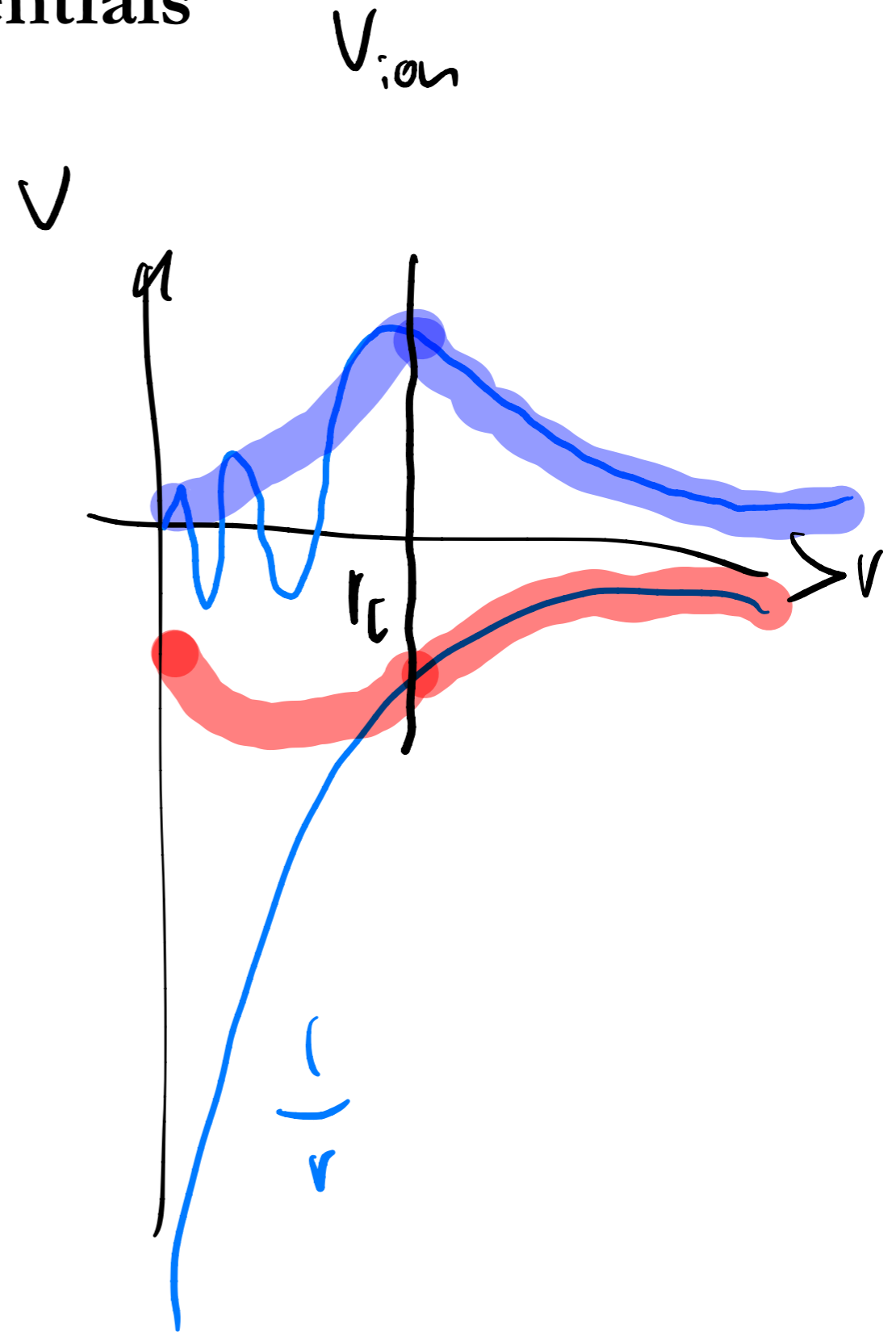


Pseudopotentials

- The pseudopotential and the wave function
- Real potential and wave function are shown in blue
- Pseudopotential and pseudo wave function in red
- Outside the cutoff region (vertical black line) the two are identical

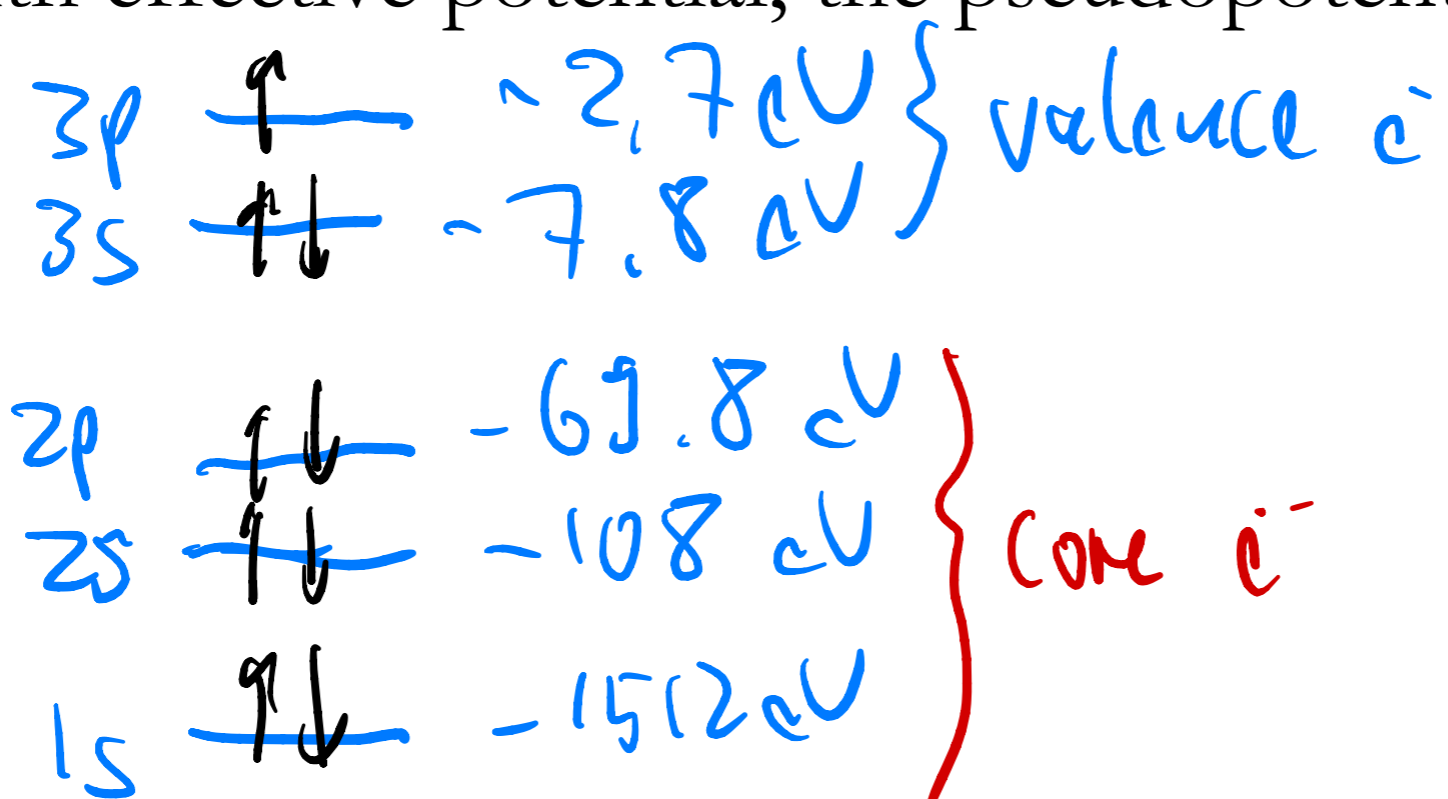


Pseudopotentials

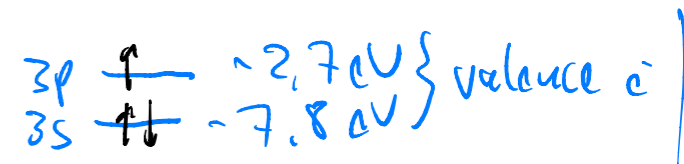
frozen core approx

- Electrons in the inner shells do not contribute to bonding
- Core electrons are effectively frozen
- Replace Coulomb potential between electrons and nuclei with effective potential, the pseudopotential

Al
Z=13



Pseudo Al
Z=3



$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}} \right] \varphi_i = \epsilon_i \varphi_i$$

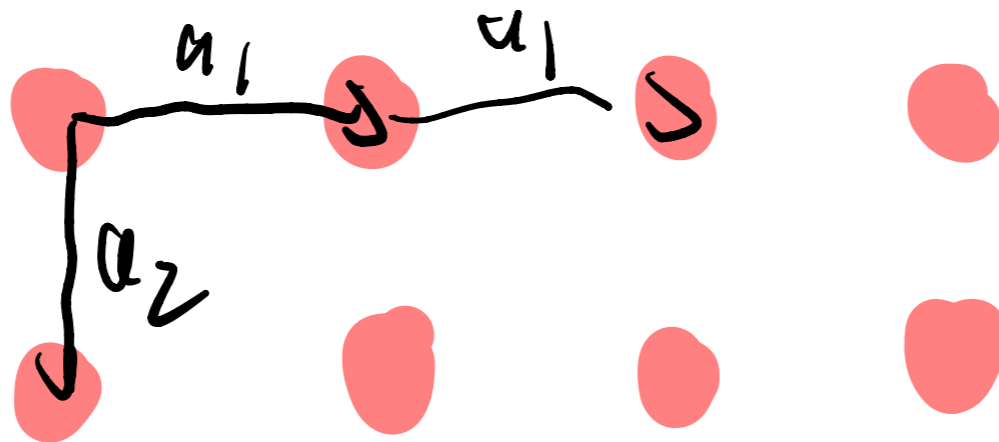
$$\left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}^{\text{pseudo}} \right] \varphi_i^{\text{pseudo}} = \epsilon_i \varphi_i^{\text{pseudo}}$$

Solids: Real and reciprocal lattices

- we assume: all atoms sit on equilibrium positions
- simplification: *infinite* and *periodic* lattice of atoms
- fundamental concept to describe this: Bravais lattice
- Bravais lattice: **all** the points that can be reached by:

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

- here: n_1, n_2, n_3 are integer numbers
- vectors \mathbf{a} are called “primitive vectors”, choice is not unique

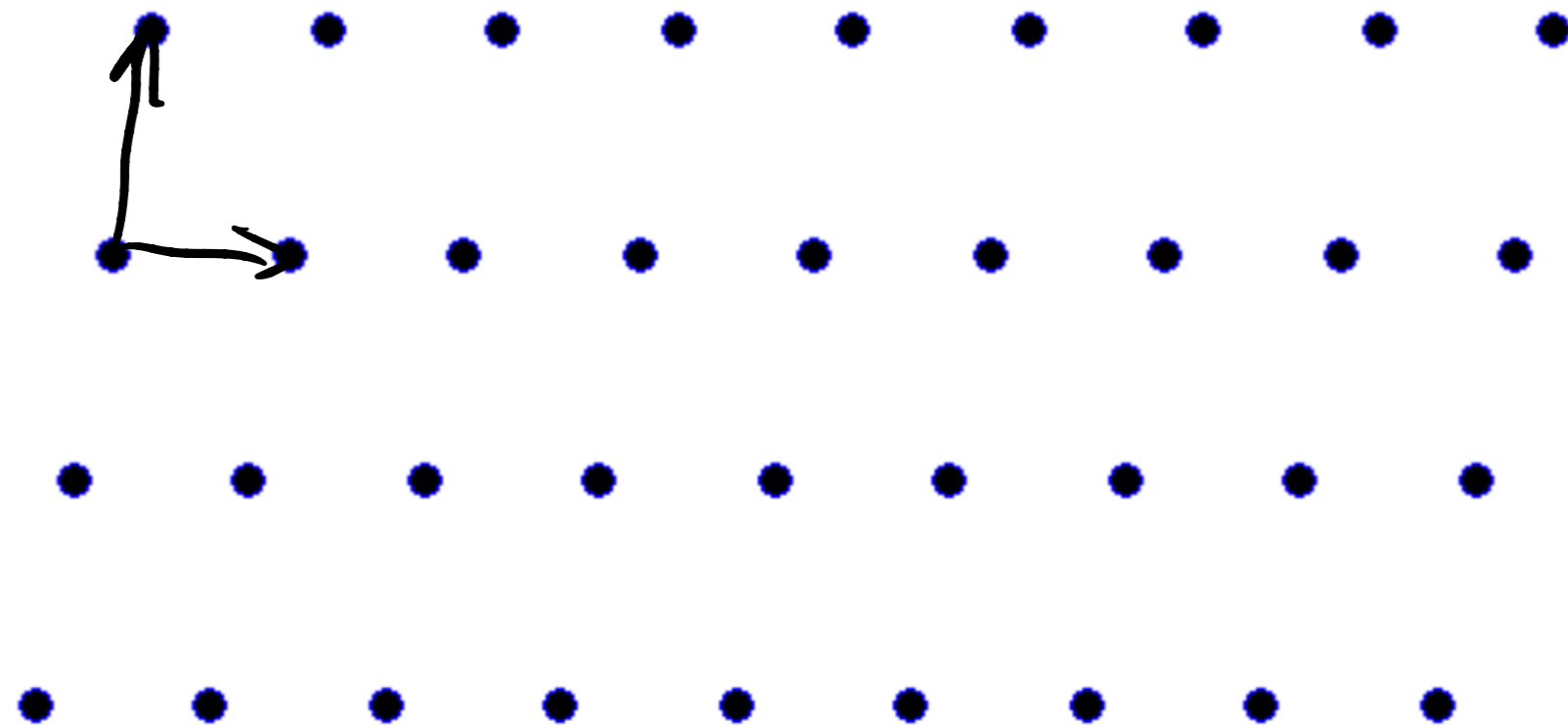


Solids: Real and reciprocal lattices

- Bravais lattice: all the points that can be achieved by:

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

- at each of these \mathbf{R} there can be either one atom (or multiple - see next slide):



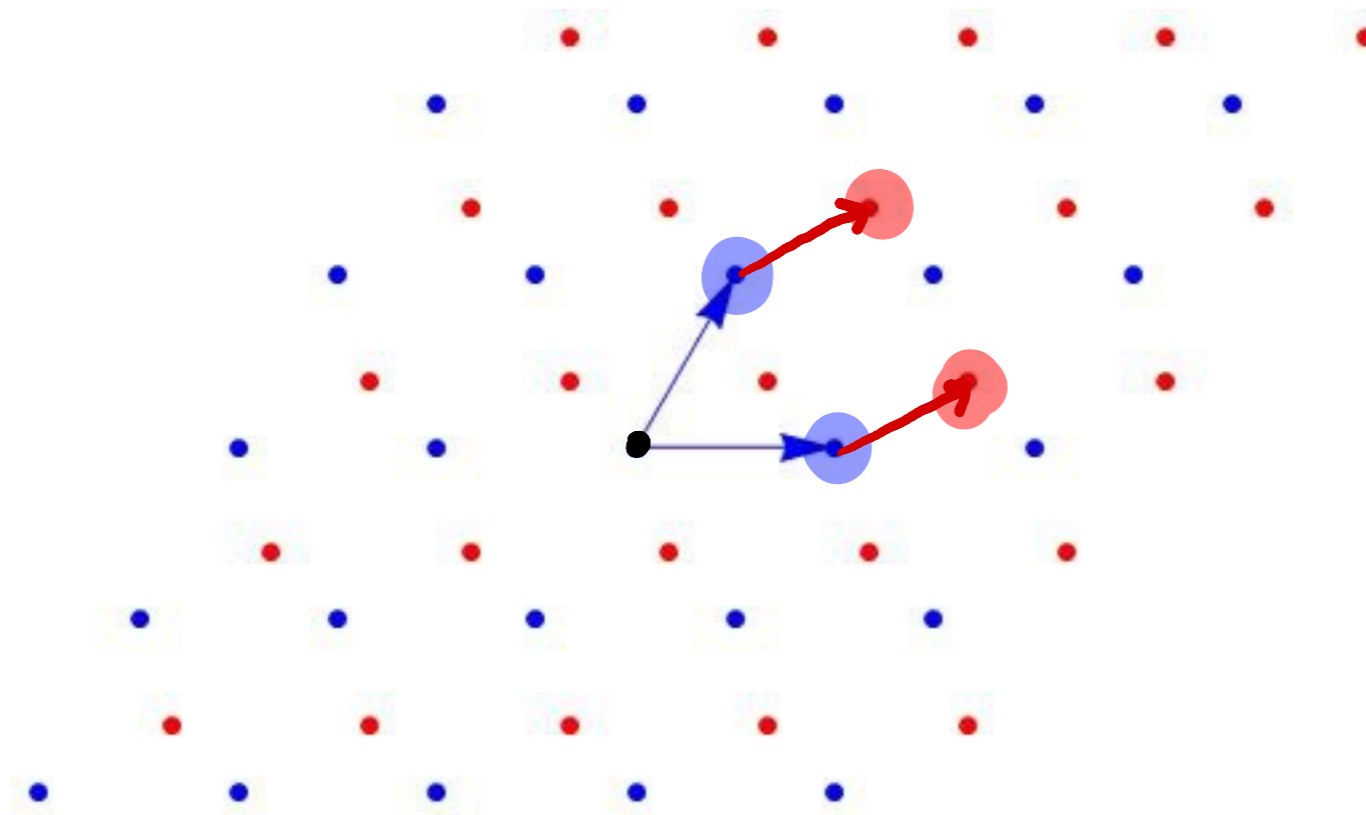
- but it is the same object for all \mathbf{R}

Solids: Real and reciprocal lattices

- Bravais lattice: all the points that can be achieved by:

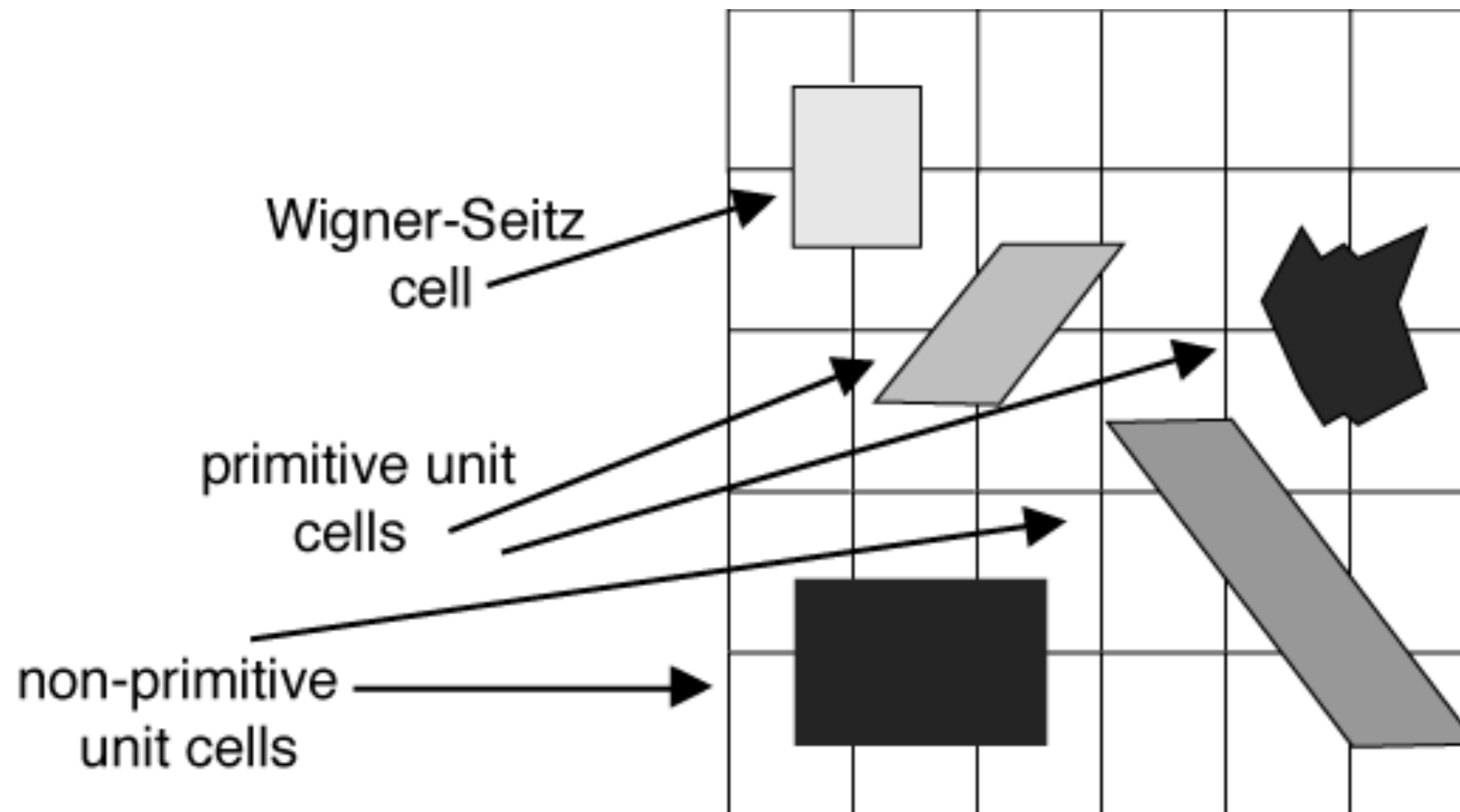
$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

- at each of these \mathbf{R} there can be either one atom, or many atoms, molecules, ...; this is called “atomic basis”
- Basis is the same object for all points \mathbf{R} of the lattice



Solids: Real and reciprocal lattices

- primitive (unit) cell: the volume that can, if repeated infinitely many times, fill the entire space without gaps and without overlap
- choice of the \mathbf{a} vectors not unique, primitive cell is not unique

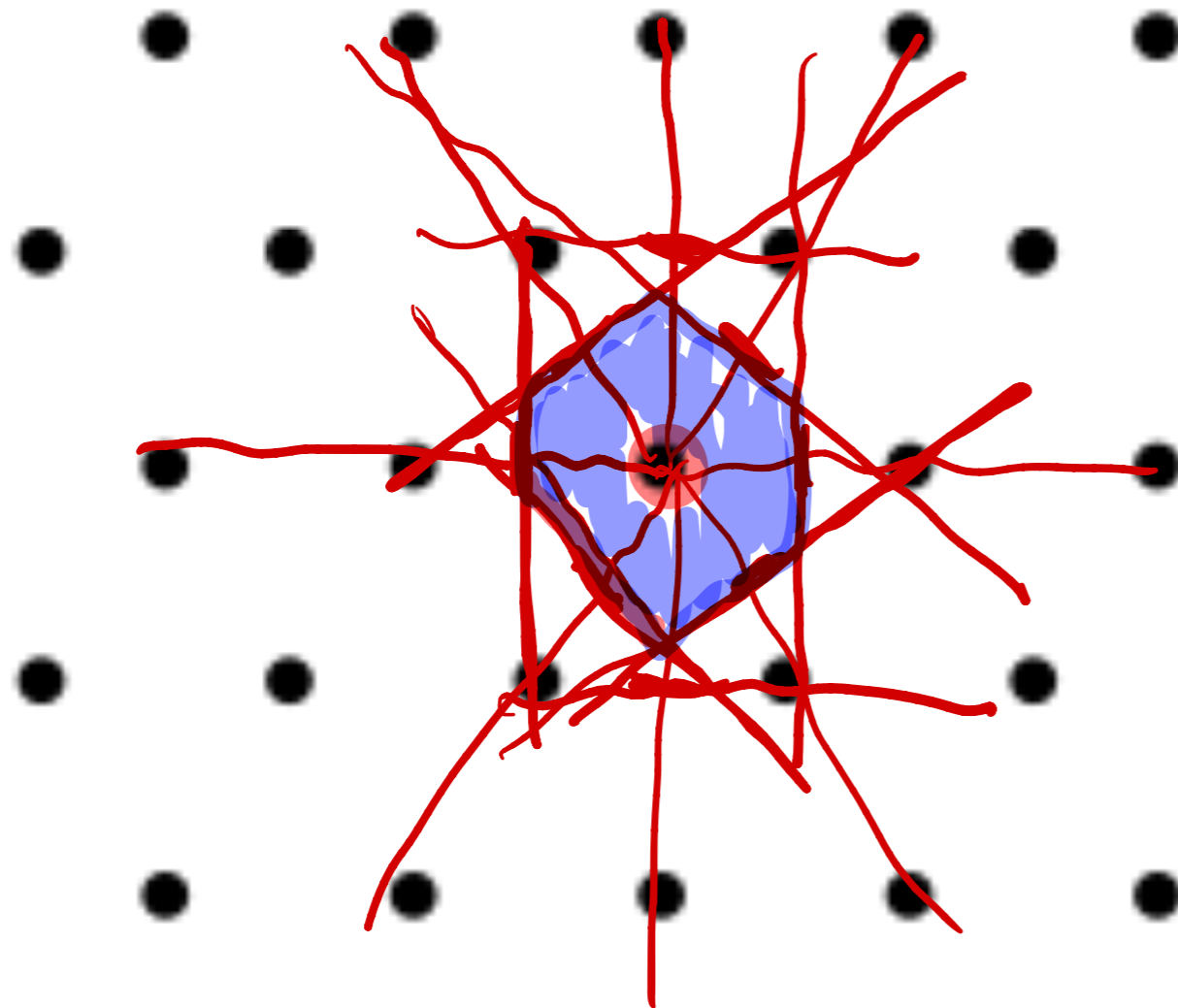


(c) http://users-phys.au.dk/philip/pictures/solid_crystalstructures/unitcells.gif

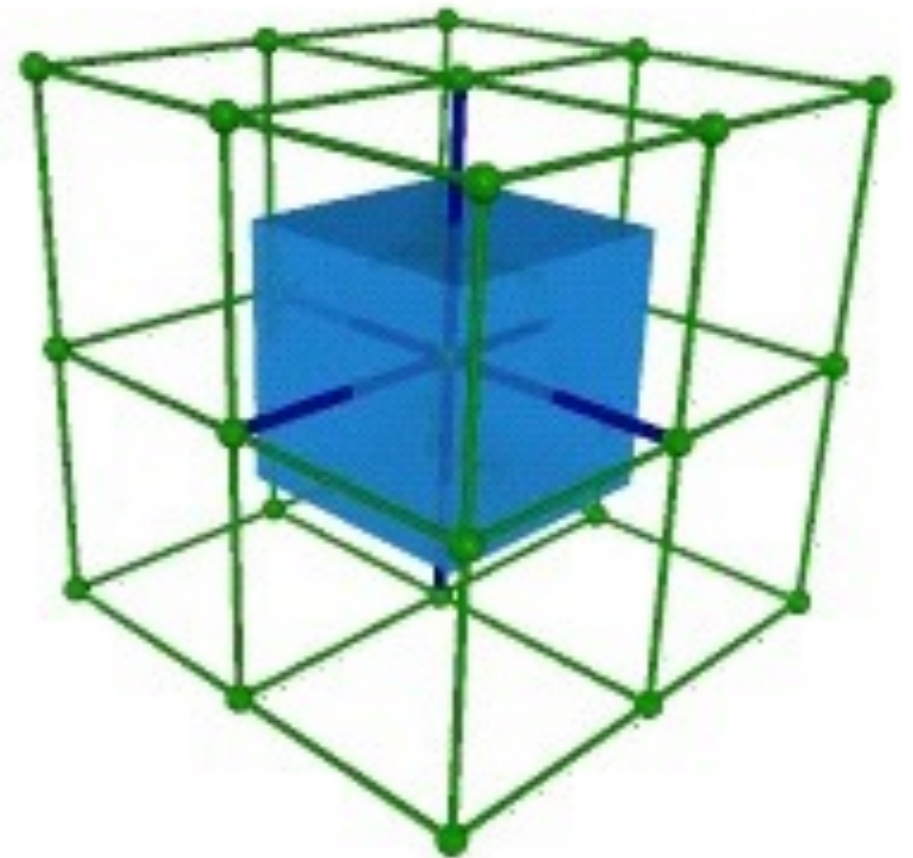
Solids: Real and reciprocal lattices

- recipe to construct primitive cell: Wigner-Seitz construction
- find all the volume that is closer to a given lattice point than to **any** other lattice point

• 2D:



• 3D:



Towards a Band Theory of Solids: Reciprocal Lattice

- a specific reciprocal lattice refers to a specific real-space lattice
- example: fcc \leftrightarrow bcc, cubic \leftrightarrow cubic, ...
 - fcc and bcc are reciprocal to each other
 - reciprocal lattice of cubic lattice is cubic
- if direct lattice vectors are known, reciprocal lattice vectors follow from:

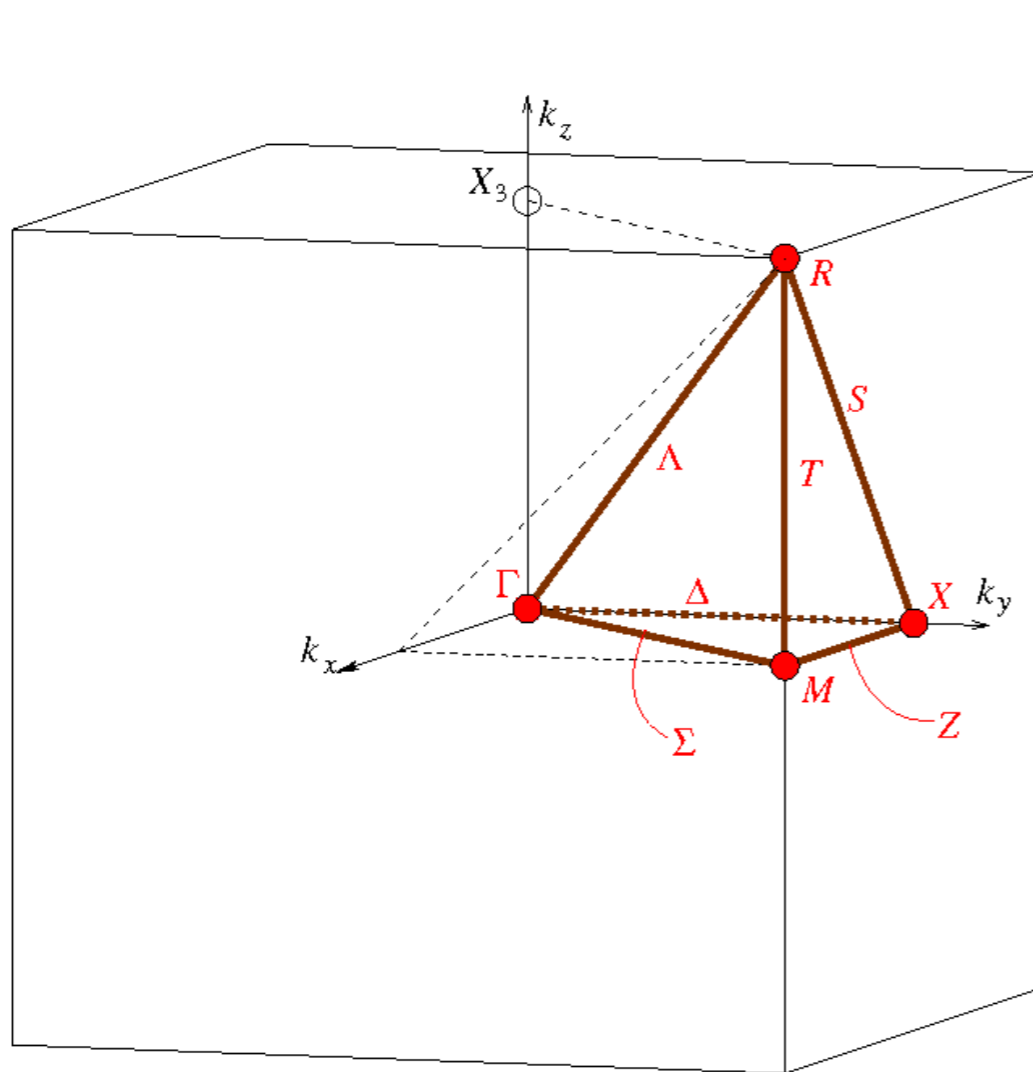
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

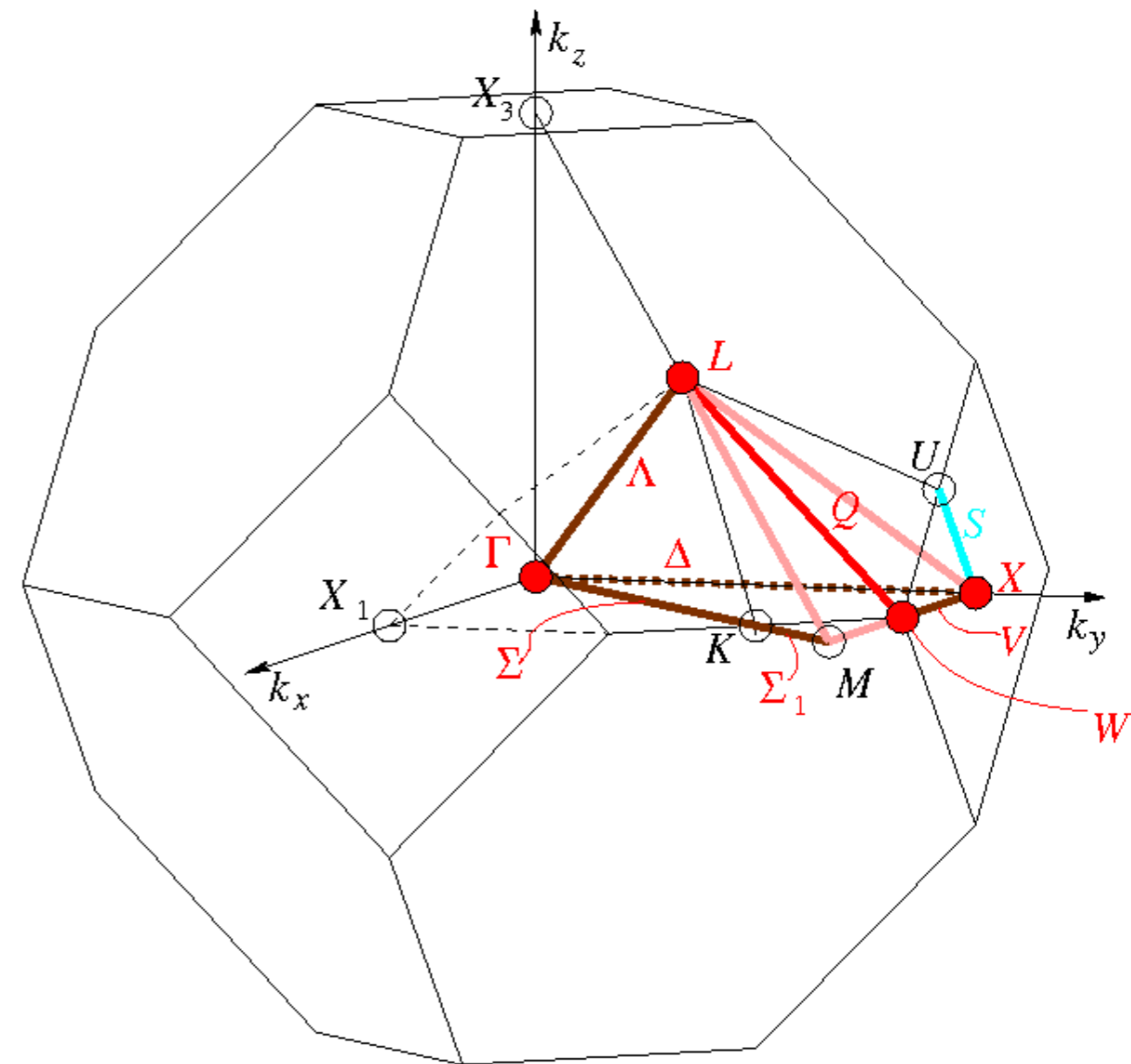
$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

Towards a Band Theory of Solids: Reciprocal Lattice

- Wigner-Seitz cell of reciprocal lattice: Brillouin zone



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Bloch theorem for solids

- we assume: all atoms sit on equilibrium positions
- this leads to a *periodic* lattice of atoms (potential for electrons)
- Bloch theorem:
- if the potential is periodic, i.e., $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$ then wave function is of the form:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r})$$

$$u_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R})$$

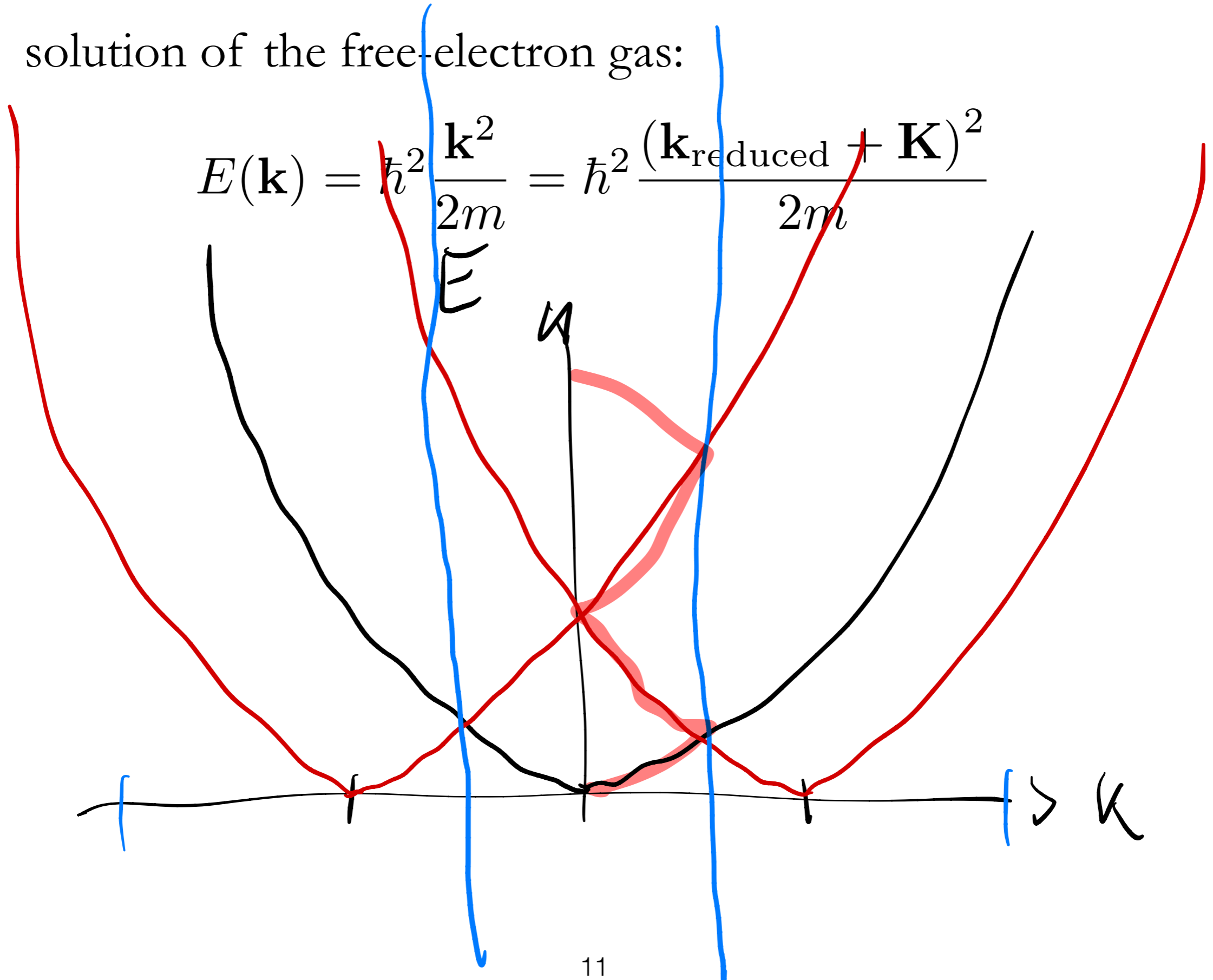
- this is true for *all* periodic potentials

$$E = \frac{\hbar^2 k^2}{2m} = \frac{(\text{reduced } k + K)^2}{2m}$$

Band structure in solids

- solution of the free-electron gas:

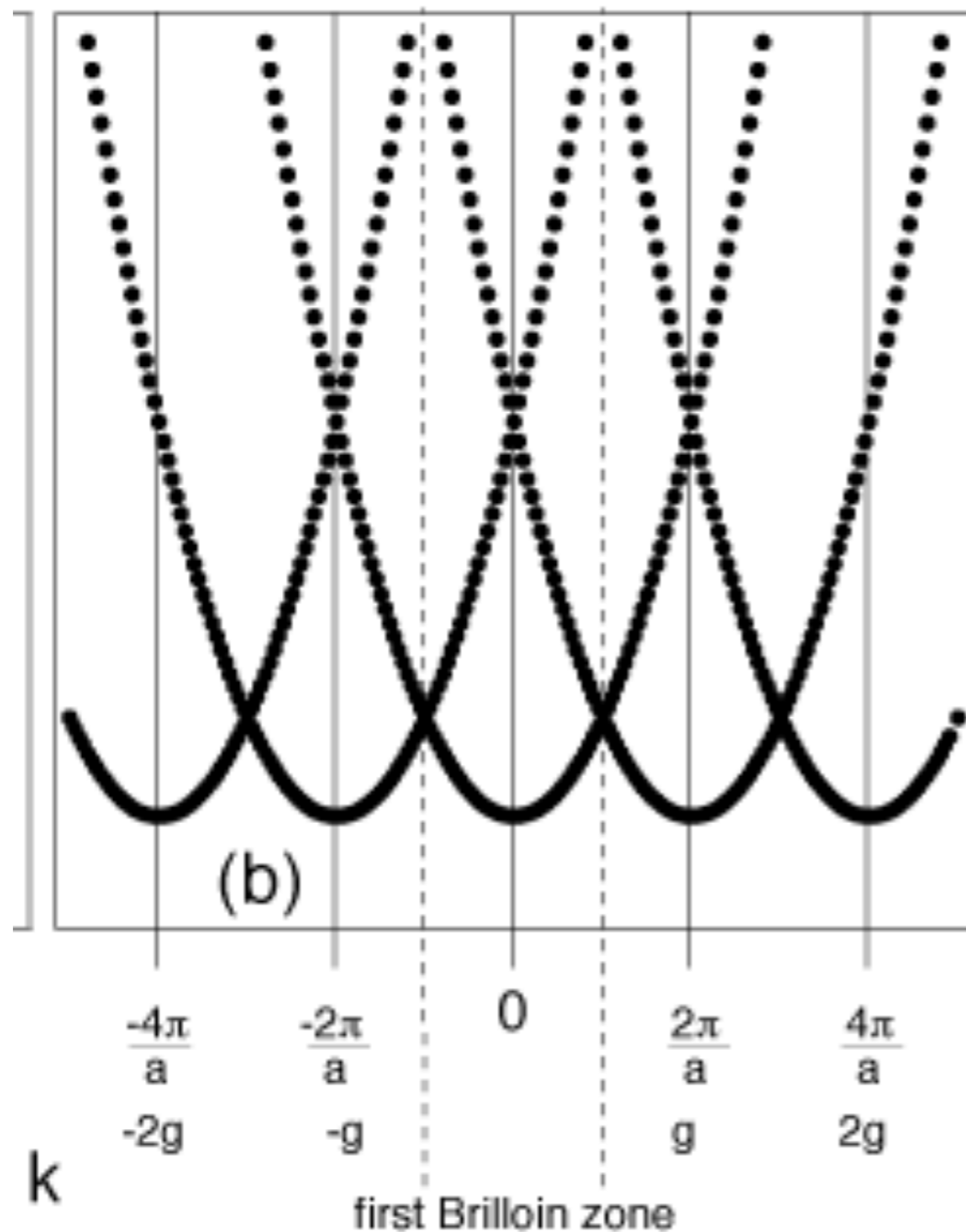
$$E(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} = \frac{\hbar^2 (\mathbf{k}_{\text{reduced}} + \mathbf{K})^2}{2m}$$



Band structure in solids

- solution of the free-electron gas:

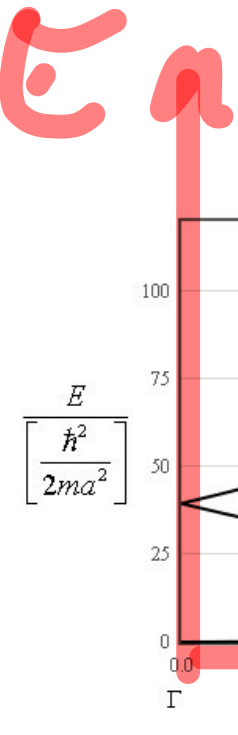
$$E(\mathbf{k}) = \hbar^2 \frac{\mathbf{k}^2}{2m} = \hbar^2 \frac{(\mathbf{k}_{\text{reduced}} + \mathbf{K})^2}{2m}$$



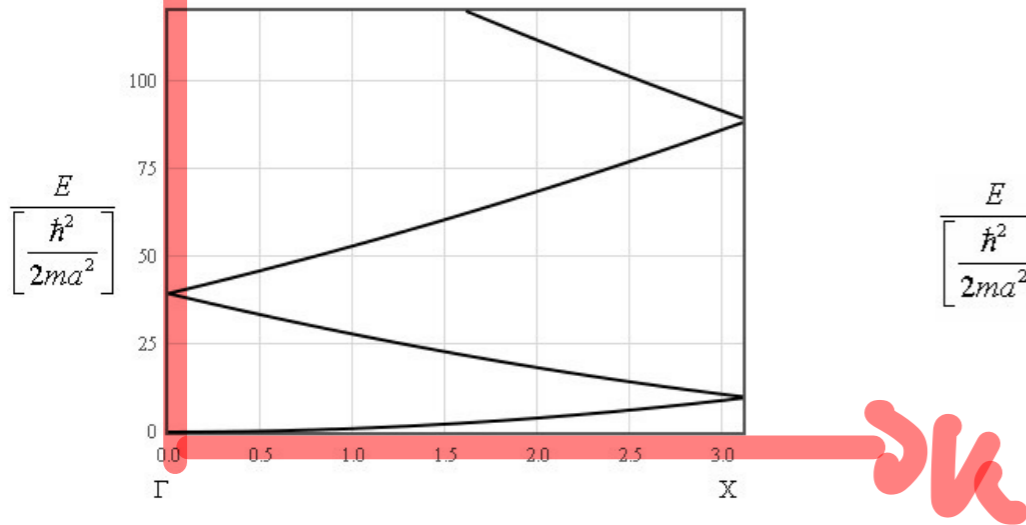
(c) <http://users-phys.au.dk/philip/pictures/physicsfigures/node8.html>

Band structure in solids: Empty lattice approximation

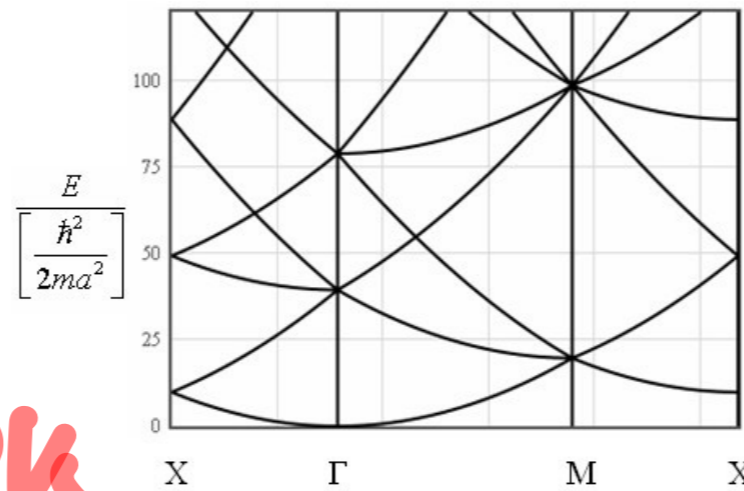
- lattice is periodic, but no atoms are present
- plot solutions for different lattice types: don't show periodicity



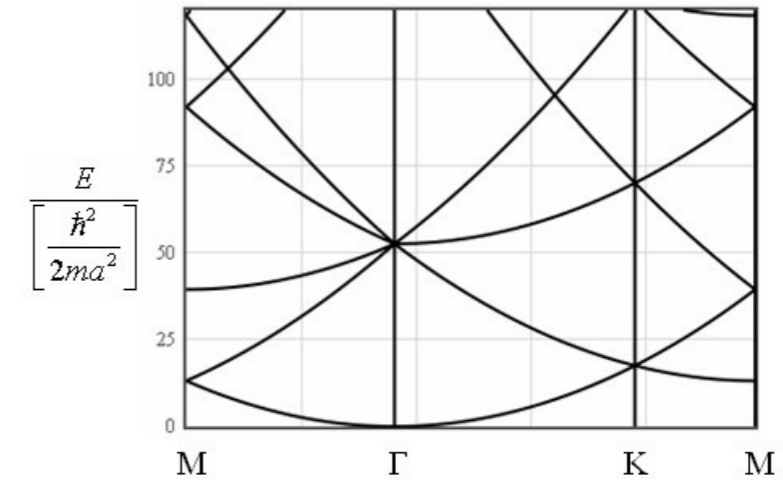
1D



2D (square)



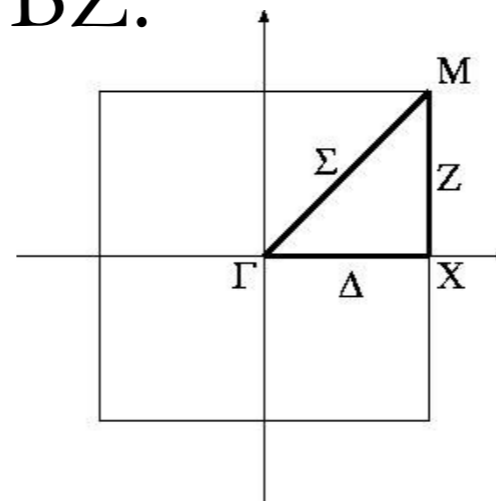
2D (hexagonal)



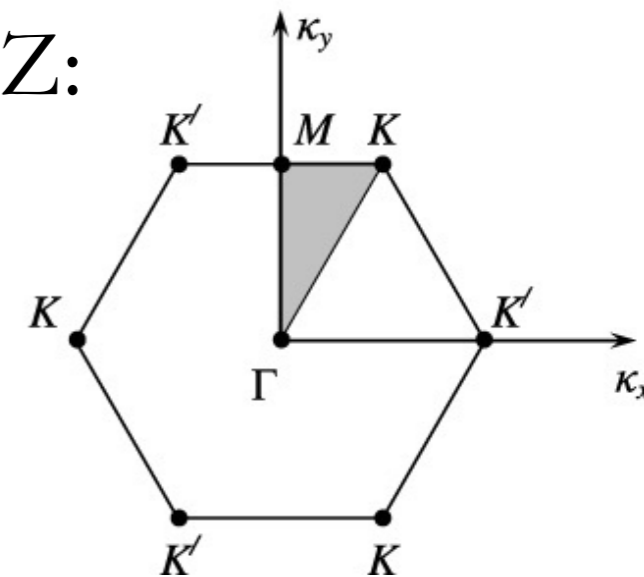
(c) <http://lamp.tu-graz.ac.at/~hadley/ss1/empty/empty.php>

$$E(\mathbf{k}) = \hbar^2 \frac{\mathbf{k}^2}{2m} = \hbar^2 \frac{(\mathbf{k}_{\text{reduced}} + \mathbf{K})^2}{2m}$$

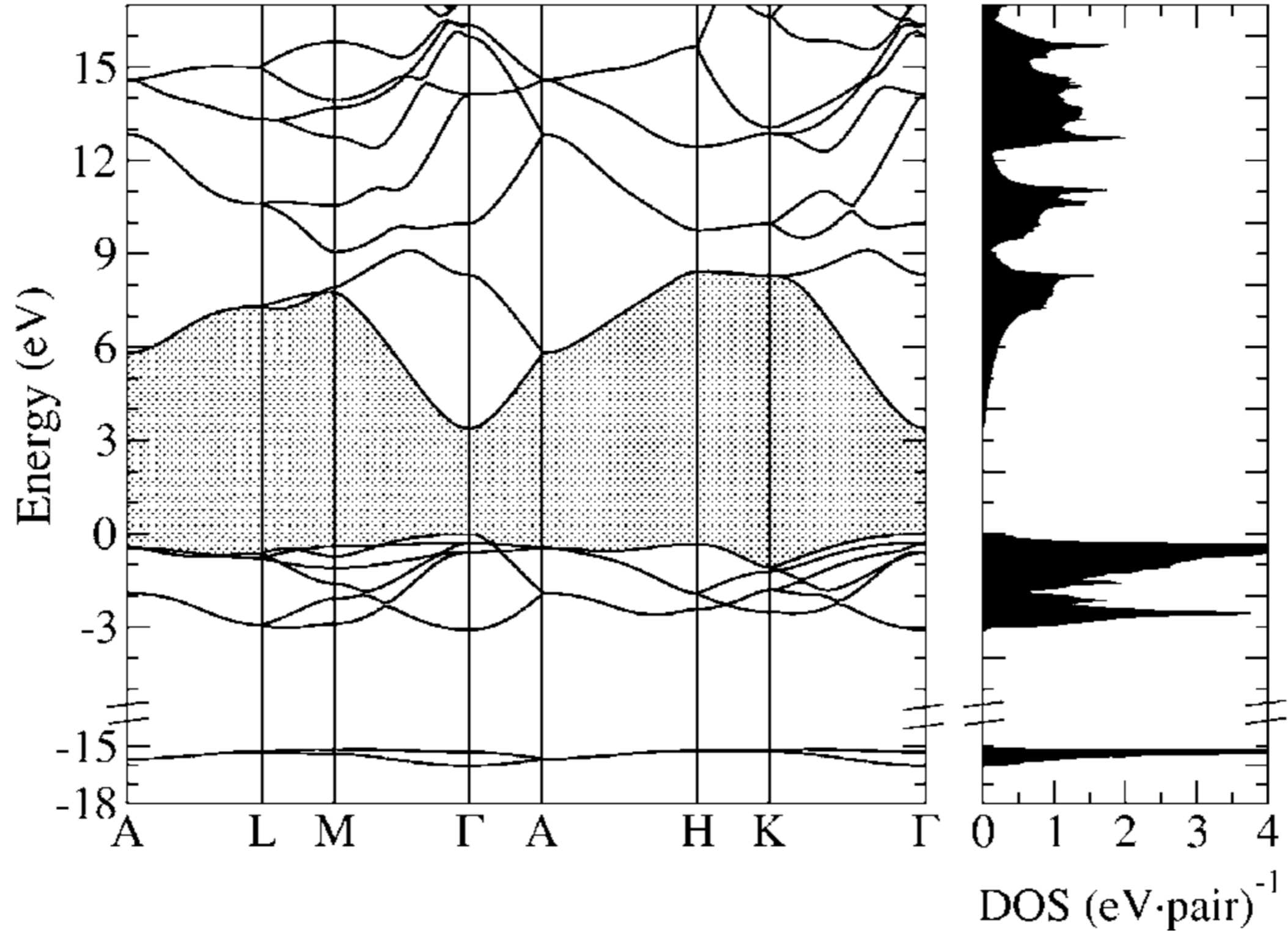
BZ:



BZ:



Band Structure and DOS for a real material



(c) Phys. Rev. B 73, 245212 (2006)

Basis Sets

Basis set choices:

- For molecules: use atomic orbitals, or localized functions like Gaussians
- For solids, periodic functions such as sines and cosines (i.e., plane waves)
- Use Bloch Theorem for periodic solids:

arbitrary phase factor

point k in Brillouin Zone

$$[\mathcal{H}, \mathcal{T}_{\mathbf{R}}] = 0 \quad \Rightarrow \quad \varphi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r})$$

Hamiltonian and translation operator commute

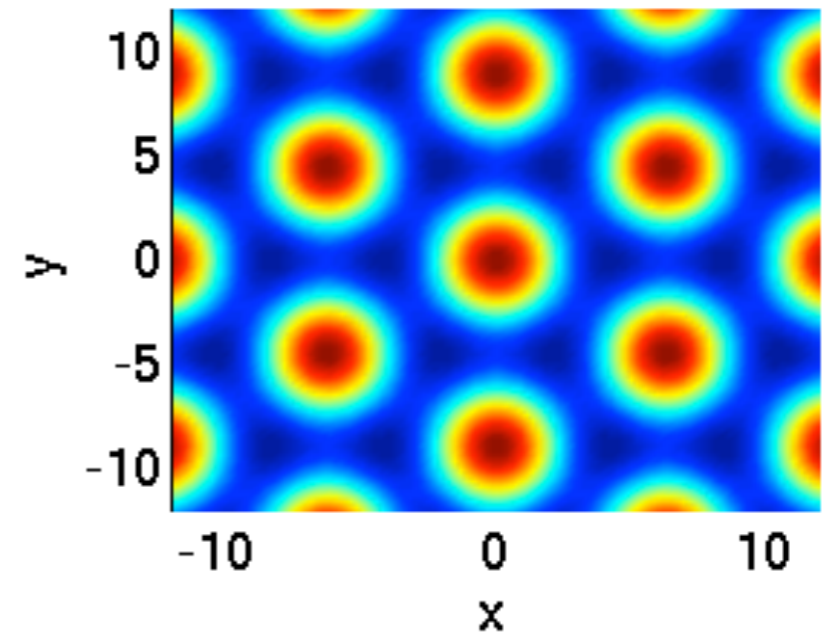
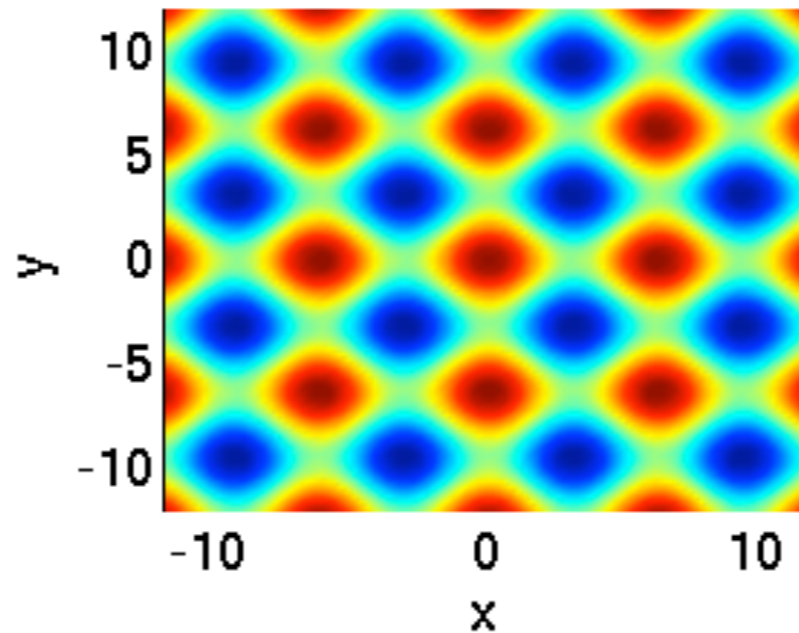
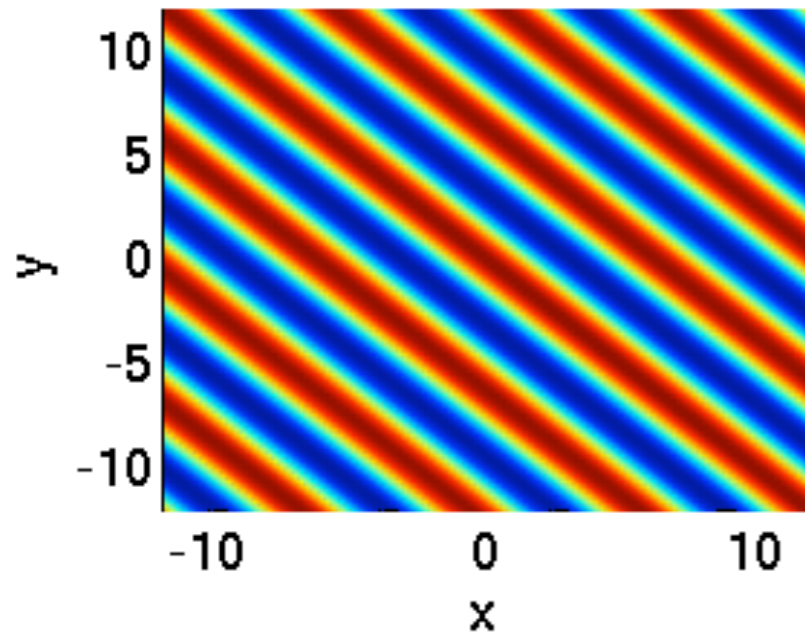
wavefunction of electron n at wavevector k in Brillouin Zone (Wigner-Seitz cell in reciprocal space)

$$u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}| < G_{\max}} c_{\mathbf{G}}(\mathbf{r}) \exp(i\mathbf{G} \cdot \mathbf{r})$$

Basis Sets: Plane waves

Superposition of plane waves to represent orbitals:

$$u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}| \leq G_{\max}} c_{nk}(\mathbf{G}) \exp(i \mathbf{G} \cdot \mathbf{r})$$



Basis Sets

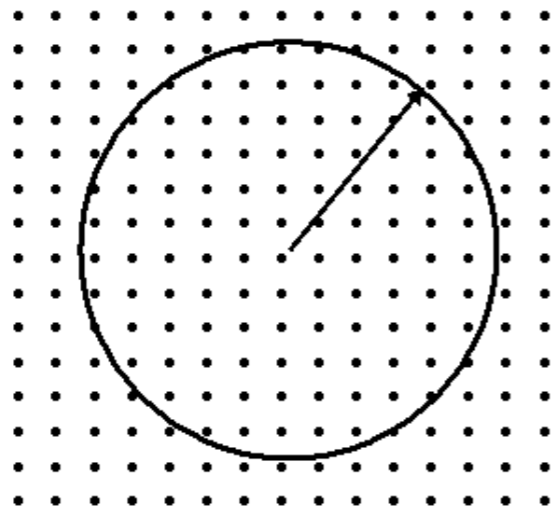
Superposition of plane waves to represent orbitals:

$$u_{nk}(\mathbf{r}) = \sum_{|\mathbf{G}| \leq G_{\max}} c_{nk}(\mathbf{G}) \exp(i \mathbf{G} \cdot \mathbf{r})$$

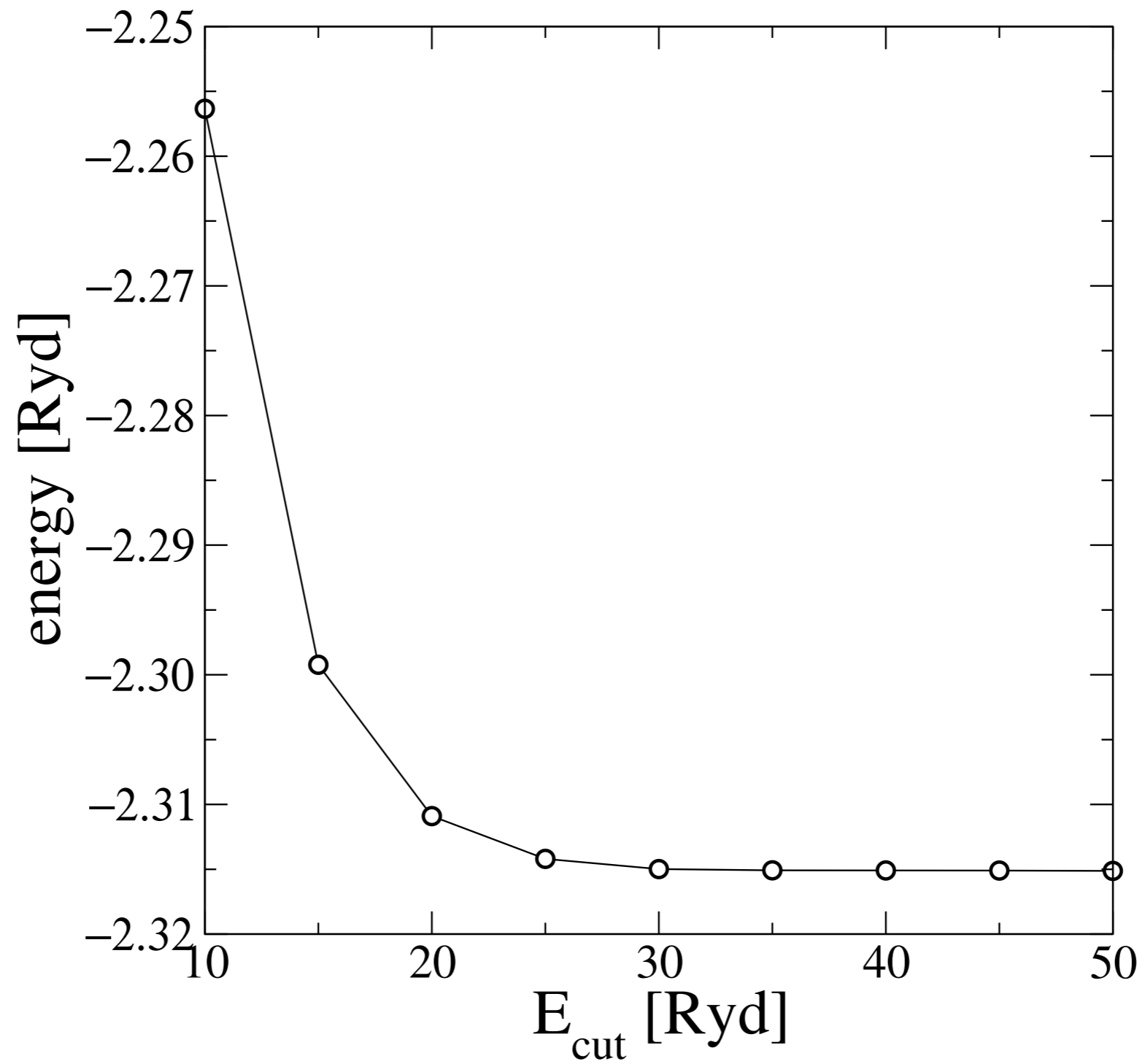
A particular plane wave: $f_i(\mathbf{r}) = c_{i,\mathbf{k}+\mathbf{G}} e^{-i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}}$

Its kinetic energy: $E_{kin} = f_i(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] f_i(\mathbf{r}) = \frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2$

- Low KE plane waves typically contribute more than higher KE
=> we can truncate the approximation to $u_{nk}(\mathbf{r})$ at E_{cut}



Quantum Espresso: Plane-wave cutoff convergence



Plane waves: Real-space quantities

The wavefunction (and energy) of each electron depends on both its quantum number n and its position \mathbf{k} within the Brillouin Zone

$$\hat{h}_{\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r}) = \varepsilon_{n,\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r})$$

Real-space quantities are computed by a discrete sum over n and integration over \mathbf{k} within the Brillouin Zone (approximated over a grid at finite \mathbf{k} -points)

e.g. density, $n(\mathbf{r})$

$$n(\mathbf{r}) = \frac{V_{\text{cell}}}{(2\pi)^3} \int_{\text{1BZ}} \left(\sum_{n=1}^{N_{\text{el}}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2 \right) d\mathbf{k}$$

Quantum Espresso: k-point convergence

