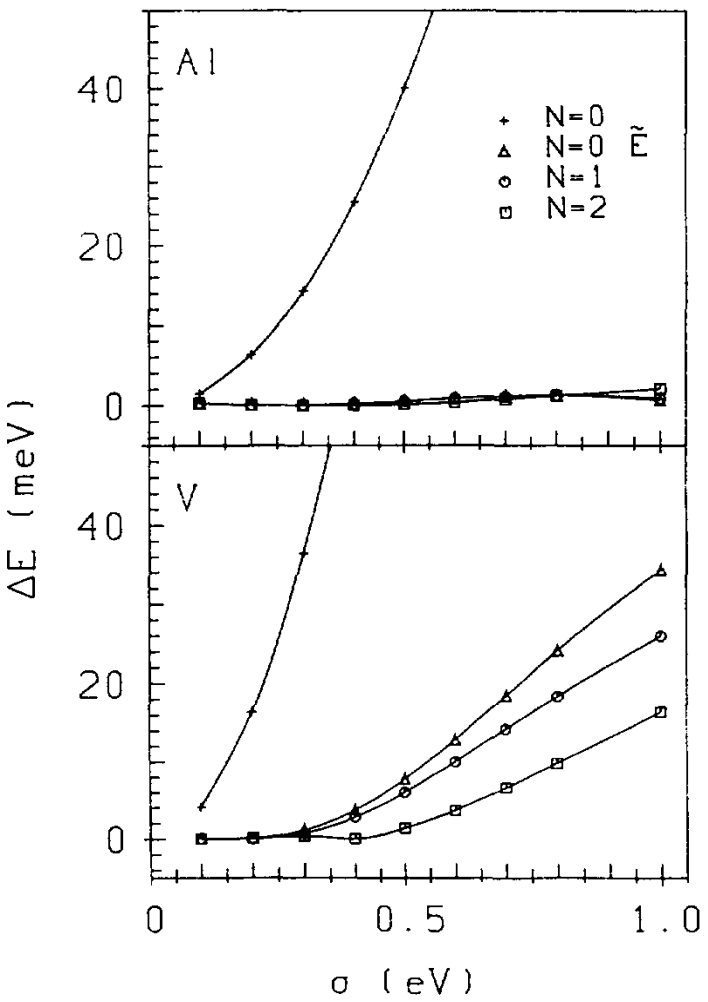
Example - hexagonal cell



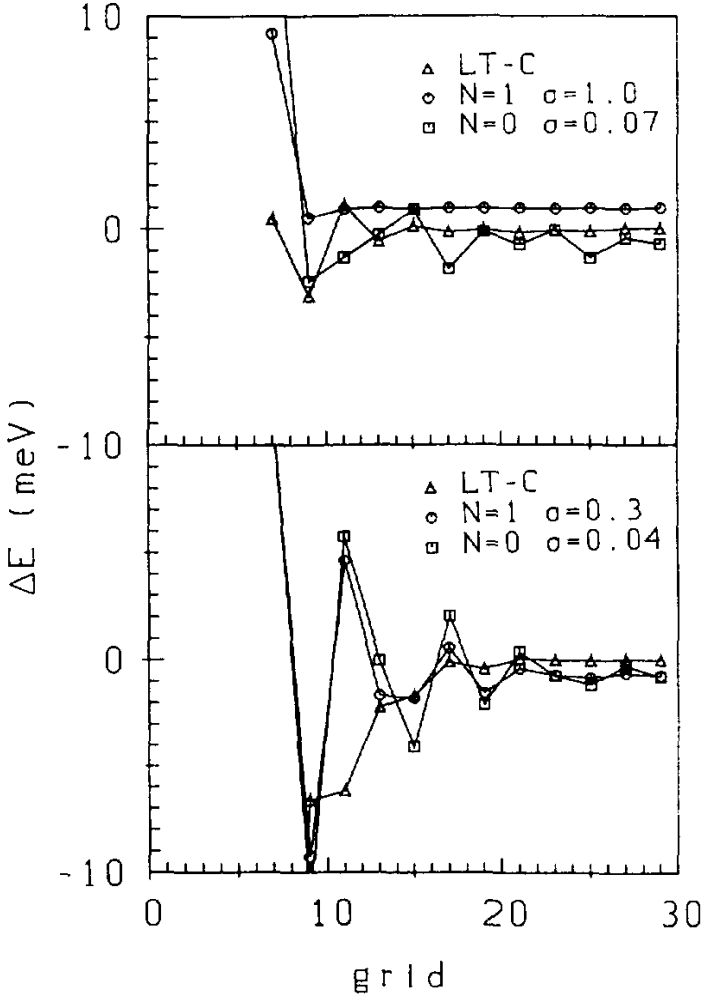
- in certain cell geometries (e.g. hexagonal cells) even meshes break the symmetry
- symmetrization results in non equally distributed k-points
- Gamma point centered mesh preserves symmetry

Convergence tests

with respect to σ . . .



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



G.Kresse, J. Furthmüller, Computat. Mat. Sci. **6**, 15 (1996).