Solids

Solids

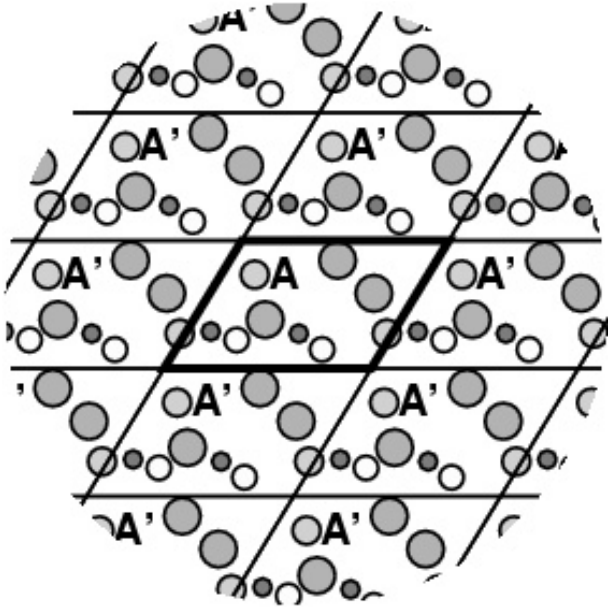
Outline

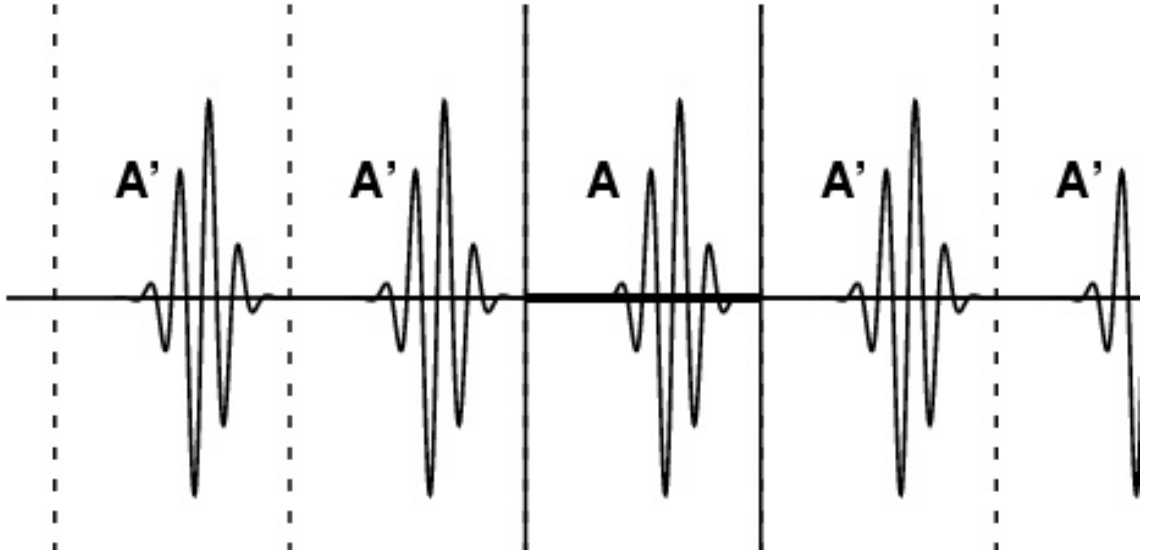
- k point sampling
- Broadening of / fractional occupation numbers
- Translations in Ewald summation

Solids

PBC

- Real materials contain $\approx 10^{23}$ atoms/cm^3
- In practical calculations $\approx 10^3$ atoms possible
- Trick: Periodic boundary conditions

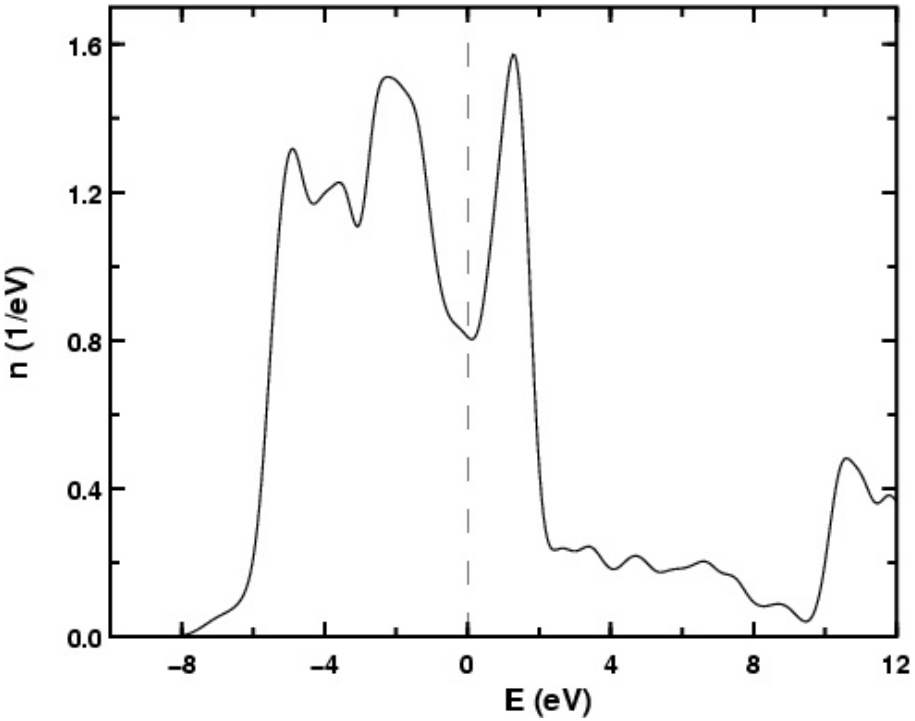


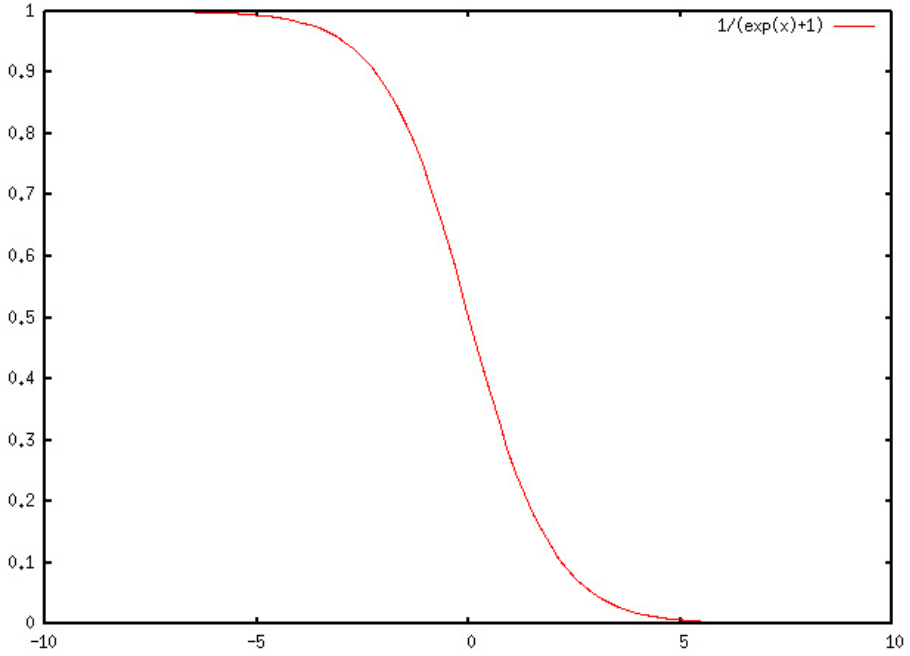


Solids

Metals

- Metals and semi-metals have a vanishing electronic band gap
- Thus both minimum-energy (low-temperature) excitations and convergence problems in achieving convergence
- Solution: Fractional occupation numbers



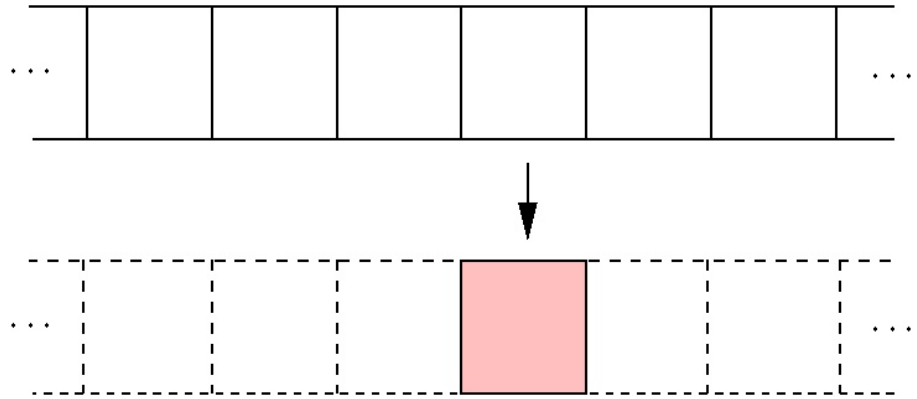


Bloch's theorem

- Bloch's theorem: The eigenstates in a periodic potential can be chosen to be

$$\boxed{\psi_{i\mathbf{k}}(\mathbf{r}) = e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} u_{i\mathbf{k}}(\mathbf{r})}$$

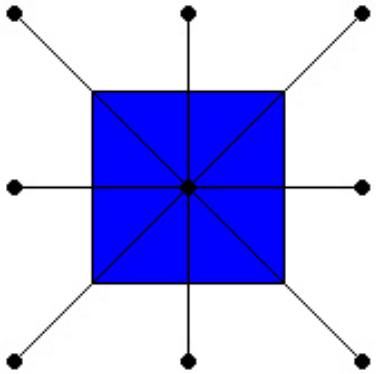
- Another way of looking it: Fold back the "infinite sum" over cells into the 1st Brillouin zone



- Integrals over whole space become integrals over the 1st Brillouin zone only:

$$\int_{\Omega} d\Omega \Rightarrow \int_{\mathbf{k}} d\mathbf{k}$$

Brillouin zone = region of space closest to the centre of the reciprocal space tha any other multiple of reciprocal lattice vectors $\mathbf{L} = i_1\mathbf{b}_1 + i_2\mathbf{b}_2 + i_3\mathbf{b}_3$



Brillouin zone integration

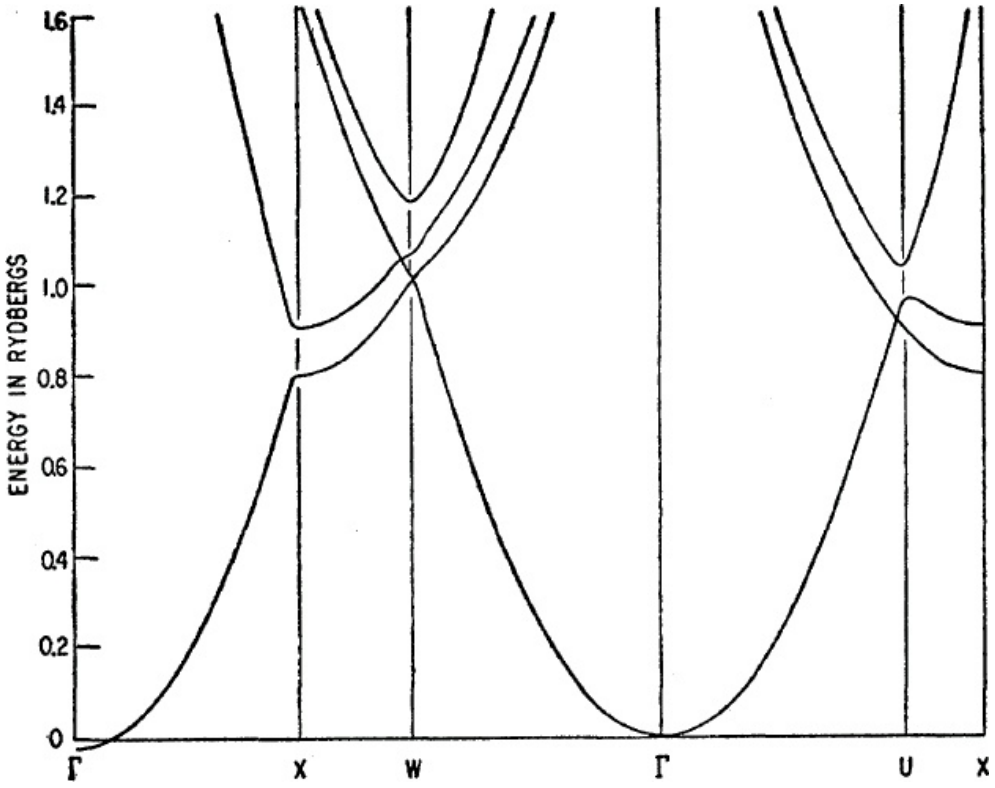
- One can reduce the integral to go over the irreducible part of the BZ only
- Different ways to perform integral $\int_{\mathbf{k}\in\mathrm{IBZ}} d\mathbf{k}$
  - (Linear) Tetrahedron method
  - Random k points (no one's using this anymore)
  - Special $\mathbf{k}$ points
    - Chadi-Cohen $\mathbf{k}$ points
    - (Extended) Cunningham $\mathbf{k}$ points (2D-hexagonal)
    - Equi-distance or Monkhorst-Pack grids

Brillouin zone integration

Discretisation

$$\int_{\mathbf{k}} d\mathbf{k} \approx \sum_{\mathbf{k}} w_{\mathbf{k}}$$

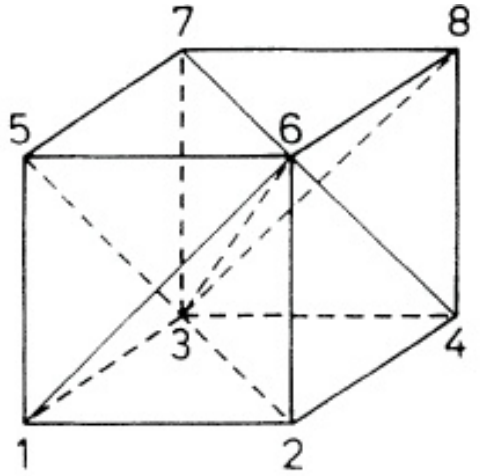
- Discretisation
- The weights are determined by the relative volume around the single $\mathbf{k}$ points

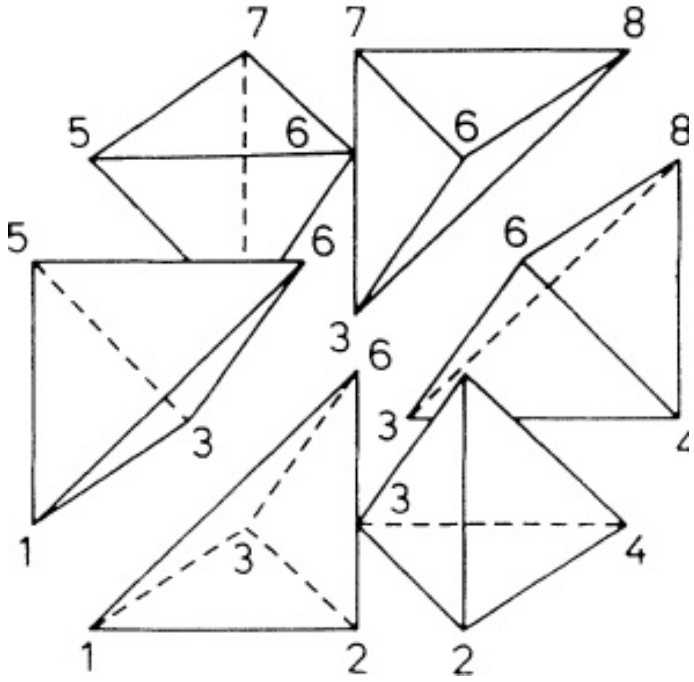


Brillouin zone integration

Linear tetrahedron method

- Divide the space into tetrahedra
- The function to be integrated is linearly interpolated within the tetrahedra
- The interpolated function is integrated

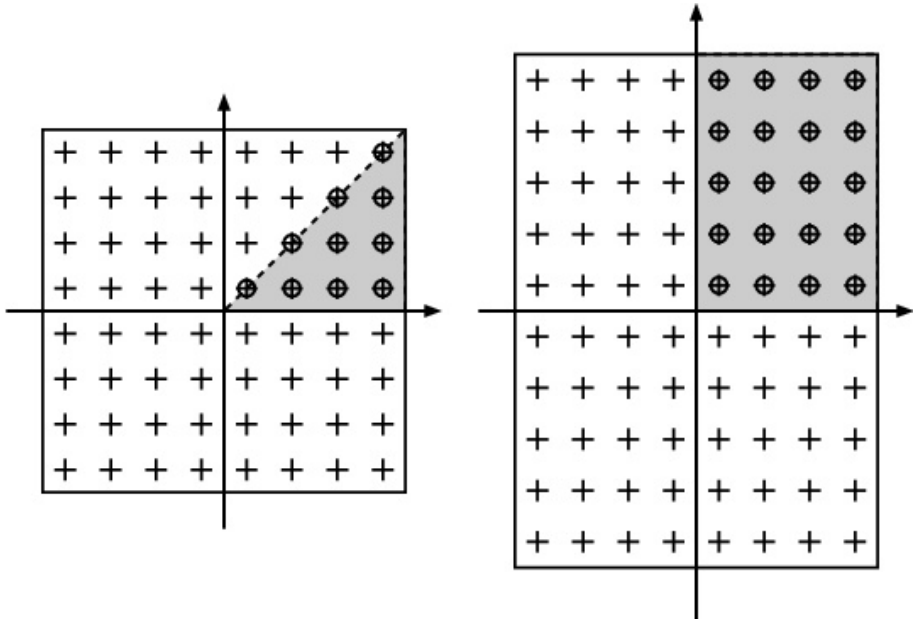




Monkhorst-Pack $\mathbf{k}$ point sets

Or, equi-distance grids

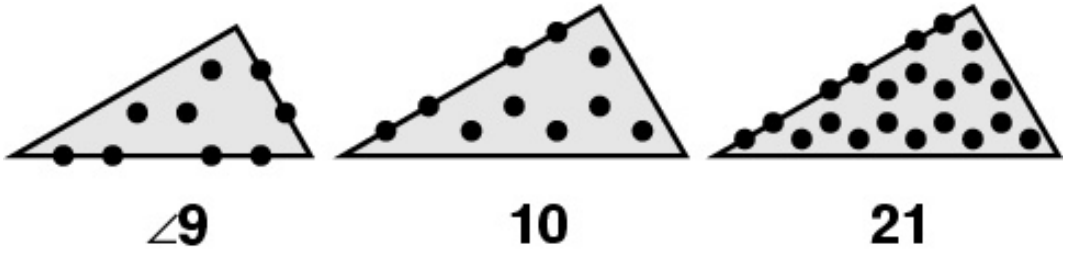
- Rectangular unit cells

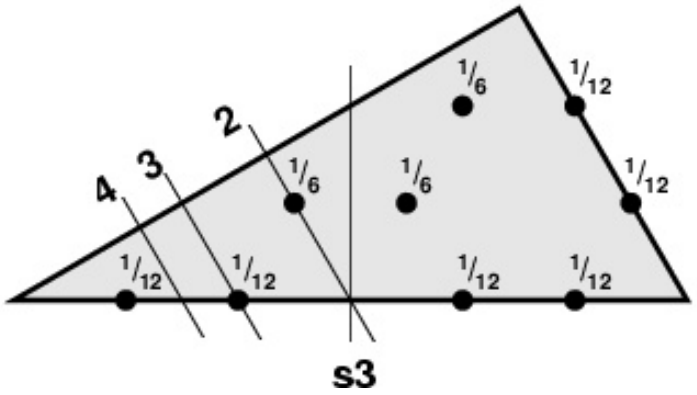


Chadi-Cohen $\mathbf{k}$ point sets

2D: (extended) Cunningham $\mathbf{k}$ point sets

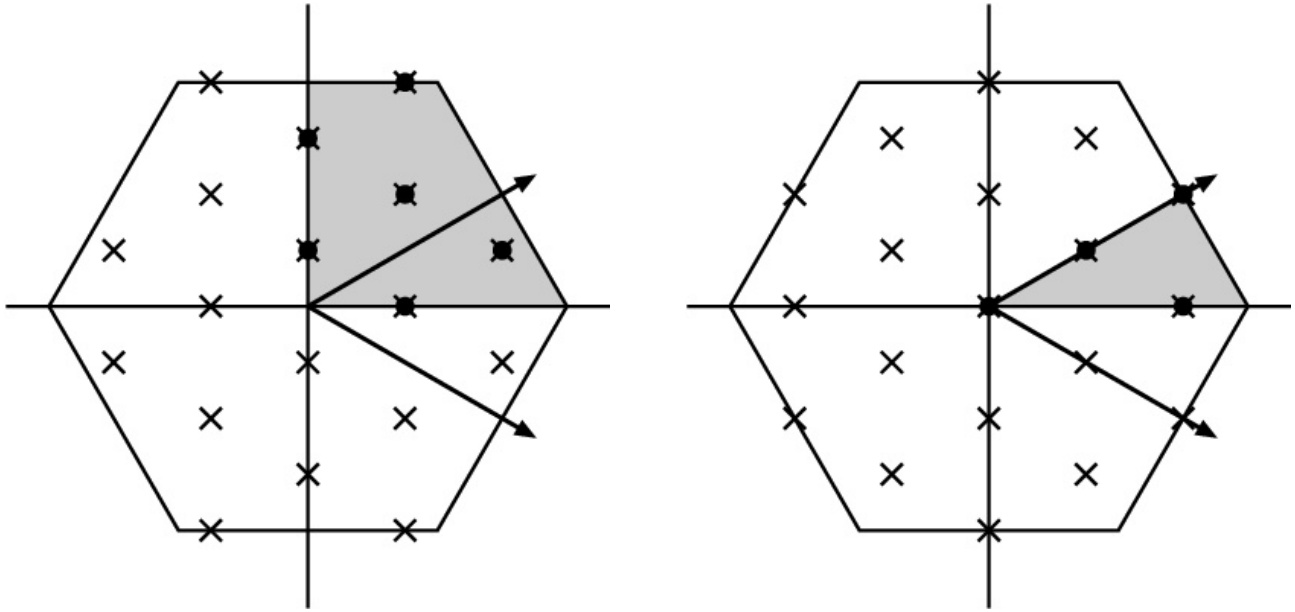
- Based on two generating vectors and their sum $\mathbf{k}_{\text{gen},1} + \mathcal{S}\mathbf{k}_{\text{gen},2}$
- In hexagonal unit cells





Hexagonal cells

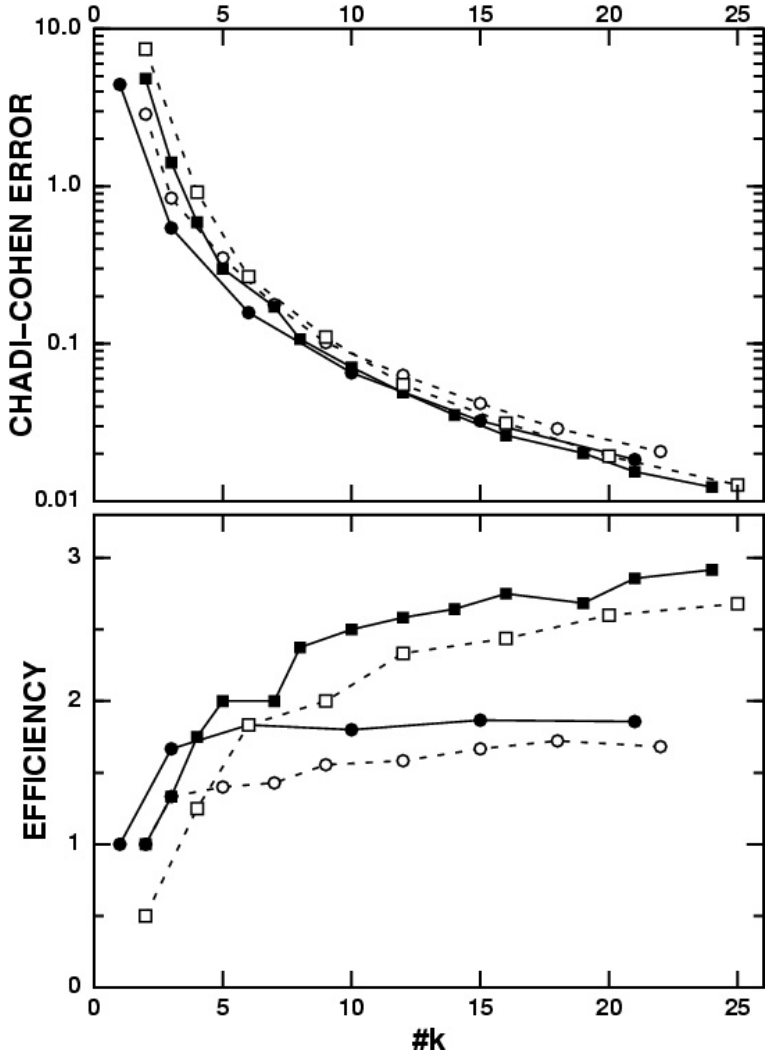
- The original Monkhorst-Pack sets always avoided point Γ; however this leads to anisotropic sampling (left). The shifted set (right), with one point at Γ, does not have this problem



- Cunningham sets do not suffer from the problem

k set test

- Mathematical test for the quality of a given set



Γ-only set

- Most of CPMD simulations use the Γ-point-only sampling
- This is justified if ...
  - the system doesn't have any dispersion, *i. e.* interaction between different cells is small
  - the cell is large enough so that even the Γ point is sampled many times
  - the system is disordered
- If you use it, try at least to estimate the error

Broadening of occupation numbers

Or, fractional occupation numbers

- The occupation numbers close to the Fermi energy are set to values between $[0 \ldots 1]$
- Thus the electrons are "at finite temperature", or excited (in a mean-field sense)
- Mermin functional is available for real temperatures
- Otherwise one has to correct for the change in energy and other quantities because of the change in the system

Fermi-Dirac broadening

- Occupation numbers

$$f\left(\frac{\varepsilon - E_F}{\sigma}\right) = \left[\exp\left(\frac{\varepsilon - E_F}{\sigma}\right) + 1\right]^{-1}$$

- New variational "free energy"

$$F = E - \sum_{i\mathbf{k}} \sigma S\left(f_{i\mathbf{k}}\right)$$

- Entropy

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

- Smearing parameter

$$\sigma = k_B T$$

  In practise $\sigma \approx 0.05 \ldots 0.2$ eV

- For more accurate energy "extrapolate to 0 K":

$$E\left(T \to 0\right) \approx \frac{1}{2}\left(F + E\right)$$

Gaussian smearing

- Occupation numbers

$$f\left(\frac{\varepsilon - E_F}{\sigma}\right) = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{\varepsilon - E_F}{\sigma}\right)\right]$$

- Entropy and free energy cannot be written in terms of f

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

- Smearing parameter σ has no physical interpretation

Other smearing schemes

- Methfessel & Paxton
  - Expansion of step function in a complete set of orthogonal functions
- "Cold" smearing
  - Not symmetric around Fermi energy
- Both can yield negative occupation numbers

Translations in Ewald sum

- Overlap between nuclear Gaussian's in electrostatic energy:

$$E_{\text{ovrl}} = E'_{I,J} \sum_{\mathbf{L}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|} \text{erfc}\left(\frac{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|}{\sqrt{R_I^{c2} + R_I^{c2}}} \right)$$

  - The default in `CPMD` is to use the minimum convention, *i. e.* only the closest neighbour is included
  - More $\mathbf{L}$'s can be included using keyword '`TESR`'

Free energy functional

- `CPMD` contains a free energy functional for calculating metals

$$F\left(N,V,T\left[n\left(\mathbf{r}\right)\right]\right)=-2k_BT\sum_i \ln\left[1+e^{-\beta(\varepsilon-\mu)}\right]+\mu N-\frac{1}{2}E_H-\int_{\mathbf{r}} v_{xc}\left(\mathbf{r}\right)\, n\left(\mathbf{r}\right)\, d\mathbf{r}+E_{xc}$$

- Requires the usage of iterative diagonalisation (Lanczos or Davidson)

- If using, please remember the mixing

Solids: Summary

- The idea of k points:
  - Replace the infinite volume with integral over the 1st Brillouin zone only
  - Replace the integral by weighted sum
- The occupation numbers around the Fermi energy are broadened in order to
  - simulate temperature
  - improve convergence
- In `CPMD FREE ENERGY FUNCTIONAL` for calculating metals