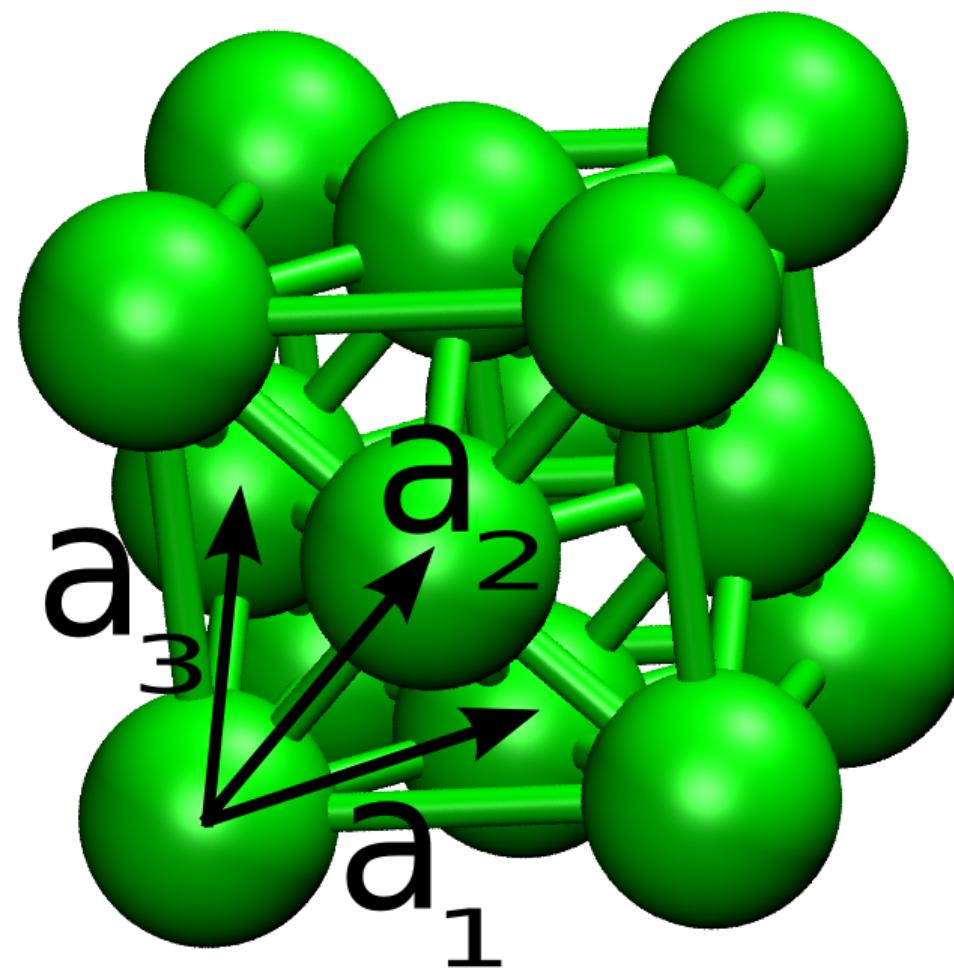


Implementing DFT in Plane-Wave basis

Fabien Bruneval

Service de Recherches de Métallurgie Physique
CEA Saclay
France

DFT for periodic systems



Outline

A DFT code adapted to periodic systems:



- Self-consistency in KS equations
- Crystal structure
- \mathbf{k} -points
- Plane-Waves
- Supercells

Solving KS equations

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

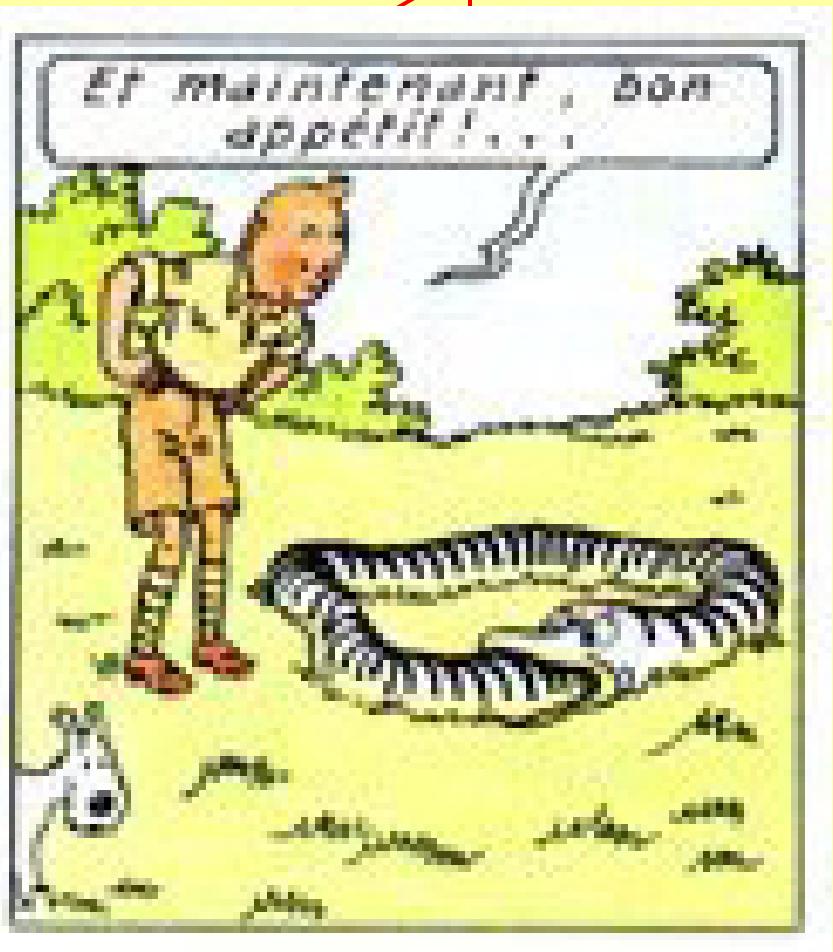
depends on the density
non linear equations

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

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

Energy, Forces, Band structure, Electronic density

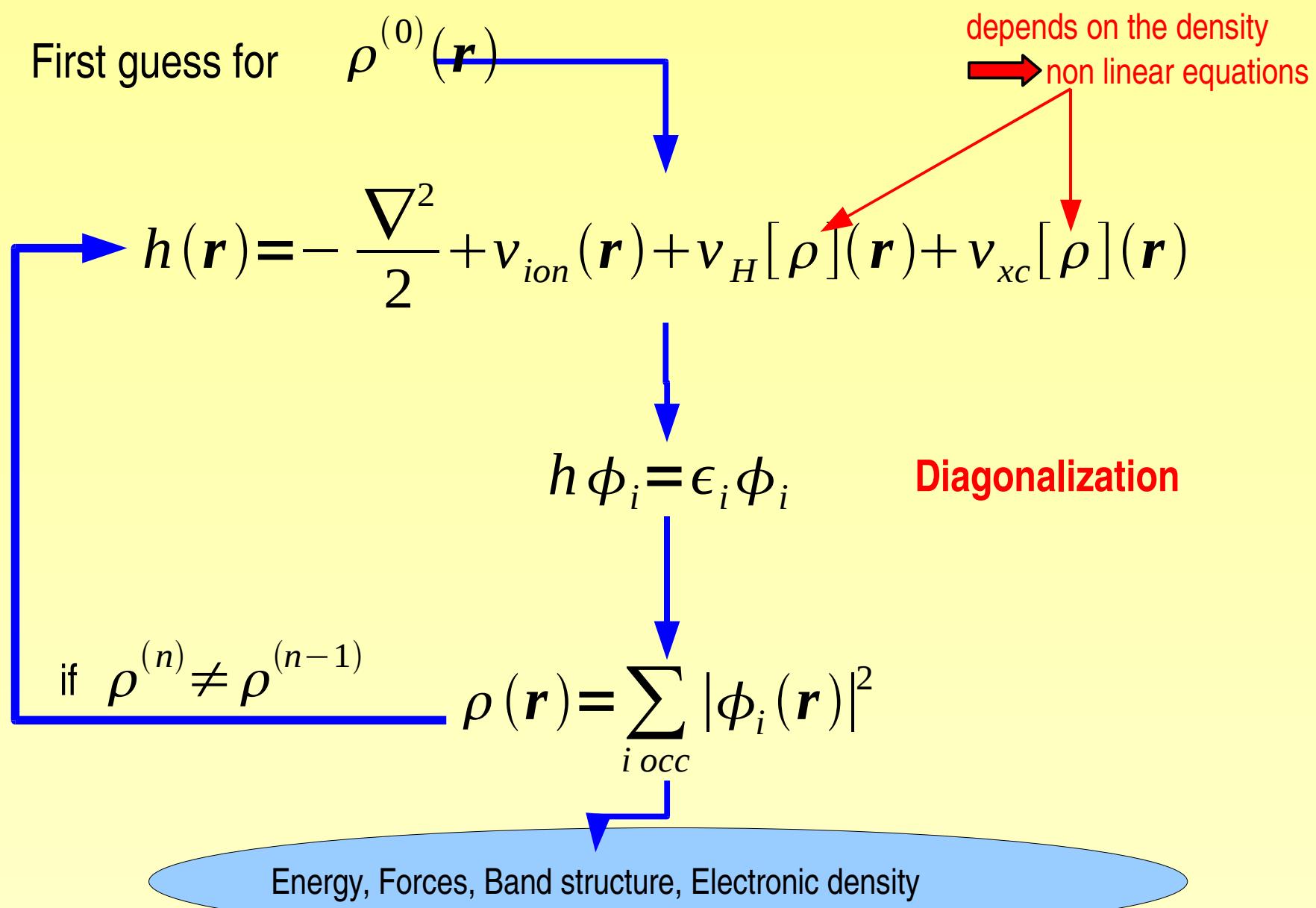
Solving KS equations



depends on the density
→ non linear equations

Energy, Forces, Band structure, Electronic density

Solving KS equations



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A DFT code adapted to periodic systems:



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

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

Direct lattice vector:

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

Periodic potential:

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

Reciprocal lattice axis:

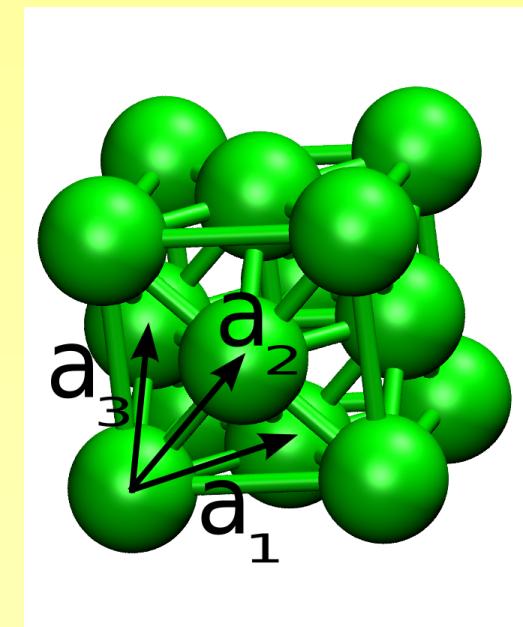
$$\mathbf{b}_1 = \frac{2\pi}{\Omega} \mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{b}_2 = \frac{2\pi}{\Omega} \mathbf{a}_3 \times \mathbf{a}_1$$

$$\mathbf{b}_3 = \frac{2\pi}{\Omega} \mathbf{a}_1 \times \mathbf{a}_2$$

Reciprocal lattice:

$$\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \quad \rightarrow \quad e^{i \mathbf{G} \cdot \mathbf{R}} = 1$$



Bloch theorem and k-points

Bloch theorem:

$$\phi_{\mathbf{k}i}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}i}(\mathbf{r})$$

where \mathbf{k} is in the first Brillouin zone

$u_{\mathbf{k}i}(\mathbf{r})$ is a periodic function with crystal periodicity

Any **periodic operator** and, in particular, the Hamiltonian, is **diagonal** in \mathbf{k} .

$$\begin{aligned} \langle \mathbf{k} i | h | \mathbf{k}' j \rangle &= \int d\mathbf{r} e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} h(\mathbf{r}) u_{\mathbf{k}i}^*(\mathbf{r}) u_{\mathbf{k}'j}(\mathbf{r}) \\ &= \sum_{\mathbf{R}} \int_{\Omega} d\mathbf{r} e^{i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{r} + \mathbf{R})} \\ &\quad \times h(\mathbf{r} + \mathbf{R}) u_{\mathbf{k}i}^*(\mathbf{r} + \mathbf{R}) u_{\mathbf{k}'j}(\mathbf{r} + \mathbf{R}) \end{aligned}$$

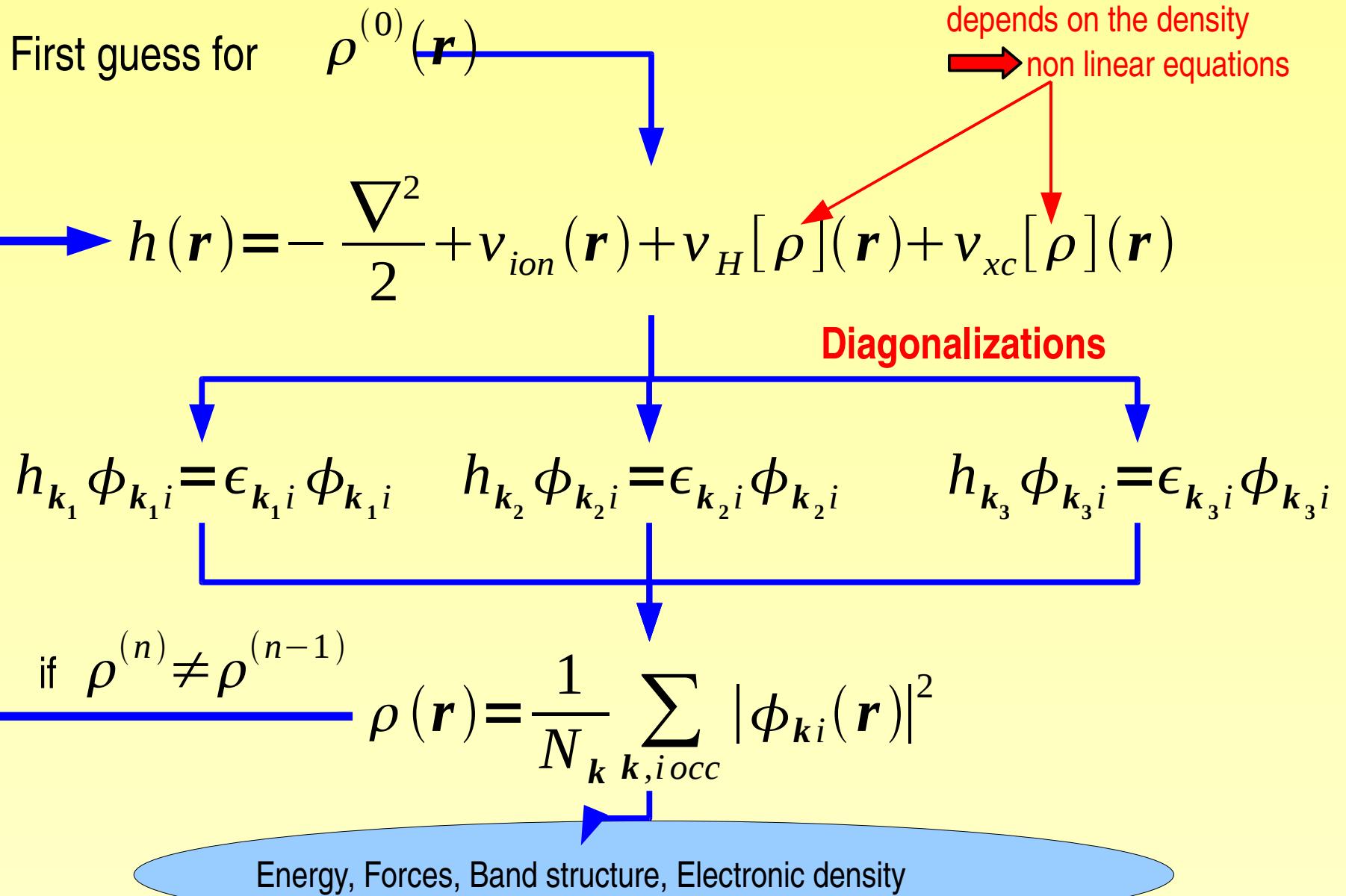
k-points allow to split the calculations

$$\rightarrow \langle \mathbf{k} i | h | \mathbf{k}' j \rangle = \delta_{\mathbf{k} \mathbf{k}'} \langle \mathbf{k} i | h | \mathbf{k} j \rangle$$

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



Brillouin Zone integration

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

$$\rho(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{k} \in BZ} \sum_{i \text{ occ}} |\phi_{\mathbf{k}i}(\mathbf{r})|^2$$


to be exact, it should be

$$\rho(\mathbf{r}) = \frac{1}{V_{BZ}} \int_{V_{BZ}} d\mathbf{k} \sum_{i \text{ occ}} |\phi_{\mathbf{k}i}(\mathbf{r})|^2$$

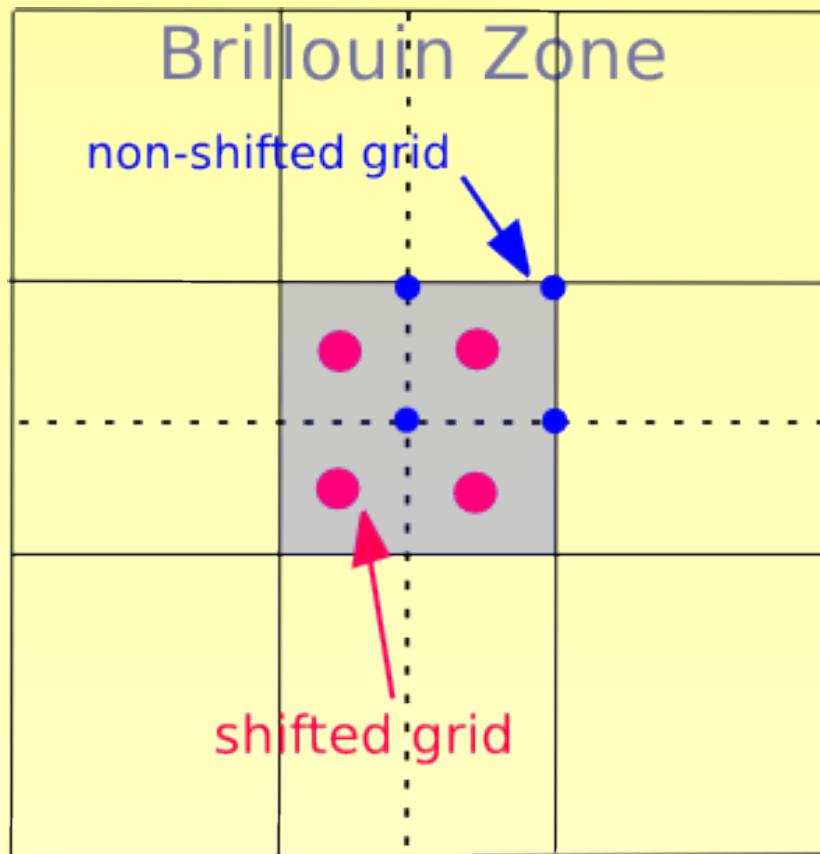
We have to find a set of points in the BZ, which makes the limit as fast as possible:

$$\frac{1}{N} \sum_{\mathbf{k} \in BZ} \rightarrow \frac{1}{V_{BZ}} \int_{V_{BZ}} d\mathbf{k}$$

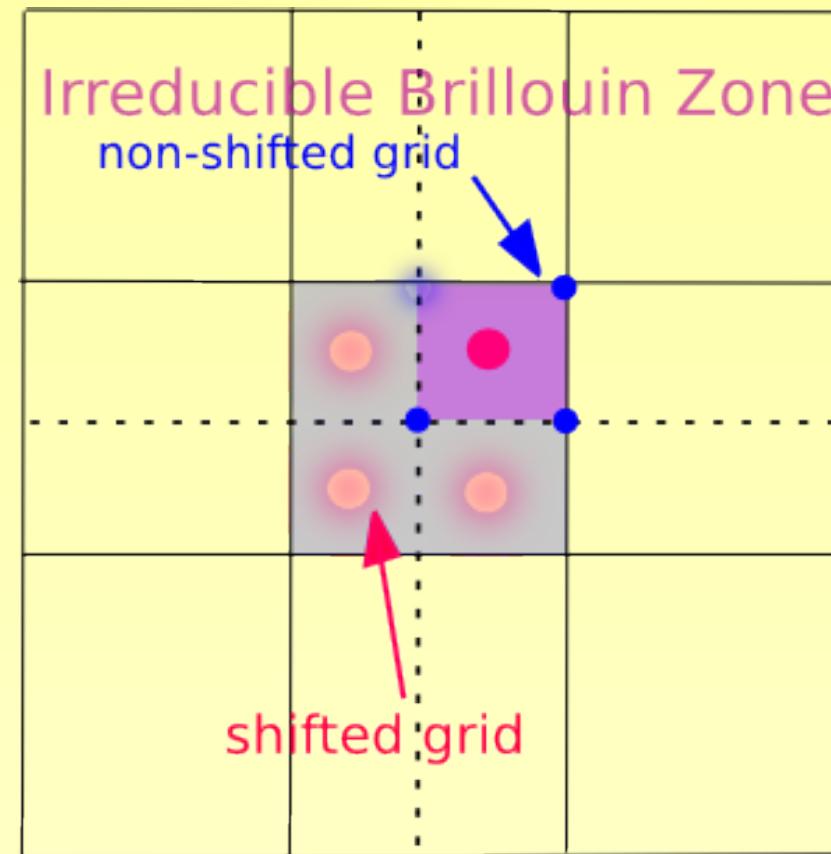
Brillouin Zone integration

$$\frac{1}{N_k} \sum_k \rightarrow \frac{1}{V_{BZ}} \int d\mathbf{k}$$

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



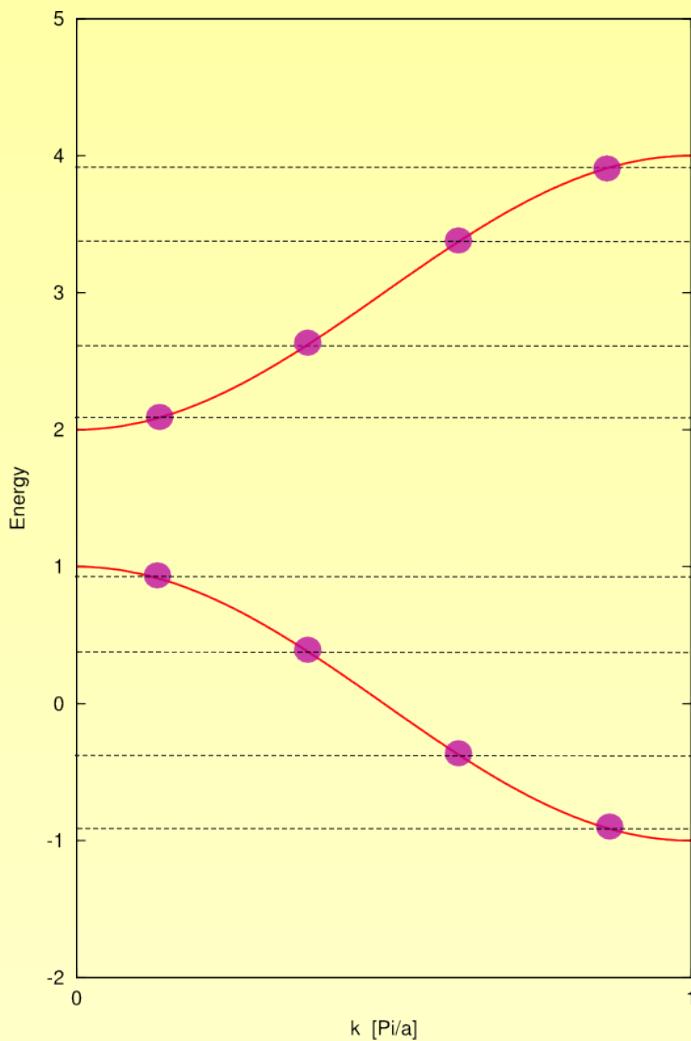
2x2 with shift 0.5 0.5



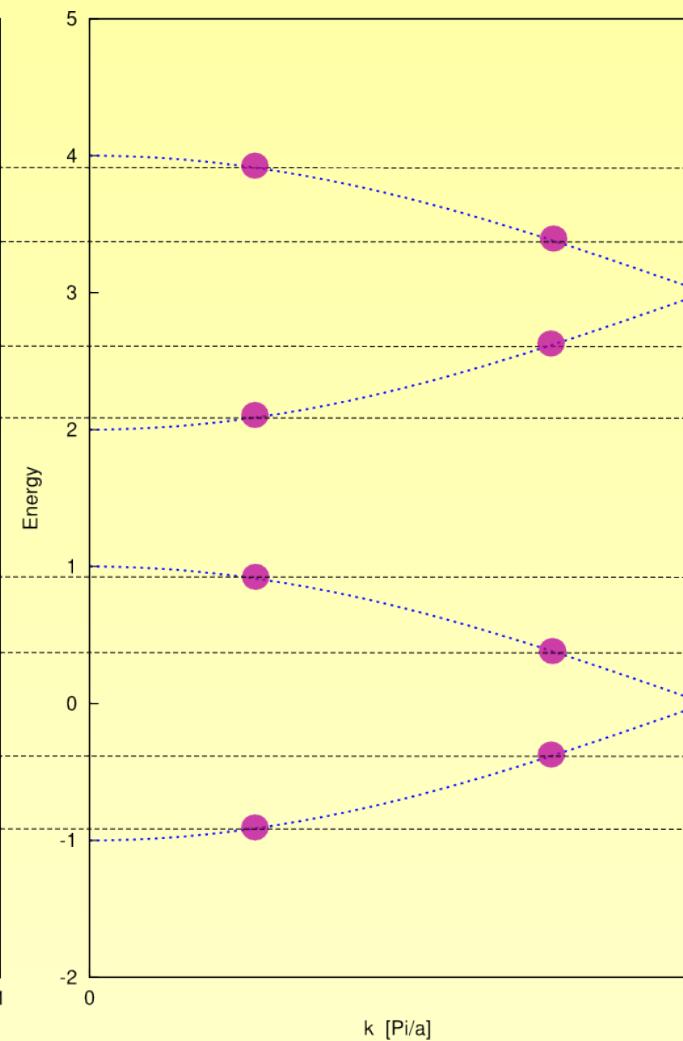
2x2 with shift 0. 0.

Equivalence k-points/larger cells

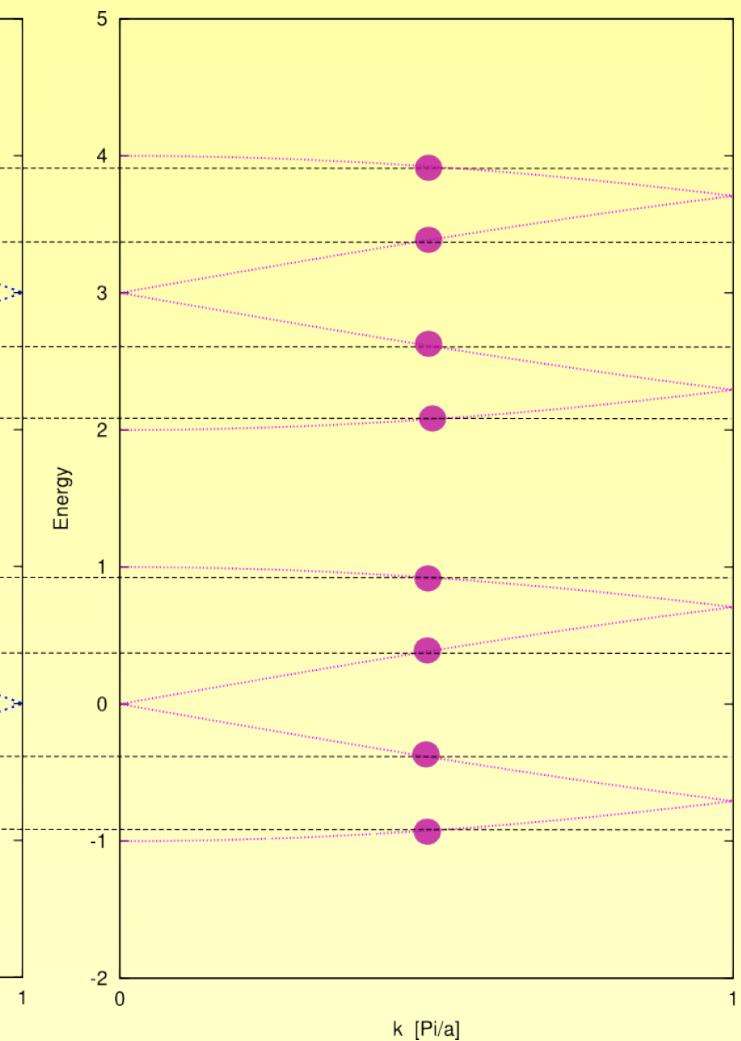
1 unit cell



2 unit cells



4 unit cells



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- k-points
- **Plane-Waves**
- Supercells

Bloch theorem again

$$\phi_{\mathbf{k}i}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}i}(\mathbf{r})$$

where \mathbf{k} is in the first Brillouin zone

$u_{\mathbf{k}i}(\mathbf{r})$ is a periodic function with crystal periodicity

$u_{\mathbf{k}i}(\mathbf{r})$ is periodic and can be expanded in a **Fourier series**

$$u_{\mathbf{k}i}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{\mathbf{k}i}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

where \mathbf{G} is on the reciprocal lattice:

$$\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$$

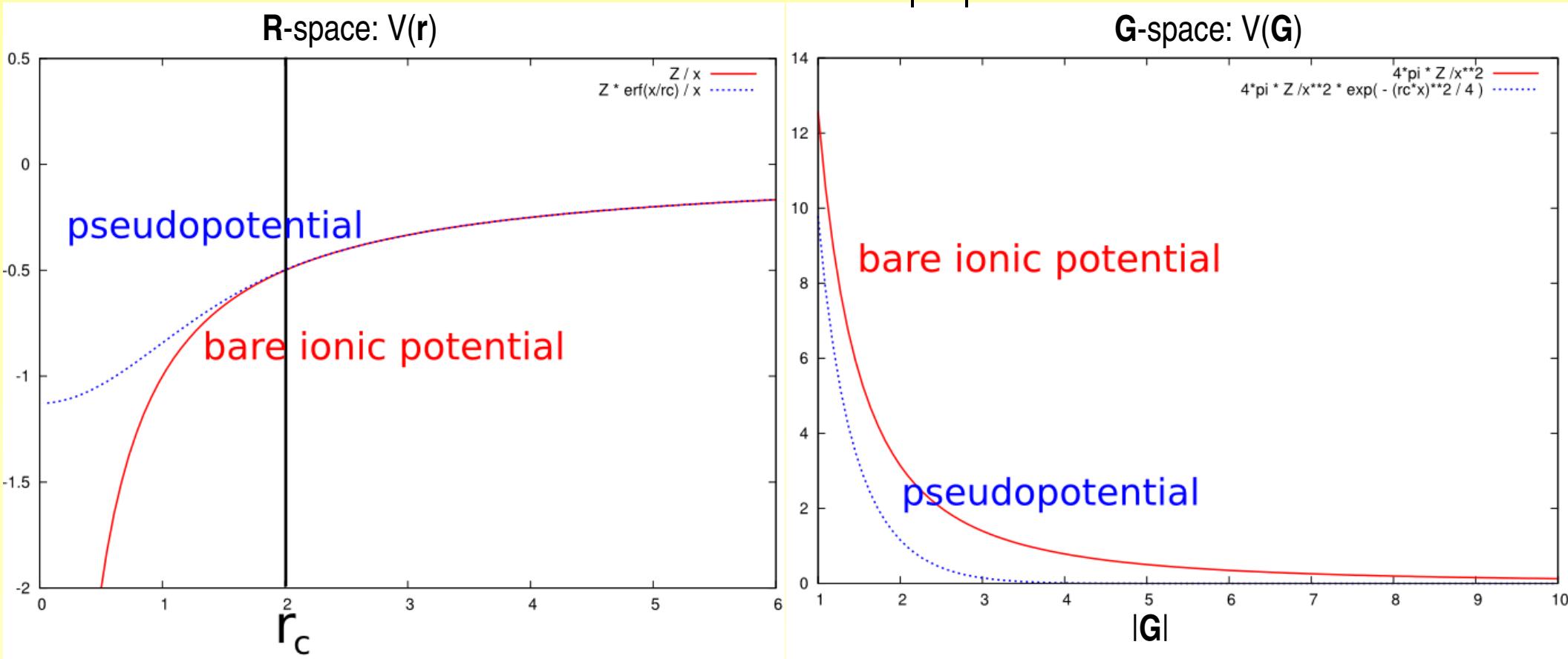
$$\phi_{\mathbf{k}i}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{\mathbf{k}i}(\mathbf{G}) e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}}$$

Potentials in plane-waves

Example of the ionic potential:

$$V_{ion}(\mathbf{r}) = \frac{Z}{|\mathbf{r}|}$$

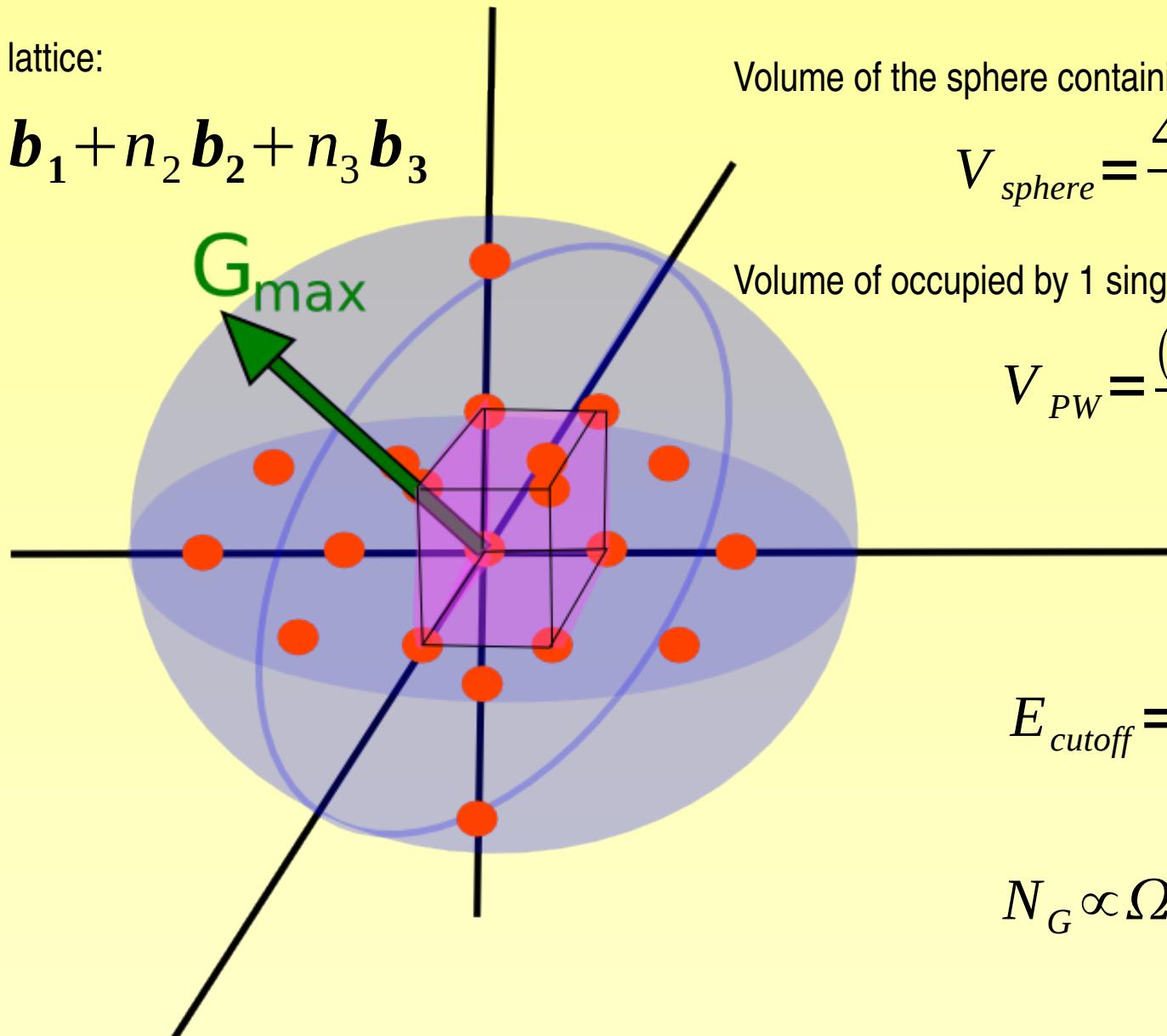
$$\tilde{V}_{ion}(\mathbf{G}) = 4\pi \frac{Z}{|\mathbf{G}|^2}$$



Plane Waves

Reciprocal lattice:

$$\mathbf{G} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$$



Volume of the sphere containing all PW:

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

Volume of occupied by 1 single PW:

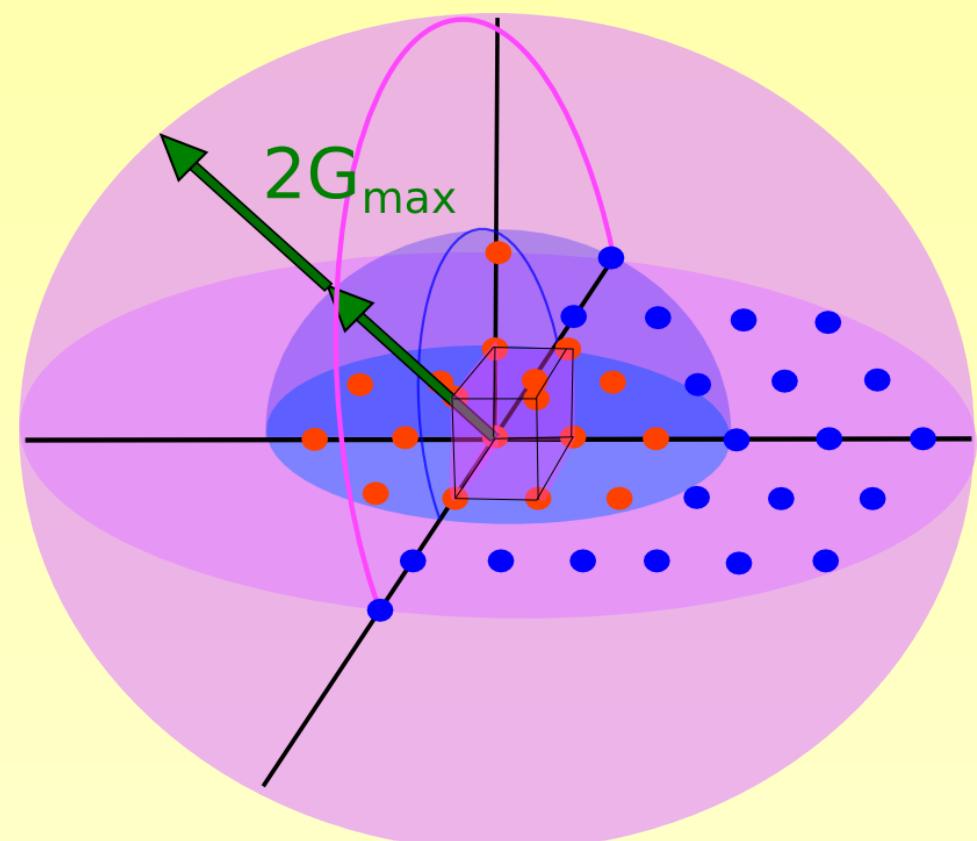
$$V_{PW} = \frac{(2\pi)^3}{\Omega}$$

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

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

Cutoff for the density

$$\begin{aligned}
 \rho(\mathbf{r}) &= \frac{1}{N_k} \sum_{\mathbf{k} iocc} \phi_{\mathbf{k} i}(\mathbf{r}) \phi_{\mathbf{k} i}^*(\mathbf{r}) \\
 &= \frac{1}{N_k \Omega} \sum_{\mathbf{k} iocc} \sum_{\mathbf{G} \leq G_{max}} \sum_{\mathbf{G}' \leq G_{max}} c_{\mathbf{k} i}(\mathbf{G}) c_{\mathbf{k} i}^*(\mathbf{G}') e^{i(\mathbf{G}-\mathbf{G}').\mathbf{r}} \\
 &= \sum_{\mathbf{G}_0 \leq 2G_{max}} \tilde{\rho}(\mathbf{G}_0) e^{i\mathbf{G}_0 \cdot \mathbf{r}}
 \end{aligned}$$



PW: an orthogonal basis set

The wavefunctions are a linear combination of orthogonal basis functions:

$$|\mathbf{k} i\rangle = \sum_{|\mathbf{G}| \leq G_{max}} c_{\mathbf{k} i}(\mathbf{G}) |\mathbf{k} + \mathbf{G}\rangle$$

and

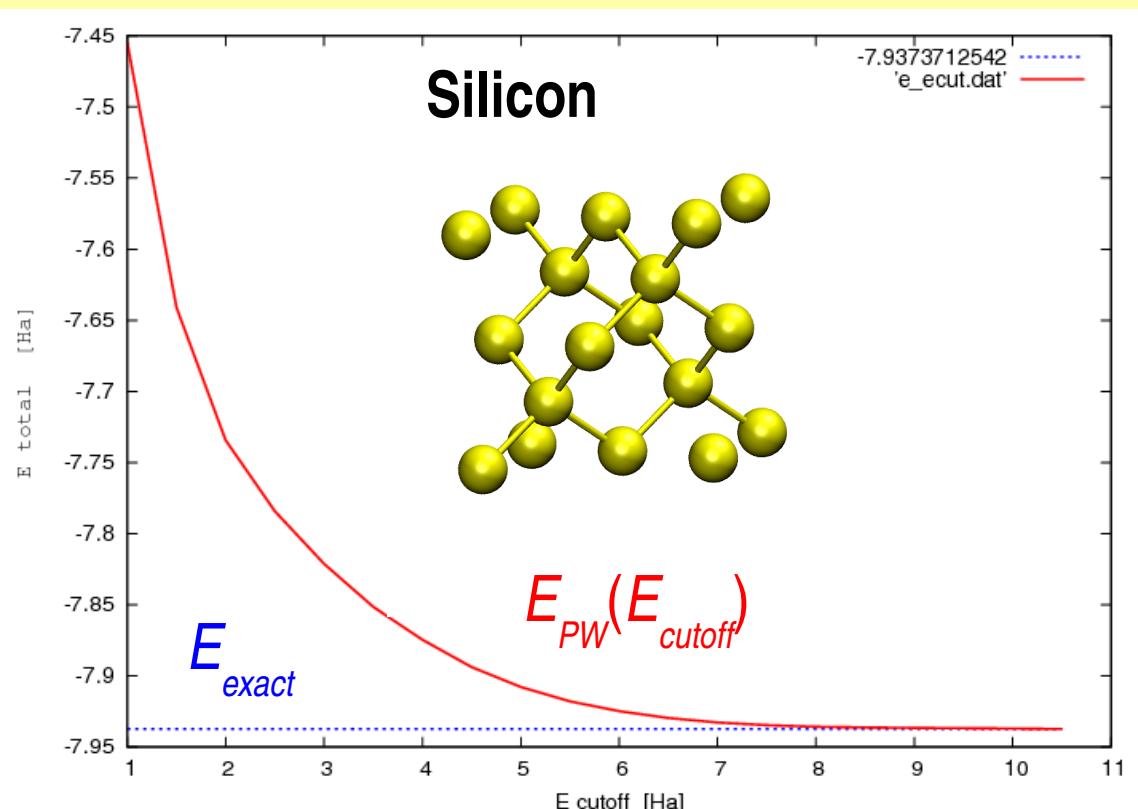
$$\langle \mathbf{k} + \mathbf{G} | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}} = \delta_{\mathbf{G}\mathbf{G}'}$$

Variational principle:

$$E_{ground\ state} \leq E(E_{cutoff} = x Ha)$$

PW: an orthogonal basis set

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



Gaussian basis sets of quantum-chemistry:

- 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

$$f(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{f}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}$$

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

$$= \frac{1}{N_r} \sum_{\mathbf{r}_i \in \Omega} e^{-i\mathbf{G} \cdot \mathbf{r}_i} f(\mathbf{r}_i)$$

Discrete Fourier Transform

It is exact as long as $N_{\mathbf{G}} = N_r$

This means that

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

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.

Unit cell

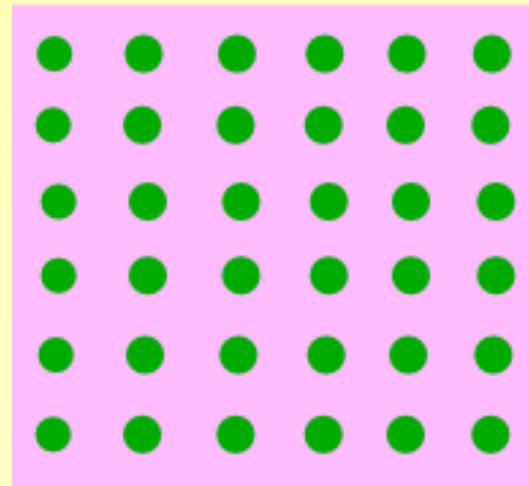
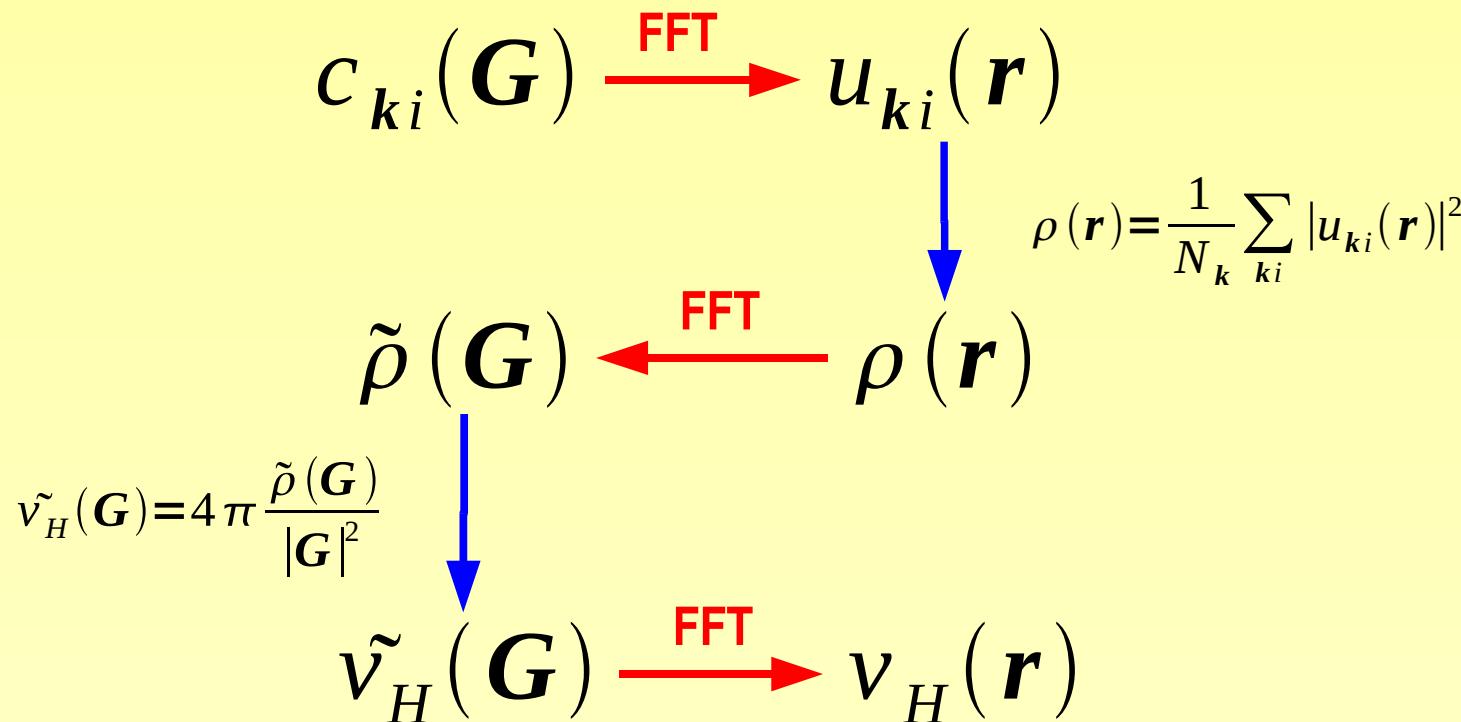


Illustration of the use FFTs

We need to calculate the Hartree potential:

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$



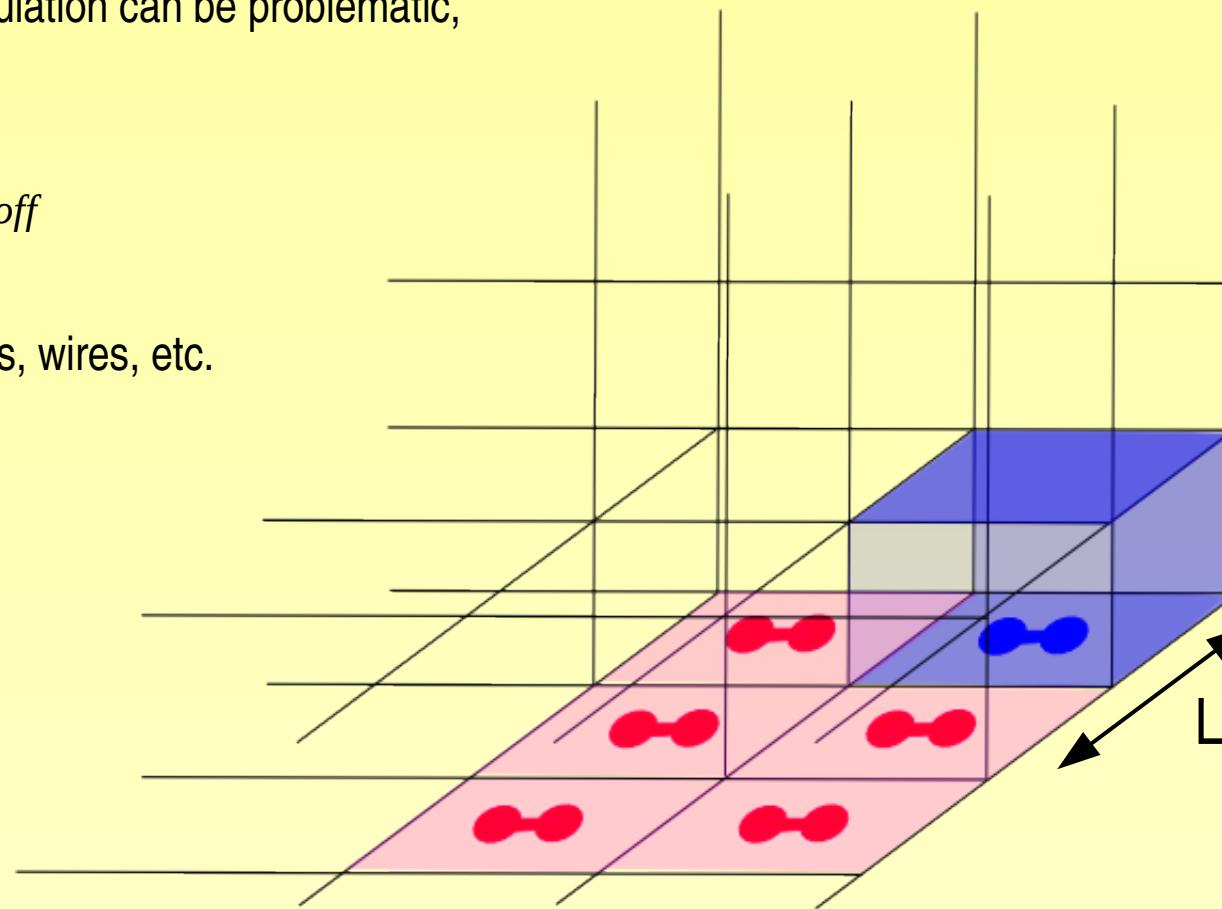
Supercell technique

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
- \mathbf{k} -points:
 - Monkhorst-Pack grid (like 4x4x4 shift 0.5 0.5 0.5)
 - Equivalence between \mathbf{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