Implementing DFT in Plane-Wave basis

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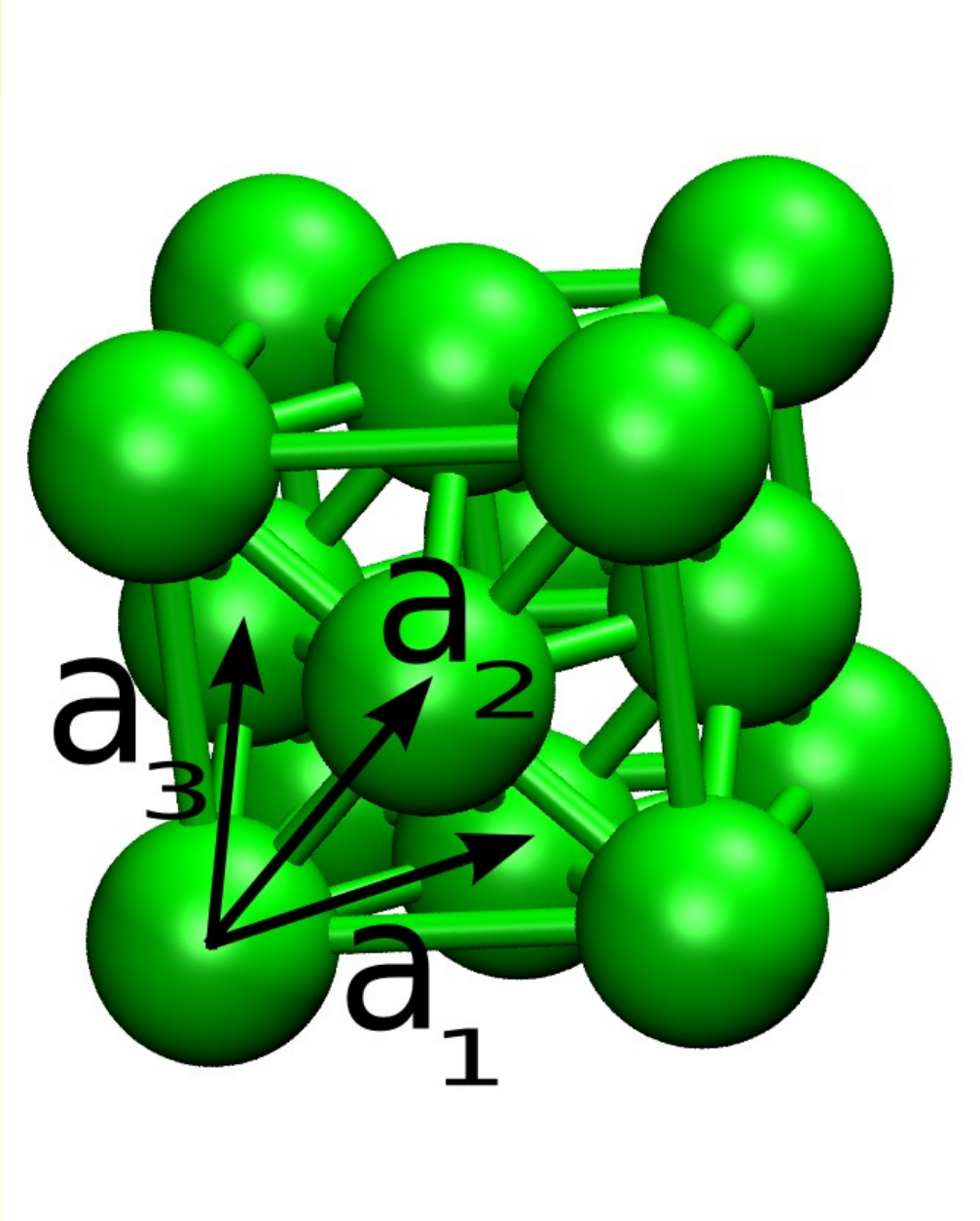
DFT for periodic systems



Outline

A DFT code adapted to periodic systems:

- Self-consistency in KS equations
- Crystal structure
- **k**-points
- Plane-Waves
- Supercells

Solving KS equations

depends on the density
non linear equations

$$h(\boldsymbol{r}) = -\frac{\nabla^2}{2} + v_{ion}(\boldsymbol{r}) + v_H[\rho](\boldsymbol{r}) + v_{xc}[\rho](\boldsymbol{r})$$

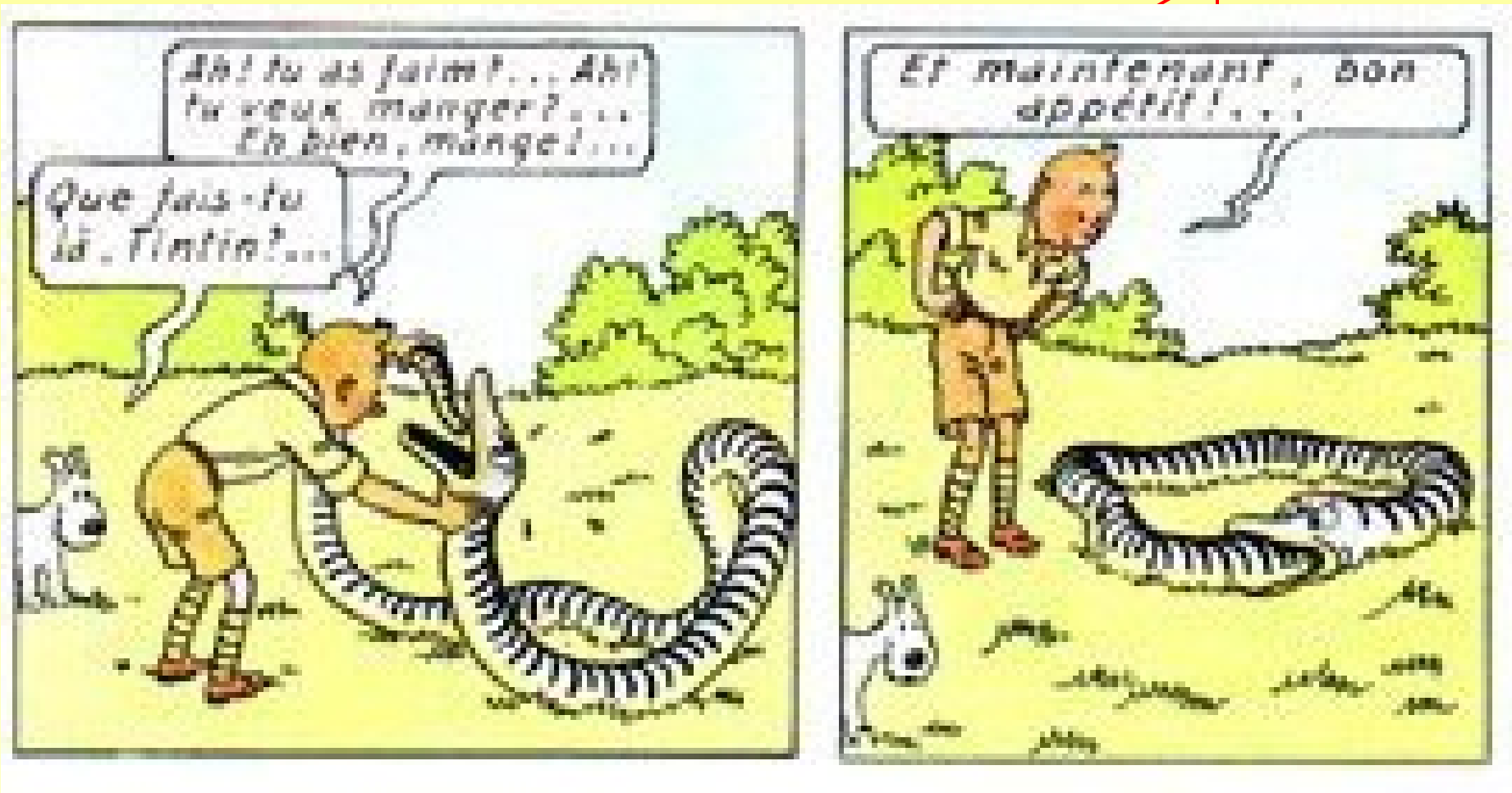
$$h(\boldsymbol{r})\phi_i(\boldsymbol{r}) = \epsilon_i \phi_i(\boldsymbol{r})$$

$$\rho(\boldsymbol{r}) = \sum_{i\,occ} |\phi_i(\boldsymbol{r})|^2$$

Energy, Forces, Band structure, Electronic density

Solving KS equations

depends on the density
➡ non linear equations



Energy, Forces, Band structure, Electronic density

Solving KS equations

First guess for $\rho^{(0)}(\boldsymbol{r})$

depends on the density
➡ non linear equations

$$h(\boldsymbol{r}) = -\frac{\nabla^2}{2} + v_{ion}(\boldsymbol{r}) + v_H[\rho](\boldsymbol{r}) + v_{xc}[\rho](\boldsymbol{r})$$

$$h\phi_i = \epsilon_i \phi_i$$

Diagonalization

$$\rho(\boldsymbol{r}) = \sum_{i\ occ} |\phi_i(\boldsymbol{r})|^2$$

if $\rho^{(n)} \neq \rho^{(n-1)}$

Energy, Forces, Band structure, Electronic density

Outline

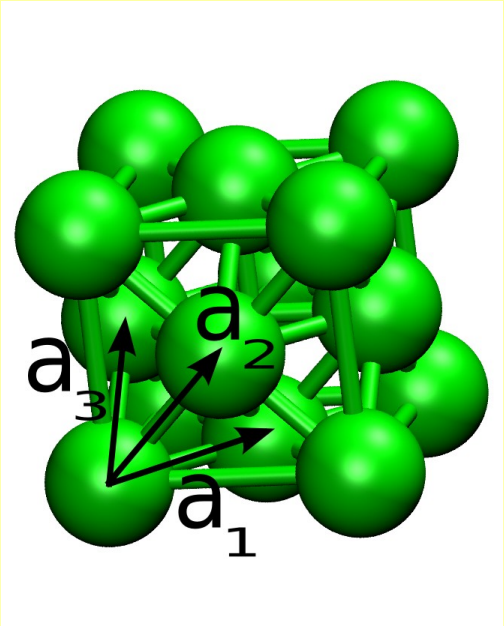
A DFT code adapted to periodic systems: abinit.org

- Self-consistency in KS equations
- **Crystal structure**
- **k**-points
- Plane-Waves
- Supercells

Crystal structure

Crystal axis: $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$

Direct lattice vector: $$\boldsymbol{R} = n_1 \boldsymbol{a_1} + n_2 \boldsymbol{a_2} + n_3 \boldsymbol{a_3}$$



Periodic potential: $$V(\boldsymbol{r} + \boldsymbol{R}) = V(\boldsymbol{r})$$

Reciprocal lattice axis:

$$\boldsymbol{b_1} = \frac{2\pi}{\Omega} \boldsymbol{a_2} \times \boldsymbol{a_3}$$

$$\boldsymbol{b_2} = \frac{2\pi}{\Omega} \boldsymbol{a_3} \times \boldsymbol{a_1}$$

$$\boldsymbol{b_3} = \frac{2\pi}{\Omega} \boldsymbol{a_1} \times \boldsymbol{a_2}$$

Reciprocal lattice:

$$\boldsymbol{G} = n_1 \boldsymbol{b_1} + n_2 \boldsymbol{b_2} + n_3 \boldsymbol{b_3} \quad \Rightarrow \quad e^{i \boldsymbol{G} . \boldsymbol{R}} = 1$$

Bloch theorem and k-points

Bloch theorem:

$$\phi_{ki}(\boldsymbol{r}) = e^{i\boldsymbol{k}.\boldsymbol{r}} u_{ki}(\boldsymbol{r})$$

where ***k*** is in the first Brillouin zone
$u_{ki}(\boldsymbol{r})$ is a periodic function with crystal periodicity

Any **periodic operator** and, in particular, the Hamiltonian, is **diagonal** in **k**.

$$\langle \boldsymbol{k}\, i | h | \boldsymbol{k}'\, j \rangle = \int_V d\boldsymbol{r}\, e^{i(\boldsymbol{k}'-\boldsymbol{k}).\boldsymbol{r}} h(\boldsymbol{r}) u^*_{\boldsymbol{k}\, i}(\boldsymbol{r}) u_{\boldsymbol{k}'\, j}(\boldsymbol{r})$$

$$= \sum_{\boldsymbol{R}} \int_{\Omega} d\boldsymbol{r}\, e^{i(\boldsymbol{k}'-\boldsymbol{k}).(\boldsymbol{r}+\boldsymbol{R})}$$

$$\times h(\boldsymbol{r}+\boldsymbol{R}) u^*_{\boldsymbol{k}i}(\boldsymbol{r}+\boldsymbol{R}) u_{\boldsymbol{k}'\, j}(\boldsymbol{r}+\boldsymbol{R})$$

k-points allow to split the calculations

$$\langle \boldsymbol{k}\, i | h | \boldsymbol{k}'\, j \rangle = \delta_{\boldsymbol{k}\,\boldsymbol{k}'} \langle \boldsymbol{k}\, i | h | \boldsymbol{k}\, j \rangle$$

The Hamiltonian has blocks of non interacting **k**-points:

$$H = \begin{pmatrix} h_{\mathbf{k}_1} & 0 & 0 & \\ 0 & h_{\mathbf{k}_2} & 0 & \\ 0 & 0 & h_{\mathbf{k}_3} & \\ & & & \ddots \end{pmatrix}$$

Solving KS equations with k-points

First guess for $\rho^{(0)}(\boldsymbol{r})$

depends on the density
non linear equations

$$h(\boldsymbol{r}) = -\frac{\nabla^2}{2} + v_{ion}(\boldsymbol{r}) + v_H[\rho](\boldsymbol{r}) + v_{xc}[\rho](\boldsymbol{r})$$

Diagonalizations

$$h_{\boldsymbol{k}_1}\phi_{\boldsymbol{k}_1 i} = \epsilon_{\boldsymbol{k}_1 i}\phi_{\boldsymbol{k}_1 i} \qquad h_{\boldsymbol{k}_2}\phi_{\boldsymbol{k}_2 i} = \epsilon_{\boldsymbol{k}_2 i}\phi_{\boldsymbol{k}_2 i} \qquad h_{\boldsymbol{k}_3}\phi_{\boldsymbol{k}_3 i} = \epsilon_{\boldsymbol{k}_3 i}\phi_{\boldsymbol{k}_3 i}$$

if $\rho^{(n)} \neq \rho^{(n-1)}$

$$\rho(\boldsymbol{r}) = \frac{1}{N_{\boldsymbol{k}}} \sum_{\boldsymbol{k},i\,occ} |\phi_{\boldsymbol{k}i}(\boldsymbol{r})|^2$$

Energy, Forces, Band structure, Electronic density

Brillouin Zone integration

Many quantities of the scheme require **averaging in the BZ**,
e.g. kinetic term, electronic density:

$$\rho(\boldsymbol{r}) = \frac{1}{N_{\boldsymbol{k}}} \sum_{\boldsymbol{k} \in BZ} \sum_{i\,occ} |\phi_{\boldsymbol{k}\,i}(\boldsymbol{r})|^2$$

to be exact, it should be $\rho(\boldsymbol{r}) = \frac{1}{V_{BZ}} \int_{V_{BZ}} d\boldsymbol{k} \sum_{i\,occ} |\phi_{\boldsymbol{k}\,i}(\boldsymbol{r})|^2$

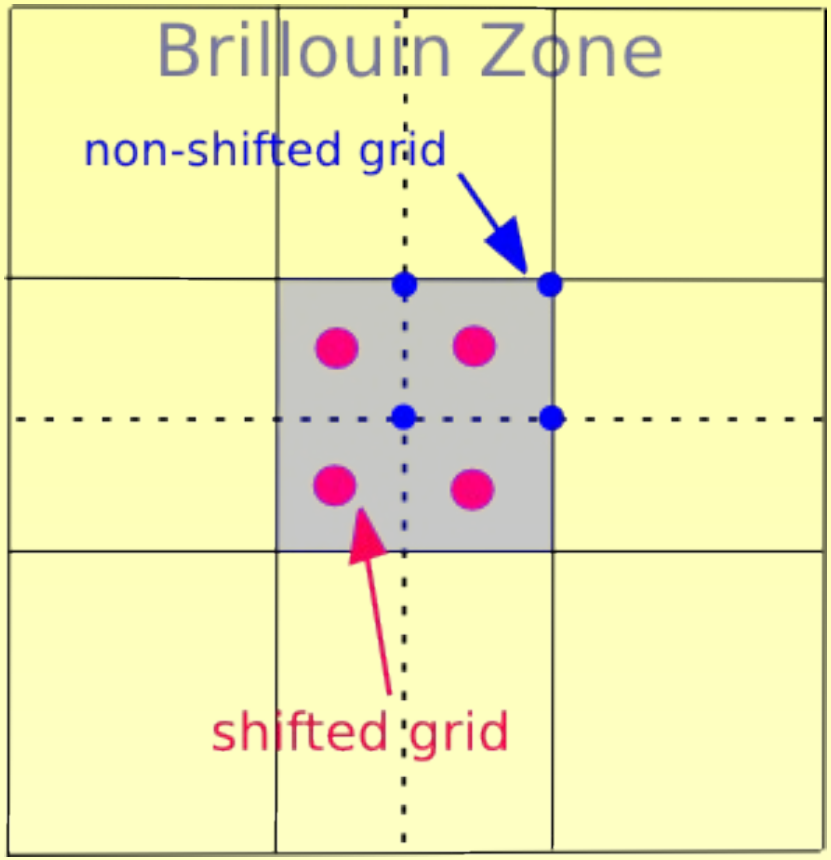
We have to find a set of points in the BZ, which makes the limit as fast as possible:

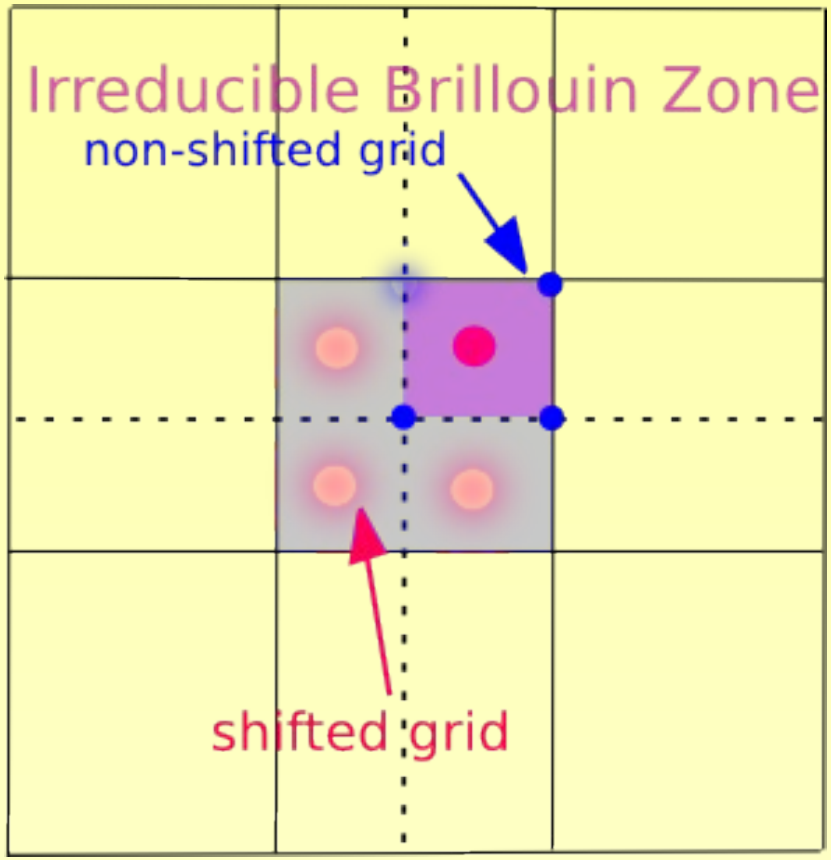
$$\frac{1}{N_{\boldsymbol{k}}} \sum_{\boldsymbol{k} \in BZ} \rightarrow \frac{1}{V_{BZ}} \int_{V_{BZ}} d\boldsymbol{k}$$

Brillouin Zone integration

$$\frac{1}{N_{\boldsymbol{k}}}\sum_{\boldsymbol{k}} \rightarrow \frac{1}{V_{BZ}}\int_{V_{BZ}} d\boldsymbol{k}$$

Monkhorst-Pack technique, *Phys. Rev. B* **13**, 5188 (1976)





2x2 with shift 0.5 0.5

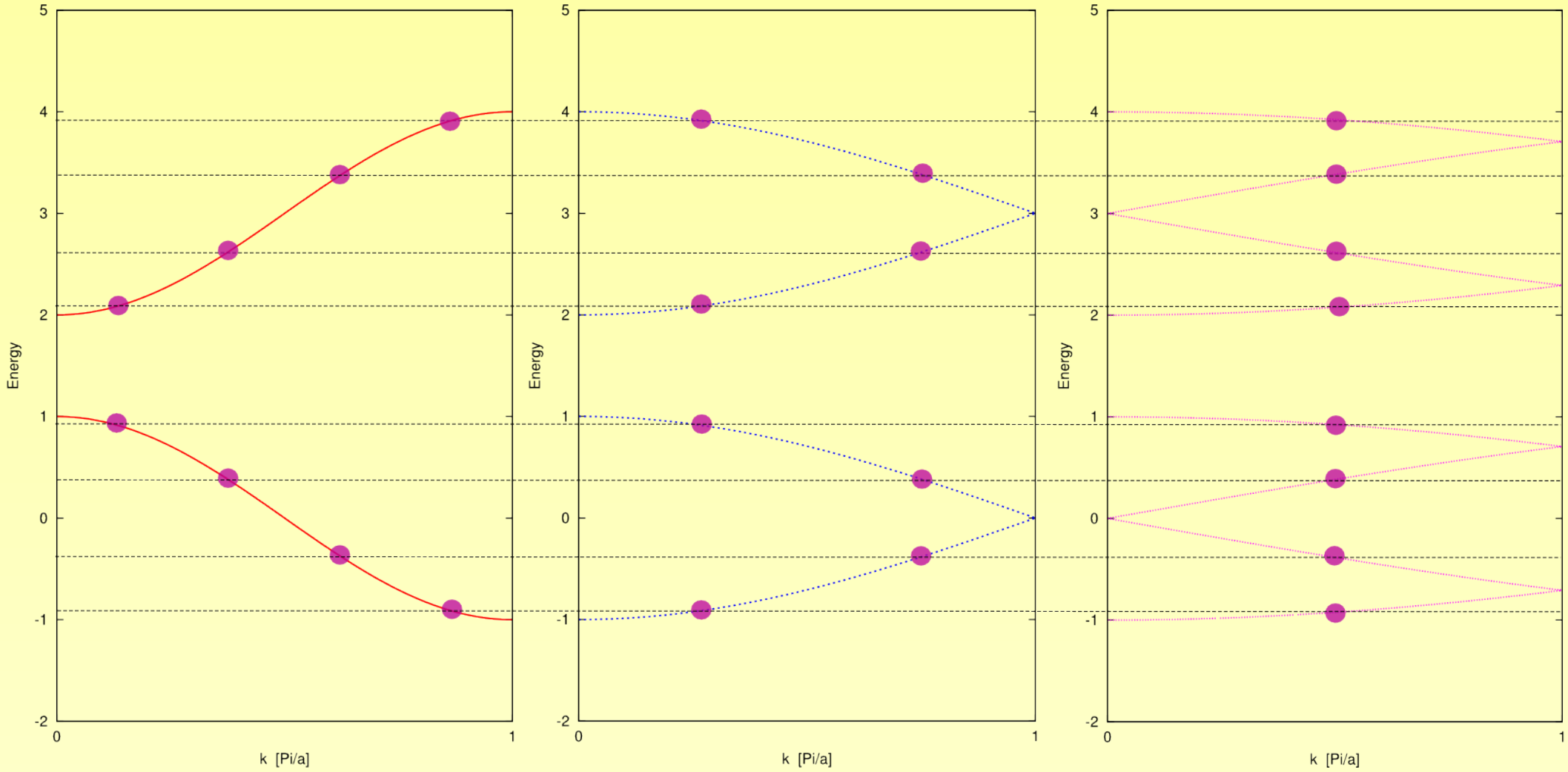
2x2 with shift 0. 0.

Equivalence k-points/larger cells

1 unit cell

2 unit cells

4 unit cells



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A DFT code adapted to periodic systems:

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- **k**-points
- **Plane-Waves**
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Bloch theorem again

$$\phi_{ki}(\boldsymbol{r}) = e^{i\boldsymbol{k}.\boldsymbol{r}} u_{ki}(\boldsymbol{r})$$

where **k** is in the first Brillouin zone
$u_{ki}(\boldsymbol{r})$ is a periodic function with crystal periodicity

$u_{ki}(\boldsymbol{r})$ is periodic and can be expanded in a **Fourier series**

$$u_{ki}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} c_{ki}(\boldsymbol{G}) e^{i\boldsymbol{G}.\boldsymbol{r}}$$

where **G** is on the reciprocal lattice: $\boldsymbol{G} = n_1 \boldsymbol{b_1} + n_2 \boldsymbol{b_2} + n_3 \boldsymbol{b_3}$

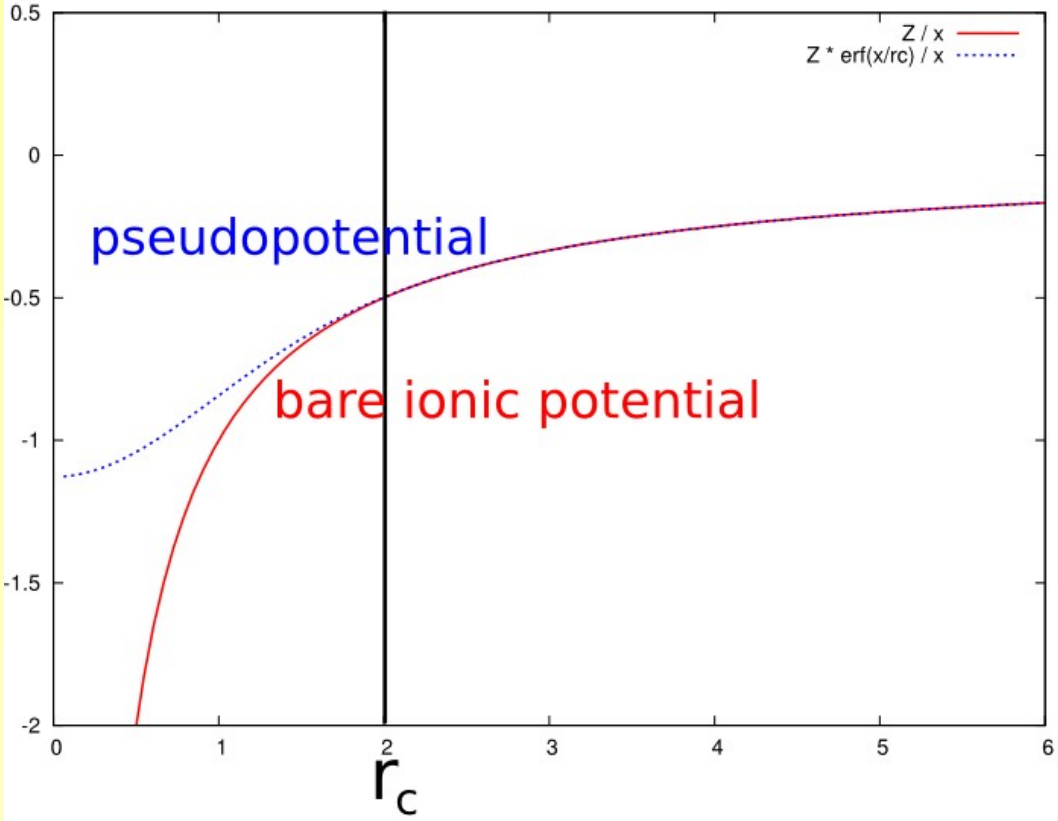
$$\phi_{ki}(\boldsymbol{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{G}} c_{ki}(\boldsymbol{G}) e^{i(\boldsymbol{k}+\boldsymbol{G}).\boldsymbol{r}}$$

Potentials in plane-waves

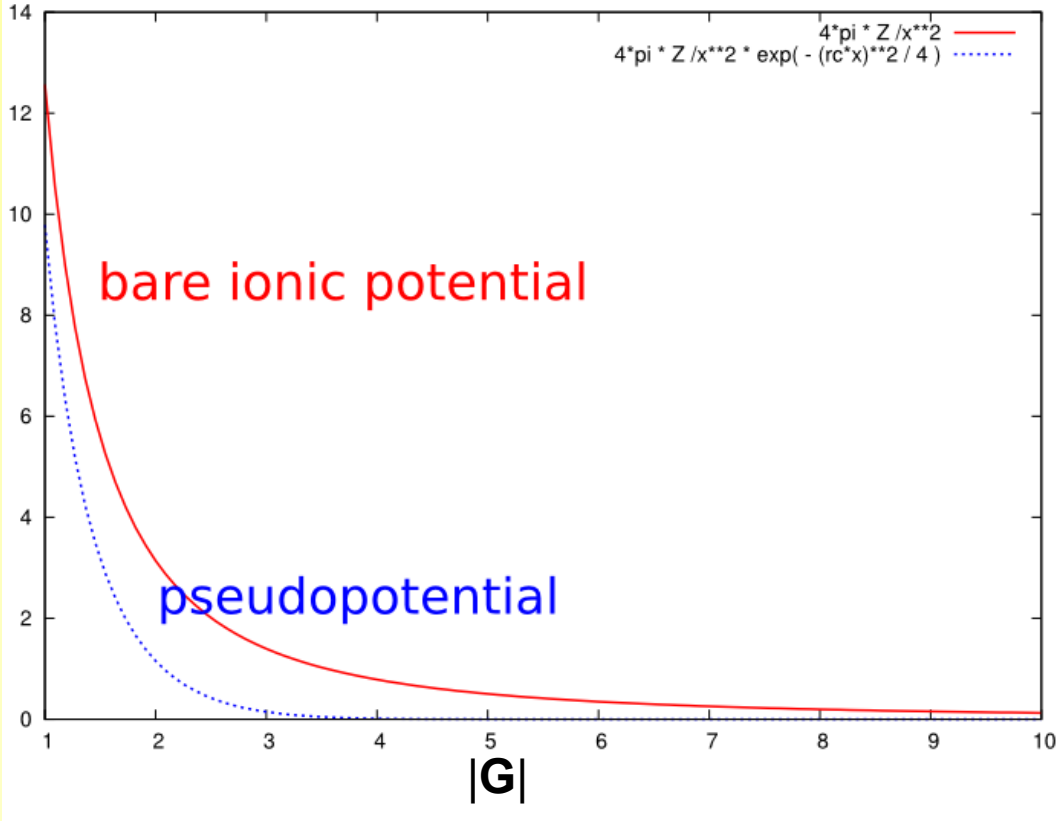
Example of the ionic potential: $V_{ion}(\boldsymbol{r}) = \frac{Z}{|\boldsymbol{r}|}$

$$\tilde{V_{ion}}(\boldsymbol{G}) = 4\pi \frac{Z}{|\boldsymbol{G}|^2}$$

R-space: V(**r**)



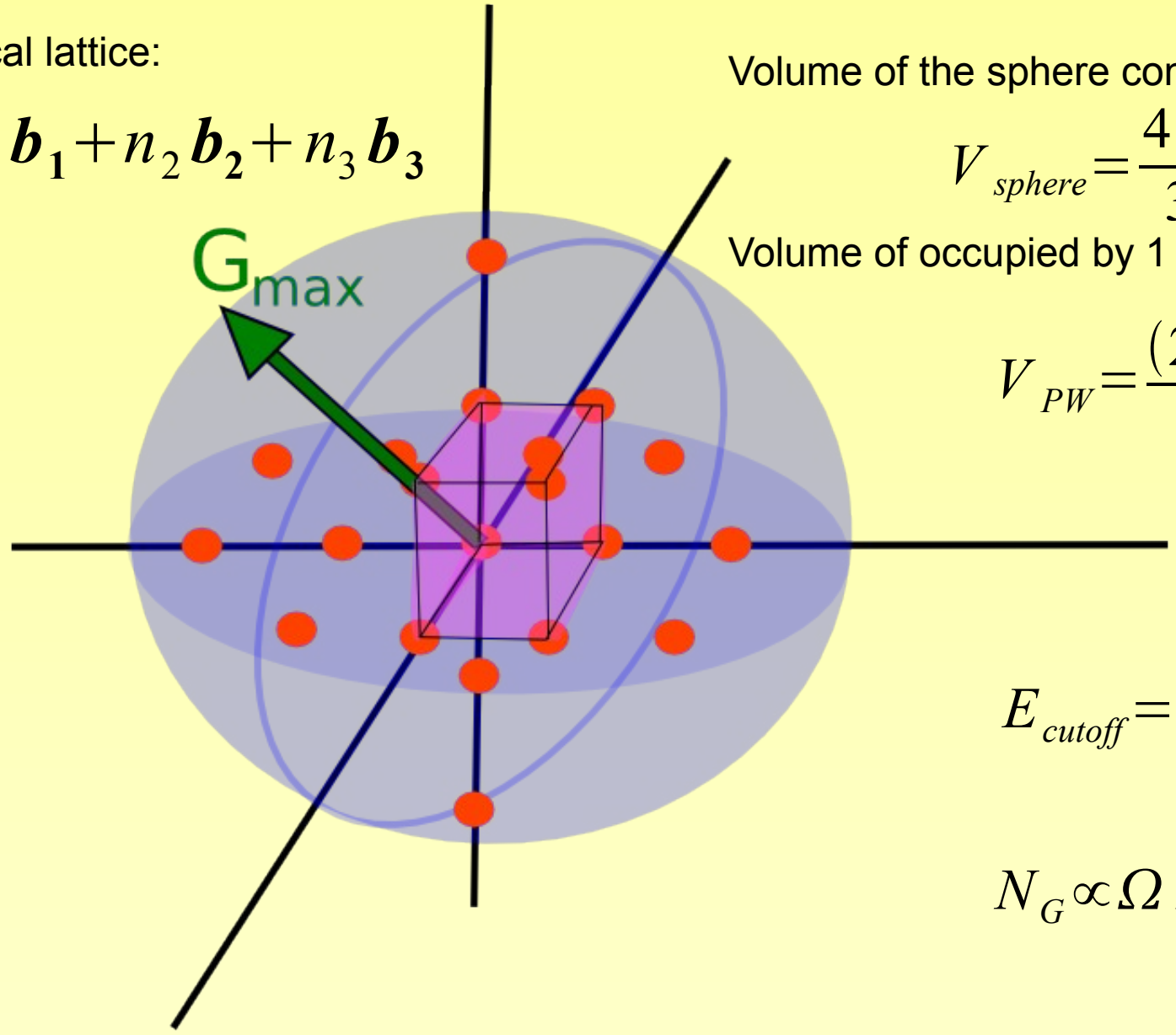
G-space: V(**G**)



Plane Waves

Reciprocal lattice:

$$\boldsymbol{G} = n_1 \boldsymbol{b_1} + n_2 \boldsymbol{b_2} + n_3 \boldsymbol{b_3}$$



Volume of the sphere containing all PW:

$$V_{sphere} = \frac{4\pi}{3} G_{max}^3$$

Volume of occupied by 1 single PW:

$$V_{PW} = \frac{(2\pi)^3}{\Omega}$$

$$E_{cutoff} = \frac{G_{max}^2}{2}$$

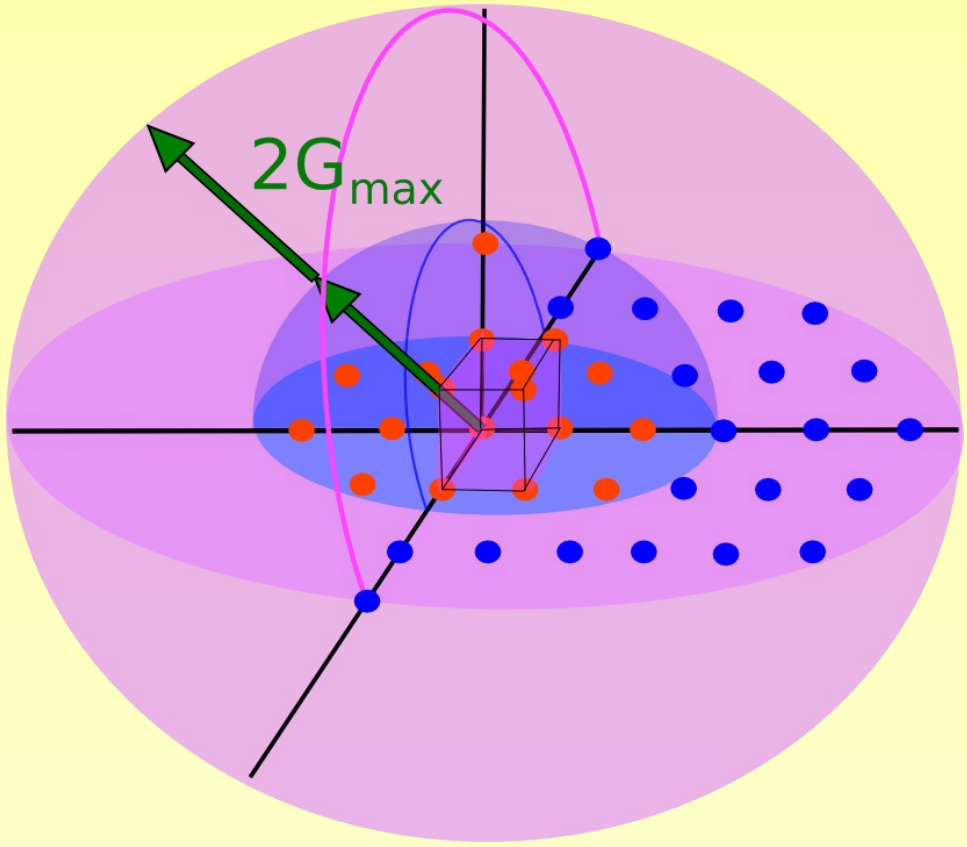
$$N_G \propto \Omega \, E_{cutoff}^{3/2}$$

Cutoff for the density

$$\rho(\boldsymbol{r}) = \frac{1}{N_{\boldsymbol{k}}} \sum_{\boldsymbol{k} i \, occ} \phi_{\boldsymbol{k}i}(\boldsymbol{r}) \phi^{*}_{\boldsymbol{k}i}(\boldsymbol{r})$$

$$= \frac{1}{N_{\boldsymbol{k}} \Omega} \sum_{\boldsymbol{k} i \, occ} \sum_{\boldsymbol{G} \leqslant G_{max}} \sum_{\boldsymbol{G}' \leqslant G_{max}} c_{\boldsymbol{k}i}(\boldsymbol{G}) c^{*}_{\boldsymbol{k}i}(\boldsymbol{G}') e^{i(\boldsymbol{G}-\boldsymbol{G}').\boldsymbol{r}}$$

$$= \sum_{\boldsymbol{G}_0 \leqslant 2G_{max}} \tilde{\rho}(\boldsymbol{G}_0) e^{i \boldsymbol{G}_0 . \boldsymbol{r}}$$



PW: an orthogonal basis set

The wavefunctions are a linear combination of orthogonal basis functions:

$$|\boldsymbol{k}\, i\rangle = \sum_{|\boldsymbol{G}| \leqslant G_{max}} c_{\boldsymbol{k}\, i}(\boldsymbol{G})\, |\boldsymbol{k}+\boldsymbol{G}\rangle$$

and

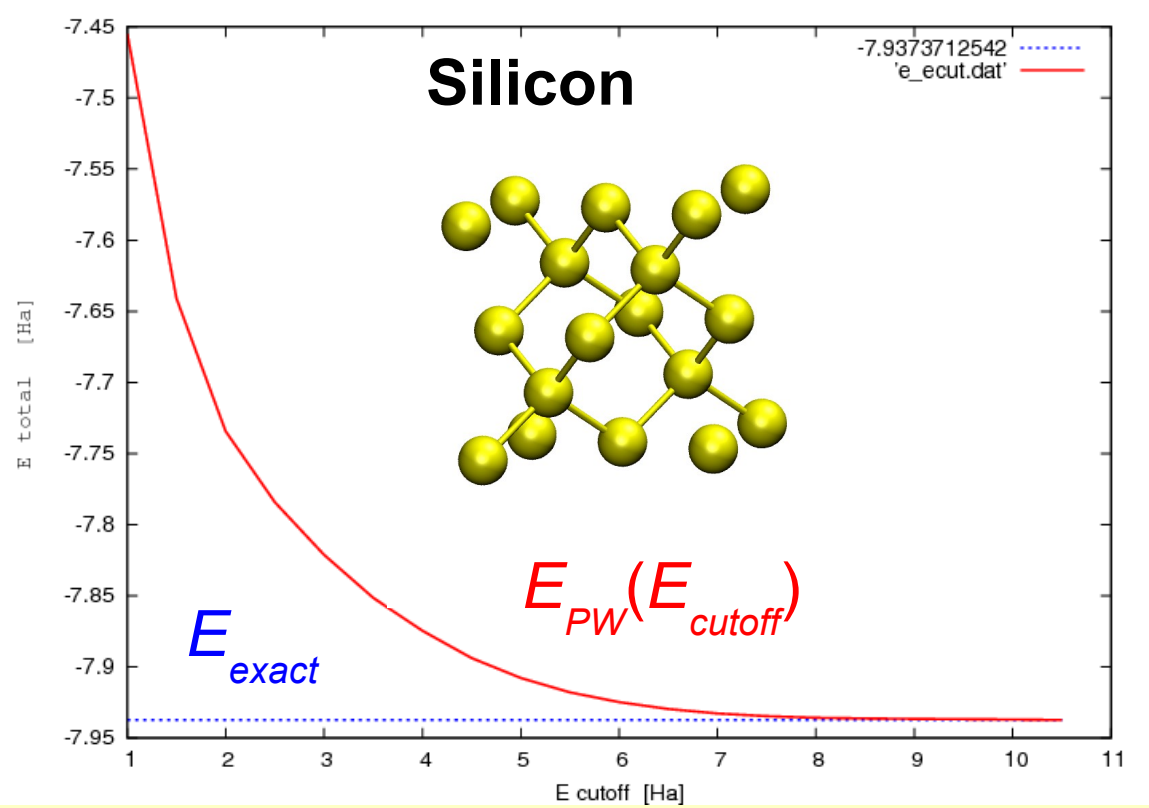
$$\langle \boldsymbol{k}+\boldsymbol{G} | \boldsymbol{k}+\boldsymbol{G}' \rangle = \frac{1}{\Omega} \int_{\Omega} d\,\boldsymbol{r}\, e^{i(\boldsymbol{G}'-\boldsymbol{G}).\boldsymbol{r}} = \delta_{\boldsymbol{G}\boldsymbol{G}'}$$

Variational principle:

$$E_{ground\ state} \leqslant E\left(E_{cutoff} = x\, Ha\right)$$

PW: an orthogonal basis set

Adding more PW or increasing the cutoff energy makes **ALWAYS** the result more accurate



Gaussian basis sets of quantum-chemisrty:

STO-3G
STO-6G
3-21G
6-31G
6-31+G*
6-311+G*
6-311++G**
cc-pVDZ
cc-pVTZ
cc-pVQZ
aug-cc-pVDZ
aug-cc-pVTZ
aug-cc-pVQZ
Dünning SVP
Dünning DVP
Dünning TVP
Dünning TVPP

PW makes life easier thanks to the FFTs

$$f(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \tilde{f}(\boldsymbol{G}) e^{i\boldsymbol{G}.\boldsymbol{r}}$$

$$\tilde{f}(\boldsymbol{G}) = \frac{1}{\Omega} \int_{\Omega} d\boldsymbol{r}\, e^{-i\boldsymbol{G}.\boldsymbol{r}} f(\boldsymbol{r})$$

$$= \frac{1}{N_{\boldsymbol{r}}} \sum_{\boldsymbol{r}_i \in \Omega} e^{-i\boldsymbol{G}.\boldsymbol{r}_i} f(\boldsymbol{r}_i)$$

Discrete **F**ourier **T**ransform

It is exact as long as $N_{\boldsymbol{G}} = N_{\boldsymbol{r}}$

This means that

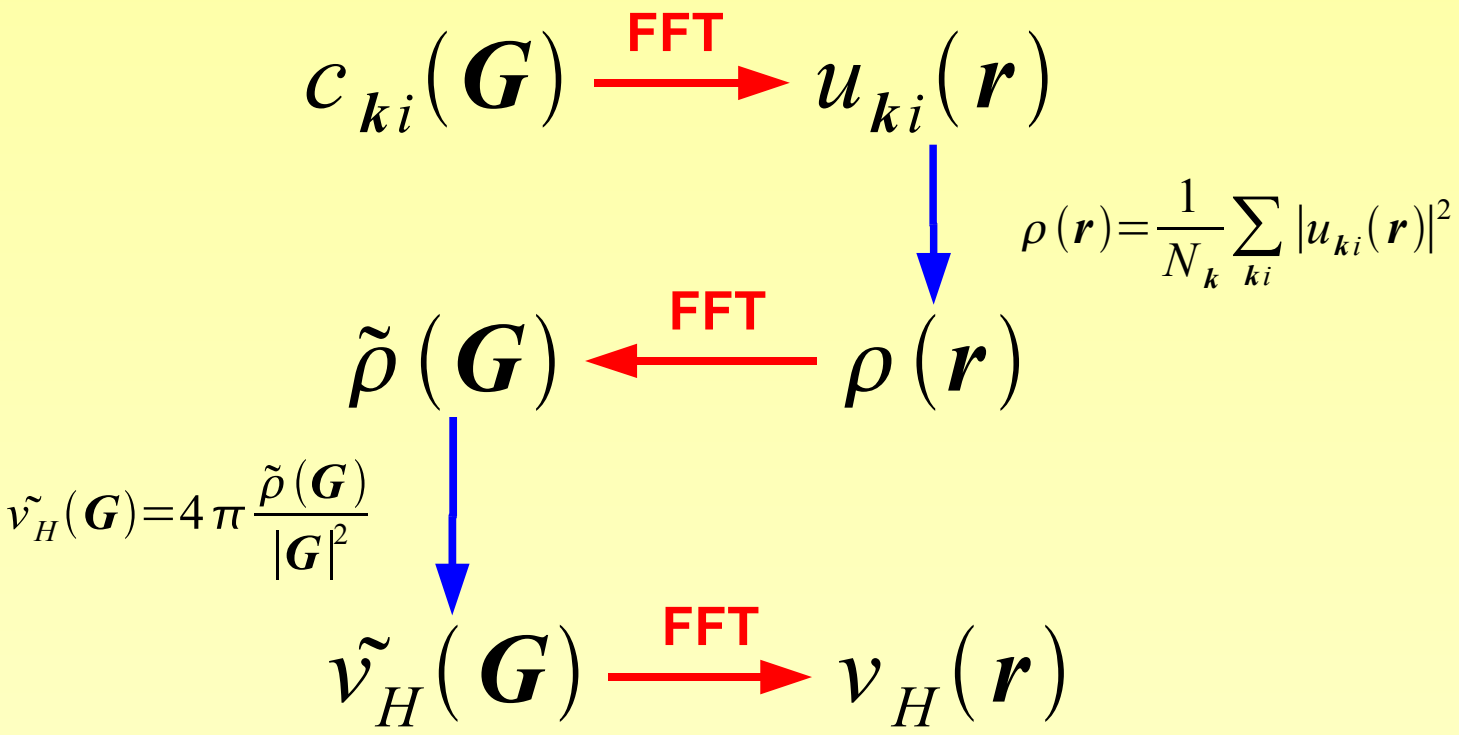
$$\tilde{f}(\boldsymbol{G}) = DFT^{-1}\left[DFT\left[\tilde{f}(\boldsymbol{G})\right]\right]$$

The fast version of DFT is the famous **Fast FT** with scales as O(N log N) instead of N^2.

This enforces the use of regular grid in real space.

Illustration of the use FFTs

We need to calculate the Hartree potential: $v_H(\boldsymbol{r}) = \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}$



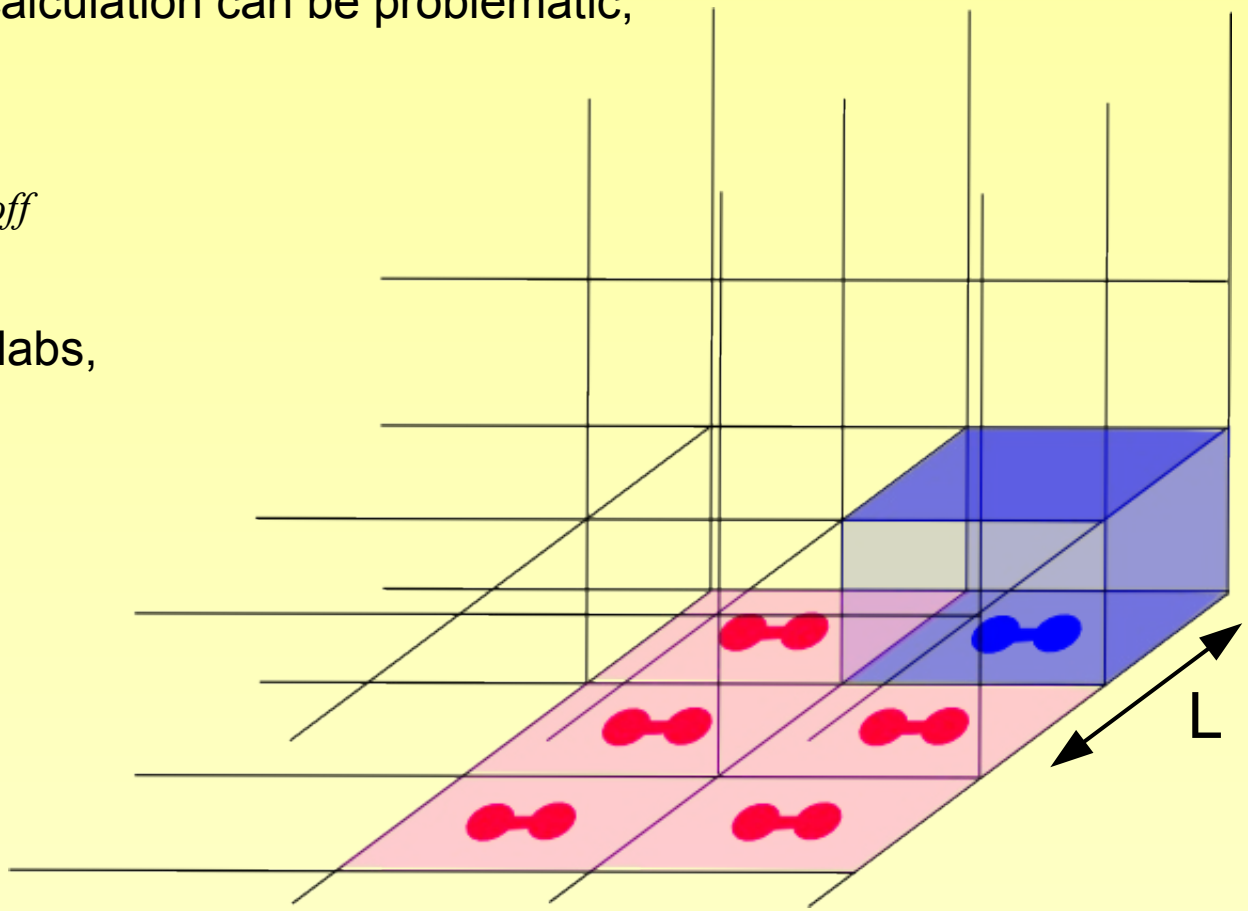
Supercell technique

How to simulate a finite system with periodic boundary conditions?

The cost of the calculation can be problematic, since

$$N_G \propto \Omega E_{cutoff}^{3/2}$$

Still useful for slabs, wires, etc.



Recap

- Self-consistent loop
- **k**-points:
  - Monkhorst-Pack grid (like 4x4x4 shift 0.5 0.5 0.5)
  - Equivalence between **k**-points and larger cells
- Plane-Waves
  - PW are an orthogonal basis set
  - Cutoff energy for wavefunctions
  - Intensive use of FFT's to increase efficiency