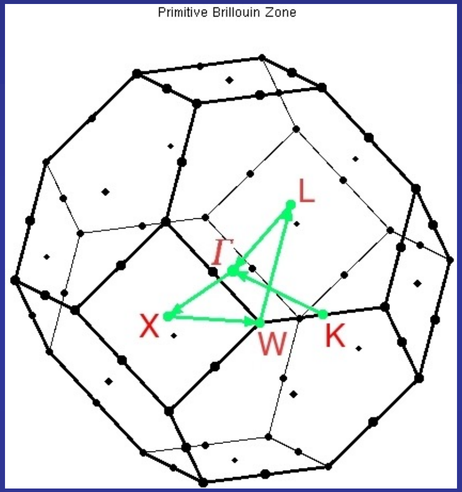
K-point sampling, smearing, metals

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r}) \qquad u_{n,\vec{k}}(\vec{r}+\vec{R}) = u_{n,\vec{k}}(\vec{r})$$



Javier Junquera

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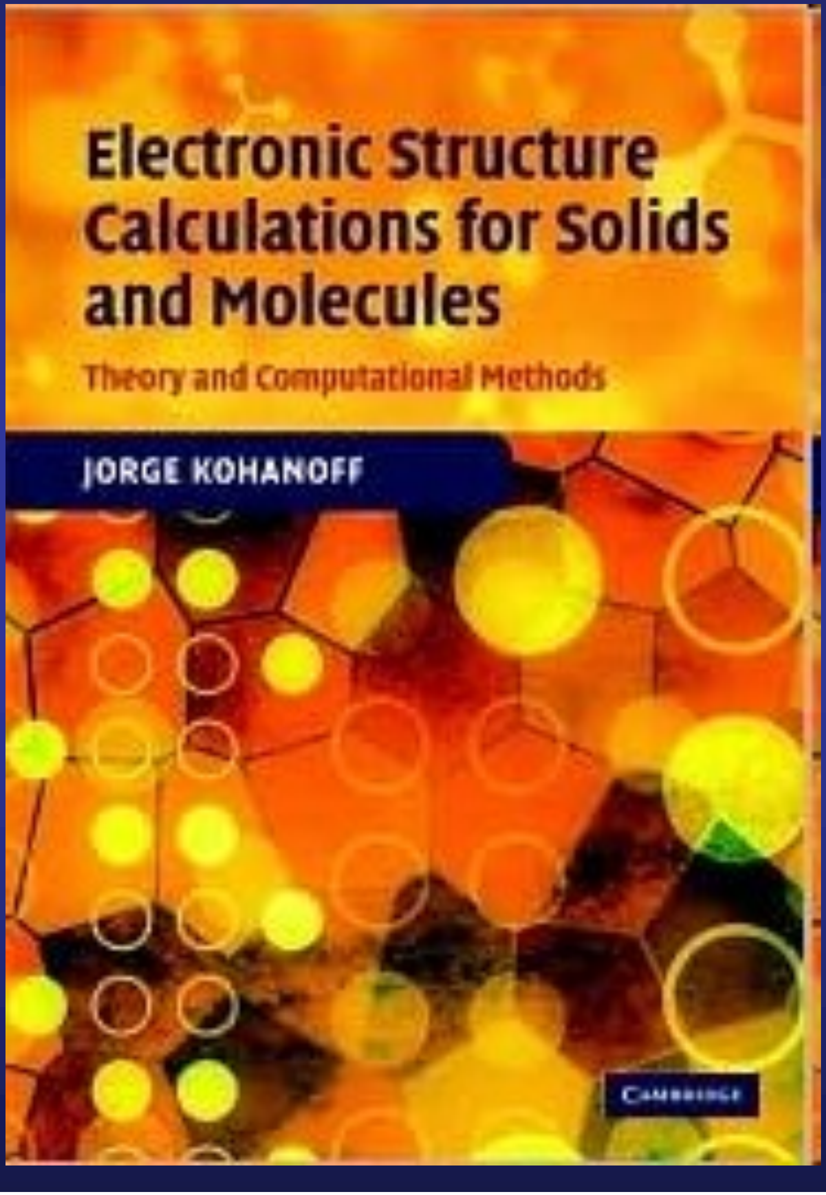
8th African School on Electronic Structure Methods and Applications
ASESMA 2025, Accra (Ghana), June 10th 2025

Bibliography used in the present lecture



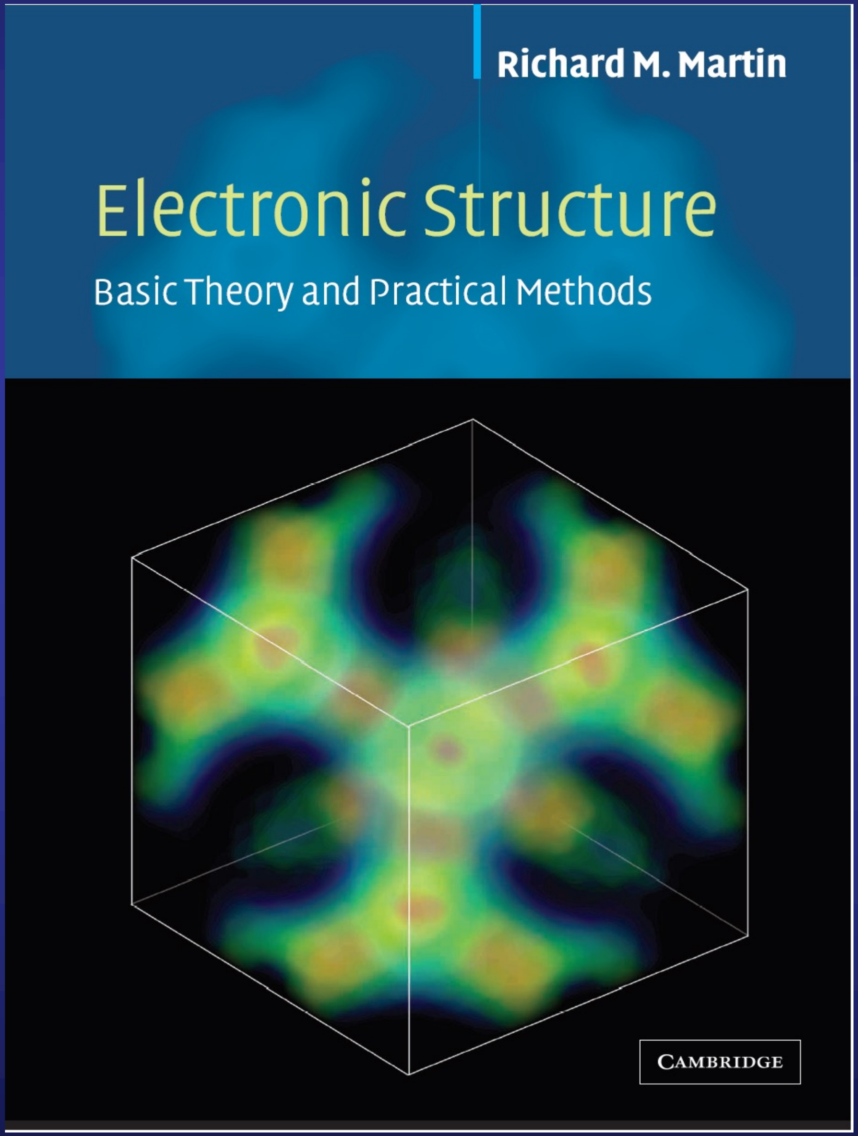
Electronic Structure Calculations for Solids and Molecules

Theory and Computational Methods

JORGE KOHANOFF

CAMBRIDGE

Bibliography used in the present lecture



Richard M. Martin

Electronic Structure

Basic Theory and Practical Methods

CAMBRIDGE

Periodic systems are idealizations of real systems
Conceptual problems

NO exactly periodic systems in Nature

(periodicity broken at the boundary)

BUT

- Condensed systems (solids, liquids, amorphous) and systems of lower dimensionalities (surfaces, wires, dots) are **macroscopic objects** constituted by a **huge number of atoms ($N_A=6\times10^{23}$).** In fact they can be treated as infinity

- The great majority of the **physical quantities** are **unaffected by** the existence of a **border.** In other words, they are **independent** of the **truncation** of the sample's **surface.** We should expect that the bulk properties to be unaffected by the presence of its surface.

Crystalline solids: an ordered state of matter in which the position of the nuclei are repeated periodically in space

Periodic repetition of a given unit

Rules that describe the repetition (translations)

Single atoms

Groups of atoms

Molecules

Ions

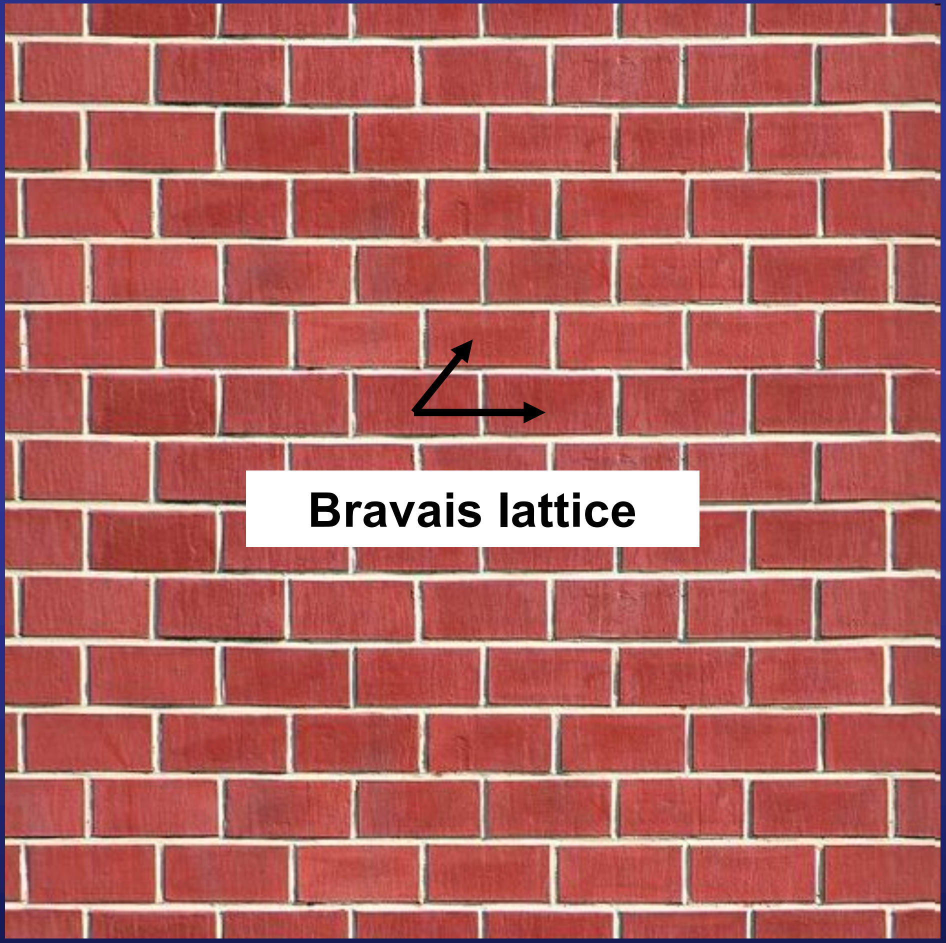
Specified by the types and positions of the nuclei in one repeated unit cell

Crystal structure = Bravais lattice + basis

(Ordered state of matter)

Crystalline solids: an ordered state of matter in which the position of the nuclei are repeated periodically in space

Periodic repetition of a given unit



Bravais lattice

Single atom

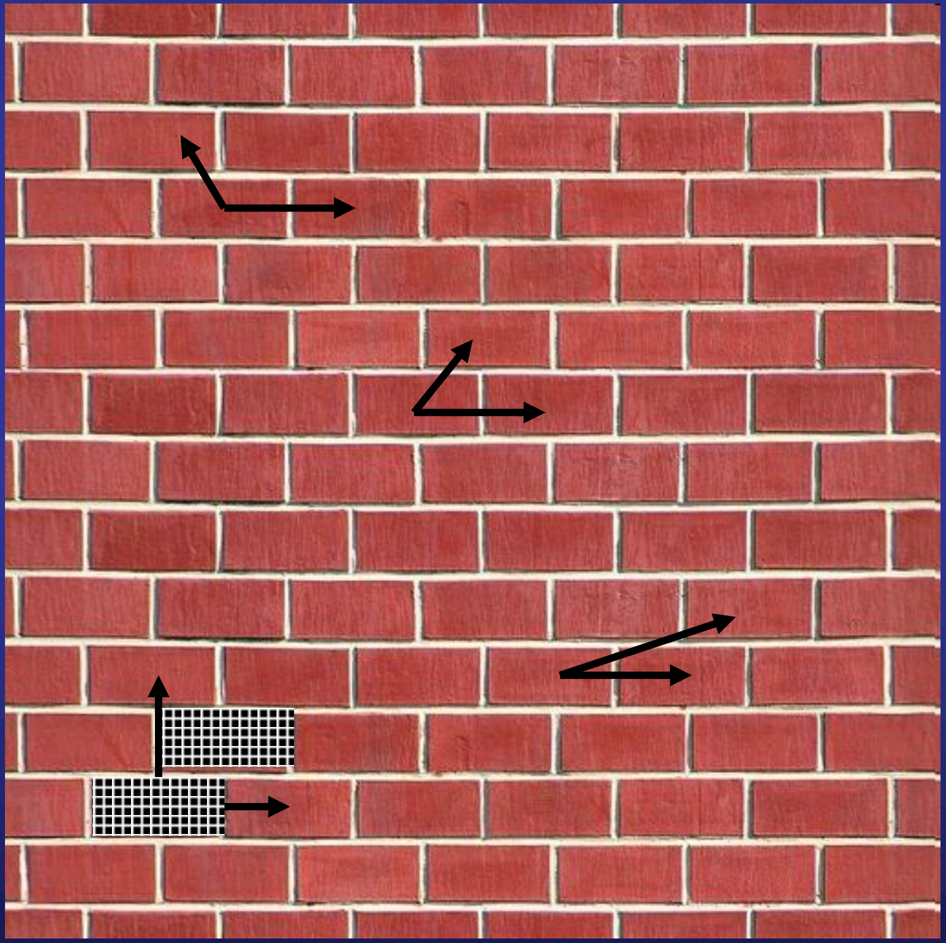
Groups of atoms

Molecules

Ions

There are infinitely many ways of characterizing a crystalline solid

Periodic repetition of a given unit



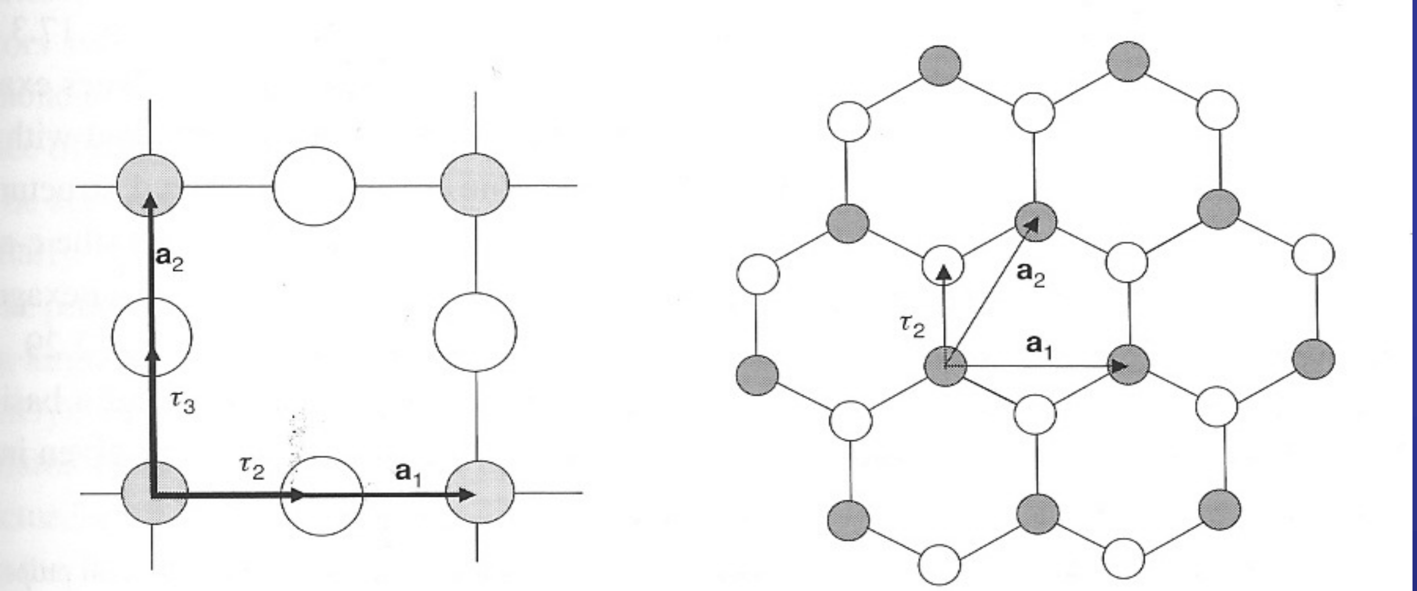
Infinite number of choices for the primitive translation vectors

Examples of two dimensional periodic systems: square and triangular lattices

CuO_2 planes

Graphene

(Single plane of graphite)



Square lattice

Three atoms per unit cell

Triangular lattice

Two atoms per unit cell

Periodic systems are idealizations of real systems
Computational problems

1. In a periodic solid:

∞ Number of atoms

∞ Number and electrons

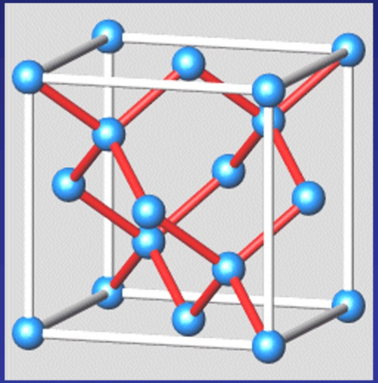
$\Downarrow$

∞ Number of wave functions ??

2. Wave function will be extended over the entire solid

Bloch theorem will rescue us!!

A periodic potential commensurate with the lattice.
The Bloch theorem



$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

Bloch Theorem: The eigenstates of the one-electron Hamiltonian in a periodic potential can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice.

$$\psi_{n,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{n,\vec{k}}(\vec{r}) \qquad u_{n,\vec{k}}(\vec{r} + \vec{R}) = u_{n,\vec{k}}(\vec{r})$$

Periodicity in reciprocal space

$\vec{G}$ ≡Reciprocal lattice vector

$$\left\{ \begin{array}{l} \psi_{n,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n,\vec{k}}(\vec{r}) \\ \\ \varepsilon_{n,\vec{k}+\vec{G}} = \varepsilon_{n,\vec{k}} \end{array} \right.$$

Both the Bloch wave functions and the eigenvalues are periodic functions in reciprocal space

$$\psi_{n\,\vec{k}+\vec{G}}(\vec{r}) = \psi_{n\,\vec{k}}(\vec{r})$$

$$E_n(\vec{k}+\vec{G}) = E_n(\vec{k})$$

The wave vector $\vec{k}$ appearing in Bloch’s theorem can always be confined to the first Brillouin zone

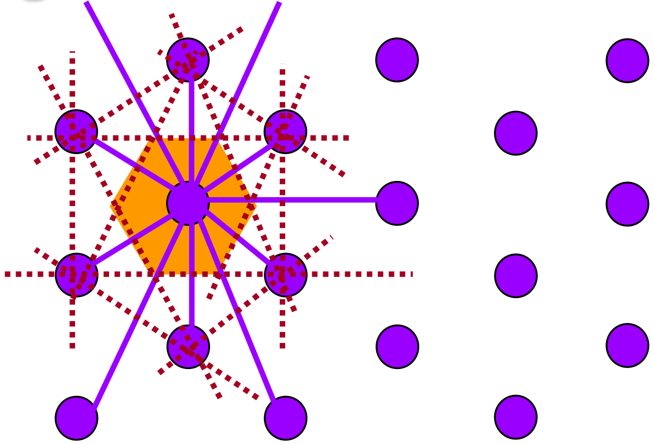
Any vector $\vec{k}'$ not in the first Brillouin zone can be written as

$$\vec{k}' = \vec{k} + \vec{G}$$

where $\vec{G}$ is a reciprocal lattice vector and $\vec{k}$ lie in the first Brillouin zone

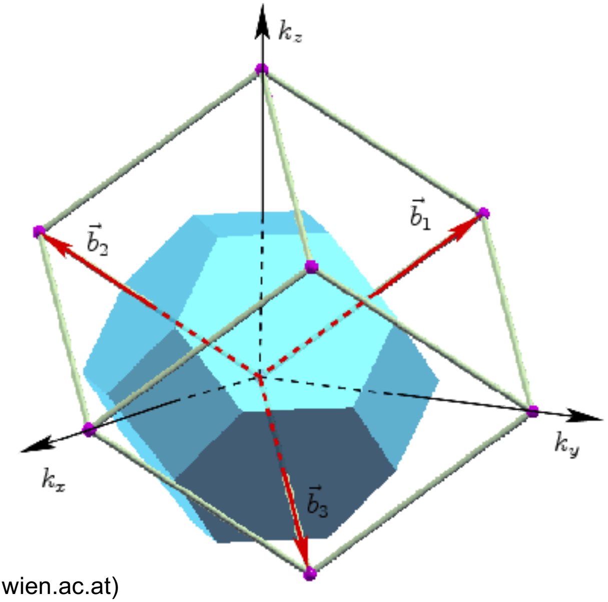
Concept of Brillouin zone

- **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)

The wave vector k and the band index n allow us to label each electron (good quantum numbers)

The Bloch theorem changes the problem

Instead of computing an infinite number of electronic wave functions

Finite number of wave functions at an infinite number of k-points in the 1BZ

Many magnitudes require integration of Bloch functions over Brillouin zone (1BZ)

Charge density

$$\rho(\vec{r}) = \sum_i \int_{BZ} n_i(\vec{k}) |\psi_{i\vec{k}}(\vec{r})|^2 d\vec{k}$$

Band structure energy

$$E_{BS} = \sum_i \int_{BZ} n_i(\vec{k}) \varepsilon_i(\vec{k}) d\vec{k}$$

In principle: we should know the eigenvalues and/or eigenvectors at all the k-points in the first BZ

In practice: electronic wave functions at k-points that are very close together will be almost identical $\Rightarrow$

It is possible to represent electronic wave functions over a region of k-space by the wave function at a single k-point.

$$\int d\vec{k} \longrightarrow \sum_{\vec{k}} \Delta\vec{k}$$

Brillouin zone sampling

Brillouin zone sampling

In practice, sum over a finite number: BZ “sampling”

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

For computational reasons, we want the number of k’s to be small

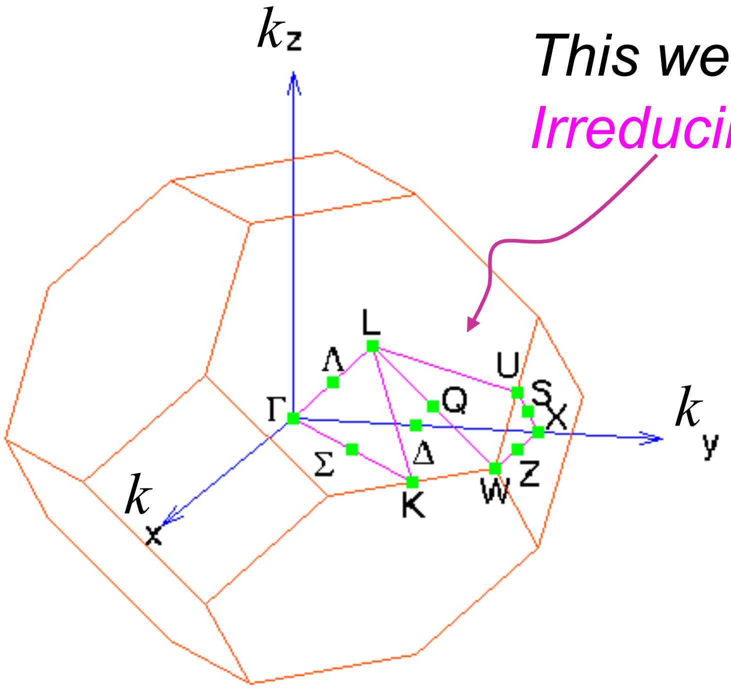
Number needed depends on band structure

Need to test convergence with respect to the k-point sampling

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

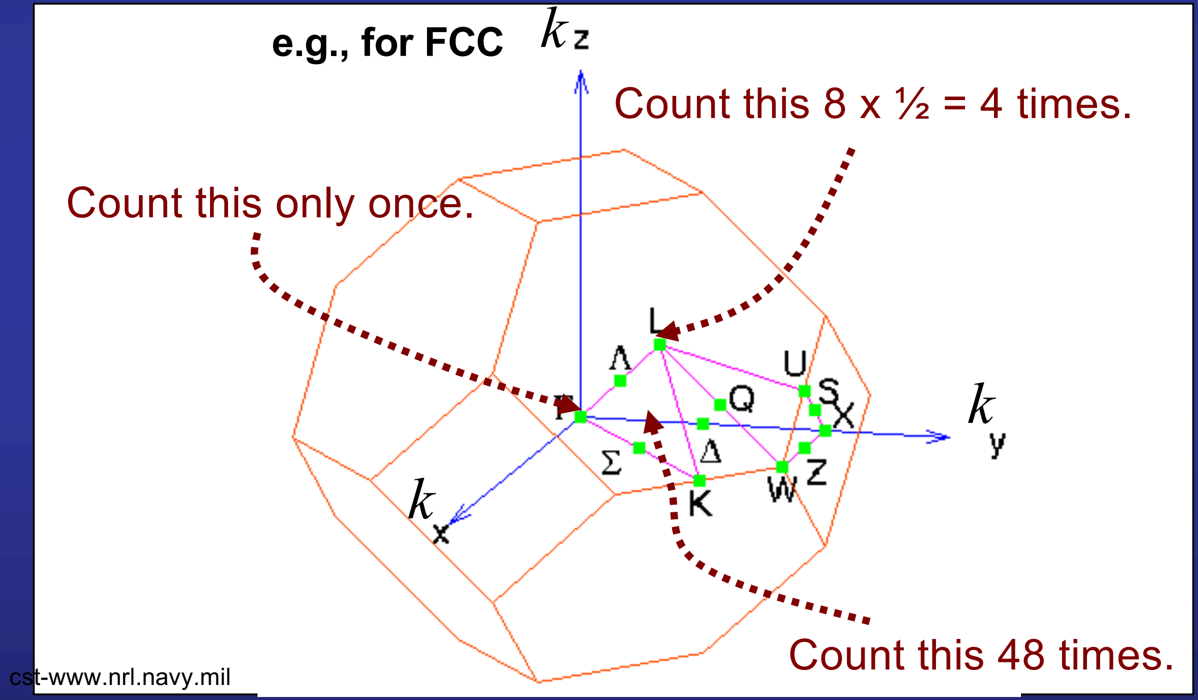


This wedge is the Irreducible Brillouin zone.

cst-www.nrl.navy.mil

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

Count this 8 x ½ = 4 times.

Count this only once.

Count this 48 times.

cst-www.nrl.navy.mil

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

Recipes to compute sets of spetial k-points for the different symmetries to accelate the convergence of BZ integrations

Using just one k-point

Baldereschi and the "mean value point"

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)

Monkhorst-Pack

Phys. Rev. B 13 5188 (1976)

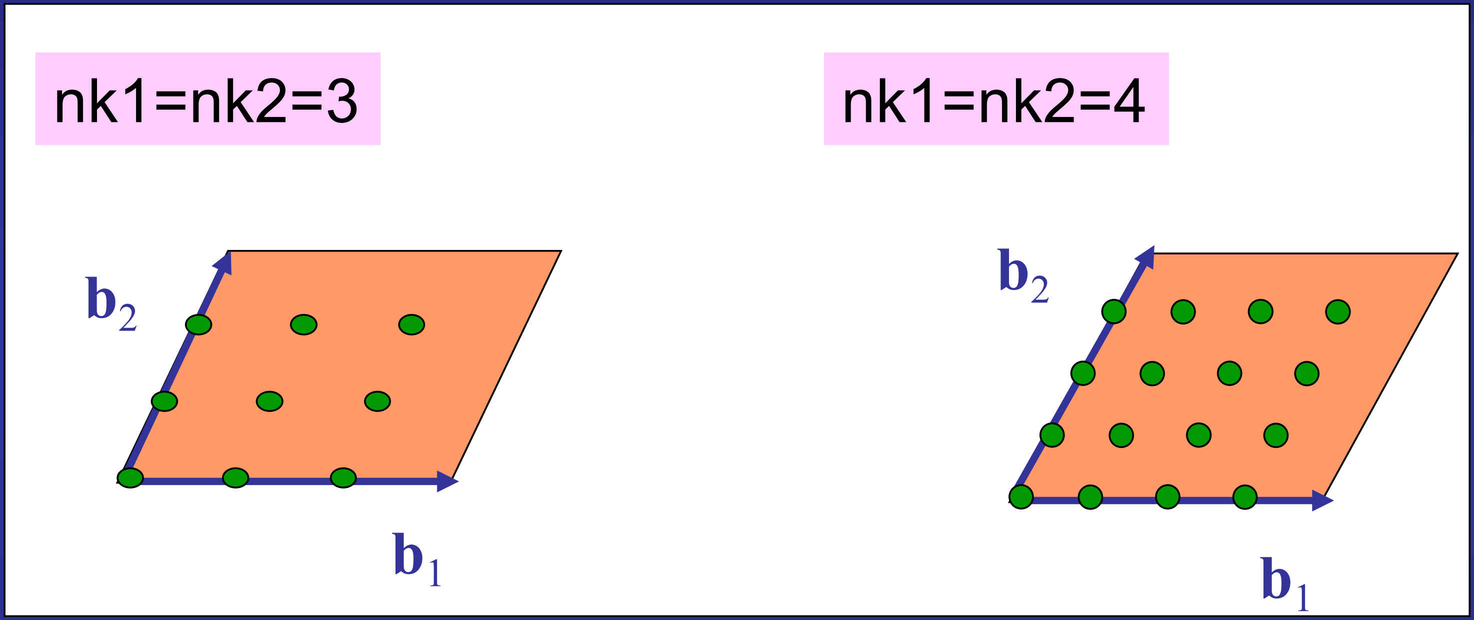
$$\vec{k} = c_1 \vec{b}_1 + c_2 \vec{b}_2 + c_3 \vec{b}_3$$

$$c_i = \frac{2n_i - N_i - 1}{2N_i}, \quad \text{with } n_i = 1, 2, \cdots, N_i$$

The magnitude of the error introduced by sampling the Brillouin zone with a finite number of k-points can always be reduced by using a denser set of points

Monkhorst-Pack k-points

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



Note: This is slightly different from way grid defined in original paper [Phys. Rev. B 13 5188 (1976)]

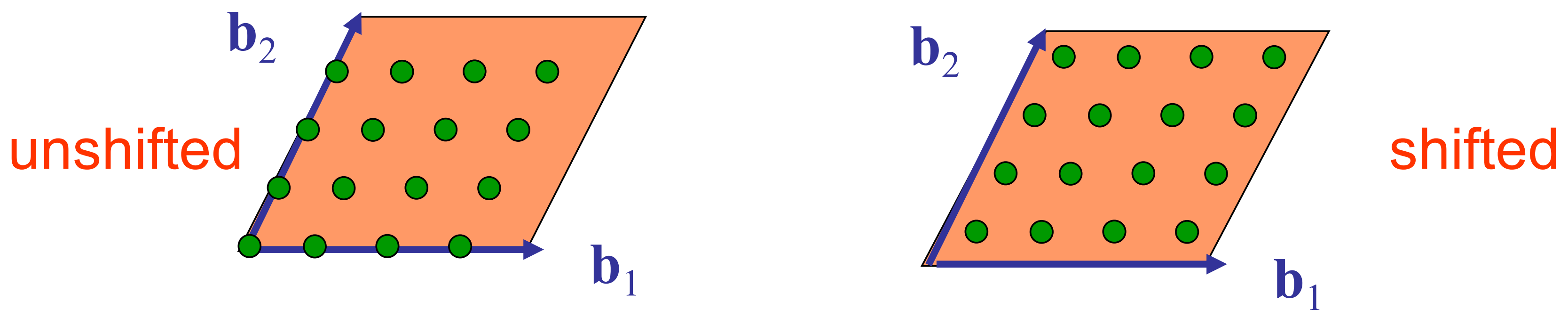
where odd/even grids include/don't include the zone center Γ

Unshifted & Shifted Grids

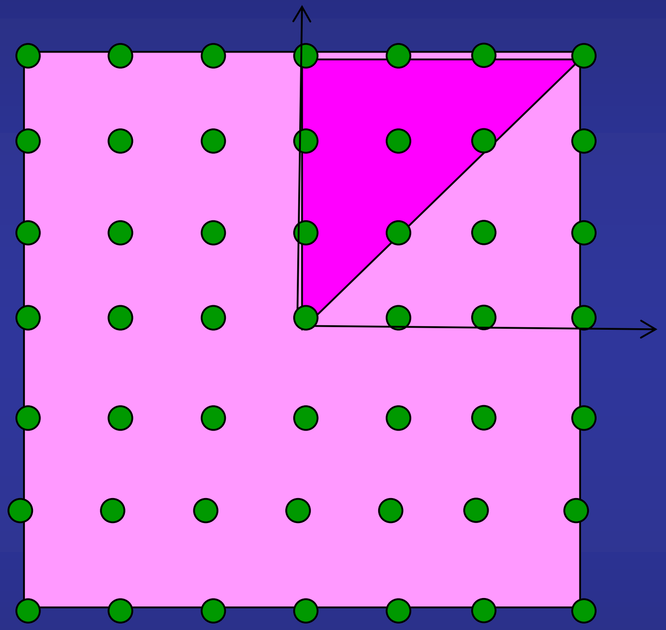
Can choose to shift grid so that it is not centered at Γ

Can get comparable accuracy with fewer k-points in IBZ

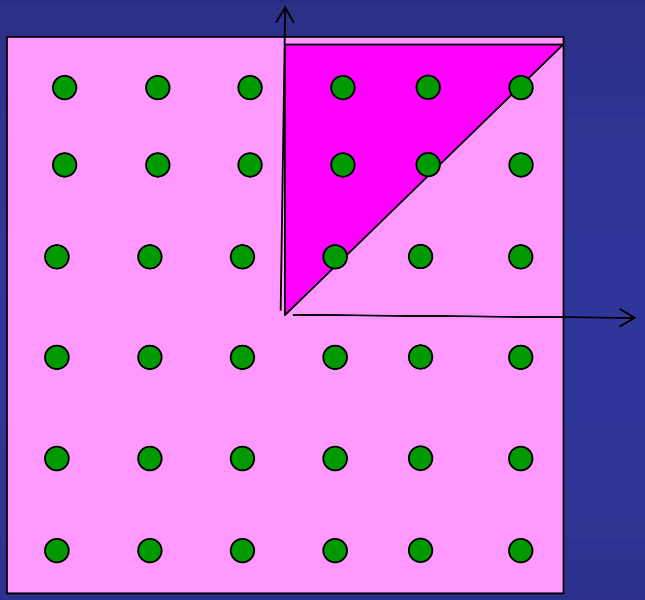
For some Bravais lattice types, shifted grid may not hav full symmetry



Why it might be better to use a shifted grid



Unshifted



Shifted

10 pts in IBZ

6 pts in IBZ

The number of citations allow us to gauge the importance of the works on DFT

11 papers published in APS journals since 1893 with >1000 citations in APS journals (~5 times as many references in all science journals)

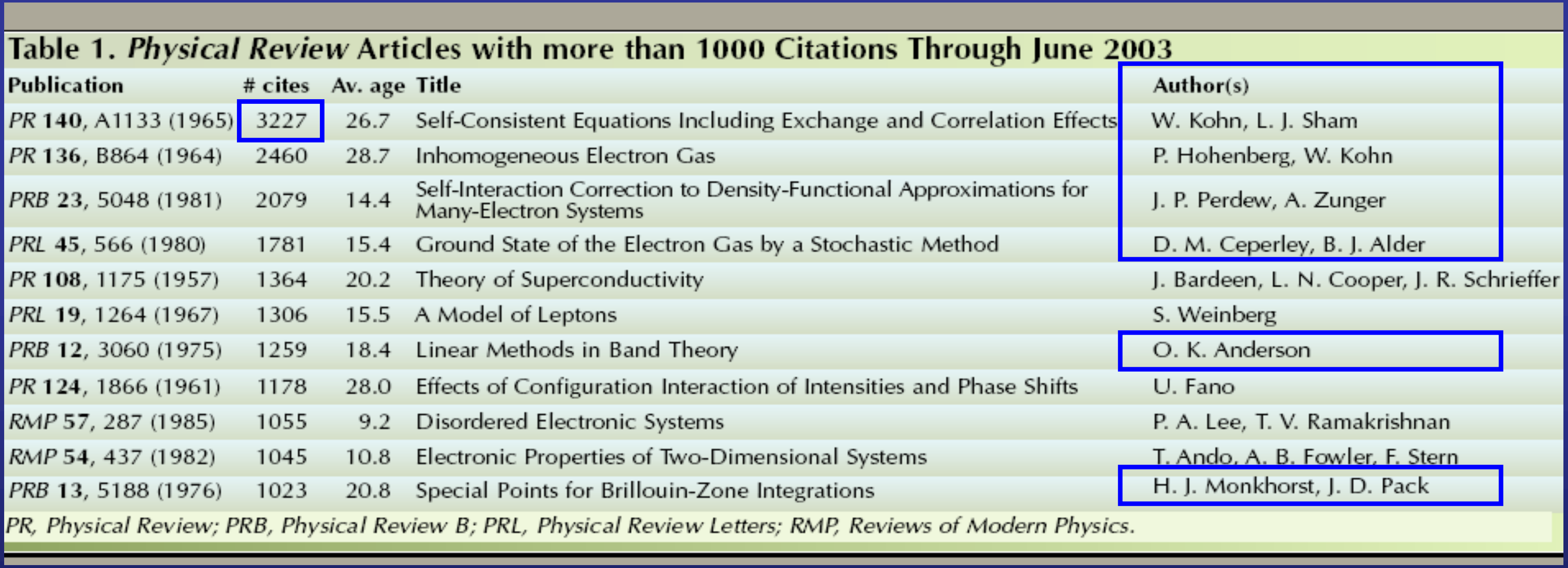


Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

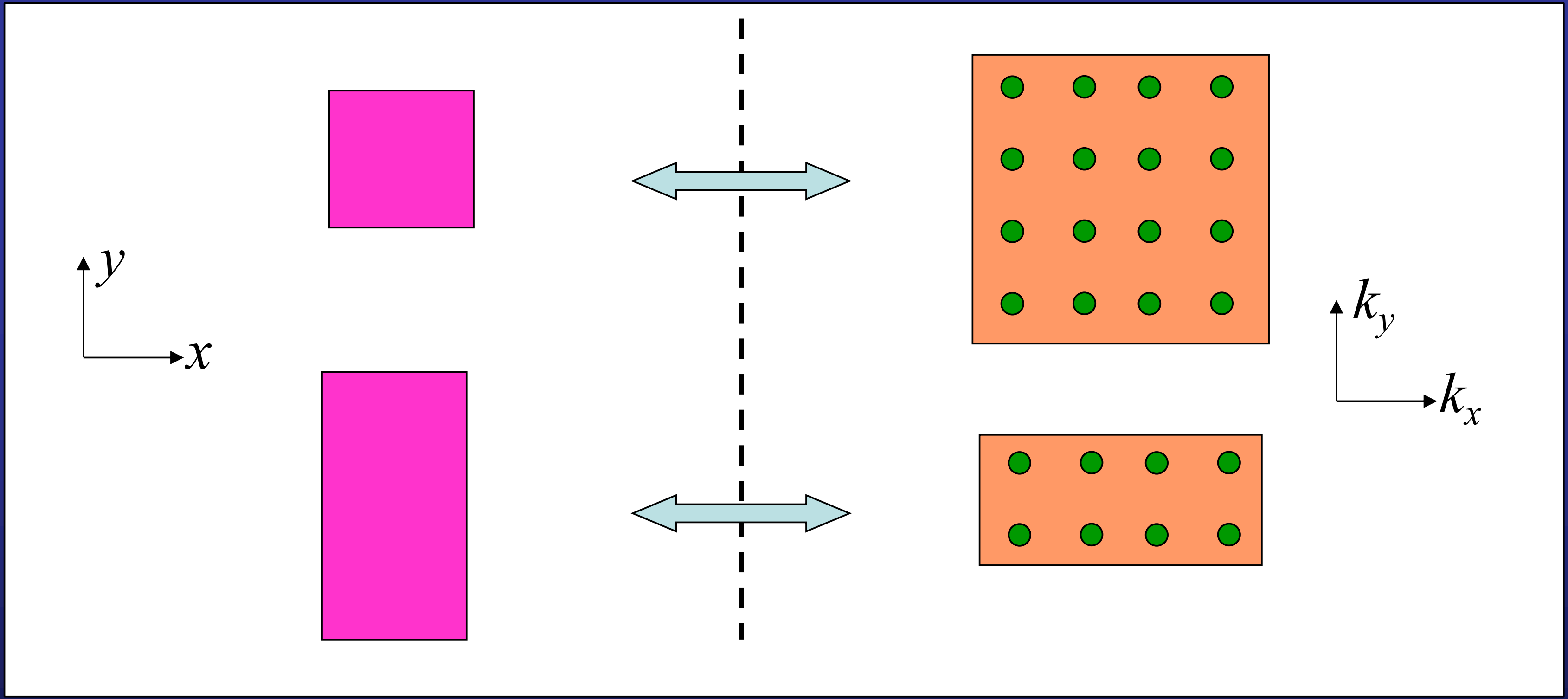
PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

From Physics Today, June, 2005

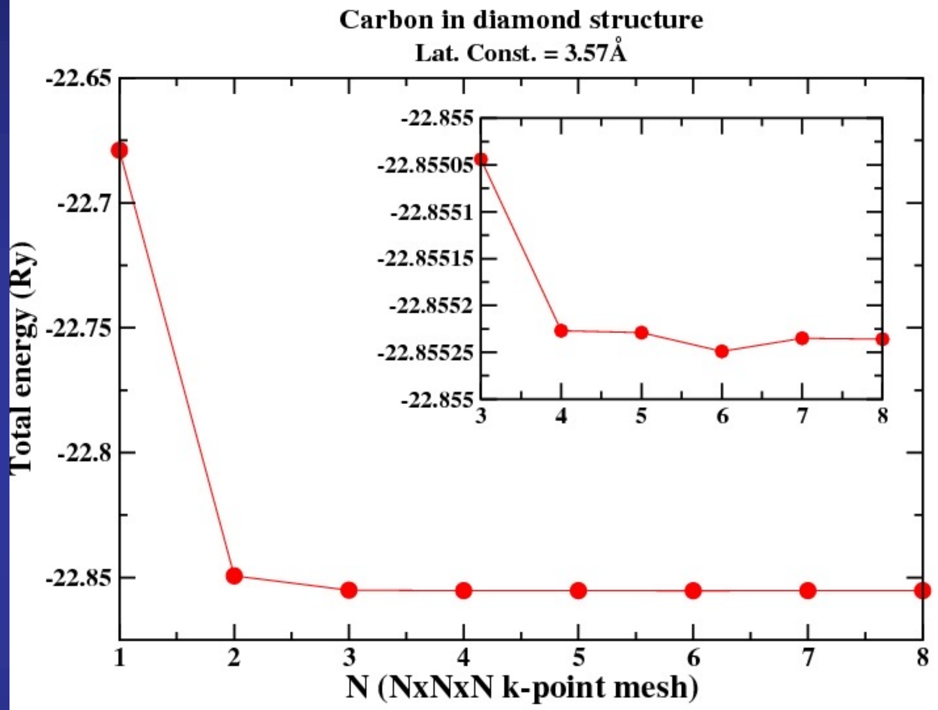
Choosing grid divisions

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!



Convergence with respect to BZ sampling



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

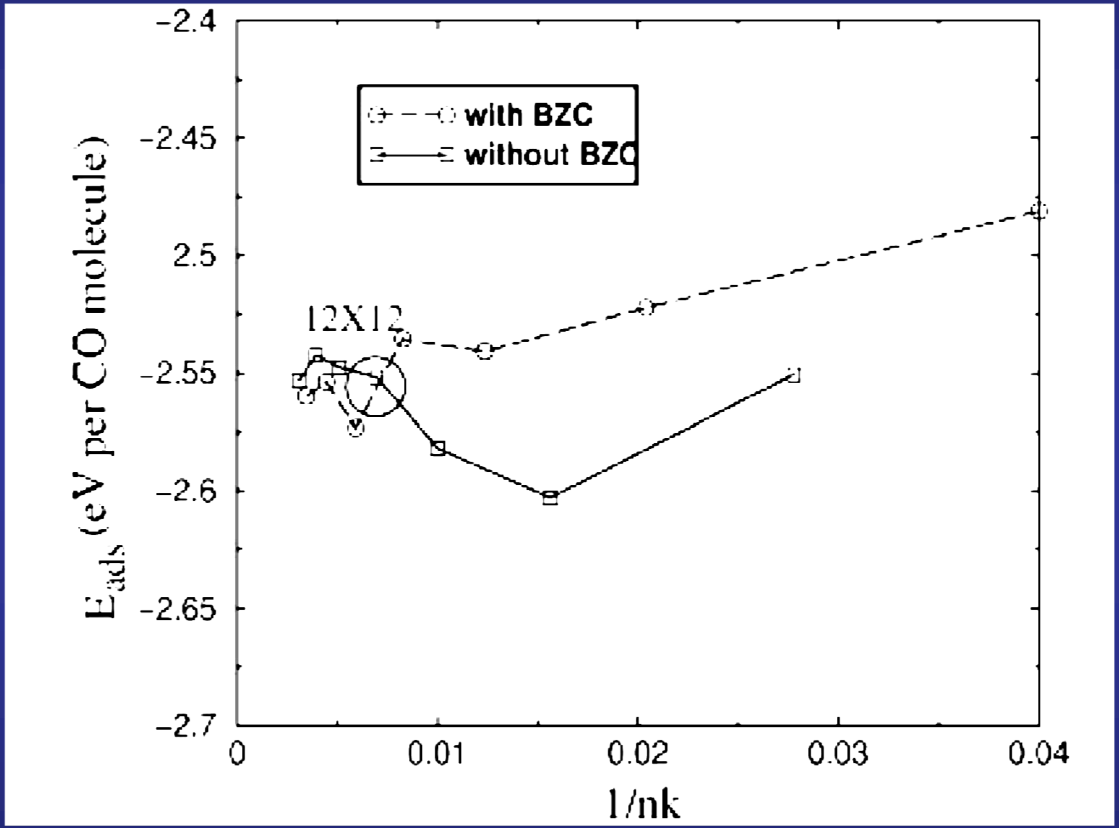
Comparing energies of structures having different symmetries: take care of BZ samplings

The BZ sampling of all the structures must be sampled with the same accuracy

Since for unit cells of different shapes it is not possible to choose exactly the same k-point sampling, a usual strategy is to try and maintain the same density of k-points

Convergence with respect to BZ sampling

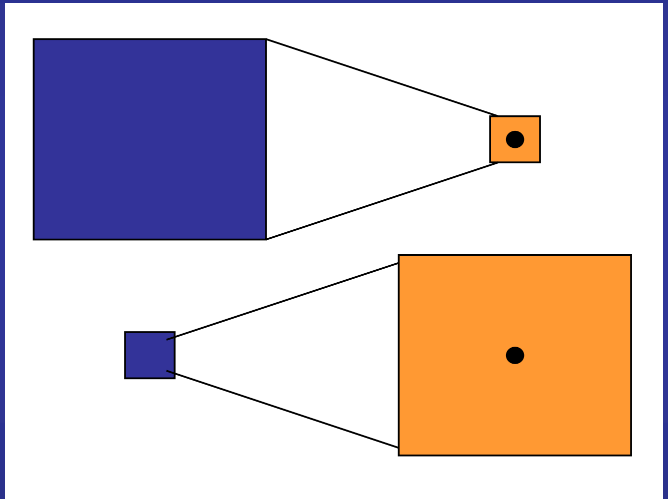
Adsorption energy of CO on Ir(100):



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

When the sampling in k is essential?

Small systems **Metals** **Magnetic systems**



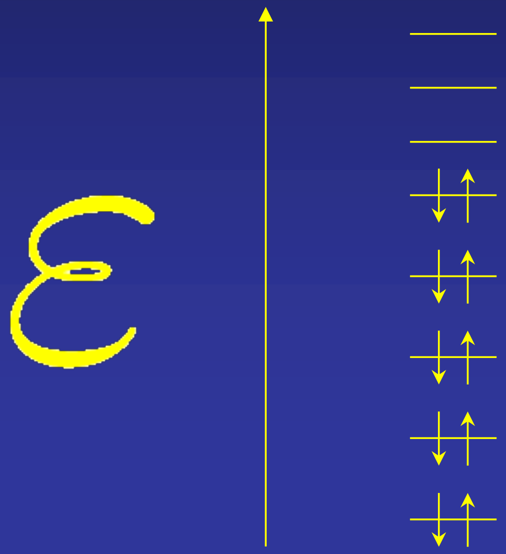
Real space ↔ Reciprocal space

Good description of the Bloch states at the Fermi level

Even in same insulators:

Perovskite oxides

The one-particle eigenstates are filled following the "Aufbau" principle: from lower to higher energies



$$n^\sigma(\vec{r}) = \sum_i \underset{\big\downarrow}{f_i^\sigma} \left|\psi_i^\sigma(\vec{r})\right|^2$$

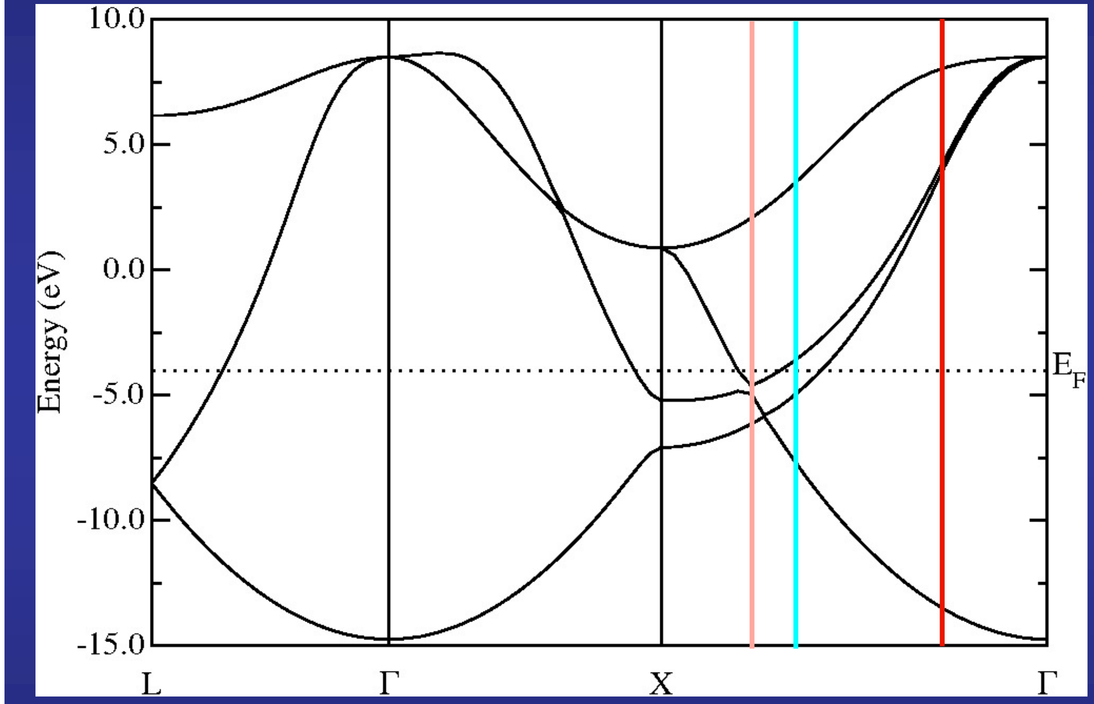
Occupation numbers

The ground state has one (or two if spin independent) in each of the orbitals with the lowest eigenvalues

Fermi surface sampling for metallic systems

The determination of the Fermi level might be delicate for metallic systems

Band structure of bulk Al



For this k-point, three bands are occupied

For this k-point, two bands are occupied

For this k-point, one band is occupied

Slightly different choices of k-points can lead to bands entering or exiting the sum, depending if a given eigenvalue is above or below the Fermi level.

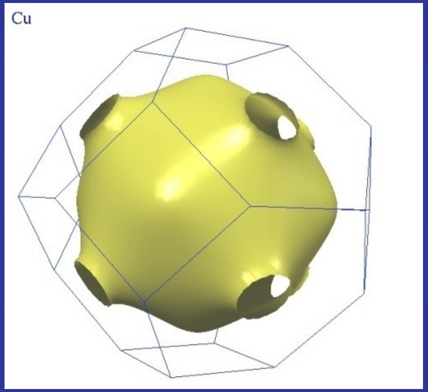
For a sufficiently dense Brillouin zone sampling, this should not be a problem

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.



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…

The Free Energy

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

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

- What we actually want is $E(\sigma\rightarrow 0)$
- $E(\sigma\rightarrow 0)=\frac{1}{2}(F+E)$ (deviation O(T^3))

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

Difficulties in the convergence of the self-consistence procedure with metals: smearing the Fermi surface

For the k-points close to the Fermi surface, the
highest occupied bands can enter or exit the sums
from one iterative step to the next, just because the
adjustement of the Fermi energy

⇓

Instability of the self-consistent procedure

Solution 1: Use small self-consistent mixing coefficients

Solution 2: Smear the Fermi surface introducing a distribution of occupation number

The occupations are not any longer 1 (if below E_F) or 0 (if above E_F)

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

Difficulties in the convergence of the self-consistence procedure with metals: smearing the Fermi surface

For the k-points close to the Fermi surface, the highest occupied bands can enter or exit the sums from one iterative step to the next, just because the adjustement of the Fermi energy

$\Downarrow$

Instability of the self-consistent procedure

Solution 1: Use small self-consistent mixing coefficients

Solution 2: Smear the Fermi surface introducing a distribution of occupation number

The occupations are not any longer 1 (if below E_F) or 0 (if above E_F)

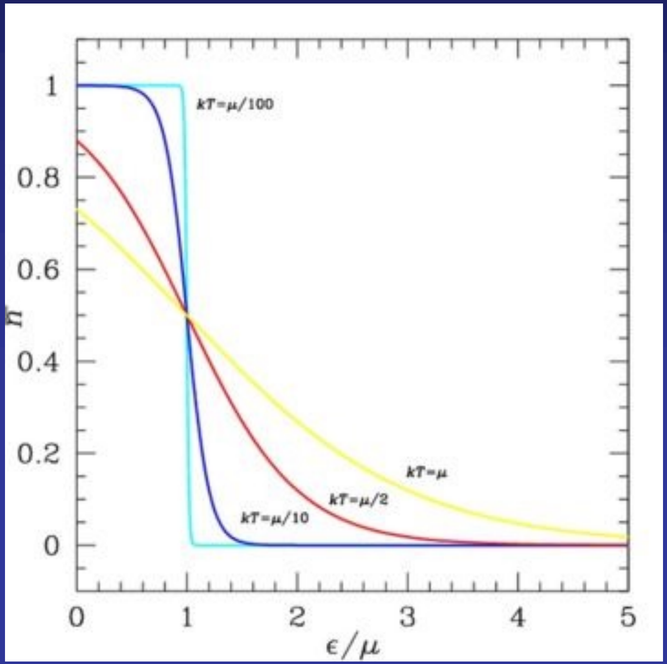
Gaussians C. –L. Fu and K. –M. Ho, Phys. Rev. B 28, 5480 (1989)

Fermi functions

$$n_i(\vec{k}) = \frac{1}{e^{(\varepsilon_i(\vec{k})-E_F)/k_BT_e} + 1}$$

Smearing the Fermi surface: the Electronic Temperature

$$n_i(\vec{k}) = \frac{1}{e^{(\varepsilon_i(\vec{k})-E_F)/k_B T_e} + 1}$$



$k_B T_e$ is a ***broadening energy parameter*** that is adjusted to avoid instabilities in the convergence of the self-consistent procedure. It is a **technical issue**. Due to its analogy with the Fermi distribution, this parameter is called the **Electronic Temperature**

For a finite T_e, the BZ integrals converge faster but to incorrect values. After self-consistency has been obtained for a relatively large value of T_e, this has to be reduced until the energy becomes independent of it.

Gaussian Smearing

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

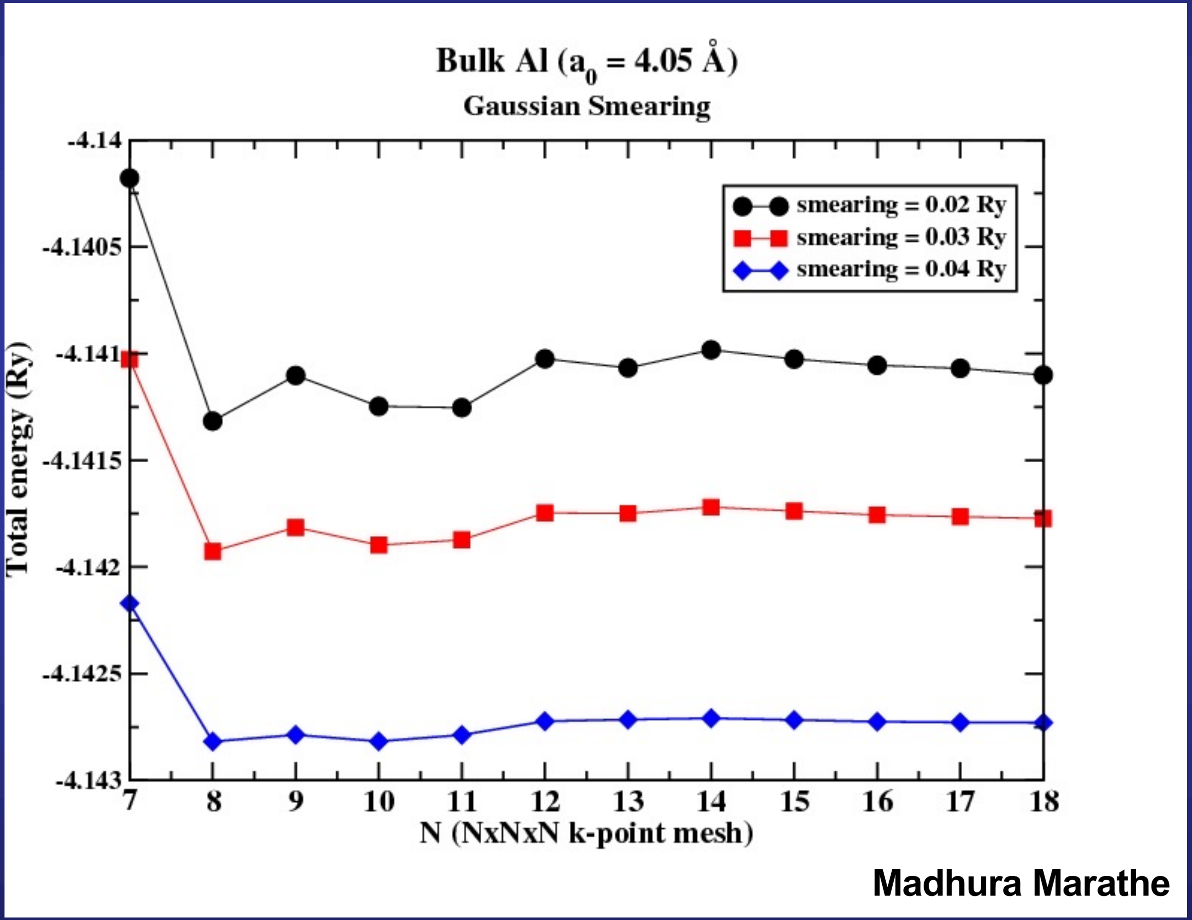
$$f(E) = \frac{1}{2}\left[1 - \text{erf}\left(\frac{E - \mu}{\sigma}\right)\right]$$

(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 <u>right</u> answer!

Convergence with respect to grid and smearing

Gaussian smearing



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Better Smearing Functions

Methfessel & Paxton:

Methfessel & Paxton, Phys. Rev. B 40 3616 (1989)

Can have a successive series of better (but smooth) approximations to the step function.

E converges fast [with respect to σ] to $E(\sigma \rightarrow 0)$

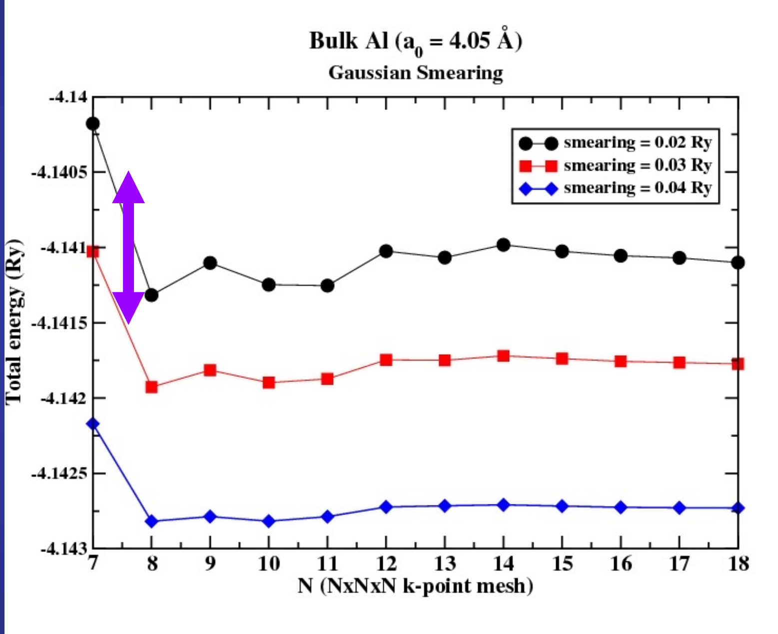
Marzari & Vanderbilt:

Marzari & Vanderbilt, Phys Rev. Lett. 82, 3296 (1999).

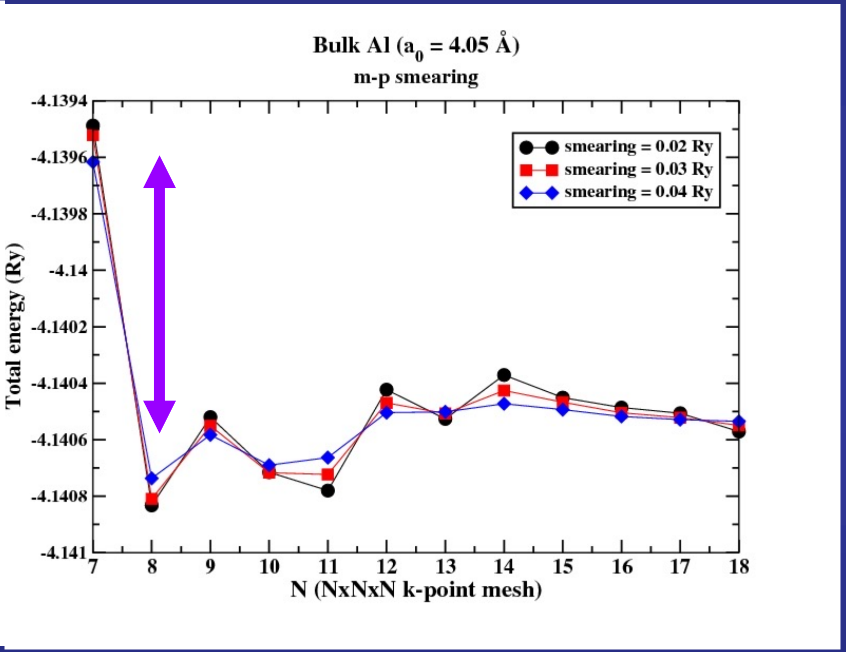
Unlike Methfessel-Paxton, don't have negative occupancies.

Convergence wrt grid & smearing

Gaussian



Methfessel-Paxton:



↕ represents an energy difference of 1 mRy

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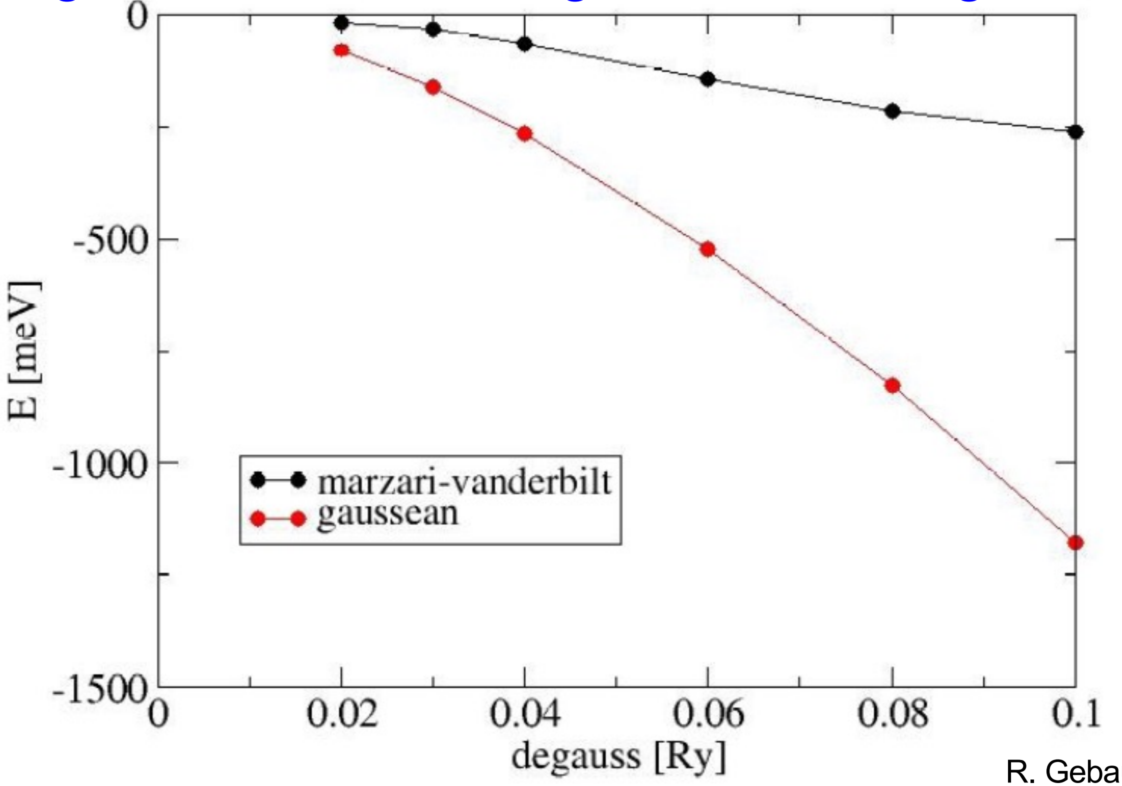
Convergence with respect to k-points and smearing width

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.

Intrinsically aperiodic systems simulated with periodic boundary conditions: the supercell approach

How can we simulate systems where the periodicity is broken?

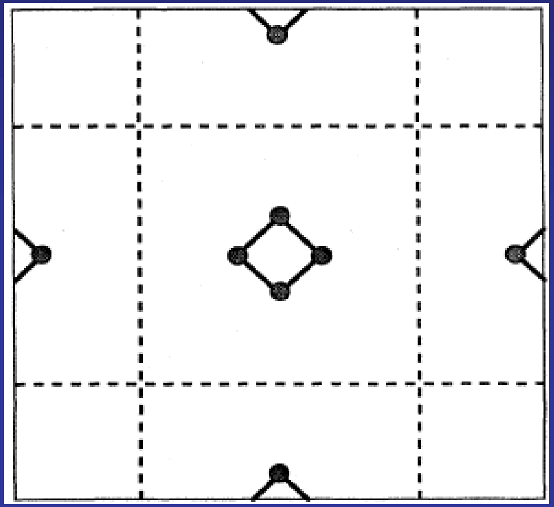
- **Defects:**
  - **Point defects (interstitials, vacancies,…)**
  - **Extended defects (surfaces, edges, steps,…)**
- **Molecules or clusters**

Solution:

Supercell approach + periodic boundary conditions

Make sure that the physical and chemical properties are converged with respect to the size of the supercell

The supercell approach for molecules or clusters



Introduce a vacuum region that should be large enough that periodic images corresponding to adjacent replicas of the supercell do not interact significantly

Make sure that the physical and chemical properties are converged with respect to the size of the supercell

M. C. Payne *et al*., Rev. Mod. Phys. 64, 1045 (1992)

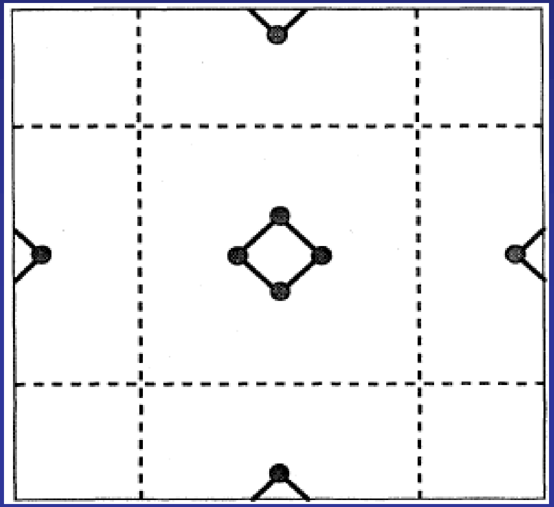
Sometimes convergence is difficult to achieve

Charged molecules: the electrostatic energy of an infinitely periodically replicated charged system diverges.

Typical solution: compensate the charge with a uniformly spread of background charge of opposite sign (a jellium)

In Siesta, use the input variable **NetCharge** (for SC, FCC, BCC)

The supercell approach for molecules or clusters



Introduce a vacuum region that should be large enough that periodic images corresponding to adjacent replicas of the supercell do not interact significantly

Make sure that the physical and chemical properties are converged with respect to the size of the supercell

M. C. Payne *et al.*, Rev. Mod. Phys. 64, 1045 (1992)

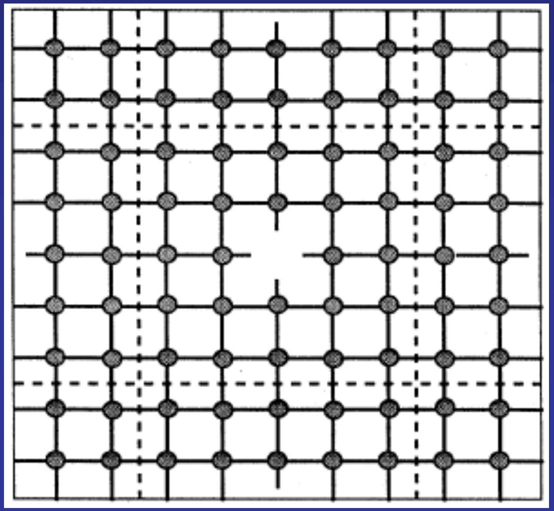
Sometimes convergence is difficult to achieve

Neutral polar molecules: the electrostatic interaction between dipoles decays as R^{-3} and the quadropole-quadropole interaction decays as R^{-5}

Mechanism to eliminate the undesired inter-cell interactions can be devised modifying the Poisson equation that determines the electrostatic potential.

G. Makov and M. C. Payne, Phys. Rev. B 51, 4014 (1995)

The supercell approach for point defects

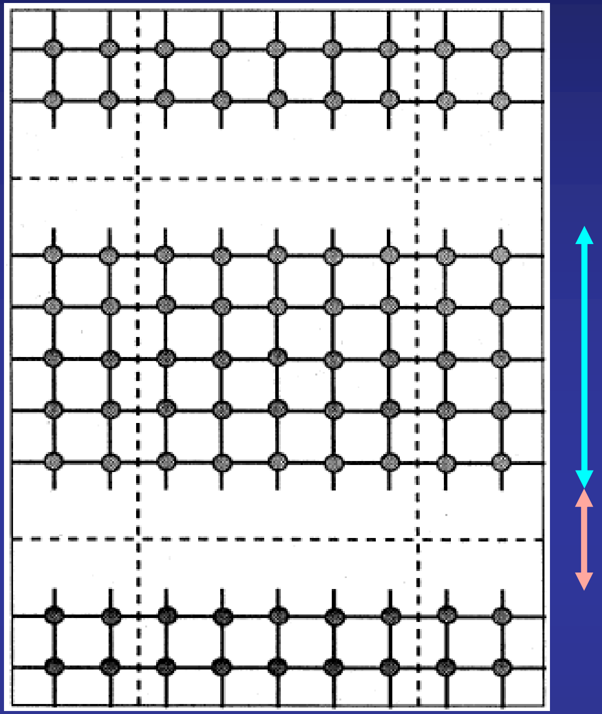


M. C. Payne *et al.*, Rev. Mod. Phys. 64, 1045 (1992)

Introduce a **piece of bulk.** The amount of bulk should be large enough that the periodic images of the defect do not interact significantly

Charged defects present the same problems of convergence as charged molecules

The supercell approach for surfaces: the slab geometry



The semi-infinite bulk is represented by a slab with two surfaces

The slab has to be large enough that the two surfaces do not interact with each other

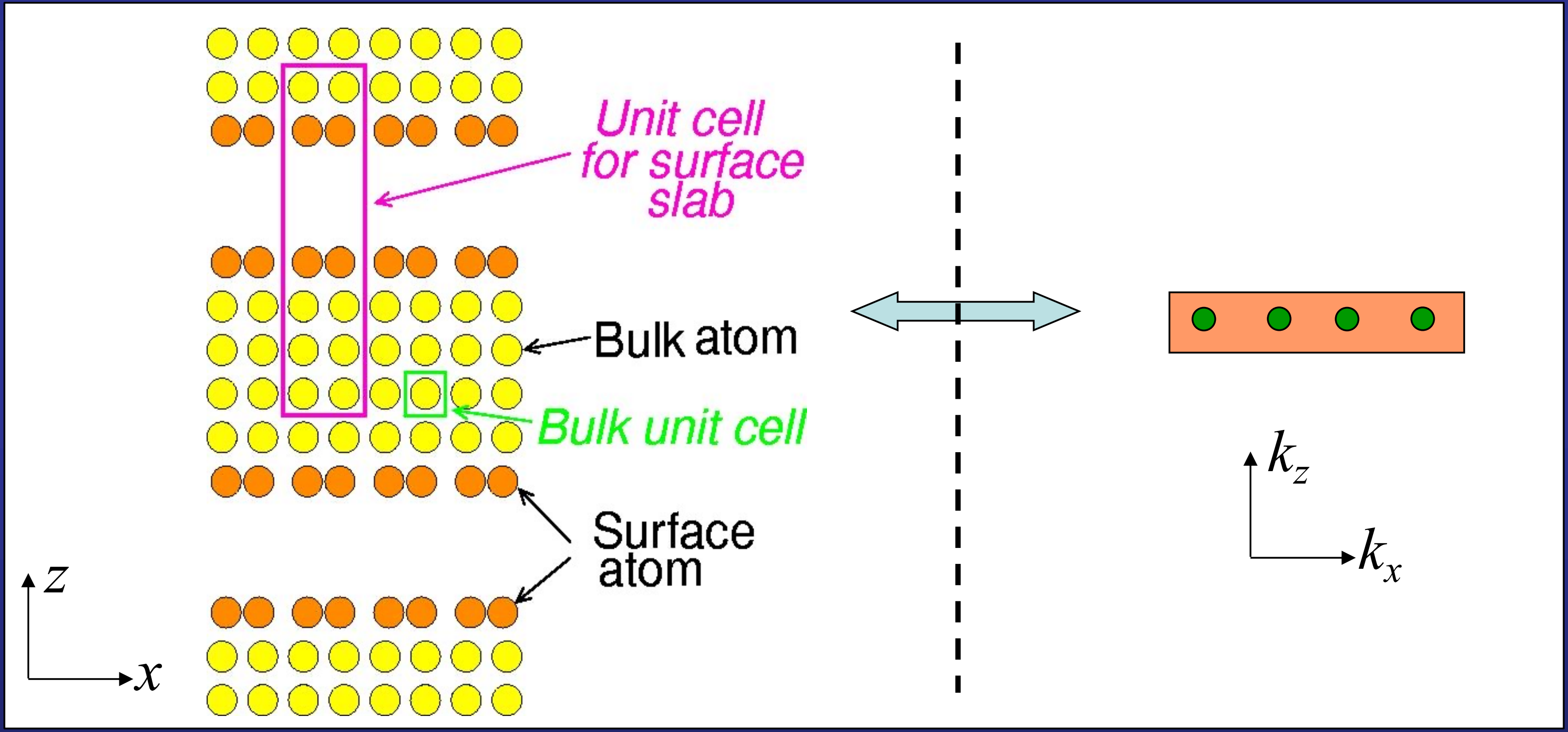
The vacuum between periodic replicas has also to be large enough, specially in charged or polarized slabs

M. C. Payne *et al*., Rev. Mod. Phys. 64, 1045 (1992)

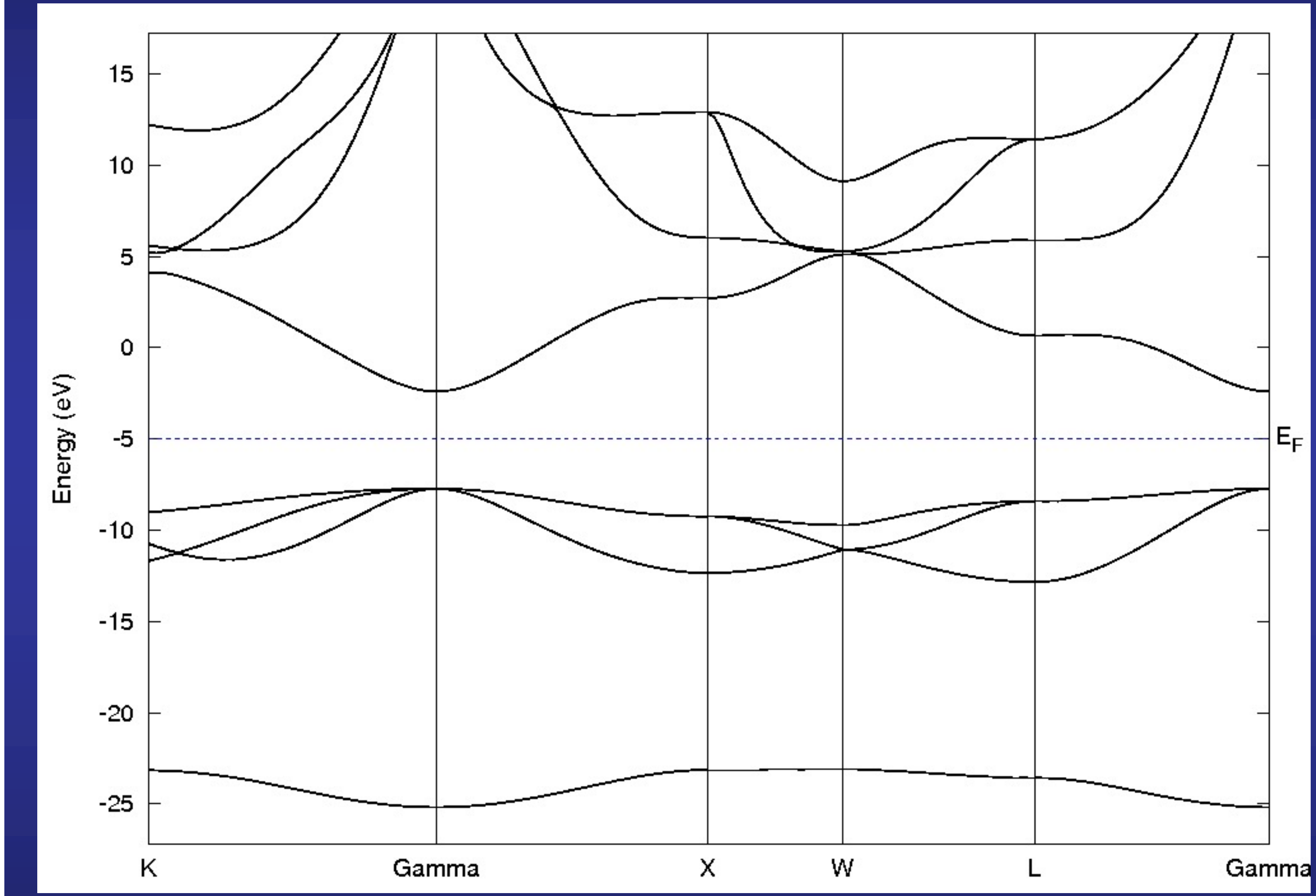
Usually, semiconductor and insulators require larger supercells than metals

Choosing grid divisions

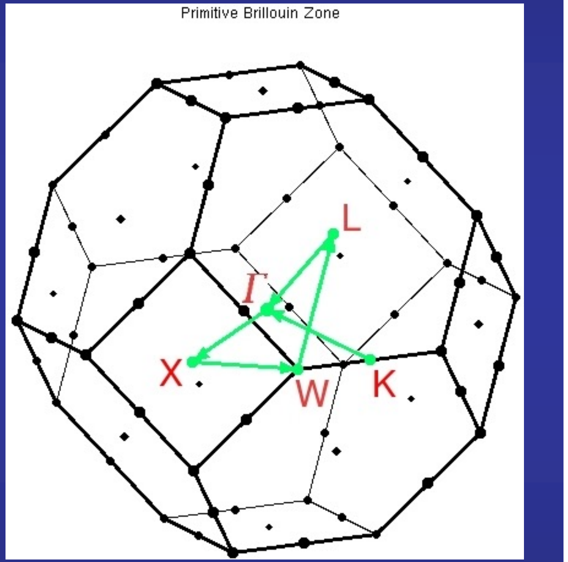
For artificially periodic supercells, choose only 1 division along the dimensions that have been extended (in real space) by introducing vacuum region.



Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone



MgO band structure



The Fermi energy lies in a gap ⇒ insulator

Theo. direct gap = 5.3 eV

Expt. Gap = 7.8 eV

(LDA band gap understimation)

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 with respect to 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)

How to set up the k-point sampling in Siesta

Spetial set of k-points: Accurate results for a small number of k-points

Monkhorst-Pack

Variables that control the fineness of the grid

kgrid_cutoff

```
kgrid_cutoff        10.0 Ang
```

A real-space radius that plays a role equivalent to the plane-wave cutoff in real space grids

(Moreno and Soler 92)

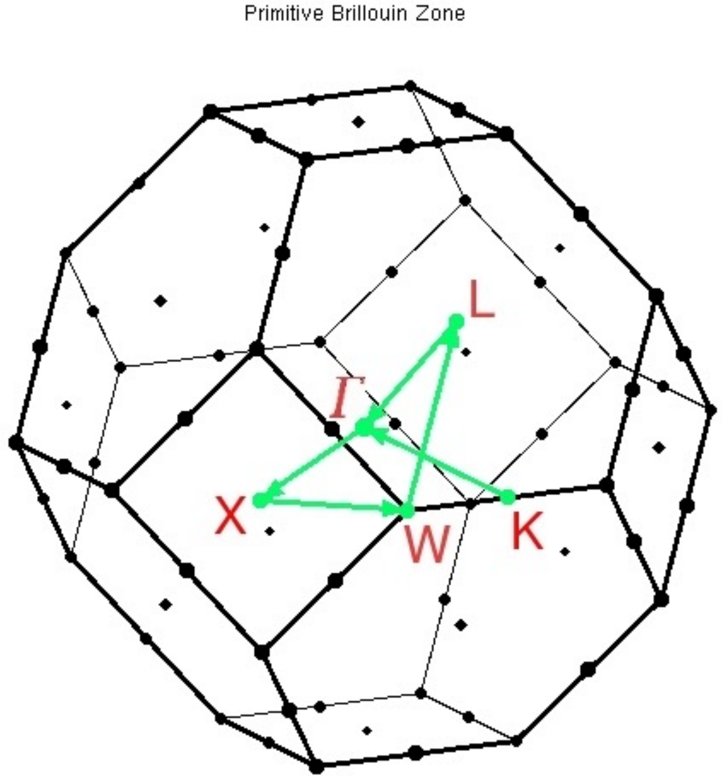
kgrid_Monkhorst_Pack

```
%block kgrid_Monkhorst_Pack
   4    0    0   0.5
   0    4    0   0.5
   0    0    4   0.5
%endblock kgrid_Monkhorst_Pack
```

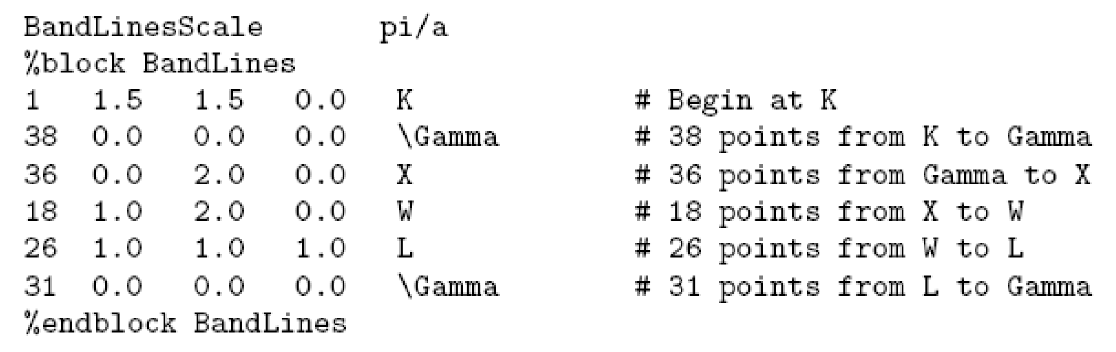
The origin of the k-grid might be displaced to reduce the number of inequivalent k-points

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone

First-Brillouin zone of a FCC , with the high symmetry points



New variables to plot the band structure



```
BandLinesScale        pi/a
%block BandLines
1    1.5    1.5    0.0    K             # Begin at K
38   0.0    0.0    0.0    \Gamma        # 38 points from K to Gamma
36   0.0    2.0    0.0    X             # 36 points from Gamma to X
18   1.0    2.0    0.0    W             # 18 points from X to W
26   1.0    1.0    1.0    L             # 26 points from W to L
31   0.0    0.0    0.0    \Gamma        # 31 points from L to Gamma
%endblock BandLines
```