



Introduction to electronic structure simulations

Lecture 8

Pseudo-potentials

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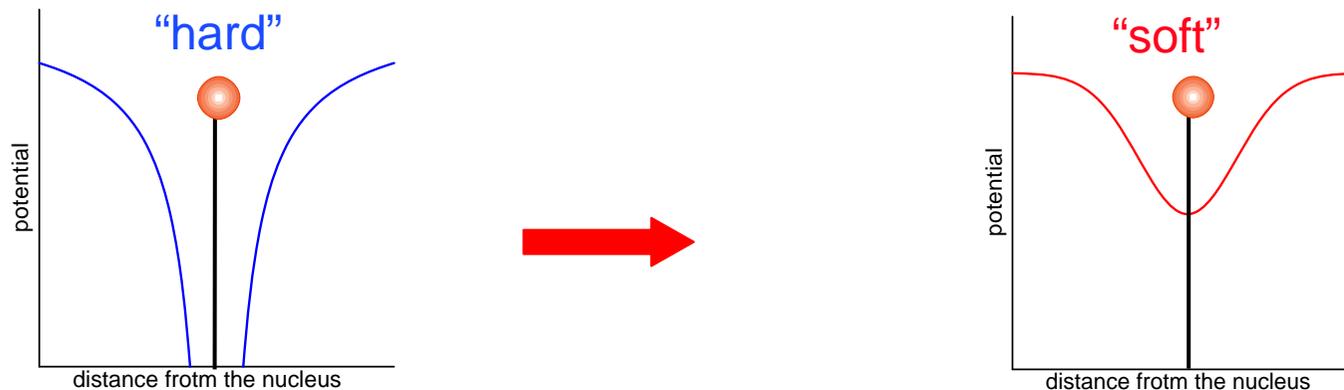
Outline

- Introductory remarks
- Why do we need pseudo-potentials?
- The concept of pseudo-potentials
- Flavors of pseudo-potentials:
 - Empirical pseudo-potentials
 - Ab initio norm-conserving pseudo-potentials
 - Ultra-soft pseudo-potentials
 - Projected augmented wave method
- Comparison of different pseudo-potentials: which pseudo-potential should be chosen?



Pseudo-potentials : introductory remarks

- The fundamental idea of a “pseudo-potential” is the replacement of one problem with another: instead of a strong Coulomb potential of the nucleus we introduce a much “softer” potential. Why? Will we clear in the following discussion



- The concept has a long history (the idea dates back to E. Fermi's papers published in the 1930s). Empirical pseudo-potentials were successfully used in many analytical (and numerical) band structure calculations in the 1950-1970s. Ab-initio transferable and accurate pseudo-potentials developed in the 1980th-1990th made plane-wave DFT calculations possible.
- Nowadays widely in use: there are many different types of pseudo-potentials



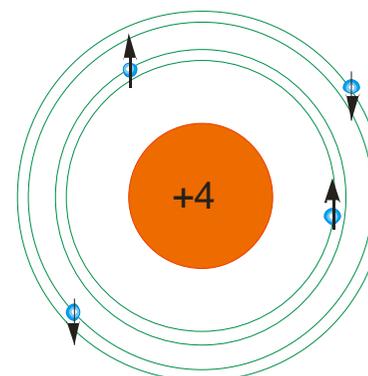
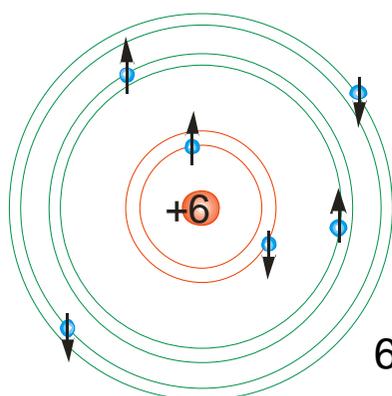
The basic idea

- Assume we want to simulate a carbon system from first-principles

We know that the valence electrons are responsible for bonding

C: $1s^2 2s^2 2p^2$

C (pseudo core): $2s^2 2p^2$



- To make simulations simpler (we will discuss later on what the problems are) let's group all the electrons around the nuclear core into an effective ionic core, and keep only the valence electrons that contribute to the bonding of the solid.
- Even if we know nothing about quantum mechanics, obviously, we cannot simply change the ion charge and assume that the electron-ion interaction is still Coulombic: For example, no difference between C and Si would be expected:

Si: $1s^2 2s^2 2p^6 3s^2 3p^2$



Si: (pseudo core) $3s^2 3p^2$

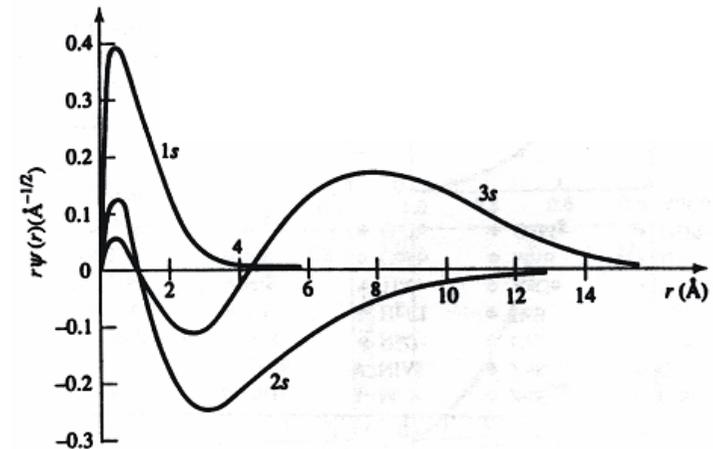
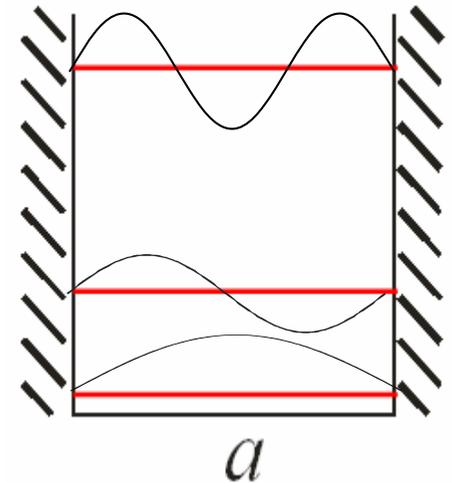
- The effective potential (pseudopotential) should be constructed with account for all the core electrons



Why do we need pseudo-potentials?

- Assume first that we use plane waves as basis functions
 - Recall that electron wave functions in the atom (except for 1s, 2p, 3d, etc.) oscillate due to the orthogonality of a state to all states with lower energies
 - The higher the state in the atom, the more the electron wave function oscillate, as in a 1D quantum well
 - This is due to the Pauli principle: the probability to find a valence electron near the nucleus is small, as the core electrons are there; thus electron function must be orthogonal
 - The oscillations are close to the nucleus, at distances being much shorter than where the valence electrons are
 - Bonding is due to the valence electrons

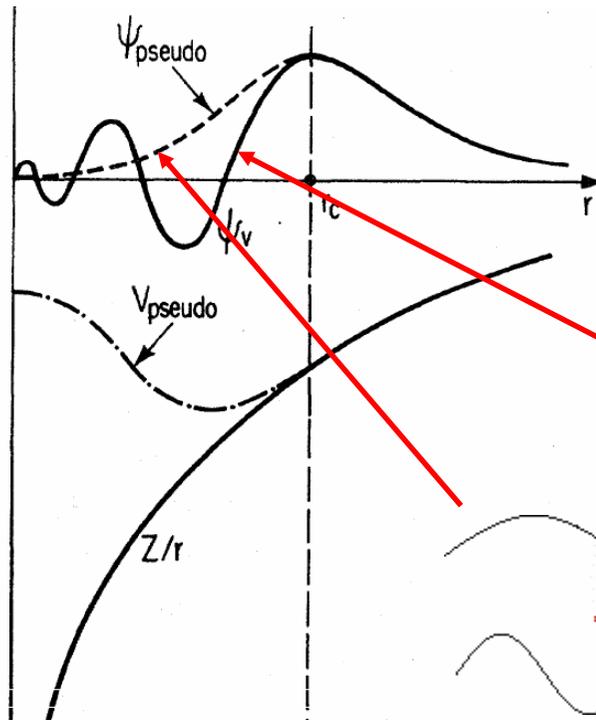
So, let's construct a new much weaker potential which would give the correct behavior of the electron WF in the "bonding" region, and nearly zero probability for the valence electron to be close to the nucleus (and no oscillations of WF)!





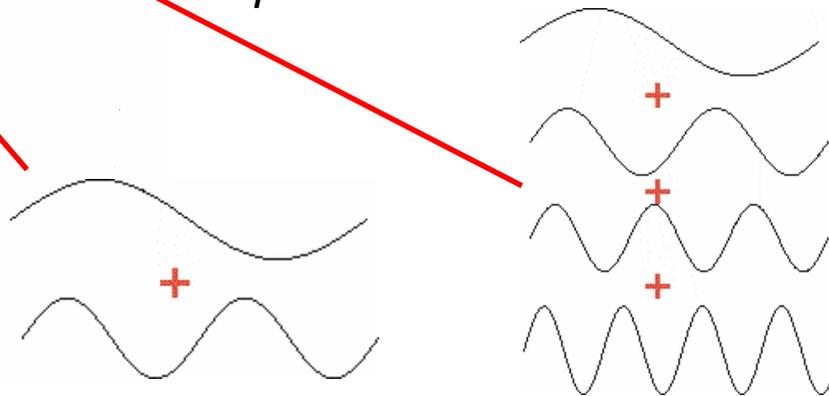
Why do we need pseudopotentials?

- Working with plane waves:



Once more, if we can construct a new much weaker potential which would give the correct behavior of the electron WF in the “bonding” region, and nearly zero probability for the valence electron to be close to the nucleus, and no oscillations of the WF, we will need much fewer plane waves!

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} e^{i\mathbf{q}\mathbf{r}} C_{\mathbf{q}}$$



Huge speed-up!

(actually, the PP concept makes PW calculations feasible)

- Working with real-space basis functions

- We can decrease the number of basis functions
- We can decrease the number eigen functions (occupied) required in HF and DFT calculations

Also substantial speed-up!



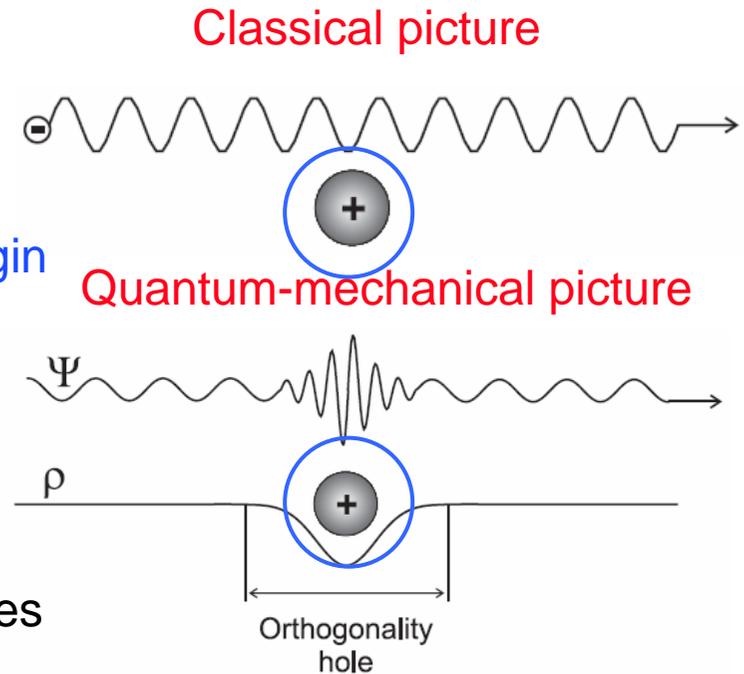
The concept of pseudo-potentials

- Let's summarize everything we have discussed up to now:
 - The pseudo-potential is a potential which replaces the all-electron + nucleus potential inside a defined core region
 - It is much weaker than the original nuclear potential since the latter is “screened” by the core electrons
 - It represents the nucleus+core electrons so that outside the core region the total potential and the pseudo-potential have the same behavior: same scattering properties for the valence electrons
 - It is very convenient to use the pseudo-potential in a plane wave representation
 - It avoids the solution of the K-S and HF equations for the core electrons: computationally more efficient even for real-space basis function
 - PPs can be generated in atomic calculations, and then used to compute properties of solids/molecules taking into account valence electrons only
- Important:
 - The choice of pseudo-potential is not unique
 - Lots of freedom to construct a computationally efficient pseudo-potential



Pseudo-potentials and the scattering problem

- The pseudo-potential problem can be discussed in terms of the electron scattering in a localized spherical potential.
- Pseudo-potentials have quantum mechanical origin (orthogonality hole)
- Two important remarks:
 - All scattering properties can be formulated concisely in terms of the “phase shift” which determines the cross-section and all the properties of the wave-function outside the localized region
 - All the properties of the wavefunctions outside the scattering region are invariant to changes in the phase shift by any multiple of 2π : we can then use this freedom to define potentials whose pseudo-wavefunctions have the same scattering properties of the true wavefunctions outside the scattering region, as defined by a cut-off radius R_c , and that behave much more smoothly inside the core.





Empirical pseudo-potentials

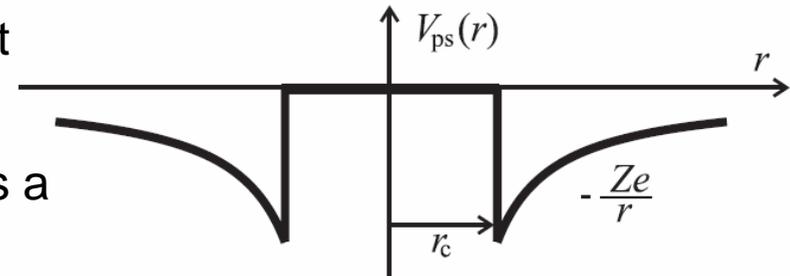
- Model ion potentials with the parameters fit to reproduce the reference data

- Example: “Empty core” potential of Ashcroft

N.W. Ashcroft, *Phys. Lett.* 23 (1966) 48

- Repulsion/zero potential in the core area is a corollary of the “orthogonality hole”

- This is a **local** potential (independent of l)



$$V_{ps} = 0 \text{ if } r < R_c$$

$$V_{ps} = -\frac{Z}{r} \text{ if } r > R_c$$

- Recall the radial Schroedinger equation depends on the angular momentum l

$$-\frac{1}{2} \frac{d^2}{dr^2} \phi(r) + \left(\frac{l(l+1)}{2r^2} + V(r) - E \right) \phi(r) = 0 \quad \phi = rR(r)$$

- More general form of the potential is $V = \sum_{lm} |lm\rangle V_l \langle lm|$ where

$|lm\rangle$ spherical harmonics V_l the pseudo-potential corresponding to a certain harmonic

- These are **nonlocal** potentials (l -dependent)



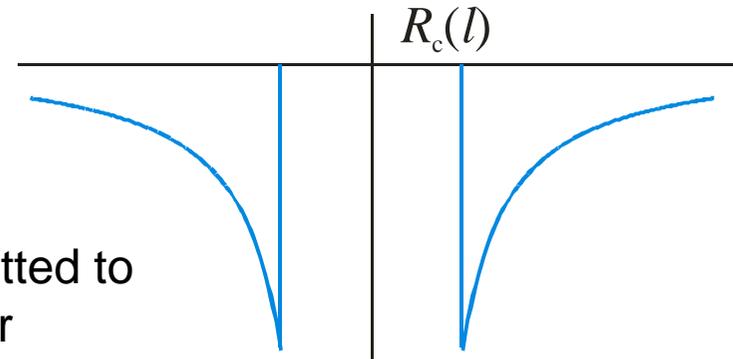
Empirical pseudo-potentials (2)

- Non-local model pseudo-potentials:

- Modified Ashcroft potential: $R_c(l)$

- Only one parameter, the core radius, fitted to match the experimental lattice parameter

- Reasonably good cohesive energy and bulk moduli of various solids

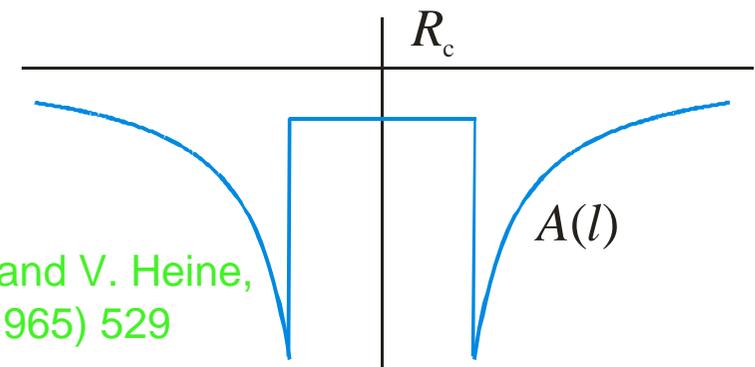


- Abarenkov and Heine potential:

$$V_{ps}(r) = \sum_l A_l |l\rangle\langle l| \text{ if } r < R_c$$

$$V_{ps} = -\frac{Z}{r} \text{ if } r > R_c$$

I.V. Abarenkov and V. Heine,
Phil. Mag. 12 (1965) 529



- One parameter per angular momentum component l of the core electrons:

- Can be easily parametrized in terms of Fourier components using a limited number of \mathbf{k} vectors in the BZ



Empirical pseudo-potentials (3)

- Note that the pseudo-potentials considered above are discontinuous at the core radius $R_c(l)$
 - Unphysical
 - Leads to long-ranged oscillations of their Fourier transforms, hindering their use in PW calculations
- Solution: The evanescent core potential

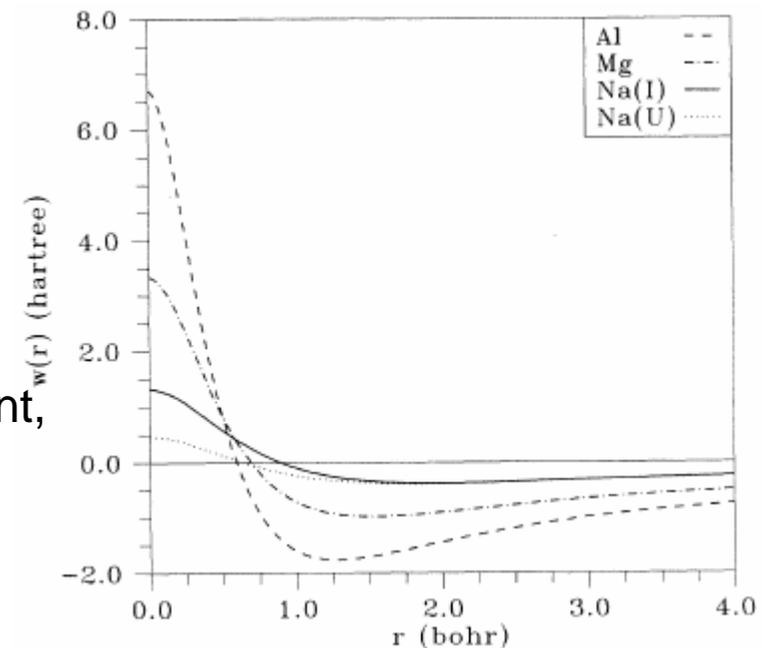
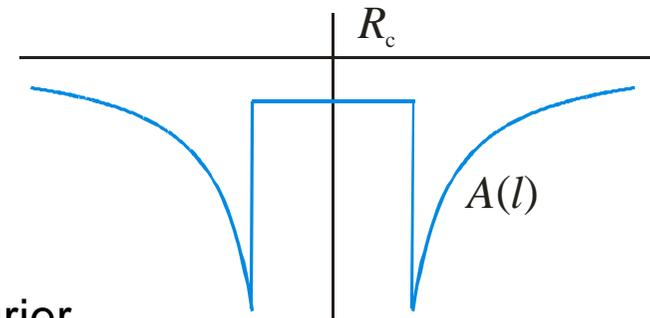
C. Fiolhais et al. Phys. Rev. B 51, 14001–14011 (1995)

$$w(r) = -\frac{z}{R} \left\{ \frac{1}{x} [1 - (1 + \beta x)e^{-\alpha x}] - Ae^{-x} \right\}$$

$$x = r/R$$

R , A , α , β are parameters (some of them dependent, so actually two parameters must be fitted):

- The approach gives reasonable results for many materials, but it is still empirical...





Orthogonalized plane-waves

- Orthogonalized Plane Waves (OPW) were introduced by Herring in 1940; the method enabled first quantitative calculations of materials properties (1959)

W.C. Herring, *Phys. Rev.* 57 (1940) 1169; J.C. Phillips and L. Kleinman, *Phys. Rev.* 116 (1959) 287.

- Very general approach for construction of basis functions for valence states: exploits the idea that core states and valence states are essentially distinct and can be separated
- Let's represent the true wave function ψ , as the sum of a smooth wave function ϕ and a sum over occupied core states:

$$\psi = \phi + \sum_t b_t \phi_t$$

- ψ the true wave function
- ϕ a smooth wave function (originally, plane waves)
- ϕ_t occupied core states (in principle, any localized functions)

- From the orthogonality condition $\langle \phi_t | \psi \rangle = 0$: $b_t = -\langle \phi_t | \phi \rangle$

$$\psi = \phi - \sum_t \langle \phi_t | \phi \rangle \phi_t$$

- Substituting into the Schroedinger equation: $H\psi = E\psi$, $H = p^2/2m + V_c$



Orthogonalized plane-waves (2)

- We arrive at $H\phi - \sum_t \langle \phi_t | \phi \rangle E_t \phi_t = E\phi - E \sum_t \langle \phi_t | \phi \rangle \phi_t$, or equivalently

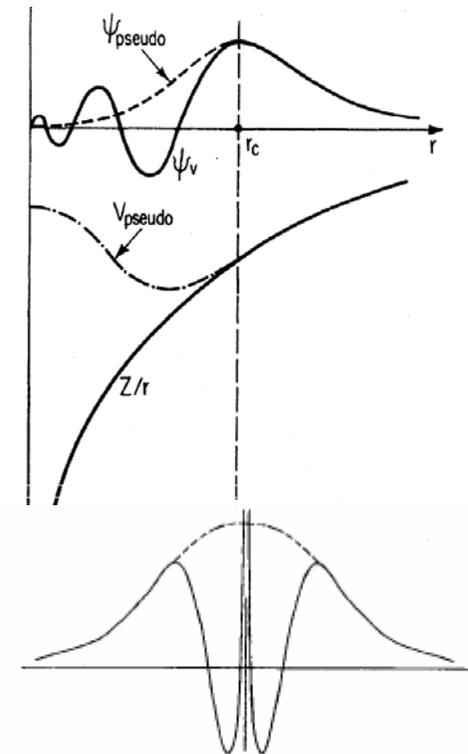
$$H\phi + \sum_t (E - E_t) \langle \phi_t | \phi \rangle \phi_t = E\phi$$

- By re-grouping the terms : $(H + V_R)\phi = E\phi$

$$V_R\phi = \sum_t (E - E_t) \langle \phi_t | \phi \rangle \phi_t$$

- V_R a short-ranged non-Hermitian **repulsive** potential
- E is not a pseudo energy but the **true energy**: the energy corresponding to the true wave function
- The Schroedinger equation reads:

$$\left(\frac{p^2}{2m} + V_c + V_R \right) \phi = \left(\frac{p^2}{2m} + V \right) \phi = E\phi$$
 - As V is a sum of repulsive V_R and attractive V_c potentials it is much softer than the original attractive potential V_c !
 - The pseudo-function has no radial nodes!



Example of a 3s orbital and the pseudo-function



Angular momentum dependent pseudo-potentials

- The pseudo-potential is, in general, spatially non-local and depends on two different electron coordinates r and r' :
$$V_R(\mathbf{r}, \mathbf{r}') = \sum_t (E - E_t) |\phi_t(\mathbf{r})\rangle \langle \phi_t(\mathbf{r}')|$$
- Since we sum up over the occupied core states, it can be broken down into angular momentum components by summing over the core states according to their orbital angular momentum symmetry

Spherical harmonics

$$V = \sum_{lm} |lm\rangle V_l \langle lm|, \quad \text{and} \quad V_l = V_l(r, r')$$

- $V_l = V_l(r, r')$ **Non-local** pseudo-potential
- $V_l = V_l(r) \delta(r-r')$ **Semi-local** pseudo-potential
- $V_l = V_l(r) V_l(r')$ **Separable** pseudo-potential
- A pseudo-potential that uses the same potential for all the angular momentum components of the wave function is called a **local** pseudo-potential

L. Kleinman and D.M. Bylander, PRL 48 (1982) 1425.

A simple way has been discovered to put model pseudopotentials, $V(\vec{r}) = \sum_{lm} |Y_{lm}\rangle V_l(r) \times \langle Y_{lm}|$, into a form which reduces the number of integrals of $V(\vec{r})$ required for an energy-band calculation from $mn(n+1)/2$ to mn for each l in the sum (where n is the number of plane waves used in the expansion and m the number of points in the Brillouin zone at which the calculation is performed). The new form may be chosen to improve the accuracy of the pseudopotential when used in other chemical environments.



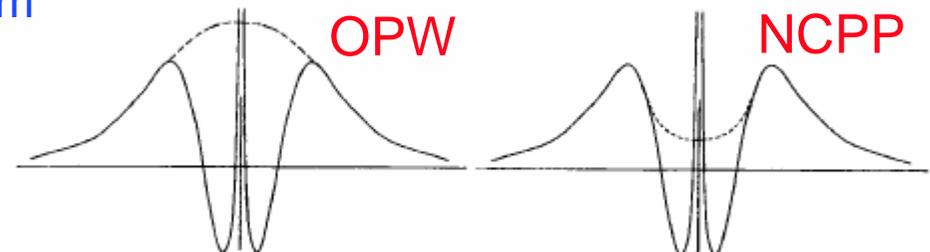
Ab initio norm-conserving pseudo-potentials

- A crucial step toward realistic and transferable PPs was the introduction of *ab initio* PPs (as opposed to empirical PPs with the parameters normally chosen to fit the data for solids) constructed to fit the valence properties for the atom **calculated** in a rigorous manner

- Such PPs were generated from atomic calculations that are themselves *ab initio*

Ab initio PPs are Norm Conserving Pseudo-potentials (NCPP)

- Norm conserving PPs are normalized (as discussed below) and are the solutions of the Schrodinger equation with a model potential chosen to reproduce the valence properties of the atom given by the all-electron calculation - no need to add a smooth and a hard part as in OPW
- Pseudo-wavefunctions are orthogonal and are thus solution of a set of the Kohn-Sham equation of the usual form
- Normally not as smooth as OPW-like functions





Norm-conservation conditions

D. R. Hamann, M. Schlueter, and C. Chiang, "Norm-conserving pseudopotentials," Phys. Rev. Lett. 43 (1979):1494-1497.

- Requirements for a “good” ab initio pseudo-potential:

1. All-electron and pseudo valence eigenvalues agree for the chosen atomic reference configuration.

$$\varepsilon_l^{\text{PP}} = \varepsilon_{nl}^{\text{AE}}$$

2. All-electron pseudo valence wavefunctions agree beyond a chosen core radius R_c .

3. The logarithmic derivatives of the all-electron and pseudo wave functions agree at R_c .

4. The integrated charge inside R_c , for each wavefunction agrees (norm-conservation).

5. The first energy derivative of the logarithmic derivatives of the all-electron and pseudo wave functions agrees at R_c .

- Besides this,

- pseudo WF should not have nodal surfaces



Norm-conservation conditions (2)

- Points (1) and (2) guarantee that the NCPP and the true potential are the same outside the core region
- Point (3) follows since the wave function and its radial derivative are continuous at R_c for any smooth potential
- Point (4) imposes the conservation of the charge in the core region:

$$Q_l = \int_0^{R_c} dr r^2 |\psi_l(r)|^2 = \int_0^{R_c} dr \phi_l(r)^2$$

Note that all-electron (AE) and pseudo wave functions are different inside the core region

- Point (4) also means that the normalized pseudo-orbital and true orbital are equal outside the core region (different from OPW functions which are equal to the true functions only if it is not normalized)
- Point (5) is crucial for the generation of a good transferable potential



Constructing norm-conserving pseudo-potential

- How to construct a pseudo-potential:
 - Solve the atomic all-electron problem for a given electronic configuration where each state l, m is treated independently
 - Ab initio self consistent calculation
 - Approximation: choice of the exchange and correlation functional
 - Approximation: spherical Hartree and exchange/correlation potentials
 - Relativistic effects normally neglected (can be included if necessary)

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_{\text{KS}}^{\text{AE}} [n^{\text{AE}}] (r) \right] r R_{nl}^{\text{AE}}(r) = \varepsilon_{nl}^{\text{AE}} r R_{nl}^{\text{AE}}(r)$$

$$v_{\text{KS}}^{\text{AE}} [n^{\text{AE}}] (r) = -\frac{Z}{r} + v_{\text{Hartree}} [n^{\text{AE}}] (r) + v_{\text{xc}} [n^{\text{AE}}] (r)$$

- Construct the pseudo wave function using

- Continuity condition

$$R_l^{\text{PP}}(r) = R_{nl}^{\text{AE}}(r) \quad \text{if } r > r_l$$

- Norm-conservation condition $\int_0^{r_l} dr |R_l^{\text{PP}}(r)|^2 r^2 = \int_0^{r_l} dr |R_{nl}^{\text{AE}}(r)|^2 r^2$, if $r < r_l$,



Constructing norm-conserving pseudo-potential (2)

- Knowing the pseudo wave function, the pseudo-potential can be constructed by the inversion of the radial Kohn-Sham equation with the account of the valence electron density:

$$w_l(r) = w_{l,\text{scr}}(r) - v_{\text{Hartree}} [n^{\text{PP}}](r) - v_{\text{xc}} [n^{\text{PP}}](r)$$

$$w_{l,\text{scr}}(r) = \varepsilon_l^{\text{PP}} - \frac{l(l+1)}{2r^2} + \frac{1}{2rR_l^{\text{PP}}(r)} \frac{d^2}{dr^2} [rR_l^{\text{PP}}(r)]$$

- Cutoff radii are a measure of the quality of the pseudo-potential
 - Smallest possible value: the outermost nodal surface (realistic but strong)
 - Large values: smooth but not accurate, angular momentum-independent
- The actual choice: the trade-off between efficiency and accuracy
- Pseudo-potentials are usually written as a sum of a local potential (non l -dependent) and a non-local part (l -dependent):
- The local part reproduces the behavior of the all-electron potential for large r ($r \rightarrow \infty$).



Hamann pseudo-potential

D. R. Hamann, M. Schlutter and C. Chiang, PRL 43 (1979):1494-1497

- Intermediate pseudo-potential is introduced

$$\begin{aligned} \bar{w}_l(r) + v_{\text{Hartree}} [n^{\text{PP}}](r) + v_{\text{xc}} [n^{\text{PP}}](r) &= \\ &= v_{\text{KS}}^{\text{AE}} [n^{\text{AE}}](r) \left[1 - f\left(\frac{r}{r_l}\right) \right] + c_l f\left(\frac{r}{r_l}\right) \end{aligned}$$

where $f(x) = e^{-x^\lambda}$, and $\lambda = 4.0$ or $\lambda = 3.5$

- The KS equations are solved using this PP and constants c_l are adjusted to obey

$$\varepsilon_l^{\text{PP}} = \varepsilon_{nl}^{\text{AE}} \quad \frac{d}{dr} \ln [r R_{nl}^{\text{AE}}(r)] \Big|_{r=\tilde{r}_l} = \frac{d}{dr} \ln [r \bar{R}_l(r)] \Big|_{r=\tilde{r}_l}$$

- To impose norm-conservation, the final pseudo wave functions are defined as a correction to the intermediate wave-function

$$R_l^{\text{PP}}(r) = \gamma_l [\bar{R}_l(r) + \delta_l g_l(r)]$$

$$\gamma_l = R_{nl}^{\text{AE}}(r) / \bar{R}_l(r) \quad r > \tilde{r}_l$$

$$g_l(r) = r^{l+1} f(r/r_l)$$

constants δ_l are adjusted to conserve the norm



Hamann pseudo-potential (2)

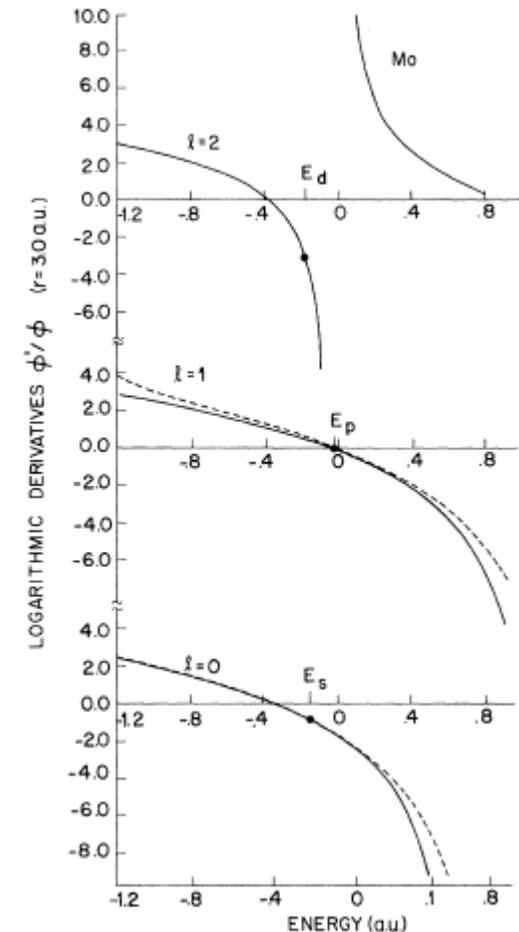
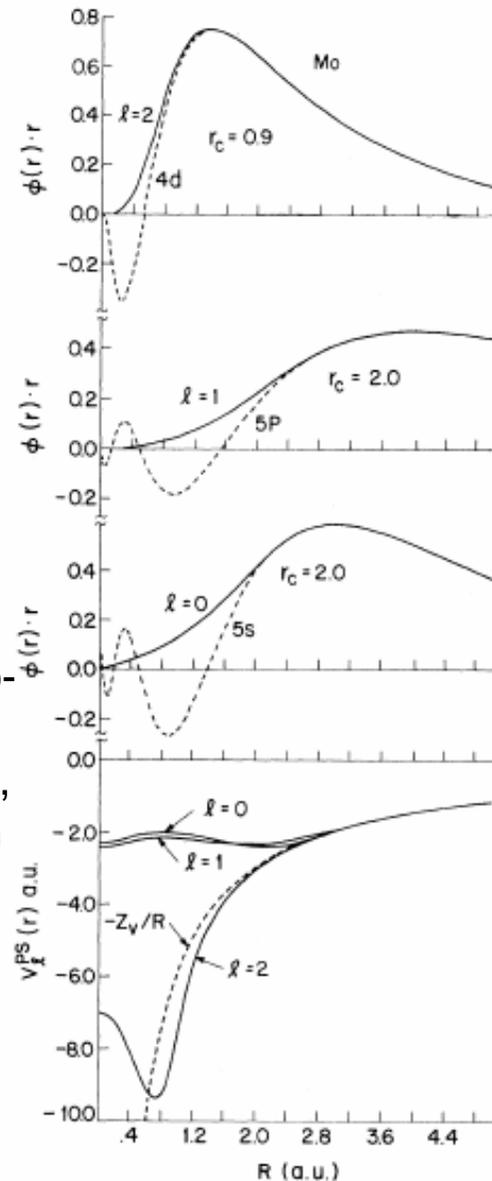
Example of norm-conserving pseudo-potentials, pseudo-functions, and logarithmic derivative for Mo.

Left bottom: $V_l(r)$ in Rydbergs for angular momentum $l = 0, 1, 2$ compared to Z_{ion}/r (dashed).

Left top: All-electron valence radial functions $\phi(r) = r\psi(r)$ (dashed and norm-conserving pseudo-functions).

Right: Logarithmic derivative of the pseudo-potential compared to the full atom calculation; the points indicate the energies, E , where they are fitted. The derivative with respect to the energy is also correct due to the norm-conservation condition.

From: D. R. Hamann, M. Schlutter and C. Chiang, PRL 43 (1979):1494-1497





Troullier-Martins pseudo-potentials

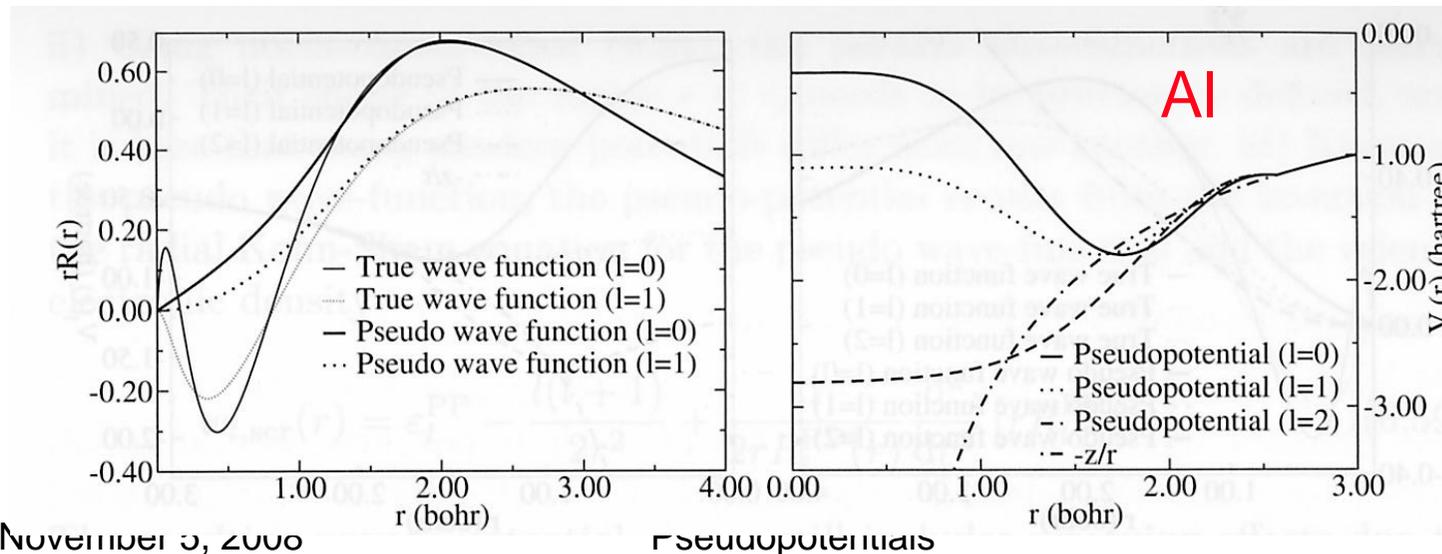
N. Troullier and J.L. Martins PRB 43 (1993) 1991

- Simpler than Hamann's approach
- Softer pseudo-potentials for 2p states of the first row elements
- Softer pseudo-potentials for d valence states of the transition metals
- However, it introduces additional constraints

Pseudo WF:
$$R_l^{PP}(r) = \begin{cases} R_{nl}^{AE}(r) & , \text{ if } r > r_l \\ r^l e^{p(r)} & , \text{ if } r < r_l \end{cases}$$

Coefficients defined from the continuity conditions and zero curvature of the PP at the origin

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

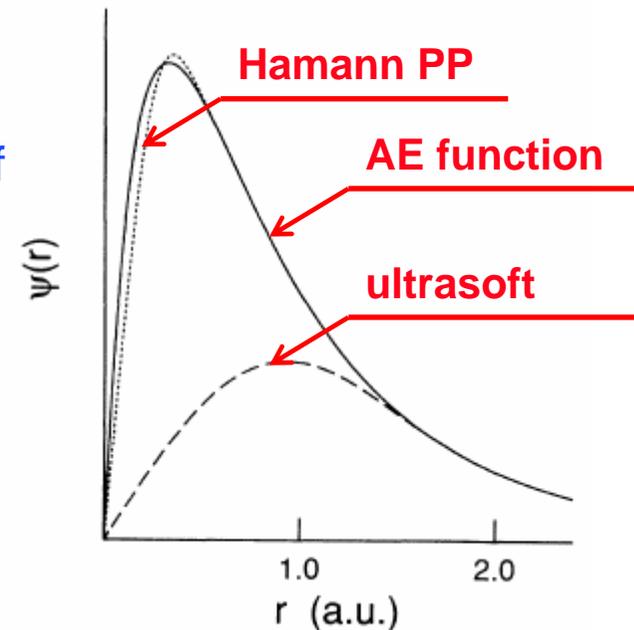




Ultrasoft pseudo-potentials

D. Vanderbilt, Phys. Rev. B 41, 7892–7895 (1990)
P. Blöchl, Phys. Rev. B 41, 5414–5416 (1990)

- Norm-conserving PPs can be very accurate, but they are usually not very smooth, so that pseudo WF are somewhat bumpy due to norm conservation
- Problematic for 2p, 3d, etc states at the beginning of the atomic shell, as no core states with the same angular momentum: the WF are nodeless and extend into the core region
- Different approach: ultra-soft PPs
 - Similar in spirit to OPW (a smooth valence function + an auxiliary function around the core)
 - The norm-conservation condition is relaxed, the core auxiliary functions are not orthogonal and do not conserve the charge



2p radial function for oxygen (LDA)



Ultrasoft pseudo-potentials (2)

(Non-strict derivation, just the basic idea)

- We introduce a new function $\tilde{\phi} = r\tilde{\psi}$ that is not norm conserving (indices l, m are omitted). $\phi = r\psi$ is the norm-conserving function

- The difference in the norm equation:

$$\Delta Q_{s,s'} = \int_0^{R_c} dr \Delta Q_{s,s'}(r) \quad \Delta Q_{s,s'}(r) = \phi_s^*(r)\phi_{s'}(r) - \tilde{\phi}_s^*(r)\tilde{\phi}_{s'}(r)$$

- We can define a new non-local potential operator

$$\delta \hat{V}_{\text{NL}}^{\text{US}} = \sum_{s,s'} D_{s,s'} |\beta_s\rangle \langle \beta_{s'}| \quad D_{s,s'} = B_{s,s'} + \varepsilon_{s'} \Delta Q_{s,s'} \quad B_{s,s'} = \langle \psi_s | \chi_{s'} \rangle \quad \beta_s = \sum_{s'} B_{s,s'}^{-1} \chi_{s'}$$

$$\chi_{lm}^{\text{PS}}(\mathbf{r}) \equiv \left\{ \varepsilon_l - \left[-\frac{1}{2} \nabla^2 + V_{\text{local}}(r) \right] \right\} \psi_{lm}^{\text{PS}}(\mathbf{r}) \quad \delta \hat{V}_{\text{NL}} = \sum_{lm} \frac{|\chi_{lm}^{\text{PS}}\rangle \langle \chi_{lm}^{\text{PS}}|}{\langle \chi_{lm}^{\text{PS}} | \psi_{lm}^{\text{PS}} \rangle}$$

- So that the smooth functions are solutions of the generalized eigenvalue problem

$$[\hat{H} - \varepsilon_s \hat{S}] \tilde{\psi}_s = 0 \quad \hat{H} = -\frac{1}{2} \nabla^2 + V_{\text{local}} + \delta \hat{V}_{\text{NL}}^{\text{US}} \quad \hat{S} = \hat{\mathbf{I}} + \sum_{s,s'} \Delta Q_{s,s'} |\beta_s\rangle \langle \beta_{s'}|$$

- Each pseudo-WF can now be generated independently with only the constraint of matching at a given cut-off radius, so allowing a choice of larger cut-offs for improved smoothness

- Final functions are then normalized to the correct charge and the non-local potential is modified



General remarks on pseudo-potentials

- There is no one “best pseudo-potential” for a given atom. There might be many best choices, each optimized for some particular use.
- In general, there are two competing factors:
 - Accuracy and transferability generally lead to the choice of a small cut-off radius and a “hard” pseudo-potentials, since we want to describe accurately the behavior near the ion. Demanding on the dimension of the plane-wave basis set!
 - Smoothness generally leads to a choice of a larger cut-off radius and “soft” pseudo-potentials so that the wave functions can be described well by fewer basis functions

As often in atomistic simulations, a trade-off between accuracy and computational efficiency!

- All the above is also relevant for real-space calculations using PPs!



Projector-Augmented plane-Wave method

- The main disadvantage of the techniques based on energy-independent PP calculations: it is not possible to restore the actual wave function
- Alternative scenario: Projector-Augmented plane-Wave (PAW) method
- Similar to the ultra-soft PP method, it introduces projectors and auxiliary functions.
- The method also defines a functional for the total energy that also involves auxiliary functions
- The method keeps the full AE wave function: the whole wave function for each electron is calculated (as opposed to only valence pseudo-wave functions in the techniques based on PPs).
- All integrals are evaluated as a combination of integrals of smooth functions extending through space plus localized contributions evaluated over muffin-tin spheres, as in the augmented plane wave (APW) approach



Projector-Augmented plane-Wave method (2)

- The main idea: The full valence electron function φ_v is split into three parts:

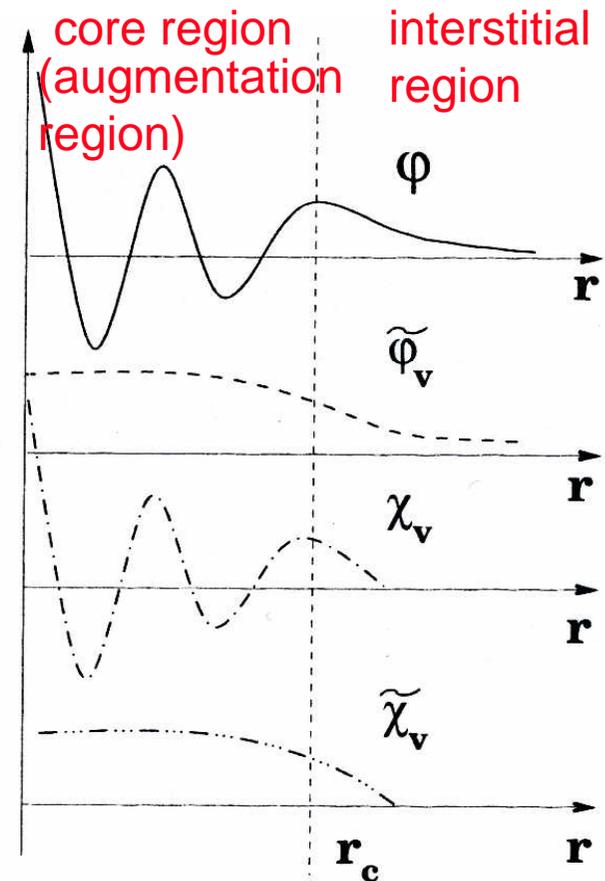
$$\varphi_v = \tilde{\varphi}_v + \chi_v - \tilde{\chi}_v$$

- $\tilde{\varphi}_v$ Is smooth everywhere; is exact outside the core region (augmentation region)
- χ_v is exact inside the augmentation region, smoothly tends to zero outside; incorporates all the necessary node structure of the exact function
- $\tilde{\chi}_v$ the net part is also smooth

- Electron density, KS equations and the total electron energy can be partitioned appropriately
- APW approach:

$$e^{-i\mathbf{K}\cdot\mathbf{r}} = 4\pi \sum_{lm} i^l j_l(Kr) Y_{lm} * (\theta_K, \phi_K) Y_{lm}(\theta, \phi)$$

$$\psi_{\mathbf{k}} = \sum_{\mathbf{G}} c_{\mathbf{G}} \psi_{\mathbf{k}+\mathbf{G}}^{APW} \quad \psi_{\mathbf{K}}^{APW} = 4\pi \sum_{lm} \frac{j_l(KR_s)}{R_l(R_s, \epsilon)} i^l R_l(r, \epsilon) Y_{lm} * (\theta_K, \phi_K) Y_{lm}(\theta, \phi)$$





PAW for small molecules

From G. Kresse's presentations, see VASP main page

<http://cms.mpi.univie.ac.at/vasp-workshop/slides/documentation.htm>

	PAW	hard	AE
H ₂	1.447		1.446 ^a
Li ₂	5.120		5.120 ^a
Be ₂	4.520		4.521 ^a
Na ₂	5.663		5.67 ^a
CO	2.141	2.128	2.129 ^a
N ₂	2.076	2.068	2.068 ^a
F ₂	2.633	2.621	2.615 ^a
P ₂	3.570		3.572 ^a
H ₂ O	1.839	1.835	1.833 ^a
$\alpha(\text{H}_2\text{O})(^\circ)$	105.3	104.8	105.0 ^a
BF ₃	2.476	2.470	2.464 ^b
SiF ₄	2.953	2.948	2.949 ^b

- results for the bond length of several molecules obtained with the PAW and AE approaches
- using standard PAW potentials (and hard PAW potentials)
- well converged relaxed core AE calculations yield identical results

^a NUMOL, R.M. Dickson, A.D. Becke, J. Chem. Phys. **99**, 3898 (1993).

^b GAUSSIAN94, S. Goedecker, et al., Phys. Rev. B **54**, 1703 (1996).



US-PP vs PAW potentials

From G. Kresse's presentations, see VASP main page
<http://cms.mpi.univie.ac.at/vasp-workshop/slides/documentation.htm>

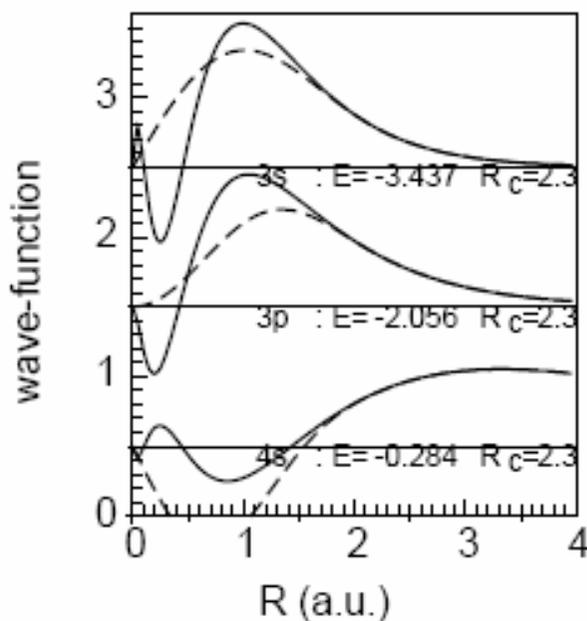
- The general rule is to use PAW potentials wherever possible
- Less parameters involved in the construction of PAW potentials
 - improved accuracy for:
 - magnetic materials
 - alkali and alkali earth elements, early 3d elements to left of periodic table
 - lanthanides and actinides
- General construction scheme is similar for US-PP and PAW
- Note that the potentials can be different depending on which method LDA/GGA was used in the parametrization calculations



Alkali and alkali earth metals

From G. Kresse's presentations, see VASP main page
<http://cms.mpi.univie.ac.at/vasp-workshop/slides/documentation.htm>

- an accurate treatment of these elements in ionic compounds is very important: oxides e.g. perovskites
- strongly ionised 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 3s and 4s states equally well in any pseudopotential description (mutual orthogonality)

in PAW, this is no problem at all, and the energy cutoffs remain modest (for Ca 200 eV)



PAW versus US-PP potentials

From G. Kresse's presentations, see VASP main page
<http://cms.mpi.univie.ac.at/vasp-workshop/slides/documentation.htm>

- the PAW potentials are generally of similar hardness across the periodic table
- most of the PAW potentials were optimised to work at a cutoff of 250-300 eV
- PAW potentials are usually slightly harder than US-PP
- for compounds where often species with very different covalent radii are mixed, the PAW potentials are clearly superior
- for one component systems the US-PP might be slightly faster (at the price of a somewhat reduced precision)
- for the US-PP the radial cutoff were chose according to the covalent radius (periodic table)
- the US-PP become progressively softer when you move down in the periodic table