Pseudopotentials (Part I):

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Overview

- the very basics

    - periodic boundary conditions

    - the Bloch theorem

    - plane waves

    - pseudopotentials

- determining the electronic groundstate

- effective forces on the ions

general road-map to the things you will hear in more detail later

Periodic boundary conditions

- as almost all plane wave codes VASP uses always periodic boundary conditions

- the interaction between repeated images must be handled by a sufficiently large vacuum region

- sounds disastrous for the treatment of molecules
  but large molecules can be handled with a comparable or even better performance than by e.g. Gaussian
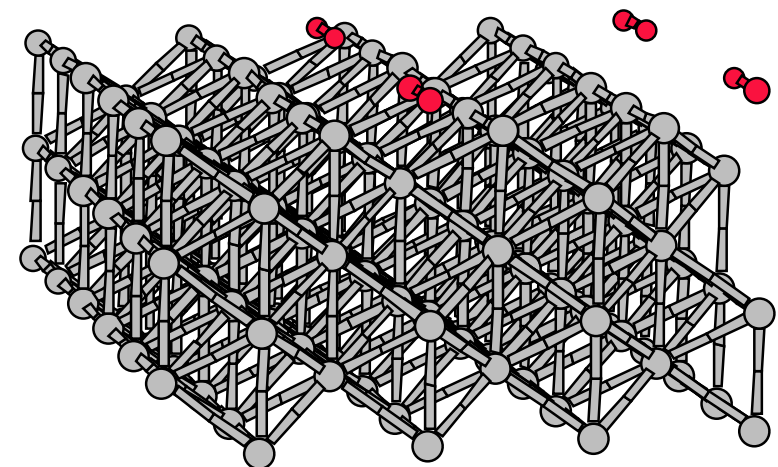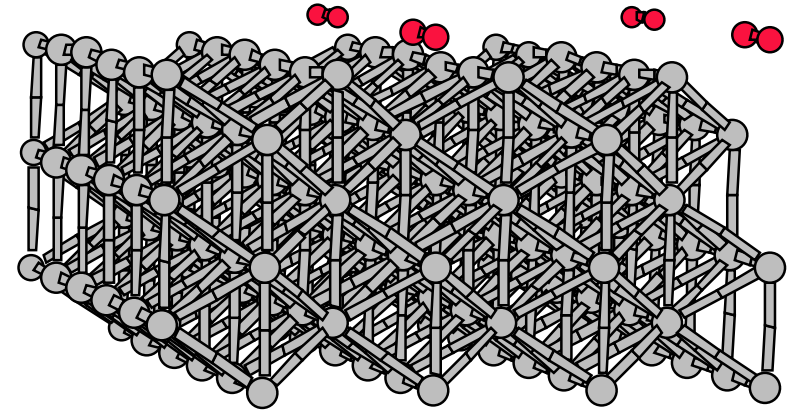
The Bloch theorem

- the translational invariance implies that a good quantum number exists, which is usually termed $\mathbf{k}$

  $\mathbf{k}$ corresponds to a vector in the Brillouin zone

- all electronic states can be indexed by this quantum number

$$\Psi_{\mathbf{k}}$$

- in a one-electron theory, one can introduce a second index, corresponding to the one electron band n

$$\psi_{n,\mathbf{k}}(\mathbf{r})$$

  the Bloch theorem implies that the (single electron) wavefunctions observe the equations

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

  where τ is any translational vector leaving the Hamiltonian invariant

The DFT Hamiltonian

- the charge density is determined by integrating over the entire Brillouin zone and summing over the filled bands

$$\rho_e(\mathbf{r}) = \sum_n^\infty \int d^3\mathbf{k} f_{n,\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r}) \psi_{n,\mathbf{k}}^*(\mathbf{r})$$

where the charge density is cell periodic (can be seen by inserting the Bloch theorem) and $f_{n,\mathbf{k}} = (1 + \exp(\beta(\varepsilon_{n,\mathbf{k}} - \varepsilon_{\text{Fermi}})))^{-1}$ are the Fermi-weights

- the KS-DFT equations (Schrödinger like) are given by

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V^{\text{eff}}(\mathbf{r}, \{\rho_\mathbf{e}(\mathbf{r}')\}) \right) \psi_{n,\mathbf{k}}(\mathbf{r}) = \varepsilon_{n,\mathbf{k}} \psi_{n,\mathbf{k}}(\mathbf{r})$$

$$V^{\text{eff}}(\mathbf{r}, \{\rho_\mathbf{e}(\mathbf{r}')\}) = \mathbf{e^2} \int \frac{\rho_\mathbf{e}(\mathbf{r}') + \rho_{\text{ion}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathbf{d^3r'} + \mathbf{V}_{\text{xc}}(\rho_\mathbf{e}(\mathbf{r}))$$

ρ_{ion} is the ionic charge distribution

Plane waves

- introduce the cell periodic part $u_{n,\mathbf{k}}$ of the wavefunctions

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

  $u_{n,\mathbf{k}}(\mathbf{r})$ is cell periodic (insert into Bloch theorem)

- all cell periodic functions are now written as a sum of plane waves

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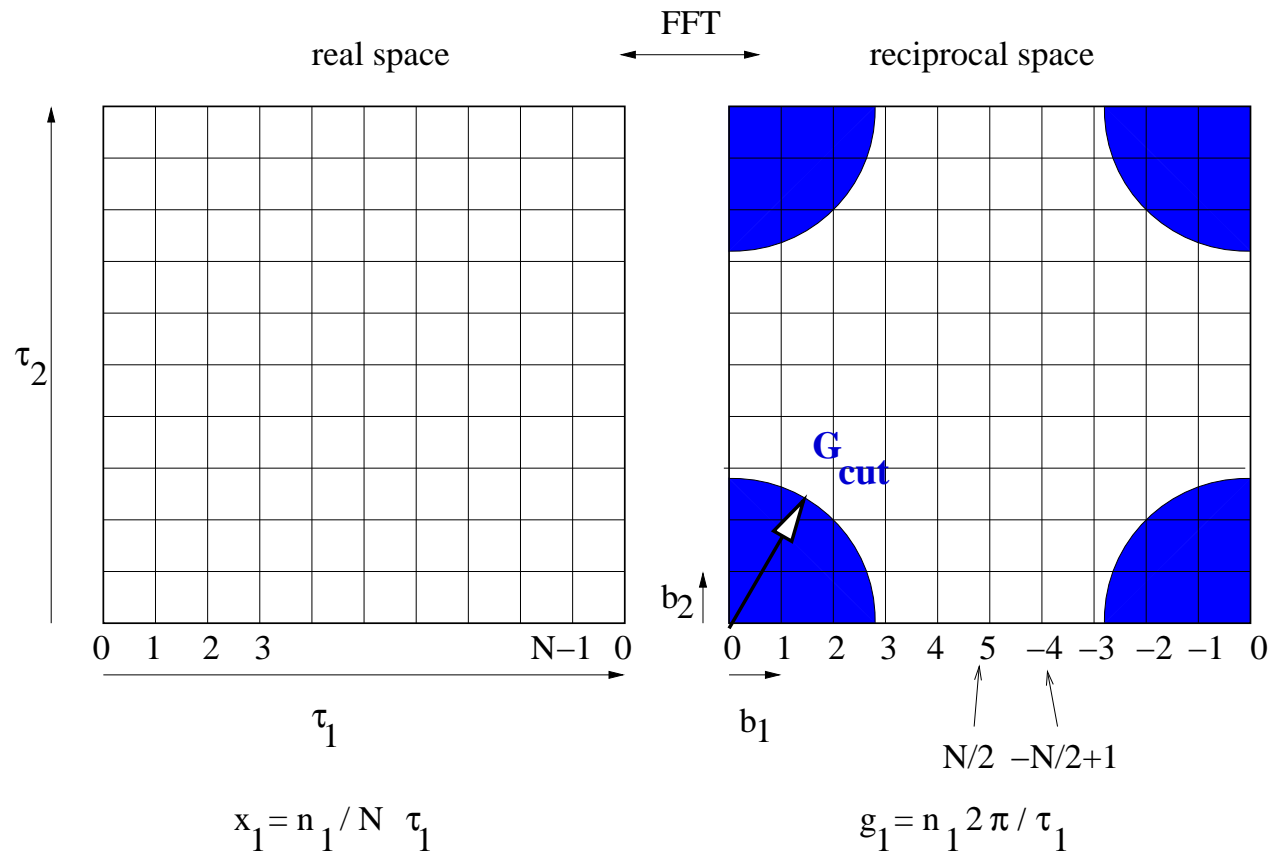
$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}},$$

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}}e^{i\mathbf{G}\mathbf{r}},$$

- in practice only those plane waves $|\mathbf{G}+\mathbf{k}|$ are included which satisfy

$$\frac{\hbar^2}{2m_e}|\mathbf{G}+\mathbf{k}|^2 < E_{\text{cutoff}}$$

Fast Fourier transformation

real space   FFT   reciprocal space

τ_2

τ_1

0 1 2 3 N−1 0

$x_1 = n_1 / N \; \tau_1$

b_2

b_1

G_{cut}

0 1 2 3 4 5 −4 −3 −2 −1 0

N/2 −N/2+1

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

$$C_{\mathbf{r}n\mathbf{k}} = \sum_{\mathbf{G}} C_{\mathbf{G}n\mathbf{k}} e^{i\mathbf{G}\mathbf{r}} \qquad C_{\mathbf{G}n\mathbf{k}} = \frac{1}{N_{\text{FFT}}} \sum_{\mathbf{r}} C_{\mathbf{r}n\mathbf{k}} e^{-i\mathbf{G}\mathbf{r}} \qquad \psi_{n,\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} C_{\mathbf{r}n\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}.$$

Why are plane waves so convenient

- historical reason:

  many elements exhibit a band-structure that can be interpreted in a free electron picture (metallic s and p elements)

  the pseudopotential theory was initially developed to cope with these elements (pseudopotential perturbation theory)

- practicle reason:

  the total energy expressions and the Hamiltonian $\mathbf{H}$ are dead simple to implement

  a working pseudopotential program can be written in a few weeks using a modern rapid prototyping language

- computational reason:

  because of it's simplicity the evaluations of $\mathbf{H}\psi$ is exceedingly efficient using FFT's

Computational reason

evaluation of $\mathbf{H}\psi_{n,\mathbf{k}}(\mathbf{r})$

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V(\mathbf{r})\right)\psi_{n,\mathbf{k}}(\mathbf{r})$$

and using the convention $\langle\mathbf{r}|\mathbf{G}+\mathbf{k}\rangle = \frac{1}{\Omega^{1/2}}e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}} \to \langle\mathbf{G}+\mathbf{k}|\psi_{n,\mathbf{k}}\rangle = C_{\mathbf{G}n\mathbf{k}}$
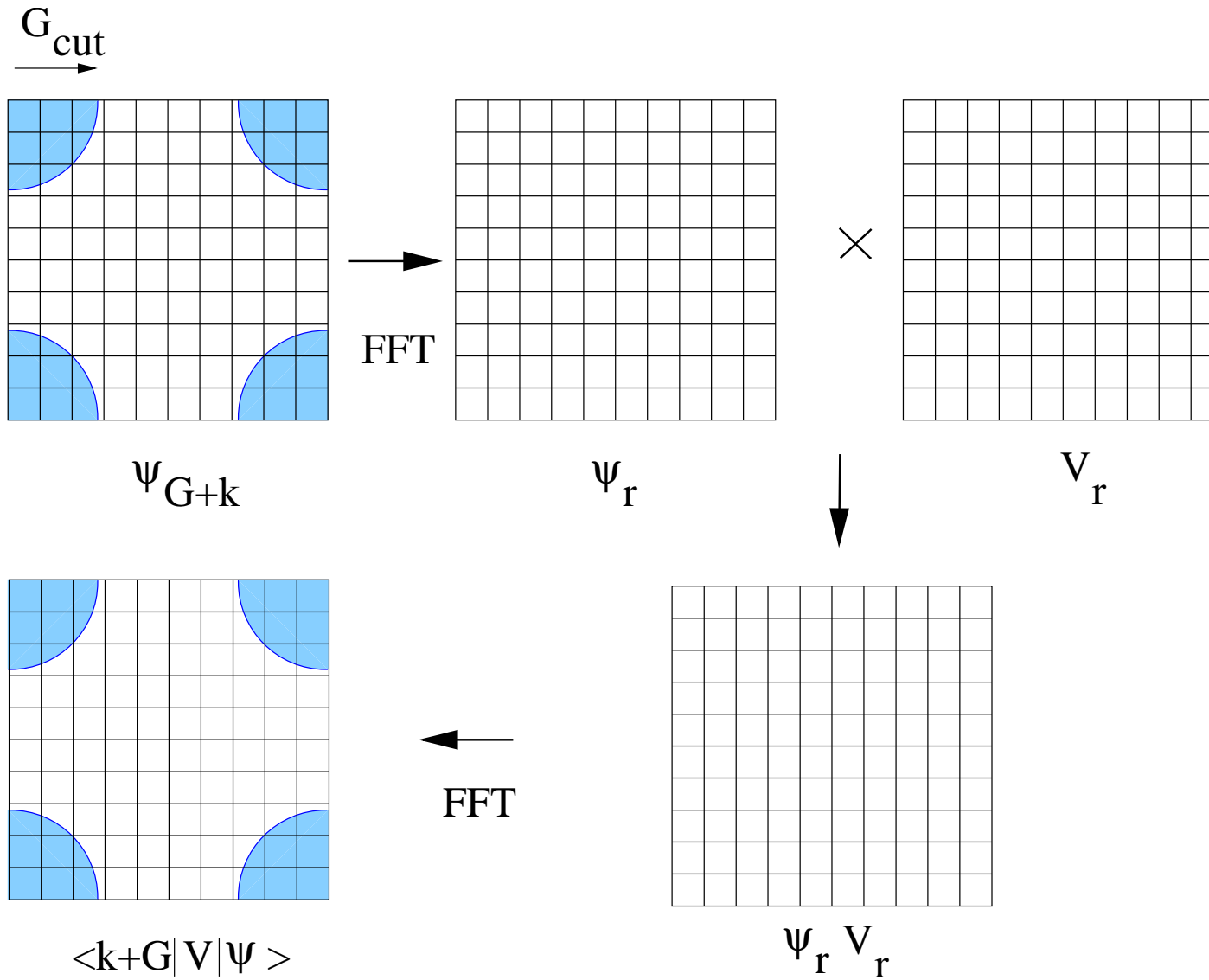
- kinetic energy:

$$\langle\mathbf{G}+\mathbf{k}| - \frac{\hbar^2}{2m_e}\Delta|\psi_{n,\mathbf{k}}\rangle = \frac{\hbar^2|\mathbf{G}+\mathbf{k}|^2}{2m_e}C_{\mathbf{G}n\mathbf{k}} \qquad N_{\text{planewaves}}$$

- local potential:

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

- if $\mathbf{H}$ would be stored as a matrix with $N_{\text{planewaves}} \times N_{\text{planewaves}}$ components
  $N_{\text{planewaves}} \times N_{\text{planewaves}}$ operations would be required

Local part of Hamiltonian

G_{cut}

Ψ_{G+k} FFT → Ψ_r × V_r

$\langle k+G|V|\Psi\rangle$ ← FFT $\Psi_r \, V_r$

Pseudopotential approximation

- the number of plane waves would exceed any practicle limits except for H and Li
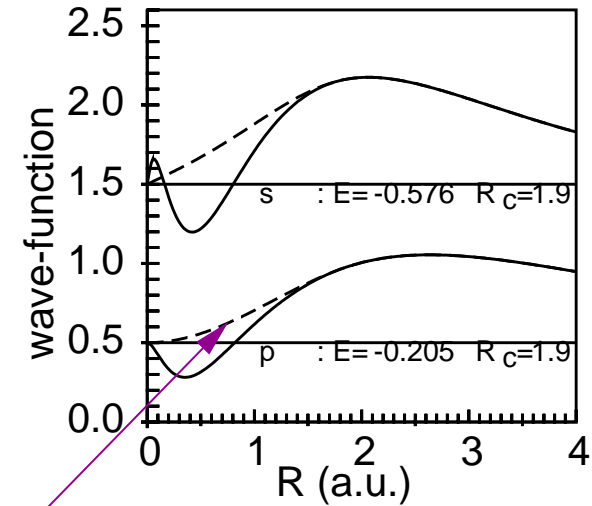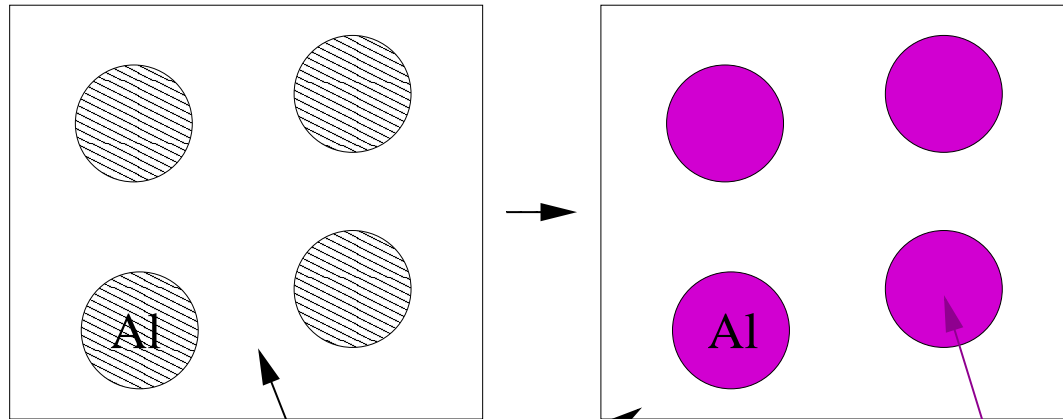
  $\Rightarrow$ pseudopotentials instead of exact potentials must be applied

- three different types of potentials are supported by VASP

  – norm-conserving pseudopotentials

  – ultra-soft pseudopotentials

  – PAW potentials

  they will be discussed in more details in later sessions

- all three methods have in common that they are presently frozen core methods

  i.e. the core electrons are pre-calculated in an atomic environment and kept frozen in the course of the remaining calculations

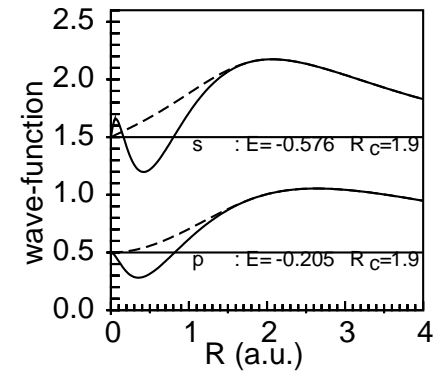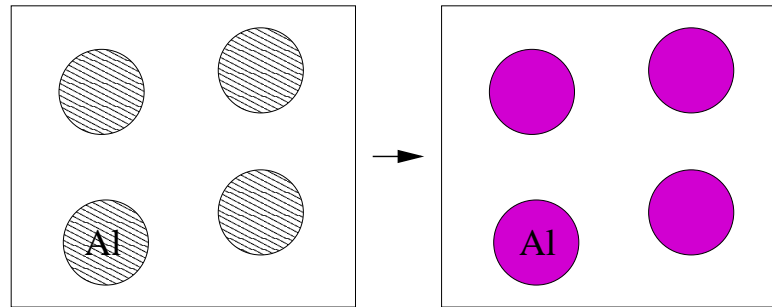# Pseudopotential: essential idea

exact potential (interstitial region)   pseudopotential

Al	effectiv Al atom	PAW Al atom
3p	2p	3p
3s	1s	3s
2p		
2s	2p and 1s are	nodal structure
1s	nodeless !!!!	is retained

Scattering approach

- solve the Schrödinger equation in the interstitial region only, using energy and angular momentum dependent boundary conditions at the spheres

$$\frac{\partial \phi_l(r,\varepsilon)}{\partial r} \frac{1}{\phi_l(r,\varepsilon)}\bigg|_{r_c} = \frac{\partial \log \phi_l(r,\varepsilon)}{\partial r}\bigg|_{r_c}$$

  ϕ_l are the regular solutions of the radial Schrödinger equation inside the spheres for the angular momentum quantum number l and the energy ε

- details of the wavefunctions (number of nodes in the spheres) do not enter

- pseudopotential: select one specific energy ε in the centre of the valence band and replace the exact wavefunction ϕ_l by a pseudo-wavefunction with $\tilde{\phi}_l$

$$\frac{\partial \log \phi_l(r,\varepsilon)}{\partial r}\bigg|_{r_c} = \frac{\partial \log \tilde{\phi}_l(r,\varepsilon)}{\partial r}\bigg|_{r_c}$$
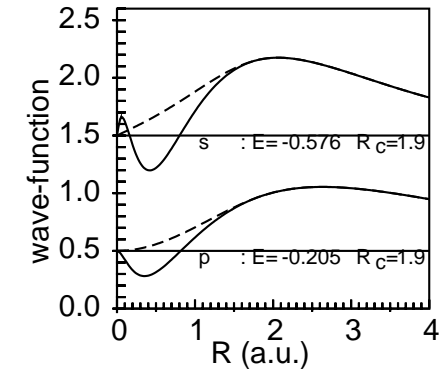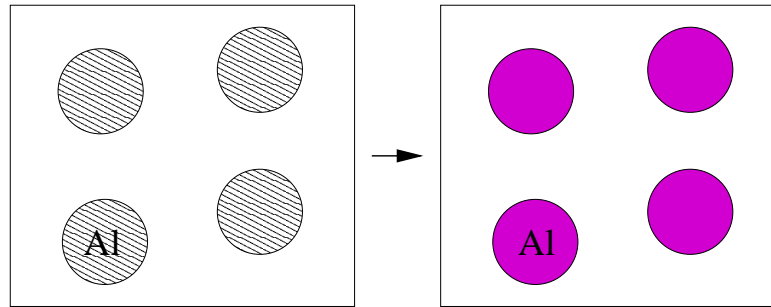
- obviously one would like to get the right distribution of charge between the spheres and the interstitial region as well

$\rightarrow$ norm-conserving pseudopotentials

$$\int_0^{r_c} \phi_l(r,\varepsilon)\phi_l^*(r,\varepsilon)4\pi r^2 dr = \int_0^{r_c} \tilde{\phi}_l(r,\varepsilon)\tilde{\phi}_l^*(r,\varepsilon)4\pi r^2 dr$$

- norm-conservation has another important consequence

the scattering properties are not only correct at the reference energy ε but also in a small energy interval around ε

$$\frac{\partial}{\partial\varepsilon}\left.\frac{\partial\log\phi_l(r,\varepsilon)}{\partial r}\right|_{r_c} = \frac{\partial}{\partial\varepsilon}\left.\frac{\partial\log\tilde{\phi}_l(r,\varepsilon)}{\partial r}\right|_{r_c} \qquad \forall l$$

Pseudopotential generation

- all-electron calculation for a reference atom

- chose energies ε_l at which the pseudisation is performed
  usually these are simply the eigen-energies of the bound valence states, but in
  principle any energy can be chosen (centre of valence band)

- replace the exact wavefunction by a node less pseudo-wavefunction observing the
  following four requirements:

$$\tilde{\phi}(r_c)^{(n)} = \phi(r_c)^{(n)} \qquad \text{for } n = 0, ..., 2 \qquad (n) \text{ is the } n.\text{th derivative}$$

$$4\pi \int_0^{r_c} \tilde{\phi}(r)^2 \, r^2 dr = 4\pi \int_0^{r_c} \phi(r)^2 \, r^2 dr \qquad \text{norm-conservation condition}$$

- this pseudopotential conserves exactly the scattering properties of the original atom
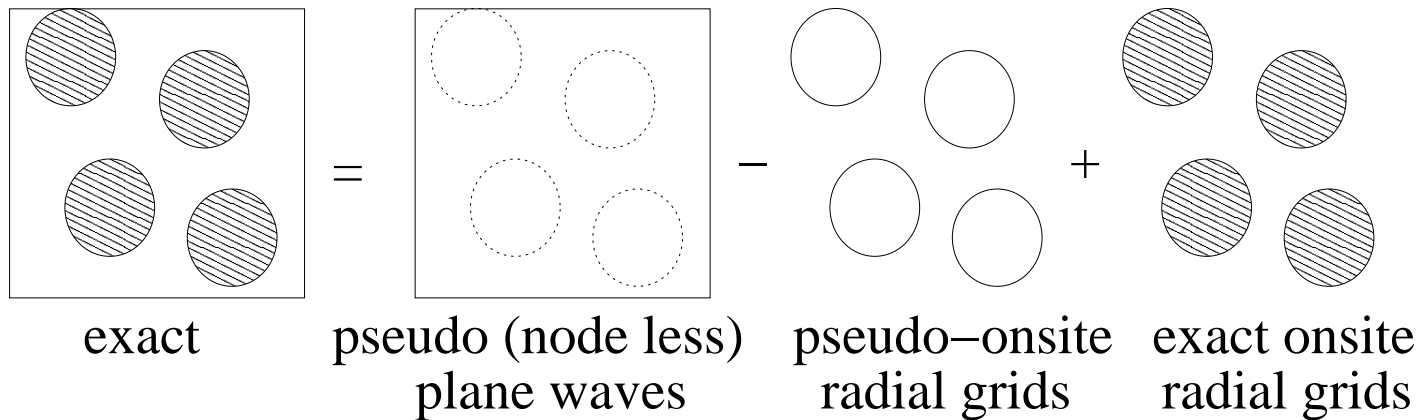 in the atomic configuration

  but it is an approximation in another environment

Projector augmented wave method

- wave function (and energy) are decomposed into three terms:

$$|\psi_n\rangle \quad = \quad |\tilde{\psi}_n\rangle \quad - \sum_{\text{atoms}} |\tilde{\phi}_{lm\varepsilon}\rangle c_{lm\varepsilon} + \sum_{\text{atoms}} |\phi_{lm\varepsilon}\rangle c_{lm\varepsilon}$$

| exact | pseudo (node less) plane waves | pseudo−onsite radial grids | exact onsite radial grids |

no interaction between different spheres and plane waves $\Rightarrow$ efficient

- decomposition into three terms holds for
  - wave functions   – kinetic energy

  - charge densities   – Hartree.- and exchange correlation energy

Determining the electronic groundstate

- by iteration – self consistency (old fashioned)

- start with a trial density ρ_e, set up the Schrödinger equation, and solve the Schrödinger equation to obtain wavefunctions $\psi_n(\mathbf{r})$
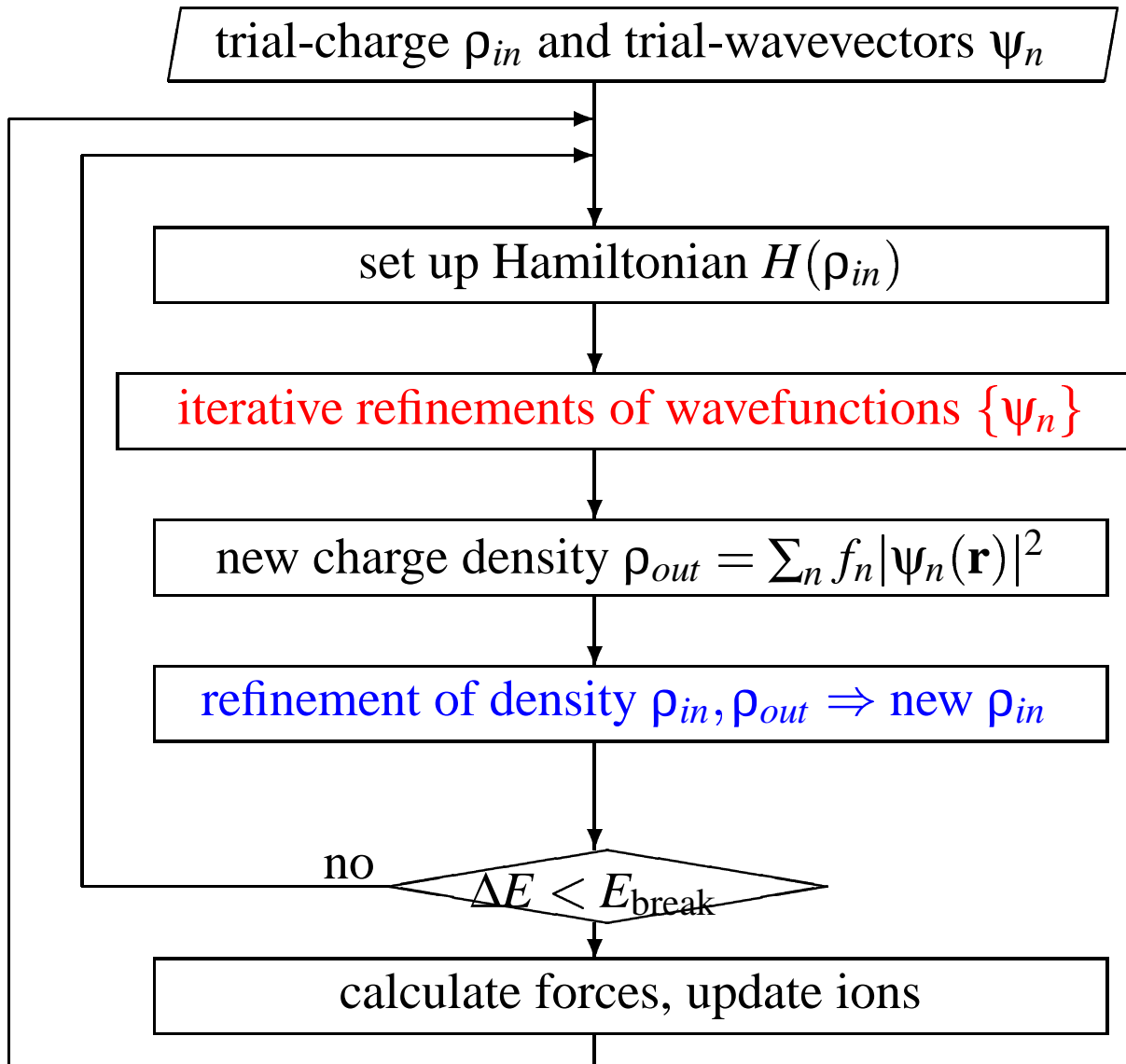
$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V^{\text{eff}}(\mathbf{r}, \{\rho_{\mathbf{e}}(\mathbf{r}')\}) \right) \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r}) \qquad n = 1, ..., N_e/2$$

- as a result one obtains a new charge density $\rho_e(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2$ and a new one electron potential:

$$V^{\text{eff}}(\mathbf{r}, \{\rho_e(\mathbf{r}')\}) = e^2 \int \frac{\rho_e(\mathbf{r}') + \rho_{\text{ion}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + V_{\text{xc}}(\rho_e(\mathbf{r}))$$

new Schrödinger equation $\Rightarrow$ iteration

Self-consistency scheme

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}

no $\quad \Delta E < E_{\text{break}}$

calculate forces, update ions

- two subproblems
  optimization of $\{\psi_n\}$ and ρ_{in}

- refinement of density:
  DIIS algorithm
  P. Pulay, Chem. Phys. Lett. **73**, 393 (1980).

- refinement of wavefunctions:
  blocked Davidson like algorithm

What have all iterative matrix diagonalisation schemes in common ?

- one usually starts with a set of trial vectors (wavefunctions) representing the filled states and a few empty one electron states

$$\{\psi_n | n = 1,.., N_{\text{bands}}\}$$

  these are initialised using a random number generator

- then the wavefunctions are improved by adding a certain amount of the residual vector to each

  the residual vector is defined as

$$|R(\psi_n)\rangle = (\mathbf{H} - \varepsilon_{\text{app}}\mathbf{S})|\psi_n\rangle \qquad \varepsilon_{\text{app}} = \langle\psi_n|\mathbf{H}|\psi_n\rangle$$

  $\mathbf{H}\psi_n$ is exactly operation discussed before (efficient)

- adding a small amount of the residual vector

$$\psi_n \rightarrow \psi_n + \lambda R(\psi_n)$$

 is in the spirit of the steepest descent approach ("Jacobi relaxation")

We know the groundstate, what now ?

Hellman-Feynmann theorem allows to calculate the ionic forces and the stress tensor

- by moving along the ionic forces (steepest descent) the ionic groundstate can be calculated

- we can displace ions from the ionic groundstate, and determine the forces on all other ions

    $\Rightarrow$ effective inter-atomic force constants and vibrational frequencies

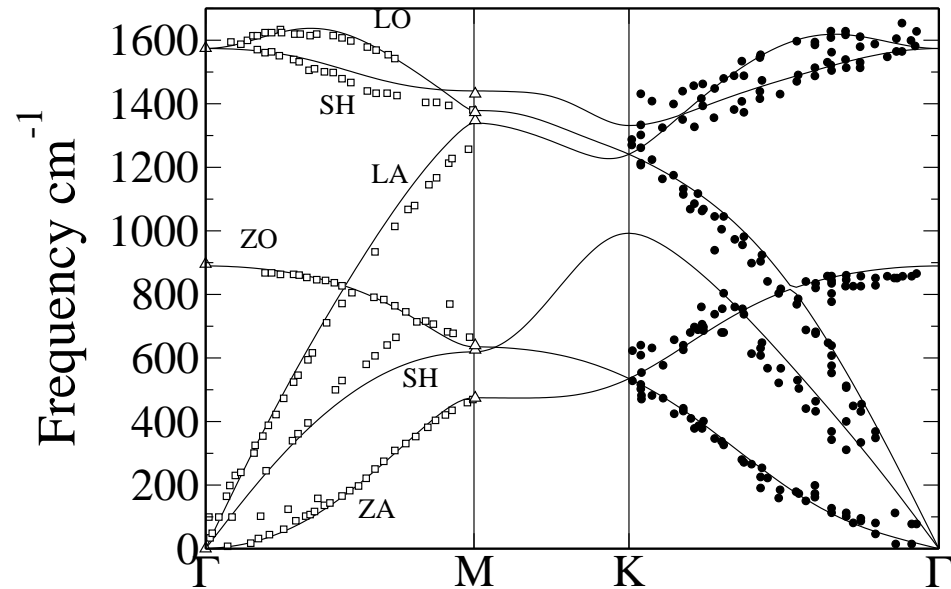- molecular dynamics by using Newtons equation of motion

Vibrational properties

- the vibrational frequencies are calculated using a brute force method:
  in the supercell all "selected
  atoms" are displaced from
  their groundstate position
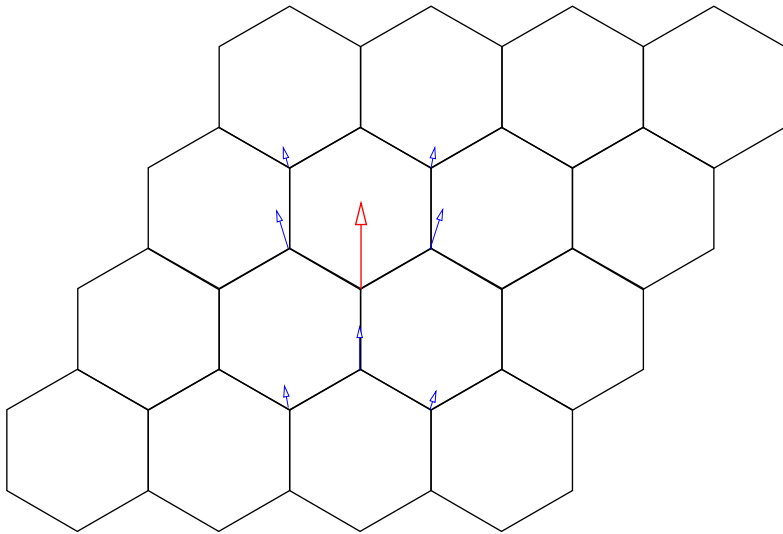
  forces $\Rightarrow$ force constants

not possible presently

- symmetry is not used !!!

- works well for molecules, but has to be applied with great care to solids