Pseudopotentials (Part II) and PAW

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Overview

- pseudopotential basics
- normconserving pseudopotentials

  adopted pseudization strategy

  G. Kresse, and J. Hafner, J. Phys.: Condens. Matter **6** (1994)
- from normconserving to ultrasoft pseudopotentials
- the PAW method

  G. Kresse, and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
- 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

  `(rhfsps)`

- pseudization of valence wave functions

  `(rhfsps)`

- 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

$$\tilde{\phi}(r) = \begin{cases} \sum_i \alpha_i \beta_i(r) & r < r_c \\ \phi(r) & r >= r_c \end{cases}$$

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

- possibly impose normconservation 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)

$$\boxed{\tilde{\phi}(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + c_8 r^8 + c_{10} r^{10} + c_{12} r^{12}}$$

  - spherical Bessel-functions (RRKJ—Rappe, Rabe, *et. al.*)

$$\boxed{\tilde{\phi}(r) = \sum_{i=1}^{3(4)} \alpha_i \, j_l(q_i' r)} \qquad \text{with } q_i' \text{ such that} \quad \frac{j_l(q_i' r_c)'}{j_l(q_i' r_c)} = \frac{\phi(r_c)'}{\phi(r_c)},$$

- 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

$$\tilde{\phi}(r) = \sum_{i=1}^{3(4)} \alpha_i \, j_l(q_i' r)$$

find maximum $q_i \Rightarrow$ $\boxed{E_{\rm cut} \approx \frac{\hbar^2}{2m_e} \max(q_i)^2 \times 1.5}$

- 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

required to speed up the calculations D.M. Bylander, et al., Phys. Rev. B **46**, 13756 (1992)

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

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

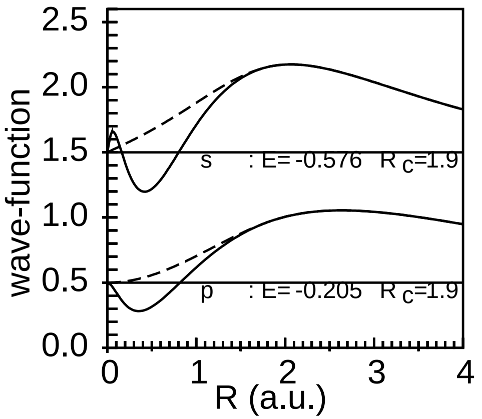
- the factorized Hamiltonian is given by

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

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

one recognizes immediately that: $\langle\tilde{\phi}|\left(-\frac{\hbar^2}{2m_e}\Delta + V_{\rm loc} + |p\rangle D\langle p|\right)|\tilde{\phi}\rangle = \varepsilon\langle\tilde{\phi}|\tilde{\phi}\rangle$

What have we acchived at this point



- the exact wavefunction has been replaced by it's pseudo counterpart and a "pseudo" Hamiltonian has been constructed

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V_{\mathrm{AE}}\right)|\phi\rangle = \varepsilon|\phi\rangle \Rightarrow$$

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

- at the energy ε, ϕ and $\tilde{\phi}$ are identical outside of the cutoff radius
- ϕ and $\tilde{\phi}$ have the same norm inside the cutoff radius $\rightarrow$ at the energy $\varepsilon + \delta\varepsilon$ ϕ 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 $\boxed{\langle p_i | \tilde{\phi}_j \rangle = \delta_{ij} \qquad \text{for all } i, j}$

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

- factorized Hamiltonian is given by

$$H = -\frac{\hbar^2}{2m_e}\Delta + V_{\text{loc}} + \sum_{ij} |p_i\rangle D_{ij} \langle p_j|$$

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

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:

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

- 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

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

  off-diagonal elements are averaged to make the matrix D symmetric

US pseudopotentials, very similar to NC pseudopotentials

- pseudize at two reference energies
- construct two projectors such that $\boxed{\langle p_i|\tilde{\phi}_j\rangle = \delta_{ij} \qquad \text{for all } i,j}$

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

- the factorized Hamiltonian and overlap operator are given by

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

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

one can show that: $\langle\tilde{\phi}_i|H|\tilde{\phi}_j\rangle = \langle\tilde{\phi}_i|S|\tilde{\phi}_j\rangle\varepsilon_j$

What does all that mean?

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

$$
\begin{aligned}
D_{ij} &= \langle\tilde{\phi}_i|\left(\frac{\hbar^2}{2m_e}\Delta - V_{\text{loc}} + \varepsilon_j\right)|\tilde{\phi}_j\rangle + \varepsilon_j Q_{ij} \\
&= \langle\tilde{\phi}_i|\frac{\hbar^2}{2m_e}\Delta - V_{\text{loc}}|\tilde{\phi}_j\rangle + \varepsilon_j(\langle\tilde{\phi}_i|\tilde{\phi}_j\rangle + Q_{ij}) \\
&= -\langle\tilde{\phi}_i| - \frac{\hbar^2}{2m_e}\Delta + V_{\text{loc}}|\tilde{\phi}_j\rangle + \varepsilon_j(\langle\tilde{\phi}_i|\tilde{\phi}_j\rangle + \langle\phi_i|\phi_j\rangle - \langle\tilde{\phi}_i|\tilde{\phi}_j\rangle) \\
&= -\langle\tilde{\phi}_i| - \frac{\hbar^2}{2m_e}\Delta + V_{\text{loc}}|\tilde{\phi}_j\rangle + \langle\phi_i|\varepsilon_j|\phi_j\rangle \\
&= -\underbrace{\langle\tilde{\phi}_i| - \frac{\hbar^2}{2m_e}\Delta + V_{\text{loc}}|\tilde{\phi}_j\rangle}_{\text{energy pseudo onsite}} + \underbrace{\langle\phi_i| - \frac{\hbar^2}{2m_e}\Delta + V_{\text{AE}}|\phi_j\rangle}_{\text{energy AE onsite}}
\end{aligned}
$$

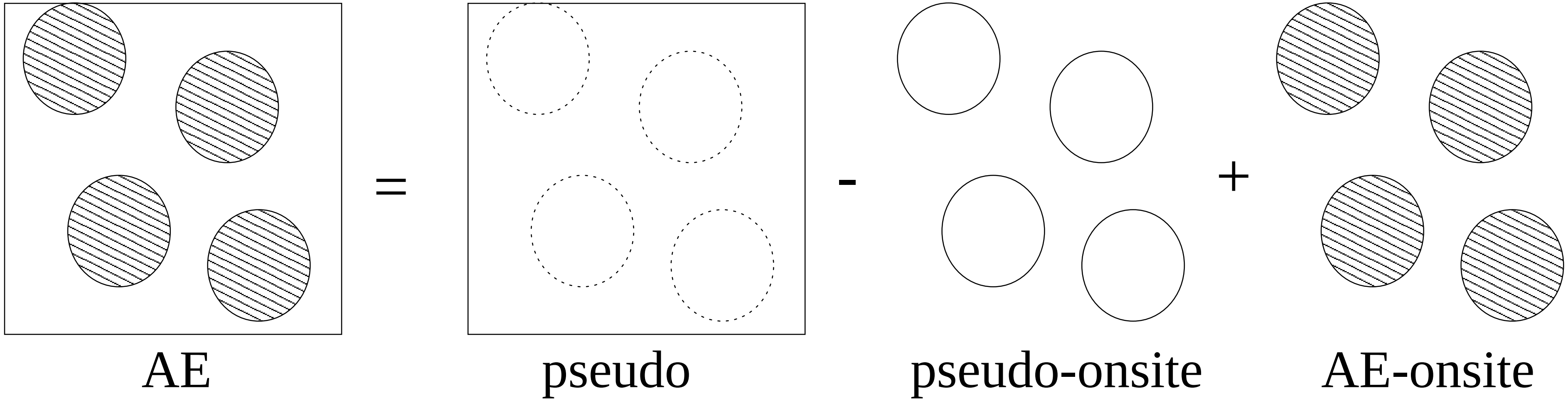
US-PP: what they really do

- character of wave function: $\boxed{c_i = \langle \tilde{p}_i | \tilde{\Psi}_n \rangle}$ $\qquad \langle p_i | \tilde{\phi}_j \rangle = \delta_{ij}$

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

- energy is the sum of three terms

$$E \quad = \quad -\Delta + V_{\mathrm{loc}} \qquad - \rho_{ij} \langle \tilde{\phi}_i | -\Delta + V_{\mathrm{loc}} | \tilde{\phi}_j \rangle + \rho_{ij} \langle \phi_i | -\Delta + V_{\mathrm{AE}} | \phi_j \rangle$$



- 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

$$\boxed{\rho_{ij} = \langle \tilde{\Psi}_n | p_i \rangle \langle p_j | \langle \tilde{\Psi}_n \rangle}$$

- PAW inspired formulation

Practical considerations

- the US-PP method can not 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:

  exact AE wave functions ⇒ norm-conserving wave functions

  $$\phi(r) \Rightarrow \phi^{\mathrm{norm-conserving}}(r)$$

  augmentation charge: $Q_{ij}(r) = \phi_i^{\mathrm{nc}}(r)\phi_j^{\mathrm{nc}}(r) - \tilde{\phi}_i(r)\tilde{\phi}_j(r)$

- these US-PP's yield exactly the same results as the corresponding NC-PP's, but at much lower cutoffs

Why are US-PP's softer

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

$$\boxed{\tilde{\phi}(r) = \sum_{i=1}^{2} \alpha_i \, j_l(q_i' r)} \qquad \text{with } q_i' \text{ such that} \qquad \frac{j_l(q_i' r_c)'}{j_l(q_i' r_c)} = \frac{\phi(r_c)'}{\phi(r_c)},$$

- additionally r_c can be increased compared to NC potentials

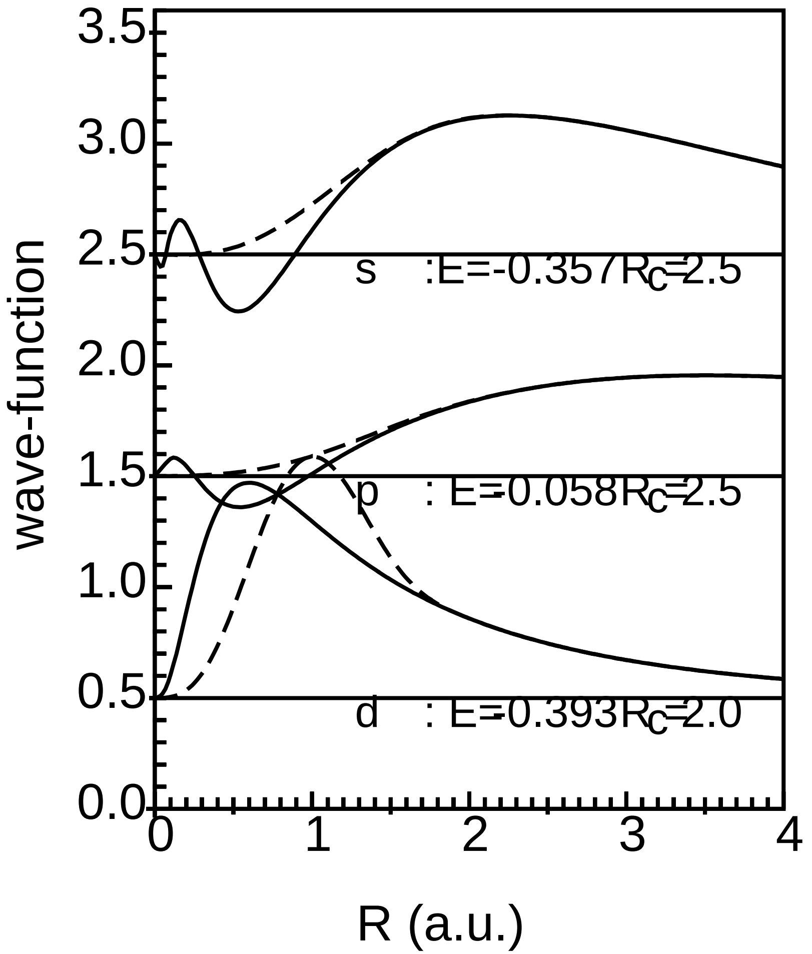
  there is no need to represent the charge distribution of the AE wave function, since this is done by the augmentation

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

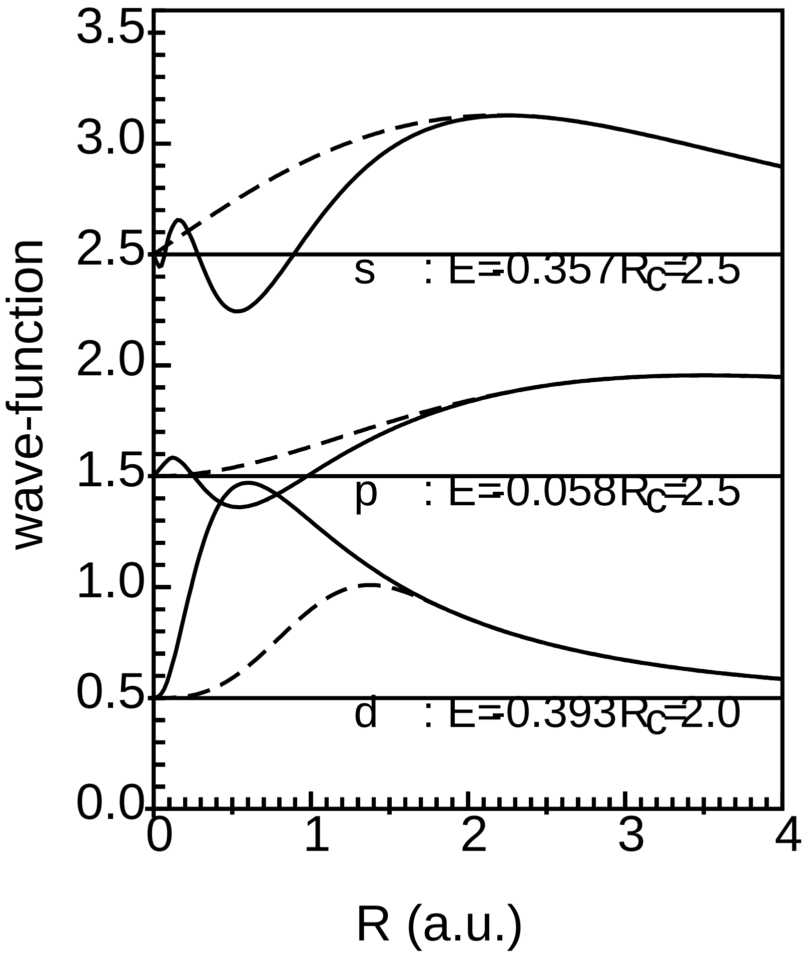
- basis sets are roughly a factor 2-3 smaller

Example for this behavior

e.g. Cu (NC)



Cu (US)



The role of the local potential

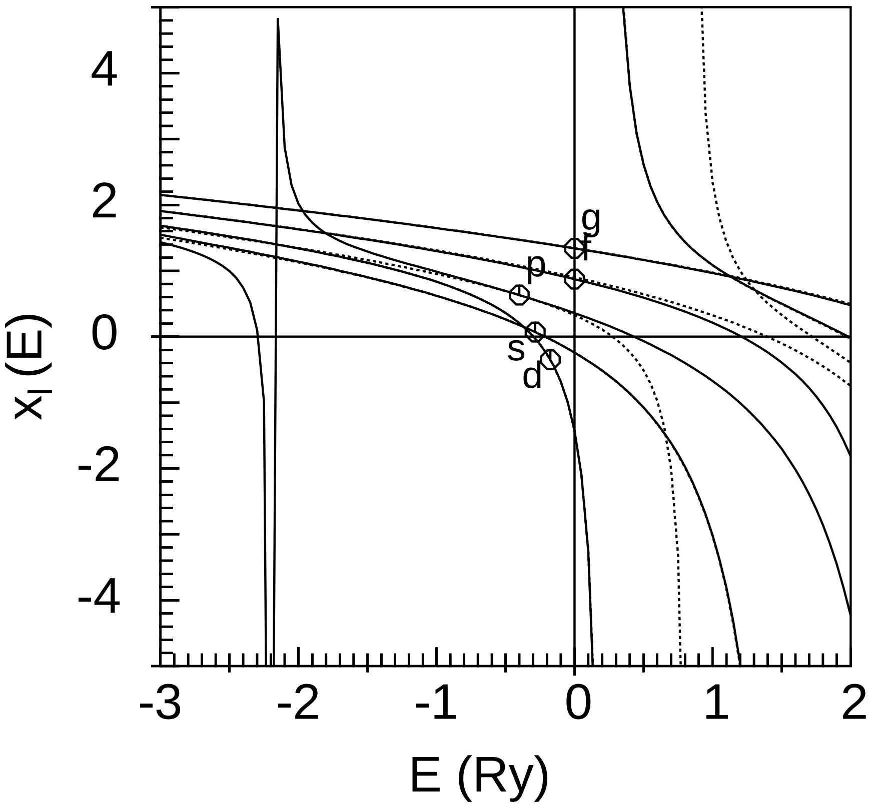
- the local potential needs to describe scattering properties for radial quantum numbers not included in the projectors
  - much underestimated problem
  - resulting errors can be 1-2 % in the lattice constant
- the tails of d electrons (transition metals) or p electrons (oxygen) overlap into the pseudization region

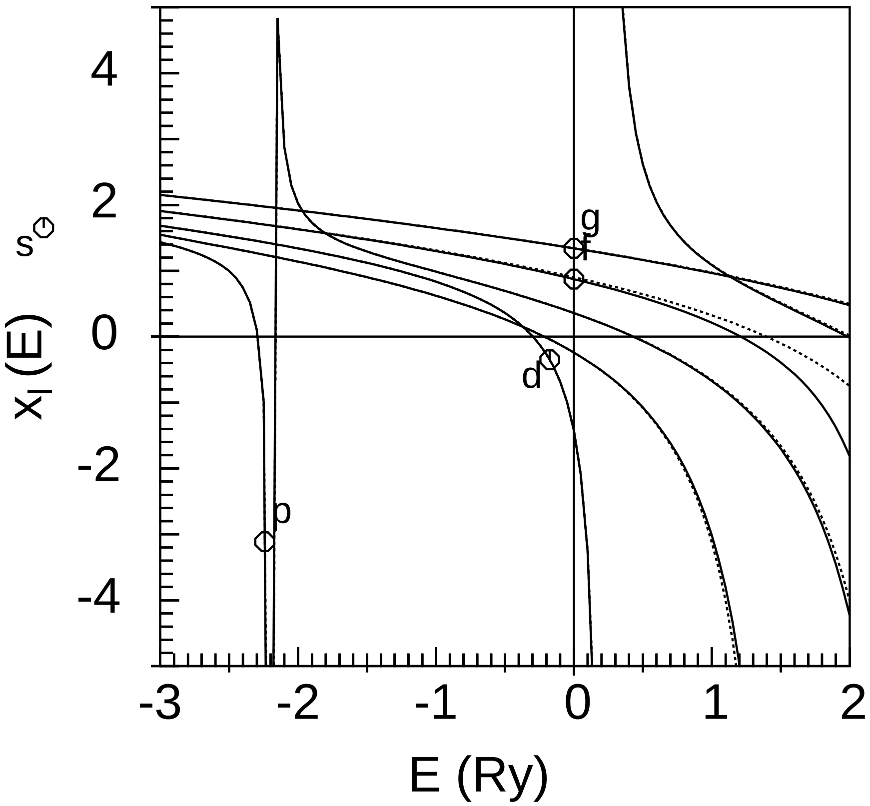
  they are picked up as high l components (FLAPW)
- ideally one would like to use very attractive local potentials

  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





- solution: treat semi-core states as valence

Pseudopotential generation in practice: the PSCTR *file*

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

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

  Description
l     E      TYP  RCUT     TYP  RCUT
0   0         15   1.13  23   1.40
0   0         15   1.13  23   1.40
1   0         15   1.13  23   1.55
1   0         15   1.13  23   1.55
2   0.0       7    1.55  7    1.55
```

PAW: basic idea

P.E. Blöchl, Phys. Rev. B**50**, 17953 (1994)

- Kohn-Sham equation

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

- frozen core approximation

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

$$\boxed{|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_{lm\varepsilon}^{\text{sites}} \left(|\phi_{lm\varepsilon}\rangle - |\tilde{\phi}_{lm\varepsilon}\rangle\right)\langle \tilde{p}_{lm\varepsilon}|\tilde{\Psi}_n\rangle}$$

- lm is an index for the angular and magnetic quantum numbers

  ε refers to a particular reference energy

- $\tilde{p}_{lm\varepsilon}$ projector function $\quad\quad$ $\tilde{\phi}_{lm\varepsilon}$ partial wave

PAW: basic idea

- <u>transformation:</u> $|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum(|\phi_{lm\varepsilon}\rangle - |\tilde{\phi}_{lm\varepsilon}\rangle)\langle\tilde{p}_{lm\varepsilon}|\tilde{\Psi}_n\rangle$
- 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

$$\boxed{c_{lm\varepsilon} = \langle\tilde{p}_{lm\varepsilon}|\tilde{\Psi}_n\rangle}$$

- inside each sphere the wavefunctions can be determined:

$$|\tilde{\Psi}_n\rangle^{\text{sphere}} = (\approx)\sum_{lm\varepsilon}|\tilde{\phi}_{l'm'\varepsilon'}\rangle c_{lm\varepsilon}$$

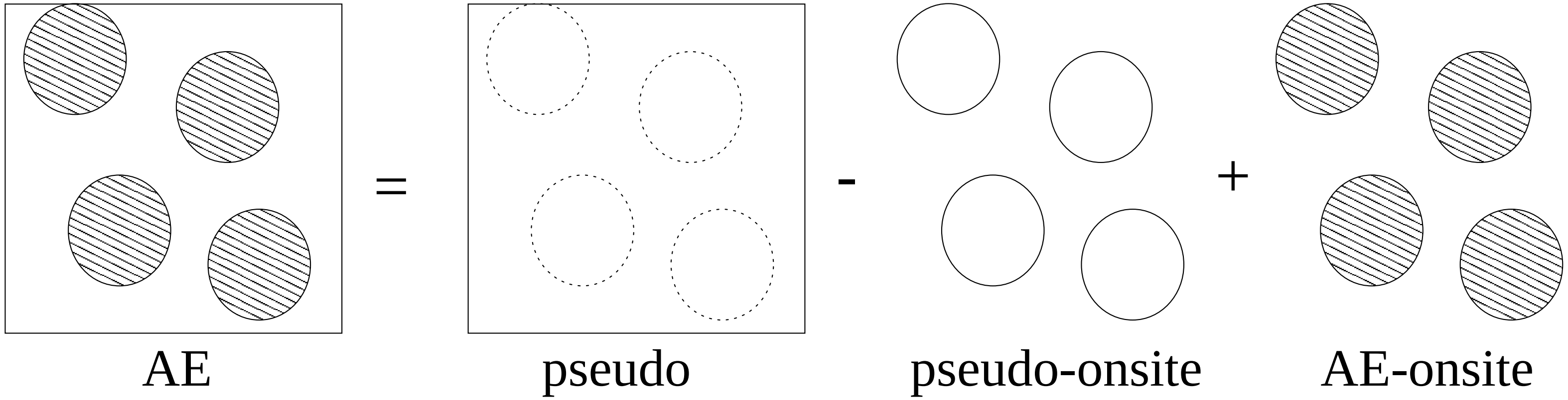
$$|\Psi_n\rangle^{\text{sphere}} = (\approx)\sum_{lm\varepsilon}|\phi_{l'm'\varepsilon'}\rangle c_{lm\varepsilon}$$

- the projector functions must be dual to the pseudo-wavefunction

$$\langle\tilde{p}_{lm\varepsilon}|\tilde{\phi}_{l'm'\varepsilon'}\rangle = \delta_{l,l'}\delta_{m,m'}\delta_{\varepsilon,\varepsilon'}$$

PAW: addidative augmentation

- character of wavefunction: $\boxed{c_{lm\varepsilon} = \langle \tilde{p}_{lm\varepsilon} | \tilde{\Psi}_n \rangle}$
- $|\Psi_n\rangle \quad = \quad |\tilde{\Psi}_n\rangle \quad - \sum |\tilde{\phi}_{lm\varepsilon}\rangle c_{lm\varepsilon} + \sum |\phi_{lm\varepsilon}\rangle c_{lm\varepsilon}$



- 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 ($i = lm\epsilon$)

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle \tilde{p}_i | \tilde{\Psi}_n\rangle .$$

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

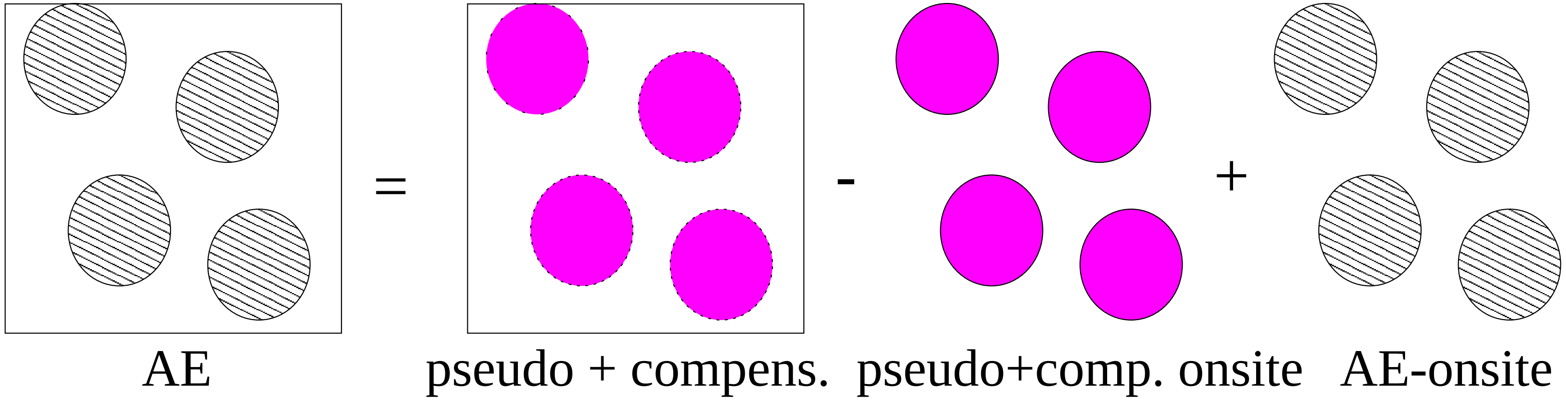
$$\boxed{\underbrace{\sum_n f_n \langle \tilde{\Psi}_n | -\Delta | \tilde{\Psi}_n \rangle}_{\tilde{E}} \underbrace{- \sum_{\text{site}} \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\Delta | \tilde{\phi}_j \rangle}_{\tilde{E}^1} \underbrace{+ \sum_{\text{site}} \sum_{(i,j)} \rho_{ij} \langle \phi_i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

- ρ_{ij} is an on-site density matrix: $\rho_{ij} = \sum_n f_n c_i^* c_j$

Hartree energy

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

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

$\tilde{n}^1$ pseudo-charge at one site $\hat{n}^1$ compensation charge at site

PAW energy functional

P.E. Blöchl, Phys. Rev. B**50**, 17953 (1994).

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

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

- $\tilde{E}$ 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

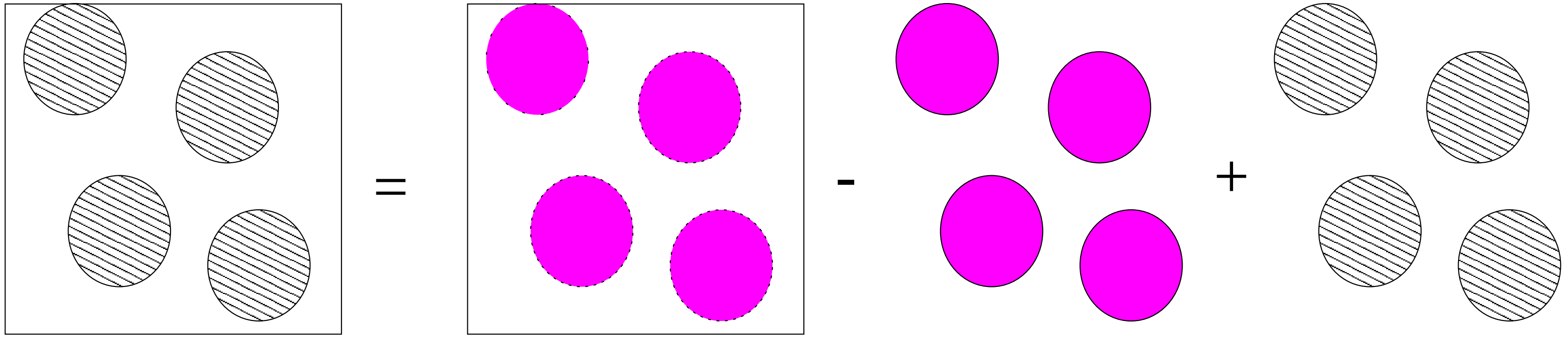
- E^1 and $\tilde{E}^1$ are evaluated on radial grids centered around each ion

  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

General scheme



AE   pseudo + compens.   pseudo+comp. onsite   AE-onsite

applies to all quantities

US-PP

D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

- 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:

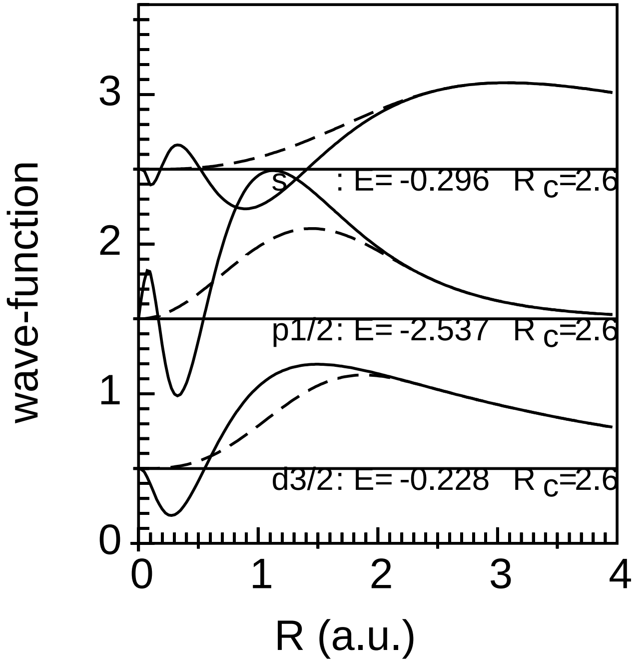
  the more the environment differs from the reference state the less accurate US-PP are

- 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

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

they must obey

$$\langle \tilde{p}_i | \tilde{\phi}_n \rangle = \delta_{i,n}$$

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

PAW — US-PP method: molecules

- 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

	US-PP(data base)	US-PP(special)	PAW	AE
H_2		1.447	1.447	1.446[a]
Li_2		5.127	5.120	5.120[a]
Be_2		4.524	4.520	4.521[a]
Na_2		5.667	5.663	5.67 [a]
CO	2.163	2.141 (2.127)	2.141 (2.128)	2.129[a]
N_2	2.101	2.077 (2.066)	2.076 (2.068)	2.068[a]
F_2	2.696	2.640 (2.626)	2.633 (2.621)	2.615[a]
P_2	3.576	3.570	3.570	3.572[a]
H_2O		1.840 (1.834)	1.839 (1.835)	1.833[a]
$\alpha(H_2O)(^\circ)$		105.3 (104.8)	105.3 (104.8)	105.0[a]
BF_3		2.476 (2.470)	2.476 (2.470)	2.464[b]
SiF_4		2.953 (2.948)	2.953 (2.948)	2.949[b]

values in paranthese were obtained with hard potentials at 700 eV

[a] NUMOL, R.M. Dickson, A.D. Becke, J. Chem. Phys. **99**,3898 (1993), [b] Gaussian94

PAW — AE methods: molecules - energetics

400 eV plane wave cutoff

xc meth	PBE PAW	PBE AE[a]	rPBE[b] PAW	rPBE[b] AE[a]	exp
CO	11.65	11.66	11.15	11.18	11.24
N_2	10.39	10.53	10.09	10.09	9.91
NO	7.31	7.45	6.95	7.01	6.63
O_2	6.17	6.14-6.24	5.75	5.78	5.22

[a] S. Kurth, J.P. Perdew, P. Blaha, Int. J. Quantum Chem. 75, 889 (1999).

[b] revised Perdew Burke Ernzerhof functional, B. Hammer, L.B. Hansen, J.K. Norskov, Phys. Rev. B 59, 7413 (1999).

PAW — US-PP method: bulk, semiconductors

results for the equilibrium lattice constant *a*, cohesive energy E_{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

	$a(\AA^3)$	E_{coh}(eV)	B (MBar)
diamond			
US-PP(current)	3.53	-10.15	4.64
PAW(current)	3.53	-10.13	4.63
LAPW^a	3.54	-10.13	4.70
PAW^a	3.54	-10.16	4.60
silicon			
US-PP(current)	5.39	-5.96	0.95
PAW(current)	5.39	-5.96	0.95
LAPW^a	5.41	-5.92	0.98
PAW^a	5.38	-6.03	0.98

PAW — US-PP method: bulk, metals

results for the equilibrium lattice constant *a*, cohesive energy E_{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

	$a(\AA^3)$	E_{coh}(eV)	*B* (MBar)
bcc V			
US-PP(current)	2.93	-9.41	2.02
PAW(current)	2.93	-9.39	2.09
LAPW[a]	2.94	-9.27	2.00
PAW[a]	2.94	-9.39	2.00
fcc Ca			
US-PP(current)	5.34	-2.20	0.0181
PAW(3s3p val)	5.34	-2.19	0.0187
PAW(3p val)	5.34	-2.20	0.0187
LAPW[a]	5.33	-2.20	0.019
PAW[a]	5.32	-2.24	0.019

PAW — US-PP method: bulk, ionic compounds

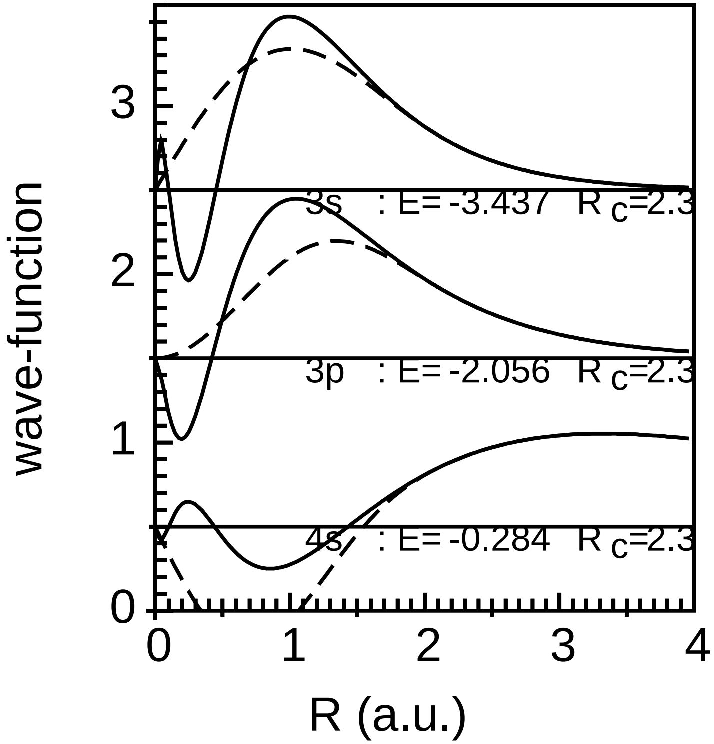
results for the equilibrium lattice constant *a*, cohesive energy E_{coh} (with respect to non spin polarised atoms) and bulk modulus *B* for several materials calculated with the the PAW, US-PP, and the FLAPW approach

	$a(\AA^3)$	E_{coh}(eV)	B (MBar)
CaF_2			
US-PP(current)	5.36	-6.32	0.97
PAW(3s3p val)	5.35	-6.32	1.01
PAW(3p val)	5.31	-6.36	1.00
LAPW[a]	5.33	-6.30	1.10
PAW[a]	5.34	-6.36	1.00

[a] N.A.W. Holzwarth, et al.; Phys. Rev. B 55, 2005 (1997)

Semi-core states; alkali and alkali earth metals

- from a practicle 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



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

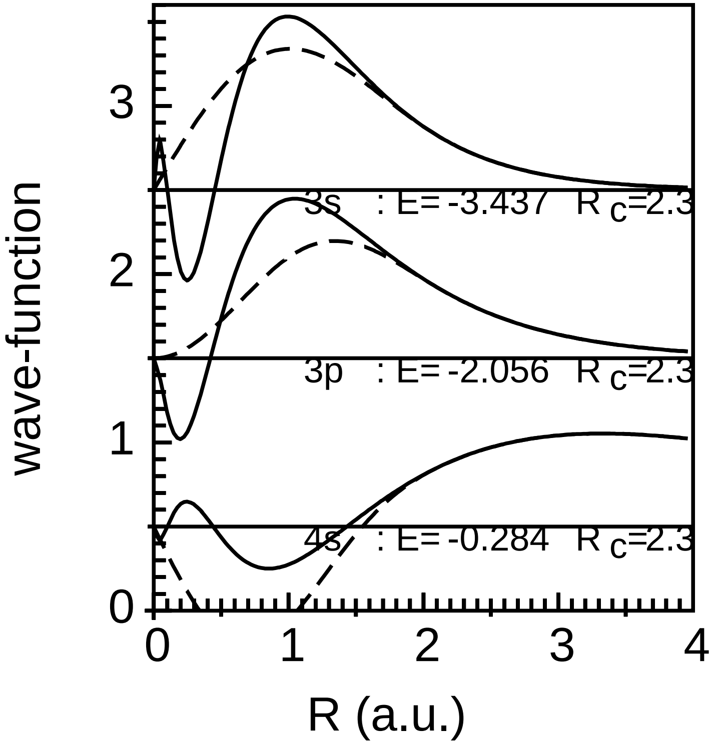
general problem for pseudopotentials

Semi core states

in VASP, NC wavefunctions describe the augmentation charges

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

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:

$\Delta E_m = E_{\mathrm{M}}(\mathrm{gs}) - E_{\mathrm{NM}}(4s^1 3d^{n-1})$ (in eV)

		US-PP	PAW	AE
O	gs	$2s^2 2p^4$	$2s^2 2p^4$	$2s^2 2p^4$
	ΔE_m	1.55	1.40	1.41
N	gs	$2s^2 2p^3$	$2s^2 2p^3$	$2s^2 2p^3$
	ΔE_m	3.14	2.88	2.89
Fe	gs	$3d^{6.2} 4s^{1.8}$	$3d^{6.2} 4s^{1.8}$	$3d^{6.2} 4s^{1.8}$
	ΔE_m	2.95	2.77	2.76
Co	gs	$3d^{7.7} 4s^{1.3}$	$3d^{7.7} 4s^{1.3}$	$3d^{7.7} 4s^{1.3}$
	ΔE_m	1.40	1.32	1.31
Ni	gs	$3d^9 4s^1$	$3d^9 4s^1$	$3d^9 4s^1$
	ΔE_m	0.54	0.52	0.52

for atoms the magnetisation is wrong by 5-10% with US-PP

Bulk properties of Fe

energy differences between different phases of Fe

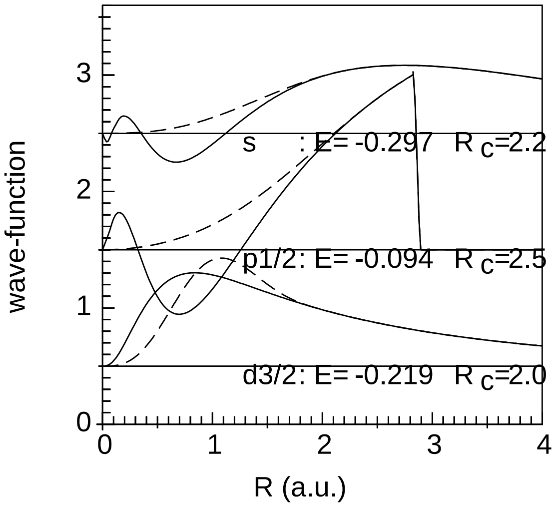
	FLAPW[a]	PAW	US-AE	US-PP
bcc Fe NM		373	372	369
bcc Fe FM	-73	-73	-73	-191
fcc Fe NM	78	61	62	62
hcp Fe NM		0	0	0

[a] FLAPW, L. Stixrude and R.E. Cohen, Geophys. Res. Lett. **22**, 125, (1995).

- 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
  - α-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



— 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 artifically 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

CeO_2	PAW	FLAPW	Exp
a (Å^3)	5.47 Å	5.47 Å	5.41 Å
B	172 GPa i	176 GPa	236 GPa

UO_2	PAW	FLAPW	Exp
a (Å^3)	5.425 Å		5.46 Å
B	200 GPa		209 GPa

Computational costs, efficiency

- code complexity of the kernel of course increases with PAW

local pseudopotentials	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

type	cutoff	time	total error per atom
NC-PP	140 eV	514 sec	400 meV
NC-PP	240 eV	1030 sec	10 meV
US-PP	140 eV	522 sec	10 meV
PAW	140 eV	528 sec	10 meV

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