

Sampling the Brillouin-zone:

Martijn MARSMAN

Institut für Materialphysik and
Center for Computational Materials Science

Universität Wien, Sensengasse 8, A-1090 Wien, Austria



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:

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

To evaluate computationally

integrals \Rightarrow weighted sum over special k-points

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

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):

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

sum over symmetry-equivalent \mathbf{R}

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

SPW \Leftrightarrow "shell" of lattice vectors

- develop $f(\mathbf{k})$ 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

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

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

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

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

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

$\Rightarrow \bar{f}$ = 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:

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

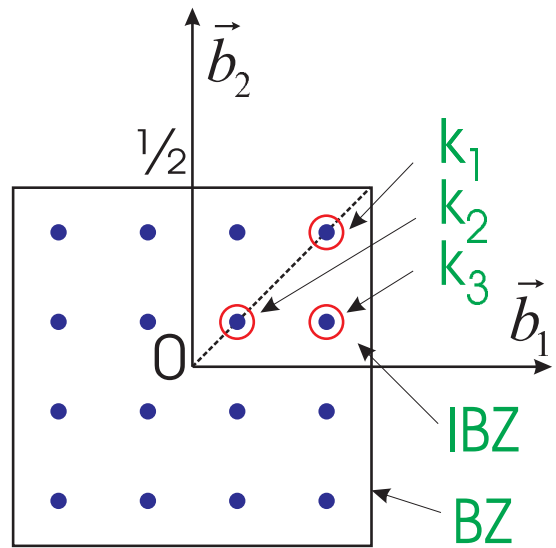
$$u_r = \frac{2r - q_r - 1}{2q_r} \quad r = 1, 2, \dots, q_r$$

\mathbf{b}_i reciprocal lattice-vectors

q_r determines number of
k-points in r-direction

Example:

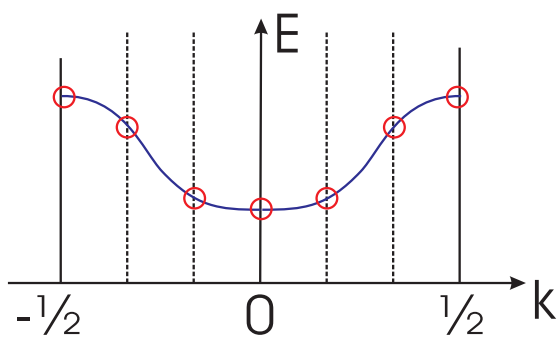
- quadratic 2-dimensional lattice
- $q_1 = q_2 = 4 \Rightarrow 16$ k-points
- only 3 inequivalent k-points (\Rightarrow IBZ)
 - $4 \times \mathbf{k}_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$
 - $4 \times \mathbf{k}_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$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



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

Interpretation:

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



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

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

Common meshes :

Two choices for the center of the mesh

- centered on Γ ($\Rightarrow \Gamma$ 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.

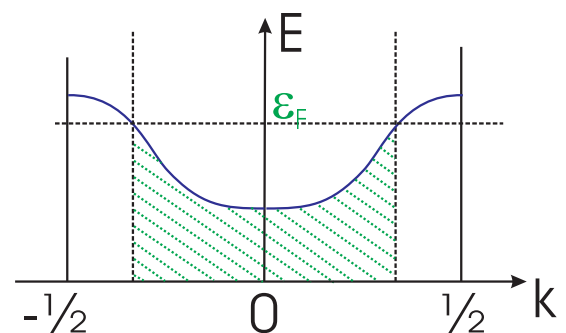
Solution: replace step function by a smoother function.

Example: bandstructure energy

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

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

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



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

Fermi-Dirac function

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

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

σ smearing parameter.

can be interpreted as finite temperature via (3).

⇒ calculations at finite temperature are possible (Mermin 1965)

Consistency:

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

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

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

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

$$(1), (4) \rightarrow (5) \quad \frac{\partial E}{\partial f_n} - \sigma \frac{\partial S}{\partial f_n} - \mu = 0$$

$$(2) \rightarrow (6) \quad \frac{\partial S}{\partial f} = -[\ln f + 1 - \ln(1 - f) - 1] = \ln \frac{1-f}{f}$$

$$(7) \quad \frac{\partial E}{\partial f_n} = \varepsilon_n$$

$$(5) - (7) \rightarrow (8) \quad \varepsilon_n - \sigma \ln \frac{1-f_n}{f_n} - \mu = 0$$

$$(8) \rightarrow (9) \quad \exp\left[\frac{\varepsilon_n - \mu}{\sigma}\right] = \frac{1}{f_n} + 1$$

$$(9) \rightarrow f_n = \frac{1}{\exp\left(\frac{\varepsilon_{n\mathbf{k}} - \mu}{\sigma}\right) + 1}$$

Gaussian smearing

broadening of energy-levels with Gaussian function.

⇒ f becomes an integral of the Gaussian function:

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

no analytical inversion of the error-function erf exists

⇒ entropy and free energy cannot be written in terms of f .

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

- σ 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 $\sigma \rightarrow 0$.

$$(1) \quad F(\sigma) \approx E(0) + \gamma\sigma^2$$

$$(2) \quad F(\sigma) = E(\sigma) - \sigma S(\sigma)$$

$$(3) \quad S(\sigma) = -\frac{\partial F(\sigma)}{\partial \sigma} \approx -2\gamma\sigma$$

$$(1) - (3) \rightarrow (4) \quad E(\sigma) \approx E(0) - \gamma\sigma^2$$

$$(1), (4) \quad E(0) \approx \hat{E}(\sigma) = \frac{1}{2} (F(\sigma) + E(\sigma))$$

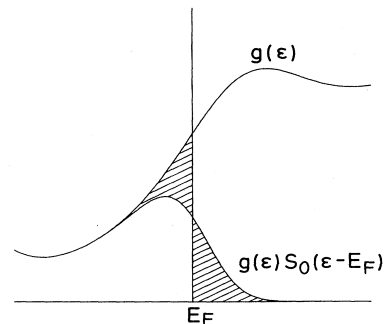
Method of Methfessel and Paxton (1989)

Idea:

expansion of stepfunction in a complete set of orthogonal functions

⇒ term of order 0 = integral over Gaussians

⇒ generalization of Gaussian broadening with functions of higher order.



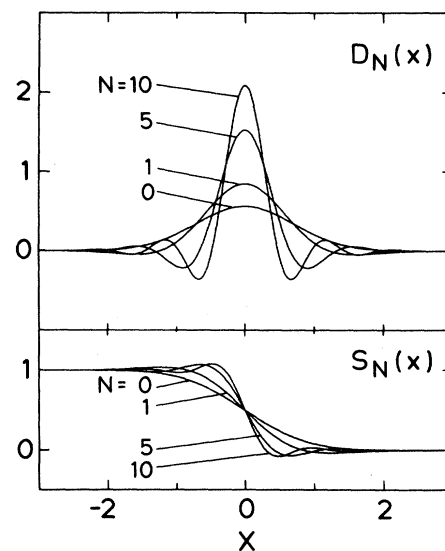
$$f_0(x) = \frac{1}{2}(1 - \text{erf}(x))$$

$$f_N(x) = f_0(x) + \sum_{m=1}^N A_m H_{2m-1}(x) e^{-x^2}$$

$$S_N(x) = \frac{1}{2} A_N H_{2N}(x) e^{-x^2}$$

$$\text{with: } A_n = \frac{(-1)^n}{n! 4^n \sqrt{\pi}}$$

H_N : Hermite-polynomial of order N



advantages:

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

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

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" ($S = \sigma \sum_n S_N(f_n)$) describes deviation of $F(\sigma)$ from $E(\sigma)$.

\Rightarrow if $S < \text{few meV}$

then $\hat{E}(\sigma) \approx F(\sigma) \approx E(\sigma) \approx E(0)$.

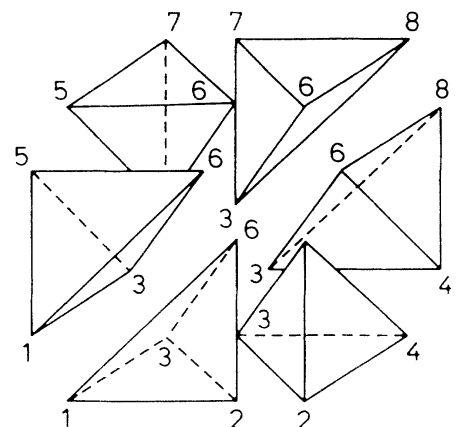
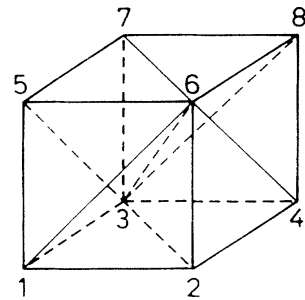
\Rightarrow forces correct within that limit.

- in practice: smearings of order $N=1$ or 2 are sufficient

Linear tetrahedron method

Idea:

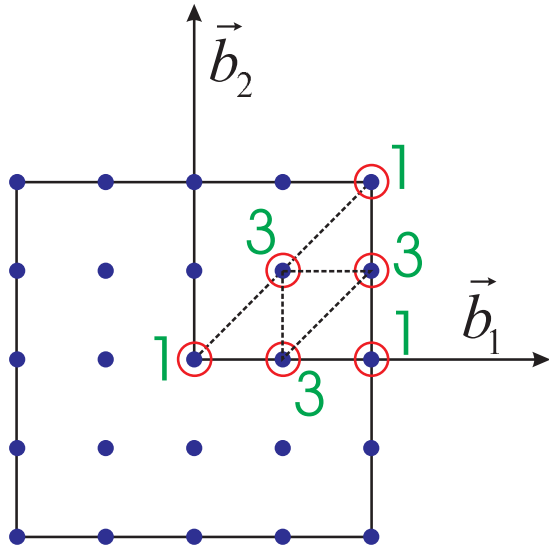
1. dividing up the Brillouin-zone into tetrahedra
2. Linear interpolation of the function to be integrated X_n within these tetrahedra
3. integration of the interpolated function \bar{X}_n



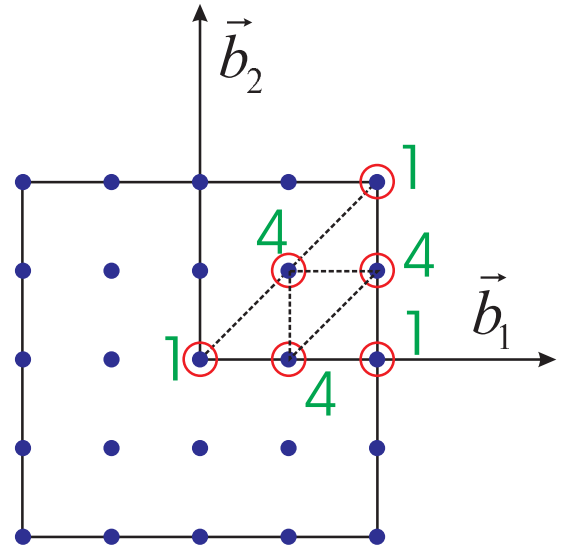
ad 1.

How to select mesh for tetrahedra

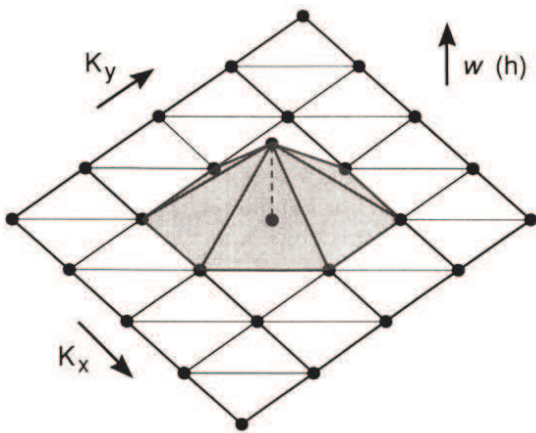
map out the IBZ



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

$$\omega_{nj} = \frac{1}{\Omega_{\text{BZ}}} \int_{\Omega_{\text{BZ}}} d\mathbf{k} c_j(\mathbf{k}) f(\epsilon_n(\mathbf{k}))$$

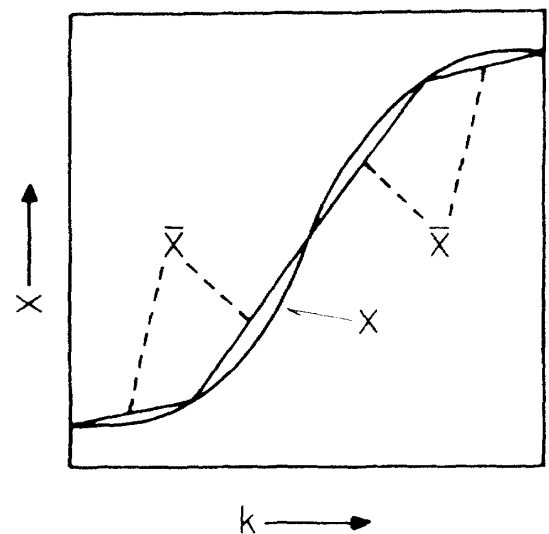
⇒ effective weights ω_{nj} for k-points.

⇒ 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:

$$\delta\omega_{\mathbf{k}n} = \sum_T \frac{1}{40} D_T(\epsilon_F) \sum_{j=1}^4 (\epsilon_{jn} - \epsilon_{\mathbf{k}n})$$

j corners (k-point) of the tetrahedron T

$D_T(\mu)$ DOS for the tetrahedron T at ϵ_F .

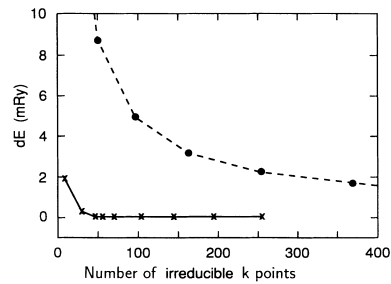
Result:

- 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

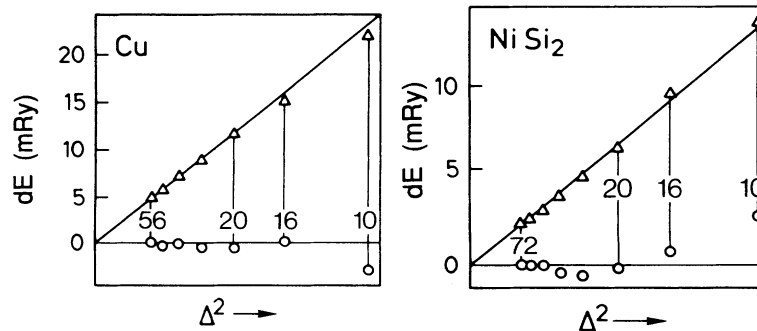
Convergence tests

(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: Monkhorst or Gammapoint (centered)

4th line: mesh parameter

5th line: 0 0 0 (shift)

mesh parameter

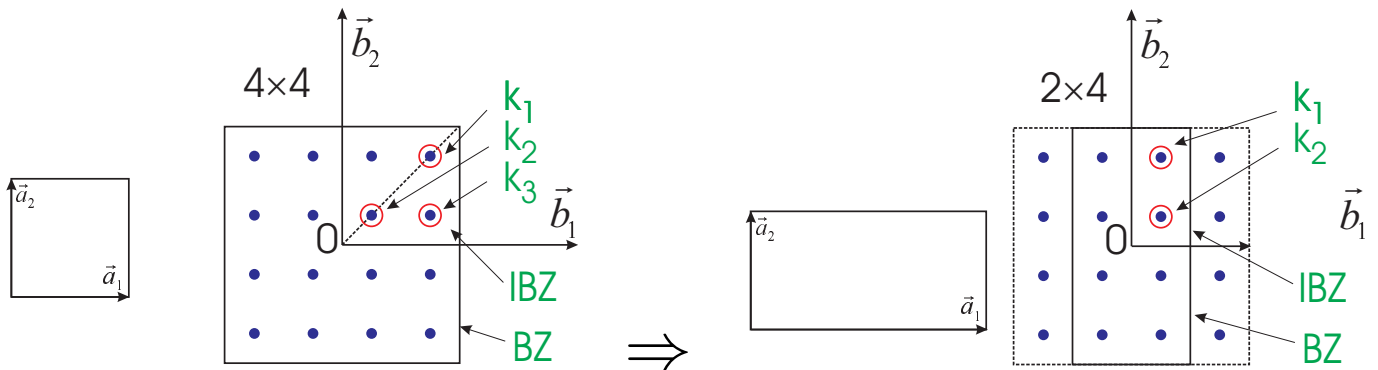
- determine the number of intersections in each direction
- longer axes in real-space \Leftrightarrow shorter axes in k-space

\Rightarrow less intersections necessary for equally spaced mesh

Consequences:

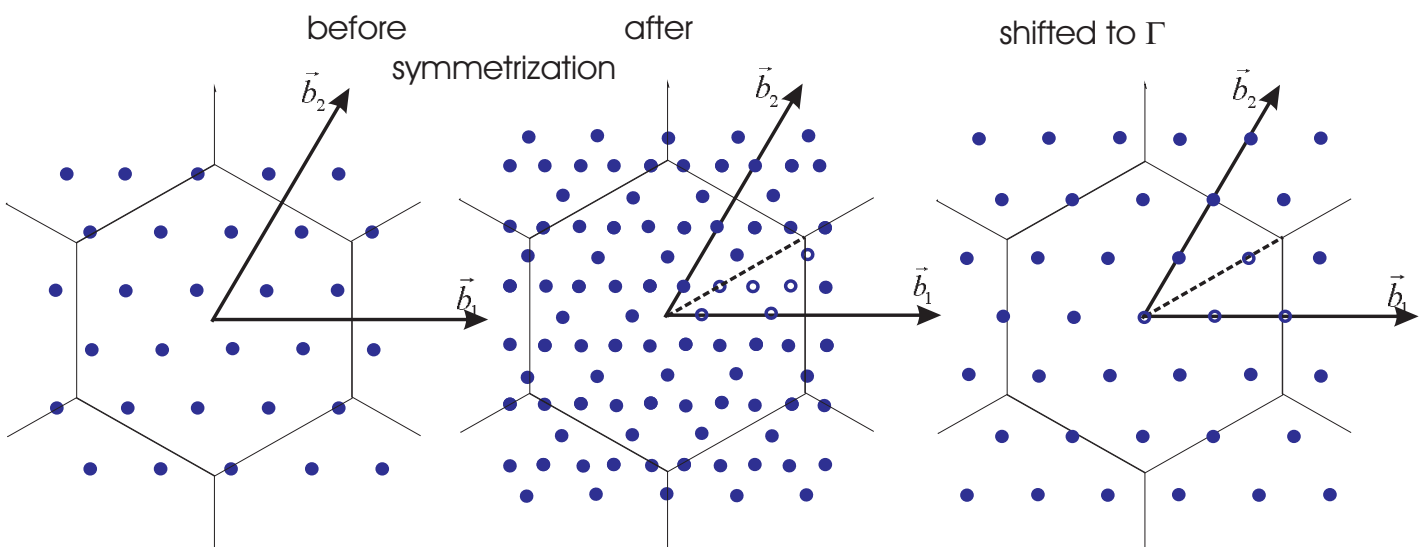
- molecules, atoms (large supercells)
 $\Rightarrow (1 \times 1 \times 1) (\equiv \Gamma)$ is enough.
- surfaces (one long direction \Rightarrow 2-D Brillouin-zone)
 $\Rightarrow (x \times y \times 1)$ for the direction corresponding to the long direction.
- "typical" values (never trust them!):
metals: $(9 \times 9 \times 9)/\text{atom}$
semiconductors: $(4 \times 4 \times 4)/\text{atom}$

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

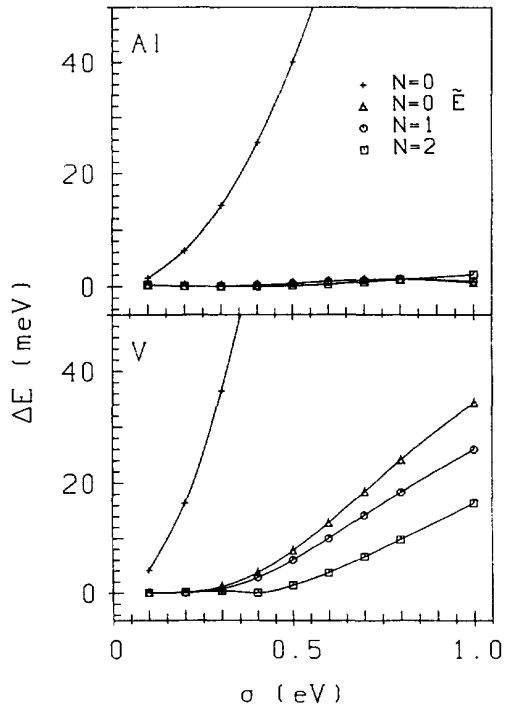
Example - hexagonal cell



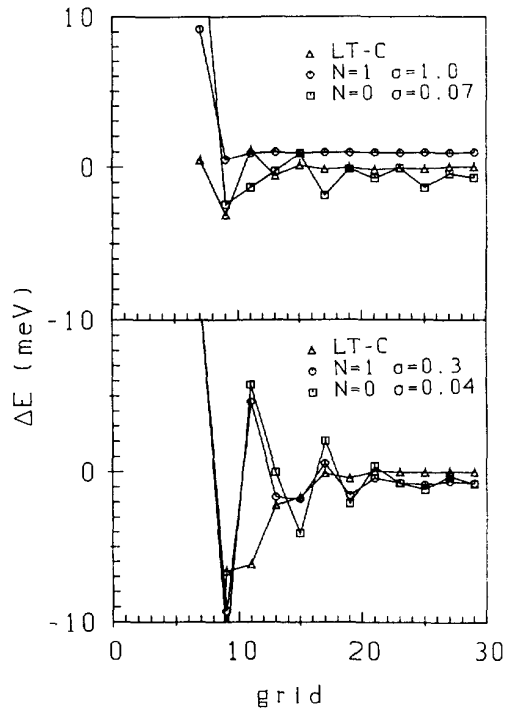
- in certain cell geometries (e.g. hexagonal cells) even meshes break the symmetry
- symmetrization results in non equally distributed k-points
- Gamma point centered mesh preserves symmetry

Convergence tests

with respect to $\sigma \dots$



\dots and number of k-points in the IBZ



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