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 \( k \)
  \( k \) corresponds to a vector in the Brillouin zone
- all electronic states can be indexed by this quantum number
  \[ \Psi_k \]
- in a one-electron theory, one can introduce a second index, corresponding to the one electron band \( n \)
  \[ \psi_{n,k}(\mathbf{r}) \]
  the Bloch theorem implies that the (single electron) wavefunctions observe the equations
  \[ \psi_{n,k}(\mathbf{r} + \mathbf{\tau}) = \psi_{n,k}(\mathbf{r}) e^{i k \mathbf{\tau}}, \]
  where \( \mathbf{\tau} \) 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

\[ \rho_e(r) = \sum_n \int d^3k f_{n,k} \psi_{n,k}(r) \psi_{n,k}^*(r) \]

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

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

\[ \left( -\frac{\hbar^2}{2m_e} \Delta + V^{\text{eff}}(r, \{\rho_e(r')\}) \right) \psi_{n,k}(r) = \varepsilon_{n,k} \psi_{n,k}(r) \]

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

\( \rho_{\text{ion}} \) is the ionic charge distribution.
**Plane waves**

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

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

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

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

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

\[ \rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}, \]

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

- 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

\[ x_1 = \frac{n_1}{N} \quad \tau_1 \]

\[ \nu_1 = \frac{n_1 \pi}{\tau_1} \]

\[ C_{rnk} = \sum_G C_{Gnk} e^{iGr} \quad C_{Gnk} = \frac{1}{N_{\text{FFT}}} \sum_r C_{rnk} e^{-iGr} \quad \psi_{n,k}(\mathbf{r}) = \frac{1}{\Omega^{1/2}} C_{rnk} e^{i\mathbf{k} \cdot \mathbf{r}}. \]
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)

- **practical reason:**
  the total energy expressions and the Hamiltonian $H$ 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 $H\psi$ is exceedingly efficient using FFT’s
Computational reason

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

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

and using the convention $\langle r|G+k\rangle = \frac{1}{\Omega^{1/2}} e^{i(G+k)r} \rightarrow \langle G+k|\psi_{n,k}\rangle = C_{Gnk}$

- kinetic energy:

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

- local potential:

$$\langle G+k|V|\psi_{n,k}\rangle = \frac{1}{N_{\text{FFT}}} \sum_r V_r C_{r\nu k} e^{-iGr} \quad N_{\text{FFT}} \log N_{\text{FFT}}$$

- if $H$ 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

\[ \psi_{G+k} \xrightarrow{\text{FFT}} \psi_r \xrightarrow{} V_r \]

\[ \langle k+G|V|\psi \rangle \xrightarrow{\text{FFT}} \psi_r V_r \]
- the number of plane waves would exceed any practicle limits except for H and Li
  \[ \Rightarrow \text{pseudopotentials instead of exact potentials must be applied} \]

- 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**

![Diagram showing exact potential (interstitial region) vs pseudopotential]

- **Al**
  - 3p
  - 3s

- **effectiv Al atom**
  - 2p
  - 1s

- **PAW Al atom**
  - 3p
  - 3s

2p and 1s are nodeless !!!!

nodal structure is retained

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G. Kresse, Pseudopotentials (Part I)
Scattering approach

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

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

\( \phi_l \) are the regular solutions of the radial Schrödinger equation inside the spheres for the angular momentum quantum number \( l \) and the energy \( \varepsilon \)

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

- pseudopotential: select one specific energy \( \varepsilon \) in the centre of the valence band and replace the exact wavefunction \( \phi_l \) by a pseudo-wavefunction with \( \tilde{\phi}_l \)

\[
\frac{\partial \log \tilde{\phi}_l(r, \varepsilon)}{\partial r} \bigg|_{r_c} = \frac{\partial \log \phi_l(r, \varepsilon)}{\partial r} \bigg|_{r_c}
\]
• obviously one would like to get the right distribution of charge between the spheres and the interstitial region as well
→ 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 \( \varepsilon \) but also in a small energy interval around \( \varepsilon \)

\[
\left. \frac{\partial}{\partial \varepsilon} \left( \frac{\partial \log \phi_l(r, \varepsilon)}{\partial r} \right) \right|_{r_c} = \left. \frac{\partial}{\partial \varepsilon} \left( \frac{\partial \log \tilde{\phi}_l(r, \varepsilon)}{\partial r} \right) \right|_{r_c} \quad \forall l
\]
Pseudopotential generation

- all-electron calculation for a reference atom
- chose energies $\varepsilon_l$ 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:
  \[ \tilde{\phi}(r_c)^{(n)} = \phi(r_c)^{(n)} \quad \text{for} \ n = 0, \ldots, 2 \quad (n) \text{ is the } n\text{.th derivative} \]
  \[ 4\pi \int_0^{r_c} \tilde{\phi}(r)^2 r^2 dr = 4\pi \int_0^{r_c} \phi(r)^2 r^2 dr \quad \text{norm-conservation condition} \]
- 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**:

\[
|\psi_n\rangle = |\tilde{\psi}_n\rangle - \sum_{\text{atoms}} |\tilde{\phi}_{lme}\rangle c_{lme} + \sum_{\text{atoms}} |\phi_{lme}\rangle c_{lme}
\]

\[
\text{exact} \quad = \quad \text{pseudo (node less) plane waves} \quad - \quad \text{pseudo–onsite radial grids} \quad + \quad \text{exact onsite radial grids}
\]

no interaction between different spheres and plane waves ⇒ **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 \( \rho_e \), set up the Schrödinger equation, and solve the Schrödinger equation to obtain wavefunctions \( \psi_n(r) \)

\[
\left( -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r, \{\rho_e(r')\}) \right) \psi_n(r) = \varepsilon_n \psi_n(r) \quad n = 1, \ldots, N_e/2
\]

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

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

new Schrödinger equation \( \Rightarrow \) iteration
**Self-consistency scheme**

- **trial-charge** $\rho_{in}$ and **trial-wavevectors** $\psi_n$

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

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

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

- **refinement of density** $\rho_{in}, \rho_{out} \Rightarrow \text{new } \rho_{in}$

- **refinement of wavefunctions**: blocked Davidson like algorithm

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

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

\[ \{ \psi_n | n = 1, \ldots, N_{\text{bands}} \} \]

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

\[ |R(\psi_n)\rangle = (H - \varepsilon_{\text{app}} S) |\psi_n\rangle \quad \varepsilon_{\text{app}} = \langle \psi_n | H | \psi_n \rangle \]

\[ H \psi_n \] 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 Newton's 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.

\[
\begin{array}{cccccc}
\text{LO} & \text{SH} & \text{LA} & \text{ZO} & \text{SH} & \text{ZA} \\
\end{array}
\]

Forces $\Rightarrow$ force constants

- Symmetry is not used !!!

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

Not possible presently
Pseudopotentials (Part II) and PAW

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Overview

- pseudopotential basics
- normconserving pseudopotentials
  adopted pseudization strategy
- from normconserving to ultrasoft pseudopotentials
- the PAW method
- where to be careful?
  - local pseudopotentials
  - simultaneous representation of valence and semi-core states
  - magnetic calculations
Normconserving pseudopotentials: General strategy

- all-electron calculation for a reference atom
  (rhfsp)
- pseudization of valence wave functions
  (rhfsp)
- chose local pseudopotential and factorize
  (fourpot3)
- un-screening of atomic potential to obtained ionic pseudopotential
  (fourpot3)
Pseudization of valence wave functions

different schemes have been proposed in literature, but the general strategy is always similar

- calculate exact all-electron wave function \( \phi(r) \)
- replace exact \( \phi(r) \) inside pseudization radius by a suitable “soft” pseudo wave function \( \tilde{\phi}(r) \) must fulfill some continuity conditions

\[
\tilde{\phi}(r) = \begin{cases} 
\sum_i \alpha_i \beta_i(r) & r < r_c \\
\phi(r) & r \geq r_c 
\end{cases}
\]

\( \tilde{\phi}(r_c)^{(n)} = \phi(r_c)^{(n)} \) for \( n = 0, \ldots, 2 \)

- possibly impose norm conservation condition

\[
4\pi \int_0^{r_c} \tilde{\phi}(r)^2 r^2 \, dr = 4\pi \int_0^{r_c} \phi(r)^2 r^2 \, dr
\]
Which expansion set should one use?

- many different basis sets have been proposed in the literature
  presently the two most prominent ones are
  - polynomials (Troullier and Martins)
    \[ \tilde{\phi}(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12} \]
  - spherical Bessel-functions (RRKJ—Rappe, Rabe, et. al.)
    \[ \tilde{\phi}(r) = \sum_{i=1}^{3(4)} \alpha_i j_l(q'_i r) \]
    with \( q'_i \) such that \( \frac{j_l(q'_i r_c)'}{j_l(q'_i r_c)} = \frac{\phi(r_c)'}{\phi(r_c)} \),

- the last one is the standard scheme for VASP pseudopotentials
  the basis set I use is generally minimal (3 or sometimes 4 Bessel-functions)
  for PAW and US pseudopotentials only 2 spherical Bessel-functions are required
Why are spherical Bessel-functions so convenient

close analogy between plane waves and spherical Bessel-functions

- the required cutoff can be calculated directly from the expansion set

\[ \tilde{\phi}(r) = \sum_{i=1}^{3(4)} \alpha_i j_i(q_i^l r) \]

find maximum \( q_i \) ⇒ \( E_{\text{cut}} \approx \frac{\hbar^2}{2m_e} \max(q_i)^2 \times 1.5 \)

- I always use a minimal basis set

in the original RRKJ scheme, more spherical Bessel-functions were used, and the wave functions were optimized for a selected cutoff

our tests indicate that this is contra-productive
Factorization


- chose local reference potential $V_{\text{loc}}$
- construct a projector such that $\langle p|\tilde{\phi}\rangle = 1$

$$|p\rangle \propto \left(-\frac{\hbar^2}{2m_e}\Delta + V_{\text{loc}} - \varepsilon\right)|\tilde{\phi}\rangle$$

- the factorized Hamiltonian is given by

$$H = -\frac{\hbar^2}{2m_e}\Delta + V_{\text{loc}} + |p\rangle\langle p|$$

with

$$D = \langle \tilde{\phi}| \left(\frac{\hbar^2}{2m_e}\Delta - V_{\text{loc}} + \varepsilon\right)|\tilde{\phi}\rangle$$

one recognizes immediately that:

$$\langle \tilde{\phi}| \left(-\frac{\hbar^2}{2m_e}\Delta + V_{\text{loc}} + |p\rangle\langle p|\right)|\tilde{\phi}\rangle = \varepsilon \langle \tilde{\phi}|\tilde{\phi}\rangle$$
What have we accomplished at this point

- The exact wavefunction has been replaced by its pseudo counterpart and a “pseudo” Hamiltonian has been constructed

\[
\left( -\frac{\hbar^2}{2m_e} \Delta + V_{AE} \right) |\phi\rangle = \epsilon |\phi\rangle \Rightarrow
\]

\[
\left( -\frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} + |p\rangle D\langle p| \right) |\tilde{\phi}\rangle = \epsilon |\tilde{\phi}\rangle
\]

- At the energy \( \epsilon \), \( \phi \) and \( \tilde{\phi} \) are identical outside of the cutoff radius

- \( \phi \) and \( \tilde{\phi} \) have the same norm inside the cutoff radius \( \rightarrow \) at the energy \( \epsilon + \delta \epsilon \phi \) and \( \tilde{\phi} \) are identical outside of the cutoff radius
**Two reference energies**

- Pseudize at two reference energies: \( \{ \phi_i | i = 1, 2 \} \)

- Construct two projectors such that
  \[ \langle p_i | \tilde{\phi}_j \rangle = \delta_{ij} \quad \text{for all } i, j \]

  \[ |p_i\rangle = \sum_j \alpha_{ij} \left( -\frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} - \varepsilon_j \right) |\tilde{\phi}_j\rangle \]

- Factorized Hamiltonian is given by
  \[ H = -\frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} + \sum_{ij} |p_i\rangle D_{ij} \langle p_j| \]

  \[ D_{ij} = \langle \tilde{\phi}_i | \left( -\frac{\hbar^2}{2m_e} \Delta - V_{\text{loc}} + \varepsilon_j \right) |\tilde{\phi}_j\rangle \]

  One recognizes immediately that:
  \[ \langle \tilde{\phi}_i | H | \tilde{\phi}_j \rangle = \varepsilon_j \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle \]
Two reference energies: practical considerations

- the pseudo wavef. must fulfill a **generalized normconserv. condition**:

\[
4\pi \int_0^{r_c} \tilde{\phi}_i(r)\tilde{\phi}_j(r)r^2 dr = 4\pi \int_0^{r_c} \phi_i(r)\phi_j(r)r^2 dr \quad \forall i, j
\]

- in the VASP PP generation program only

\[
\int_0^{r_c} \tilde{\phi}_i(r)\tilde{\phi}_i(r)r^2 dr = \int_0^{r_c} \phi_i(r)\phi_i(r)r^2 dr
\]

is enforced

- to correct for this error, augmentation charges would be required, but these are neglected

as a result \(D_{ij}\) is not Hermitian

\[
D_{ij} = \langle \tilde{\phi}_i | \left( \frac{\hbar^2}{2m_e} \Delta - V_{\text{loc}} + \varepsilon_j \right) | \tilde{\phi}_j \rangle
\]

off-diagonal elements are averaged to make the matrix \(D\) symmetric
US pseudopotentials, very similar to NC pseudopotentials

- psuedize at two reference energies
- construct two projectors such that \( \langle p_i | \tilde{\phi}_j \rangle = \delta_{ij} \) for all \( i, j \)

\[
|p_i\rangle = \sum_j \alpha_{ij} \left( -\frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} - \epsilon_j \right)|\tilde{\phi}_j\rangle
\]

- the factorized Hamiltonian and overlap operator are given by

\[
H = -\frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} + \sum_{ij} |p_i \rangle D_{ij} \langle p_j | \quad S = 1 + \sum_{ij} |p_i \rangle Q_{ij} \langle p_j |
\]

\[
D_{ij} = \langle \tilde{\phi}_i | \left( \frac{\hbar^2}{2m_e} \Delta - V_{\text{loc}} + \epsilon_j \right) |\tilde{\phi}_j \rangle + \epsilon_j Q_{ij}
\]

\[
Q_{ij} = \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle
\]

one can show that: \( \langle \tilde{\phi}_i | H | \tilde{\phi}_j \rangle = \langle \tilde{\phi}_i | S | \tilde{\phi}_j \rangle \epsilon_j \)
What does all that mean?

let us look again at the definition of $D_{ij}$

$$D_{ij} = \langle \tilde{\phi}_i | \left( \frac{\hbar^2}{2m_e} \Delta - V_{\text{loc}} + \varepsilon_j \right) | \tilde{\phi}_j \rangle + \varepsilon_j Q_{ij}$$

$$= \langle \tilde{\phi}_i | \frac{\hbar^2}{2m_e} \Delta - V_{\text{loc}} | \tilde{\phi}_j \rangle + \varepsilon_j (\langle \tilde{\phi}_i | \tilde{\phi}_j \rangle + Q_{ij})$$

$$= -\langle \tilde{\phi}_i | - \frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} | \tilde{\phi}_j \rangle + \varepsilon_j (\langle \tilde{\phi}_i | \tilde{\phi}_j \rangle + \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle)$$

$$= -\langle \tilde{\phi}_i | - \frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} | \tilde{\phi}_j \rangle + \langle \phi_i | \varepsilon_j | \phi_j \rangle$$

$$= -\langle \tilde{\phi}_i | - \frac{\hbar^2}{2m_e} \Delta + V_{\text{loc}} | \tilde{\phi}_j \rangle + \langle \phi_i | - \frac{\hbar^2}{2m_e} \Delta + V_{\text{AE}} | \phi_j \rangle$$

energy pseudo onsite

energy AE onsite
**US-PP: what they really do**

- Character of wave function:  
  \[ c_i = \langle \tilde{p}_i | \tilde{\Psi}_n \rangle \quad \langle p_i | \tilde{\phi}_j \rangle = \delta_{ij} \]

  onsite occupancy matrix (or density matrix):  
  \[ \rho_{ij} = \langle \tilde{\Psi}_n | p_i \rangle \langle p_j | \tilde{\Psi}_n \rangle \]

- Energy is the sum of three terms
  \[ E = -\Delta + V_{\text{loc}} - \rho_{ij} \langle \tilde{\phi}_i | - \Delta + V_{\text{loc}} | \tilde{\phi}_j \rangle + \rho_{ij} \langle \phi_i | - \Delta + V_{\text{AE}} | \phi_j \rangle \]

- US-PP method is in principle an exact frozen core all-electron method.
Mixed basis set with an implicit dependency

- US-PP’s carry a small rucksack, with two additional sets of basis functions defined around each atomic site
  - one for the soft pseudo-wave functions \( \{ \tilde{\phi}_i \} \)
  - one for the AE wave functions \( \{ \phi_i \} \)

- for each atomic sphere the energy is evaluated using these two sets and the calculated energy is subtracted and added, respectively

- the onsite occupancy matrix (density matrix) for these two sets is calculated from the plane wave coefficients

\[
\rho_{ij} = \langle \tilde{\Psi}_n | p_i \langle p_j | \tilde{\Psi}_n \rangle
\]

- PAW inspired formulation
Practical considerations

- The US-PP method cannot be implemented exactly, since currently no method exists to handle the rapid variations of the all-electron wave functions.
  A regular grid does not work, maybe wavelets would be an option.

- In practice, I therefore adopt a modified prescription for US-PP’s:

  \[
  \phi(r) \Rightarrow \phi_{\text{norm-conserving}}(r)
  \]

  Augmentation charge:
  \[
  Q_{ij}(r) = \phi_{i}^{\text{nc}}(r)\phi_{j}^{\text{nc}}(r) - \tilde{\phi}_{i}(r)\tilde{\phi}_{j}(r)
  \]

- These US-PP’s yield exactly the same results as the corresponding NC-PP’s, but at much lower cutoffs.

G. Kresse, Pseudopotentials (Part II) and PAW
Why are US-PP’s softer

• pseudo wave function is represented as a sum of two spherical Bessel functions instead of three

\[ \tilde{\phi}(r) = \sum_{i=1}^{2} \alpha_i j_l(q_i' r) \]

with \( q_i' \) such that

\[ \frac{j_l(q_i' r_c)'}{j_l(q_i' r_c)} = \frac{\phi(r_c)'}{\phi(r_c)}, \]

• additionally \( r_c \) can be increased compared to NC potentials

there is no need to represent the charge distribution of the AE wave function, since this is done by the augmentation

the pseudo wave functions follow remarkably well the AE wave functions, even for values much smaller than \( r_c \)

• basis sets are roughly a factor 2-3 smaller
Example for this behavior

e.g. Cu (NC)

Cu (US)
The role of the local potential

- the local potential needs to describe scattering properties for radial quantum numbers not included in the projectors
  - much underestimated problem
  - resulting errors can be 1-2% in the lattice constant
- the tails of d electrons (transition metals) or p electrons (oxygen) overlap into the pseudization region
  - they are picked up as high l components (FLAPW)
- ideally one would like to use very attractive local potentials
  - but $\rightarrow$ ghost-state problem
- in most cases, compromises must be made
Ghost-state problems

- particularly severe for alkali, alkali-earth and early transition metals
- the more attractive the local potential and the smaller $r_c$, the more likely it is to have a ghost-state; Zr example

\[ x_l(E) \]

\[ s, p, d, f, g \]

\[ E \text{ (Ry)} \]

\[ x_l(E) \]

\[ s, p, d, f, g \]

\[ E \text{ (Ry)} \]
solution: treat semi-core states as valence

Pseudopotential generation in practice: the PSCTR file

TITEL = US 0
LULTRA = T use ultrasoft PP?
RWIGS = 1.40 nn distance

ICORE = 2
NE = 100
LCOR = .TRUE.
QCUT = -1

Description

<table>
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<th>E</th>
<th>TYP</th>
<th>RCUT</th>
<th>TYP</th>
<th>RCUT</th>
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<td>23</td>
<td>1.40</td>
</tr>
<tr>
<td>0 0</td>
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</tr>
<tr>
<td>1 0</td>
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<td>23</td>
<td>1.55</td>
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<tr>
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<td>1.13</td>
<td>23</td>
<td>1.55</td>
</tr>
<tr>
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<td>7</td>
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<td>7</td>
<td>1.55</td>
</tr>
</tbody>
</table>

- Kohn-Sham equation

\[ E = \sum_n f_n \langle \Psi_n \rangle - \frac{1}{2} \Delta \langle \Psi_n \rangle + E_H [n + n_Z] + E_{xc}[n]. \]

- frozen core approximation

for the valence electrons, a transformation from the pseudo to the AE wavefunction is defined:

\[ |\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_{\text{sites}} (|\phi_{lm\varepsilon}\rangle - |\tilde{\phi}_{lm\varepsilon}\rangle) \langle \tilde{\rho}_{lm\varepsilon} | \tilde{\Psi}_n\rangle \]

- $lm$ is an index for the angular and magnetic quantum numbers
- $\varepsilon$ refers to a particular reference energy
- $\tilde{\rho}_{lm\varepsilon}$ projector function
- $\tilde{\phi}_{lm\varepsilon}$ partial wave
**PAW: basic idea**

- **transformation:** \(|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum (|\phi_{lm\epsilon}\rangle - |\tilde{\phi}_{lm\epsilon}\rangle) \langle \tilde{p}_{lm\epsilon}|\tilde{\Psi}_n\rangle\)

- the “character” of an arbitrary pseudo-wavefunction \(\tilde{\Psi}_n\) at one site can be calculated by multiplication with the projector function at that site
  \[c_{lm\epsilon} = \langle \tilde{p}_{lm\epsilon}|\tilde{\Psi}_n\rangle\]

- inside each sphere the wavefunctions can be determined:
  \(|\tilde{\Psi}_n\rangle^{\text{sphere}} = (\approx) \sum_{lm\epsilon} |\tilde{\phi}_{l'm'e'}\rangle c_{lm\epsilon}\)
  \(|\Psi_n\rangle^{\text{sphere}} = (\approx) \sum_{lm\epsilon} |\phi_{l'm'e'}\rangle c_{lm\epsilon}\)

- the projector functions must be dual to the pseudo-wavefunction
  \[\langle \tilde{p}_{lm\epsilon}|\tilde{\phi}_{l'm'e'}\rangle = \delta_{l,l'} \delta_{m,m'} \delta_{\epsilon,\epsilon'}\]
**PAW: addidative augmentation**

- character of wavefunction: 
  \[ c_{lmc} = \langle \tilde{p}_{lmc} | \tilde{\Psi}_n \rangle \]

- \[ |\Psi_n\rangle = |\tilde{\Psi}_n\rangle - \sum |\tilde{\phi}_{lmc}\rangle c_{lmc} + \sum |\phi_{lmc}\rangle c_{lmc} \]

- same trick works for
  - wavefunctions
  - charge density
  - kinetic energy
  - exchange correlation energy
  - Hartree energy
Derivation of the PAW method is straightforward

- for instance, the kinetic energy is given by
  \[
  E_{\text{kin}} = \sum_n f_n \langle \Psi_n | - \Delta | \Psi_n \rangle
  \]

- by inserting the transformation \((i = lm\epsilon)\)
  \[
  |\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i \langle |\phi_i\rangle - |\tilde{\phi}_i\rangle \rangle \langle \tilde{p}_i | \tilde{\Psi}_n \rangle.
  \]

  into \(E_{\text{kin}}\) one obtains: \(E_{\text{kin}} = \tilde{E} - \tilde{E}^1 + E^1\) (assuming completeness)

- \(\rho_{ij}\) is an on-site density matrix: \(\rho_{ij} = \sum_n f_n c_i^* c_j\)
the pseudo-wavefunctions do not have the same norm as the AE wavefunctions inside the spheres

to deal with long range electrostatic interactions between spheres

a soft compensation charge \( \hat{n} \) is introd. (similar to FLAPW)

Hartree energy becomes: \( E_H = \tilde{E} - \tilde{E}^1 + E^1 \)

\[ E_H[\hat{n} + \hat{n}^1] - \sum_{\text{sites}} E_H[\hat{n} + \hat{n}^1] + \sum_{\text{sites}} E_H[n^1 + \hat{n}^1] \]

\( \hat{n}^1 \) pseudo-charge at one site     \( \hat{n}^1 \) compensation charge at site
PAW energy functional


- total energy becomes a sum of three terms $E = \tilde{E} + E^1 - \tilde{E}^1$

\[
\tilde{E} = \sum_n f_n \langle \tilde{\Psi}_n \rangle - \frac{1}{2} \Delta \langle \tilde{\Psi}_n \rangle + E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] +
\]

\[
E_H[\tilde{n} + \hat{n}] + \int v_H[\tilde{n}_Zc](\tilde{n}(r) + \hat{n}(r)) \, d^3r + U(R, Z_{ion})
\]

\[
\tilde{E}^1 = \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i \rangle - \frac{1}{2} \Delta \langle \tilde{\phi}_j \rangle + E_{xc}[\tilde{n}_1 + \hat{n} + \tilde{n}_c] +
\]

\[
\overline{E_H[\tilde{n}_1 + \hat{n}]} + \int_{\Omega_r} v_H[\tilde{n}_Zc](\tilde{n}_1(r) + \hat{n}(r)) \, d^3r \right\}
\]

\[
E^1 = \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \phi_i \rangle - \frac{1}{2} \Delta \langle \phi_j \rangle + E_{xc}[n^1 + n_c] +
\]

\[
\overline{E_H[n^1]} + \int_{\Omega_r} v_H[n_{Zc}](n^1(r)) \, d^3r \right\}
\]
• $\tilde{E}$ is evaluated on a regular grid

Kohn Sham functional evaluated in a plane wave basis set

with additional compensation charges to account for the incorrect norm of the
pseudo-wavefunction (very similar to ultrasoft pseudopotentials)

$$\tilde{n} = \sum_n f_n \tilde{\Psi}_n \tilde{\Psi}_n^*$$  pseudo charge density

$\hat{n}$  compensation charge

• $E^1$ and $\tilde{E}^1$ are evaluated on radial grids centered around each ion

Kohn-Sham energy evaluated for basis sets $\{\tilde{\psi}_i\}$ and $\{\psi_i\}$

these terms correct for the shape difference between the pseudo and AE
wavefunctions

• no cross-terms between plane wave part and radial grids exist
Generals scheme

\[ \text{AE} = \text{pseudo + compens. pseudo+comp. onsite} + \text{AE-onsite} \]

applies to all quantities

- the original derivation of US-PP is somewhat “problematic”
  it’s more like accepting things than understanding them

- in fact, the equations for US-PP’s can be derived rigidly from the PAW functional
  by linearisation of the on-site terms $E^1$ and $\tilde{E}^1$ around the atomic reference
  configuration
  this shows the close relation between both approaches

- but it also indicates when US-PP’s might be problematic:
  the more the environment differs from the reference state the less accurate US-PP
  are

- our tests indicate that magnetism is the strongest perturbation

in other cases, US-PP and the PAW yield almost identical results
Construction of PAW potentials

- first an AE calculation for a reference atom is performed
- the AE wavefunctions of the valence states are pseudised

projectors are constructed as

\[ |p_i⟩ = \sum_j \alpha_{ij} \left( -\frac{\hbar^2}{2m_e} \Delta + V_{loc} - \varepsilon_j \right) |\tilde{φ}_j⟩ \]

they must obey

\[ ⟨\tilde{p}_i | \tilde{φ}_n⟩ = δ_{i,n} \]

projectors are dual to the pseudo wavefunction

- to have a rather complete set of projectors, two partial waves for each quantum channel \( lm \) are constructed
results for the bond length of several molecules obtained with the US-PP, PAW and AE approaches
• plane wave cutoffs were around 200-400 eV
• US-PP and the PAW method give the same results within 0.1-0.3%
• well converged relaxed core AE calculations yield identical results
<table>
<thead>
<tr>
<th></th>
<th>US-PP (data base)</th>
<th>US-PP (special)</th>
<th>PAW</th>
<th>AE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1.447</td>
<td>1.447</td>
<td>1.446</td>
<td></td>
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<tr>
<td>Li₂</td>
<td>5.127</td>
<td>5.120</td>
<td>5.120</td>
<td></td>
</tr>
<tr>
<td>Be₂</td>
<td>4.524</td>
<td>4.520</td>
<td>4.521</td>
<td></td>
</tr>
<tr>
<td>Na₂</td>
<td>5.667</td>
<td>5.663</td>
<td>5.67</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2.163</td>
<td>2.141 (2.127)</td>
<td>2.141  (2.128)</td>
<td>2.129</td>
</tr>
<tr>
<td>N₂</td>
<td>2.101</td>
<td>2.077 (2.066)</td>
<td>2.076  (2.068)</td>
<td>2.068</td>
</tr>
<tr>
<td>F₂</td>
<td>2.696</td>
<td>2.640 (2.626)</td>
<td>2.633  (2.621)</td>
<td>2.615</td>
</tr>
<tr>
<td>P₂</td>
<td>3.576</td>
<td>3.570</td>
<td>3.570</td>
<td>3.572</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.840 (1.834)</td>
<td>1.839 (1.835)</td>
<td>1.833</td>
<td></td>
</tr>
<tr>
<td>α(H₂O) (°)</td>
<td>105.3 (104.8)</td>
<td>105.3 (104.8)</td>
<td>105.0</td>
<td></td>
</tr>
<tr>
<td>BF₃</td>
<td>2.476 (2.470)</td>
<td>2.476 (2.470)</td>
<td>2.464</td>
<td></td>
</tr>
<tr>
<td>SiF₄</td>
<td>2.953 (2.948)</td>
<td>2.953 (2.948)</td>
<td>2.949</td>
<td></td>
</tr>
</tbody>
</table>

Values in parentheses were obtained with hard potentials at 700 eV

Superscript:

- **b** Gaussian 94
400 eV plane wave cutoff

<table>
<thead>
<tr>
<th>xc meth</th>
<th>PBE (PAW)</th>
<th>PBE (AE\textsuperscript{a})</th>
<th>rPBE\textsuperscript{b} (PAW)</th>
<th>rPBE\textsuperscript{b} (AE\textsuperscript{a})</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
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<td>11.66</td>
<td>11.15</td>
<td>11.18</td>
<td>11.24</td>
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<tr>
<td>N\textsubscript{2}</td>
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<td>10.53</td>
<td>10.09</td>
<td>10.09</td>
<td>9.91</td>
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<tr>
<td>NO</td>
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<td>7.45</td>
<td>6.95</td>
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<td>5.78</td>
<td>5.22</td>
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</table>


results for the equilibrium lattice constant \( a \), cohesive energy \( E_{\text{coh}} \) (with respect to non spin polarised atoms) and bulk modulus \( B \) for several materials calculated with the PAW, US-PP, and the FLAPW approach.

<table>
<thead>
<tr>
<th></th>
<th>( a (\text{\AA}^3) )</th>
<th>( E_{\text{coh}} ) (eV)</th>
<th>( B ) (MBar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>diamond</td>
<td>US-PP (current)</td>
<td>3.53</td>
<td>-10.15</td>
</tr>
<tr>
<td></td>
<td>PAW (current)</td>
<td>3.53</td>
<td>-10.13</td>
</tr>
<tr>
<td></td>
<td>LAPW (^a)</td>
<td>3.54</td>
<td>-10.13</td>
</tr>
<tr>
<td></td>
<td>PAW (^a)</td>
<td>3.54</td>
<td>-10.16</td>
</tr>
<tr>
<td>silicon</td>
<td>US-PP (current)</td>
<td>5.39</td>
<td>-5.96</td>
</tr>
<tr>
<td></td>
<td>PAW (current)</td>
<td>5.39</td>
<td>-5.96</td>
</tr>
<tr>
<td></td>
<td>LAPW (^a)</td>
<td>5.41</td>
<td>-5.92</td>
</tr>
<tr>
<td></td>
<td>PAW (^a)</td>
<td>5.38</td>
<td>-6.03</td>
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</tbody>
</table>
results for the equilibrium lattice constant $a$, cohesive energy $E_{\text{coh}}$ (with respect to non spin polarised atoms) and bulk modulus $B$ for several materials calculated with the the PAW, US-PP, and the FLAPW approach.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>$a$ (Å$^3$)</th>
<th>$E_{\text{coh}}$ (eV)</th>
<th>$B$ (MBar)</th>
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<tr>
<td>bcc V</td>
<td>US-PP (current)</td>
<td>2.93</td>
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</tr>
<tr>
<td></td>
<td>PAW (current)</td>
<td>2.93</td>
<td>-9.39</td>
<td>2.09</td>
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<tr>
<td></td>
<td>LAPWa</td>
<td>2.94</td>
<td>-9.27</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>PAWa</td>
<td>2.94</td>
<td>-9.39</td>
<td>2.00</td>
</tr>
<tr>
<td>fcc Ca</td>
<td>US-PP (current)</td>
<td>5.34</td>
<td>-2.20</td>
<td>0.0181</td>
</tr>
<tr>
<td></td>
<td>PAW (3s3p val)</td>
<td>5.34</td>
<td>-2.19</td>
<td>0.0187</td>
</tr>
<tr>
<td></td>
<td>PAW (3p val)</td>
<td>5.34</td>
<td>-2.20</td>
<td>0.0187</td>
</tr>
<tr>
<td></td>
<td>LAPWa</td>
<td>5.33</td>
<td>-2.20</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>PAWa</td>
<td>5.32</td>
<td>-2.24</td>
<td>0.019</td>
</tr>
</tbody>
</table>
results for the equilibrium lattice constant $a$, cohesive energy $E_{\text{coh}}$ (with respect to non spin polarised atoms) and bulk modulus $B$ for several materials calculated with the PAW, US-PP, and the FLAPW approach:

<table>
<thead>
<tr>
<th></th>
<th>$a$(Å$^3$)</th>
<th>$E_{\text{coh}}$(eV)</th>
<th>$B$ (MBar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
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<tr>
<td>US-PP(current)</td>
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<td>0.97</td>
</tr>
<tr>
<td>PAW(3s3p val)</td>
<td>5.35</td>
<td>-6.32</td>
<td>1.01</td>
</tr>
<tr>
<td>PAW(3p val)</td>
<td>5.31</td>
<td>-6.36</td>
<td>1.00</td>
</tr>
<tr>
<td>LAPW$^a$</td>
<td>5.33</td>
<td>-6.30</td>
<td>1.10</td>
</tr>
<tr>
<td>PAW$^a$</td>
<td>5.34</td>
<td>-6.36</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Semi-core states; alkali and alkali earth metals

- from a practical point of view, an accurate treatment of these elements in ionic compounds is very important: oxides e.g. perovskites
- strongly ionized, and small core radii around 2.0 a.u. (1 Å) are desirable
- e.g. Ca: one would like to treat 3s, 3p, 4s states as valence states

![Wavefunction chart]

It is very difficult to represent the charge distribution of the 3s and 4s states equally well in a pseudopotential approaches.

General problem for pseudopotentials
Semi core states

in VASP, NC wavefunctions describe the augmentation charges

\[ Q_{ij}(r) = \phi_i^{nc}(r)\phi_j^{nc}(r) - \tilde{\phi}_i(r)\tilde{\phi}_j(r) \]

it is very difficult to construct accurate NC-PP for 3s and 4s (mutual orthogonality)

node in 4s must be included in some way if one succeeds, the augmentation charges become quite hard, and require fine regular grids PAW method is the best solution to this problem
### PAW — US-PP method: atoms

Comparison of GGA PAW, US-PP and scalar relativistic all-electron calculations for O, N, Fe, Co and Ni magnetic energy:

\[ \Delta E_m = E_M(gs) - E_{NM}(4s^13d^{n-1}) \] (in eV)

<table>
<thead>
<tr>
<th></th>
<th>US-PP</th>
<th>PAW</th>
<th>AE</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>(2s^22p^4)</td>
<td>(2s^22p^4)</td>
<td>(2s^22p^4)</td>
</tr>
<tr>
<td>(\Delta E_m)</td>
<td>1.55</td>
<td>1.40</td>
<td>1.41</td>
</tr>
<tr>
<td>N</td>
<td>(2s^22p^3)</td>
<td>(2s^22p^3)</td>
<td>(2s^22p^3)</td>
</tr>
<tr>
<td>(\Delta E_m)</td>
<td>3.14</td>
<td>2.88</td>
<td>2.89</td>
</tr>
<tr>
<td>Fe</td>
<td>(3d^{6.2}4s^{1.8})</td>
<td>(3d^{6.2}4s^{1.8})</td>
<td>(3d^{6.2}4s^{1.8})</td>
</tr>
<tr>
<td>(\Delta E_m)</td>
<td>2.95</td>
<td>2.77</td>
<td>2.76</td>
</tr>
<tr>
<td>Co</td>
<td>(3d^{7.7}4s^{1.3})</td>
<td>(3d^{7.7}4s^{1.3})</td>
<td>(3d^{7.7}4s^{1.3})</td>
</tr>
<tr>
<td>(\Delta E_m)</td>
<td>1.40</td>
<td>1.32</td>
<td>1.31</td>
</tr>
<tr>
<td>Ni</td>
<td>(3d^94s^1)</td>
<td>(3d^94s^1)</td>
<td>(3d^94s^1)</td>
</tr>
<tr>
<td>(\Delta E_m)</td>
<td>0.54</td>
<td>0.52</td>
<td>0.52</td>
</tr>
</tbody>
</table>

For atoms the magnetisation is wrong by 5-10% with US-PP.
### Bulk properties of Fe

Energy differences between different phases of Fe

<table>
<thead>
<tr>
<th></th>
<th>FLAPW$^a$</th>
<th>PAW</th>
<th>US-AE</th>
<th>US-PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc Fe NM</td>
<td>373</td>
<td>372</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>bcc Fe FM</td>
<td>-73</td>
<td>-73</td>
<td>-73</td>
<td>-191</td>
</tr>
<tr>
<td>fcc Fe NM</td>
<td>78</td>
<td>61</td>
<td>62</td>
<td>62</td>
</tr>
<tr>
<td>hcp Fe NM</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>


- PAW and FLAPW give almost identical results.
- US-PP overestimates the magnetisation energy by around 5-10%.
- Calculations for other systems indicate that the accuracy of the PAW method for magnetic systems is comparable to other AE methods.
  - $\alpha$-Mn, bulk Cr and Cr surfaces, LaMnO$_3$ (perovskites).
Why do pseudopotentials fail in spin-polarised calculations

- non linear core corrections were included in the PP’s!
- pseudo-wavefunction for a normconserving pseudopotentials

![Wavefunction Plot]

- all electron
- pseudo

the peak in the d-wavefunction is shifted outward to make the PP softer

- similar compromises are usually made in US-pseudopotentials
- as a result, the valence-core overlap is artificially reduced and the spin enhancement factor $\xi(r)$ is overestimated

$$\xi(r) = \frac{m(r)}{n_{\text{valence}}(r) + n_{\text{core}}(r)}$$
## Oxides

CeO$_2$ and UO$_2$

<table>
<thead>
<tr>
<th></th>
<th>PAW</th>
<th>FLAPW</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a ($\text{Å}^3$)</td>
<td>5.47 Å</td>
<td>5.47 Å</td>
<td>5.41 Å</td>
</tr>
<tr>
<td>B</td>
<td>172 GPa</td>
<td>176 GPa</td>
<td>236 GPa</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>PAW</th>
<th>FLAPW</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>a ($\text{Å}^3$)</td>
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<td></td>
<td>5.46 Å</td>
</tr>
<tr>
<td>B</td>
<td>200 GPa</td>
<td></td>
<td>209 GPa</td>
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</table>
Computational costs, efficiency

- Code complexity of the kernel of course increases with PAW
  
<table>
<thead>
<tr>
<th>pseudopotentials</th>
<th></th>
</tr>
</thead>
</table>
  | local pseudopots  | low| 2000 lines  
  | NC-PP pseudopotential | low-medium | 7000 lines  
  | US-PP              | medium | 10 000 lines  
  | PAW                | medium-high | 15 000 lines  

- Parallelisation or error removal becomes progressively difficult

- Computational efficiency:

  Ge 64 atoms, 1 k-point (Γ), Alpha ev6 (500 MHz), 14 electronic cycles

<table>
<thead>
<tr>
<th>type</th>
<th>cutoff</th>
<th>time</th>
<th>total error per atom</th>
</tr>
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<tbody>
<tr>
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<td>140 eV</td>
<td>514 sec</td>
<td>400 meV</td>
</tr>
<tr>
<td>NC-PP</td>
<td>240 eV</td>
<td>1030 sec</td>
<td>10 meV</td>
</tr>
<tr>
<td>US-PP</td>
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<td>522 sec</td>
<td>10 meV</td>
</tr>
<tr>
<td>PAW</td>
<td>140 eV</td>
<td>528 sec</td>
<td>10 meV</td>
</tr>
</tbody>
</table>

The extra costs for PAW or US-PP’s at a fixed cutoff are small

PAW method is particularly good for transition metals and oxides
PAW advantages

- formal justification is very sound
- improved accuracy for:
  - magnetic materials
  - alkali and alkali earth elements, 3d elements (left of PT)
  - lathanides and actinides
- generation of datasets is fairly simple (certainly easier than for US-PP)
- AE wavefunction are available
- comparison to other methods:
  - all test indicate that the accuracy is as good as for other all electron methods (FLAPW, NUMOL, Gaussian)
  - efficiency for large system should be significantly better than with FLAPW