

“k-points” or Brillouin Zone Sums In Electronic Structure Calculations

Shobhana Narasimhan

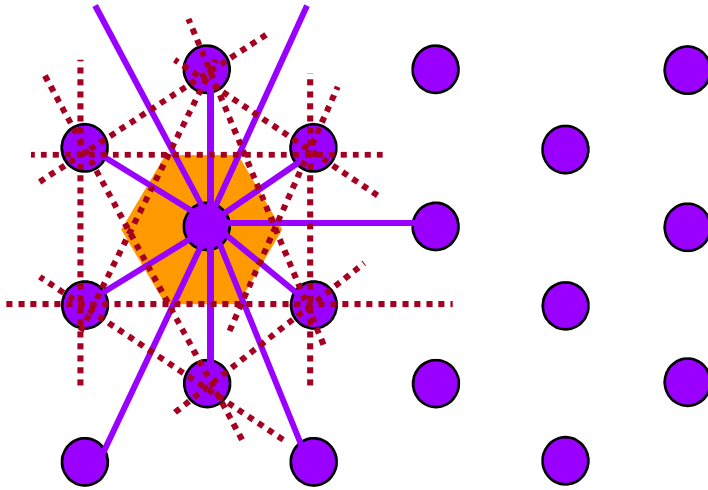
JNCASR, Bangalore, India

shobhana@jncasr.ac.in



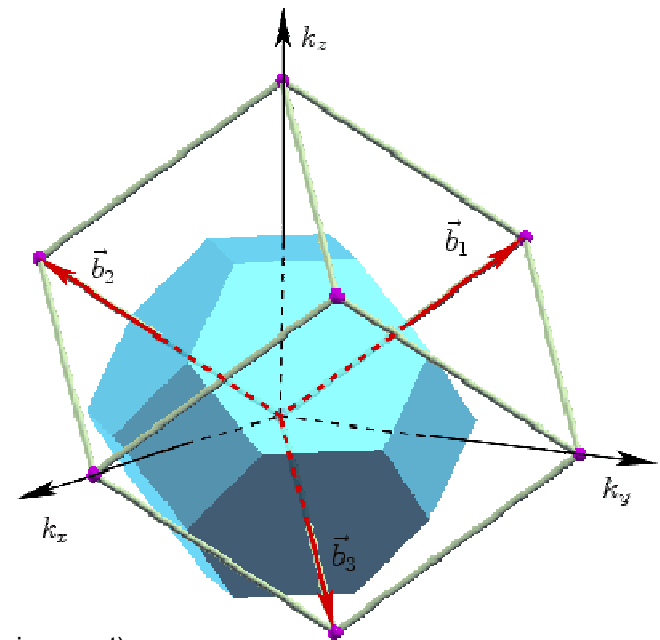
First Brillouin Zone

- 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 →



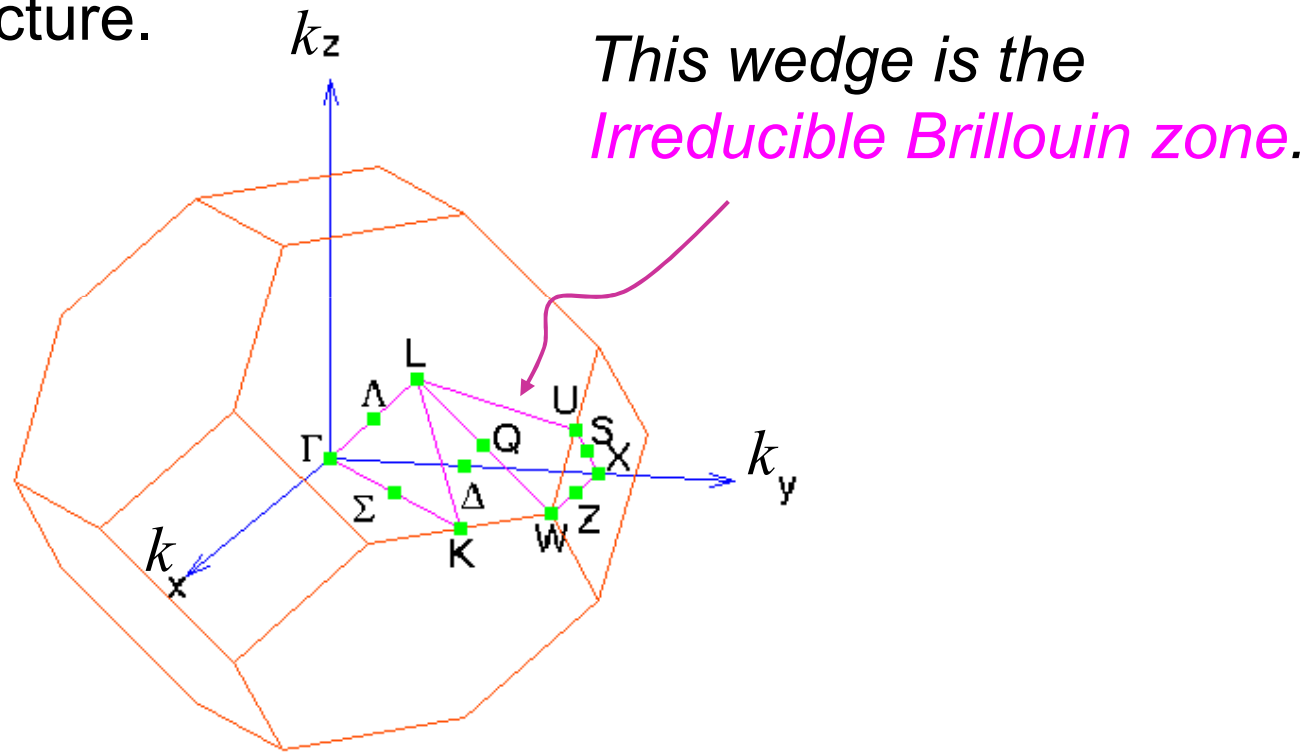
(www.iue.tuwien.ac.at)



Irreducible Brillouin Zone

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

e.g., for FCC lattice



cst-www.nrl.navy.mil



Brillouin Zone Sums

- Many quantities (e.g., density, total energy) involve integrals over \mathbf{k} :

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

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



Brillouin Zone Sums

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

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

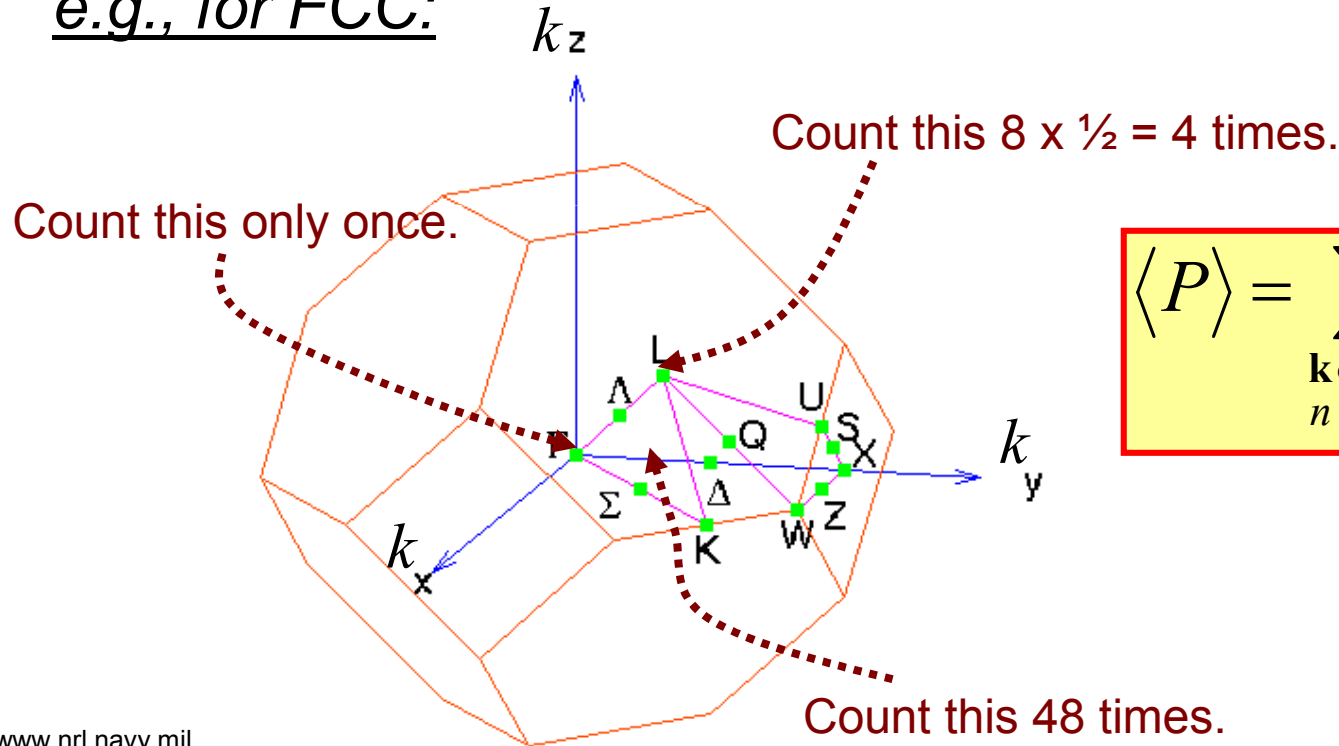
- For computational reasons, want # \mathbf{k} 's to be small.
- Number needed depends on band structure.
- Need to test convergence w.r.t. k-point sampling.



Using the Irreducible BZ; Weights

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

e.g., for FCC:



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

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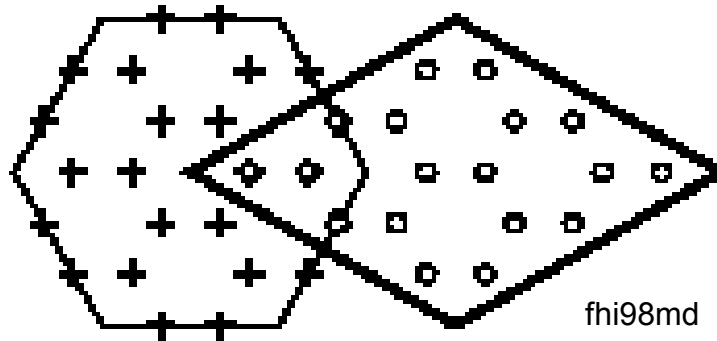


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Special Points

- 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).

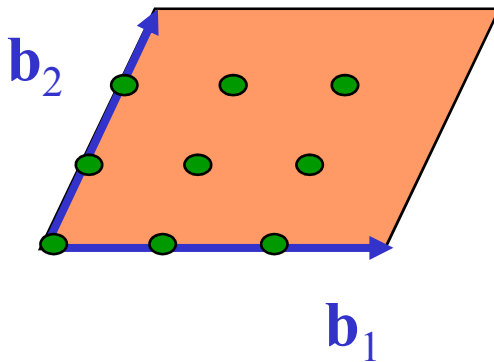
e.g. for FCC(111) surface
(2-D hexagonal lattice)



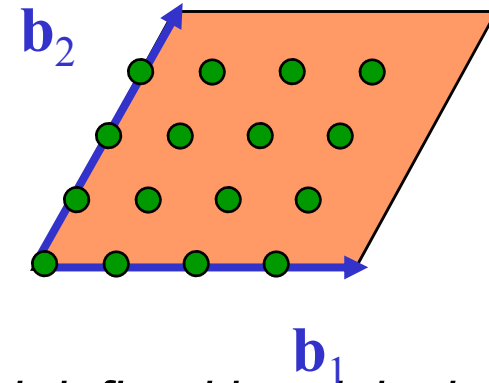
Monkhorst-Pack k-points

- Uniformly spaced grid of $nk1 \times nk2 \times nk3$ points in 1st BZ:

$$nk1=nk2=3$$



$$nk1=nk2=4$$



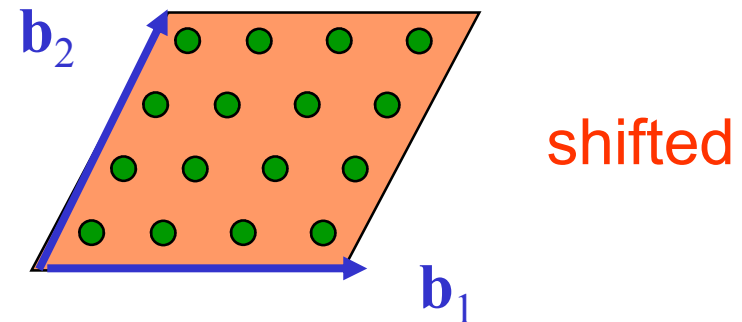
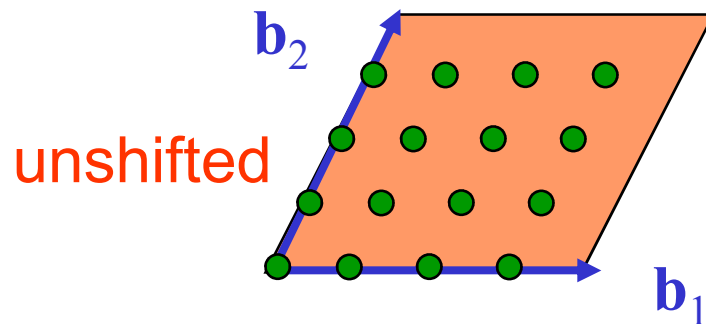
- Note: This is slightly different from way grid defined in original paper [Phys. Rev. B **13** 5188 (1976)] where odd/even grids include/don't include the zone center Γ .*

(Paper cited 10,279 times so far!)

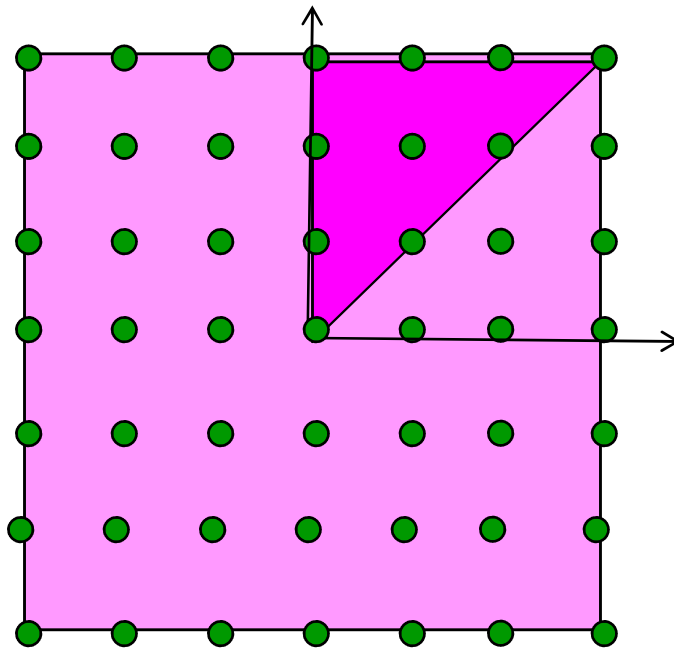


Unshifted & Shifted Grids

- 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.

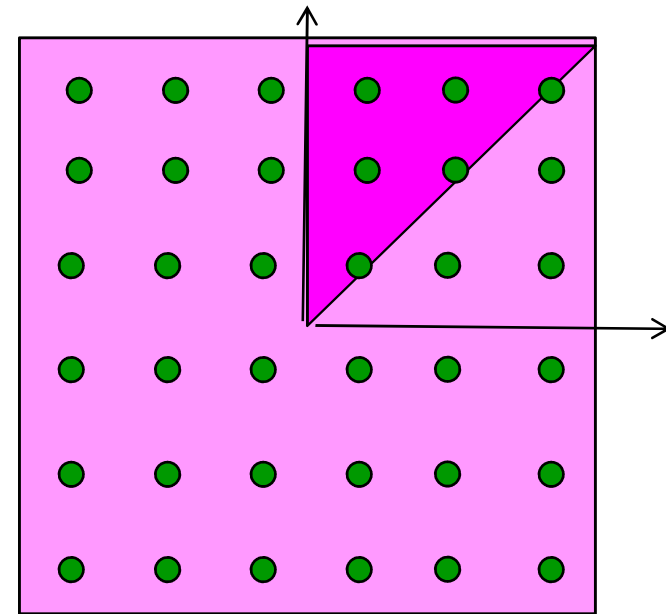


Why it might be better to use a shifted grid



Unshifted

10 pts in IBZ



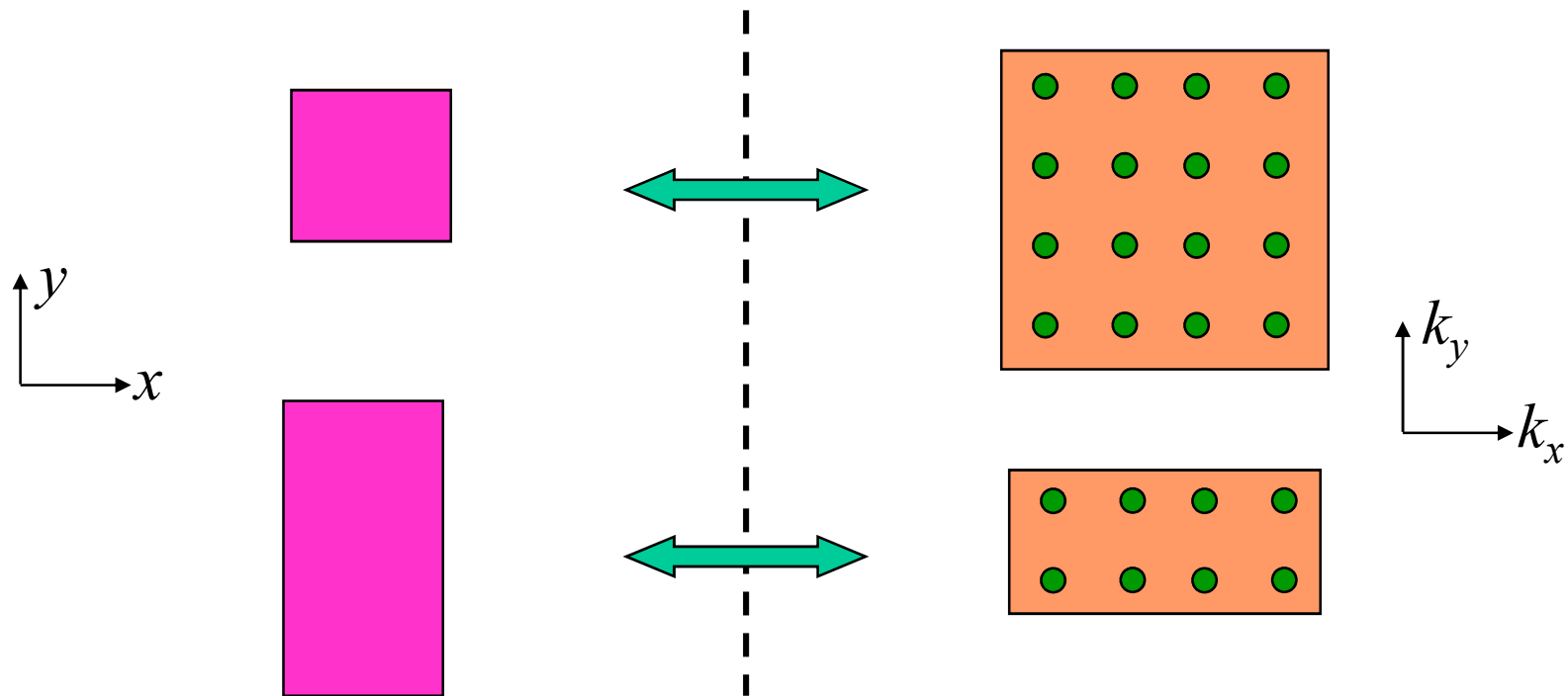
Shifted

6 pts in IBZ



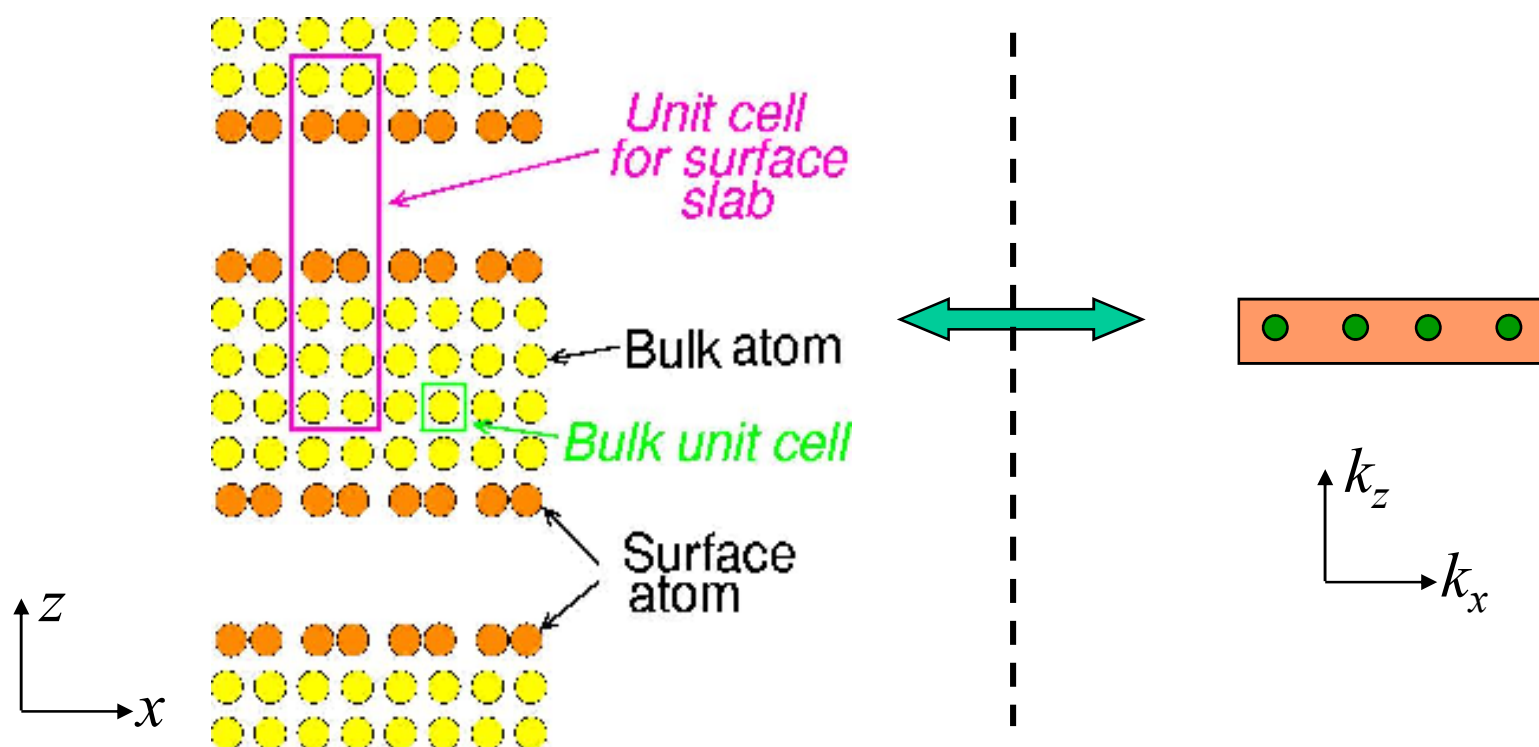
Choosing Grid Divisions

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



Choosing Grid Divisions

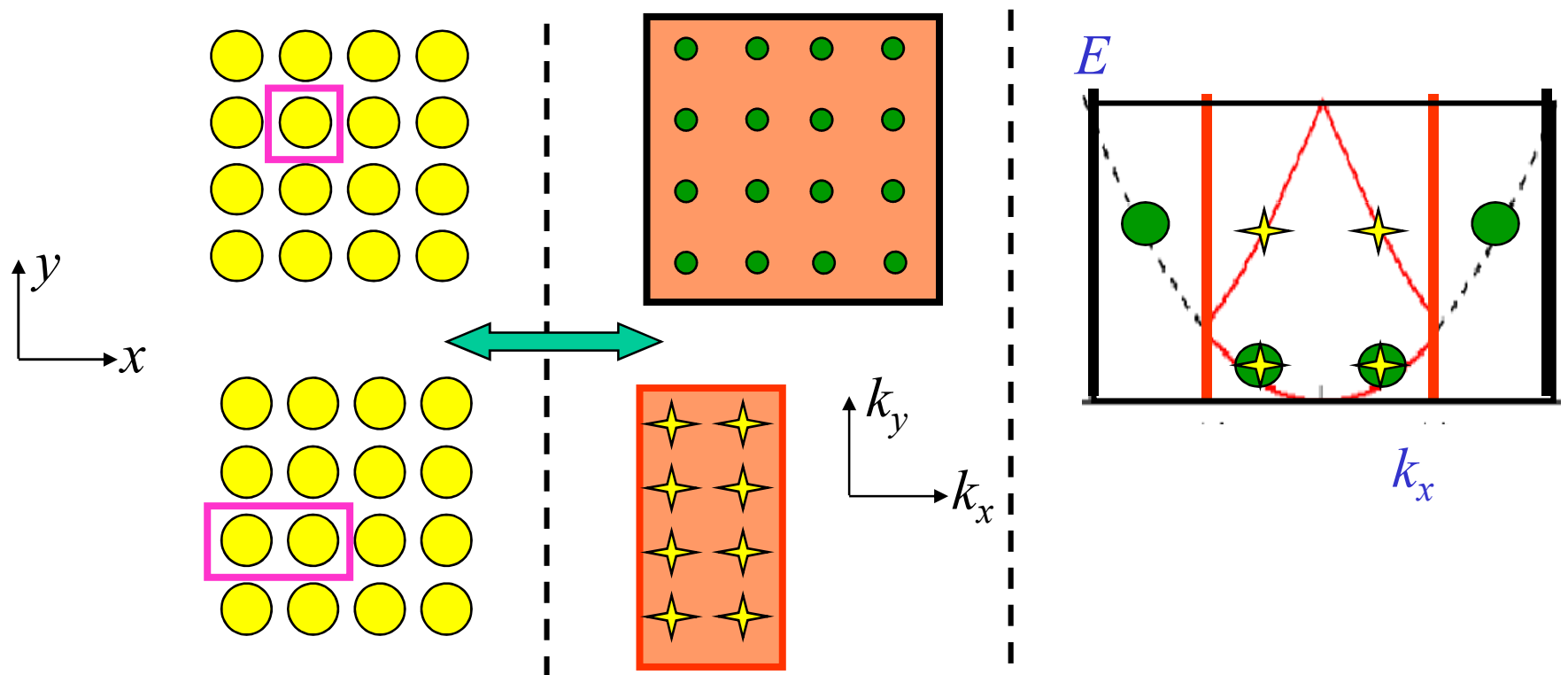
- For artificially periodic supercells, choose only 1 division along the dimensions that have been extended (in real space) by introducing vacuum region.



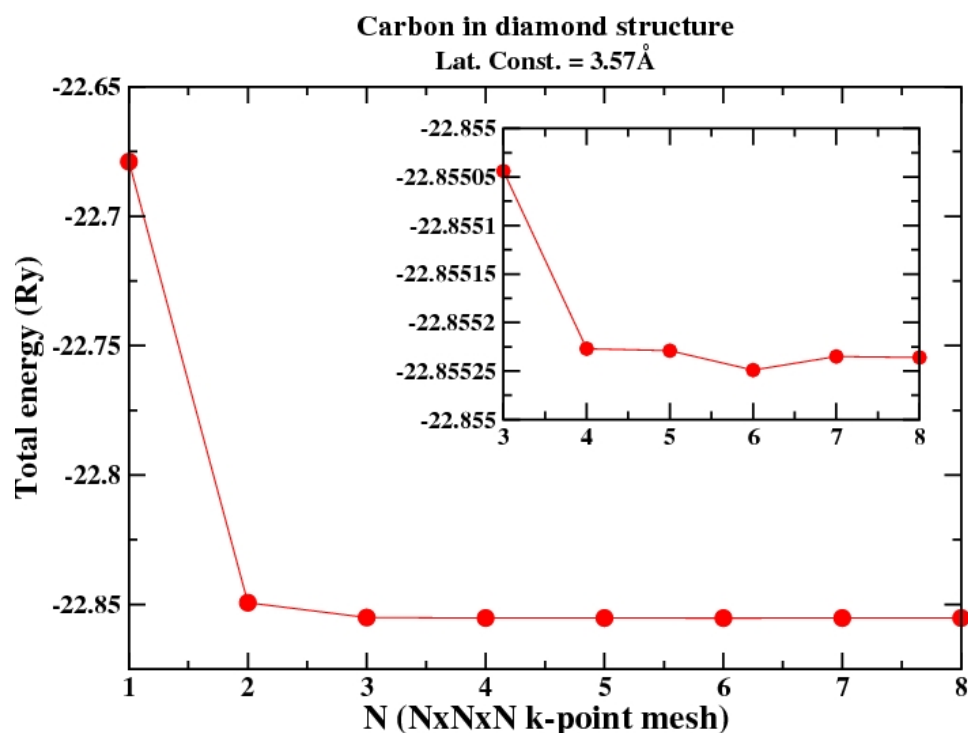
Reciprocity of Supercells & BZ Sampling

Increase supercell in real space by a factor N_i along 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



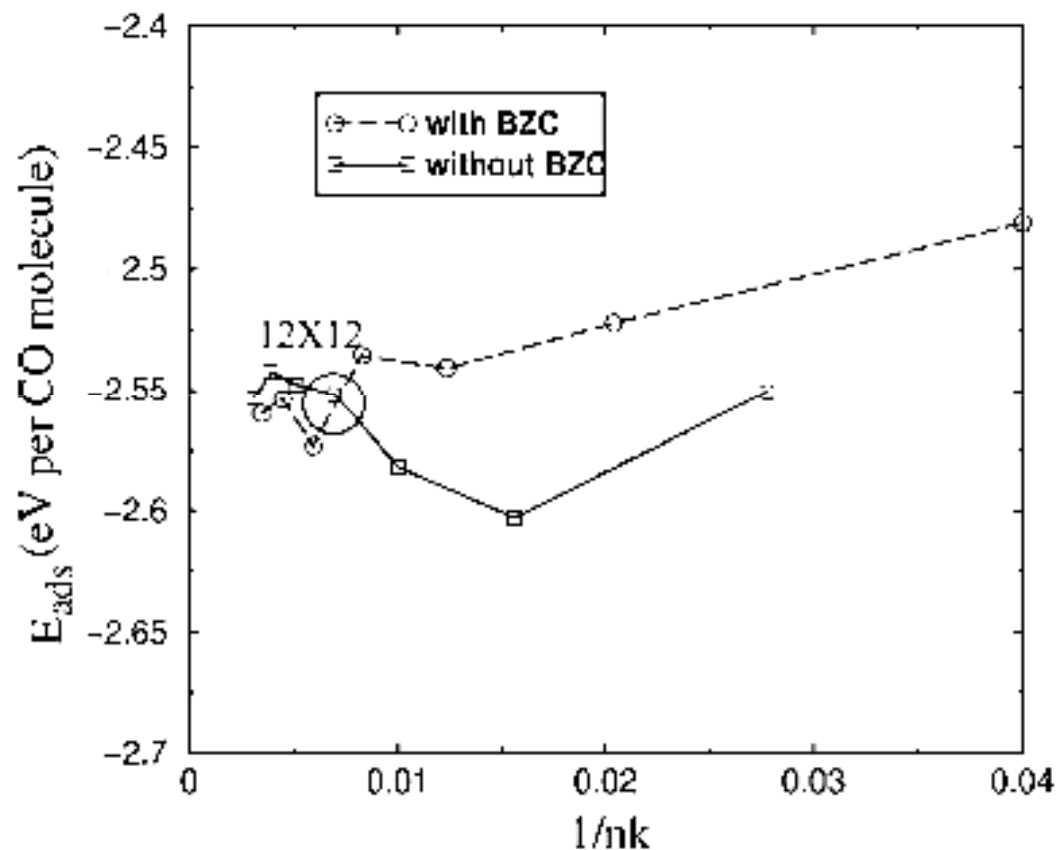
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Note: Differences in energy usually converge faster than absolute value of total energy because of error cancellation (if supercells & k-points are identical or commensurate).



Convergence wrt BZ sampling

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



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

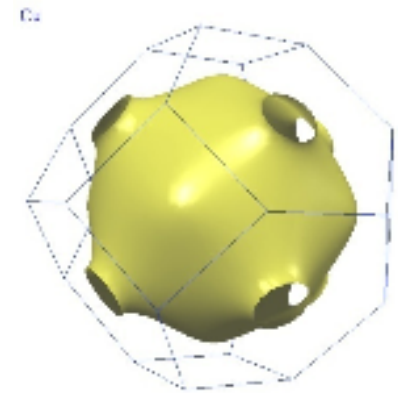


Problems with Metals

- Recall:

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

- 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

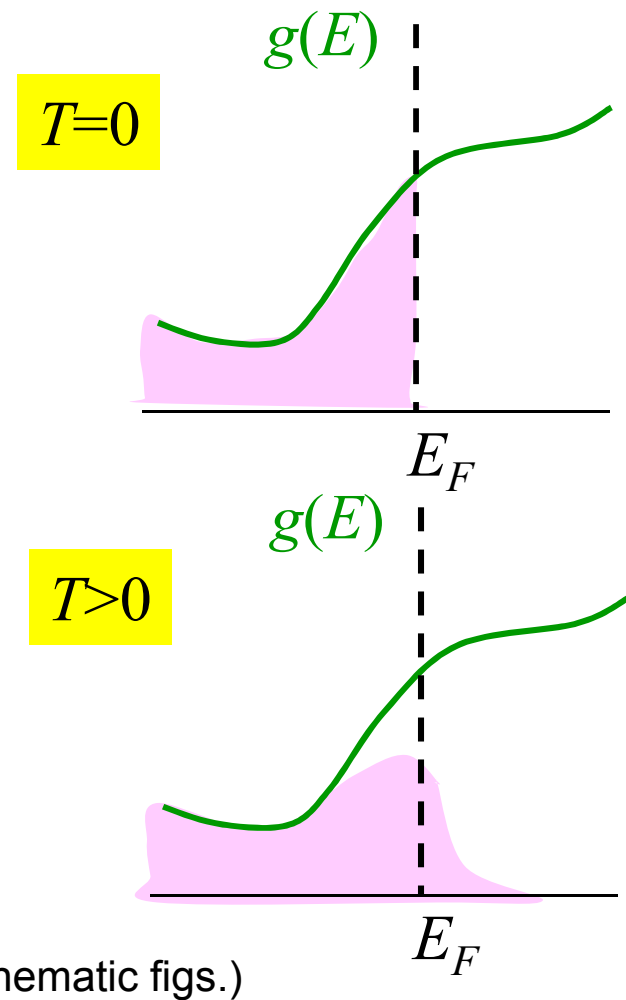


Fermi-Dirac Smearing

- 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 $T > 0$.

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

$$\sigma = k_B T$$



The Free Energy

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

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

- What we actually want is $E(\sigma \rightarrow 0)$
- $E(\sigma \rightarrow 0) = \frac{1}{2} (F + E)$ (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....

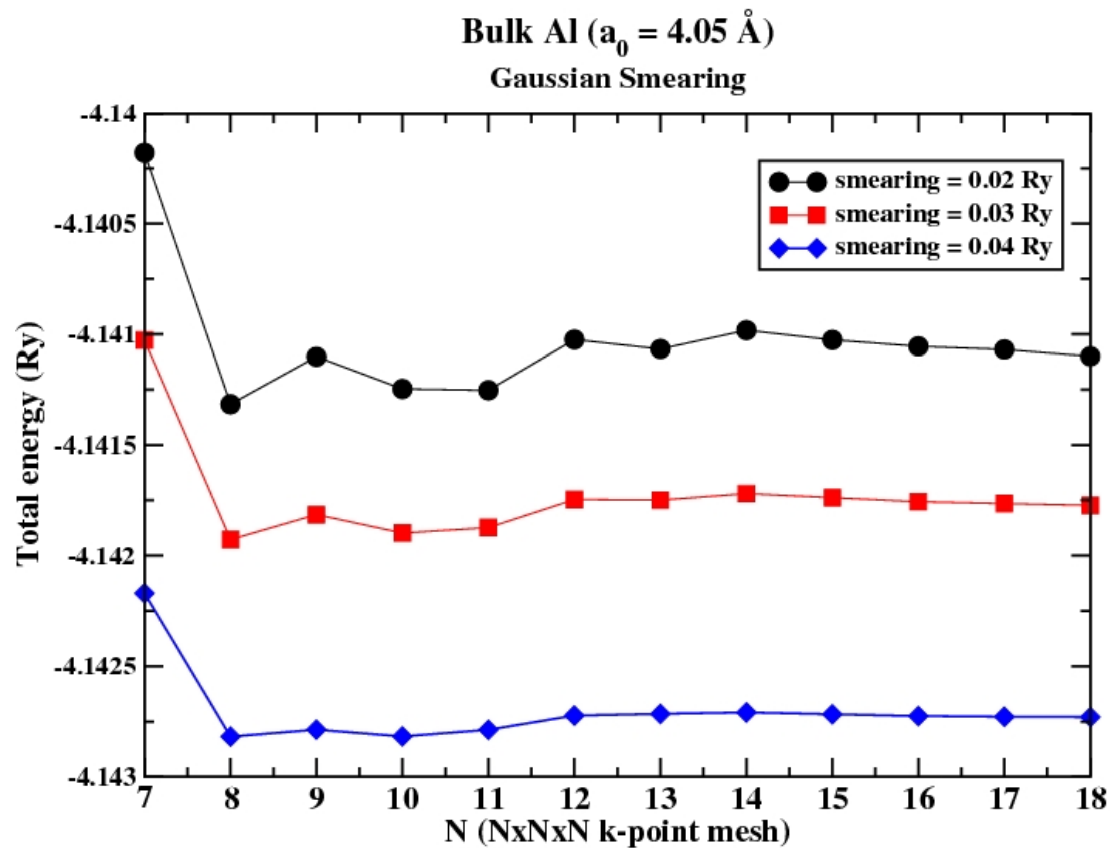
$$f(E) = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{E - \mu}{\sigma} \right) \right] \quad \text{(this is what you get if you integrate a Gaussian)}$$

- 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

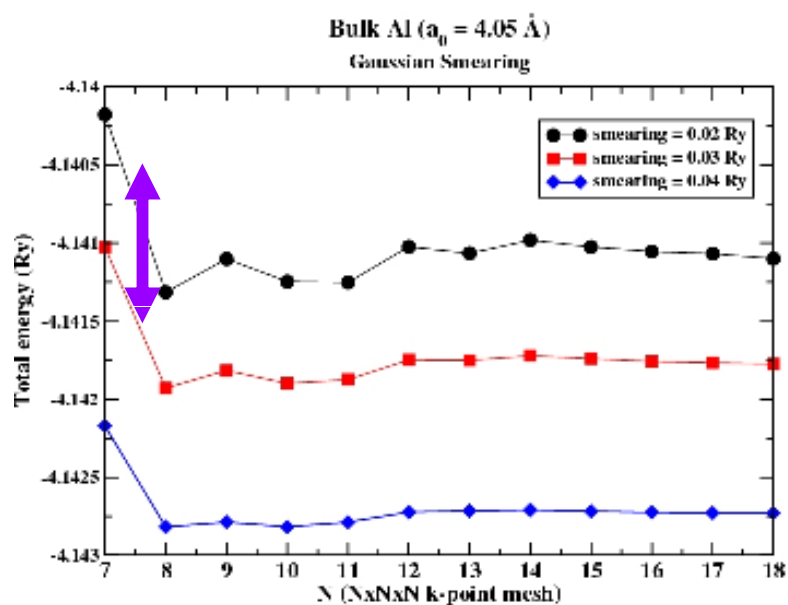
- Methfessel & Paxton:
 - Can have a successive series of better (but smooth) approximations to the step function.
 - E converges fast [wrt σ] to $E(\sigma \rightarrow 0)$
- Marzari & Vanderbilt:
 - Unlike Methfessel-Paxton, don't have negative occupancies.

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

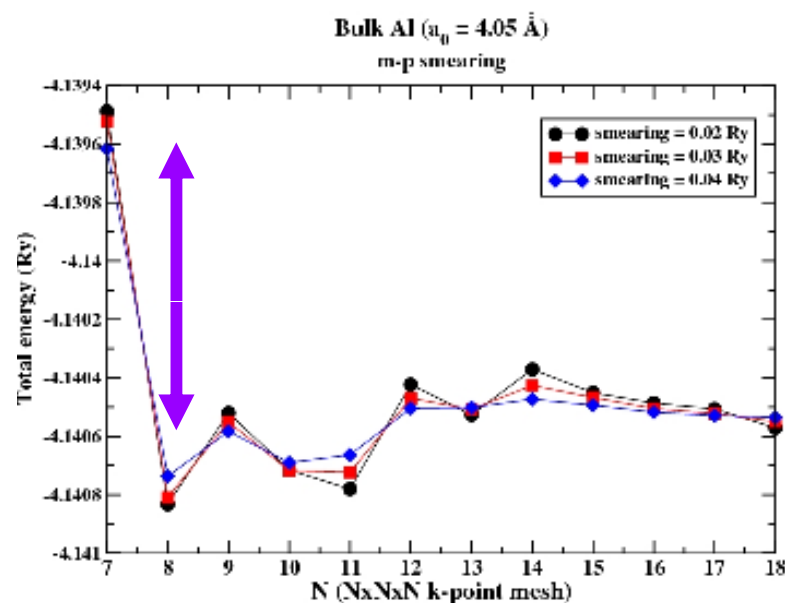


Convergence wrt grid & smearing

- Gaussian:



- Methfessel-Paxton:



represents an energy difference of 1 mRy

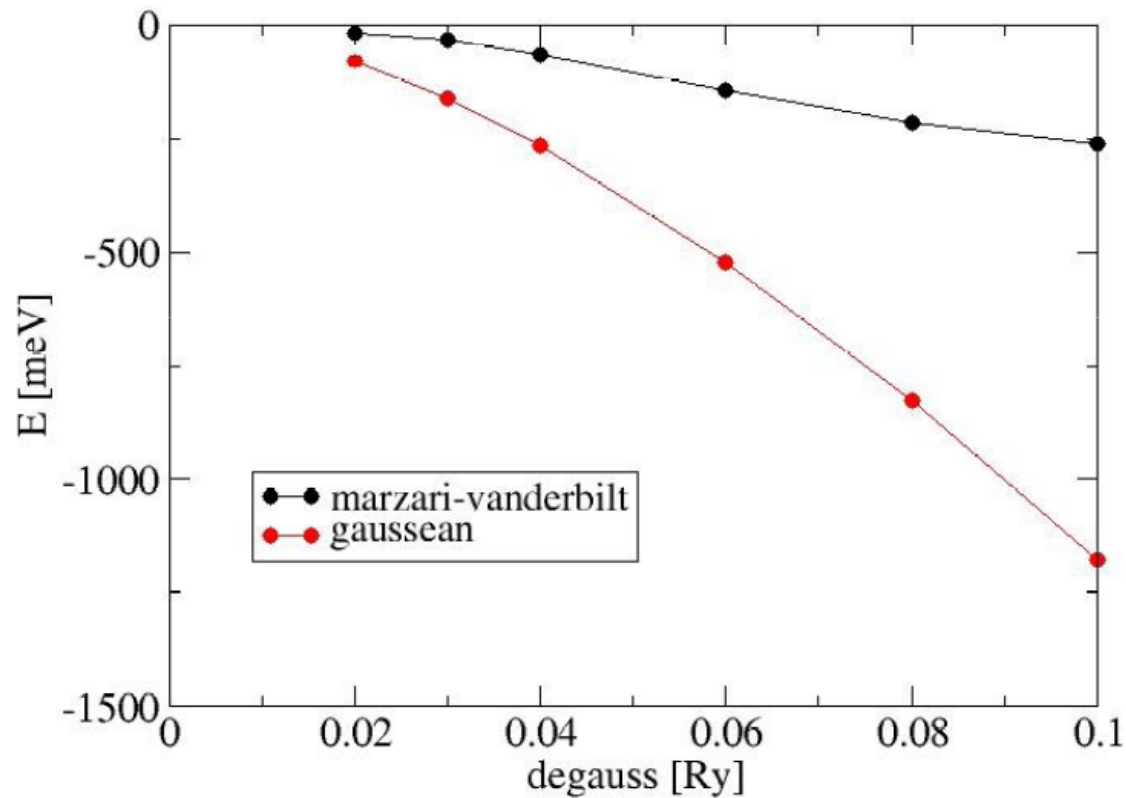
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Convergence wrt k-points & smearing width

e.g., for bcc Fe, using $14 \times 14 \times 14$ 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).

