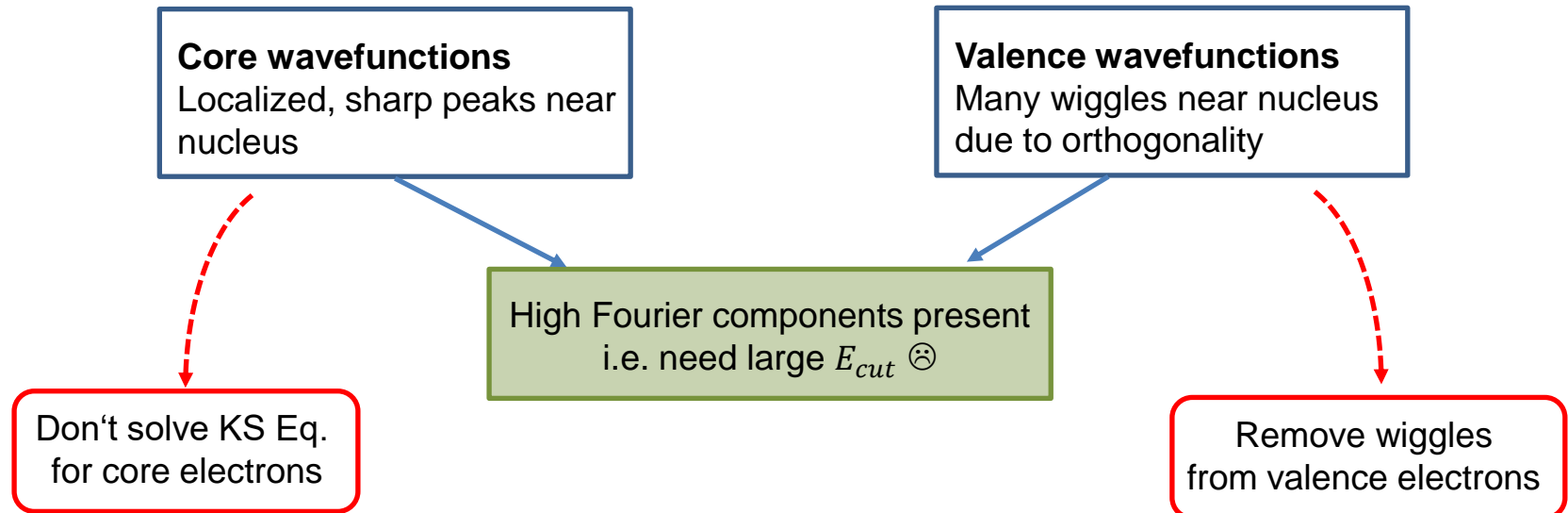# Density functional theory in solid state physics

Lecture 7

- Periodic boundary conditions: electrons occupy bands with dispersion in k-space

- Integration over Brillouin zone practically done using uniform discrete „Monkhorst-Pack" grids. Number of explicitly to-be included grid points can be reduced by crystal symmetry

- Suitable basis set to expand Kohn-sham orbitals in periodic systems: Planewaves

$$\varphi_{kn\sigma}(\vec{r}) \approx \sum_{\vec{G}}^{\vec{G}_{max}} c_{kn\sigma}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \qquad E_{cut} = \frac{\left|\vec{G}_{max}\right|^2}{2}$$

- Many advantages, but problem with basis set size

Core wavefunctions
Localized, sharp peaks near nucleus

Valence wavefunctions
Many wiggles near nucleus due to orthogonality

High Fourier components present
i.e. need large E_{cut} ☹

Don't solve KS Eq.
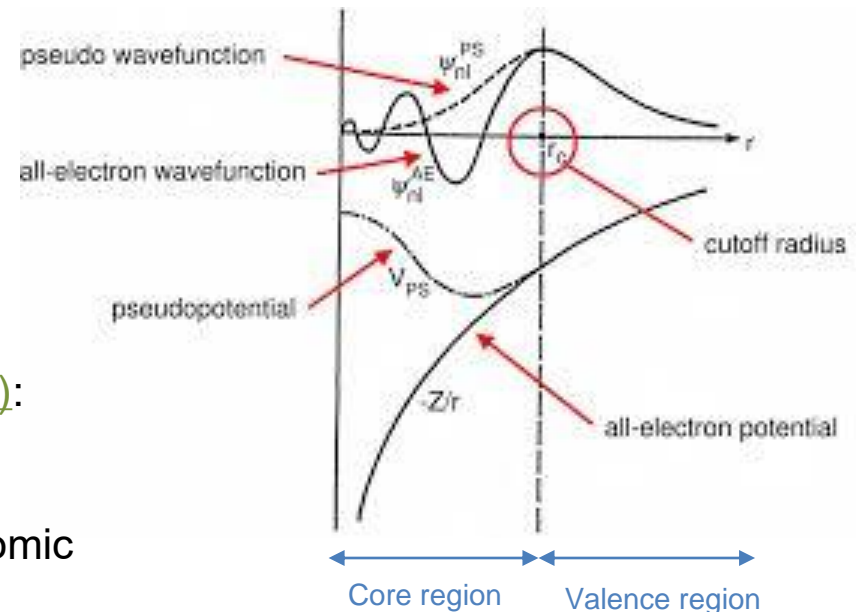for core electrons

Remove wiggles
from valence electrons

Normconserving pseudopotentials

- Pseudopotentials: Replace nucleic Coulomb potential $v(\vec{r})$ by a combined effective potential $v^{PS}(\vec{r})$ of nuclei and „frozen" core electrons

- Valence electrons feel this pseudo-potential

- Norm-conserving pseudopotentials (NCPP): For a given reference configuration,

  - reproduce the correct ‚all-electron' atomic eigenvalues, $\varepsilon_l^{ps} = \varepsilon_l^{AE}$

  - $\phi_l^{ps}(\vec{r})$ is nodeless

  - $\phi_l^{ps}(\vec{r}) = \phi_l^{ae}(\vec{r})$ for $r > r_c$

  - „normconservation", i.e. the total charge in the core region is conserved,

$$\int_{r<r_c} \left|\phi_l^{ps}(\vec{r})\right|^2 r^2 dr = \int_{r<r_c} |\phi_l^{ae}(\vec{r})|^2 r^2 dr$$

pseudo wavefunction ψ_{nl}^{PS}

all-electron wavefunction ψ_{nl}^{AE}

cutoff radius r_c

pseudopotential v_{PS}

$-Z/r$

all-electron potential

Core region   Valence region

- How are pseudopotentials typically generated?

  - Perform all-electron calculation for a free atom in a chosen reference configuration
    -> obtain all-electron wavefunctions $\phi_{lm}(\vec{r})$ and energy levels ε_{lm}

  - Pick a cutoff radius r_c and construct pseudo wavefunctions $\widetilde{\phi}_{lm}(\vec{r})$ that have the desired properties:

    Hamann: Phys. Rev. Lett. 42, 662 (1979)
    G. P. Kerker: J. Phys. C 13, 189 (1980)
    Troullier-Martins: Phys. Rev. N 43, 1993 (1991)

    all-electron wavefunction   pseudowavefunction

    $\phi_l(r)$

    $r \longrightarrow$
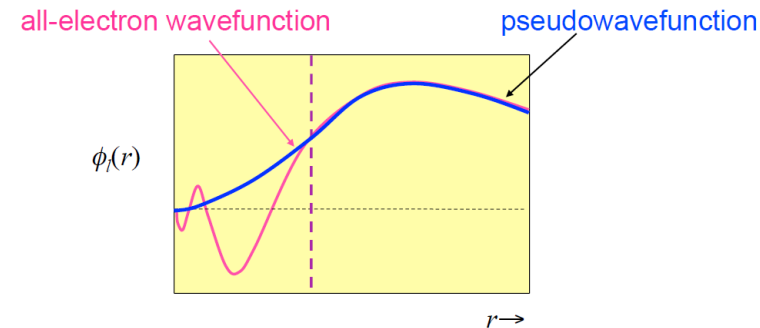
  - For each angular momentum l, construct pseudopotential by inverting the Kohn-Sham equation

    $$\left(-\frac{1}{2}\nabla^2 + u_l(\vec{r}) + v_H(\vec{r}) + v_{XC}(\vec{r}) - \varepsilon_{lm}\right)\widetilde{\phi}_{lm}(\vec{r}) = 0$$

  - Obtain pseudopotential v_l^{PS} by „unscreening": $v_l^{PS} = u_l - v_H(n^{PS}) - v_{XC}(n^{PS})$

- Different pseudopotential „channels" for different angular momenta

Accuracy vs. efficiency

- Desirable characteristics of a pseudopotential:

  - Transferability: The same pseudopotential should work well for different atomic environments and for different electronic configurations

  - Softness: The pseudopotential should give smooth pseudo wavefunctions and such allow for a low E_{cut}

    small r_c: hard but transferable pseudopotential
    large r_c: soft but less transferable pseudopotential

  - Should be „ghost-free", i.e. not produce spurious states

- Typically compromise necessary between efficiency and accuracy necessary

- Normconserving pseudopotentials often take a *non-local* form:

$$v^{ps,US}(\vec{r}) = v^{loc}(\vec{r}) + \sum_{ij} B_{ij} |\beta_i\rangle\langle\beta_j|$$

Core-localized projector functions

- Popular: Kleinman-Bylander form

$$v^{ps,NL}(\vec{r}) \approx v^{ps,KB}(\vec{r}) = v^{loc}(\vec{r}) + \sum_{l,m} v_l |\beta_{lm}\rangle\langle\beta_{lm}|$$

Local potential, same for all electrons

One projector function per *l*, electrons with different *l* feel different potential

Advantages of NC-PP

- Advantages of normconserving pseudopotentials

    - Conceptionally simple, easy to generate and implement

    - Normconserving pseudopotentials ensure the reproduction of the correct „scattering properties" within a certain range of energies

    - Good accuracy compared to ‚all-electron' calculations, relatively good transferability

    - Considerable speed-up compared to ‚all-electron', especially for transition metals and heavier elements

    - Databases of pre-generated pseudopotentials for all elements readily available

- Normconserving pseudopotentials are implemented and used in almost every DFT code aimed at solid state physics

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- Disadvantages

  - For transition metals, more localized „semi-core" states can show up, norm-conserving psps lead to high cutoff for such elements

  - Kleinman-Bylander form can lead to problems with transferability if semi-core electrons are involved

  - Often choice between transferability and efficiency necessary

Ga pseudopotential, normconserving
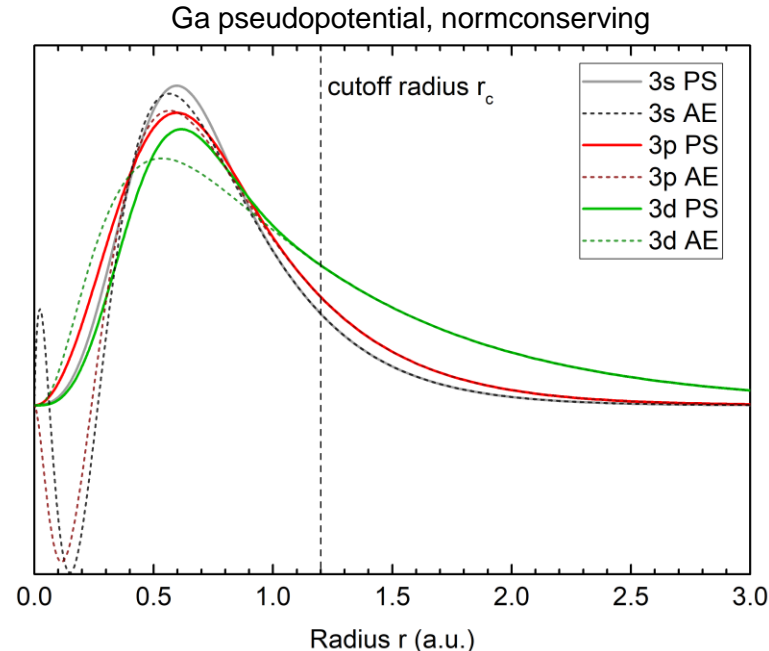
Ultrasoft pseudopotentials

- Ultrasoft pseudopotentials (Phys. Rev. B 41, 7892 (1990))

- Aim: Improve accuracy, efficiency and transferability of pseudopotentials

- Idea: Do away with normconservation

  $r > r_c$: φ^{US} identical to AE wavefunction
  $r > r_c$: choose φ^{US} to be as soft as possible

- Use atom-centered augmentation charges to compensate for error

- Justified because charge in core region is rigid, does not need to be treated self-consistently
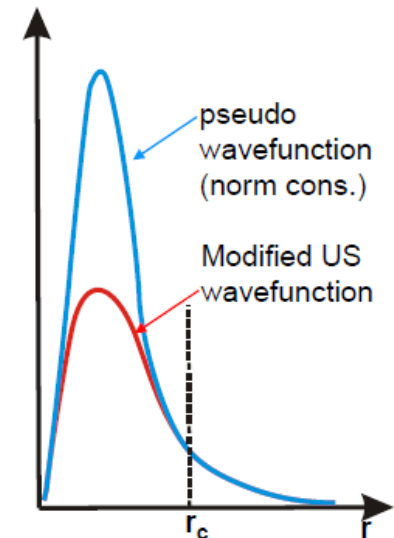
- Pseudopotential of the form
  $$v^{ps,US}(\vec{r}) = v^{loc}(\vec{r}) + \sum_{ij} D_{ij}^{US} |\beta_i\rangle\langle\beta_j|$$

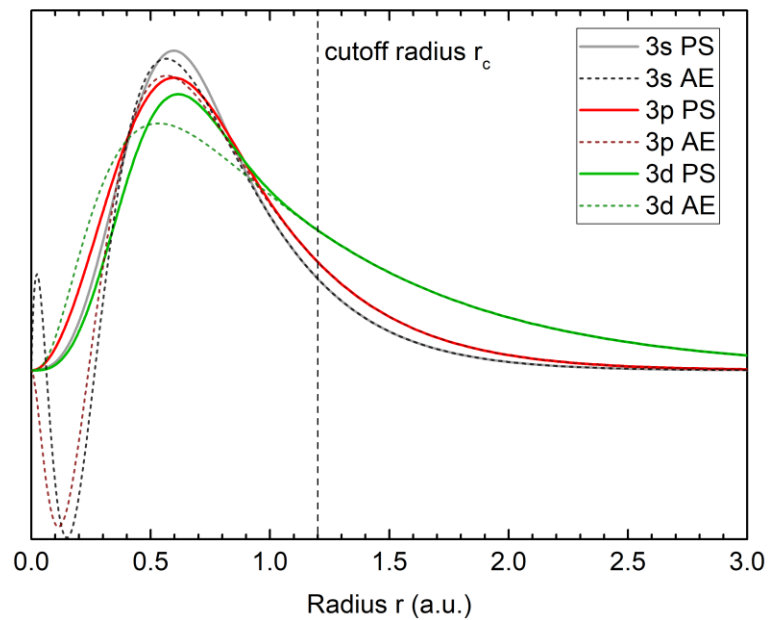 Typically 2-4 projectors per atom

- Charge density is now
  $$n(\vec{r}) = \sum_{n,k} |\varphi_{nk}|^2 + \sum_{\alpha,ij} Q_{ji}^{\alpha}(\vec{r}) \langle\varphi_{nk}|\beta_i^{\alpha}\rangle\langle\beta_j|\varphi_{nk}\rangle$$

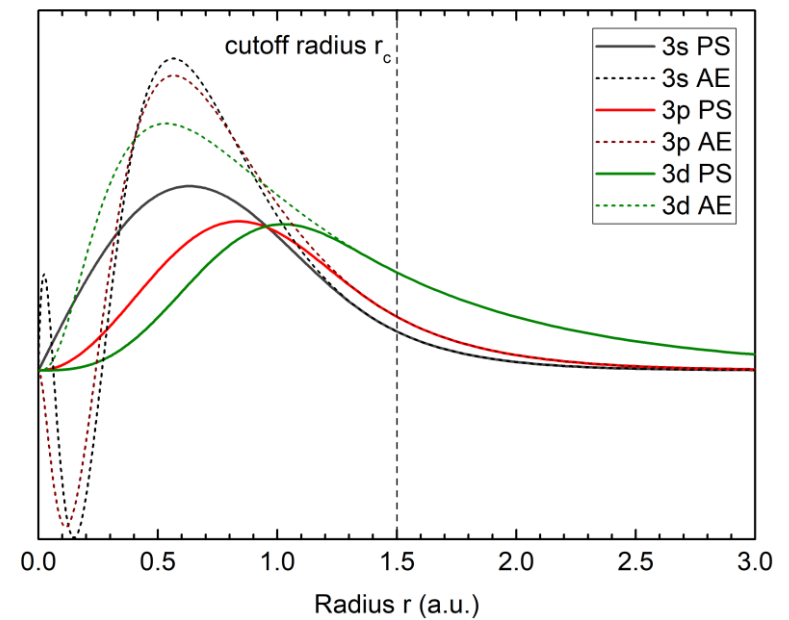 Augmentation charges, $Q_{ij}(r) = \varphi_i^{AE,*}\varphi_j^{AE} - \varphi_i^{US,*}\varphi_j^{US}$

pseudo wavefunction (norm cons.)

Modified US wavefunction

r_c

Normconserving vs ultrasoft

Ga pseudopotential, normconserving

Ga pseudopotential, ultrasoft

Pro and cons of ultrasoft PP

- Advantages:

    - Increased flexibility compared to normconserving PPs, bettwe transferability

    - Often significantly reduced cutoff energies necessary for converged results

    - Can be easier to generate ultrasoft pseudopotentials for some elements

- Disadvantages:

    - Introduction of augmentation charges leads to an increased complexity of implementations, many advanced features are far less widely implemented for ultrasoft pseudopotentials

    - Can be more difficult to generate ultrasoft pseudopotentials for some elements due to additional complexity

- Ultrasoft pseudopotentials can be read and used by most pseudopotential codes aimed at solid state physics

- Several libraries of pre-generated ultrasoft pseudopotentials available

Porjector augmented waves

- Generalization of ultrasoft psps: Projected augmented waves (PAW)

- Divide AE wavefunction into a „planewave" part and „one-center terms" localized to „augmentation spheres" around each atoms

- AE observables can be derived from pseudo wvfns using linear transformation T

AE wavefunction

Augmentation sphere

Soft pseudo-wavefunction

„pseudo partial wave"

„AE partial wave" (tabulated)

$$|\varphi^{AE}\rangle = |\varphi^{PS}\rangle + \sum_i \left(\left|\phi_i^{AE}\right\rangle - \left|\phi_i^{PS}\right\rangle \right) \langle\beta_i|\varphi^{PS}\rangle = \hat{T}\,|\varphi^{PS}\rangle \qquad \langle\beta_i|\phi_j^{PS}\rangle = \delta_{ij}$$
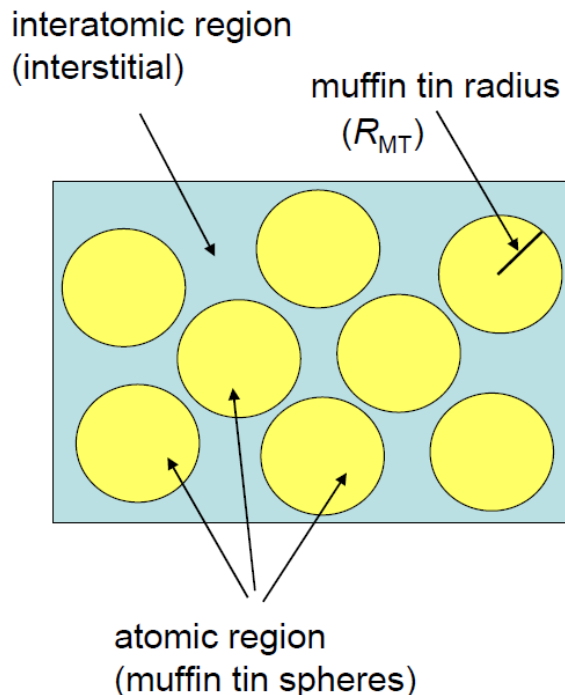
- Electron density: $n(r) = \sum_j \left|\varphi_j^{PS}\right|^2 + \sum_{j,m,n} Q_{mn}\langle\varphi_j^{PS}|\beta_m\rangle\langle\beta_n|\varphi_j^{PS}\rangle$

Usually approximated

Pros and Cons of PAWs

- Typical implementation: only onsider valence electrons, keeping core electrons frozen, using PAW potential (i.e. pseudopotentials)

- Advantages:

    - Advantages of ultrasoft pseudopotentials are kept, low cutoff energy can be achieved

    - In principle all-electron accuracy, as AE wavefunction is reconstructed

    - Works equally well for both light and heavy elements

- Disadvantage: Increased computational complexity compared to ultrasoft pseudopotentials

- Several high-quality libraries of PAW potentials are available

- Implemented in a variety of codes:

Augmentation-based AE methods

- Augmentation methods are the primary way to do all-electron simulations on solid systems

- Idea: Divide system into „core" regions and „interstitital" regions

- Linear muffin-tin orbital method (LMTO): spherically symmetric potential in core region, contant potential in interstitital region, matching solutions inside and outside of muffin tins

interatomic region
(interstitial)

muffin tin radius
(R_{MT})

atomic region
(muffin tin spheres)

- (linearized) augmented plane waves (LAPW):

  no shape-assumption for potential, wavefunctions are linear combinations of atomic orbitals in core region, valence electron ‚leak out' into interstitial region, matching at sphere boundary

  Basis set size: $R_{MT,min} G_{max} = const$

Method	Core	Interstitial
LMTO	AO	Hankel functions
(L)APW	AO	PWs
PAW	Projectors+PWs	PWs

- Advantages:

  - All electrons are treated on same footing

  - Most accurate method for use on periodic systems

  - Systematic improvement of basis set

  - Relativistic effects are straight-foward to implement

- Disadvantages:

  - Mathematically and conceptionally complex, forces difficult to implement

  - Basis changes when atoms move

  - Computationally far less efficient than pseudopotential methods
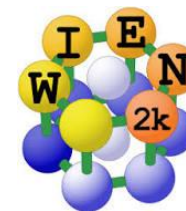
- Disadvantage of plane-wave based methods: „empty" regions are costly

- Chemistry-view to basis sets: Wavefunctions are derived from atomic orbitals, LCAO ansatz

- Examples:
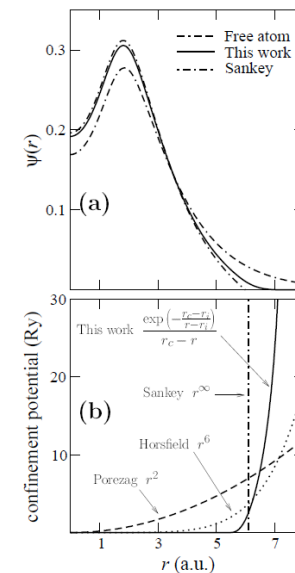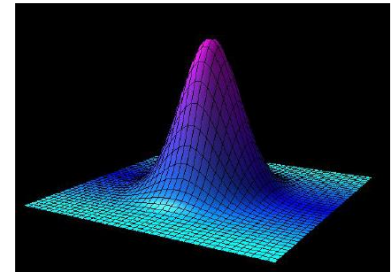
  - Gaussian-type orbitals (GTO):

    $$\varphi(\vec{r}) = r^l \underbrace{\sum_p c_p\, B(l,\alpha) e^{-\alpha r^2}}_{R_l(r)} Y_{lm}(\theta,\phi)$$

    Used in all quantum chemistry codes

  - Numerical atomic orbitals (NAO)

    $$\varphi(\vec{r}) = R_l(r) Y_{lm}(\theta,\phi)$$

    Obtain R_l from numerical solution of KS-equation of free atom, using an additional confining potential

Phys. Rev. B 64, 235111 (2001)

Pros and Cons of local basis sets

- Advantages:

  - Atom-centered and spatially localized, all-electron

  - No costs for empty space/vacuum

  - Applicable to both non-periodic and periodic systems

  - „Overlap" of orbitals efficient, analytical (GTOs) or using locality of basis (NAO)

  - Very efficient implementation of Hartree-Fock exchange

- Disadvantages:

  - Basis set is non-orthogonal and depends on atomic positions

  - No implicit periodicity

  - Difficult to improve basis set quality, „polarization" and „diffuse" orbitals

  - k-points not straight-forward to implement. *LxNxM* Monkhorst-Pack grid → *LxNxM* supercell in real space.

The SCF method in Kohn-Sham

- We now have all incredients to solve Kohn-Sham Equation and calculate ground state density and energy.

$$\sum_{\vec{G}'} \left[\frac{1}{2} \left| \vec{k} + \vec{G} \right|^2 \delta_{GG'} + v(\vec{G}, \vec{G}') + v_H(\vec{G} - \vec{G}') + v_{XC}(\vec{G} - \vec{G}') \right] c_{ik}(\vec{G}') = \varepsilon_{ik} S c_{ik}(\vec{G})$$
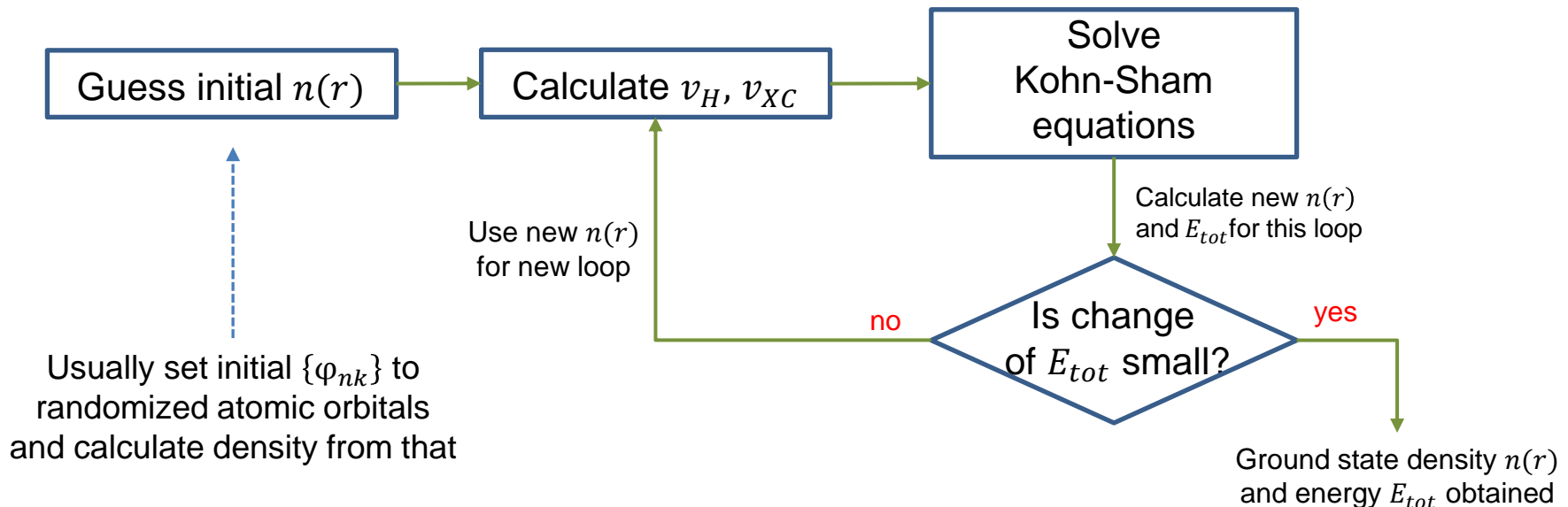
Describe this with pseudo- or PAW potentials.
Non-local PPs: $v_k^{NL-PS}(\vec{G}, \vec{G}')$

Want to only consider valence electrons

Overlap matrix,
For NC-PP: $S = I$
For US: $S = I + \sum_{mn} Q_{mn}(\vec{r}) |\beta_m\rangle\langle\beta_n|$

- How do we do this? Almost always using the SCF method

Guess initial $n(r)$ → Calculate v_H, v_{XC} → Solve Kohn-Sham equations

Calculate new $n(r)$ and E_{tot} for this loop

Use new $n(r)$ for new loop

no ← Is change of E_{tot} small? → yes

Usually set initial $\{\varphi_{nk}\}$ to randomized atomic orbitals and calculate density from that

Ground state density $n(r)$ and energy E_{tot} obtained

$$\sum_{\vec{G}'} \left[\frac{1}{2} \left| \vec{k} + \vec{G} \right|^2 \delta_{GG'} + v(\vec{G}, \vec{G}') + v_H(\vec{G} - \vec{G}') + v_{XC}(\vec{G} - \vec{G}') \right] c_{ik}(\vec{G}') = \varepsilon_{jk} S c_{jk}(\vec{G})$$

- Solving the Kohn-Sham Equations is the most expensive step in the SCF procedure

- A more practical problem: Full KS-Hamiltonian H is very large, as N^{PW} on order 10000.

- Also: H has N^{PW} x N^{PW} eigenvalues, most of which we are not interested in

- We are only interested in all occupied states, as well as (usually) a few unoccupied states close to the Fermi energy

- Idea: Instead of construction and direct diagonalization of H, use iterative approach to find $\{c_{ik}\}$ and $\{\varepsilon_{ik}\}$ in range of interest

Iterative solution of Kohn-Sham Eq.

- One-band-at-a-time approach: Use conjugate-gradients (CG) approach to find

$$\min\left[\langle c_{ik}|H|c_{ik}\rangle - \underbrace{\sum_{i\leq j}\lambda_j\langle c_{ik}|S|c_{jk}\rangle}_{\text{keep wavefunctions orthogonal}}\right]$$

for a given density $n(r)$. Do this for every band i in the range of interest
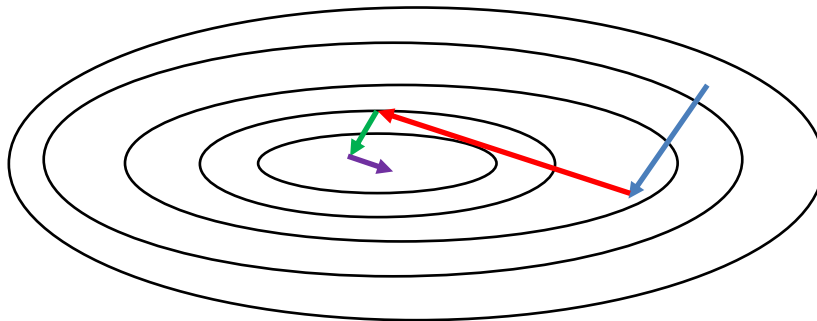
1. Minimize along „error vector"
2. find new „congugate" search direction d orthogonal to previous search direction
3. minimize along new d
4. repeat 2. and 3. until error is small enough

- Iterative (blocked) Davidson minimization and RMM-DIIS methods: Minimize several eigenvectors simultaneously.

  Much faster than CG, but sometimes less stable.

  Phys. Rev. B 54, 11169 (1996)

  *Chem. Phys. Lett. **73**, 393 (1980)*

Charge sloshing

- Another problem: SCF algorithm in the shown form almost never converges due to numerical instabilities

- Why? Typically not only one „global" energy minimum, but several local minima exist

- Energy landscape also changes with electron density, this minima can change between steps.

- Slow or no convergence of SCF method

- Might even lead to wrong „ground state", if SCF is caught in the wrong minimum

- Typically, metals or „problematic systems" are affected
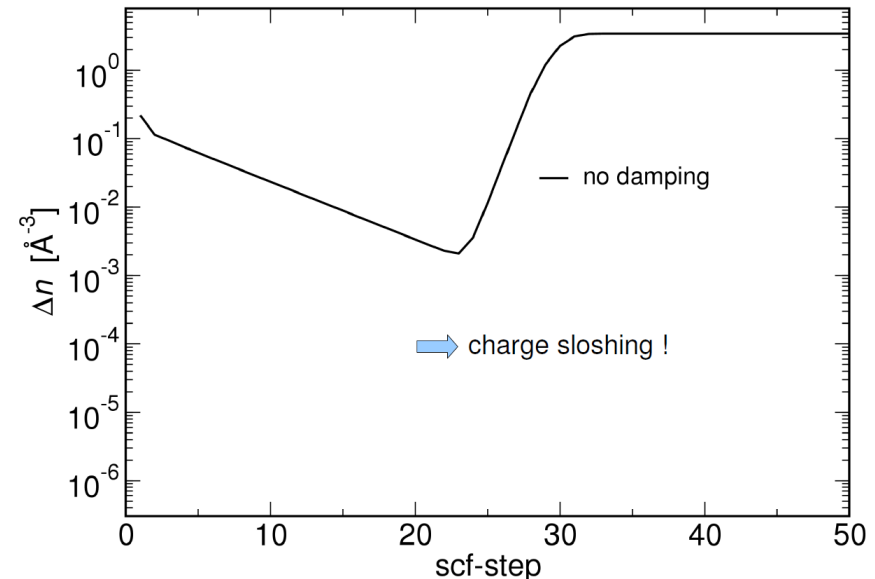
Taken from „Making electronic structure theory work"

Density mixing

- We want fast SCF convergence

- Density mixing: stabilize SCF algorithm by mixing old and new electron densities

- Linear mixing: Density entering ith SCF loop:

$$n_{in}^i(r) = \alpha n_{out}^{i-1}(r) + (1 - \alpha)n_{in}^{i-1}(r)$$

mixing parameter

Taken from „Making electronic structure theory work"
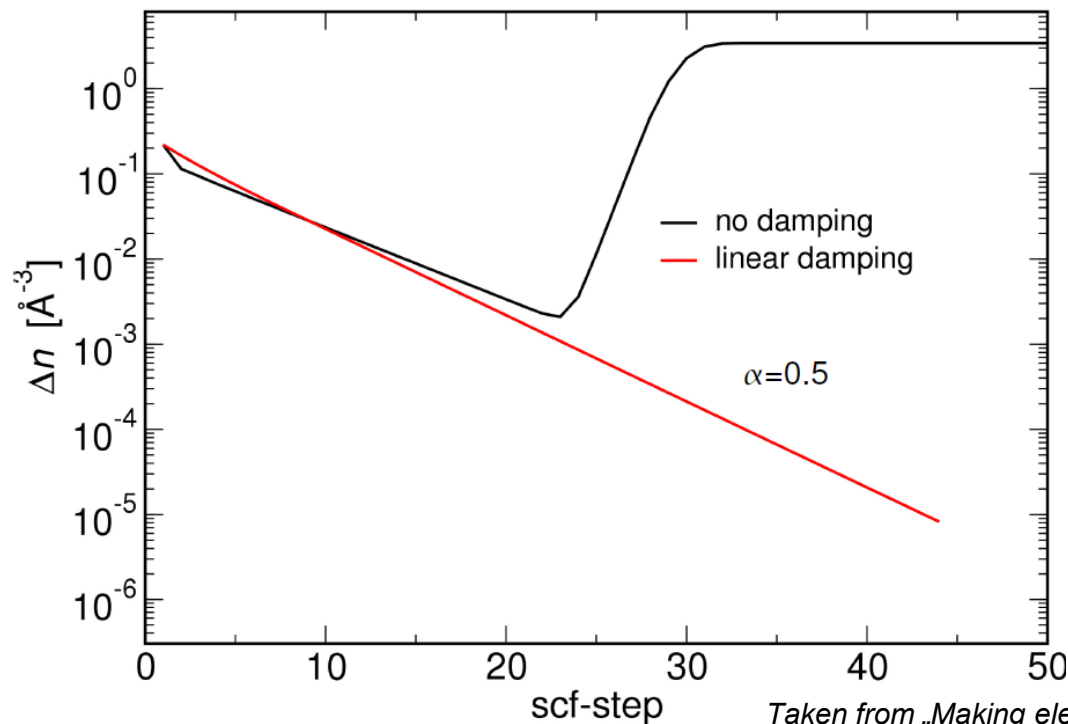
Density mixing

- We want fast SCF convergence

- Density mixing: stabilize SCF algorithm by mixing old and new electron densities

- Linear mixing: Density entering *i*th SCF loop:

$$n_{in}^i(r) = \alpha n_{out}^{i-1}(r) + (1-\alpha)n_{in}^{i-1}(r)$$

mixing parameter

- Pulay/Broyden mixing: take „history" of electron density from last M steps into account, try to find „optimal" input density

$$n_{in}^i(r) = \sum_j^M \alpha_j\left(n_{in}^{i-j} + R\left[n_{in}^{i-j}\right]\right)$$

Chem. Phys. Lett. **73**, 393 (1980)

Phys. Rev. B 38, 12807 (1988)

Residual, change between input and output density in step i-j

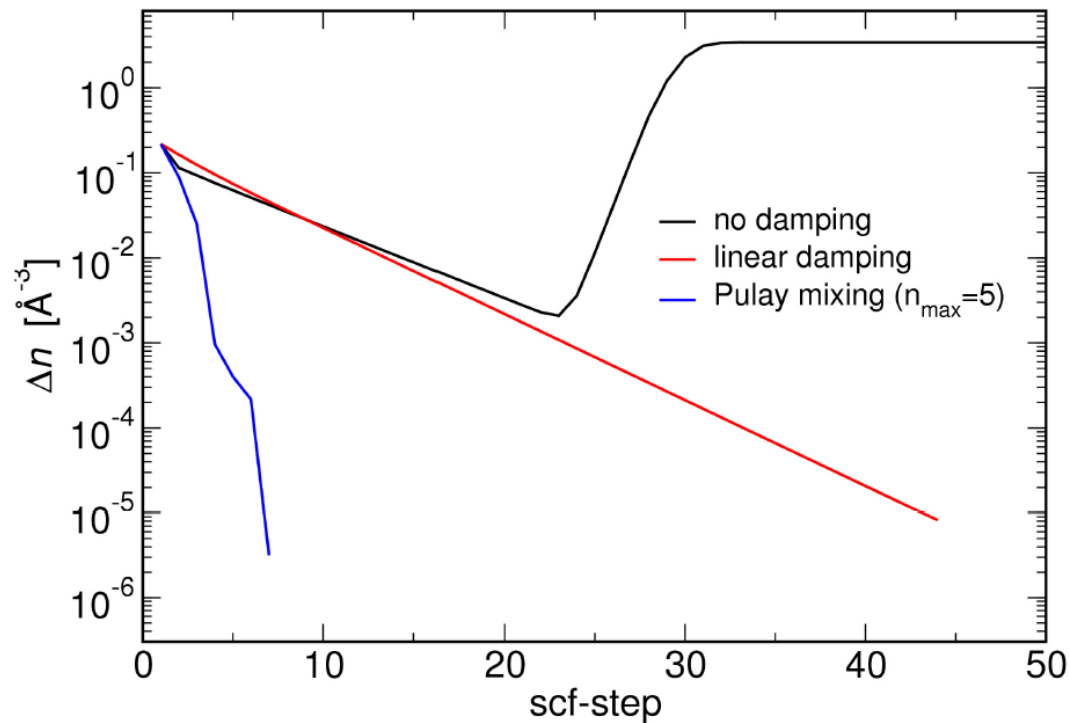- Kerker mixing: large-G components in $n(G)$ cause charge sloshing; preconditioning of density:

$$n_{in}^i(G) = n_{in}^{i-1}(G) + \alpha \frac{G^2}{G^2+G_{max}^2}(n_{out}^{i-1}(G) - n_{in}^{i-1}(G))$$

Can be combined with Pulay/Broyden mixing as well   *Phys. Rev. B 23, 3082 (1981)*

Density mixing

- Smart mixing can strongly accelerate convergence (and counter charge sloshing)

- In case of convergence problems: increase included electron density history and decrease mixing weight

Taken from „Making electronic structure theory work"