"k-points"
or Brillouin Zone Sums
In Electronic Structure Calculations

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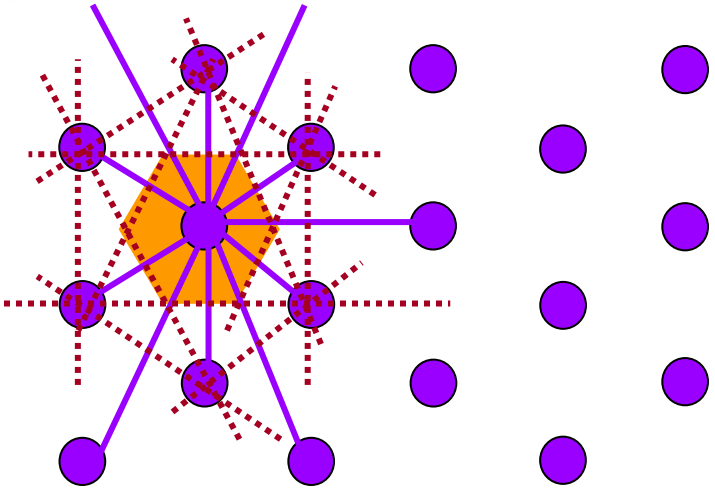
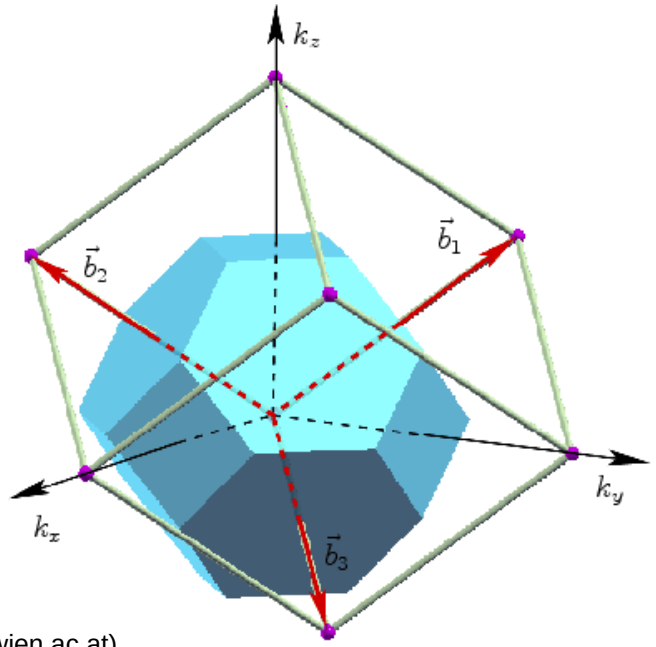
First Brillouin Zone

- Wigner-Seitz cell in reciprocal space.



(Or could choose to use parallelepiped defined by $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$)

e.g., 1st BZ for FCC lattice →



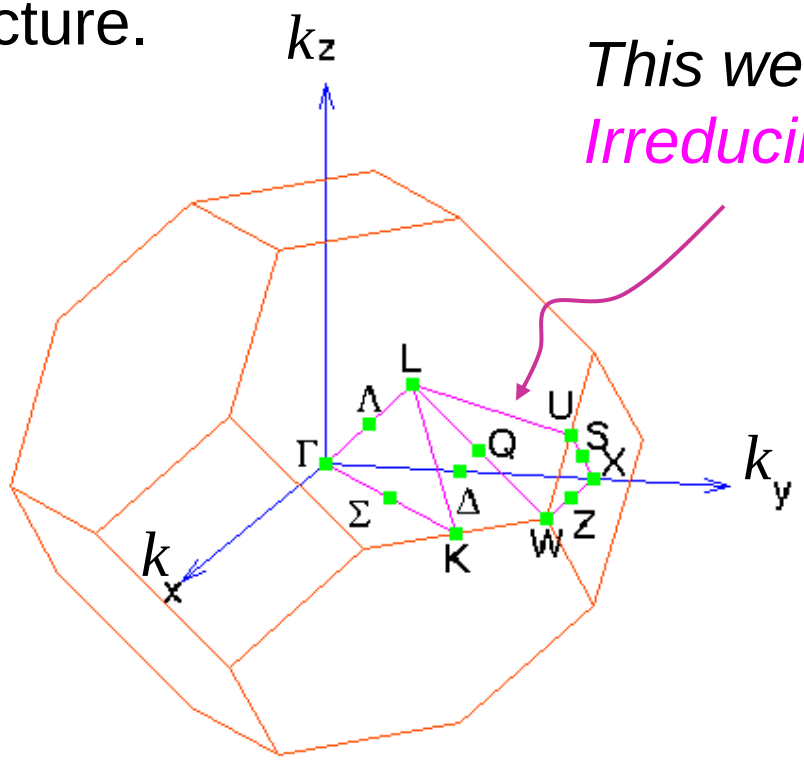
(www.iue.tuwien.ac.at)

Irreducible Brillouin Zone

- Smallest wedge of the 1st BZ such that any wave-vector **k** in the 1st BZ can be obtained from a wave-vector **k** in the IBZ by performing symmetry operations of the crystal structure.

This wedge is the Irreducible Brillouin zone.

e.g., for FCC lattice



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Brillouin Zone Sums

- Many quantities (e.g., density, total energy) involve integrals over **k:**

$$\langle P \rangle = \frac{\Omega}{(2\pi)^3} \sum_{n\,occ} \int_{BZ} P_n(\mathbf{k}) d^3k$$

- **k** (wave-vector) is in the first Brillouin zone,
- n (band index) runs over occupied manifold.
- In principle, need infinite number of **k**'s.
- In practice, sum over a finite number: BZ "Sampling".

Brillouin Zone Sums

- In practice, sum over a finite number: BZ "Sampling".

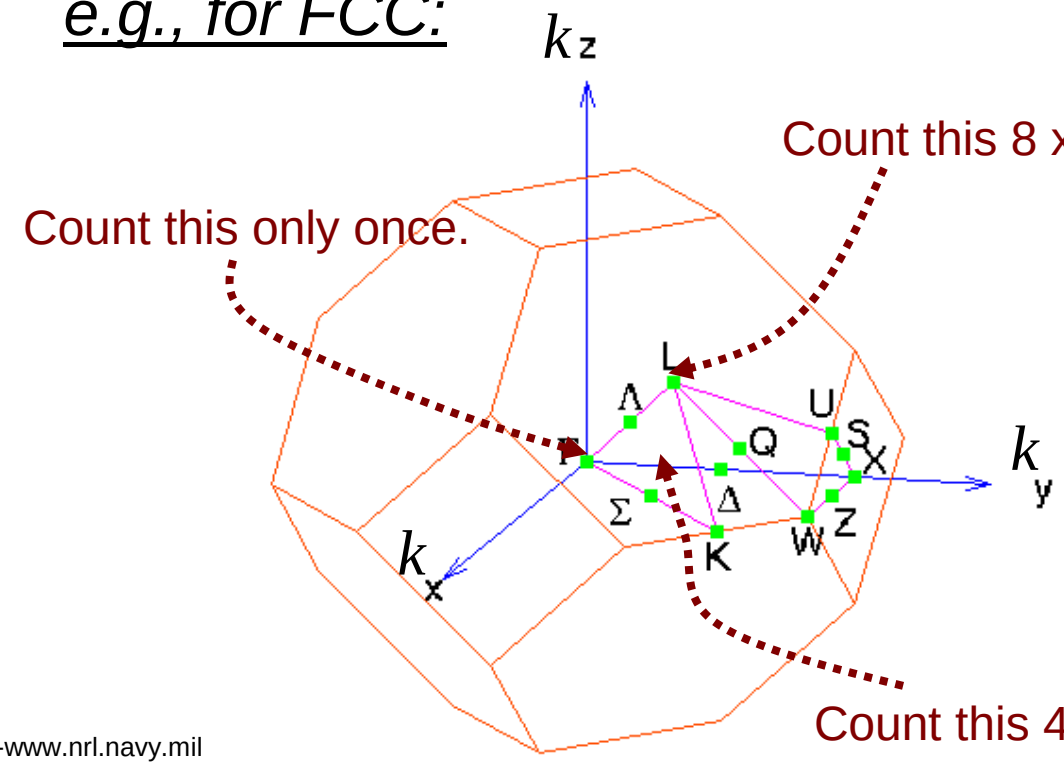
$$\langle P \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\substack{\mathbf{k} \in BZ \\ n\ occ}} P_n(\mathbf{k})$$

- For computational reasons, want # $\mathbf{k}$'s to be small.
- Number needed depends on band structure.
- Need to test convergence w.r.t. k-point sampling.

Using the Irreducible BZ; Weights

- Need not sum over **k**'s in entire BZ; can restrict to Irreducible BZ, with appropriate weights.

e.g., for FCC:



$$\langle P \rangle = \sum_{\substack{\mathbf{k} \in IBZ \\ n\ occ}} P_n(\mathbf{k}) w(\mathbf{k})$$

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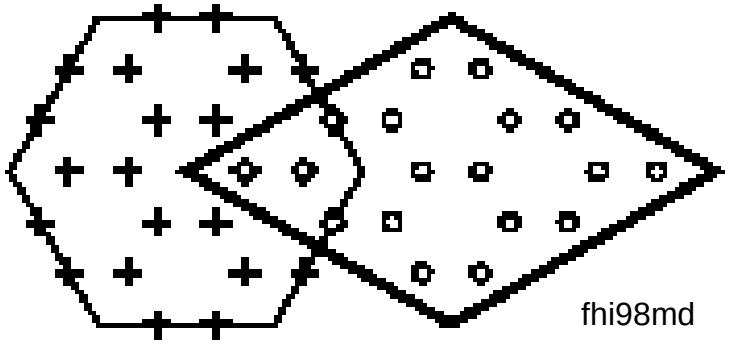
Special Points

- Can we use just one k-point?
- Just Γ (zone centre)? Usually bad choice!
- "Mean Value point": Baldereschi: Phys. Rev. B 7 5212 (1973).

- A few k-points chosen to give optimally fast convergence.
- Chadi and Cohen: Phys. Rev. B 8 5747 (1973).
- Cunningham: Phys. Rev. B 10, 4988 (1974).

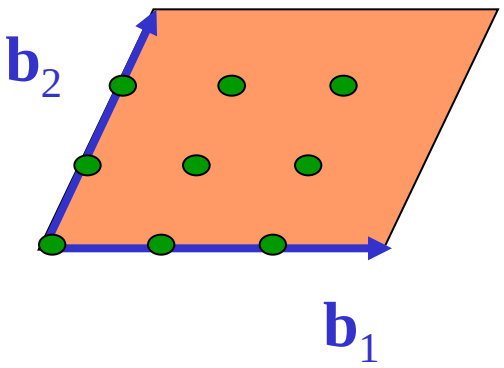
e.g. for FCC(111) surface
(2-D hexagonal lattice)



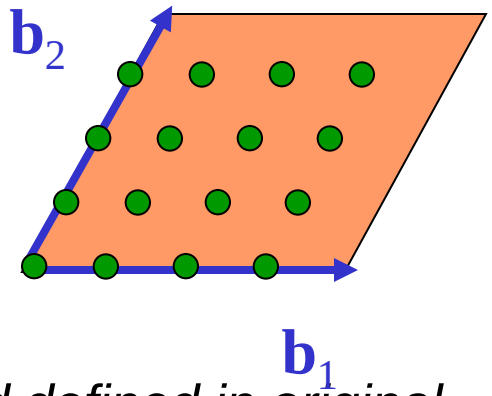
Monkhorst-Pack k-points

- Uniformly spaced grid of **`nk1 × nk2 × nk3`** points in 1st BZ:

nk1=nk2=3



nk1=nk2=4

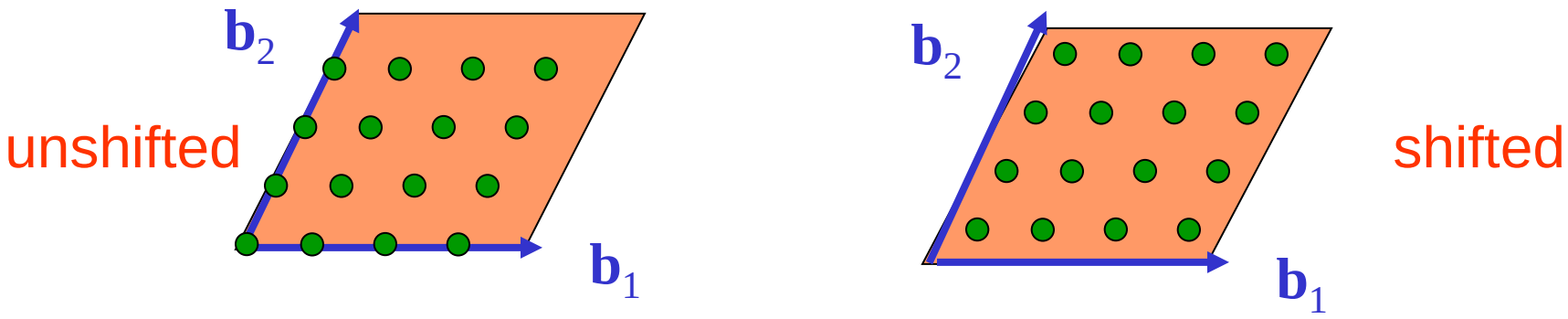


- *Note: This is slightly different from way grid defined in original paper [Phys. Rev. B **13** 5188 (1976)] where odd/even grids include/don't include* the zone center Γ.

(Paper cited 10,279 times so far!)

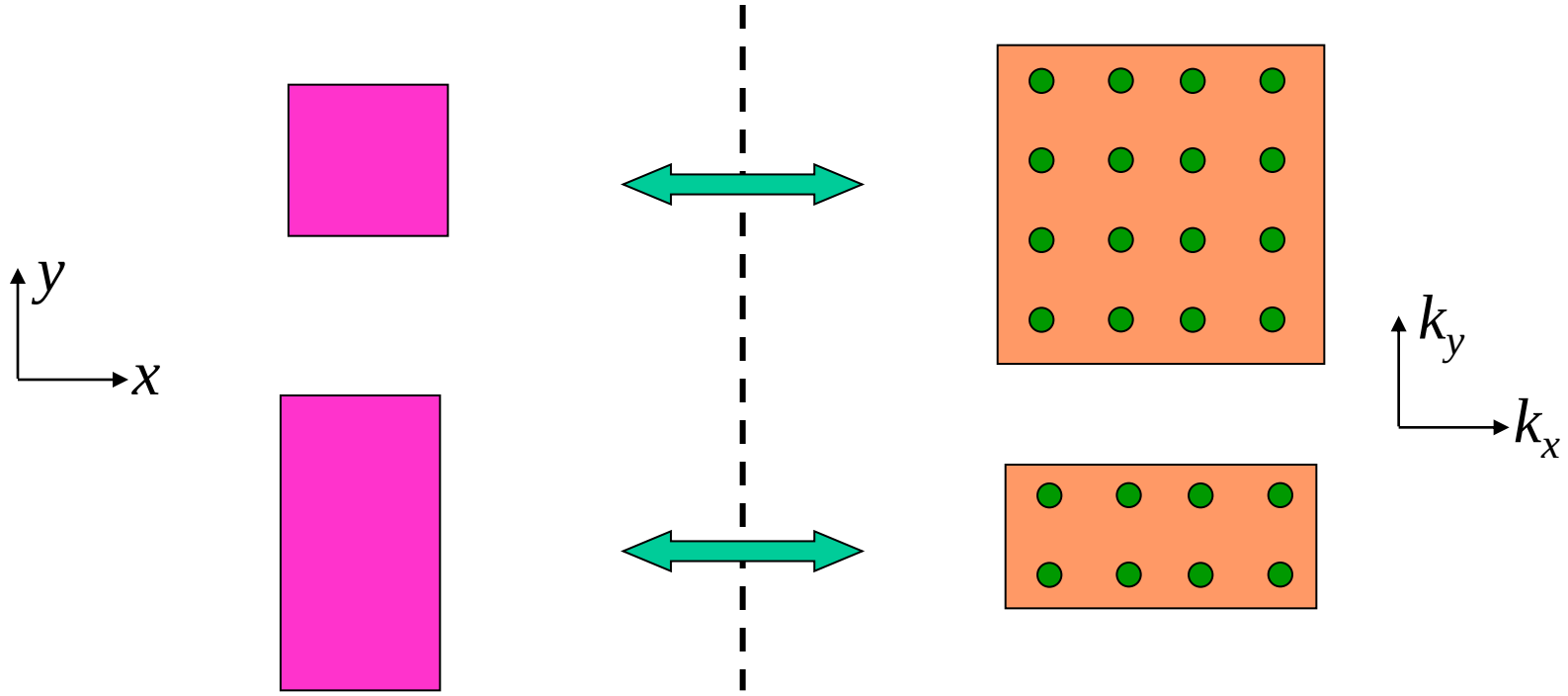
Unshifted & Shifted Grids

- Can choose to shift grid so that it is not centered at Γ.
- Can get comparable accuracy with fewer k-points in IBZ.
- For some Bravais lattice types, shifted grid may not have full symmetry.



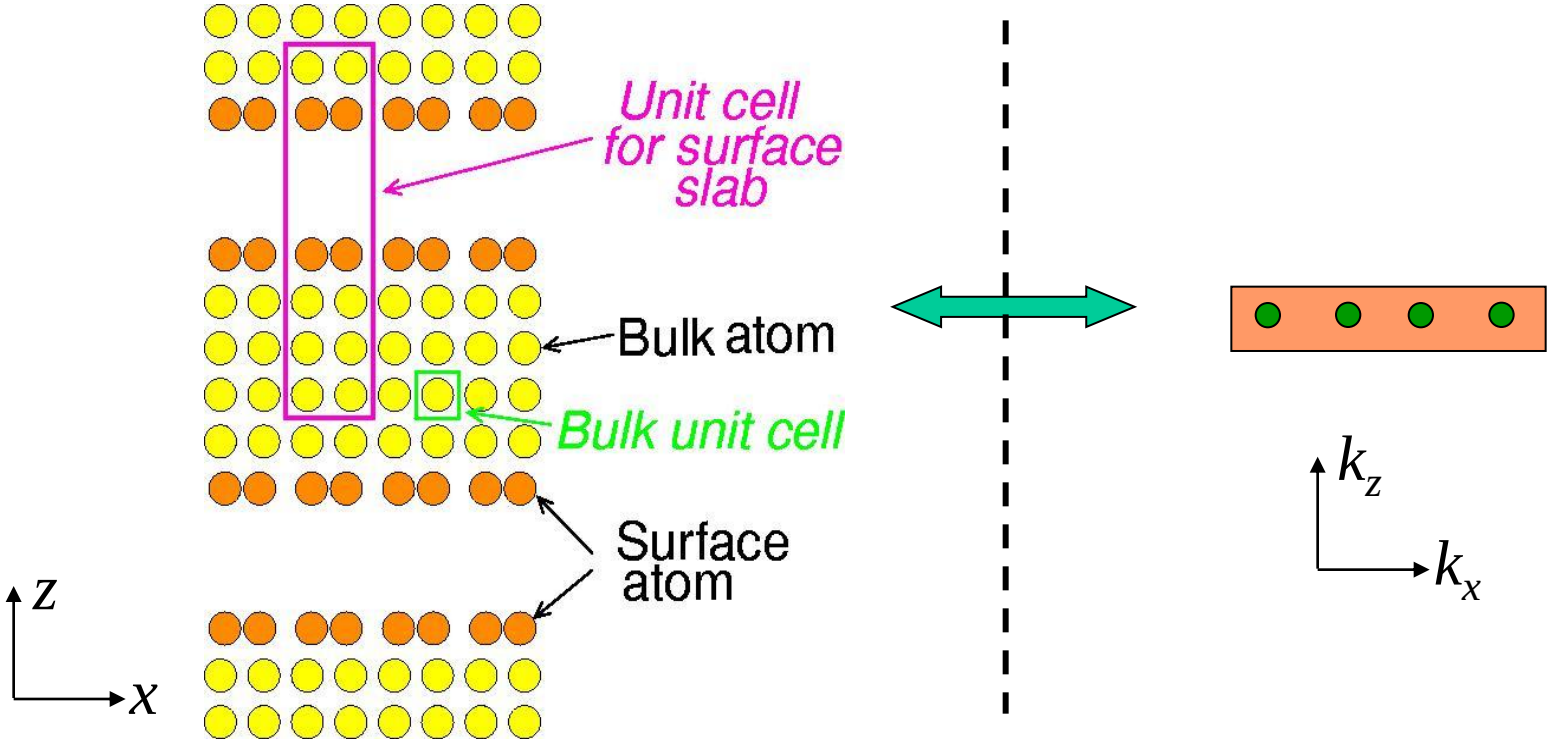
Choosing Grid Divisions

- Space grid in a way (approximately) commensurate with length of primitive reciprocal lattice vectors **b**'s.
- Remember that dimensions in reciprocal space are the inverse of the dimensions in real space!



Choosing Grid Divisions

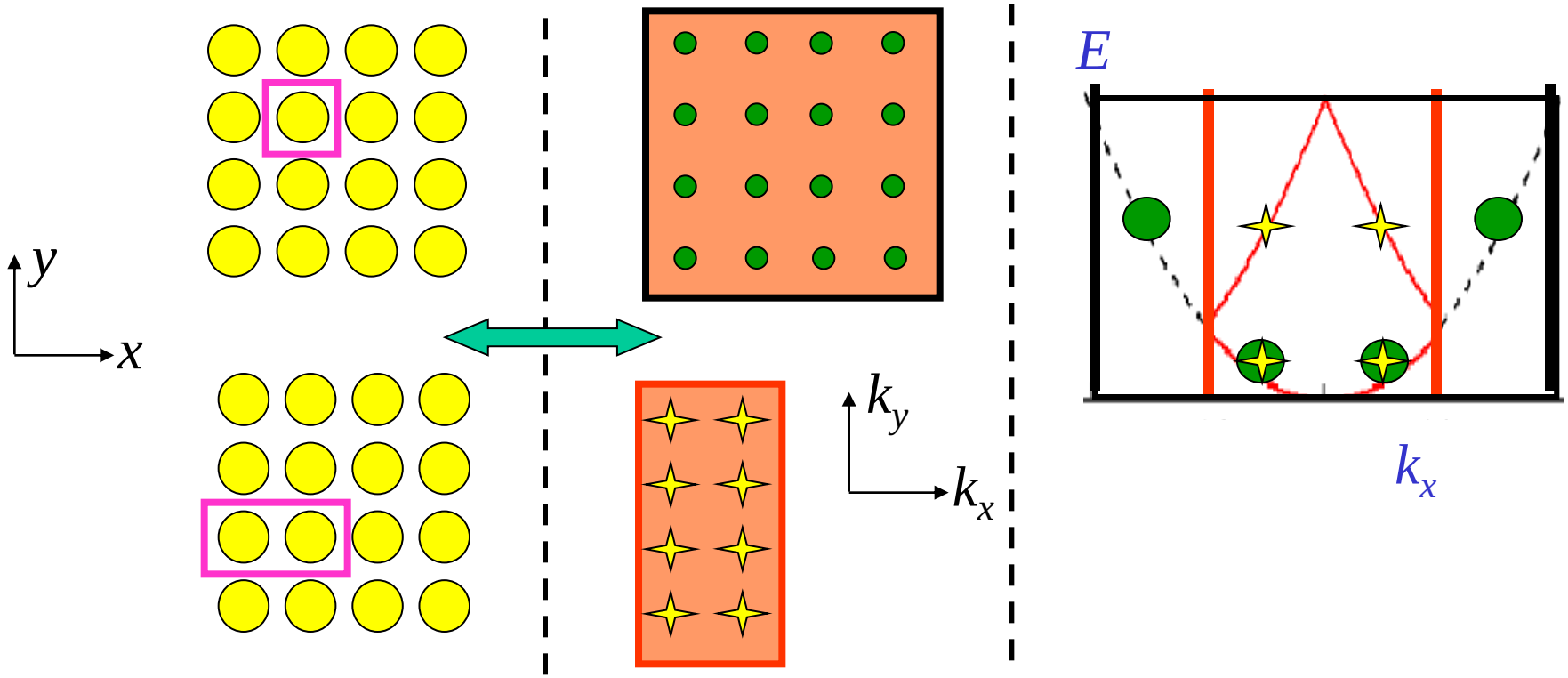
- For artificially periodic supercells, choose only 1 division along the dimensions that have been extended (in real space) by introducing vacuum region.



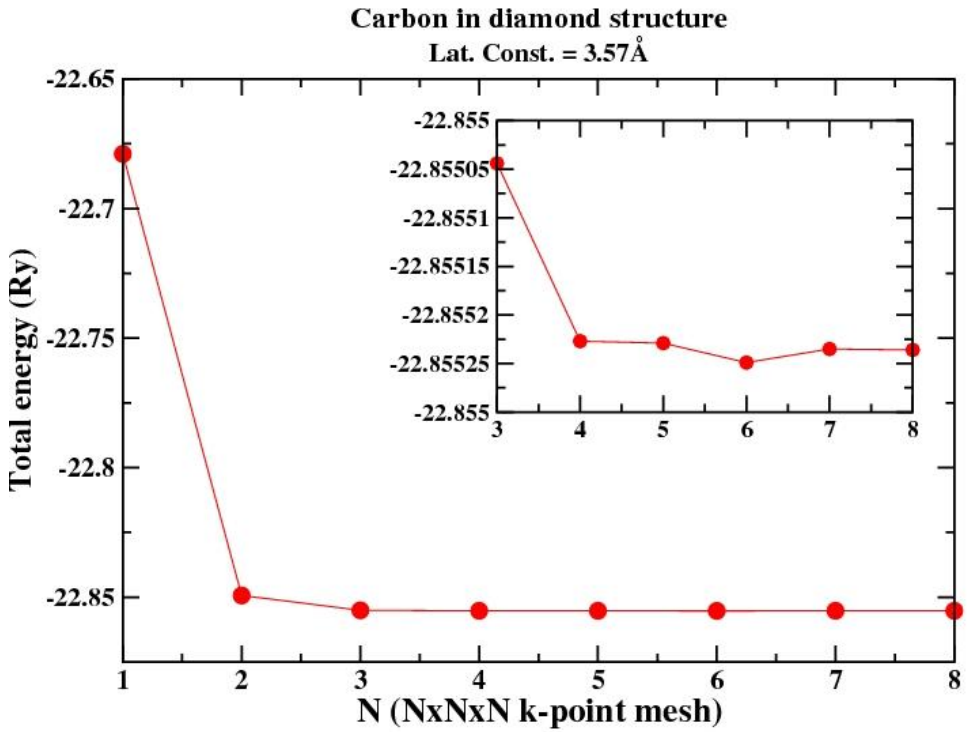
Reciprocity of Supercells & BZ Sampling

Increase supercell in real space by a factor N_i along $\boldsymbol{a}_i$

EXACTLY same results obtained by reducing # divisions in k mesh (in the new smaller BZ) by factor N_i .



Convergence wrt BZ sampling



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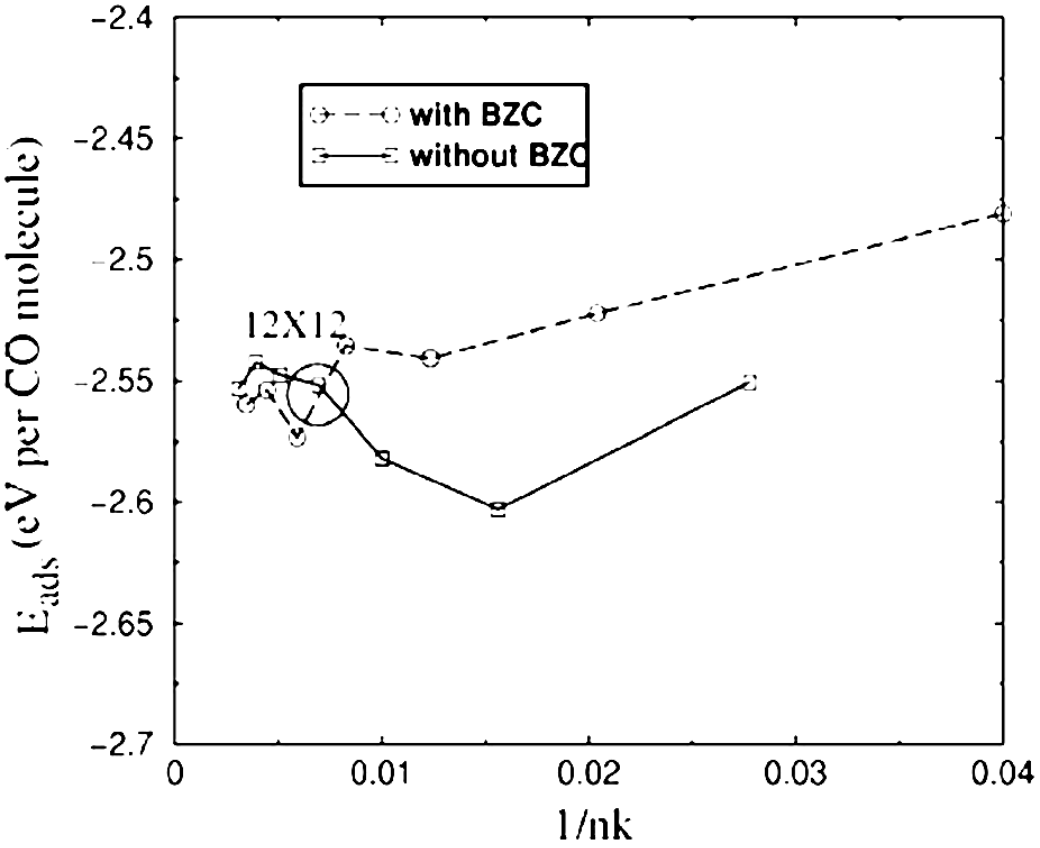
Note: Differences in energy usually converge faster than absolute value of total energy because of error cancellation (if supercells & k-points are identical or commensurate).

Convergence wrt BZ sampling

e.g., Adsorption energy of CO on Ir(100):



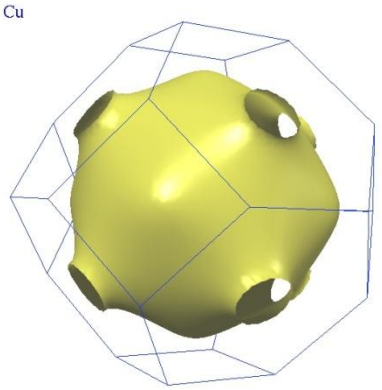
Ghosh, Narasimhan, Jenkins & King, J. Chem. Phys. **126** 244701 (2007).

Problems with Metals

- Recall:

$$\langle P \rangle = \frac{\Omega}{(2\pi)^3} \sum_{n\ occ} \int_{BZ} P_n(\mathbf{k}) d^3k$$

- For metals, at T=0, this corresponds to (for highest band) an integral over all wave-vectors contained within the Fermi surface, i.e., for highest band, sharp discontinuity in k-space between occupied and unoccupied states…need many k-points to reproduce this accurately.
- Also can lead to scf convergence problems because of band-crossings above/below Fermi level.



Fermi Surface of Cu
iramis.cea.fr

Problems with Metals

The basic problem is that anything with sharp edges or features can't be reproduced well if it is sampled coarsely…

…So smear out the quantity we are sampling into something that can be sampled coarsely…but of course…the procedure of smearing out may lead to errors…

A Smear Campaign!

- Problems arise because of sharp discontinuity at Fermi surface / Fermi energy.
- "Smear" this out using a smooth operator!
- Will now converge faster w.r.t. number of k-points (but not necessarily to the right answer!)
- The larger the smearing, the quicker the convergence w.r.t. number of k-points, but the greater the error introduced.

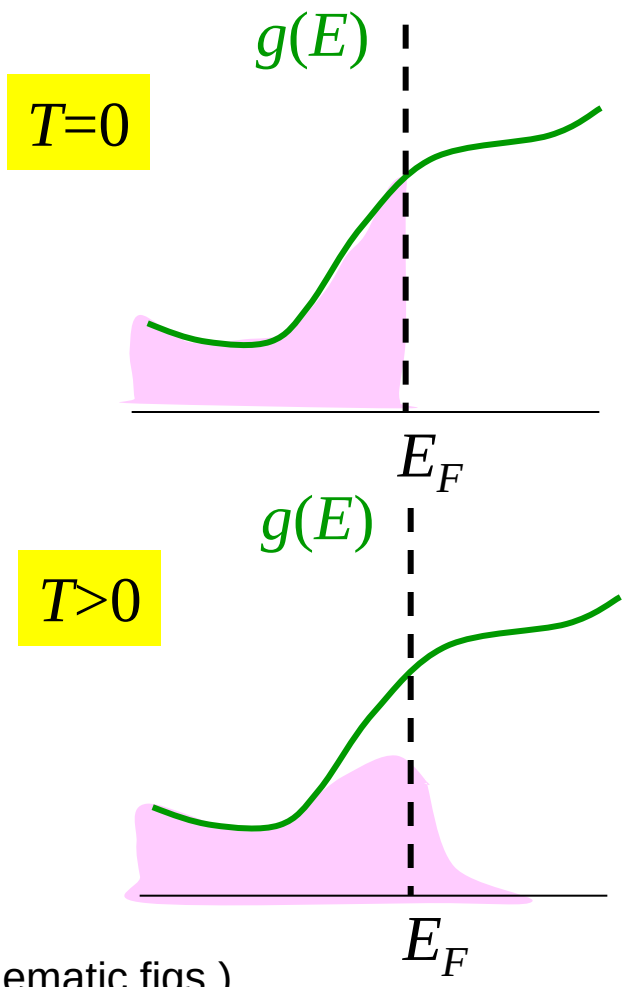
PhD Comics

Fermi-Dirac Smearing

- Recall that the Fermi surface, which is sharply defined at T=0, becomes fuzzy as T increased.
- One way of smearing: occupy with Fermi-Dirac distribution for a (fictitious) temperature T > 0.

$$f(E) = \frac{1}{e^{\left(\frac{E-\mu}{\sigma}\right)}+1}$$

$$\sigma = k_B T$$



(schematic figs.)

The Free Energy

- When occupying with a finite T distribution, what is variational (minimal) w.r.t. wavefunctions and occupations is not E but $F=E-TS$

$$S = -2k_B \sum_i \left[f_i \ln f_i + (1 - f_i) \ln(1 - f_i) \right]$$

- What we actually want is $E(\sigma \to 0)$
- $E(\sigma \to 0) = ½ (F+E)$ (deviation $O(T^3)$)

Mermin, Phys. Rev. **137** A1441 (1965).
Gillan, J. Phys. Condens. Matter **1** 689 (1989).

Gaussian Smearing

- Think of the step function as an integral of δ-fn.
- Replace sharp δ-fn. by smooth gaussian….

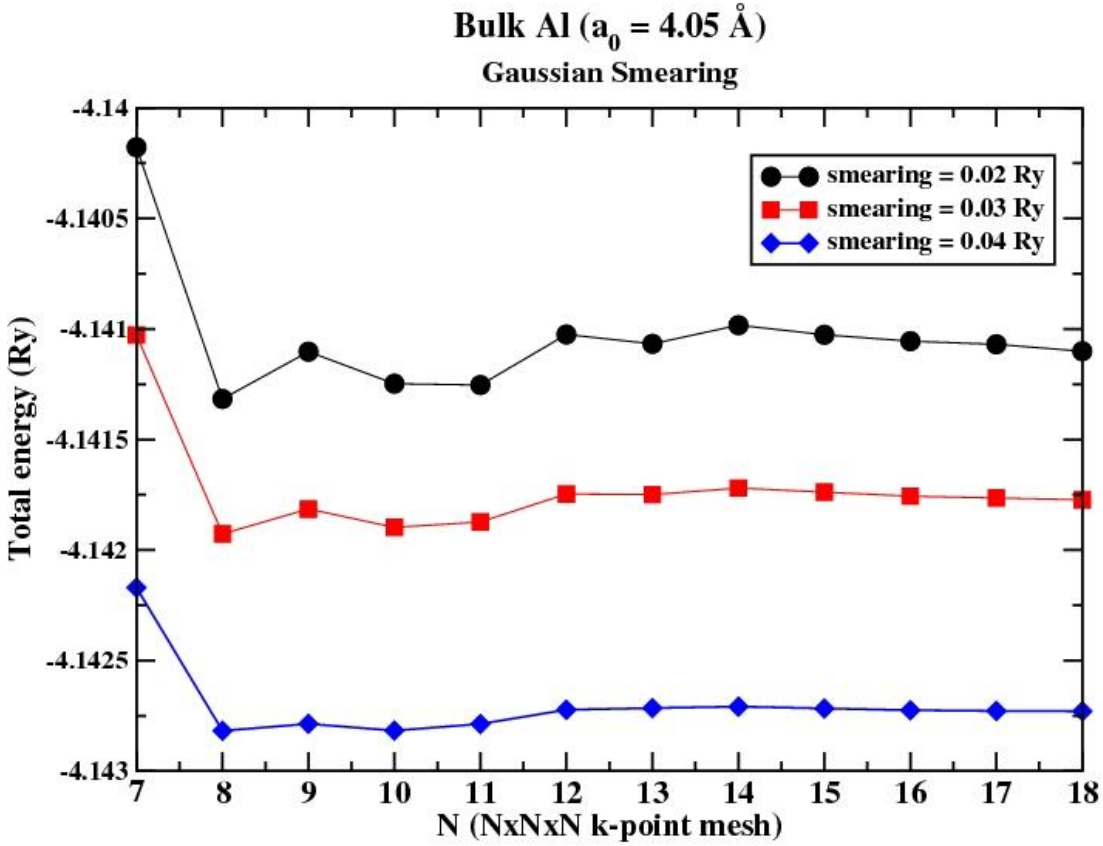
$$f(E) = \frac{1}{2}\left[1 - \text{erf}\left(\frac{E - \mu}{\sigma}\right)\right]$$

(this is what you get if you integrate a Gaussian)

- Now have a generalized free energy …E-TS, where S is a generalized entropy term.
- Converges faster (w.r.t. k-mesh) than Fermi-Dirac.
- Problem: need not converge to the right value, can get errors in forces.
- Want: fast convergence w.r.t. k-mesh to right answer!

Convergence wrt grid & smearing

- Gaussian smearing:



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Better Smearing Functions

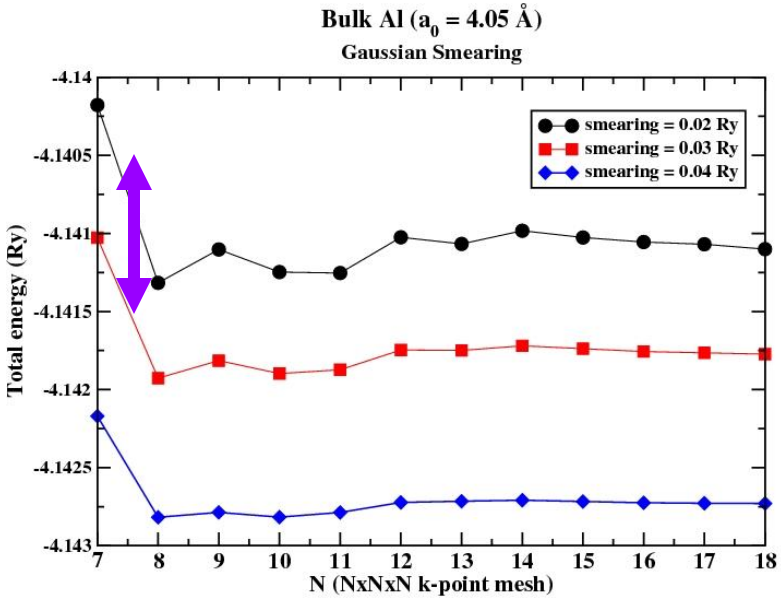
- Methfessel & Paxton:
- Can have a successive series of better (but smooth) approximations to the step function.
- E converges fast [wrt σ] to $E(\sigma \rightarrow 0)$

- Marzari & Vanderbilt:
- Unlike Methfessel-Paxton, don't have negative occupancies.

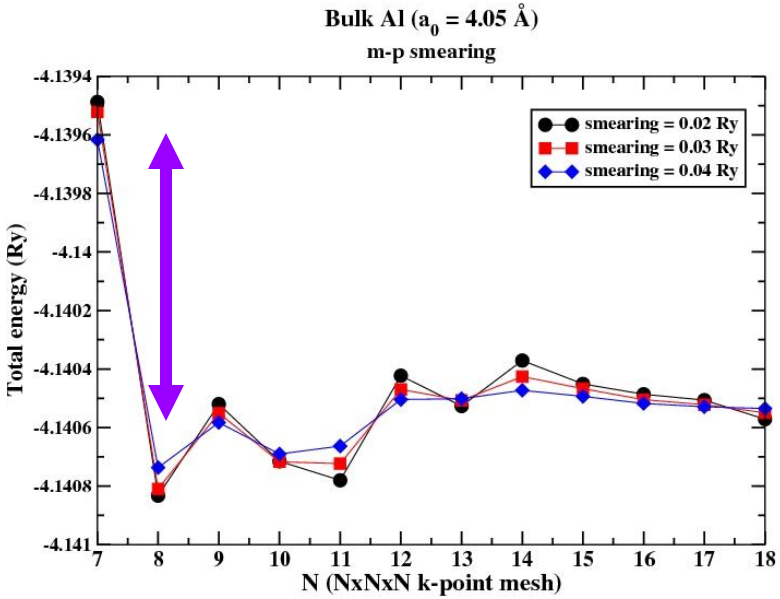
Methfessel & Paxton, Phys. Rev. B **40** 3616 (1989).
Marzari & Vanderbilt, Phys Rev. Lett. **82**, 3296 (1999).

Convergence wrt grid & smearing

- Gaussian:



- Methfessel-Paxton:



represents an energy difference of 1 mRy

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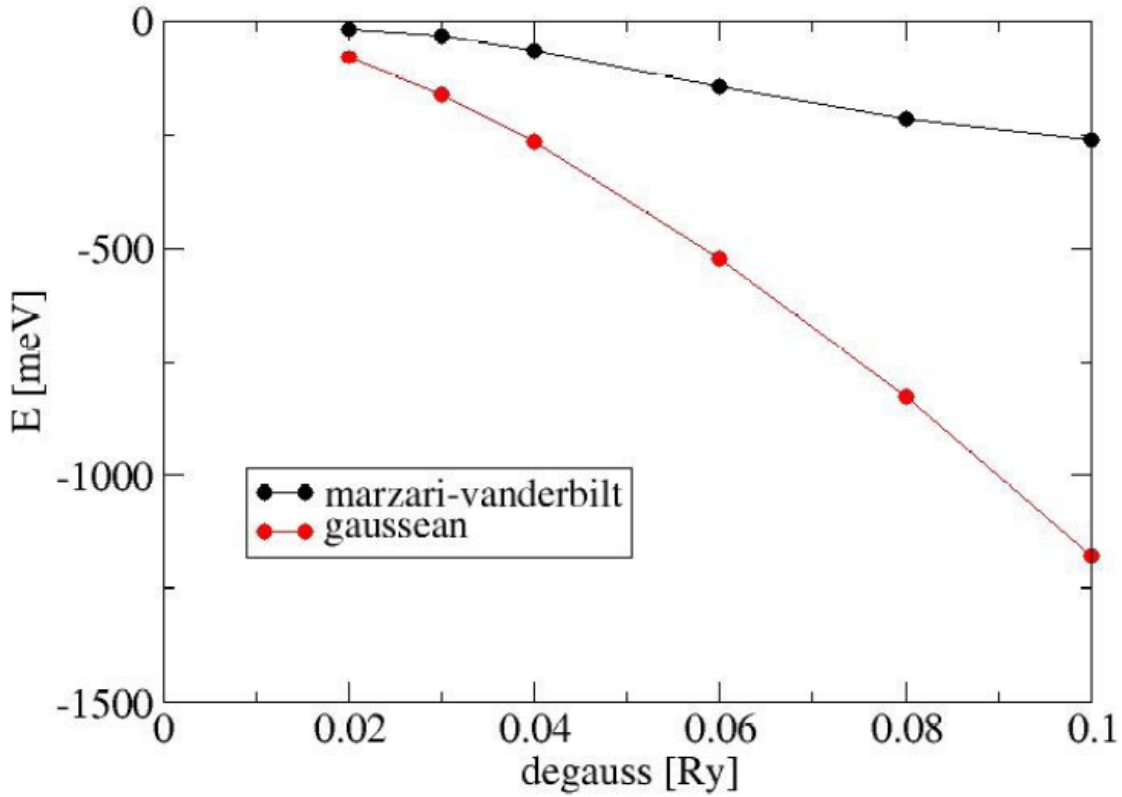
Convergence wrt k-points & smearing width

e.g., for bcc Fe, using 14 ×14 × 14 grid:



R. Gebauer

Smearing for Molecules

- Consider a molecule where HOMO is multiply degenerate and only partially occupied.
- If we don't permit fractional occupancies…the code will occupy only one (or some) of the degenerate states, resulting in wrong symmetry.
- Smearing will fix this problem.

Summary

- For extended systems, need to sum over BZ.
- Smaller the cell in real space, larger # k-points needed.
- Always need to test for convergence wrt k-points.
- More k-points needed for metals than insulators.
- Problems with metals can be aided by “smearing”.
- All of this is true for all DFT codes (not special for plane waves & pseudopotentials).