Brillouin zone sums

Shobhana Narasimhan
JNCASR, Bangalore, India
shobhana@jncasr.ac.in

Outline

- Density of states
- Brillouin zone sampling

1. Density of States

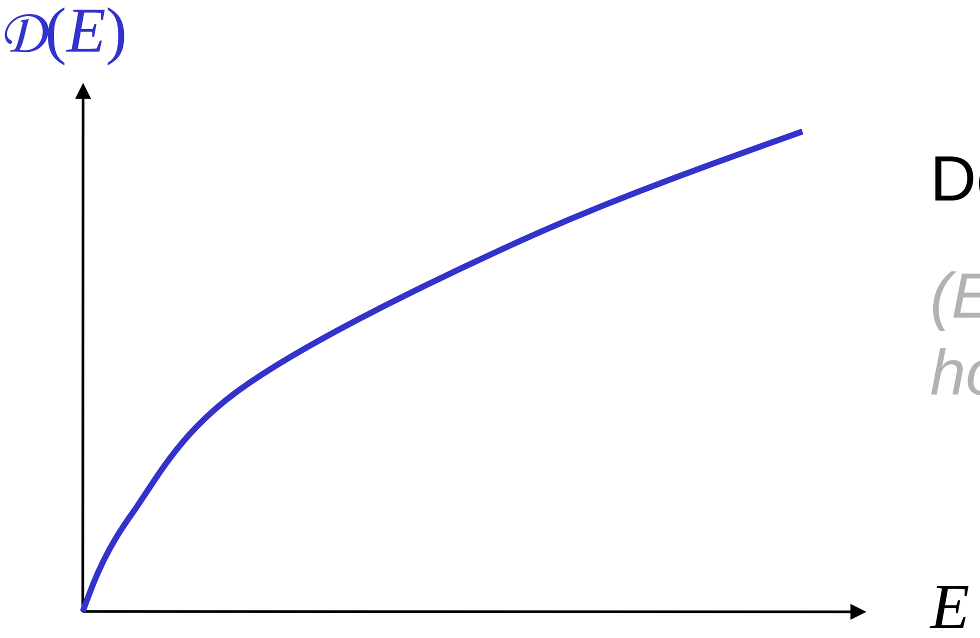
Density of States $\mathcal{D}(E)$ or $g(E)$

- $\mathcal{D}(E)dE$: Number of states available in the energy range E to $E+dE$ *(used in Kittel)*
- $g(E)dE = (1/V)\mathcal{D}(E)dE$ = number of states available, per unit volume, in the energy range E to $E+dE$ *(used in Ashcroft and Mermin)*

- Note: these definitions hold even when the electrons are not free.
- Can also define DOS for phonons, etc.

- For free electrons, since $E \propto k^2$, as $|k|$ ↑, the range of $|k|$ that corresponds to a unit interval dE will have a decreasing width.

DOS for free electrons in 3-D



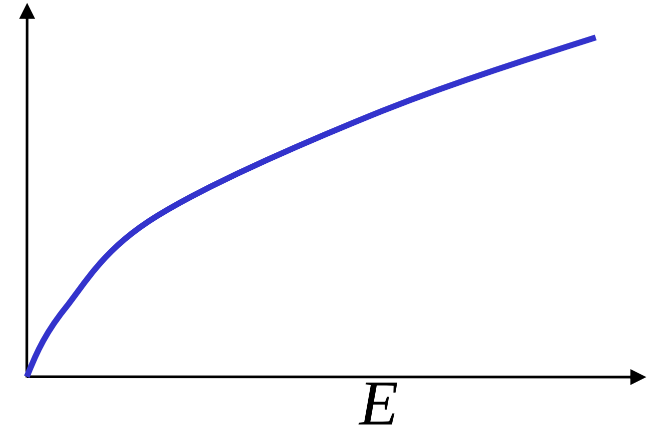
Density of states ↑ as E ↑

(Exact derivation: homework!)

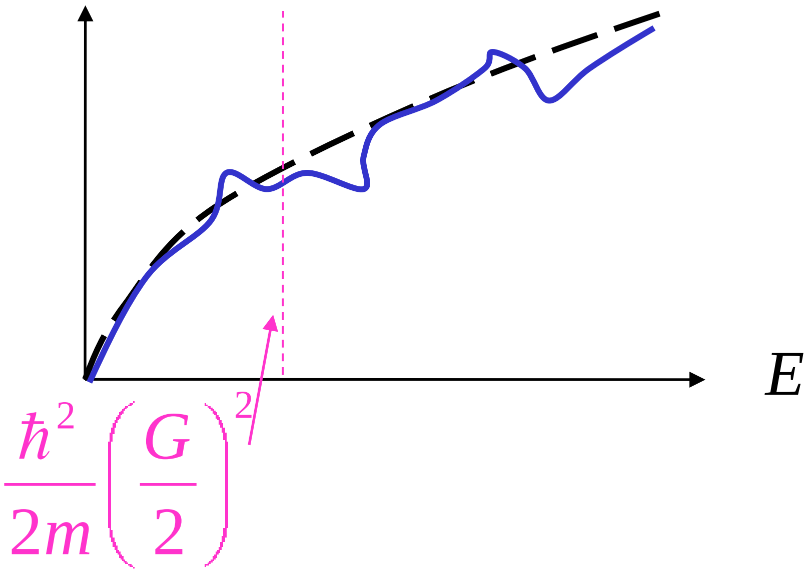
(Schematic diagram only!)

Density of States in Presence of a Periodic Potential

- Let us see some qualitative features:
- Bands get distorted in neighborhood of Bragg planes
- DOS gets blips in neighborhood of energies corresponding to Bragg planes.



Free electrons

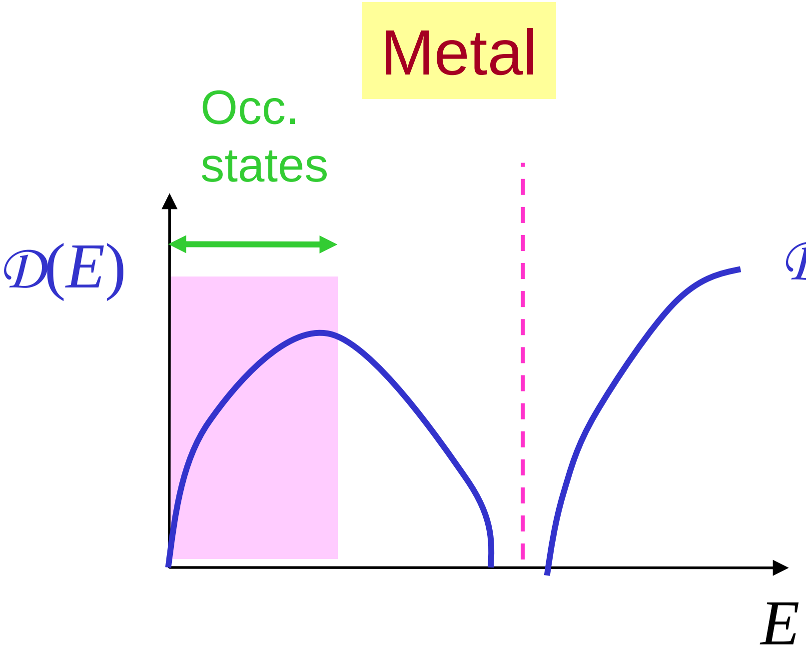


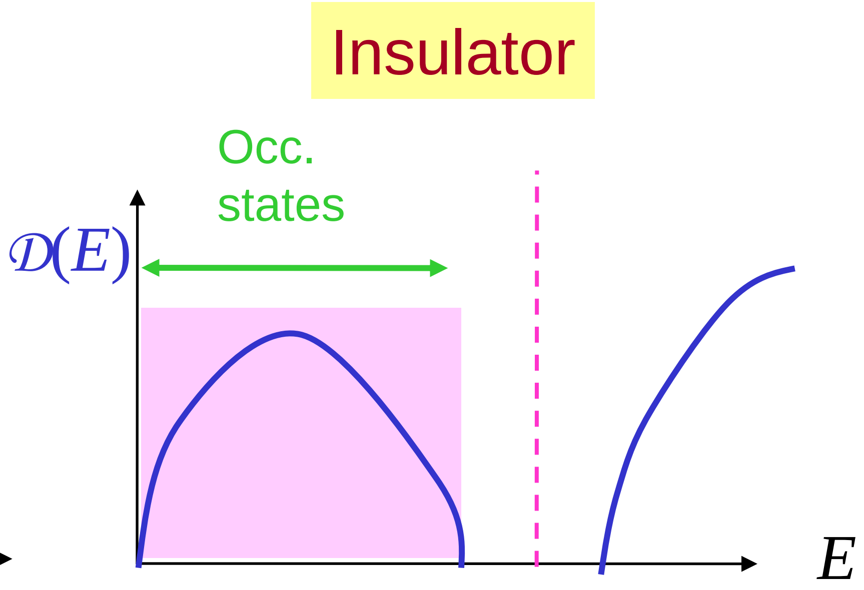
Electrons in periodic potl.

$$\frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2$$

Density of States in Presence of a Periodic Potential

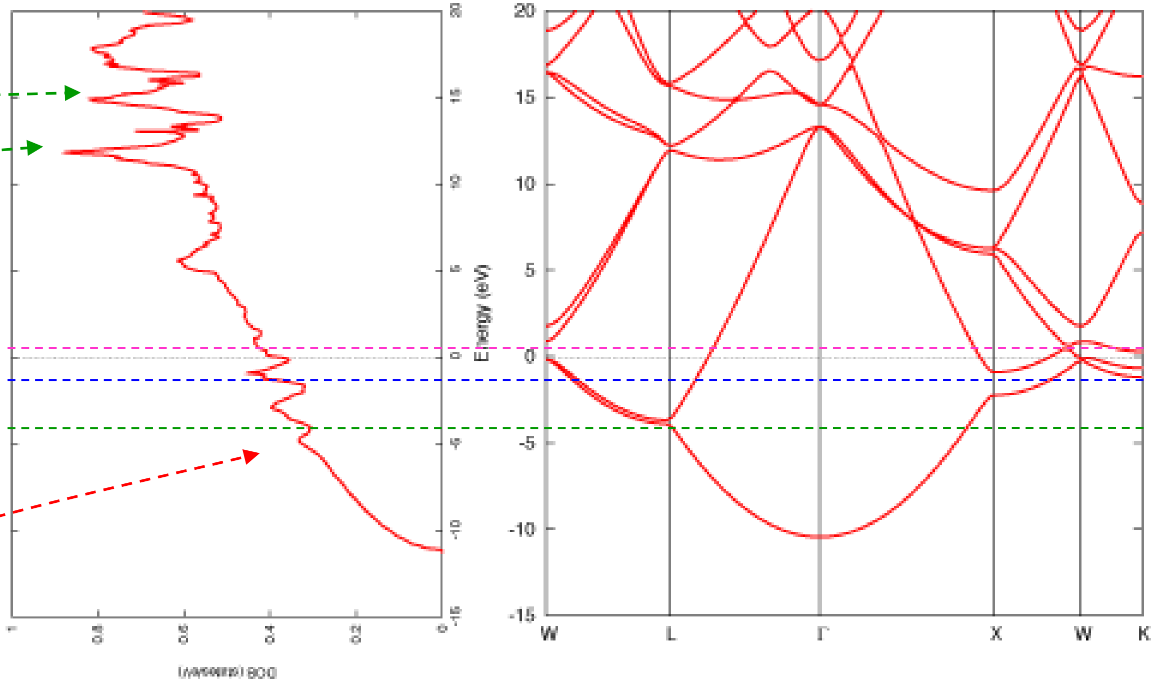
- Let us see some qualitative features:





Density of States

- For Al:



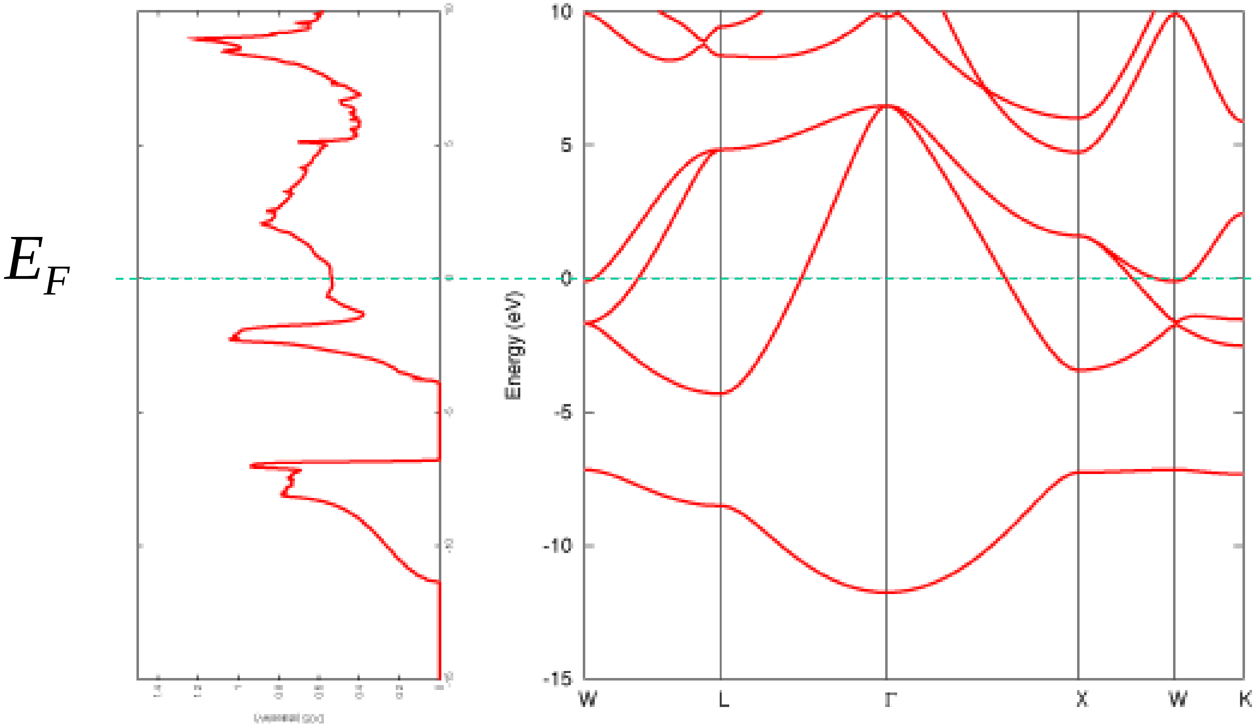
Van Hove Singularities

Density of States ("sideways"!)

www.fsis.iis.u-tokyo.ac.jp

Density of States

- For Pb:



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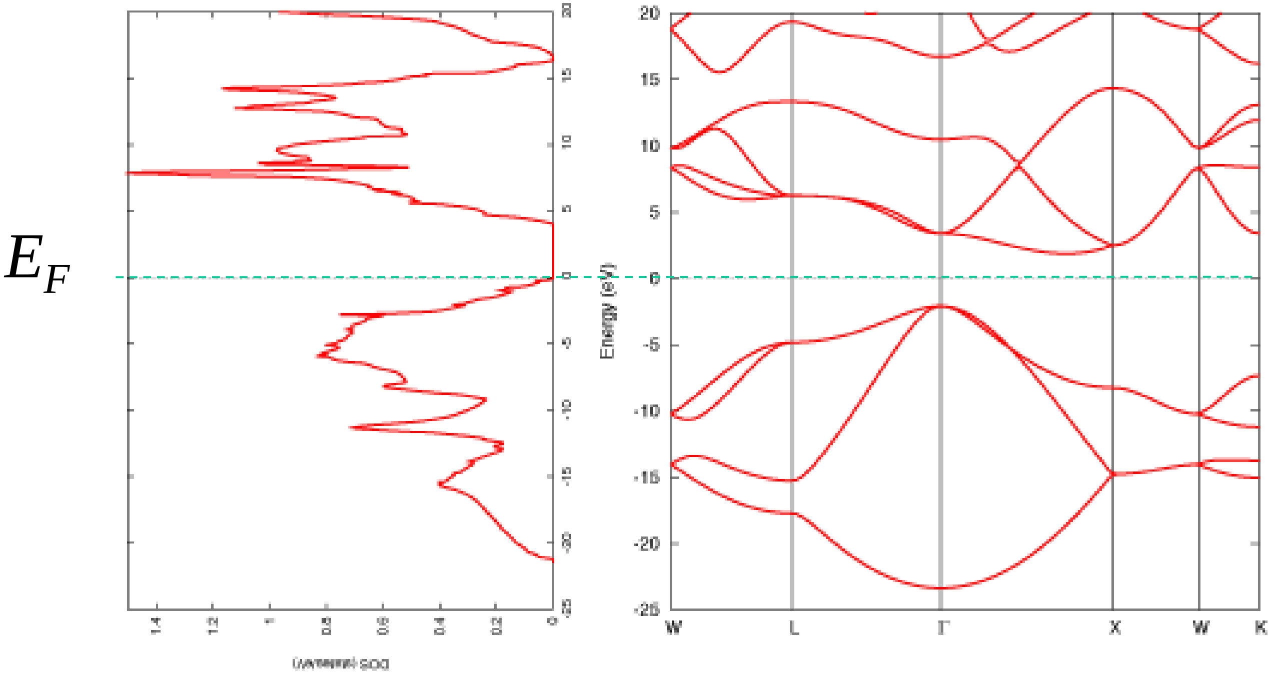
Density of States

- For C (diamond structure):



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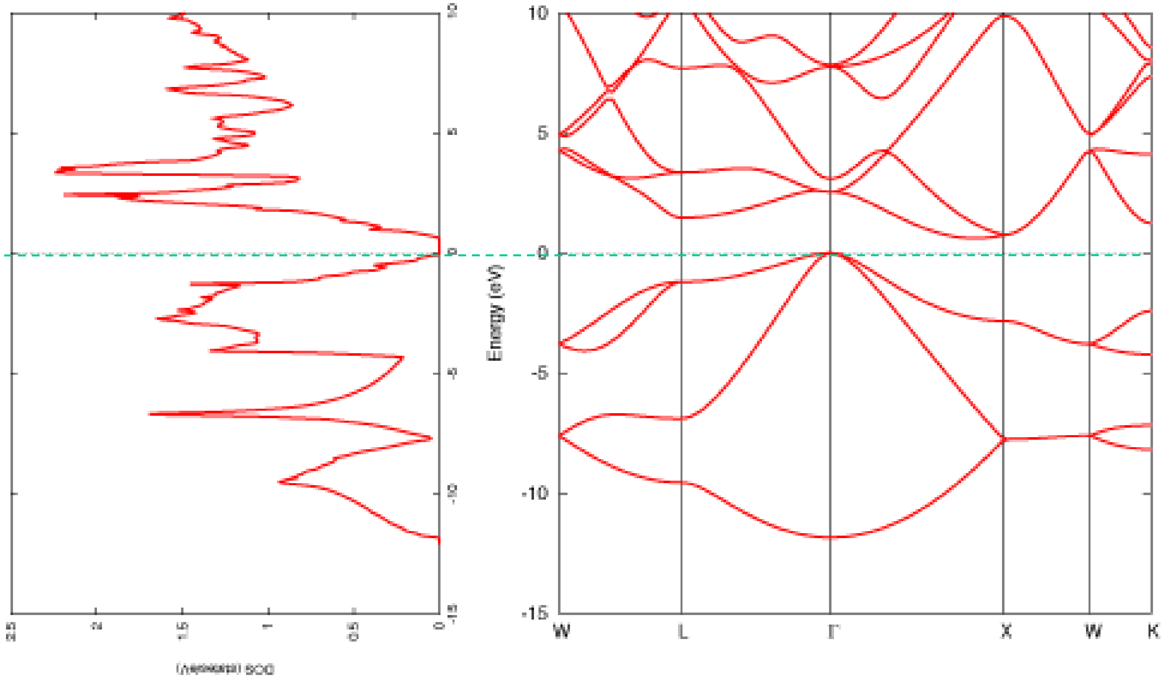
Density of States

- For Si:



E_F

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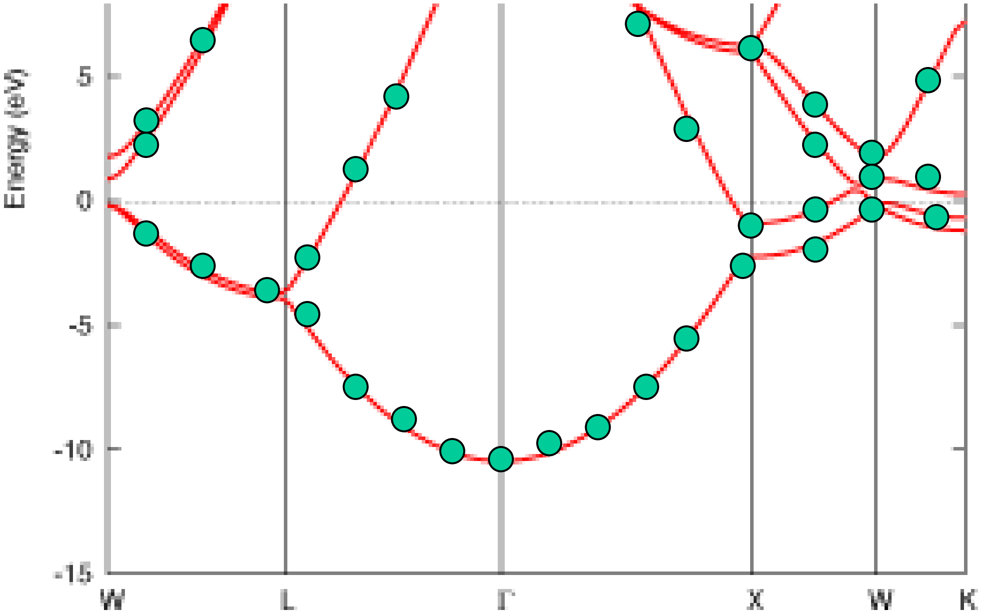
Calculating the Band Structure in Practice

- Except for some simple models where an analytical solution is possible, one calculates the band structure numerically at certain values of wave-vector **k.**

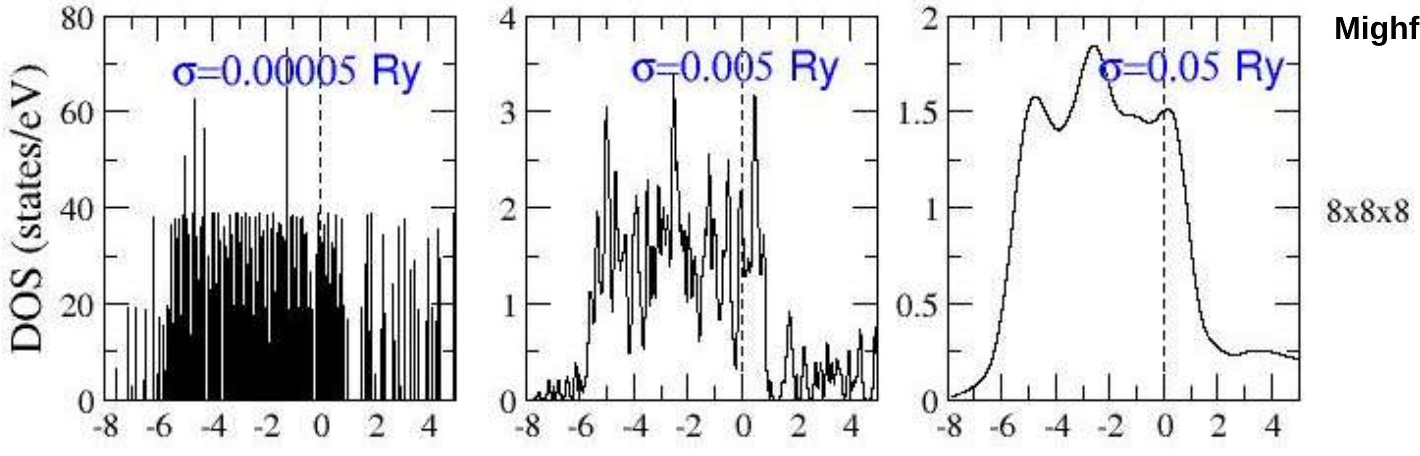


Calculating the Density of States in Practice

$$g(E) = \frac{1}{N_k} \sum_{n,\mathbf{k}\in BZ} \delta(E - \varepsilon_{n\mathbf{k}})$$

- Obtain $\varepsilon_{n\mathbf{k}}$ on a grid of k in the BZ.
- Approximate δ fn. by smeared-out function (gaussian) with a width σ.

e.g., for bulk rhodium:



Mighfar Imam

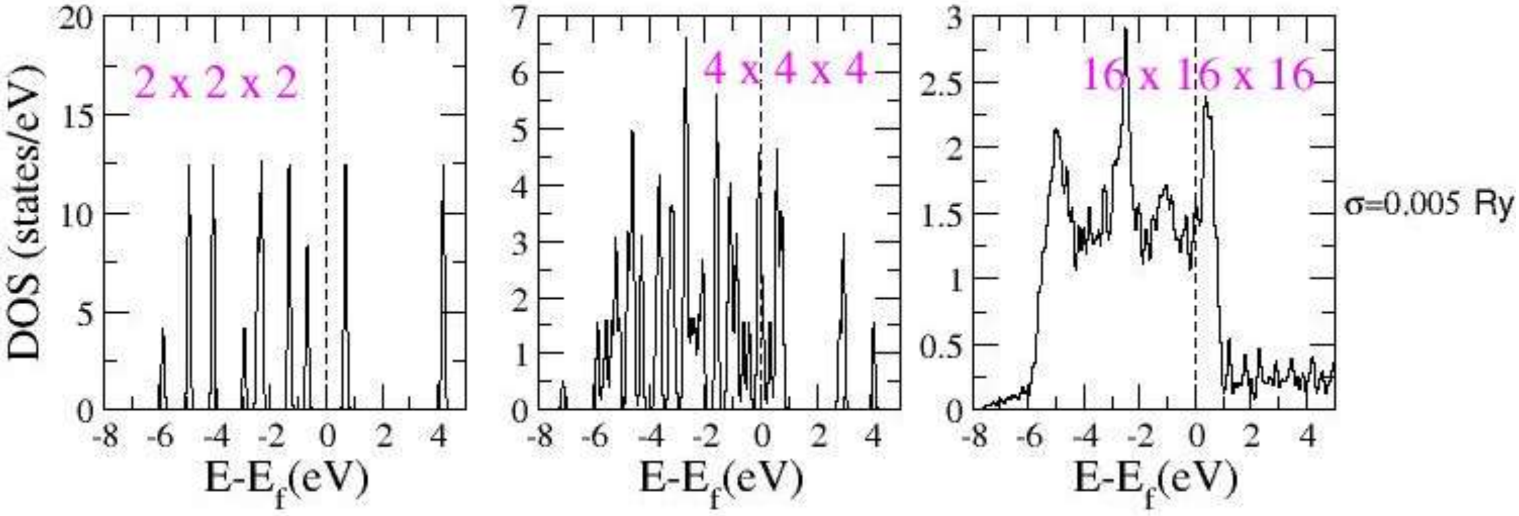
σ too small E-E_F (eV) σ too large

Calculating the Density of States in Practice

$$g(E) = \frac{1}{N_k} \sum_{n,\mathbf{k}\in BZ} \delta(E - \varepsilon_{n\mathbf{k}})$$

- Obtain $\varepsilon_{n\mathbf{k}}$ on a grid of $\mathbf{k}$ in the BZ;
- Approximate δ-fn. by smeared out function (e.g.,gaussian).
- Need a very fine grid in k-space to get sharp features ok.

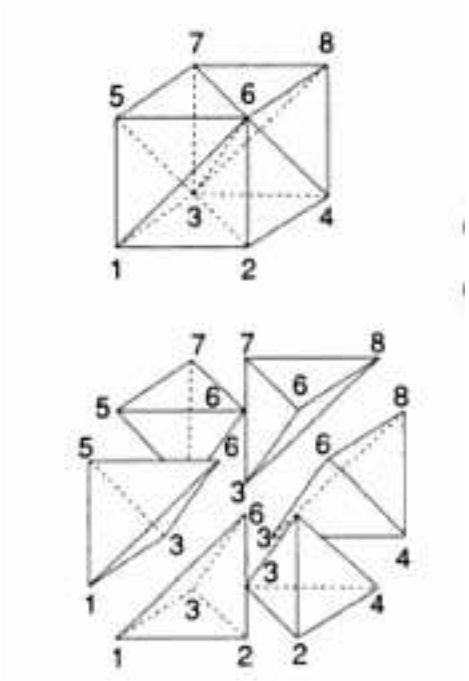
e.g., for bulk rhodium:



Mighfar Imam

Interpolating between k-points

- In order to get sharp features in the DOS (e.g., van Hove singularities) correctly, use a method that interpolates between k-points.
- e.g., the Linear Tetrahedron method.
- Tetrahedra can be used to fill all space for any grid.
- Linear interpolation between values at vertices.



Bloechl, Jepsen & Andersen

2. Brillouin Zone Sampling

Card **`K_POINTS`**

Brillouin Zone Sums

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

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

- **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".

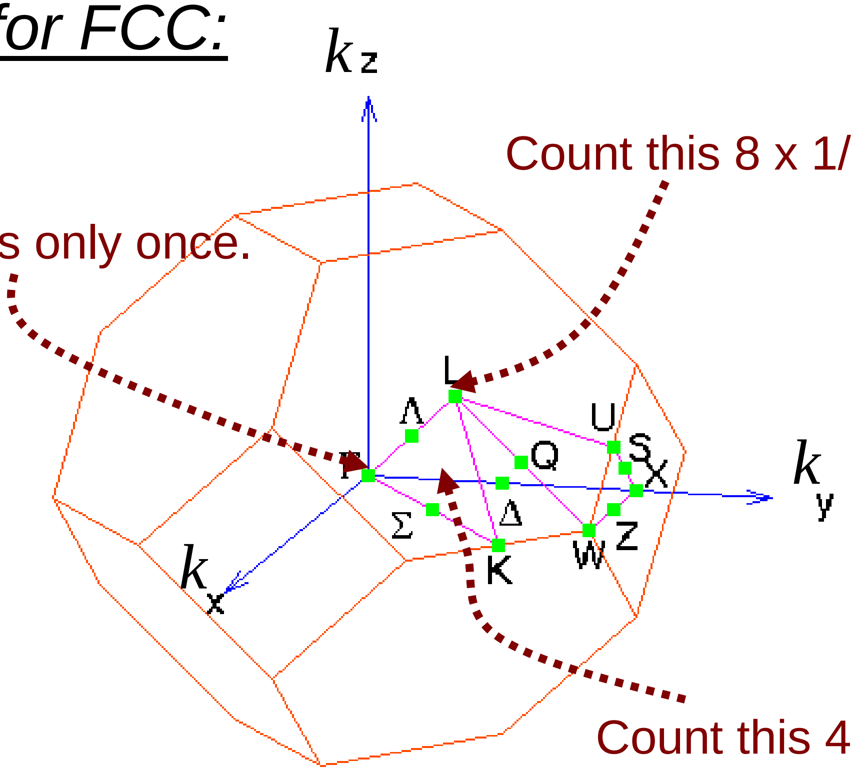
$$\boxed{\langle P \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\substack{\mathbf{k}\in BZ \\ n\,occ}} P_n(\mathbf{k})}$$

- For computational reasons, want # **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:



Count this 8 x 1/2 times.

Count this only once.

Count this 48 times.

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

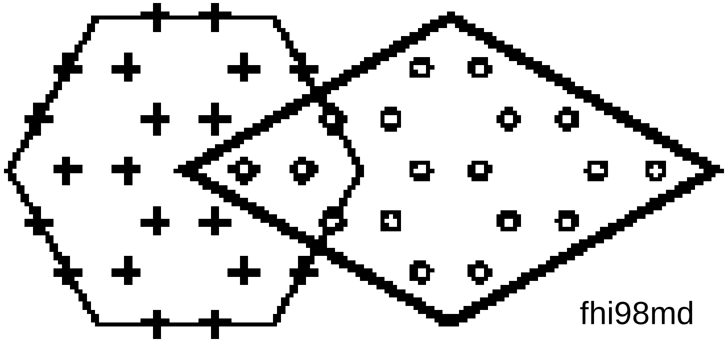
cst-www.nrl.navy.mil

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)

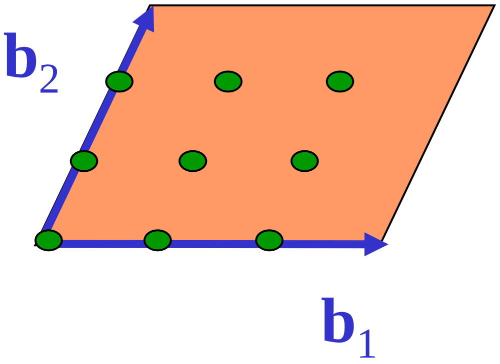


fhi98md

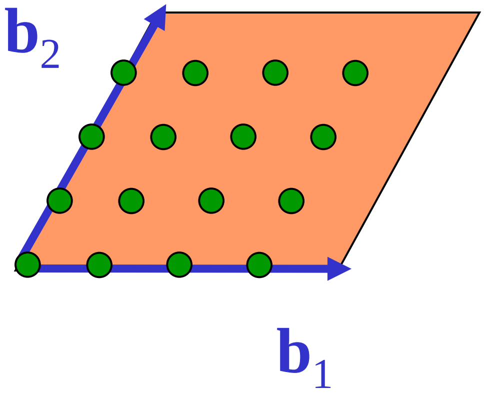
Monkhorst-Pack k-points

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

nk1=nk2=3



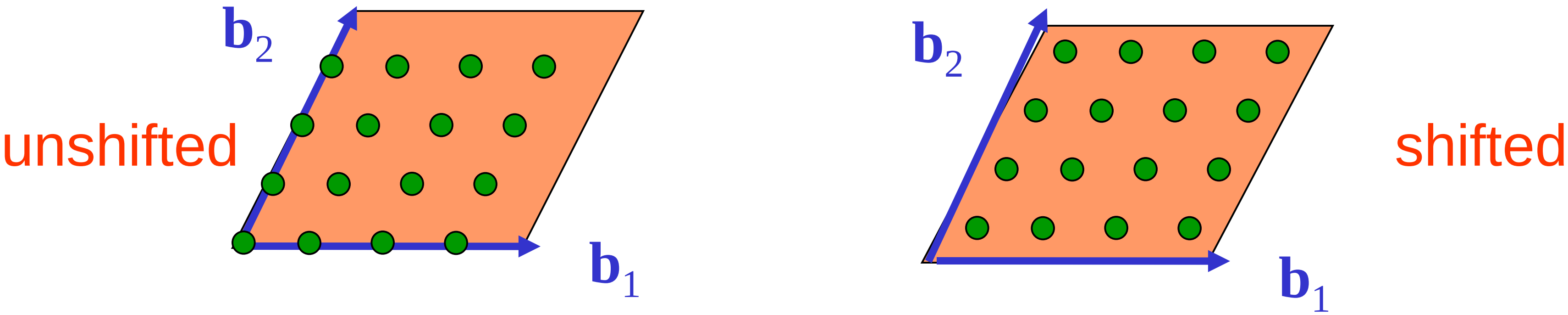
nk1=nk2=4



- *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.

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 **`ibrav`** shifted grid may not have full symmetry.

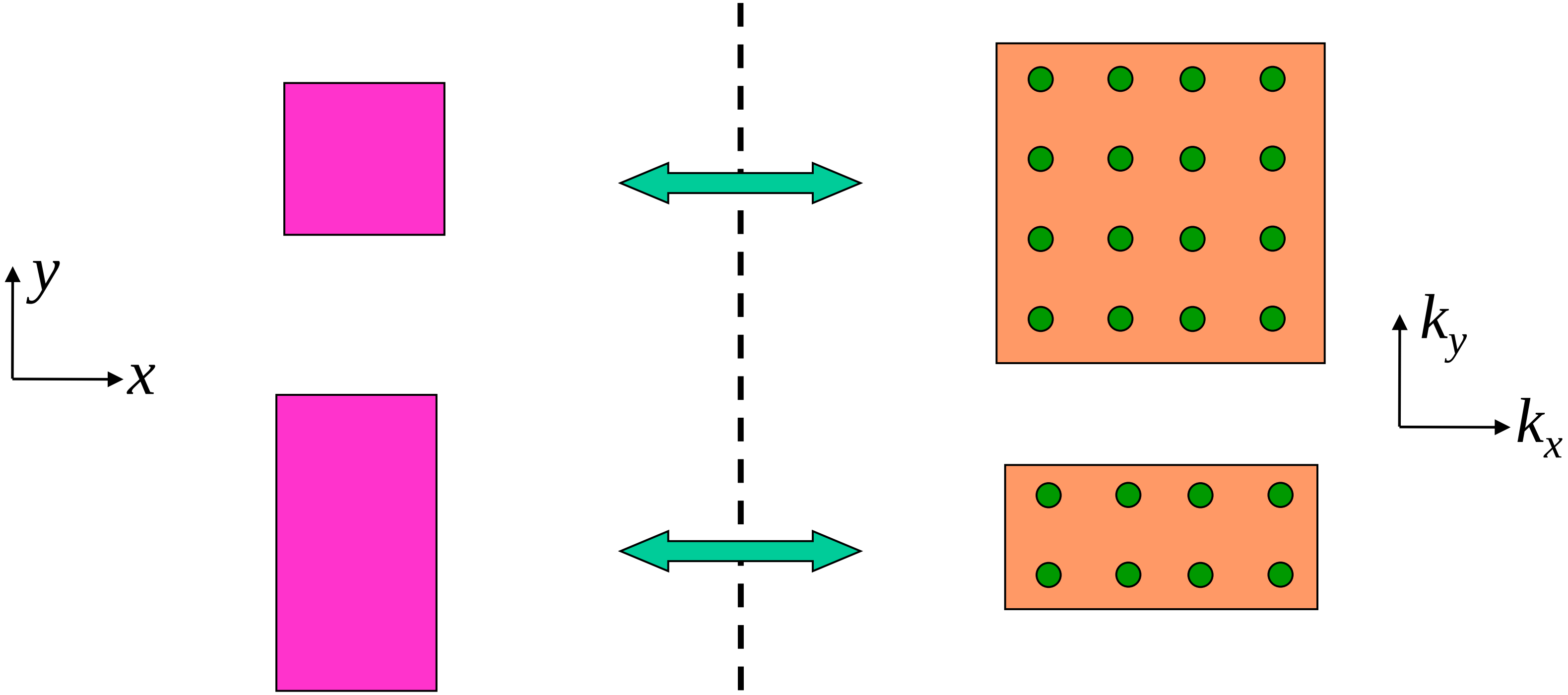


```
nk1 nk2 nk3 k1 k2 k3
```

grid divisions (nk1 nk2 nk3)   shift (k1 k2 k3)

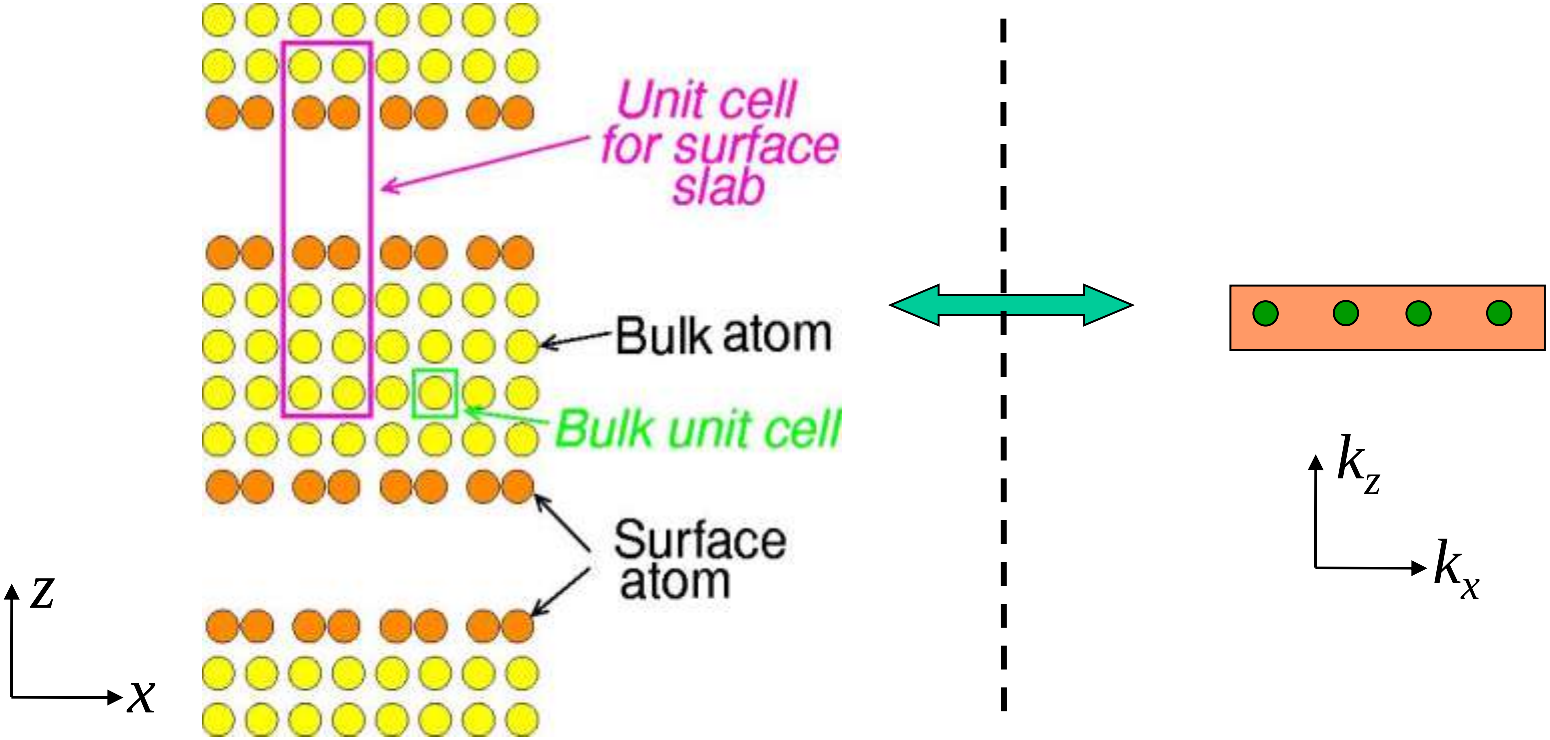
Choosing Grid Divisions

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



Choosing Grid Divisions

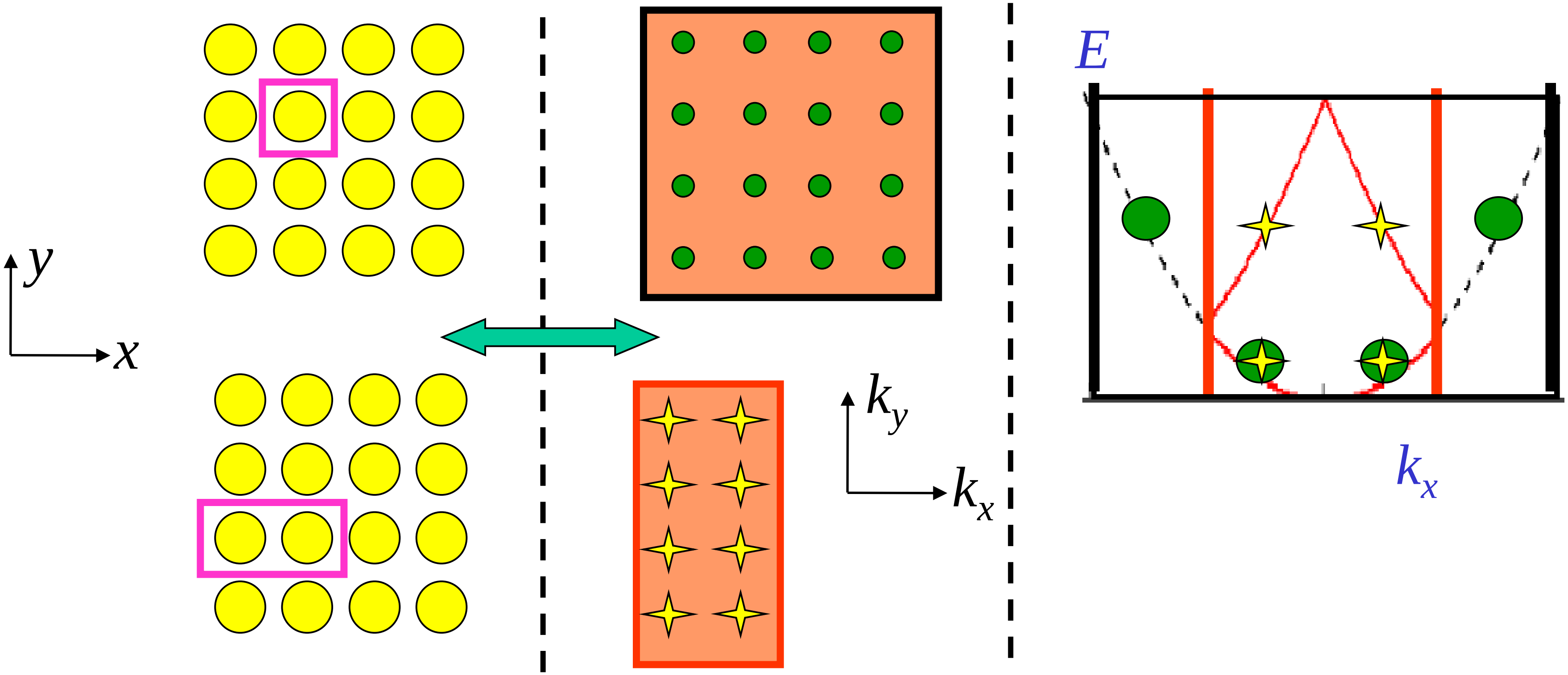
- For artificially periodic supercells, choose only 1 division along the dimensions that have been extended (in real space) by introducing vacuum region.



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 .



Specifying k-points in PWscf

`K_POINTS { tpiba|automatic|crystal|gamma }`

- `gamma`: use only **k**=0 (use different faster routines)
- `automatic`: generate Monkhorst-Pack mesh

  `nk1, nk2, nk3, k1, k2, k3:`

  grid divisions, offset (shifted/unshifted)
- `tpiba`: k-points specified, in units of 2π/*a*

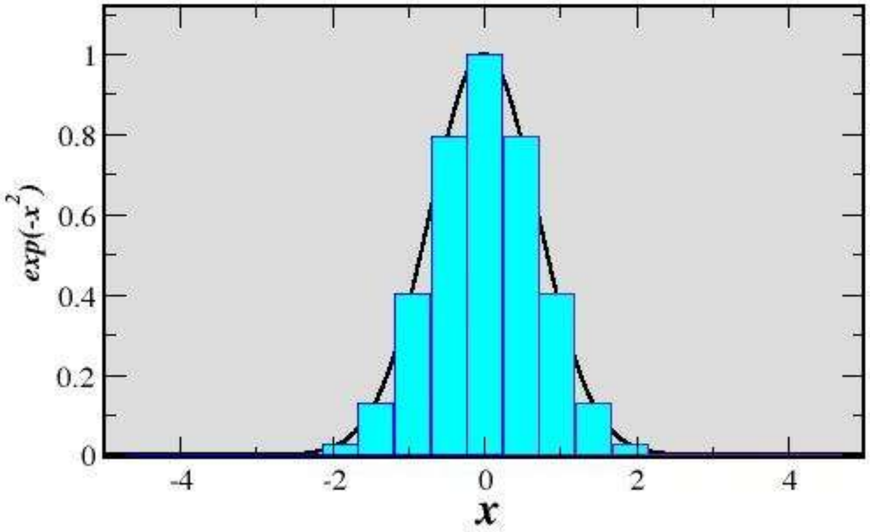
  `nks`: number of special k-points supplied

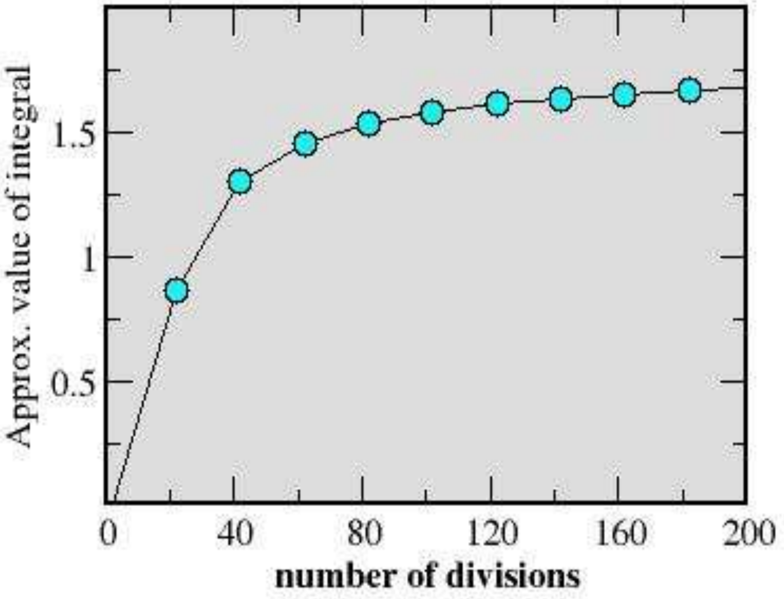
  `xk_x, xk_y, xk_z, wk:` coordinates & weights
- `crystal`: k-points specified, in units of PRLV's.

Analogy: Numerical Integration of Gaussian

Let us approximately integrate $\int_{-xcut}^{xcut} e^{-x^2} dx$

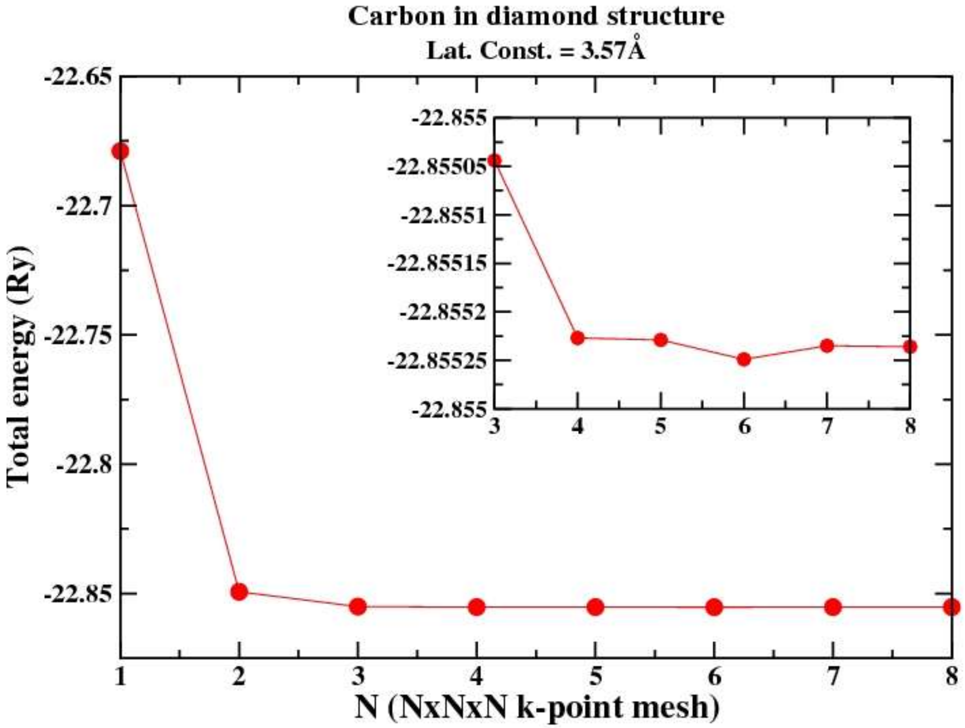
by dividing the range from -5 to 5 into *ndiv* divisions:





- •Larger *ndiv*: more accurate answer but longer cpu time.
- •Sharper the features in fn.: larger *ndiv* needed for accuracy.

Convergence wrt BZ sampling

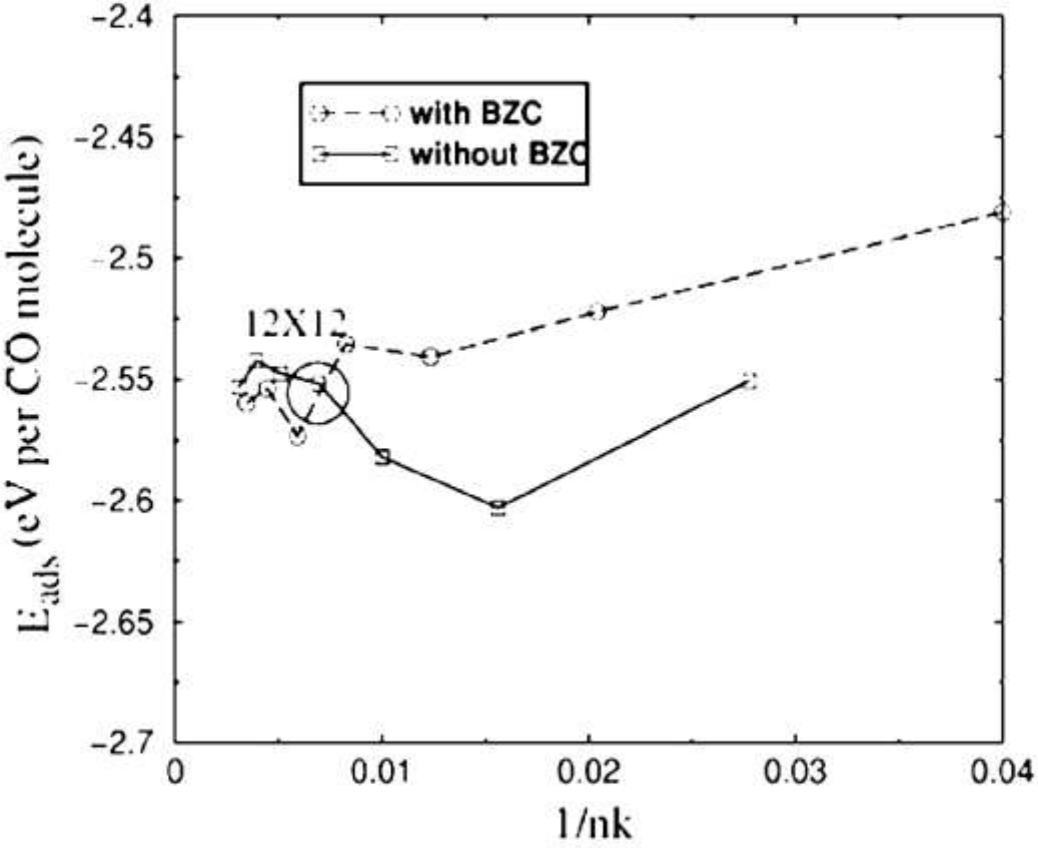


Madhura Marathe

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):



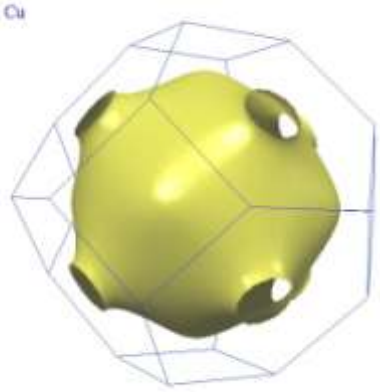
Ghosh, Narasimhan, Jenkins & King, J. Chem. Phys. **126** 244701 (2007).

Problems with Metals

- Recall:

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

- 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

How to deal with metals?

- Use LOTS of k points...this is not an ideal solution because you will need LOTS of cpu time (calculation time scales linearly with number of k-points, so for example a 10x10x10 grid will take ~15 times as much time as a 4x4x4 grid.)

- Deal with the sharp discontinuity in k-space by "smearing out" the occupations. *(Nicola Marzari will discuss later).*