Pseudo potentials

Why use pseudo potentials?

- **Reduction of basis set size**
  effective speedup of calculation

- **Reduction of number of electrons**
  reduces the number of degrees of freedom
  For example in Pt: 10 instead of 78

- **Unnecessary** "Why bother? They are inert anyway..."

- **Inclusion of relativistic effects**
  relativistic effects can be included "partially" into effective potentials

Why use pseudo potentials?
Estimate for number of plane waves

plane wave cutoff

$\updownarrow$

most localized function

1s Slater type function $\approx exp[-Zr]$
Z: effective nuclear charge

$$\phi_{1s}(\mathbf{G}) \approx \frac{16\pi Z^{5/2}}{G^2 + Z^2}$$

	Cutoff	Plane waves
H	1	1
Li	4	8
C	9	27
Si	27	140
Ge	76	663

Pseudo potentials
What is it?

- Replacement of the all-electron, $-Z/r$ problem with a Hamiltonian containing an effective potential

- It should reproduce the necessary physical properties of the full problem at the reference state

- The potential should be transferable, *i. e.* also be accurate in different environments

The construction consists of two steps of approximations

- Frozen core approximation

- Pseudisation

Frozen core approximation

- Core electrons are chemically inert

- Core/Valence separation is often not clear
  in plane wave calculations: core = all filled shells

- Core wavefunctions are transfered from atomic reference
  calculation

- Core electrons of different atoms do not overlap

Remaining problems

- Valence wavefunctions have to be orthogonalized to core states $\rightarrow$ nodal structures $\rightarrow$ high plane wave cutoff

- Pseudo potential should produce node-less functions and include Pauli repulsion

- Pseudo potential replaces Hartree and XC potential due to the core electrons

- XC functionals are not linear: approximation

$$E_{\mathsf{XC}}(n_{\mathsf{c}} + n_{\mathsf{v}}) = E_{\mathsf{XC}}(n_{\mathsf{c}}) + E_{\mathsf{XC}}(n_{\mathsf{v}})$$

This assumes that core and valence electrons do not overlap. This restriction can be overcome with the "non–linear core correction" (NLCC) discussed later.
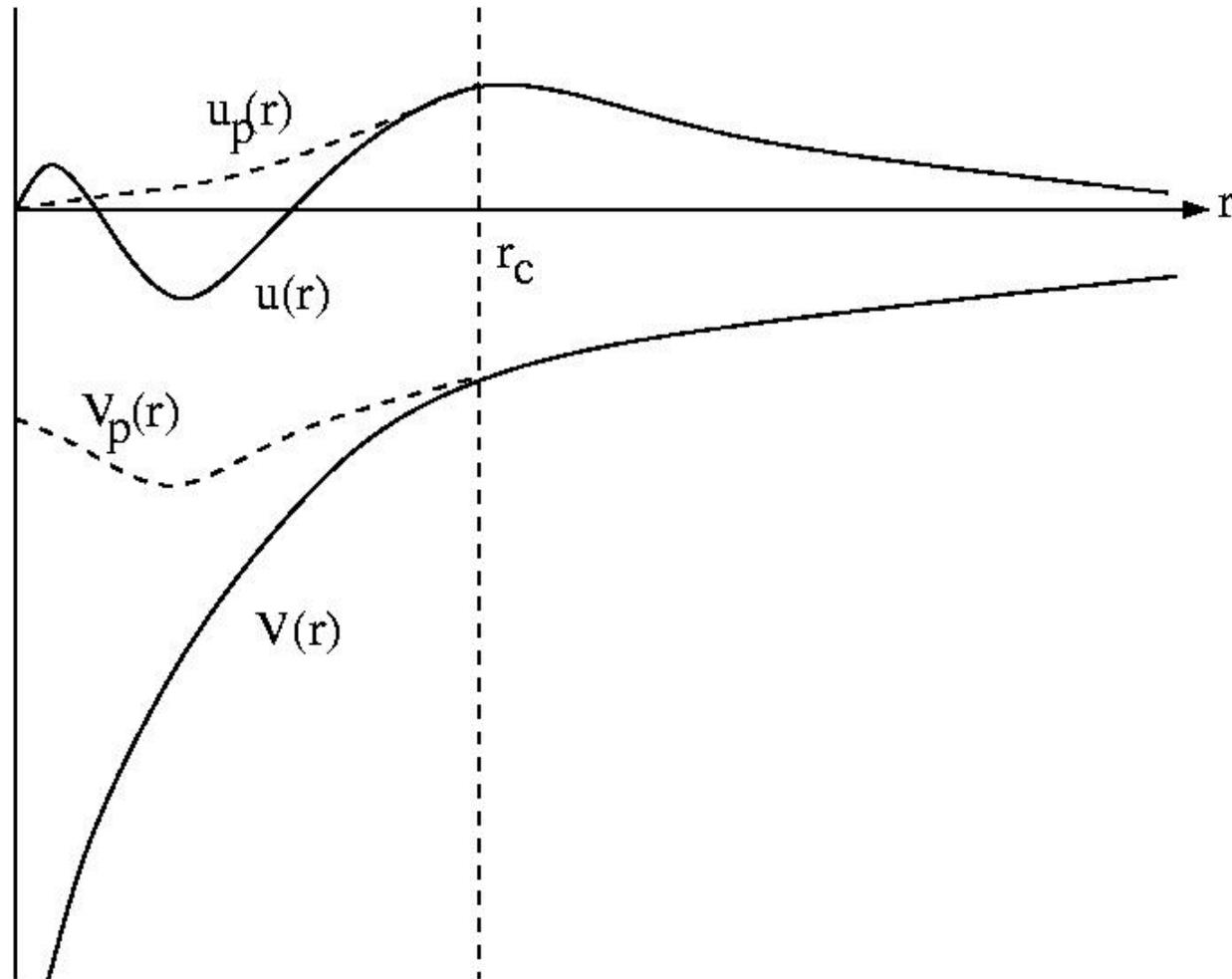
Atomic pseudo potentials

$$n(\mathbf{r}) = n_{\mathsf{C}}(\mathbf{r}) + n_{\mathsf{V}}(\mathbf{r})$$

Valence Kohn–Sham Equations

$$\boxed{\left(T + V(\mathbf{r}, \mathbf{r}') + V_{\mathsf{H}}(n_{\mathsf{V}}) + V_{\mathsf{XC}}(n_{\mathsf{V}})\right) \Phi_i^{\mathsf{V}}(\mathbf{r}) = \epsilon_i \Phi_i^{\mathsf{V}}(\mathbf{r})}$$

Pseudo potential $V(\mathbf{r}, \mathbf{r}')$ has to be chosen such that the main properties of the atom are reproduced.

Pseudization of Valence Wavefunctions

General Recipe

1. Atomic all–electron calculation (reference state)
   $\Rightarrow \Phi_i^{\text{v}}(\mathbf{r})$ and ϵ_i.

2. Pseudize $\Phi_i^{\text{v}} \Rightarrow \Phi_i^{\text{PS}}$

3. Calculate potential from

$$\left(T + V_i(\mathbf{r})\right) \Phi_i^{\text{PS}}(\mathbf{r}) = \epsilon_i \Phi_i^{\text{PS}}(\mathbf{r})$$

4. Calculate pseudo potential by unscreening of $V_i(\mathbf{r})$

$$V_i^{\text{PS}}(\mathbf{r}) = V_i(\mathbf{r}) - V_{\text{H}}(n_{\text{PS}}) - V_{\text{XC}}(n_{\text{PS}})$$

V_i^{PS} is state dependent !

Semi-local Pseudo potentials

$$V^{\mathsf{PS}}(\mathbf{r}, \mathbf{r}') = \sum_l V_l^{\mathsf{PS}}(r) \ | \, Y_{lm}(\hat{\mathbf{r}}) \rangle \langle Y_{lm}(\hat{\mathbf{r}}') \, |$$

where Y_{lm} are spherical harmonics.

If there is more than one valence state per angular momentum, the procedure has to be slightly adapted. But there is still only one V_l^{PS}. This procedure generates a pseudo potential per occupied angular momentum in the reference state.

Norm-Conserving Pseudo potentials

Hamann-Schlüter-Chiang-Recipe (HSC) Conditions

1. Real and pseudo valence eigenvalues agree for a chosen prototype atomic configuration. $\epsilon_l = \widehat{\epsilon}_l$

2. Real and pseudo atomic wave functions agree beyond a chosen core radius r_c.

$$\Psi_l(r) = \Phi_l(r) \quad \text{for } r \geq r_c$$

3. The integrals from 0 to R of the real and pseudo charge densities agree for R $\geq$ r_c for each valence state (norm conservation).

$$\langle\Phi_l|\Phi_l\rangle_R = \langle\Psi_l|\Psi_l\rangle_R \quad \text{for } R \geq r_c$$

where

$$\langle\Phi|\Phi\rangle_R = \int_0^R r^2|\phi(r)|^2 dr$$

4. The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for r $\geq$ r_c.

Property 3) and 4) are related through

$$-\frac{1}{2}\left[(r\Phi)^2\frac{d}{d\epsilon}\frac{d}{dr}ln\Phi\right]_R = \int_0^R r^2|\Phi|^2 dr$$

Recipes to Construct Norm-conserving Pseudo potentials

- **Bachelet-Hamann-Schüter (BHS) Form**

  G.B. Bachelet et al., Phys. Rev. B, **26**, 4199 (1982)

  Recipe and analytic form of V_l^{PS}

- **Kerker Recipe** G.P. Kerker, J. Phys. C **13**, L189 (1980)

  analytic pseudization function

- D. Vanderbilt, Phys. Rev. B, **32**, 8412 (1985)

- **Kinetic energy optimized pseudo potentials**
  A.M. Rappe et al., Phys. Rev. B, **41**, 1227 (1990)
  J.S. Lin et al., Phys. Rev. B, **47**, 4174 (1993)

Troullier–Martins Recipe

N. Troullier and J.L. Martins, Phys. Rev. B, **43**, 1993 (1991)

$$\Phi_l^{\mathsf{PS}}(\mathbf{r}) = r^{l+1} e^{p(r)} \quad r \leq r_c$$

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

determine c_n from

- norm–conservation

- smoothness at r_c (for $m = 0 \ldots 4$)
  $$\left. \frac{d^m \Phi}{dr^m} \right|_{r=r_c-} = \left. \frac{d^m \Phi}{dr^m} \right|_{r=r_c+}$$

- $\left. \dfrac{d\Phi}{dr} \right|_{r=0} = 0$

Separation of Local and Nonlocal Parts

$$V^{\mathsf{PS}}(\mathbf{r}, \mathbf{r}') = \sum_{L=0}^{\infty} V_L^{\mathsf{PS}}(r)|Y_L\rangle\langle Y_L|$$

Approximation: all potentials with $L > L_{\mathsf{max}}$ are equal to $V_{\mathsf{loc}}^{\mathsf{PS}}$
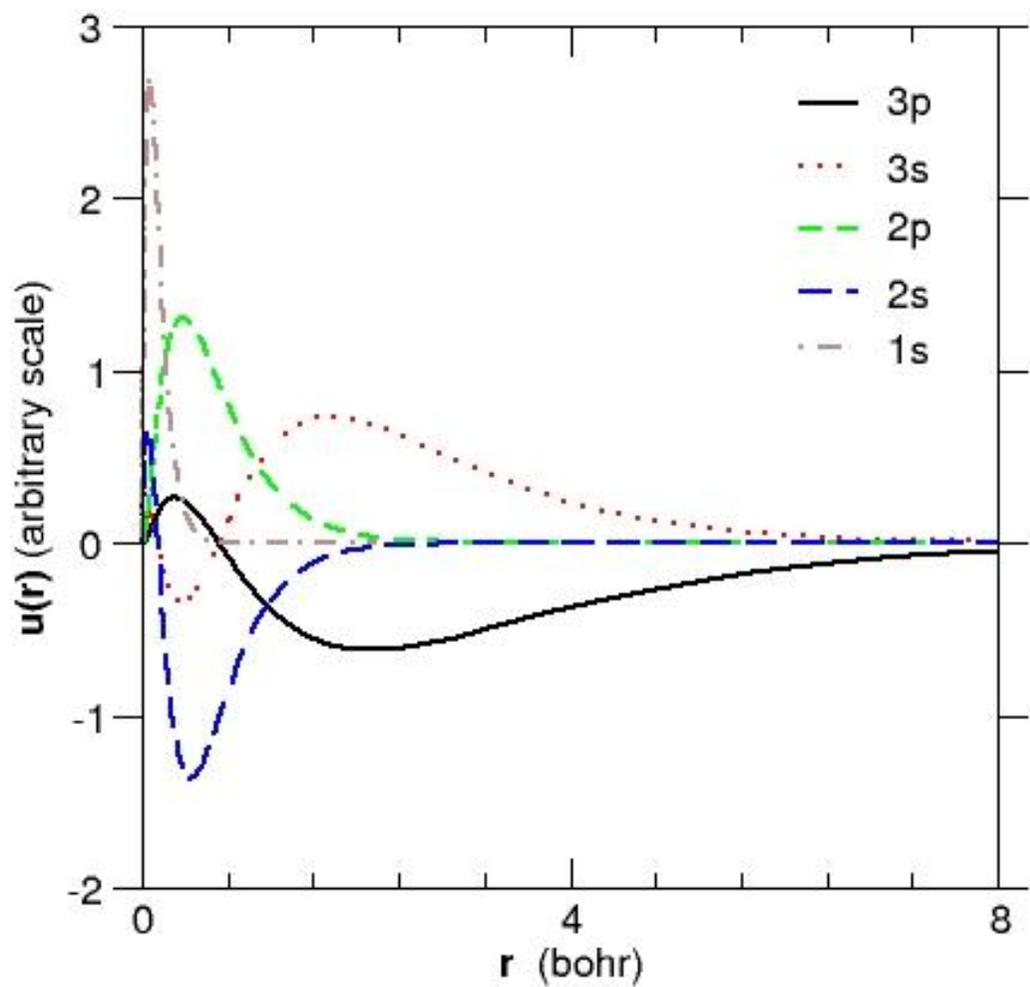
$$
\begin{aligned}
V^{\mathsf{PS}}(\mathbf{r}, \mathbf{r}') &= \sum_{L=0}^{L_{\mathsf{max}}} V_L^{\mathsf{PS}}(r)|Y_L\rangle\langle Y_L| + \sum_{L=L_{\mathsf{max}}+1}^{\infty} V_{\mathsf{loc}}^{\mathsf{PS}}(r)|Y_L\rangle\langle Y_L| \\
&= \sum_{L=0}^{L_{\mathsf{max}}} \left(V_L^{\mathsf{PS}}(r) - V_{\mathsf{loc}}^{\mathsf{PS}}(r) \right)|Y_L\rangle\langle Y_L| + \sum_{L=0}^{\infty} V_{\mathsf{loc}}^{\mathsf{PS}}(r)|Y_L\rangle\langle Y_L| \\
&= \sum_{L=0}^{L_{\mathsf{max}}} \left(V_L^{\mathsf{PS}}(r) - V_{\mathsf{loc}}^{\mathsf{PS}}(r) \right)|Y_L\rangle\langle Y_L| + V_{\mathsf{loc}}^{\mathsf{PS}}(r)
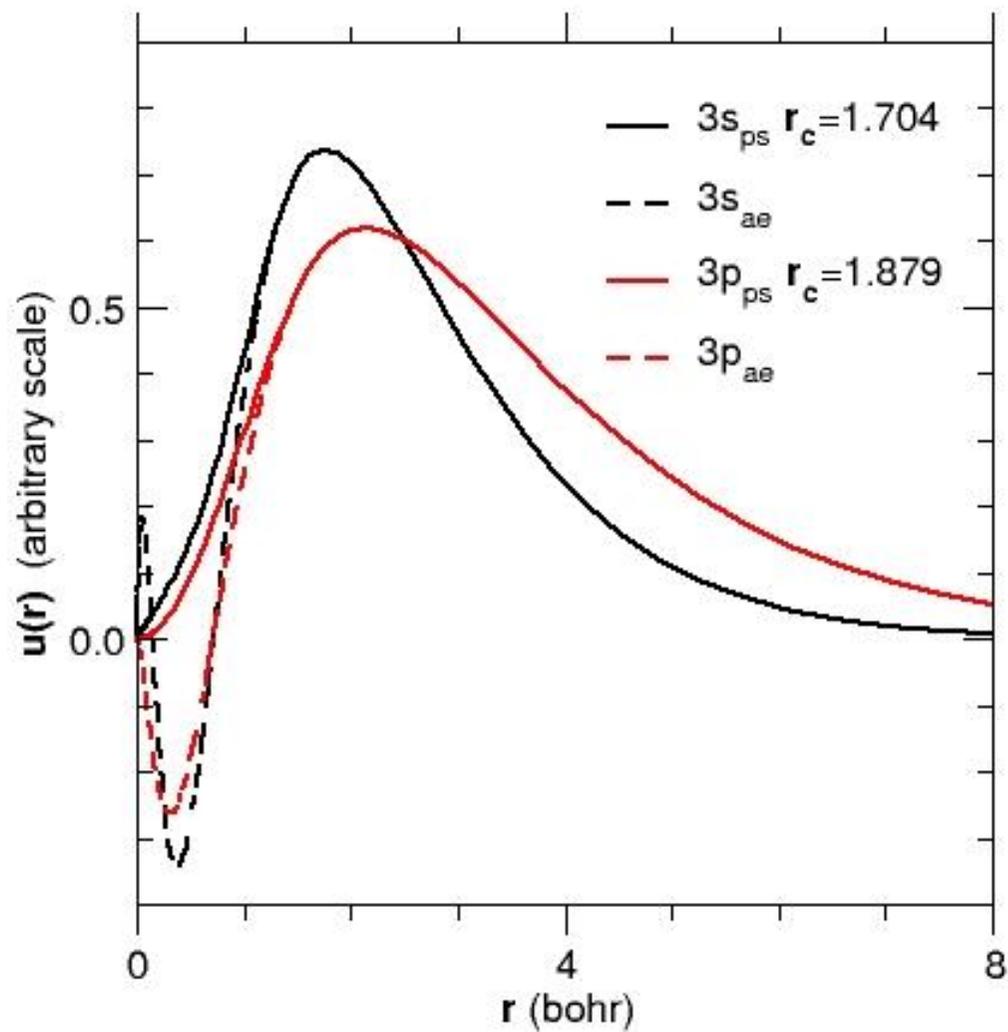\end{aligned}
$$

Final Form

$$V^{\mathsf{PS}}(\mathbf{r}, \mathbf{r}') = V_{\mathsf{loc}}^{\mathsf{PS}}(r) + \sum_{L=0}^{L_{\mathsf{max}}} \Delta V_L^{\mathsf{PS}}(r) |Y_L\rangle \langle Y_L|$$

- Local pseudo potential $V_{\mathsf{loc}}^{\mathsf{PS}}$

- Non-local pseudo potential ΔV_L^{PS}
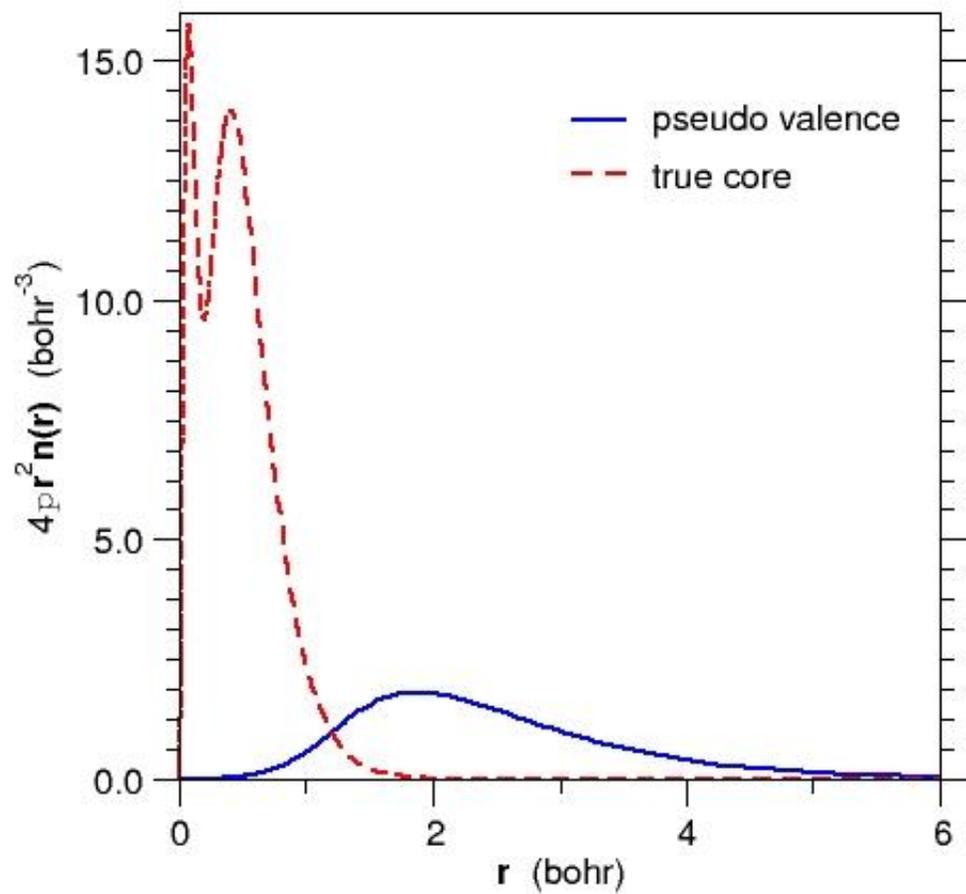
- Any L quantum number can have a non-local part

Silicon: Radial wave functions
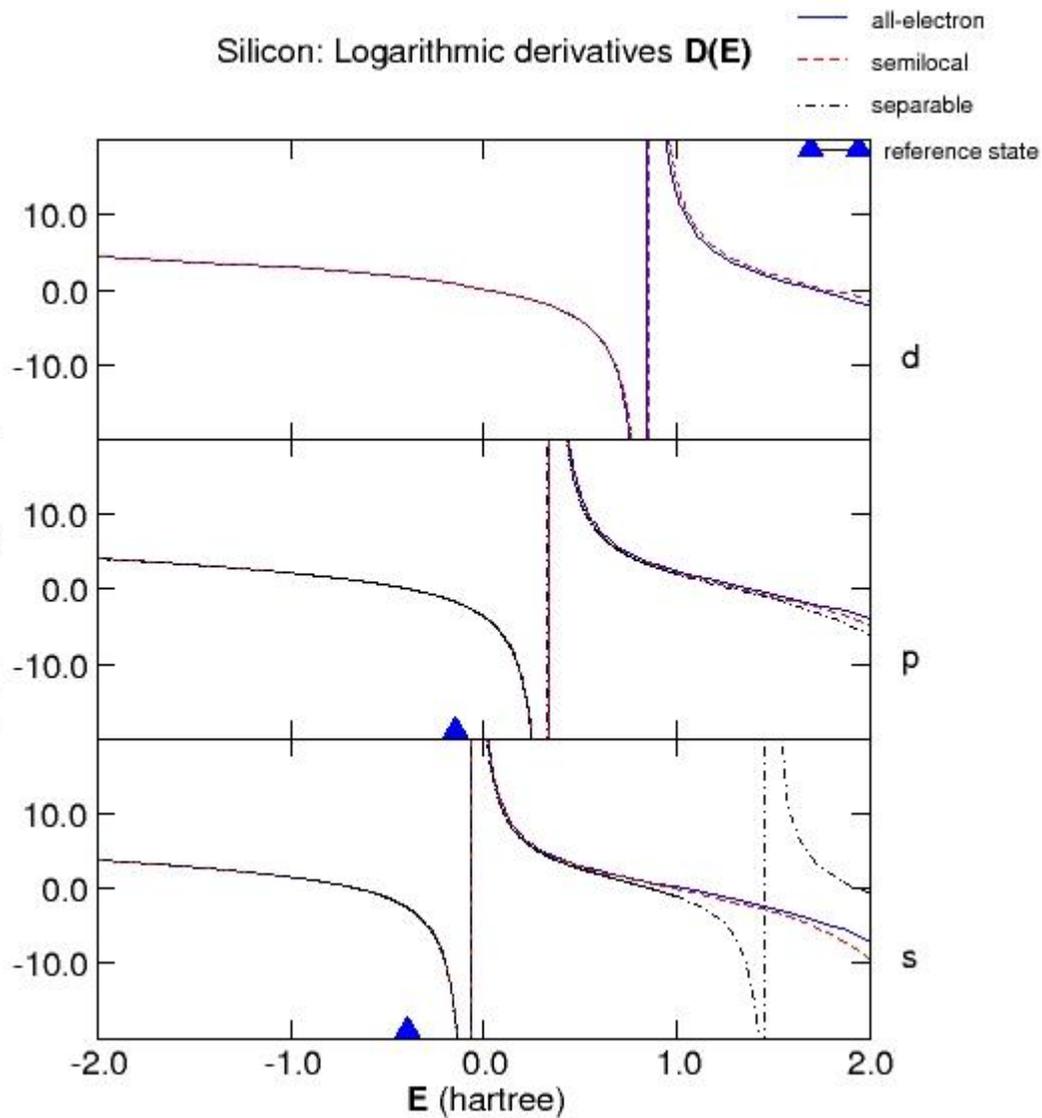
Silicon: Pseudo vs all-electron wave functions

3p
3s
2p
2s
1s

$3s_{ps}$ r_c=1.704
$3s_{ae}$
$3p_{ps}$ r_c=1.879
$3p_{ae}$

Silicon: Radial densities
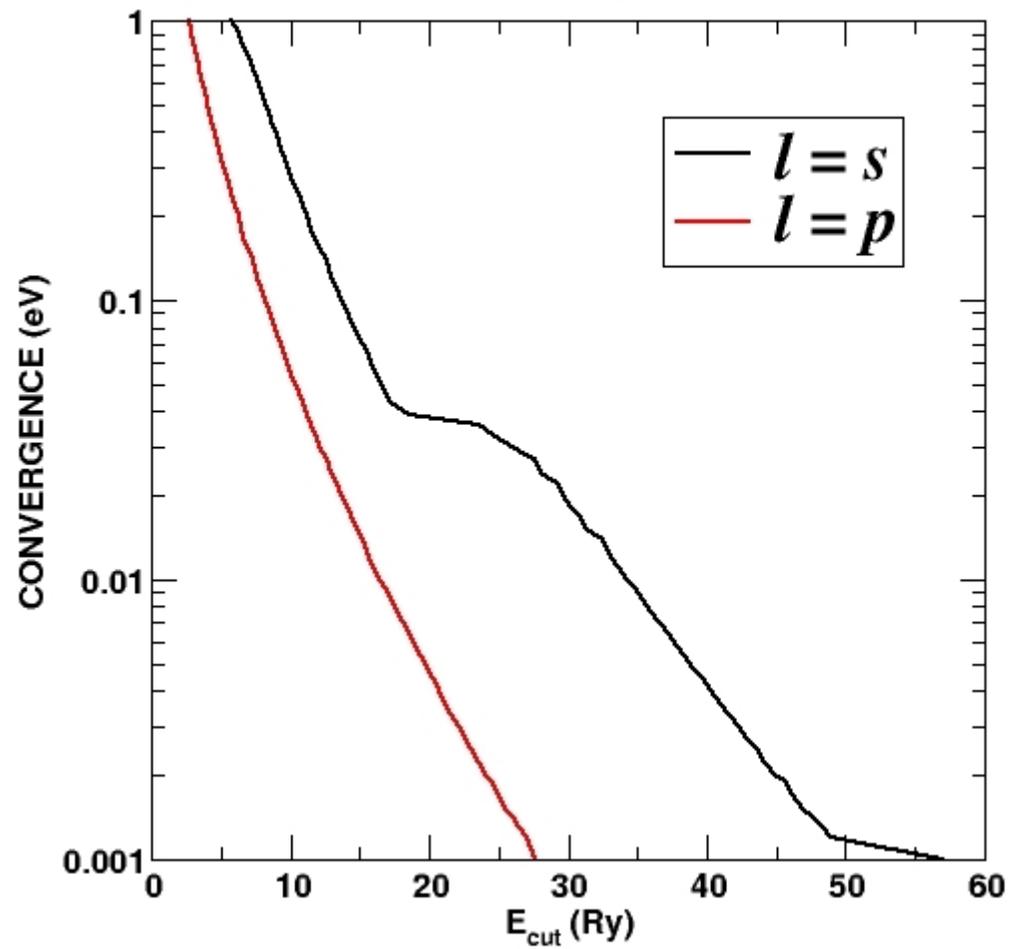
Silicon: Ionic pseudo potentials
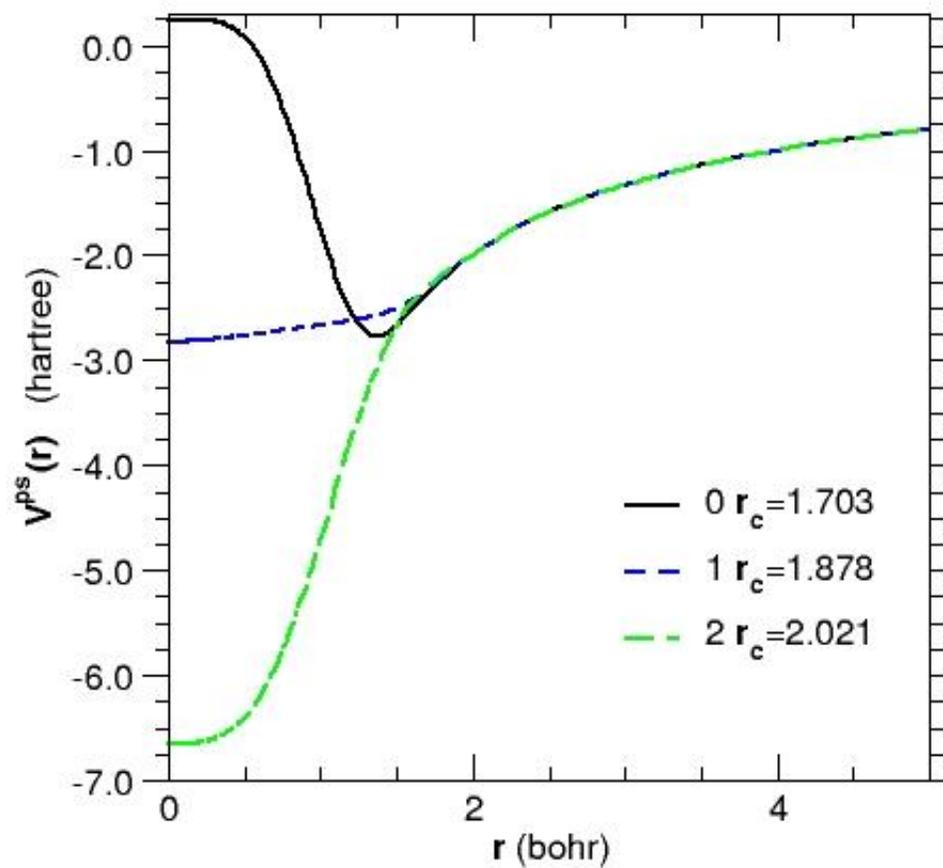
Silicon: Logarithmic derivatives D(E)

Silicon
$E_{kin}(E_{cut}) - E_{kin}(\infty)$

Non-Local PP in PW Calculations

$$E_{\mathsf{PS}} = \sum_L \sum_i f_i \int [\Phi_i \mid Y_L](r) \; \triangle V_L^{\mathsf{PS}}(r) \; [Y_L \mid \Phi_i](r) \; dr$$

$$[\Phi_i \mid Y_L](r) = \int \Phi_i(\mathbf{r}) Y_L(\hat{\mathbf{r}}) d\hat{\mathbf{r}}$$

Integral depends on r.

Gauss–Hermite Integration

$$E_{\mathsf{PS}}^{\mathsf{nl}} = \sum_L \sum_i f_i \sum_k w_k \Delta V_L^{\mathsf{PS}}(r_k) \left([\Phi_i \mid Y_L](r_k) \right)^2$$

Accurate integration requires $\approx$ 15 - 25 points.

For an atom with s and p non-local potential this requires the calculation of 60 - 100 times number of states integrals $[\Phi_i \mid Y_L](r)$.

Basis Set Expansion

Resolution of identity $1 = \sum_n |\varphi_n\rangle\langle\varphi_n|$ for a complete orthonormal basis set $\{\varphi_n\}$.

$$E_{\mathsf{PS}} = \sum_L \sum_i f_i \sum_{nm} \langle \Phi_i \mid \varphi_n \rangle$$
$$\int [\varphi_n \mid Y_L](r) \; V_L^{\mathsf{PS}}(r) \; [Y_L \mid \varphi_m](r) \; dr \langle \varphi_m \mid \Phi_i \rangle$$

Using $[\varphi_n \mid Y_L](r) = \varphi_n(r)$ we can calculate the basis set expansion of the pseudo potential

$$V_{L,nm}^{\mathsf{PS}} = \int \varphi_n(r) V_L^{\mathsf{PS}}(r) \varphi_m(r) dr$$

and get

$$E_{\mathsf{PS}} = \sum_L \sum_i f_i \sum_{nm} \langle \Phi_i \mid \varphi_n \rangle V_{L,nm}^{\mathsf{PS}} \langle \varphi_m \mid \Phi_i \rangle$$

Typical basis set expansions contain only a few functions.

Kleinman–Bylander Form

Basis set expansion with the following approximation for the identity:

$$1 = \sum_L \frac{|\varphi_L\rangle\langle\Delta V_L\varphi_L|}{\langle\varphi_L\delta V_L\varphi_L\rangle}$$

where φ_L is the pseudo–atomic wavefunction from the reference calculation.

$|\Delta V_L\varphi_L\rangle$ is localized within r_c.

Kleinman–Bylander Form

$$E_{\mathsf{PS}} = \sum_L \sum_i f_i \langle \Phi_i \mid \delta V_L \varphi_L \rangle \omega_L \langle \delta V_L \varphi_L \mid \Phi_i \rangle$$

where

$$\omega_L = \langle \varphi_L \delta V_L \varphi_L \rangle$$

For an atom with s and p non-local potential this requires the calculation of 4 times number of states integrals $\langle \delta V_L \varphi_L \mid \Phi_i \rangle$ Generalization of the Kleinman–Bylander form to more than 1 reference function by Blöchl (1990) and Vanderbilt (1990).

Ghost States

Problem: in Kleinman–Bylander form, the node-less wfn is no longer the solution with the lowest energy.

Solution: carefully tune the local part of the pseudo potential until the ghost states disappear

How to find host states: Look for following properties

- Deviations of the logarithmic derivatives of the energy of the KB–pseudo potential from those of the respective semi-local pseudo potential or all–electron potential.

- Comparison of the atomic bound state spectra for the semi-local and KB–pseudo potentials.

- Ghost states below the valence states are identified by a rigorous criteria by Gonze et al.

Dual Space Pseudo potentials

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

C. Hartwigsen et al., Phys. Rev. B, **58** 3641 (1998)

- Functional form of pseudo potential: local part + fully separable non–local part

- All functions are expanded in Gaussians

- All free parameters are globally optimized

Ultra–soft Pseudo potentials and PAW method

- Many elements require high cutoff for plane wave calculations

  - First row elements: O, F

  - Transition metals: Cu, Zn

  - f elements: Ce

- relax norm-conservation condition

$$\int n^{\mathsf{PS}}(\mathbf{r})d\mathbf{r} + \int Q(\mathbf{r})d\mathbf{r} = 1$$

- Augmentation functions $Q(\mathbf{r})$ depend on environment.

- No full un-screening possible, $Q(\mathbf{r})$ has to be recalculated for each atom and atomic position.

- Complicated orthogonalization and force calculations.

- Allows for larger r_c, reduces cutoff for all elements to about 30 Rydberg.

Non-Linear Core Correction (NLCC)

For many atoms (e.g. alkali atoms, transition metals) core states overlap with valence states. Linearization assumption for XC energy breaks down.

- Add additional states to valence

  - adds more electrons

  - needs higher cutoff

- Add core charge to valence charge in XC energy $\Rightarrow$ non–linear core correction (NLCC)
  S.G. Louie et al., Phys. Rev. B, **26** 1738 (1982)

Non-Linear Core Correction (NLCC)

$$E_{\text{xc}} = E_{\text{xc}}(n + \tilde{n}_{\text{core}}) \quad \text{where} \quad \tilde{n}_{\text{core}}(r) = n_{\text{core}}(r) \quad \text{if } r > r_0$$
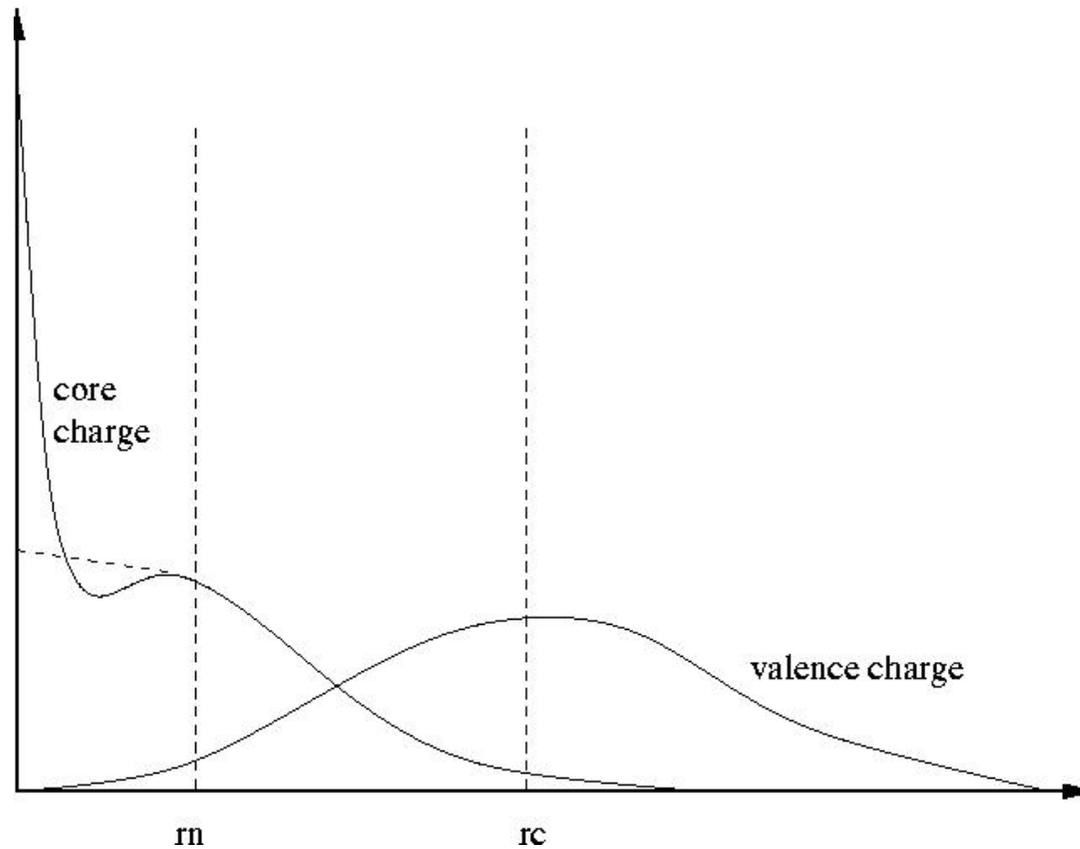
Non-Linear Core Correction (NLCC)

The total core charge of the system depends on the atomic positions.

$$\tilde{n}_{core}(\mathbf{G}) = \sum_I \tilde{n}^I_{core}(\mathbf{G}) S_I(\mathbf{G})$$

This leads to additional terms in the derivatives wrt to nuclear positions and the box matrix (for the pressure).

$$\frac{\partial E_{\mathsf{xc}}}{\partial \mathbf{R}_{I,s}} = -\Omega \sum_{\mathbf{G}} i\mathbf{G}_s V^\star_{\mathsf{xc}}(\mathbf{G}) \tilde{n}^I_{\mathsf{core}}(\mathbf{G}) S_I(\mathbf{G})$$

Specification of Pseudo potentials

- The pseudo potential recipe used and for each l value r_c and the atomic reference state

- The definition of the local potential and which angular momentum state have a non–local part

- For Gauss–Hermit integration: the number of integration points

- Was the Kleinman–Bylander scheme used ?

- NLCC: definition of smooth core charge and r_{loc}

Spin Polarized Calculations and Gradient Corrections

Spin Polarization If the frozen core approximation is valid, i.e. there is no spin polarization of core states, we can use the same pseudo potentials

Different Functionals Pseudo potentials in plane wave calculations are usually generated with the same functional as later used in the molecular calculation.

Testing of Pseudo potentials

- calculation of other atomic states

- calculation of transferability functions, logarithmic derivatives, hardness

- calculation of small molecules, compare to all electron calculations (geometry, harmonic frequencies, dipole moments)

- check of basis set convergence (cutoff requirements)

- calculation of test systems
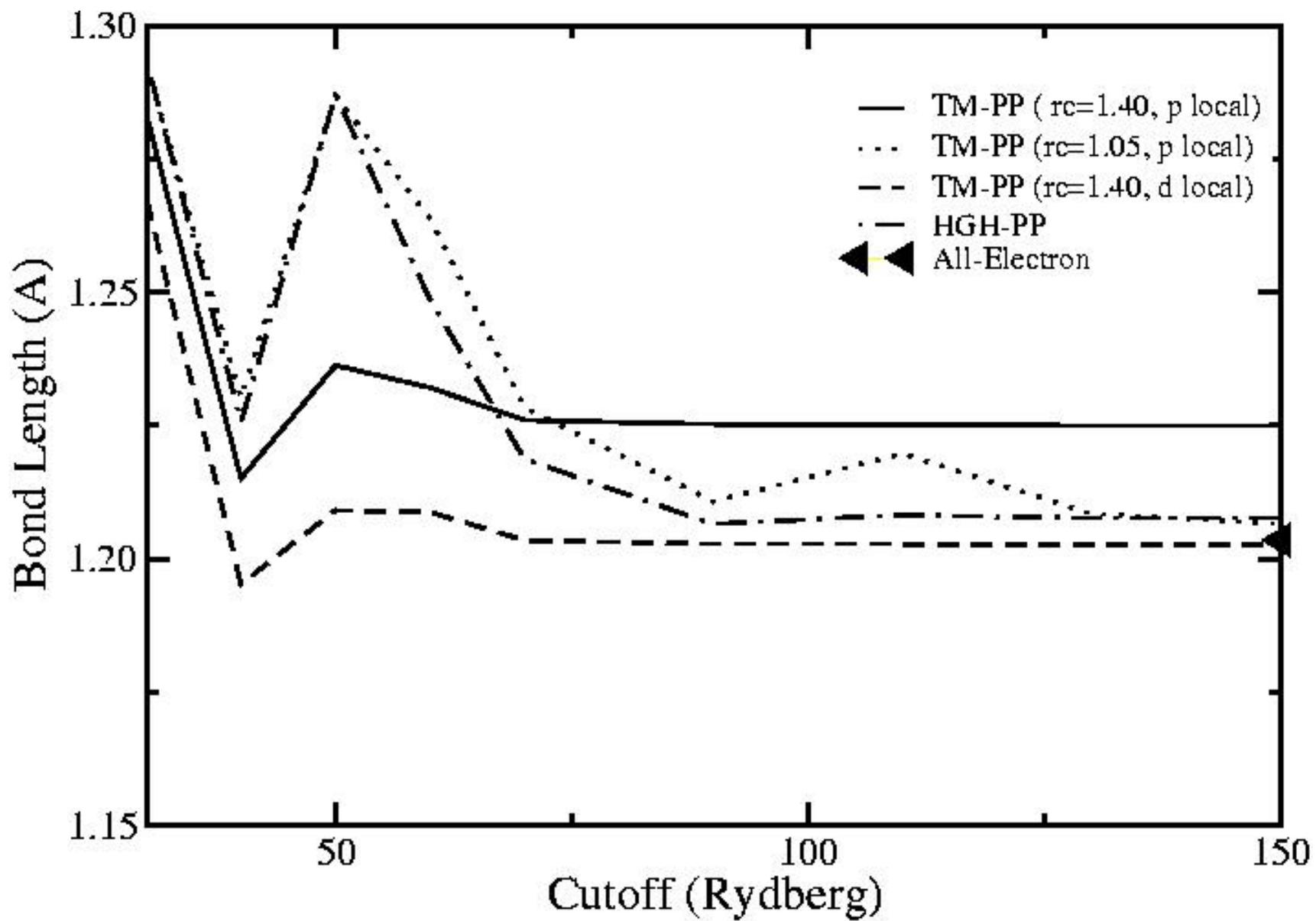
Pseudo potentials: Summary

- Pseudo potential are necessary when using plane wave basis sets in order to keep the number of the basis function manageable

- Pseudo potentials are generated at the reference state; transferability is the quantity describing the accuracy of the properties at other conditions

- The mostly used scheme in plane wave calculations is the Troullier-Martins pseudo potentials in the fully non-local, Kleinman-Bylander form

- Non-linear core correction is need if the core and valence electron densities overlap excessively

- Once created, a pseudo potential must be **tested**, **tested**, **tested**!!!