VASP: Basics
(DFT, PW, PAW, …)

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Outline

- Density functional theory
- Translational invariance and periodic boundary conditions
- Plane wave basis set
- The Projector-Augmented-Wave method
- Electronic minimization

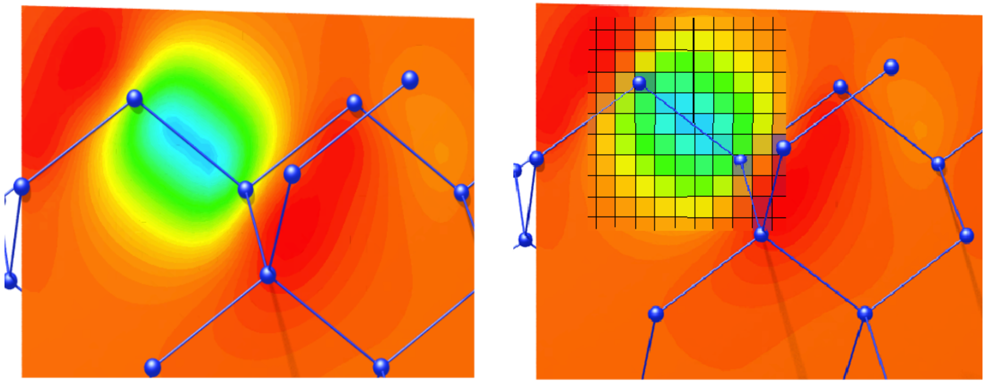
The Many-Body Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

$$\left(-\frac{1}{2}\sum_i \Delta_i + \sum_i V(\mathbf{r}_i) + \sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right)\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$$

For instance, many-body WF storage demands are prohibitive:

$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ $(\#\text{grid points})^N$



5 electrons on a 10×10×10 grid ~ 10 PetaBytes !

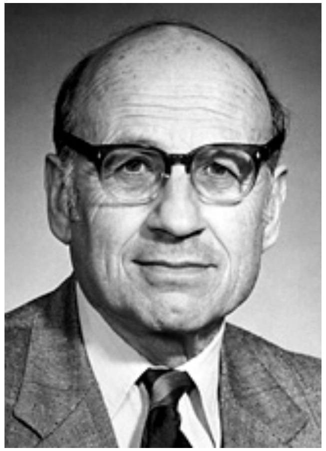
A solution: map onto “one-electron” theory:

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), ..., \psi_N(\mathbf{r})\}$$

Hohenberg-Kohn-Sham DFT

Map onto “one-electron” theory:

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), ..., \psi_N(\mathbf{r})\} \qquad \Psi(\mathbf{r}_1, ..., \mathbf{r}_N) = \prod_i^N \psi_i(\mathbf{r}_i)$$



Total energy is a functional of the density:

$$E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{\mathrm{xc}}[\rho] + E_Z[\rho] + U[Z]$$

The density is computed using the one-electron orbitals:

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2$$

The one-electron orbitals are the solutions of the Kohn-Sham equation:

$$\Big(-\frac{1}{2}\Delta + V_Z(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{\mathrm{xc}}[\rho](\mathbf{r})\Big)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

BUT:

$$E_{\mathrm{xc}}[\rho] = ??? \qquad V_{\mathrm{xc}}[\rho](\mathbf{r}) = ???$$

Exchange-Correlation

$$E_{\mathrm{xc}}[\rho] = ??? \qquad V_{\mathrm{xc}}[\rho](\mathbf{r}) = ???$$

- Exchange-Correlation functionals are modeled on the uniform-electron-gas (UEG): The correlation energy (and potential) has been calculated by means of Monte-Carlo methods for a wide range of densities, and has been parametrized to yield a density functional.

- LDA: we simply pretend that an inhomogeneous electronic density locally behaves like a homogeneous electron gas.

- Many, many, many different functionals available:
  LDA, GGA, meta-GGA, van-der-Waals functionals, etc etc

An N-electron system: N = O(10^{23})

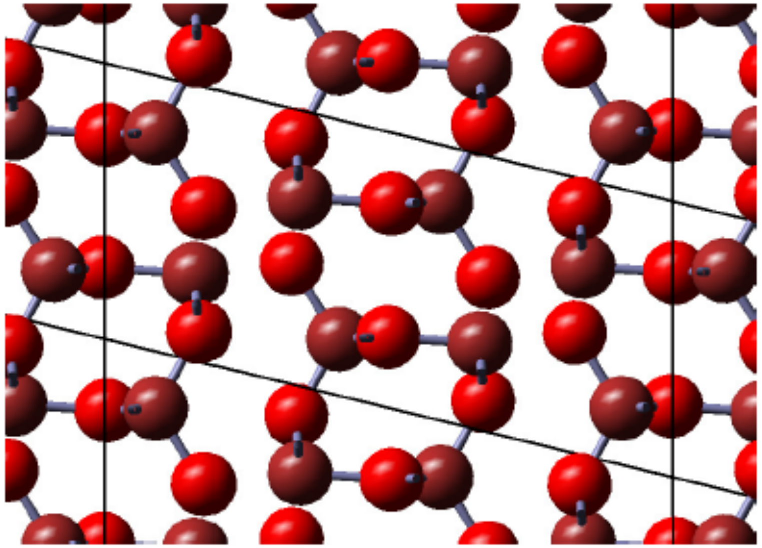
Hohenberg-Kohn-Sham DFT takes us a long way:

$$\Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \rightarrow \{\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), ..., \psi_N(\mathbf{r})\}$$

$$(\#\text{grid points})^N \qquad N \times (\#\text{grid points})$$

Nice for atoms and molecules, but in a realistic piece of solid state material N= O(10^{23})!

Translational invariance: Periodic Boundary Conditions



Translational invariance implies:

$$\psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \psi_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{R}}$$

and

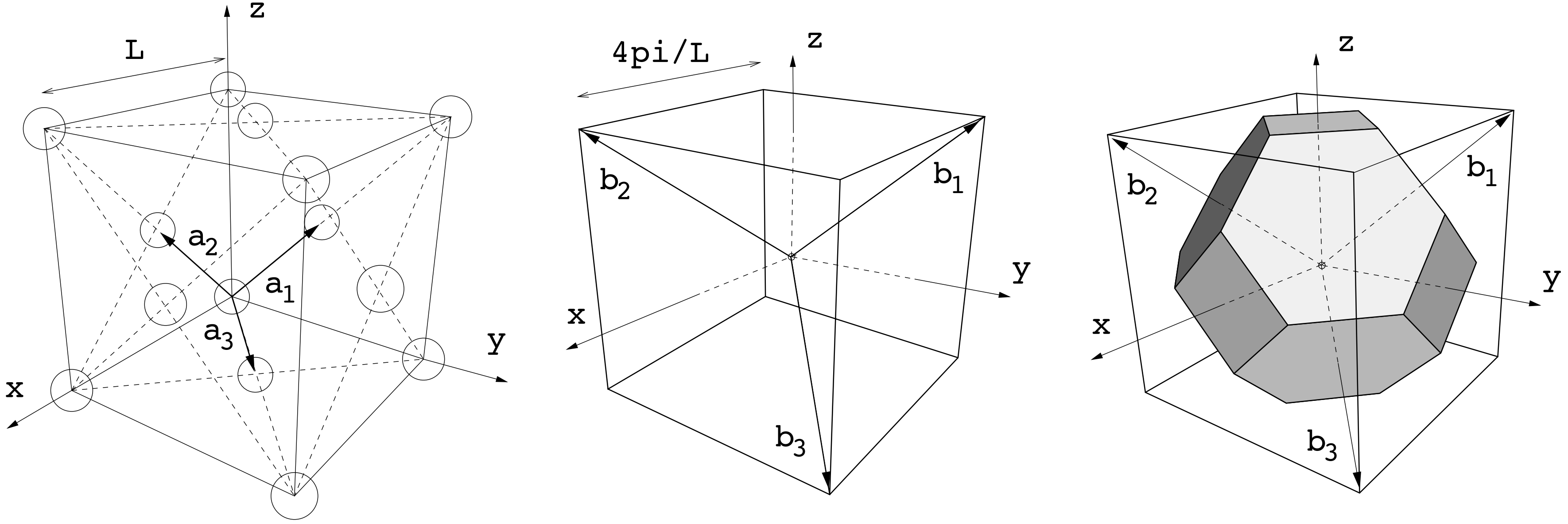
$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}$$

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

All states are labeled by *Bloch vector* **k** and the *band index* n:

- The Bloch vector **k** is usually constrained to lie within the first Brillouin zone of the reciprocal space lattice.
- The band index *n* is of the order if the number of electrons per unit cell.

Reciprocal space & the first Brillouin zone



A B C

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

$$\Omega = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 \qquad \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

Sampling the 1st BZ

The evaluation of many key quantities involves an integral over the 1st BZ.
For instance the charge density:

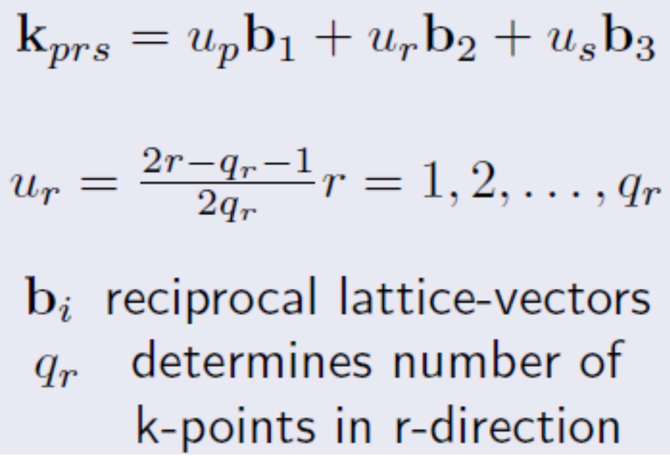
$$\rho(\mathbf{r}) = \frac{1}{\Omega_{\mathrm{BZ}}} \sum_n \int_{\mathrm{BZ}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

We exploit the fact that the orbitals at Bloch vectors **k** that are close together are almost identical and approximate the integral over the 1st BZ by a weighted sum over a discrete set of **k**-points:

$$\rho(\mathbf{r}) = \sum_{n\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k},$$

Fazit: the intractable task of determining $\Psi(\mathbf{r}_1, ..., \mathbf{r}_N)$ with N=10^{23}, has been reduced to calculating $\psi_{n\mathbf{k}}(\mathbf{r})$ at a discrete set of **k**-points in the 1st BZ, for a number of bands that is of the order if the number of electrons in the unit cell.

Idea: equally spaced mesh in the 1st Brillouin zone

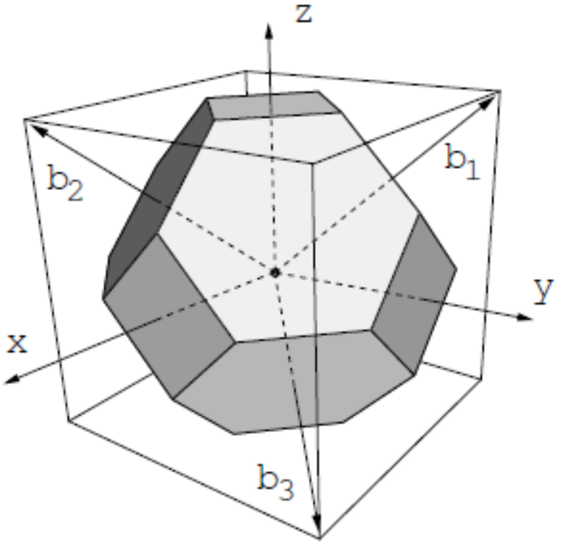


$$\mathbf{k}_{prs} = u_p\mathbf{b}_1 + u_r\mathbf{b}_2 + u_s\mathbf{b}_3$$

$$u_r = \frac{2r-q_r-1}{2q_r} r = 1, 2, \ldots, q_r$$

$\mathbf{b}_i$ reciprocal lattice-vectors

q_r determines number of k-points in r-direction



Example: a quadratic 2D lattice

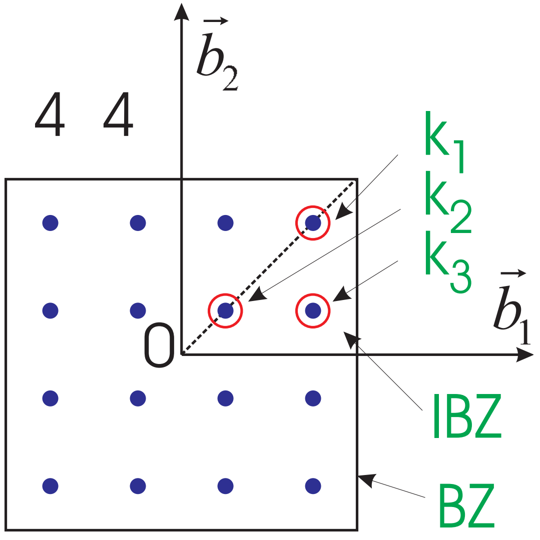
- $q_1=q_2=4$, *i.e.*, 16 points in total
- Only 3 symmetry inequivalent points:

$$4 \times \mathbf{k}_1 = (\frac{1}{8}, \frac{1}{8}) \Rightarrow \omega_1 = \frac{1}{4}$$

$$4 \times \mathbf{k}_2 = (\frac{3}{8}, \frac{3}{8}) \Rightarrow \omega_2 = \frac{1}{4}$$

$$8 \times \mathbf{k}_3 = (\frac{3}{8}, \frac{1}{8}) \Rightarrow \omega_3 = \frac{1}{2}$$

$$\frac{1}{\Omega_{\mathrm{BZ}}} \int\limits_{BZ} F(\mathbf{k})d\mathbf{k} \Rightarrow \frac{1}{4}F(\mathbf{k}_1) + \frac{1}{4}F(\mathbf{k}_2) + \frac{1}{2}F(\mathbf{k}_3)$$

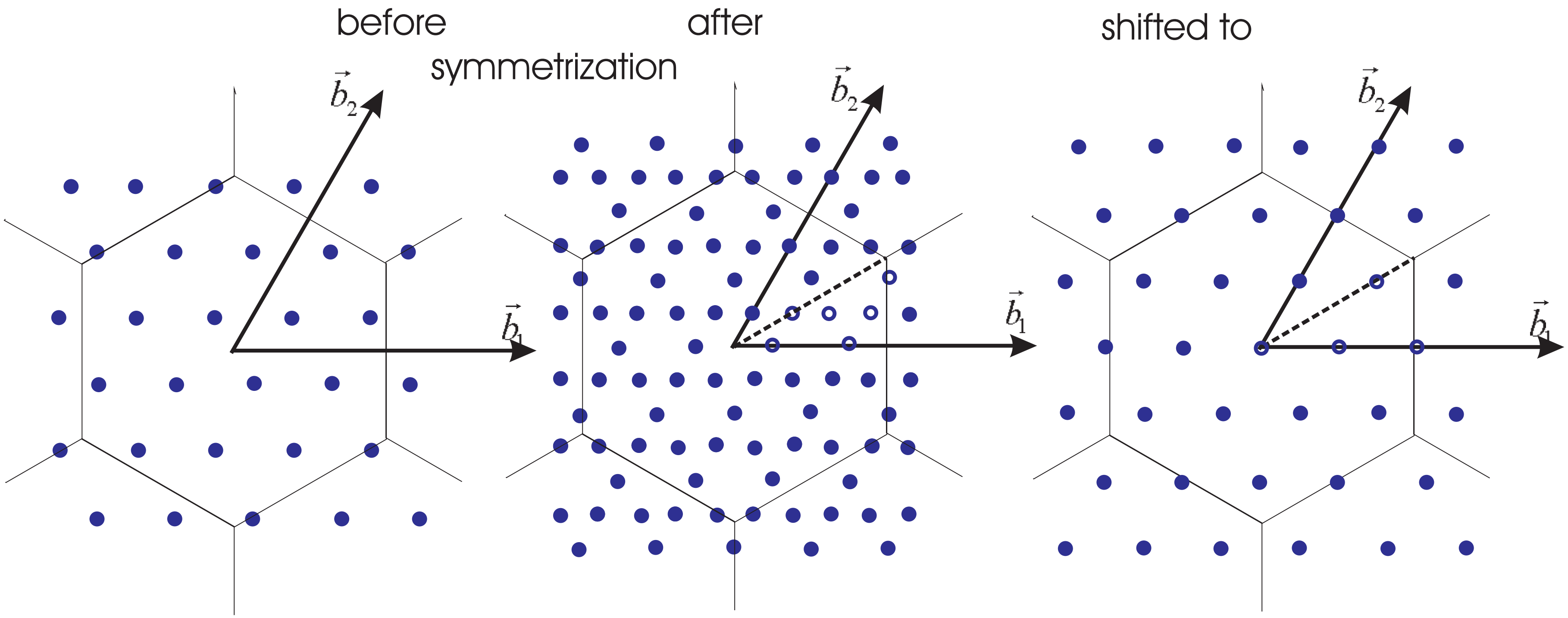


Algorithm:

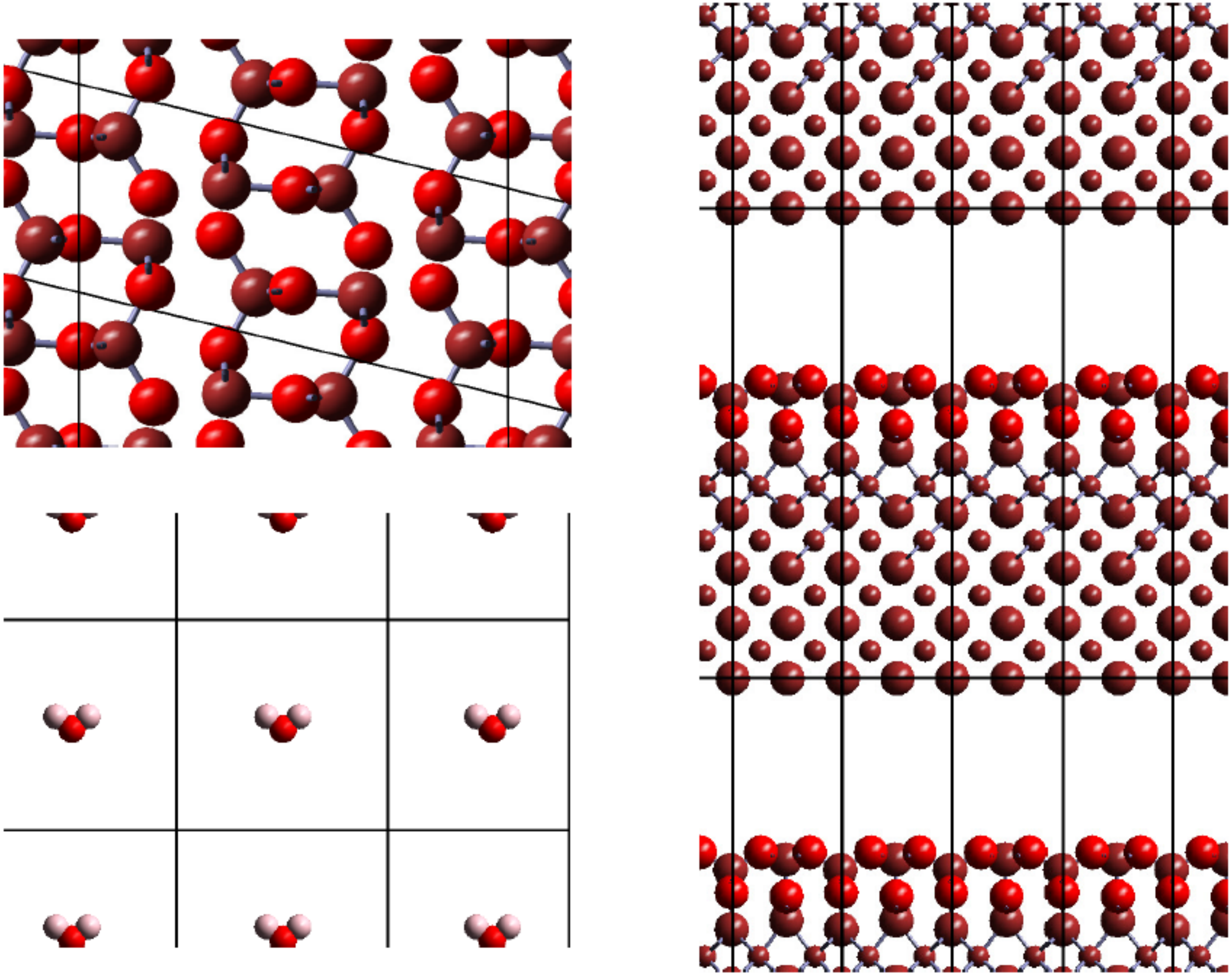
- Calculate equally spaced mesh.
- Shift the mesh if desired.
- Apply all symmetry operations of the Bravais lattice to all **k**-points.
- Extract the irreducible **k**-points (IBZ).
- Calculate the proper weighting.

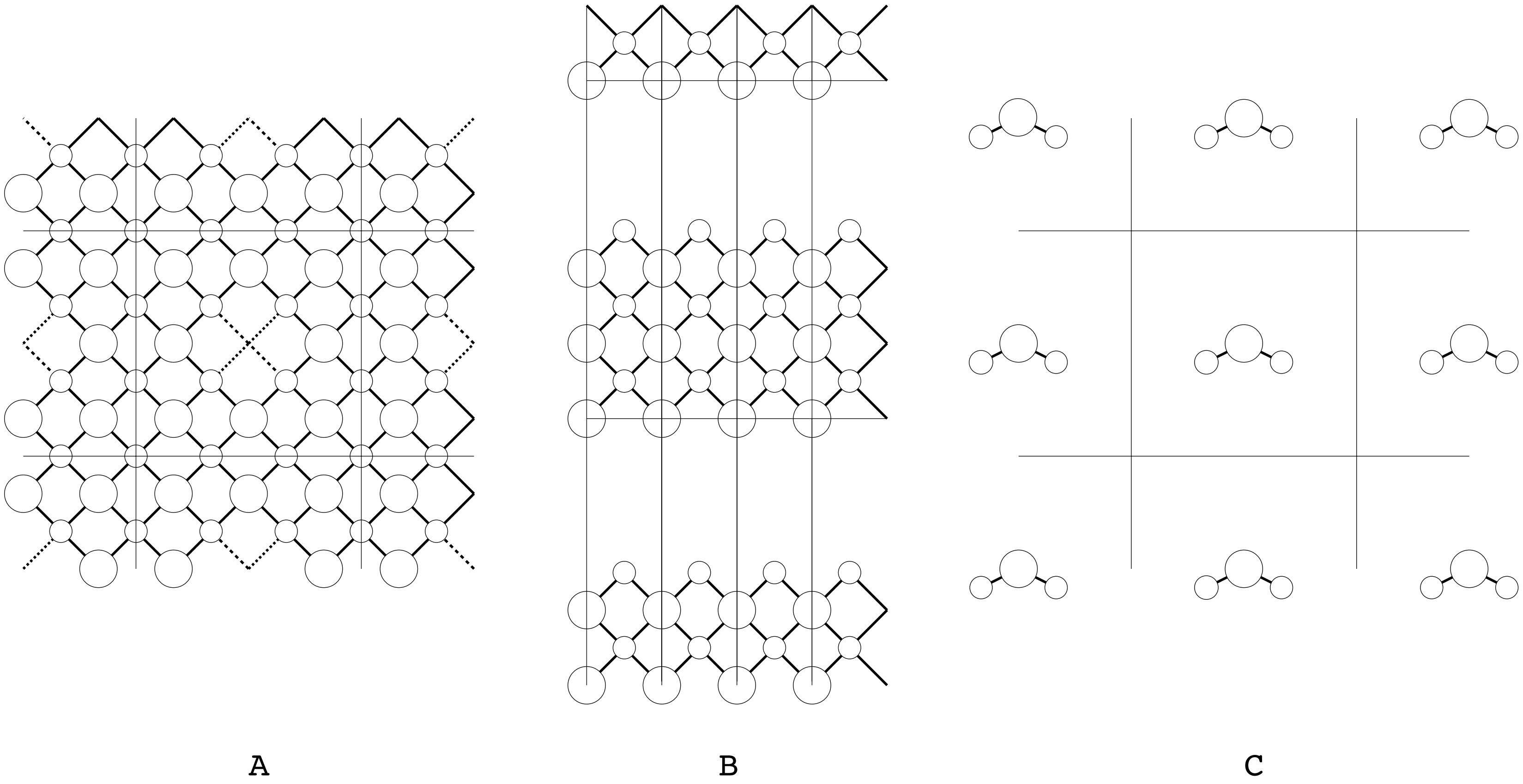
Common meshes: Two different choices for the center of the mesh.

- Centered on Γ
- Centered around Γ (can break the symmetry!)



- In certain cell geometries (*e.g.* hexagonal cells) even meshes break the symmetry.
- Symmetrization results in non-uniform distributions of **k**-points.
- Γ-point centered meshes preserve the symmetry.




A
B
C

The total energy

$$E[\rho,\{\mathbf{R},Z\}] = T_s[\{\psi_{n\mathbf{k}}[\rho]\}] + E_H[\rho,\{\mathbf{R},Z\}] + E_{\mathrm{xc}}[\rho] + U(\{\mathbf{R},Z\})$$

The kinetic energy

$$T_s[\{\psi_{n\mathbf{k}}[\rho]\}] = \sum_{n\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} \langle\psi_{n\mathbf{k}}| - \frac{1}{2}\Delta|\psi_{n\mathbf{k}}\rangle$$

The Hartree energy

$$E_{\mathrm{H}}[\rho,\{\mathbf{R},Z\}] = \frac{1}{2}\iint \frac{\rho_{eZ}(\mathbf{r})\rho_{eZ}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r}$$

where

$$\rho_{eZ}(\mathbf{r}) = \rho(\mathbf{r}) + \sum_i Z_i \delta(\mathbf{r}-\mathbf{R}_i) \qquad \rho(\mathbf{r}) = \sum_{n\mathbf{k}} w_{\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 d\mathbf{k}$$

The Kohn-Sham equations

$$\Big(-\frac{1}{2}\Delta + V_H[\rho_{eZ}](\mathbf{r}) + V_{\mathrm{xc}}[\rho](\mathbf{r})\Big)\psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$$

The Hartree potential

$$V_H[\rho_{eZ}](\mathbf{r}) = \int \frac{\rho_{eZ}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

A plane wave basis set

$$\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}} \qquad\qquad u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

All cell-periodic functions are expanded in plane waves (Fourier analysis):

$$u_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{Gr}} \qquad\qquad \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}}\sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}$$

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}e^{i\mathbf{Gr}} \qquad\qquad V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}}e^{i\mathbf{Gr}}$$

The basis set includes all plane waves for which

$$\frac{1}{2}|\mathbf{G}+\mathbf{k}|^2 < E_{\mathrm{cutoff}}$$

Transformation by means of FFT between “real” space and “reciprocal” space:

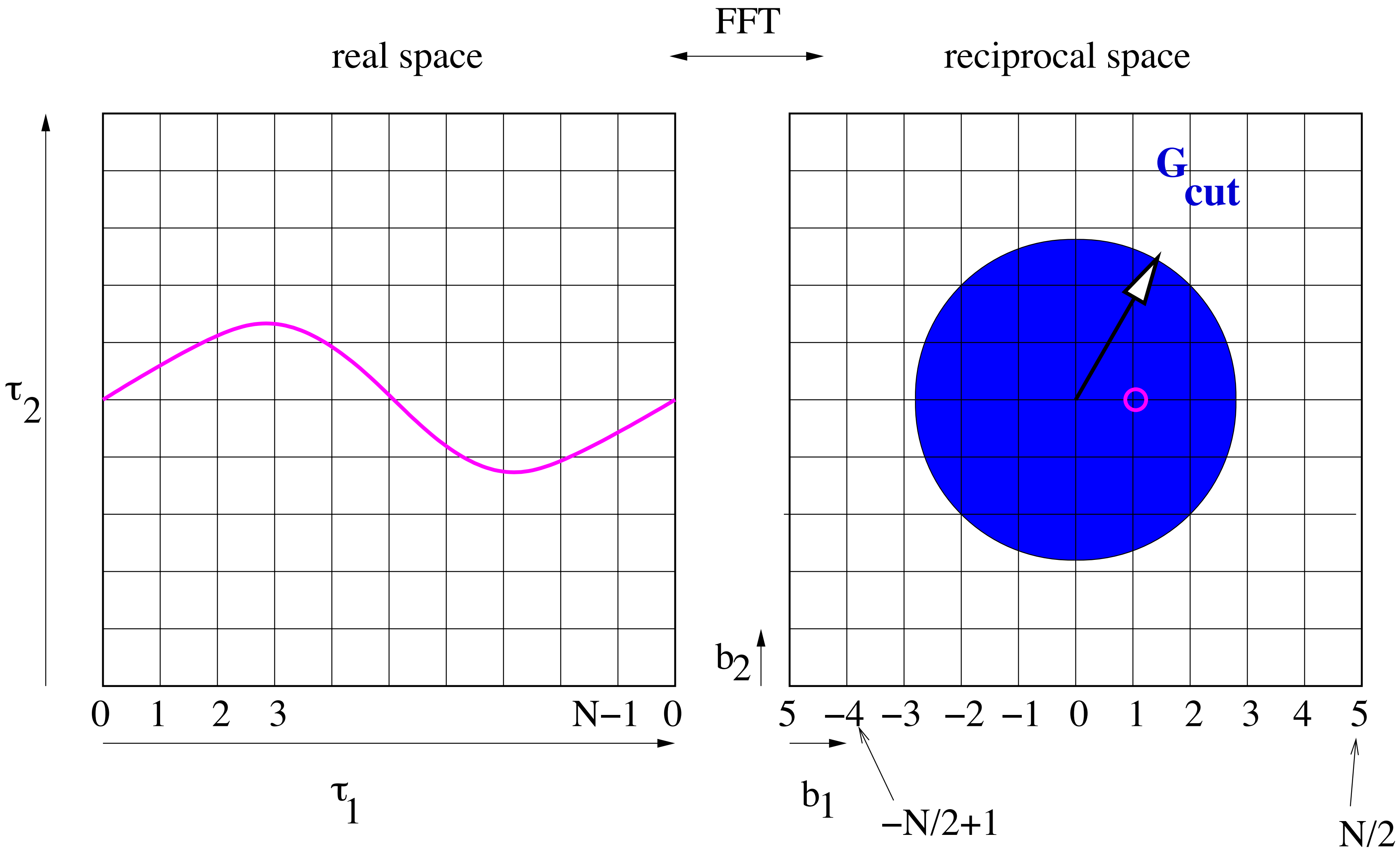
$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}}e^{i\mathbf{Gr}} \quad \overset{\mathrm{FFT}}{\longleftrightarrow} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\mathrm{FFT}}}\sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}}e^{-i\mathbf{Gr}}$$

Why use plane waves?

- Historical reason: Many elements exhibit a band-structure that can be interpreted in a free electron picture (metallic s and p elements). Pseudopotential theory was initially developed to cope with these elements (pseudopotential perturbation theory).

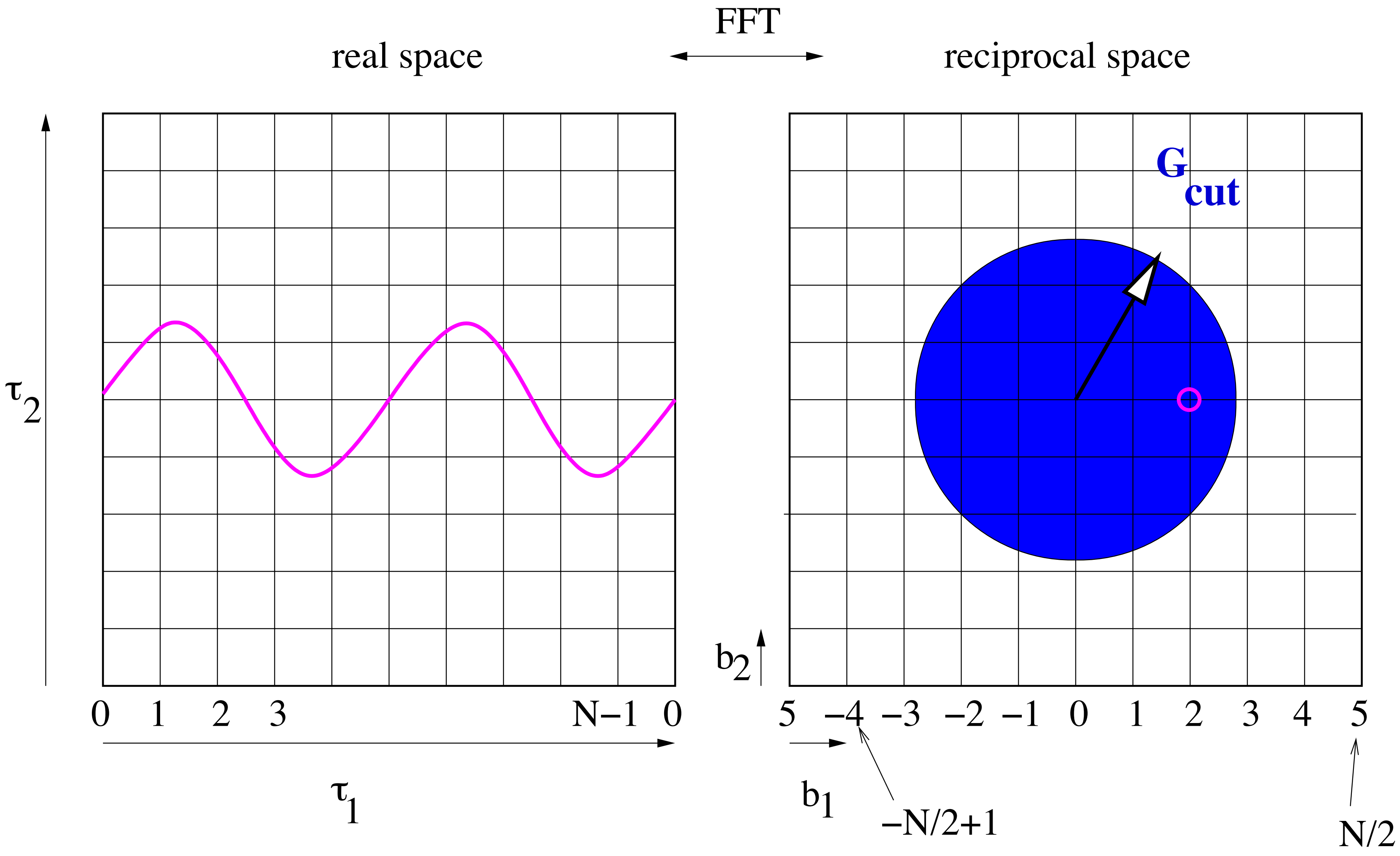
- Practical reason: The total energy expressions and the Hamiltonian are easy to implement.

- Computational reason: The action of the Hamiltonian on the orbitals can be efficiently evaluated using FFTs.



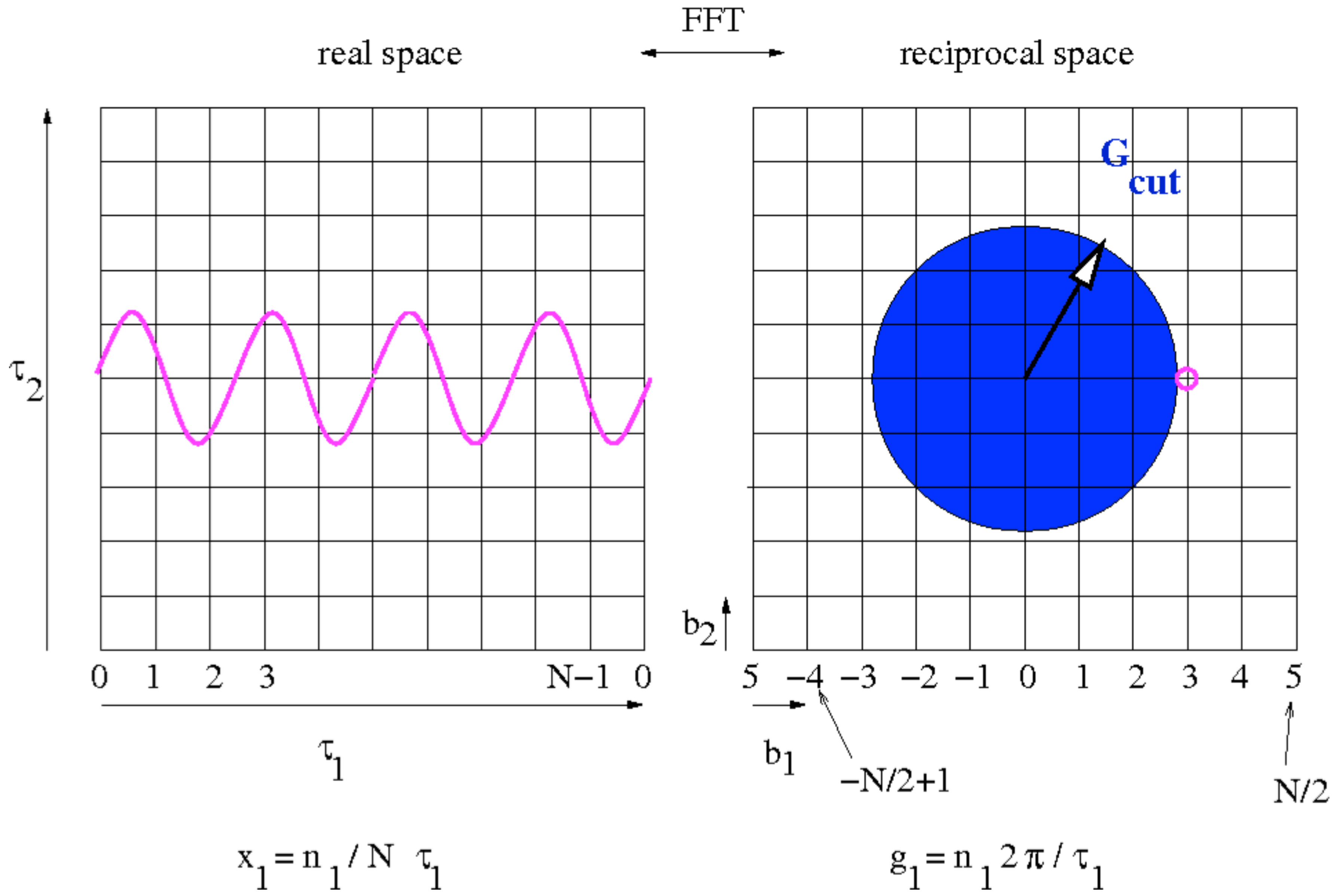
$x_1 = n_1 / N \ \tau_1$ $g_1 = n_1 \, 2\pi / \tau_1$

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \overset{\text{FFT}}{\longleftrightarrow} C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

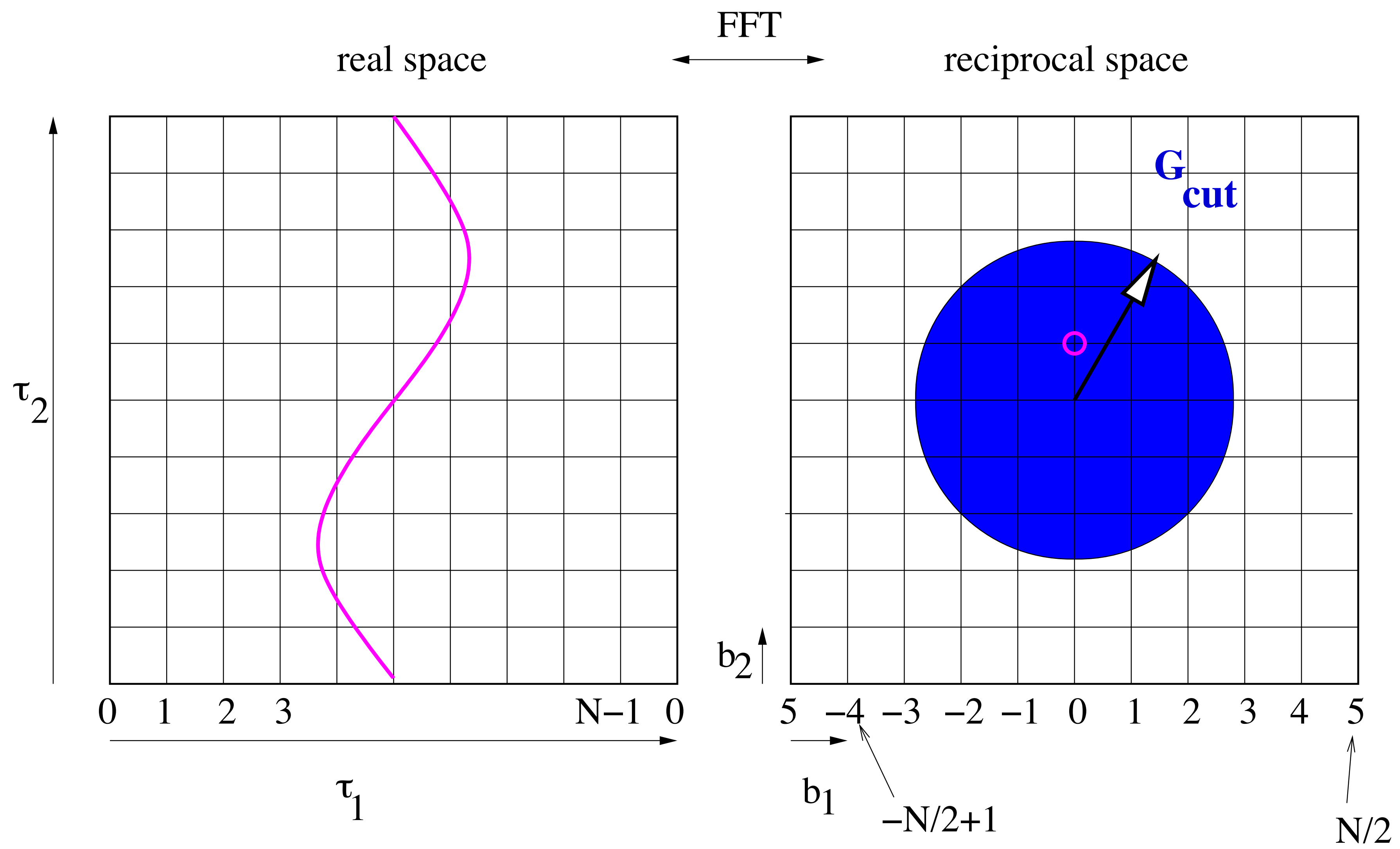


$x_1 = n_1 / N \;\; \tau_1$ $\qquad$ $g_1 = n_1 \, 2\pi / \tau_1$

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \overset{\text{FFT}}{\longleftrightarrow} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$



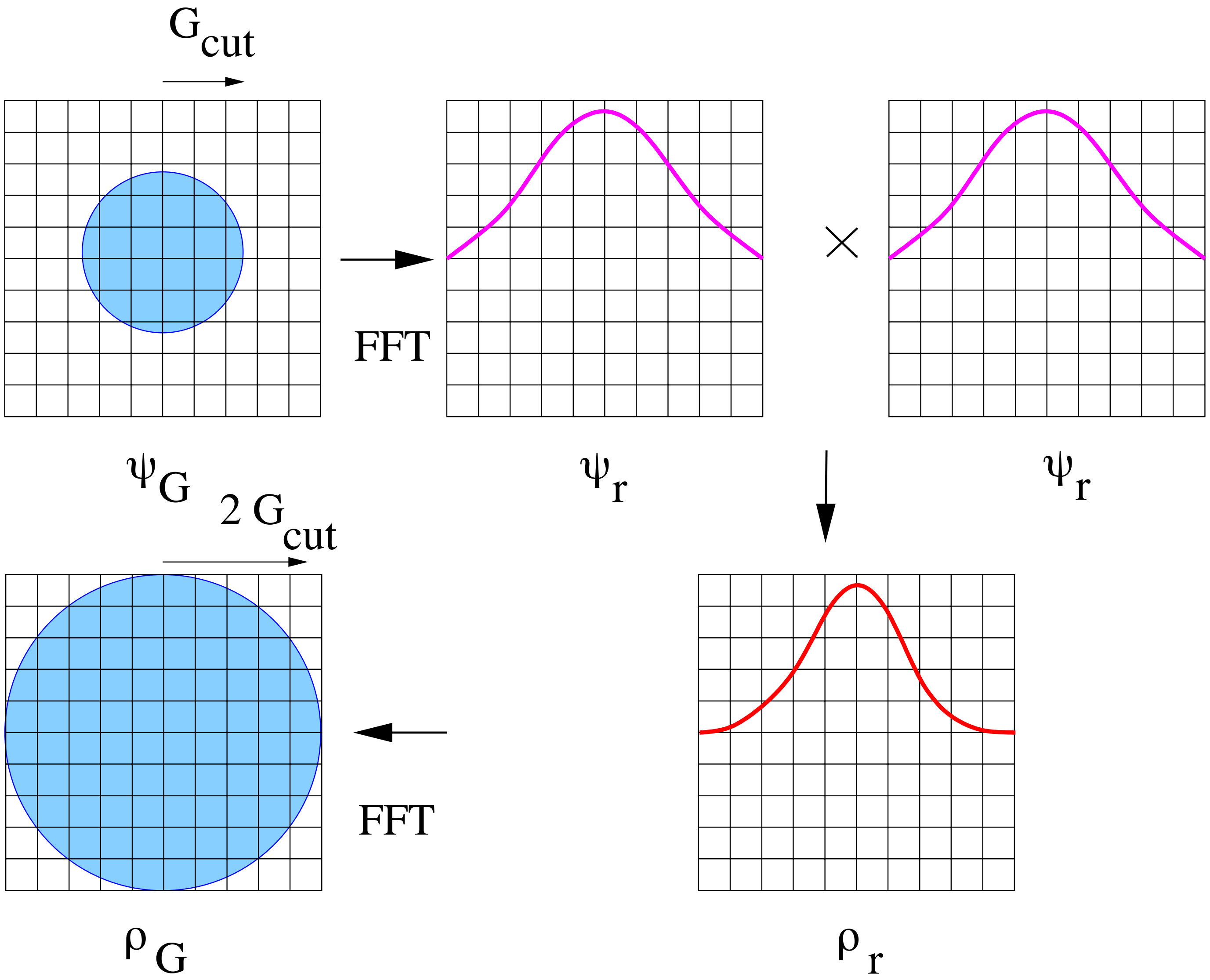
$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \overset{\text{FFT}}{\longleftrightarrow} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$



$x_1 = n_1 / N \;\; \tau_1$ $\qquad$ $g_1 = n_1 \, 2\pi / \tau_1$

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \quad \overset{\text{FFT}}{\longleftrightarrow} \quad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}}$$

The charge density



The action of the Hamiltonian

The action $\mathbf{H}|\psi_{n\mathbf{k}}\rangle$

$$\left(-\frac{1}{2}\Delta + V(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r})$$

Using the convention

$$\langle\mathbf{r}|\mathbf{G}+\mathbf{k}\rangle = \frac{1}{\Omega^{1/2}}e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}} \rightarrow \langle\mathbf{G}+\mathbf{k}|\psi_{n\mathbf{k}}\rangle = C_{\mathbf{G}n\mathbf{k}}$$

- Kinetic energy:

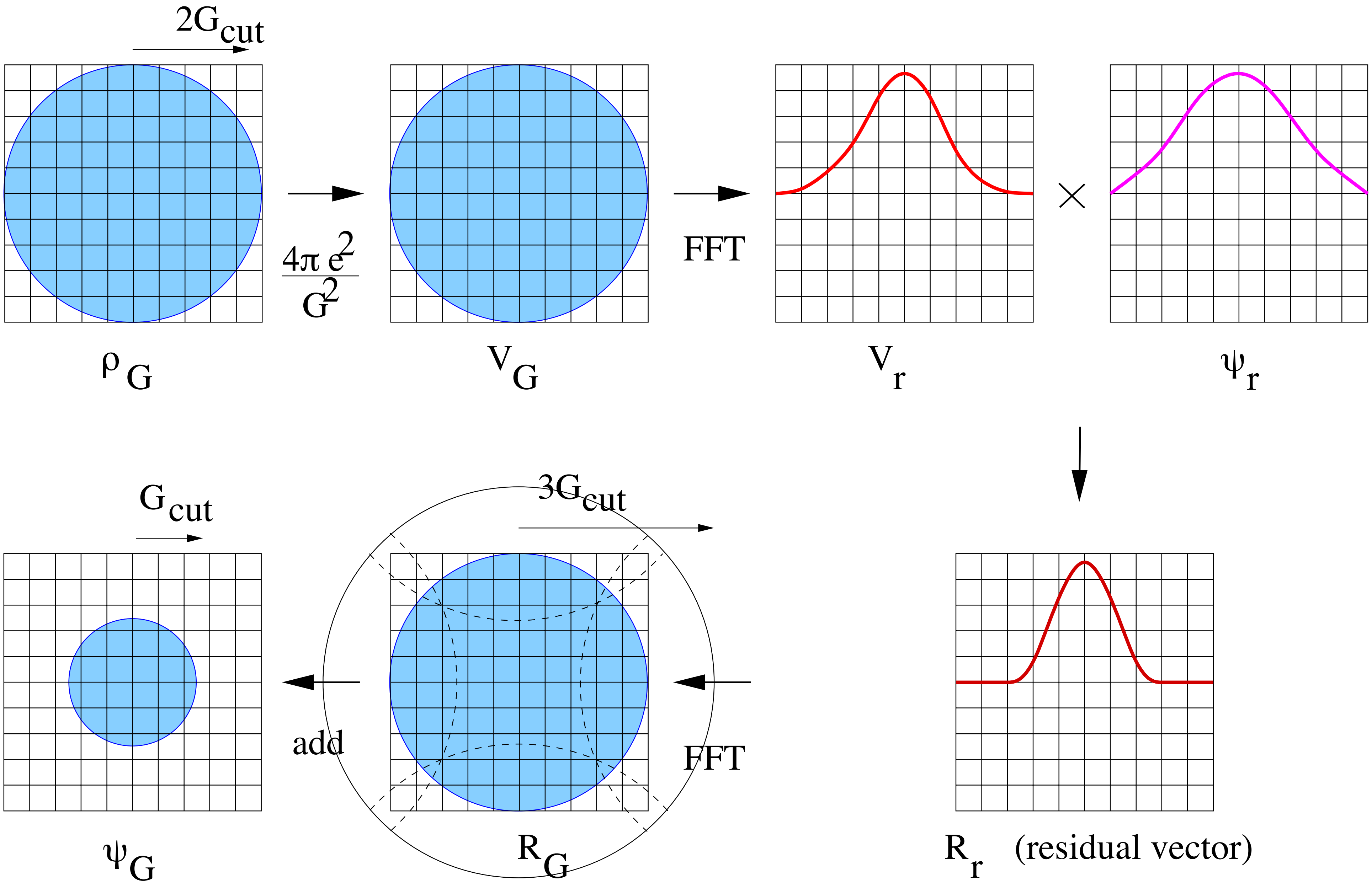
$$\langle\mathbf{G}+\mathbf{k}| -\frac{1}{2}\Delta|\psi_{n\mathbf{k}}\rangle = \frac{1}{2}|\mathbf{G}+\mathbf{k}|^2 C_{\mathbf{G}n\mathbf{k}} \qquad N_{\mathrm{NPLW}}$$

- Local potential: $V = V_{\mathrm{H}}[\rho] + V_{xc}[\rho] + V_{\mathrm{ext}}$
  - Exchange-correlation: easily obtained in real space $V_{\mathrm{xc},\mathbf{r}} = V_{\mathrm{xc}}[\rho_{\mathbf{r}}]$
  - FFT to reciprocal space $\{V_{\mathrm{xc},\mathbf{r}}\} \rightarrow \{V_{\mathrm{xc},\mathbf{G}}\}$
  - Hartree potential: solve Poisson eq. in reciprocal space $V_{\mathrm{H},\mathbf{G}} = \dfrac{4\pi}{|\mathbf{G}|^2}\rho_{\mathbf{G}}$
  - Add all contributions $V_{\mathbf{G}} = V_{\mathrm{H},\mathbf{G}} + V_{\mathrm{xc},\mathbf{G}} + V_{\mathrm{ext},\mathbf{G}}$
  - FFT to real space $\{V_{\mathbf{G}}\} \rightarrow \{V_{\mathbf{r}}\}$

  The action

$$\langle\mathbf{G}+\mathbf{k}|V|\psi_{n\mathbf{k}}\rangle = \frac{1}{N_{\mathrm{FFT}}}\sum_{\mathbf{r}} V_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}} \qquad N_{\mathrm{FFT}}\log N_{\mathrm{FFT}}$$

The action of the local potential



The Projector-Augmented-Wave method

The number of plane waves needed to describe

- tightly bound (spatially strongly localized) states,
- and rapid oscillations (nodal features) of the orbitals near the nucleus

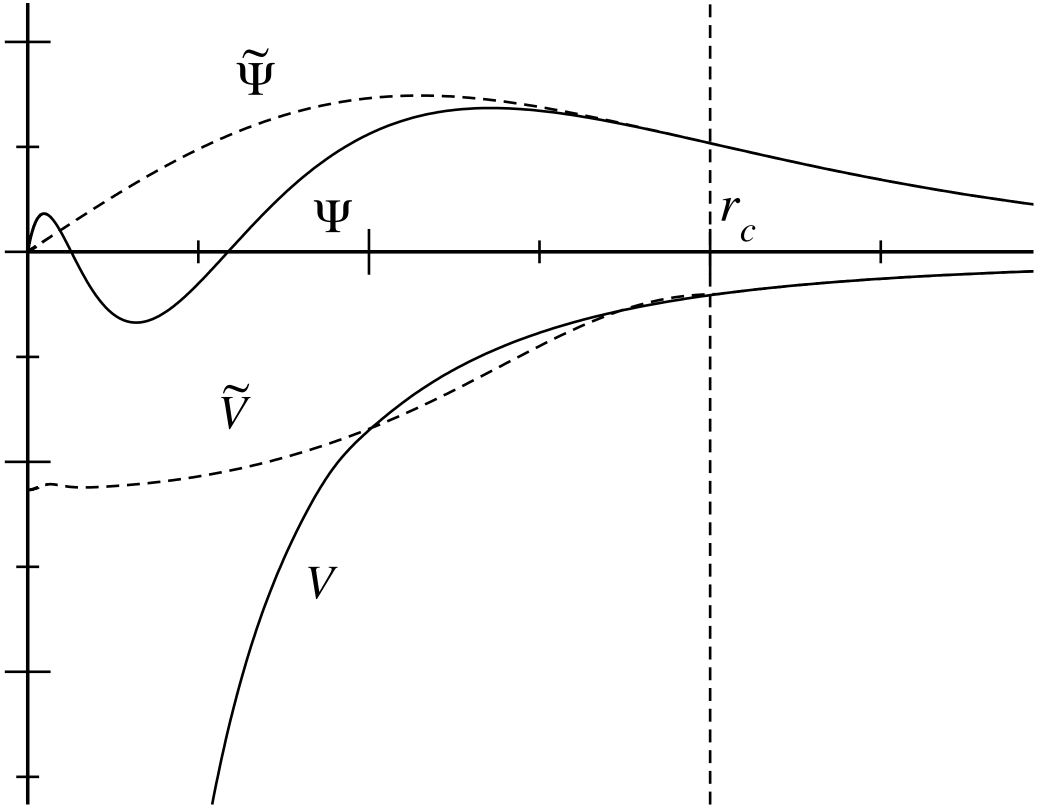
exceeds any practical limit, except maybe for Li and H.

The common solution:

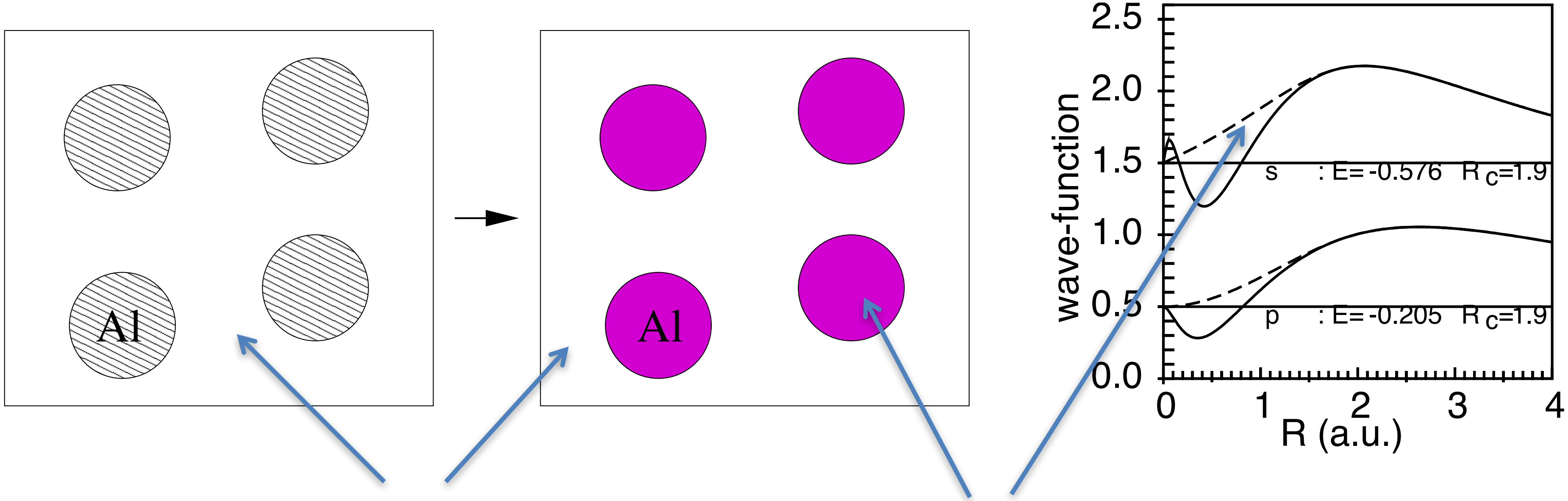
- Introduce the frozen core approximation:
  Core electrons are pre-calculated in an atomic environment and kept frozen in the course of the remaining calculations.

- Use of pseudopotentials instead of exact potentials:
  - Norm-conserving pseudopotentials
  - Ultra-soft pseudopotentials
  - The Projector-Augmented-Wave (PAW) method
    [P. E. Blöchl, Phys. Rev. **B** 50, 17953 (1994)]

Pseudopotentials: the general idea



Pseudopotentials: cont.



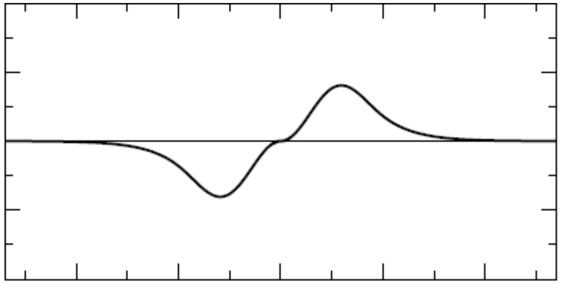
Exact potential (interstitial)

Pseudopotential

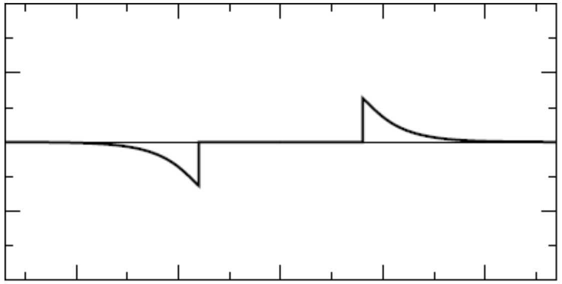
Al	effective Al atom	PAW Al atom
3p	2p	3p
3s	1s	3s
~~2p~~	2p and 1s are nodeless	nodal structure retained
~~2s~~		
~~12~~		

The PAW orbitals

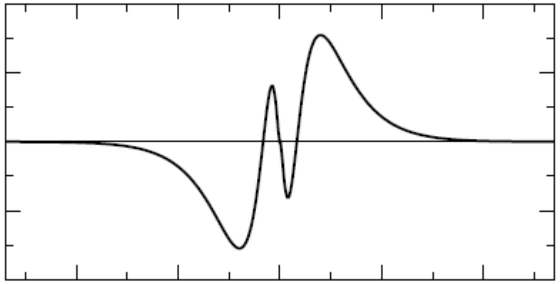
$$|\psi_n\rangle = |\widetilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\widetilde{\phi}_i\rangle)\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$$



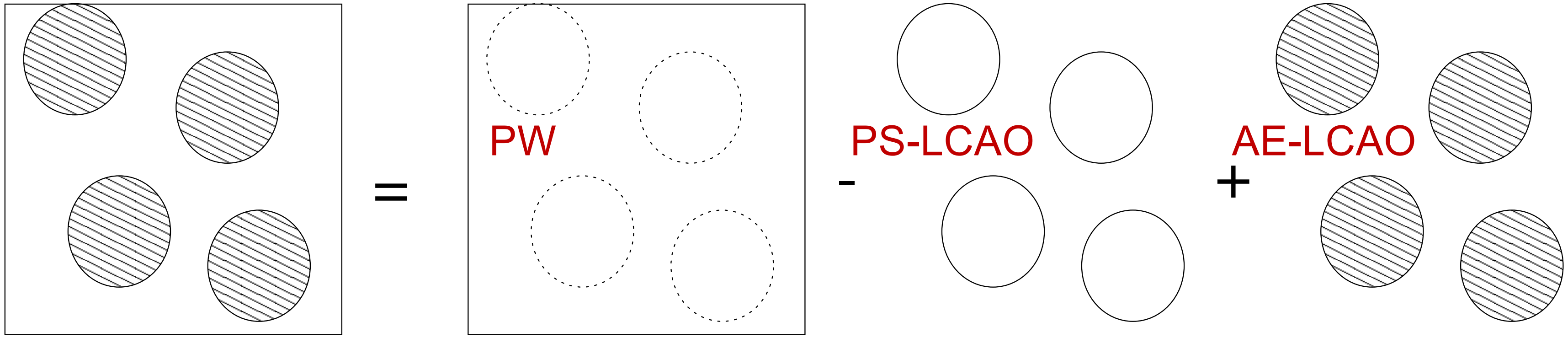
$|\widetilde{\psi}_n\rangle$



$|\widetilde{\psi}_n\rangle - \sum_i |\widetilde{\phi}_i\rangle\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$



$$|\widetilde{\psi}_n\rangle - \sum_i |\widetilde{\phi}_i\rangle\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$$
$$+ \sum_i |\phi_i\rangle\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$$



AE pseudo pseudo-onsite AE-onsite

The PAW orbitals (cont.)

$$|\psi_n\rangle = |\widetilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\widetilde{\phi}_i\rangle)\langle\widetilde{p}_i|\widetilde{\psi}_n\rangle$$

- $|\widetilde{\psi}_n\rangle$ is the pseudo (PS) orbital, expressed in a plane wave basis set
- $|\phi_i\rangle$, $|\tilde{\phi}_i\rangle$, and $|\tilde{p}_i\rangle$ are atom-centered localized functions
- The all-electron partial waves are solutions to the radial scalar relativistic non-spinpolarized Schrödinger equation:

$$(-\frac{1}{2}\Delta + v_{\text{eff}})|\phi_i\rangle = \epsilon_i|\phi_i\rangle$$

- A pseudization procedure yields:

$$|\phi_i\rangle \rightarrow |\widetilde{\phi}_i\rangle \qquad v_{\text{eff}} \rightarrow \widetilde{v}_{\text{eff}} \qquad \langle\widetilde{p}_i|\widetilde{\phi}_j\rangle = \delta_{ij}$$

The PAW orbitals (cont.)

- The pseudo partial waves obey:

$$\Big(-\frac{1}{2}\Delta + \widetilde{v}_{\mathrm{eff}} + \sum_{ij} |\widetilde{p}_i\rangle D_{ij} \langle \widetilde{p}_j|\Big)|\widetilde{\phi}_k\rangle = \epsilon_k \Big(1 + \sum_{ij} |\widetilde{p}_i\rangle Q_{ij} \langle \widetilde{p}_j|\Big)|\widetilde{\phi}_k\rangle$$

- with the so-called PAW strength parameters and augmentation charges:

$$D_{ij} = \langle \phi_i| - \frac{1}{2}\Delta + v_{\mathrm{eff}}|\phi_j\rangle - \langle \widetilde{\phi}_i| - \frac{1}{2}\Delta + \widetilde{v}_{\mathrm{eff}}|\widetilde{\phi}_j\rangle$$

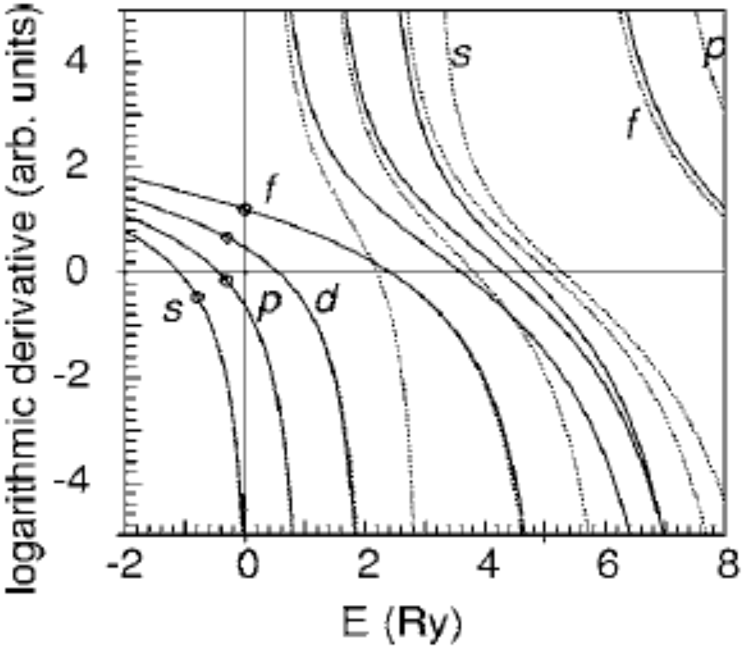
$$Q_{ij} = \langle \phi_i|\phi_j\rangle - \langle \widetilde{\phi}_i|\widetilde{\phi}_j\rangle$$

The all-electron and pseudo eigenvalue spectrum is identical!
All-electron scattering properties are reproduced over a wide energy-range.

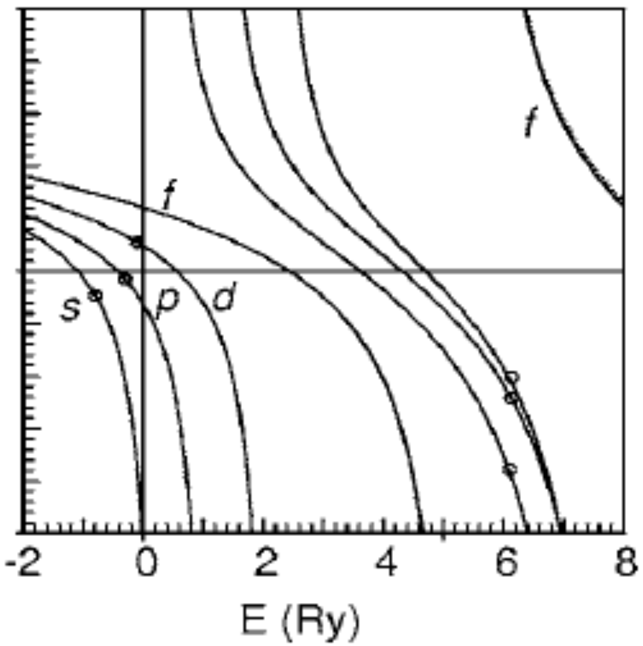
$$(-\frac{1}{2}\Delta + v_{\mathrm{eff}})|\phi_i\rangle = \epsilon_i|\phi_i\rangle$$

$$\Big(-\frac{1}{2}\Delta + \widetilde{v}_{\mathrm{eff}} + \sum_{ij}|\widetilde{p}_i\rangle D_{ij}\langle\widetilde{p}_j|\Big)|\widetilde{\phi}_k\rangle = \epsilon_k\Big(1 + \sum_{ij}|\widetilde{p}_i\rangle Q_{ij}\langle\widetilde{p}_j|\Big)|\widetilde{\phi}_k\rangle$$

Si: Troullier-Martins



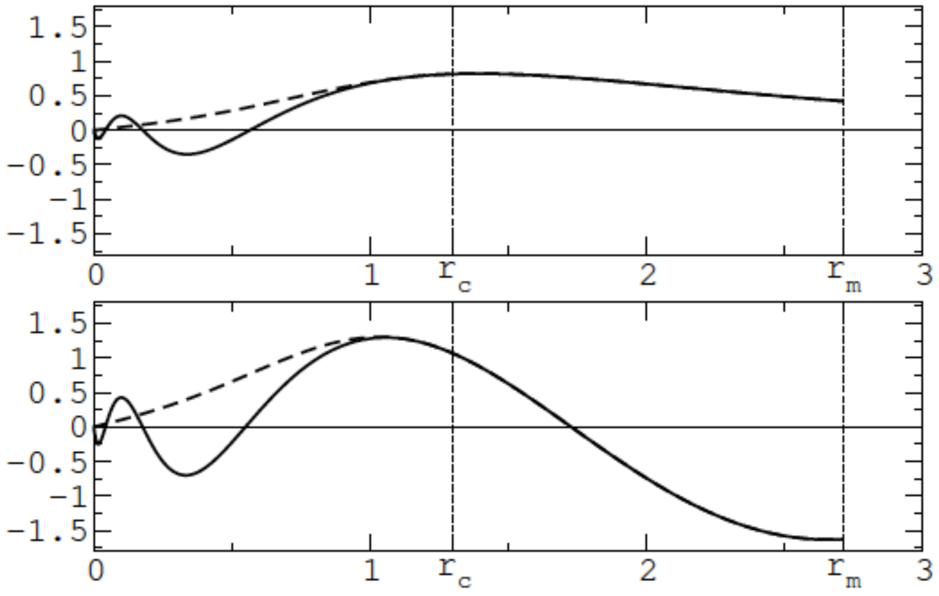
Si: PAW



$$\frac{\partial\widetilde{\phi}_l(r,\epsilon)}{\partial r}\frac{1}{\widetilde{\phi}_l(r,\epsilon)}\bigg|_{r=r_c} \approx \frac{\partial\phi_l(r,\epsilon)}{\partial r}\frac{1}{\phi_l(r,\epsilon)}\bigg|_{r=r_c}$$

- 1st *s*-channel in Mn: ε_1
  4s “bound” state

- 2nd *s*-channel in Mn: ε_2
  “non-bound” state



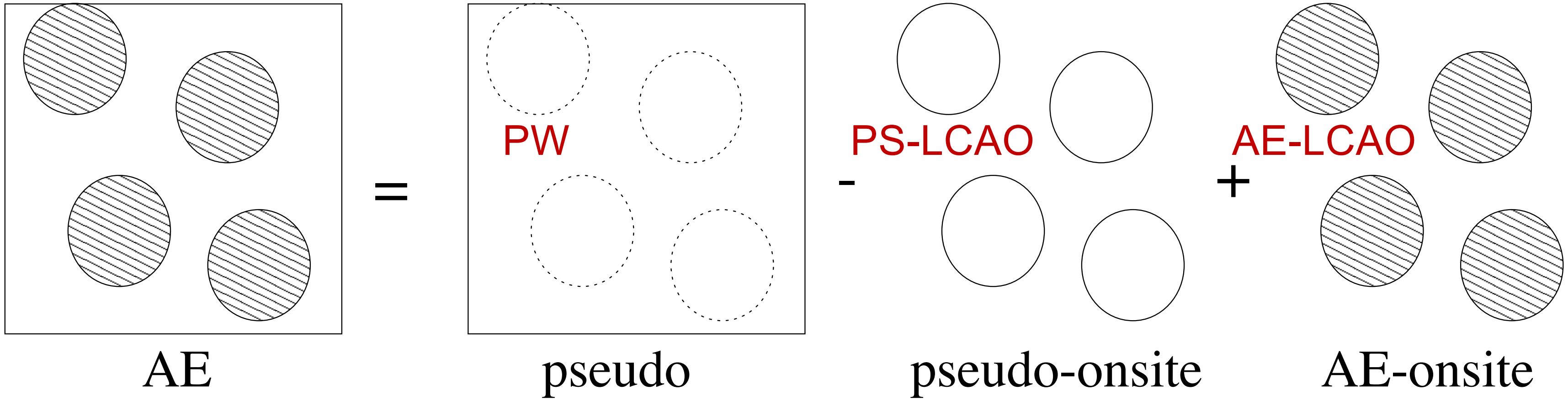
- And we use the frozen core approximation:

$$v_{\text{eff}}[\rho_v] = v_H[\rho_v] + v_H[\rho_{Zc}] + v_{xc}[\rho_v + \rho_c] \qquad \rho_v(\mathbf{r}) = \sum_i a_i |\phi_i(\mathbf{r})|^2$$

$$\widetilde{v}_{\text{eff}}[\widetilde{\rho}_v] = v_H[\widetilde{\rho}_v] + v_H[\widetilde{\rho}_{Zc}] + v_{xc}[\widetilde{\rho}_v + \widetilde{\rho}_c] \qquad \widetilde{\rho}_v(\mathbf{r}) = \sum_i a_i |\widetilde{\phi}_i(\mathbf{r})|^2$$

The PAW orbitals (cont.)

$$|\psi_n\rangle \qquad |\tilde{\psi}_n\rangle \qquad -\sum |\tilde{\phi}_{lm\epsilon}\rangle c_{lm\epsilon} \qquad +\sum |\phi_{lm\epsilon}\rangle c_{lm\epsilon}$$



where $c_{lm\epsilon} = \langle \tilde{p}_{lm\epsilon} | \tilde{\psi}_n \rangle$

This decomposition in three contributions can be achieved for all relevant quantities, *e.g.* orbitals, densities, and energies.

The kinetic energy

For instance the kinetic energy:

$$E_{\mathrm{kin}} = \sum_n f_n \langle \psi_n | -\frac{1}{2}\Delta | \psi_n \rangle$$

Inserting the PAW transformation (where *i=lmε*):

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle \tilde{p}_i | \tilde{\psi}_n \rangle$$

and assuming completeness of the one-center basis, we have

$$E_{\mathrm{kin}} = \tilde{E} - \tilde{E}^1 + E^1$$

$$\underbrace{\sum_n f_n \langle \tilde{\psi}_n | -\frac{1}{2}\Delta | \tilde{\psi}_n \rangle}_{\tilde{E}} - \underbrace{\sum_{\mathrm{site}} \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2}\Delta | \tilde{\phi}_j \rangle}_{\tilde{E}^1} + \underbrace{\sum_{\mathrm{site}} \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2}\Delta | \phi_j \rangle}_{E^1}$$

Where

$$\rho_{ij} = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle$$

are the one-center occupancies, or on-site density matrix.

Local operators

To any (semi)-local operator *A*, that acts on the true all-electron orbital, the PAW method associates a pseudo operator:

$$\tilde{A} = A + \sum_{ij} |\tilde{p}_i\rangle \left(\langle\phi_i|A|\phi_j\rangle - \langle\tilde{\phi}_i|A|\tilde{\phi}_j\rangle \right) \langle\tilde{p}_j|$$

that acts on the pseudo-orbital, such that

$$\langle\psi|A|\psi\rangle = \langle\widetilde{\psi}|\tilde{A}|\widetilde{\psi}\rangle$$

For instance the PS operator associated with the density operator ($|\mathbf{r}\rangle\langle\mathbf{r}|$)

$$|\mathbf{r}\rangle\langle\mathbf{r}| + \sum_{ij} |\tilde{p}_i\rangle \left(\langle\phi_i|\mathbf{r}\rangle\langle\mathbf{r}|\phi_j\rangle - \langle\tilde{\phi}_i|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{\phi}_j\rangle \right) \langle\tilde{p}_j|$$

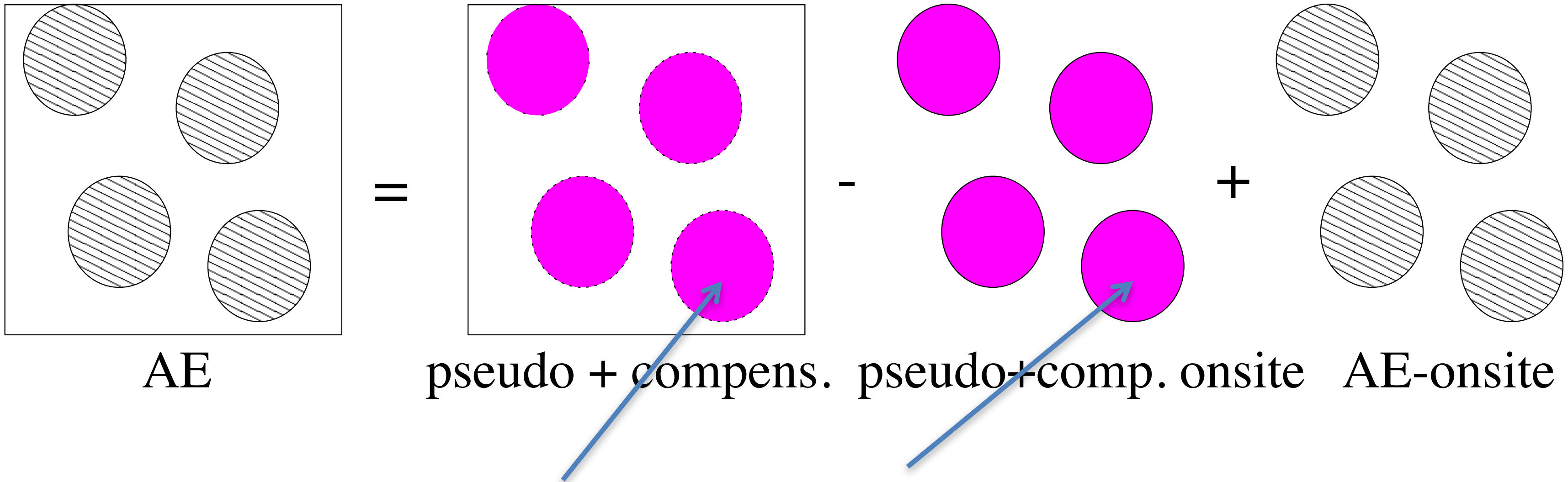
and the density

$$\begin{aligned}\langle\psi|\mathbf{r}\rangle\langle\mathbf{r}|\psi\rangle &= \langle\widetilde{\psi}|\mathbf{r}\rangle\langle\mathbf{r}|\widetilde{\psi}\rangle + \sum_{ij} \langle\widetilde{\psi}|\tilde{p}_i\rangle \left(\langle\phi_i|\mathbf{r}\rangle\langle\mathbf{r}|\phi_j\rangle - \langle\tilde{\phi}_i|\mathbf{r}\rangle\langle\mathbf{r}|\tilde{\phi}_j\rangle \right) \langle\tilde{p}_j|\widetilde{\psi}\rangle \\ &= \widetilde{\rho}(\mathbf{r}) - \widetilde{\rho}^1(\mathbf{r}) + \rho^1(\mathbf{r})\end{aligned}$$

Non-local operators are more complicated.

The Hartree energy

- The PS orbitals do not have the same norm as the AE orbitals inside of the PAW spheres.
- To correctly describe the long-range electrostatic interactions between the PAW spheres, a soft *compensation* charge is introduced in the spheres (like in the FLAPW method):



$$E_H[\tilde{\rho}+\hat{\rho}] - \sum_{\text{sites}} E_H[\tilde{\rho}^1+\hat{\rho}^1] + \sum_{\text{sites}} E_H[\rho^1]$$

- This way the Hartree energy (a non-local operator!) decomposes in the same manner as a (semi)-local operator:

$$E_H = \tilde{E}_H - \tilde{E}_H^1 + E_H^1$$

The PAW total energy

The same three-way decomposition holds for the total energy

$$E = \tilde{E} - \tilde{E}^1 + E^1$$

where

$$\begin{aligned}
\tilde{E} =& \sum_n f_n \langle \tilde{\psi}_n | -\frac{1}{2}\Delta | \tilde{\psi}_n \rangle + E_{xc}[\tilde{\rho} + \hat{\rho} + \tilde{\rho}_c] + \\
& E_H[\tilde{\rho} + \hat{\rho}] + \int v_H[\tilde{\rho}_{Zc}] \left(\tilde{\rho}(\mathbf{r}) + \hat{\rho}(\mathbf{r}) \right) \, d^3\mathbf{r} + \ U(\mathbf{R}, Z_{\text{ion}}) \\
\tilde{E}^1 =& \sum_{\text{sites}} \Bigg\{ \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2}\Delta | \tilde{\phi}_j \rangle + \overline{E_{xc}[\tilde{\rho}^1 + \hat{\rho} + \tilde{\rho}_c]} + \\
& \overline{E_H[\tilde{\rho}^1 + \hat{\rho}]} + \int_{\Omega_r} v_H[\tilde{\rho}_{Zc}] \left(\tilde{\rho}^1(\mathbf{r}) + \hat{\rho}(\mathbf{r}) \right) \, d^3\mathbf{r} \Bigg\} \\
E^1 =& \sum_{\text{sites}} \Bigg\{ \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2}\Delta | \phi_j \rangle + \overline{E_{xc}[\rho^1 + \rho_c]} + \\
& \overline{E_H[\rho^1]} + \int_{\Omega_r} v_H[\rho_{Zc}] \rho^1(\mathbf{r}) \, d^3\mathbf{r} \Bigg\}
\end{aligned}$$

The PAW total energy (cont.)

- $\tilde{E}$ is evaluated on a regular grid:

  The Kohn-Sham functional evaluated in a plane wave basis set

  with additional compensation charge to account for the incorrect norm of the PS-orbitals and to correctly describe long-range electrostatics

$\widetilde{\rho} = \sum_n f_n \widetilde{\psi}_n \widetilde{\psi}_n^*$ PS charge density

$\hat{\rho}$ Compensation charges

- $\tilde{E}^1$ and E^1 are evaluated on atom-centered radial logarithmic grids:

  The Kohn-Sham energies evaluated using localized basis sets

  These terms correct for the difference in the shape of the all-electron and pseudo orbitals:

) AE nodal features near the core

) Orthogonality between core and valence states

The essence of the PAW method: there are no cross-terms between quantities on the regular grid (PW part) and the quantities on the radial grids (LCAO part)!

The PAW total energy (cont.)

The PS orbitals (plane waves!) are the self-consistent solutions of

$$\Big(-\frac{1}{2}\Delta+\widetilde{V}_{\text{eff}}+\sum_{ij}|\widetilde{p}_i\rangle(D_{ij}+...)\langle\widetilde{p}_j|\Big)|\widetilde{\psi}_n\rangle=\epsilon_n\Big(1+\sum_{ij}|\widetilde{p}_i\rangle Q_{ij}\langle\widetilde{p}_j|\Big)|\widetilde{\psi}_n\rangle$$

where

$$D_{ij}=\langle\phi_i|-\frac{1}{2}\Delta+v^1_{\text{eff}}[\rho^1_v]|\phi_j\rangle-\langle\widetilde{\phi}_i|-\frac{1}{2}\Delta+\widetilde{v}^1_{\text{eff}}[\widetilde{\rho}^1_v]|\widetilde{\phi}_j\rangle$$

$$Q_{ij}=\langle\phi_i|\phi_j\rangle-\langle\widetilde{\phi}_i|\widetilde{\phi}_j\rangle$$

and

$$\widetilde{\rho}^1_v(\mathbf{r})=\sum_{ij}\rho_{ij}\langle\widetilde{\phi}_i|\mathbf{r}\rangle\langle\mathbf{r}|\widetilde{\phi}_j\rangle \qquad \rho^1_v(\mathbf{r})=\sum_{ij}\rho_{ij}\langle\phi_i|\mathbf{r}\rangle\langle\mathbf{r}|\phi_j\rangle$$

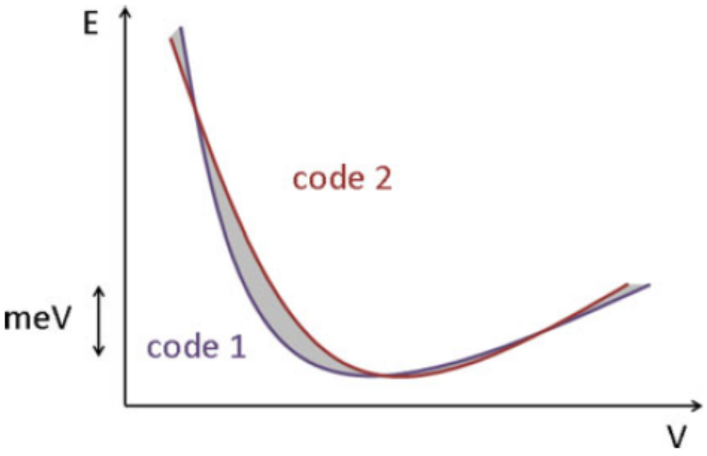
with

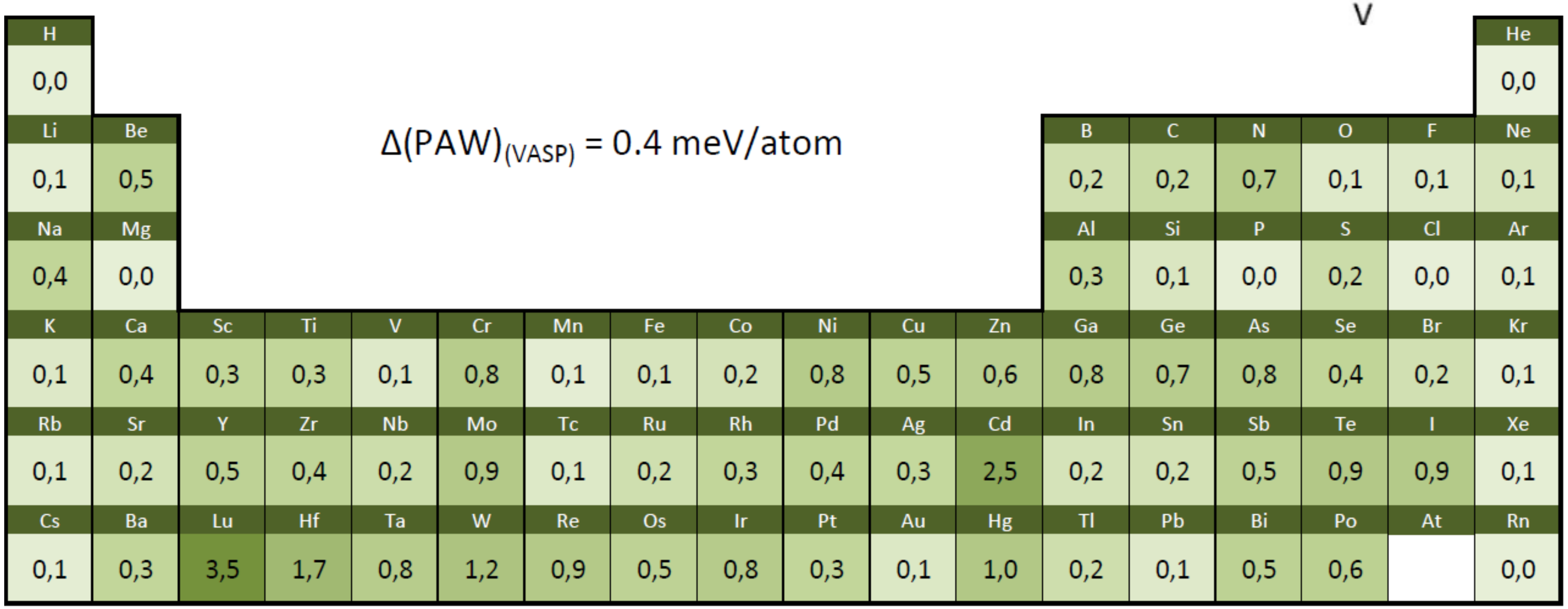
$$\rho_{ij}=\sum_n f_n\langle\widetilde{\psi}_n|\widetilde{p}_i\rangle\langle\widetilde{p}_j|\widetilde{\psi}_n\rangle$$

- The PS orbitals are the variational quantity of the PAW method!
- If the partial waves constitute a complete (enough) basis inside the PAW spheres, The all-electron orbitals will remain orthogonal to the core states.

Accuracy of the PAW method

$$\Delta = \left\langle \sqrt{\frac{\int \Delta E^2(V)\mathrm{d}V}{\Delta V}} \right\rangle$$





$\Delta(\mathrm{PAW})_{(\mathrm{VASP})}$ = 0.4 meV/atom

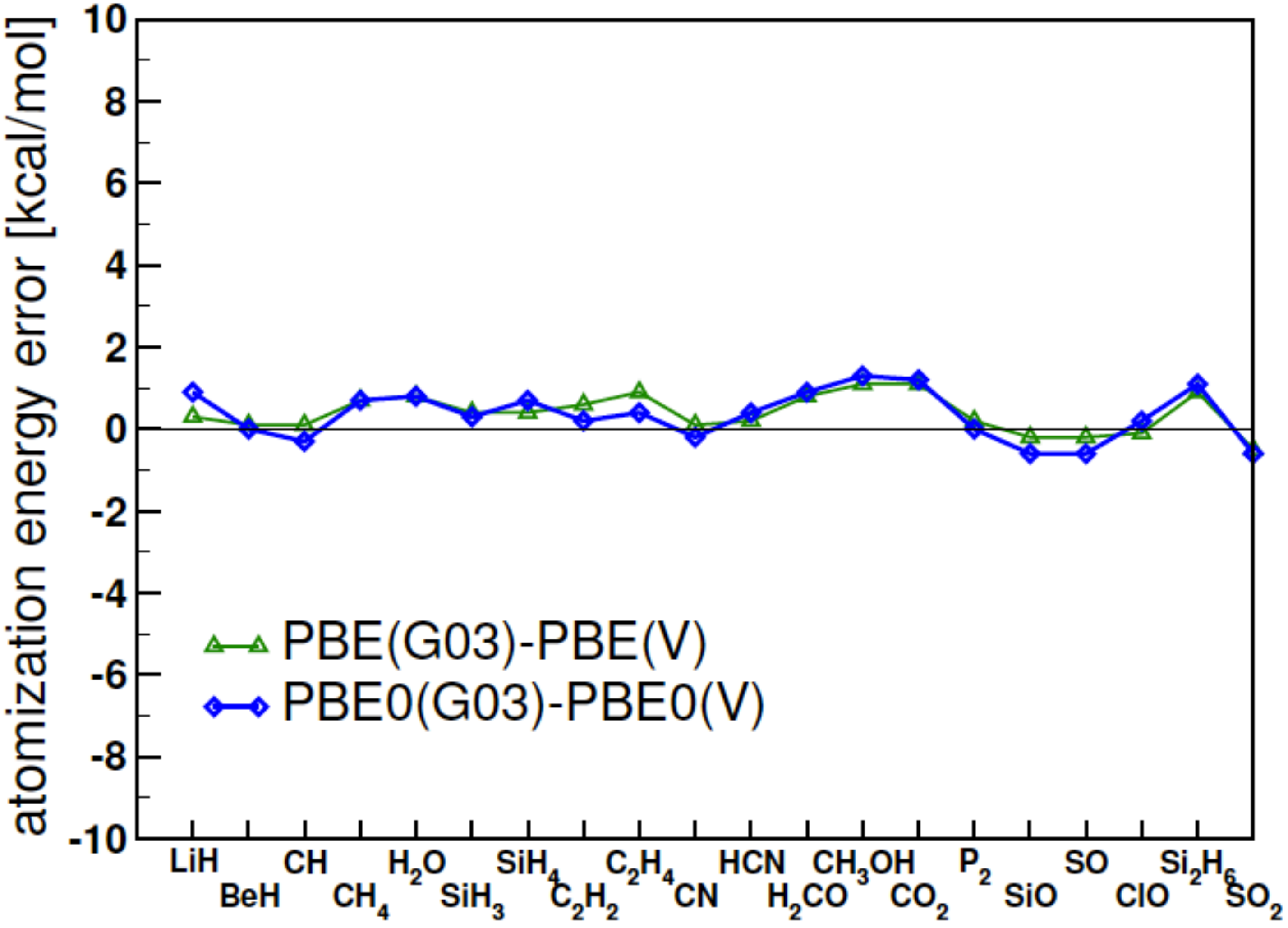
H																	He
0,0																	0,0
Li	Be											B	C	N	O	F	Ne
0,1	0,5											0,2	0,2	0,7	0,1	0,1	0,1
Na	Mg											Al	Si	P	S	Cl	Ar
0,4	0,0											0,3	0,1	0,0	0,2	0,0	0,1
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0,1	0,4	0,3	0,3	0,1	0,8	0,1	0,1	0,2	0,8	0,5	0,6	0,8	0,7	0,8	0,4	0,2	0,1
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0,1	0,2	0,5	0,4	0,2	0,9	0,1	0,2	0,3	0,4	0,3	2,5	0,2	0,2	0,5	0,9	0,9	0,1
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0,1	0,3	3,5	1,7	0,8	1,2	0,9	0,5	0,8	0,3	0,1	1,0	0,2	0,1	0,5	0,6		0,0

Δ-evaluation (PAW vs. FLAPW)

K. Lejaeghere *et al.*, Critical Reviews in Solid State and Materials Sciences 39,1 (2014)

Accuracy of the PAW method (cont.)

Subset of the G2-1 testset of small molecules: deviation of PAW w.r.t. GTO (in kcal/mol)



$|\Delta E_{\mathrm{AE}}| < 1$ kcal/mol.

Electronic minimization:
Reaching the groundstate

Direct minimization of the DFT functional (*e.g.* Car-Parrinello): start with a set of trial orbitals (random numbers) and minimize the energy by propagating the orbitals along the gradient:

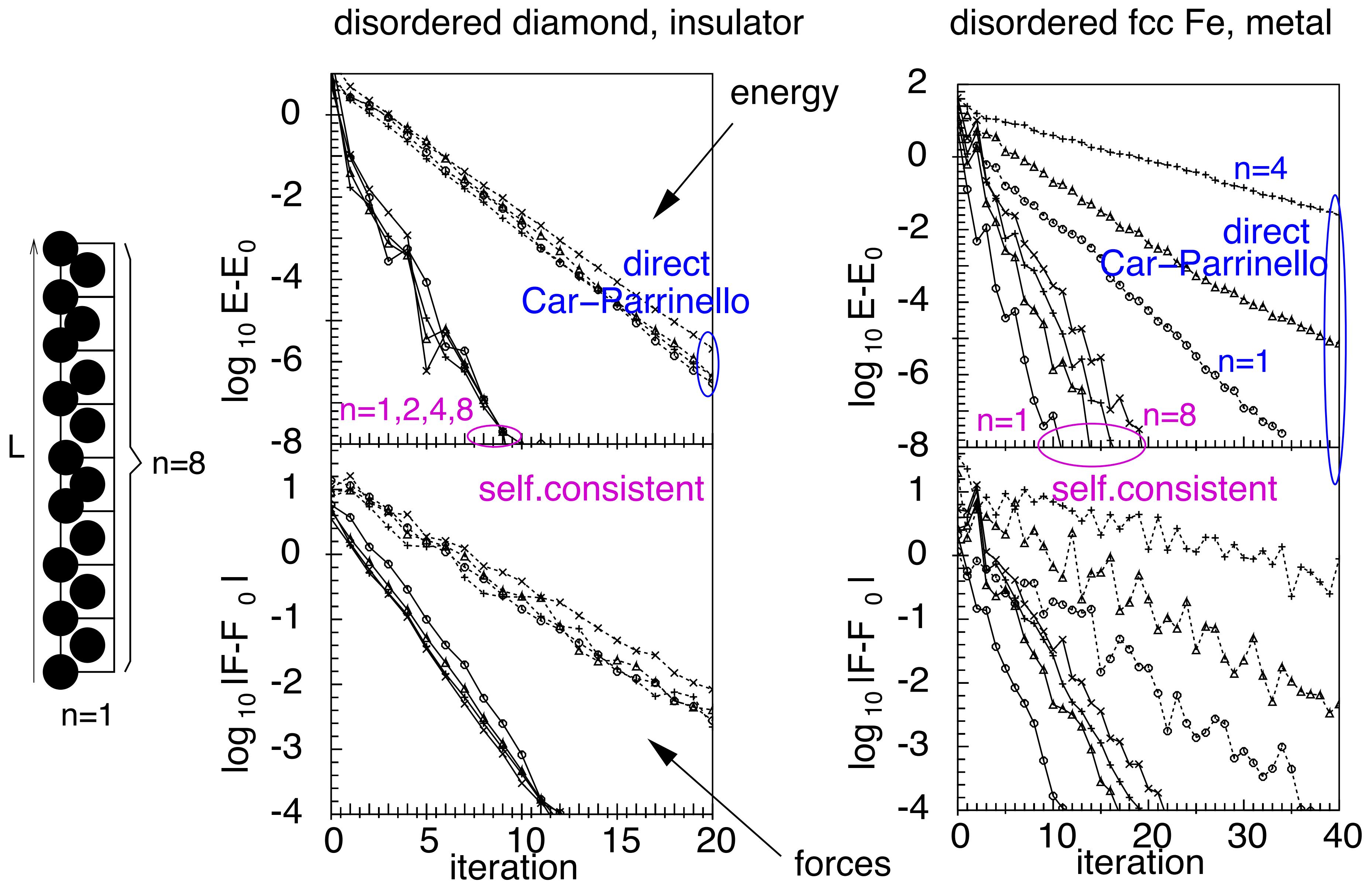
$$\text{Gradient:} \quad F_n(\mathbf{r}) = \left(-\frac{\hbar^2}{2m_e}\nabla^2 + V^{\text{eff}}(\mathbf{r}, \{\psi_n(\mathbf{r}')\}) - \epsilon_n \right) \psi_n(\mathbf{r})$$

The Self-Consistency-Cycle: start with a trial density, construct the corresponding Hamiltonian. Solve it to obtain a set of orbitals:

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + V^{\text{eff}}(\mathbf{r}, \{\rho(\mathbf{r}')\}) \right) \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r}) \qquad n = 1, ..., N_e/2$$

These orbitals define a new density, that defines a new Hamiltonian, …
iterate to self-consistency

Direct minimization vs. SCC



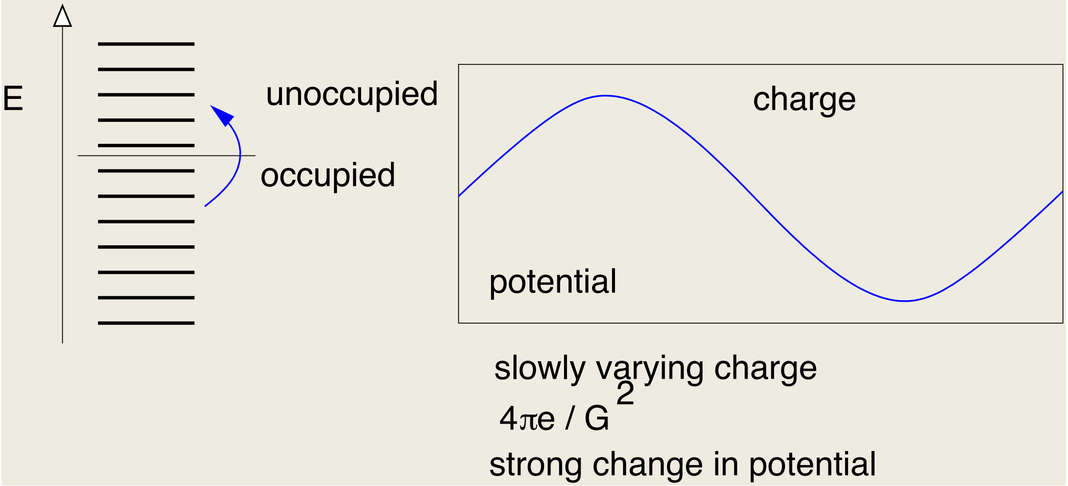
Direct minimization and charge sloshing

The gradient of the total energy with respect to an orbital is given by:

$$|g_n\rangle = f_n\Big(1 - \sum_m |\psi_m\rangle\langle\psi_m|\Big)\hat{H}|\psi_n\rangle + \sum_m \frac{1}{2}\mathbf{H}_{nm}(f_n - f_m)|\psi_m\rangle$$

where

$$\mathbf{H}_{nm} = \langle\psi_m|\hat{H}|\psi_n\rangle$$



Consider two states

$$\psi_n = e^{i(\mathbf{k}_F - \delta\mathbf{k})\mathbf{r}} \quad \psi_m = e^{i(\mathbf{k}_F + \delta\mathbf{k})\mathbf{r}}$$

and a small sub-space rotation
(2nd comp. of the gradient):

$$\psi'_n = \psi_n + \Delta s\psi_m \quad \psi'_m = \psi_m - \Delta s\psi_n$$

This leads to a long-wavelength change in the density and a very strong change in the electrostatic potential (charge sloshing):

$$\delta\rho(\mathbf{r}) = 2\Delta s \mathrm{Re}\, e^{i2\delta\mathbf{k}\cdot\mathbf{r}} \qquad \delta V_{\mathrm{H}}(\mathbf{r}) = \frac{2\Delta s\, 4\pi e^2}{|2\delta\mathbf{k}|^2}\mathrm{Re}\, e^{i2\delta\mathbf{k}\cdot\mathbf{r}}$$

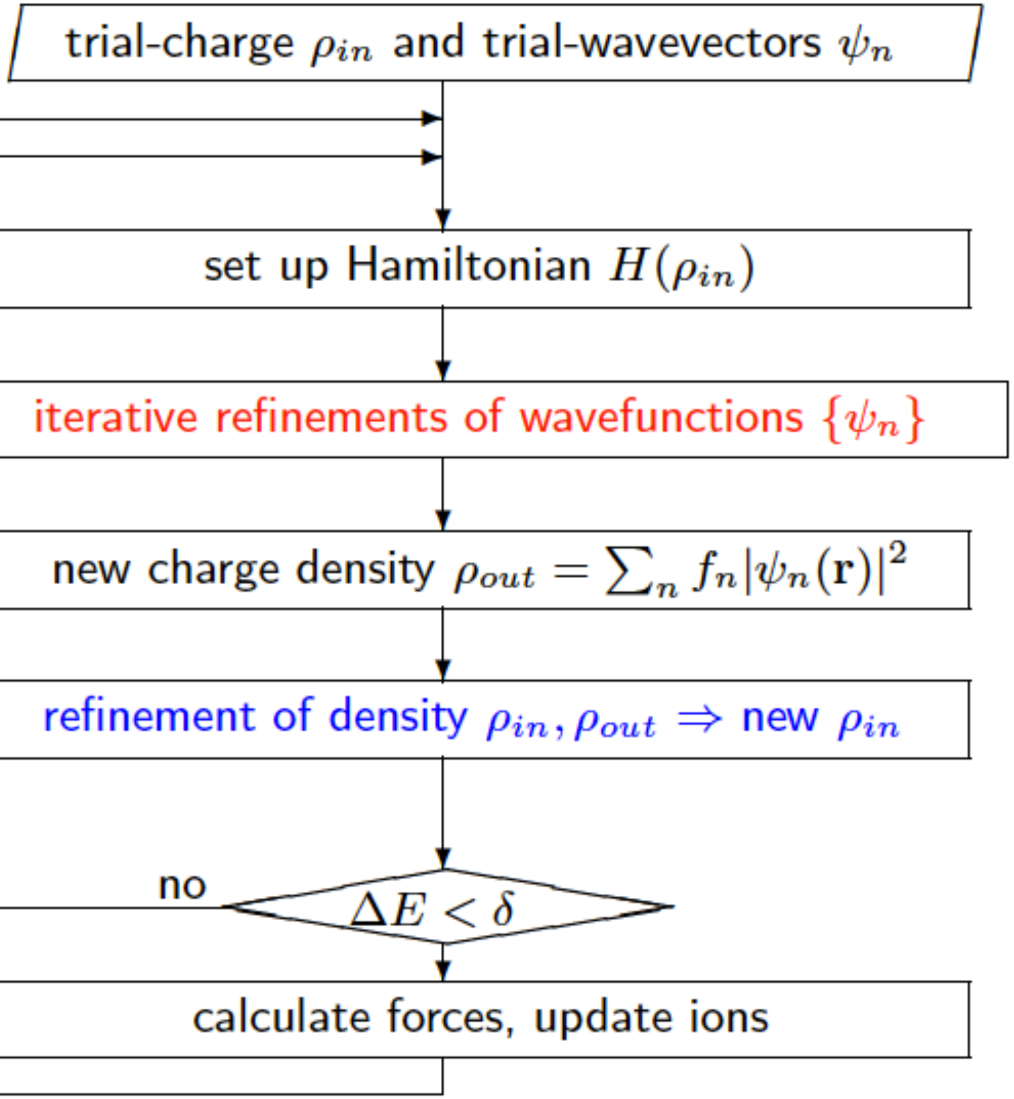
Stable step size Δs (for a simulation box with largest dimension L):

$$|\delta\mathbf{k}| \propto 1/L \longrightarrow \delta V_{\mathrm{H}} \propto L^2 \longrightarrow \Delta s \propto 1/L^2$$

The Self-Consistency-Cycle (cont.)

Two sub-problems:

- Optimization of $\{\psi_n\}$
  Iterative Diagonalization
  e.g. RMM-DIIS or
  Blocked Davidson
- Construction of ρ_{in}
  Density Mixing
  e.g. Broyden mixer



trial-charge ρ_{in} and trial-wavevectors ψ_n

set up Hamiltonian $H(\rho_{in})$

iterative refinements of wavefunctions $\{\psi_n\}$

new charge density $\rho_{out} = \sum_n f_n |\psi_n(\mathbf{r})|^2$

refinement of density $\rho_{in}, \rho_{out} \Rightarrow$ new ρ_{in}

$\Delta E < \delta$

no

calculate forces, update ions

The self-Consistency-Cycle

A naïve algorithm: express the Hamilton matrix in a plane wave basis and diagonalize it:

$$\mathbf{H} = \langle \mathbf{G} | \hat{H}[\rho] | \mathbf{G}' \rangle \rightarrow \text{diagonalize } \mathbf{H} \rightarrow \{\psi_i, \epsilon_i\} \;\; i = 1, .., N_{\mathrm{FFT}}$$

Self-consistency-cycle:

$$\rho_0 \rightarrow \mathbf{H}_0 \rightarrow \rho' \rightarrow \rho_1 = f(\rho_0, \rho') \rightarrow \mathbf{H}_1 \rightarrow ...$$

Iterate until: $\rho = \rho'$

BUT: we do not need N_{FFT} eigenvectors of the Hamiltonian (at a cost of $O(N_{FFT}^3)$). Actually we only the N_b lowest eigenstates of **H**, where N_b is of the order of the number of electrons per unit cell ($N_b << N_{FFT}$).

Solution: use iterative matrix diagonalization techniques to find the N_b lowest Eigenvector of the Hamiltonian: RMM-DIIS, blocked-Davidson, etc.

Key ingredients: Subspace diagonalization and the Residual

- Rayleigh-Ritz: diagonalization of the N_b x N_b subspace

$$\sum_m \bar{H}_{nm} B_{mk} = \sum_m \epsilon_k^{\mathrm{app}} \bar{S}_{nm} B_{mk}$$

with

$$\bar{H}_{nm} = \langle \psi_n | \hat{H} | \psi_m \rangle \qquad \bar{S}_{nm} = \langle \psi_n | \hat{S} | \psi_m \rangle$$

yields N_b eigenvectors $|\bar{\psi}_k\rangle = \sum_m B_{mk} |\psi_m\rangle$ with eigenvalues $\varepsilon_{\mathrm{app}}$.

These eigenstates are the best approximation to the exact N_b lowest eigenstates of **H** within the subspace spanned by the current orbitals.

- The Residual:

$$|R(\psi_n)\rangle = (\hat{H} - \epsilon_{\mathrm{app}} \hat{S}) |\psi_n\rangle \qquad \epsilon_{\mathrm{app}} = \frac{\langle \psi_n | \hat{H} | \psi_n \rangle}{\langle \psi_n | \hat{S} | \psi_n \rangle}$$

(its norm is measure for the error in the eigenvector)

Blocked-Davidson

- Take a subset of all bands: $\{\psi_n | n = 1, .., N\} \Rightarrow \{\psi_k^1 | k = 1, .., n_1\}$
  - Extend this subset by adding the (preconditioned) residual vectors to the presently considered subspace:

$$\{\psi_k^1 / g_k^1 = \mathbf{K}(\mathbf{H} - \epsilon_{\rm app}\mathbf{S})\psi_k^1 | k = 1, .., n_1\}$$

  - Rayleigh-Ritz optimization ("sub-space rotation") in the 2n$_1$ dimensional subspace to determine the n$_1$ lowest eigenvectors:

$$\mathrm{diag}\{\psi_k^1 / g_k^1\} \longrightarrow \{\psi_k^2 | k = 1, .., n_1\}$$

  - Extend subspace with the residuals of $\{\psi_k^2\}$

$$\{\psi_k^1 / g_k^1 / g_k^2 = \mathbf{K}(\mathbf{H} - \epsilon_{\rm app}\mathbf{S})\psi_k^2 | k = 1, .., n_1\}$$

  - Rayleigh-Ritz optimization $\Rightarrow \{\psi_k^3 | k = 1, .., n_1\}$
  - Etc …
  - The optimized set replaces the original subset:

$$\{\psi_k^m | k = 1, .., n_1\} \longrightarrow \{\psi_n | n = 1, .., n_1\}$$

- Continue with next subset: $\{\psi_k^1 | k = n_1 + 1, .., n_2\}$, etc, …

After treating all bands: Rayleigh-Ritz optimization of $\{\psi_n | n = 1, .., N\}$

Charge density mixing

We want to minimize residual vector

$$R[\rho_{\rm in}] = \rho_{\rm out}[\rho_{\rm in}] - \rho_{\rm in}$$

with

$$\rho_{\rm out}(\vec{r}) = \sum_{\rm occupied} w_k f_{nk} |\psi_{nk}(\vec{r})|^2$$

Linearization of the residual around the self-consistent density $\rho_{\rm sc}$
(linear response theory):

$$R[\rho] = -\mathbf{J}(\rho - \rho_{\rm sc}) \qquad \mathbf{J} = \mathbf{1} - \chi \underbrace{\mathbf{U}}_{\frac{\mathbf{4\pi e^2}}{\mathbf{q^2}}}$$

where **J** is the charge dielectric function.

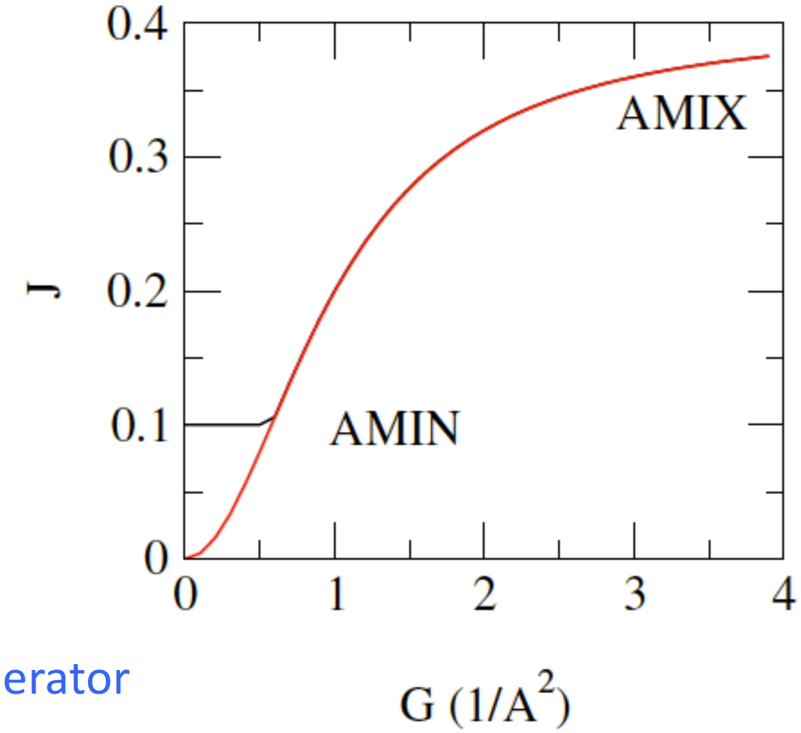
Provided we have a good approximation for the charge dielectric function, minimization of the residual is trivial:

$$R[\rho_{\rm in}] = \rho_{\rm out}[\rho_{\rm in}] - \rho_{\rm in} = -\mathbf{J}(\rho_{\rm in} - \rho_{\rm sc}) \longrightarrow \rho_{\rm sc} = \rho_{in} + \mathbf{J}^{-1} R[\rho_{\rm in}]$$

The charge dielectric function

- Use a model dielectric function that is a good initial approximation for most systems

$$\mathbf{J}^{-1} \approx \mathbf{G}_q^1 = \max(\frac{q^2\texttt{AMIX}}{q^2+\texttt{BMIX}}, \texttt{AMIN})$$



- This is combined with a convergence accelerator

  The initial dielectric function is improved using the information accumulated in each electronic mixing step.

The End

Thank you!