Pseudopotentials

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Pseudopotentials:
- what are they?
- why use them?
- why do they work (or not?)
- how to obtain?
- how to test & use?

Nuclear Potential

Electrons experience a Coulomb potential due to the nuclei.

This has a known and simple form:

$$\boxed{V_{nuc} = -\frac{Z}{r}}$$

But this leads to computational problems, especially when using a plane wave basis set!

Electrons in Atoms

- Electrons in atoms are arranged in shells.

- Quantum numbers:
  n [principal], l [angular], m_l [magnetic], m_s[spin]

- Rare gas atoms
  have certain complete subshells (inert configurations):
  He: $1s^2$ Ne: [He], $2s^2$, $2p^6$ Ar: [Ne] $3s^2$, $3p^6$
  Kr: [Ar], $3d^{10}$, $4s^2$,$4p^6$ Xe: [Kr], $4d^{10}$, $5s^2$, $5p^6$
  Rn: [Xe], $4f^{14}$, $5d^{10}$, $6s^2$,$6p^6$

- Can divide electrons in any atom into core and valence.

- This division is not always clear-cut, but usually
  core = rare gas configuration [+ filled d/f subshells]

Obtaining atomic wavefunctions

- Hydrogen(ic) atoms: solve exactly (analytically).
  Recall: $\psi_{lm}(\mathbf{r}) = \psi_l(r)Y_{lm}(\theta,\phi) = r^{-1}\phi_l(r)Y_{lm}(\theta,\phi)$

- When there are many interacting electrons: have to solve numerically.
  - Schrödinger equation / Dirac equation
  - Hartree-Fock equations
  - Kohn-Sham equations

Orthogonality

- For hydrogenic atoms, recall:

$$\psi_{lm}(\mathbf{r}) = \psi_l(r) Y_{lm}(\theta,\phi) = r^{-1}\phi_l(r) Y_{lm}(\theta,\phi)$$

- Radial part & Angular Part

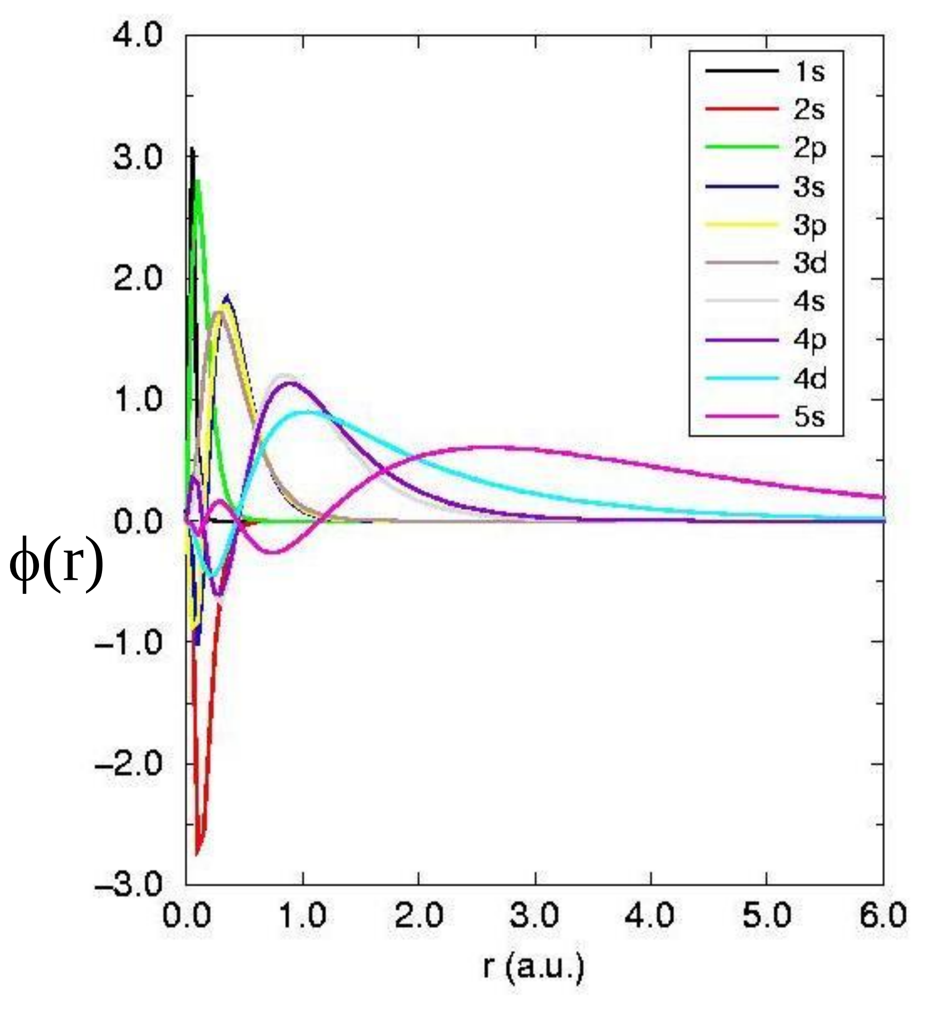
- Being eigenfunctions of a Hermitian operator, ψ_{lm}'s are orthonormal.

- Wavefunctions with same n, different l are orthogonal due to the nature of the angular part of the wavefunction.

- Wavefunctions with different n, same l are orthogonal due to the nature of the radial part of the wavefunction.

Example: wavefunctions for Ag atom

- Ground state configuration: [Kr], $4d^{10}$ $5s^{1}$ $5p^{0}$ $5d^{0}$



- Core wavefunctions sharply peaked near nucleus (so high Fourier components).
- Valence wavefunctions peaked far away from nucleus, lots of wiggles near nucleus (so high Fourier components).
- Not clear whether 4d should be considered core / valence.
- In a solid, wavefunction may also have some 5p, 5d character.
- 1s, 2p, 3d, 4f,… nodeless.

Core & Valence Electrons in Molecules & Solids

- Chemical bonds between atoms are formed by sharing / transferring electrons.
- Only the valence electrons participate in bonding.
- Wavefunctions of valence electrons can change significantly once the bond is formed.
- Wavefunctions of core electrons change only slightly when the bond is formed.
- All-electron calculations: both core and valence e^-s included (whether for atom or solid).

Problem for Plane-Wave Basis

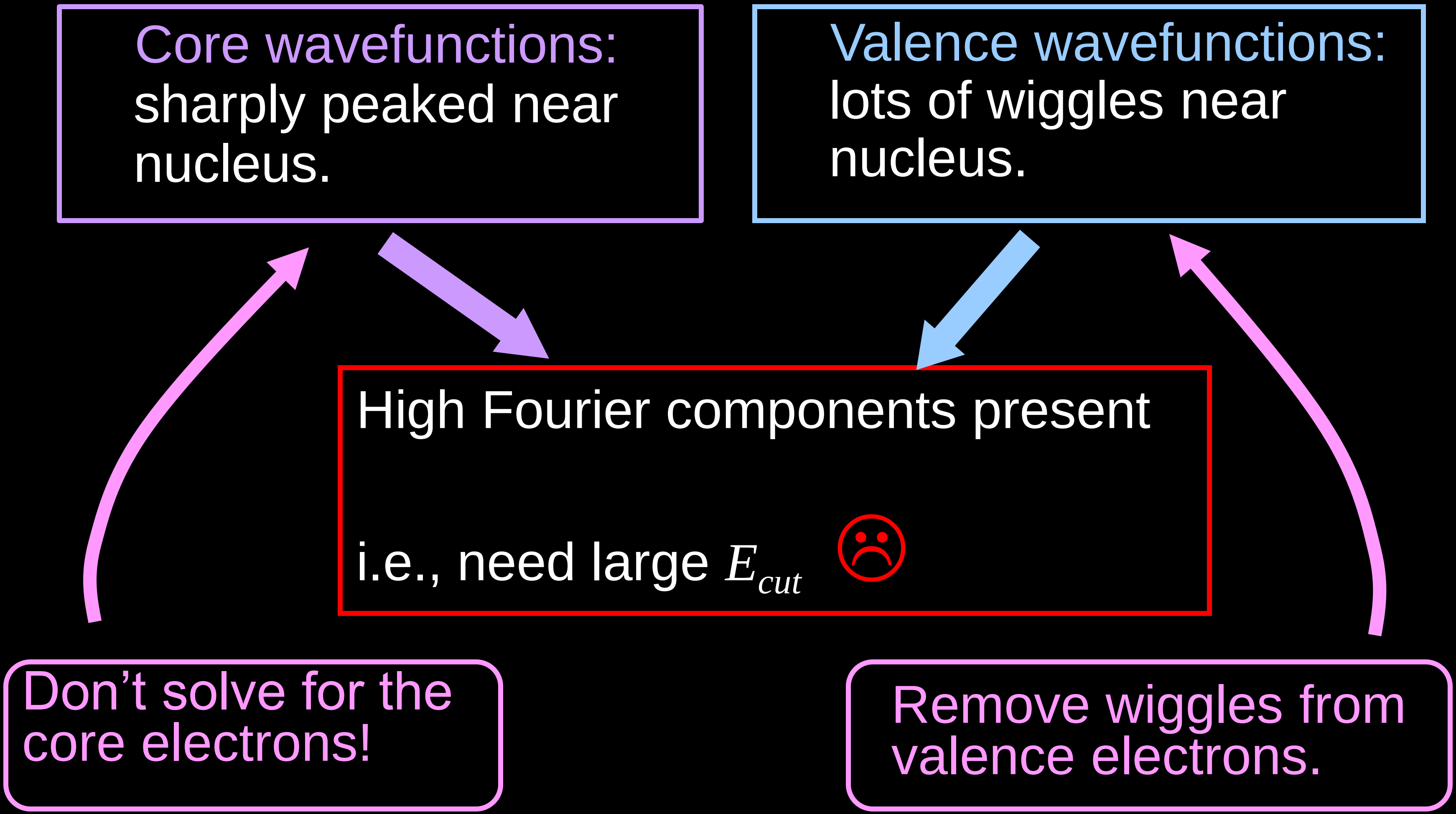
Core wavefunctions:
sharply peaked near nucleus.

Valence wavefunctions:
lots of wiggles near nucleus.

High Fourier components present

i.e., need large E_{cut} ☹

Problem for Plane-Wave Basis



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Valence wavefunctions: lots of wiggles near nucleus.

High Fourier components present

i.e., need large E_{cut} ☹

Don’t solve for the core electrons!

Remove wiggles from valence electrons.

The Pseudopotential Approximation

Frozen core: remove core-electron degrees of freedom
i.e., NOT an “All-electron” calculation.

Valence electrons see a weaker potential than the full Coulomb potential.

$$V_{nuc}(r) \rightarrow V_{ion}(r)$$

Further tailor this potential so that wavefunctions behave ‘properly’ in region of interest, yet computationally cheap.

How the Pseudopotential Helps

- When solving using a basis (especially plane waves), basis size drastically reduced (smaller matrices to diagonalize). ***

- Have to solve for fewer eigenvalues.
- No Coulomb singularity (cusp in wavefunction) at origin.

Disadvantages:

- Can lose accuracy

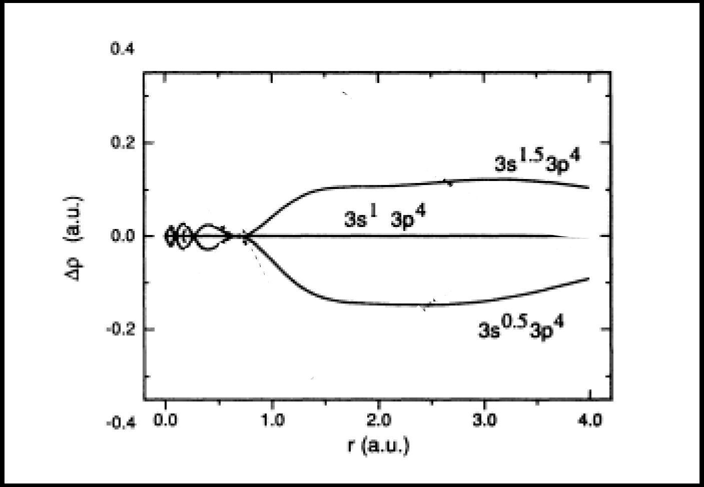
An analogy!

- "Dummy cops" used by many law-enforcement agencies!
- Stick a mannequin in uniform by the highway … if it looks like a cop, it works like a cop!
- Don't care about internal structure as long as it works right!
- But cheaper!!
- Obviously it can't reproduce all the functions of a real cop, but should be convincing enough to produce desired results….

Hey, we have them in Bangalore, too!

Is the core really frozen?

- Example: see how density for P changes when electronic configuration changed:



Goedecker & Maschke,1992

- All-electron calc.: changes in ρ mostly outside core region.
- Reproduced well by a pseudopotential.

- Pseudopotential won't work well in cases where polarizable semicore states contribute to bonding.

Wish List for a Good Pseudopotential

For accuracy:

- Should reproduce scattering properties of true potential.
- Transferable: Nice to have one pseudo-potential per element, to use in variety of chemical environments.
- Norm conserving? *(will explain)*
- *Ab initio*? (no fitting to experimental data)

For (computational) cheapness:

- Smooth / Soft: Need smaller basis set (esp. plane waves)
- 'Separable'? *(will skip)* but 'Ghost free' (should not introduce spurious states when making separable!)

Scattering

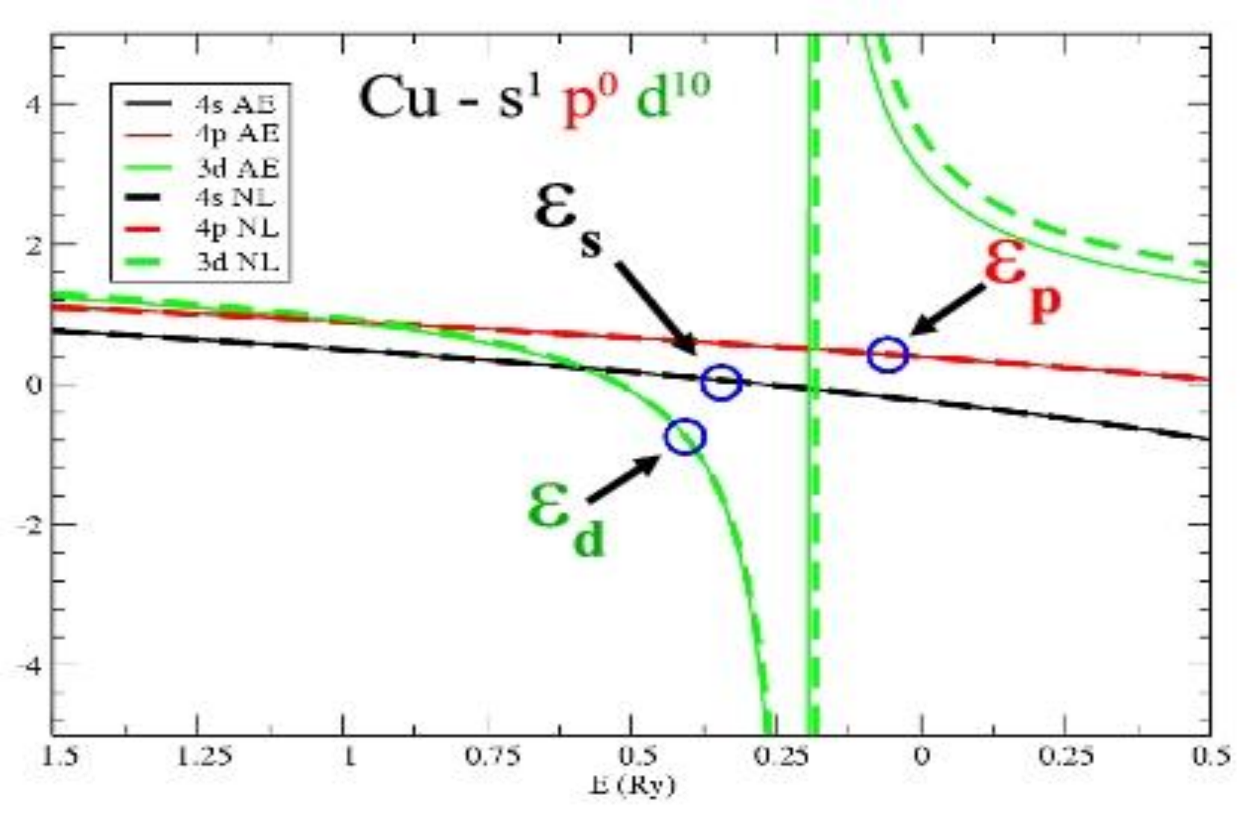
Recall (from a quantum mechanics course?):

- Scattering properties of a potential described by phase shift η_l.
- Related to logarithmic derivatives: [see, e.g. Eq. J.6, Martin]

$$\boxed{D_l(\epsilon, r) = r\frac{d}{dr}\ln\psi_l(\epsilon, r) = r\frac{d}{dr}\ln(\phi_l(\epsilon, r)/r)}$$

- Weaker potentials will have fewer bound states.
- In the pseudopotential approximation: want to make the potential weak enough that the valence electron is the lowest bound state (with that *l*), while reproducing log derivatives to the extent possible....

Log derivatives



Eric Walter

Generating an *ab initio* pseudopotential

(Note: general outline, schemes differ!)

1) Pick electronic configuration for atom (reference config.)

[e.g., may want to promote some electrons to excited states]

2) Perform all-electron calculation → $\phi_{nl}^{AE}(\mathbf{r}),\, \epsilon_{nl}^{AE}$

$$-\frac{1}{2}\frac{d^2}{dr^2}\phi_{nl}^{AE}(r) + \left[\frac{l(l+1)}{2r^2} + V_{eff}(r) - \epsilon_{nl}^{AE}\right]\phi_{nl}^{AE}(r) = 0$$

where

$$V_{eff} = -Z/r + V_H[\rho; r] + V_{XC}[\rho; r]$$

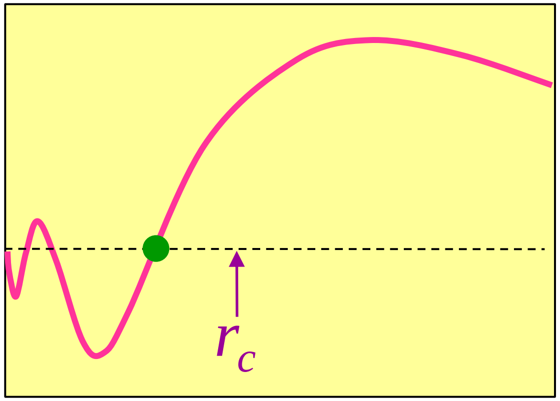
(*contd.*)

Generating an *ab initio* pseudopotential

3) Divide electrons into core and valence.

4) Pick a core radius r_c

- r_c too small → hard pseudopotential
- r_c too large → transferability poor
- r_c should be large enough to avoid overlapping cores
- r_c can be different for each l
- r_c should be larger than r for outer-most node of radial wavefunction



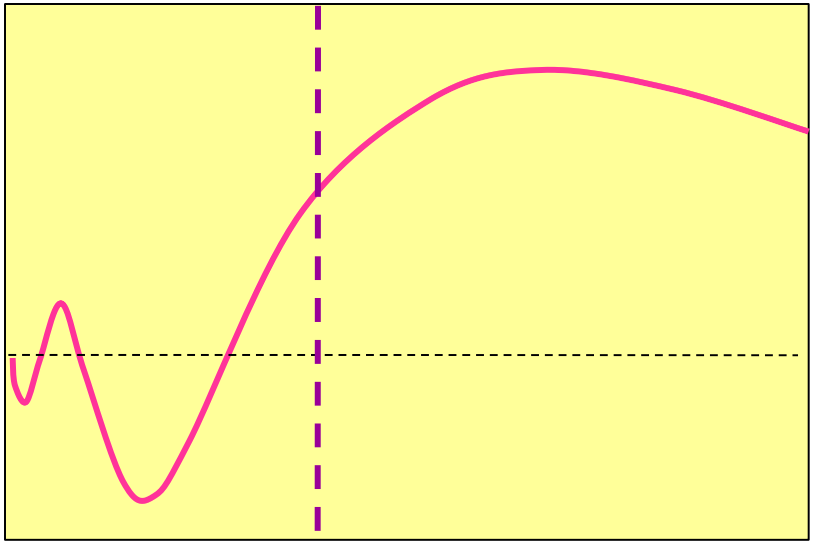
(*contd.*)

Generating an *ab initio* pseudopotential

(contd.)

5) Construct pseudowavefunction (one l *at a time):*

- Pseudowavefunction & all-electron wavefunction are identical outside the cut-off radius r_c:



Generating an *ab initio* pseudopotential

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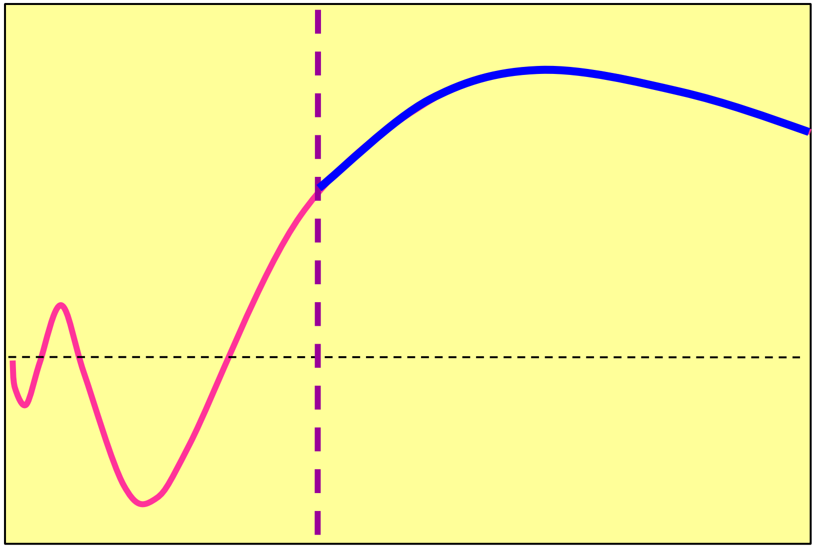

$$\phi^{AE}_{l,ref}(r) = \phi^{PS}_{l,ref}(r) \quad r \geq r_c$$

Generating an *ab initio* pseudopotential

(contd.)

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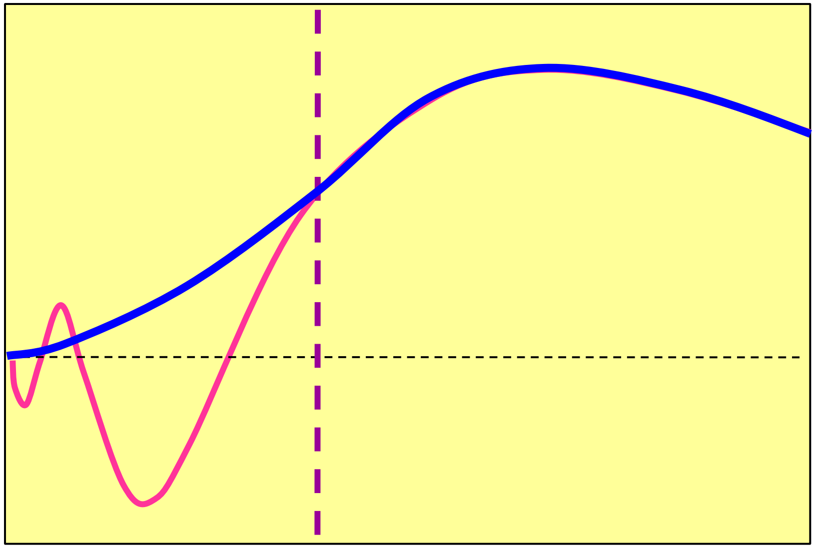


- Inside r_c , $\phi^{PS}_{l,ref}(r) = f(r)$
- Lots of freedom for choice of f (choose for right log derivatives, softness, norm conservation, etc.)

Generating an *ab initio* pseudopotential

(contd.)

6) Invert Schrödinger equation:

$$V_l^{scr}(r) = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2\phi_l(r)} \frac{d^2[\phi_l(r)]}{dr^2}$$

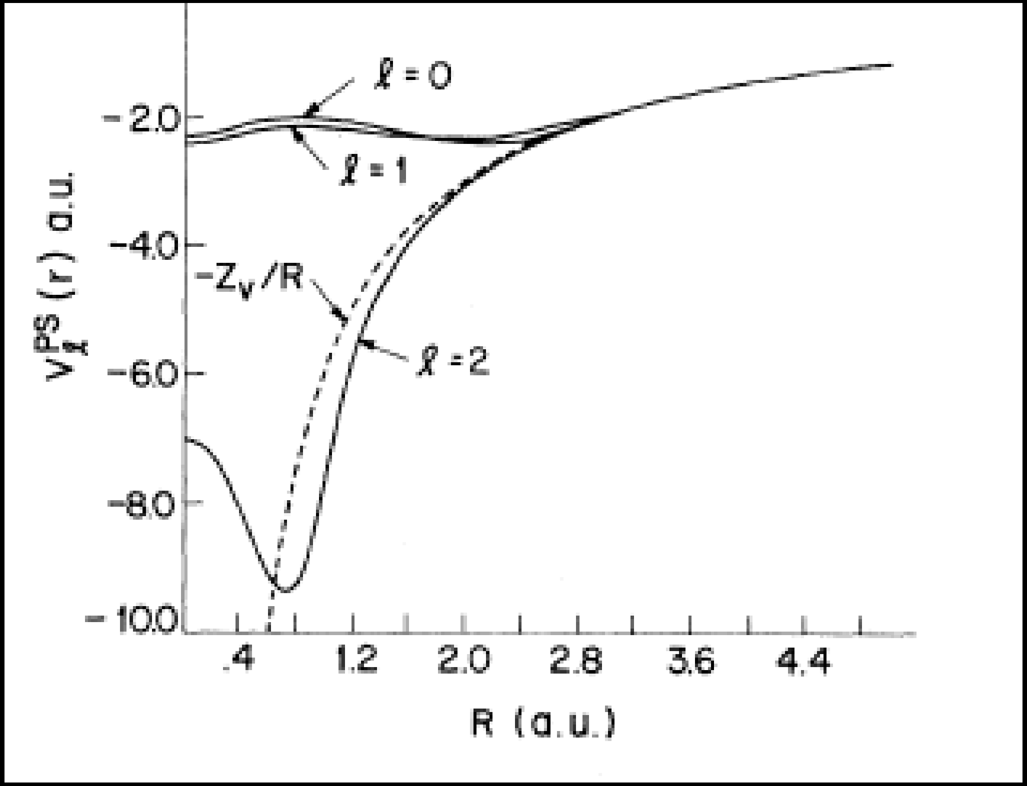
- Will get correct (all-electron) eigenvalue.
  - "Screened" pseudopotential (includes Hartree + XC potentials)

7) "Unscreen", i.e., remove Hartree and XC contributions.

$$V_l^{PS}(r) = V_l^{scr}(r) - V_H[\rho^{val}(r)] - V_{XC}[\rho^{val}(r)]$$

What does a pseudopotential look like?

Example for Mo:



- Weaker than full Coulomb potential

- No singularity at $r=0$

- Different pseudopotential for each l (example of “semilocal” pseudopotential)

- Will be V_{ext} (replacing nuclear potential)

Norm Conservation

- By construction, log derivatives satisfy:

$$D_l^{AE}(\epsilon, r_c) = D_l^{PS}(\epsilon, r_c)$$

- In addition, if we impose norm conservation:

$$\int_0^{rc} \phi^{*AE}(r)\phi^{AE}(r)dr = \int_0^{rc} \phi^{*PS}(r)\phi^{PS}(r)dr$$

then from the identity *(see e.g. pg. 214 of Martin for derivation)*:

$$\frac{\partial}{\partial\epsilon} D_l(\epsilon, r_c) = -\frac{rc}{|\phi_l(rc)|^2} \int_0^{rc} dr|\phi_l(r_c)|^2$$

we have*

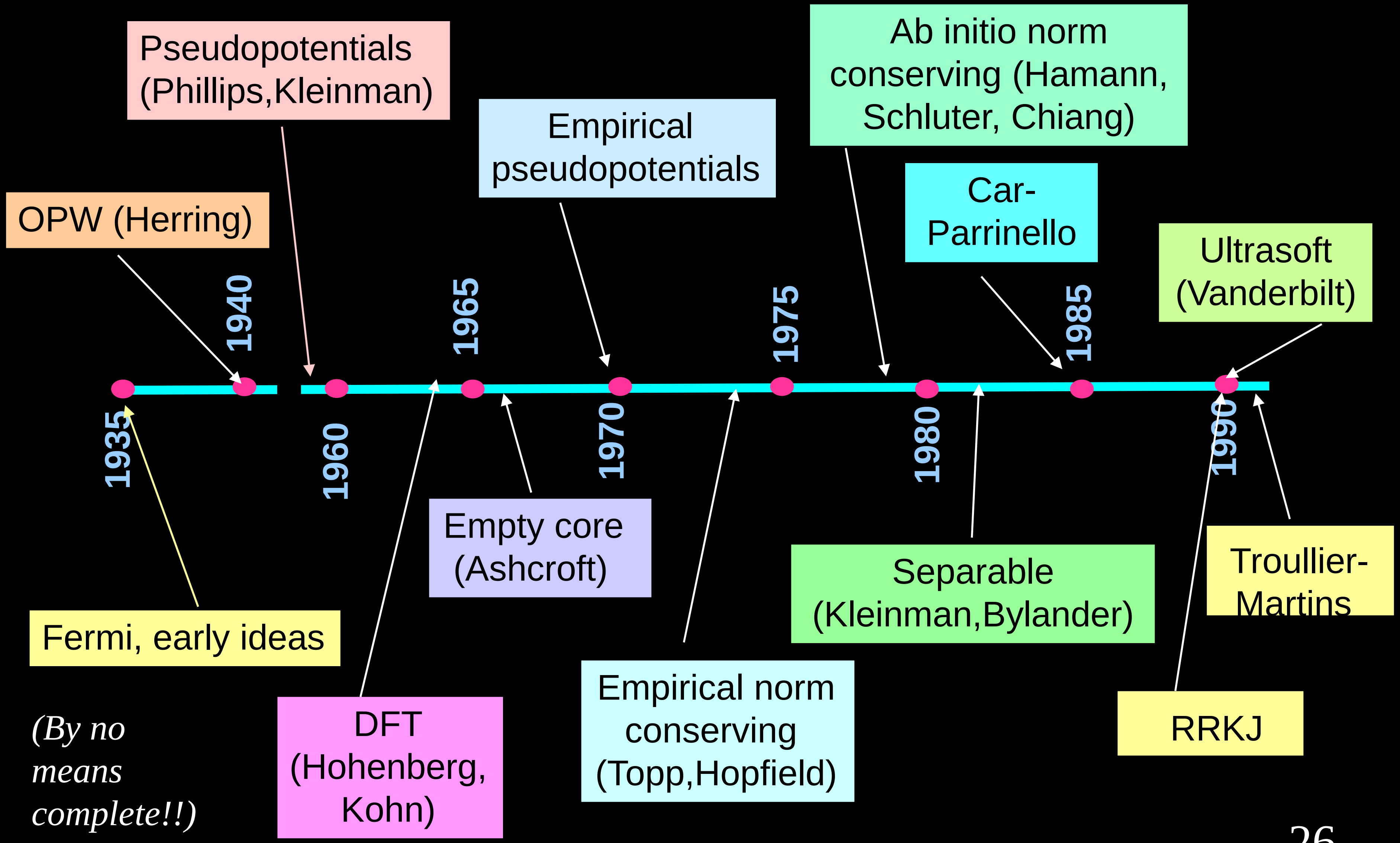
$$\frac{\partial}{\partial\epsilon} D_l^{AE}(\epsilon, r_c) = \frac{\partial}{\partial\epsilon} D_l^{PS}(\epsilon, r_c)$$

i.e., if energy is shifted slightly from that of reference eigenvalue, log derivatives ~ unchanged →

improved transferability!

- *Hamann, Schlüter, & Chiang, *PRL* **43**, 1494 (1979)

A Pseudopotential Timeline



Fermi, early ideas

OPW (Herring)

Pseudopotentials (Phillips,Kleinman)

DFT (Hohenberg, Kohn)

Empty core (Ashcroft)

Empirical pseudopotentials

Empirical norm conserving (Topp,Hopfield)

Ab initio norm conserving (Hamann, Schluter, Chiang)

Separable (Kleinman,Bylander)

Car-Parrinello

Ultrasoft (Vanderbilt)

RRKJ

Troullier-Martins

(By no means complete!!)

BHS pseudopotentials

- Bachelet, Hamann, Schlüter, *PRB 26, 4199 (1982).*
- "Pseudopotentials that work: from H to Pu"
- Ab initio, norm conserving, so good transferability (?)
- Semilocal $V_l(r)$ [local in radial coordinates, nonlocal in angular coordinates]
- Parametrized form: chosen to give nice analytical expressions with many basis sets, 9 parameters, tabulated for all elements.
- Non-linear fitting procedure, caution needed!
- Fairly hard pseudopotentials since smoothness not built in explicitly, frequently need high cut-off.

Some Popular Pseudopotentials: BHS

- Bachelet, Hamann, Schlüter, *PRB 26, 4199 (1982).*
- "Pseudopotentials that work: from H to Pu"
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Soft / Smooth Pseudopotentials

- Want to lower E_{cut} (cut-off for plane wave basis).
- Various strategies:
  - Optimize so as to minimize error in KE introduced by truncating basis (Rappe, Rabe, Kaxiras & Joannopoulos, 1990)
  - Make smooth near origin (Troullier & Martins, 1991)

- Cut-offs lowered considerably, but still higher than we would like, especially for
  - > first row elements (1s, 2p nodeless)
  - > transition metals (3d nodeless)
  - > rare-earths (4f nodeless)

Fast convergence* with soft pseudopotentials

e.g. Cu: localized d orbitals →
high cut-off needed with BHS pseudopotential

Troullier-Martins

RRKJ

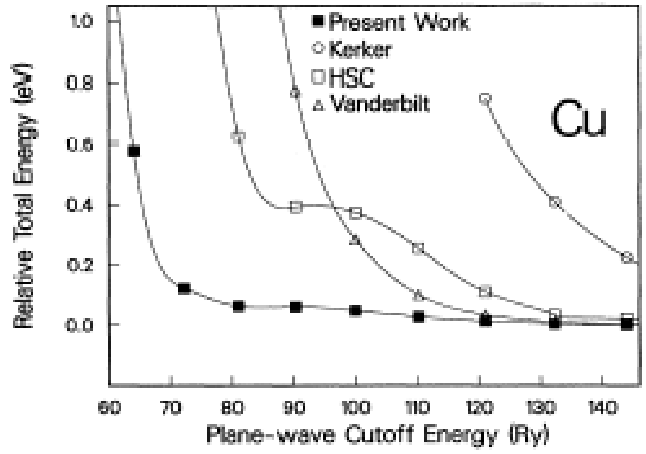


FIG. 8. The calculated total energy of fcc Cu plotted against the cutoff energy of the plane-wave basis set for the four pseudopotentials shown in Fig. 7. The total energy for all four curves are referenced to the total energy calculated at a cutoff energy of 225 Ry. The squares, circles, and triangles are the calculated data points and the curves are obtained from a spline interpolation.

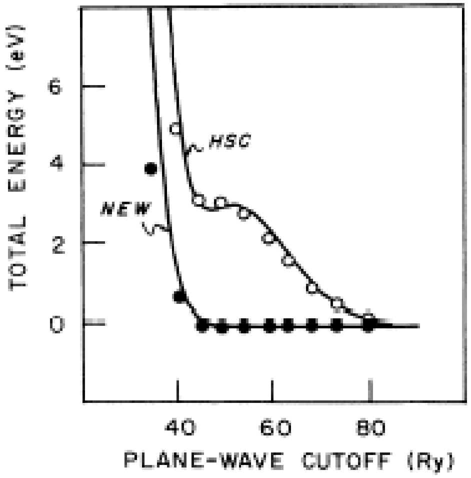


FIG. 3. Atomic (solid lines) and fcc solid (dots) total energies as a function of cutoff energy for copper in the HSC and present approaches. The zero of atomic total energy for each pseudopotential was chosen to be the total atomic energy at a cutoff energy of 324 Ry. The zero of solid total energy was chosen for each pseudopotential so that the atomic and solid total energies coincide at a cutoff energy of 80 Ry.

w.r.t. E_{cut}

Ultrasoft Pseudopotentials

- Vanderbilt, *Phys. Rev. B 41 7892 (1990).*
- Do away with norm conservation!!
- Can make ψ^{PS} extremely soft!
- Drastically reduces E_{cut}, especially for “difficult” elements.
- New separable form.
- Choose multiple energy references (to improve transferability).
- Solve generalized eigenvalue eqn.

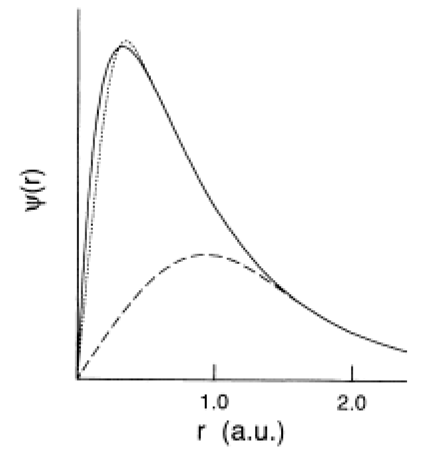


FIG. 1. Oxygen 2*p* radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Vanderbilt

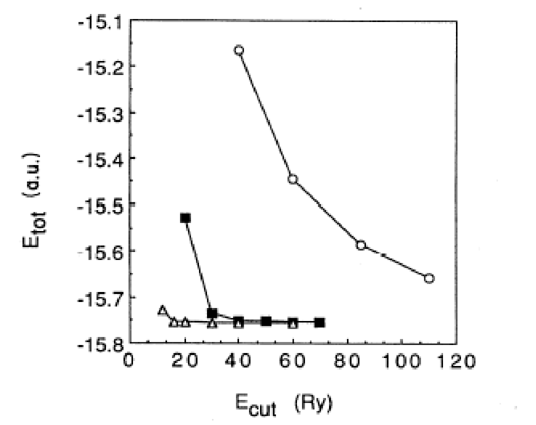


FIG. 1. Total energy of ground-state oxygen atom vs plane-wave cutoff for Bachelet-Hamann-Schlüter pseudopotential (open circles) and for Vanderbilt pseudopotential with $r_c = 1.2$ a.u. (solid squares) and $r_c = 1.8$ a.u. (open triangles).

Transferability

- Condition that pseudoatom reproduces behavior of all-electron atom in a wide variety of chemical environments.

- Recall, pseudopotential derived for reference configuration(atom with a given occupation of levels), using a reference eigenvalue.

- When eigenvalue changes from reference one:

  do scattering properties of potential change correctly? (Look at log derivatives)

- When the filling changes:

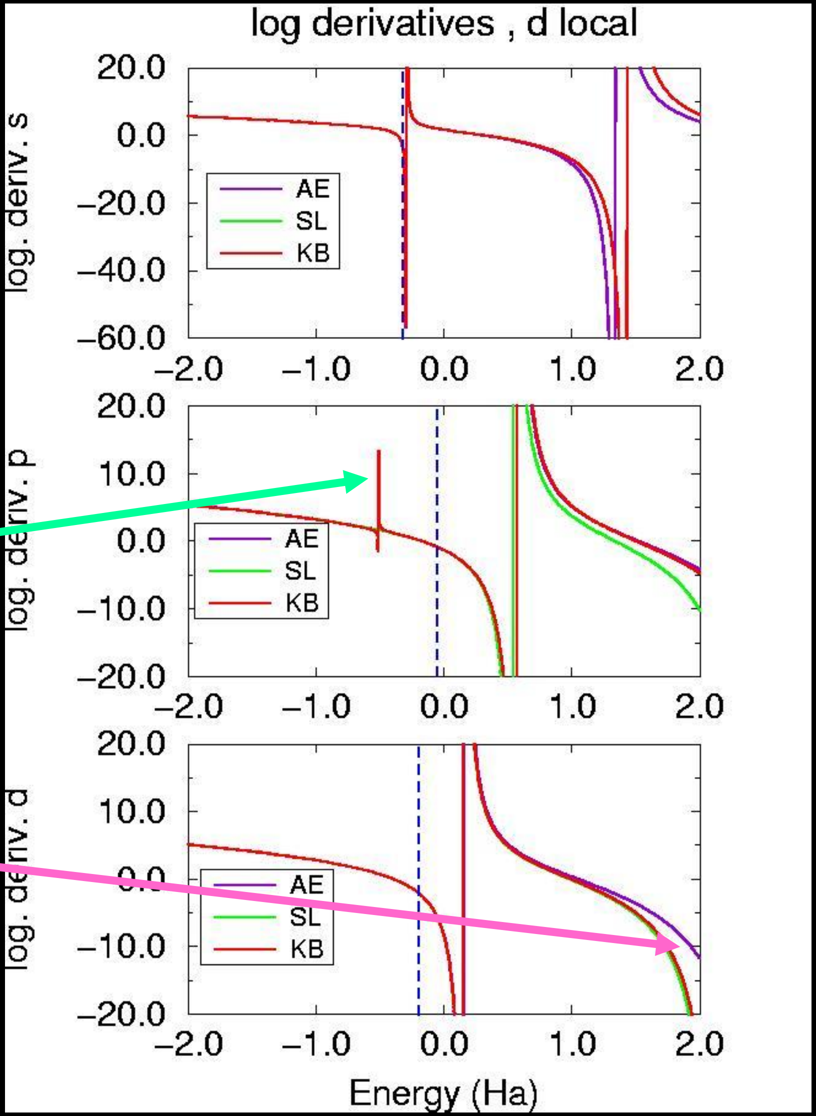
  - do eigenvalues shift correctly? (look at chemical hardness)

  - do scattering properties change correctly?

Transferability: log derivatives

- Log derivatives guaranteed to match at reference energy, check how log derivatives change with energy .

Ag



Has ghost ☹

Log derivatives don’t match ☹

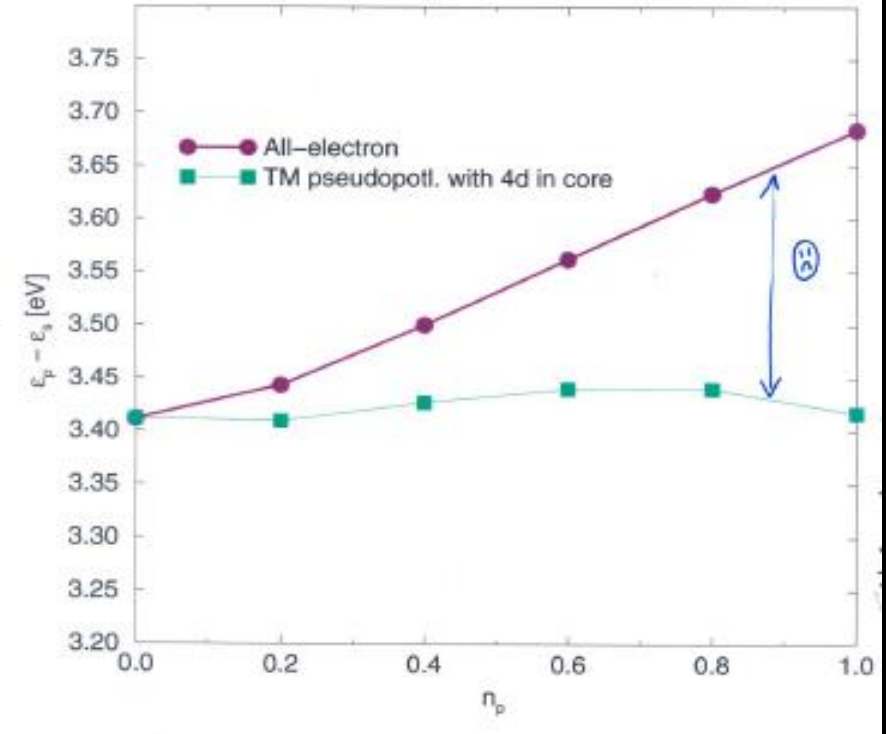
Transferability: Occupation Changes

- See how eigenvalues change with occupation

  Chemical Hardness matrix: $\eta_{ij} = \frac{1}{2}\frac{\partial \epsilon_i}{\partial f_j}$ [Teter, 1993] .

- See how 'tail norms' $N_i = \int_{rc}^{\infty} |\phi_i|^2 dr$ change with occupation: $\frac{\partial N_i}{\partial f_j}$ should be reproduced

e.g.: check transferability of a pseudopotential for Ag with 4d in core:



Non-Linear Core Correction

- Working only with ρ^{val} corresponds to linearizing the XC potential, but $V_{XC}(\rho^{val}+\rho^{core}) \neq V_{XC}(\rho^{val})+Vxc(\rho^{core})$
- This is particularly a problem when there is significant overlap between ρ^{val} and ρ^{core}
- Correction: [Louie, Froyen & Cohen, Phys. Rev. B 26 1738 (1982)]:
  - When unscreening, subtract out $V_H(\rho^{val})$ and $V_{XC}(\rho^{val}+\rho^{core})$
  - Store ρ^{core} from atomic calculation
  - Use $V_{XC}(\rho^{val}+\rho^{core})$ in all calculations
  - Okay to just use partial ρ^{core} (in region of overlap)

Bibliography

- R.M. Martin, “Electronic Structure Calculations, Basic Theory and Practical Applications”, Cambridge, 2004.
- W.E. Pickett, “Pseudopotential methods in condensed matter applications”, Computer Physics Reports 9, 115, 1989
- … and references therein