Atoms and Pseudopotentials

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Atomic wavefunctions:

- what do they look like?
- how to obtain?

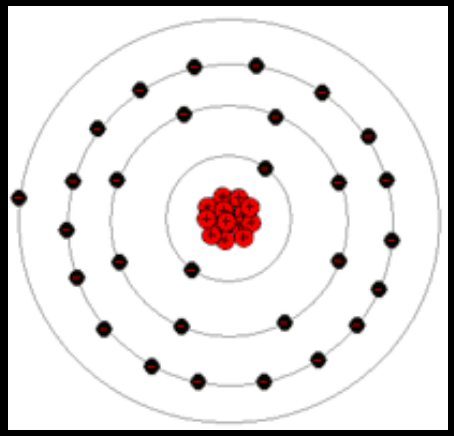
Pseudopotentials:

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

Electrons in Atoms

- Electrons in atoms are arranged in shells.

Schematic pic of Cl atom



- Quantum numbers:
  n [shells], l [subshells], m_l [orbitals], m_s

- 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]

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.
- The Pseudopotential Approximation: view matter as a sea of valence electrons moving in a background composed of rigid ions [ion = nucleus + core electrons].

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
  - Though external (Coulomb) potential is spherically symmetric, effective potential may / may not be so, but usually solve in spherical approximation.
- All-electron calculations: both core and valence e^-s included (whether for atom or solid).

Orthogonality

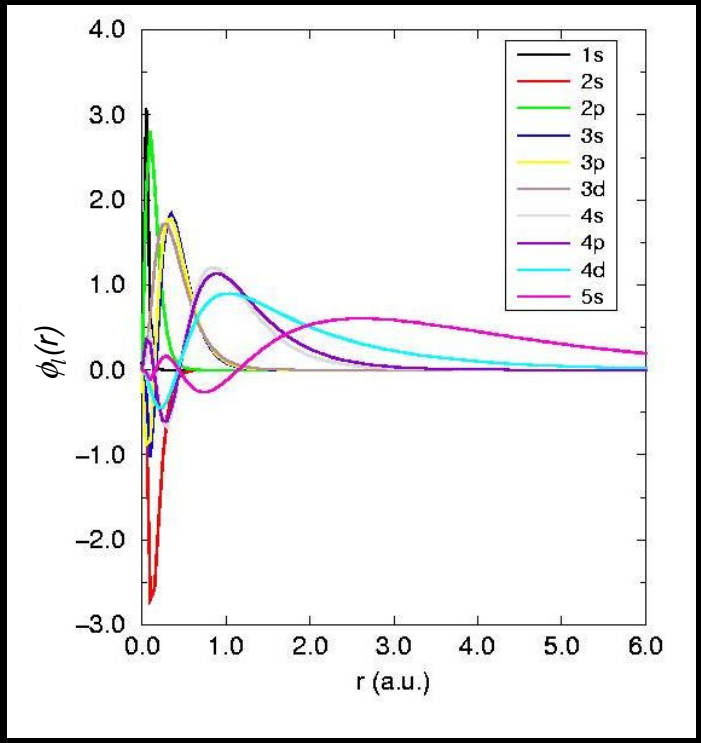
Recall:

- Eigenfunctions of a Hermitian operator form a complete orthonormal set, and the eigenvalues are real.
- For atomic wavefunctions specified by n, l:
  - Separate into radial part and angular part.
  - 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.

$$\int \phi_{nl}(r)\phi_{n'l}(r)dr = \delta_{nn'}$$

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, 3p, 4f,… are nodeless.

The Pseudopotential Approximation

- Frozen core: remove core-electron degrees of freedom.
- Valence electrons see a weaker potential than the full Coulomb potential, replaces electron-nuclear potential.
- Tailor this pseudopotential so that wavefunctions behave 'properly' in region of interest, yet computationally cheap.

(Numerical) Advantages when solving Kohn-Sham eqns.:

- Have to solve for fewer eigenvalues.
- When solving using a basis (especially plane waves), basis size drastically reduced (smaller matrices to diagonalize).
- No Coulomb singularity (cusp in wavefunction) at origin.

Disadvantages:

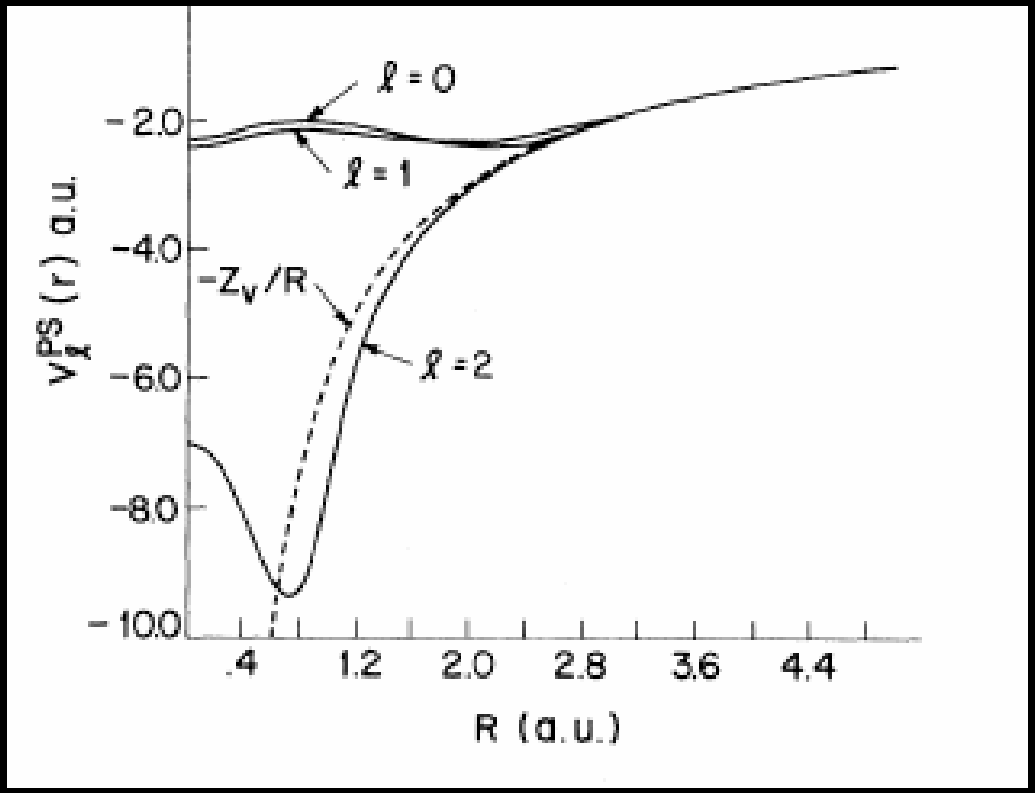
- Can lose accuracy

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….

What does a pseudopotential look like?

Example: *(will see later how to obtain….)* for Mo*:*



Hamann, Schluter & Chiang, 1979.

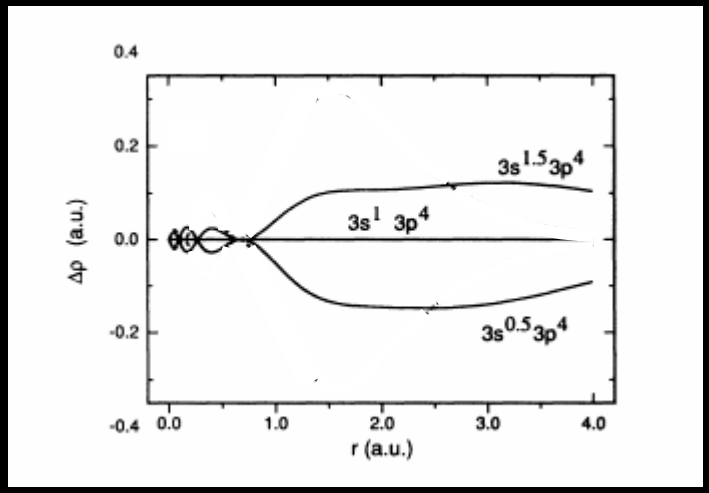
- Weaker than full Coulomb potential
- No singularity at r=0
- Different pseudopotential for each l (example of semilocal pseudopotential)
- Will be V_{ext} (replacing nuclear potential)

Why do pseudopotentials work at all?

- Core e⁻s are ~ frozen, don't participate in bonding.
- Energy correction (due to non-frozen core) is second order in $\Delta\rho = \rho_{true} - \rho_{frozen\text{-}core}$.
- Screening by core e⁻s $\rightarrow$ valence e⁻s see weaker potential.
- Cancellation of kinetic energy and potential energy in core regions.
- Pseudopotentials are constructed so that they have the same scattering properties as true potential.

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 explain)* 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:

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

- 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).

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 → $\psi_{nl}^{AE}(\mathbf{r}), \epsilon_l^{AE}$

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

where

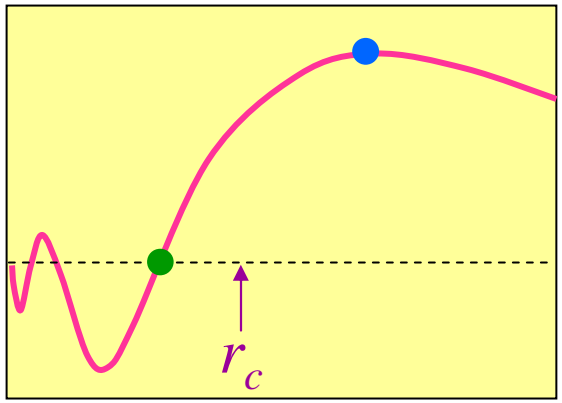
$$V_{eff} = -Z/r + V_H[\rho; r] + V_{XC}[\rho; r]$$

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 can be different for each l
- r_c should be larger than r for outer-most node of radial wavefunction
- usually pick r_c slightly inside position of peak in radial wavefunction.

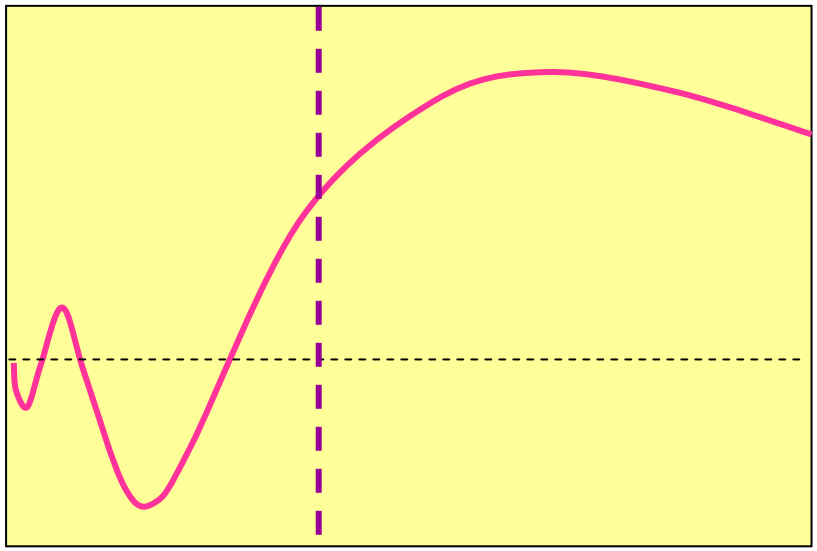


Generating an *ab initio* pseudopotential

(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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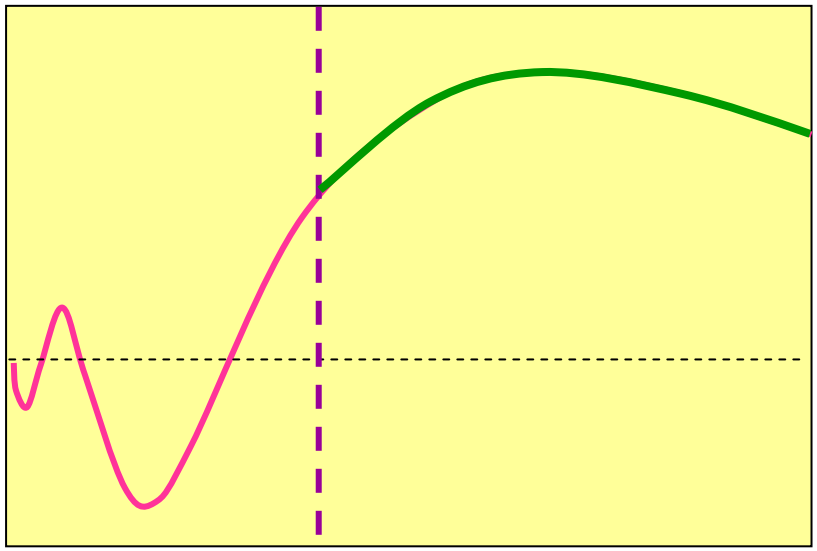

$$\psi_{l,\mathrm{ref}}^{\mathrm{AE}} = \psi_{l,\mathrm{ref}}^{\mathrm{PS}} \quad r \geq r_c$$

Generating an *ab initio* pseudopotential

(contd.)

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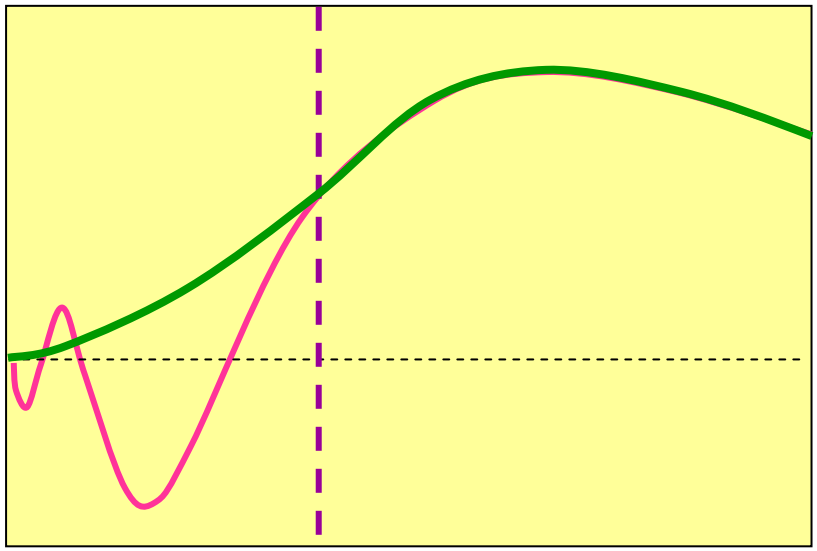


- Inside r_c , $\psi_{l,\mathrm{ref}}^{\mathrm{PS}}(r) = f(r)$
- Lots of freedom for choice of f (choose for right log derivatives, softness, norm conservation, etc.)

Generating an *ab initio* pseudopotential

(contd.)

6) Invert Schrödinger equation:

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

- Can always do (if pseudowavefunction is nodeless)
- Will get correct (all-electron) eigenvalue.
- "Screened" pseudopotential
  (includes Hartree + XC potentials)

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

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

Norm Conservation

- We always have the following conditions:

$$\psi^{\mathrm{AE}}_{l,\mathrm{ref}} = \psi^{\mathrm{PS}}_{l,\mathrm{ref}} \quad r \geq r_c$$

$$\left\{\epsilon^{\mathrm{AE}}_l\right\}_{\mathrm{ref}} = \left\{\epsilon^{\mathrm{PS}}_l\right\}_{\mathrm{ref}}$$

$$D^{\mathrm{AE}}_l(\epsilon, r_c) = D^{\mathrm{PS}}_l(\epsilon, r_c) \quad \text{where} \quad D_l(\epsilon, r) = r\frac{d}{dr}\ln\psi_l(\epsilon, r)$$

log derivatives

- In addition, if we impose norm conservation:

$$\int_0^{r_c} r^2 \psi^{*AE}_{nl}(\mathbf{r})\psi^{AE}_{nl}(\mathbf{r})d\mathbf{r} = \int_0^{r_c} \psi^{*PS}_{l}(\mathbf{r})\psi^{PS}_{l}(\mathbf{r})d\mathbf{r}$$

then it will automatically follow*:

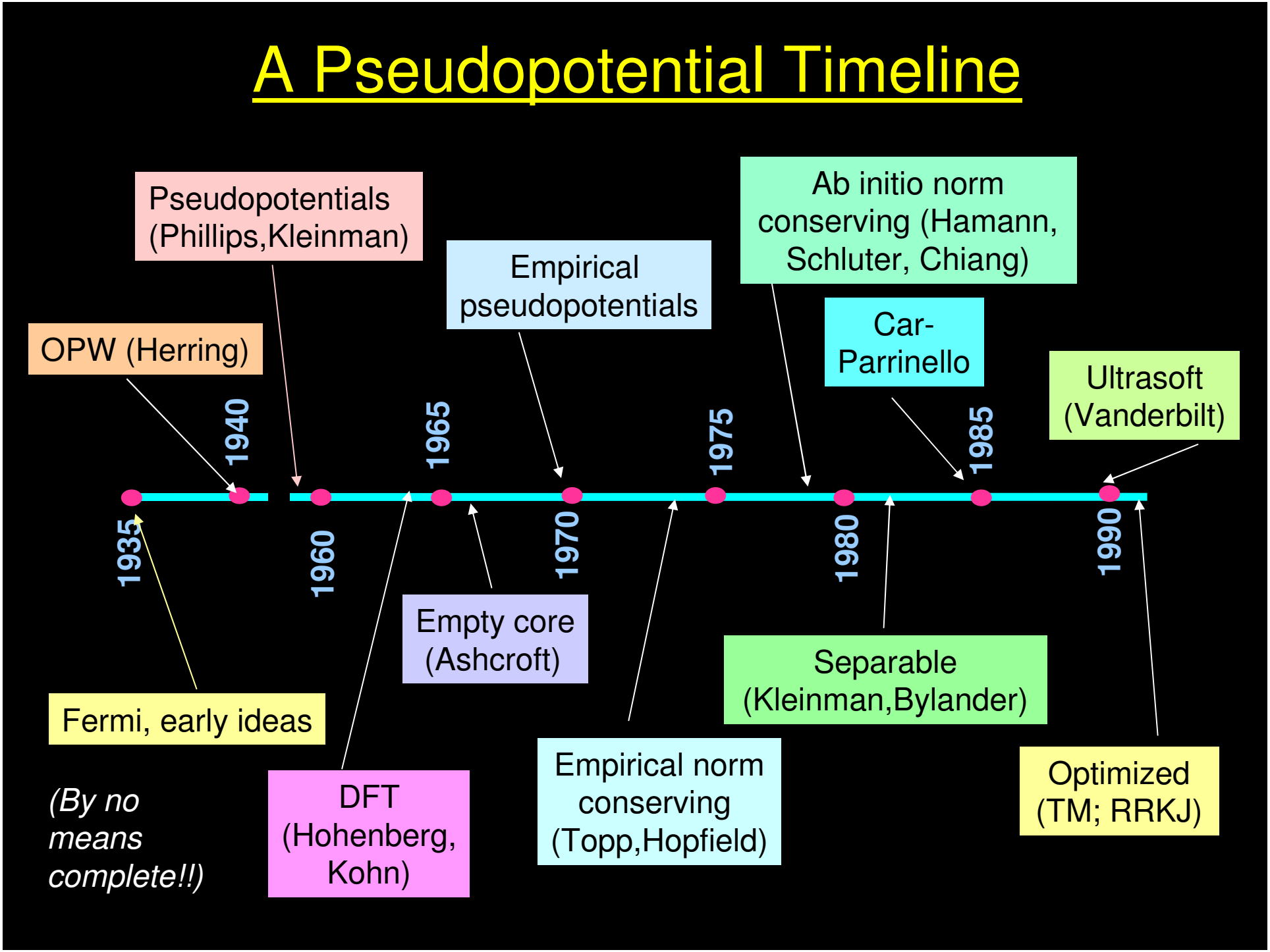
$$\frac{\partial}{\partial\epsilon}D^{\mathrm{AE}}_l(\epsilon, r_c) = \frac{\partial}{\partial\epsilon}D^{\mathrm{PS}}_l(\epsilon, r_c)$$

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



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.

Kleinman-Bylander Transformation

- Nonlocal: $V(\mathbf{r},\mathbf{r}')$ [nonlocal in r & Ω]
- Semilocal $V_l(r,r')=V_l(r)\delta(r-r')$
- Local $V(\mathbf{r},\mathbf{r}')=V_{loc}(r)\delta(r-r')\delta(\Omega,\Omega')$ [can always pull out local piece, speeds computation]
- Separable: Want $V_l(r,r') = F_l^*(r)f_lF_l(r')$ [faster to compute]
- Kleinman & Bylander (PRL 48, 1425, 1982): Way to map semilocal potential to separable potential.
- Get identical results for reference configuration (but not necessarily elsewhere!)
- Can result in ghosts (spurious bound states)
- Need ghostwatching / ghostbusting!

[Gonze,Stumpf & Scheffler, PRB 44, 8503 (1991)].

Soft / Smooth Pseudopotentials

- Want to lower E_{cut} (cut-off for plane wave basis).
- Various strategies:
  - Reduce $V(q)$ for large q (Vanderbilt, 1985).
  - Reduce $\psi(q)$ for large q (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

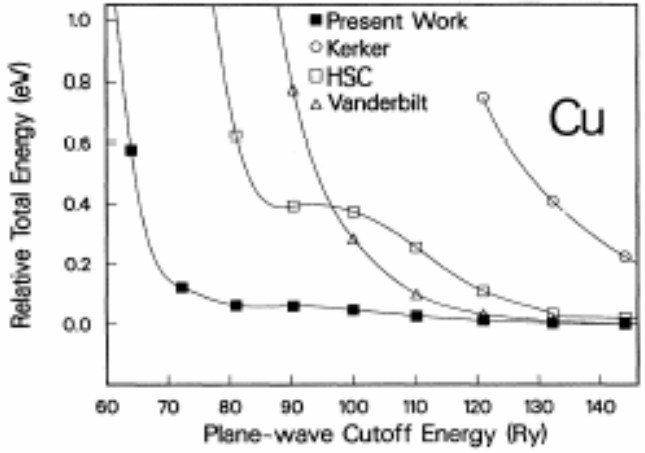


FIG. 8. The calculated total energy of fcc Cu plotted against the cutoff energy of the plane-wave basis set for the four pseudopotentials shown in Fig. 7. The total energy for all four curves are referenced to the total energy calculated at a cutoff energy of 225 Ry. The squares, circles, and triangles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

RRKJ

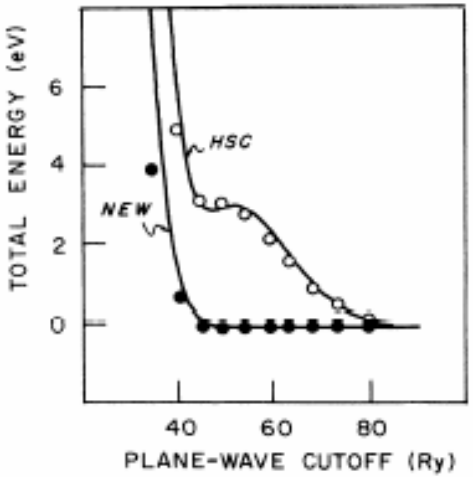


FIG. 3. Atomic (solid lines) and fcc solid (dots) total energies as a function of cutoff energy for copper in the HSC and present approaches. The zero of atomic total energy for each pseudopotential was chosen to be the total atomic energy at a cutoff energy of 324 Ry. The zero of solid total energy 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} as soft as desired!
- Drastically reduces E_{cut}, especially for "difficult" elements.
- New separable form.
- Choose multiple energy references (to improve transferability).
- Solve generalized eigenvalue eqn.

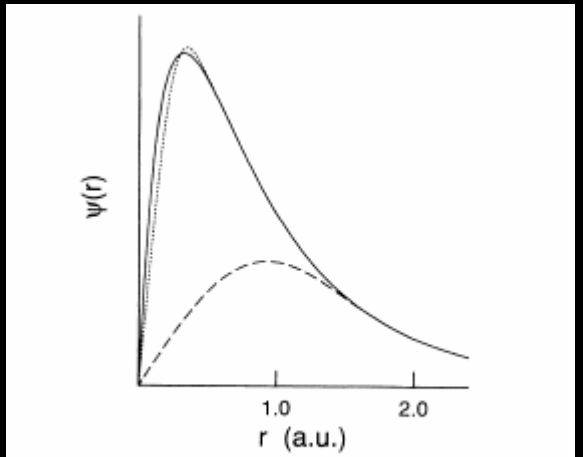


FIG. 1. Oxygen $2p$ radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Vanderbilt

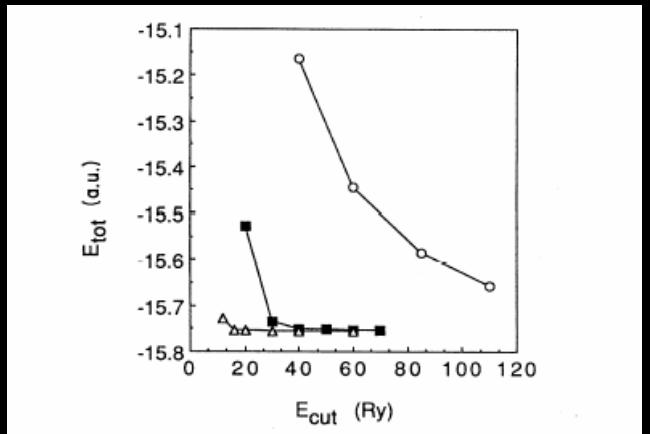


FIG. 1. Total energy of ground-state oxygen atom vs plane-wave cutoff for Bachelet-Hamann-Schlüter pseudopotential (open circles) and for Vanderbilt pseudopotential with $r_c = 1.2$ a.u. (solid squares) and $r_c = 1.8$ a.u. (open triangles).

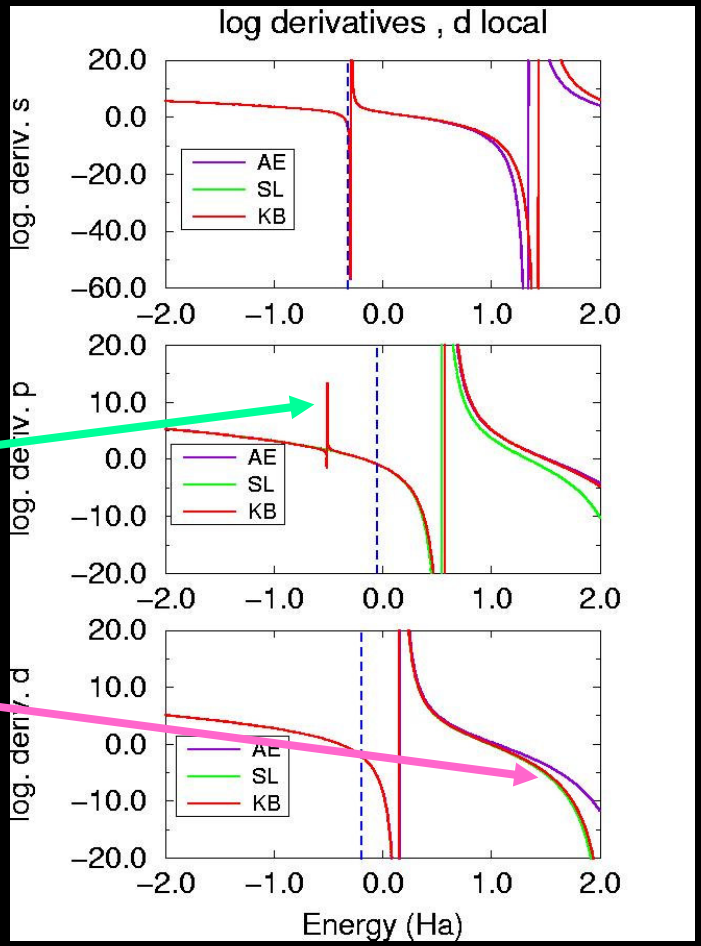
Laasonen, Car, Lee & Vanderbilt

Transferability: log derivatives

- Condition that pseudoatom reproduces behavior of all-electron atom in a wide variety of chemical environments.
- Log derivatives guaranteed to match at reference energy, check how log derivatives change with energy .

Has ghost ☹

Log derivatives don't match ☹

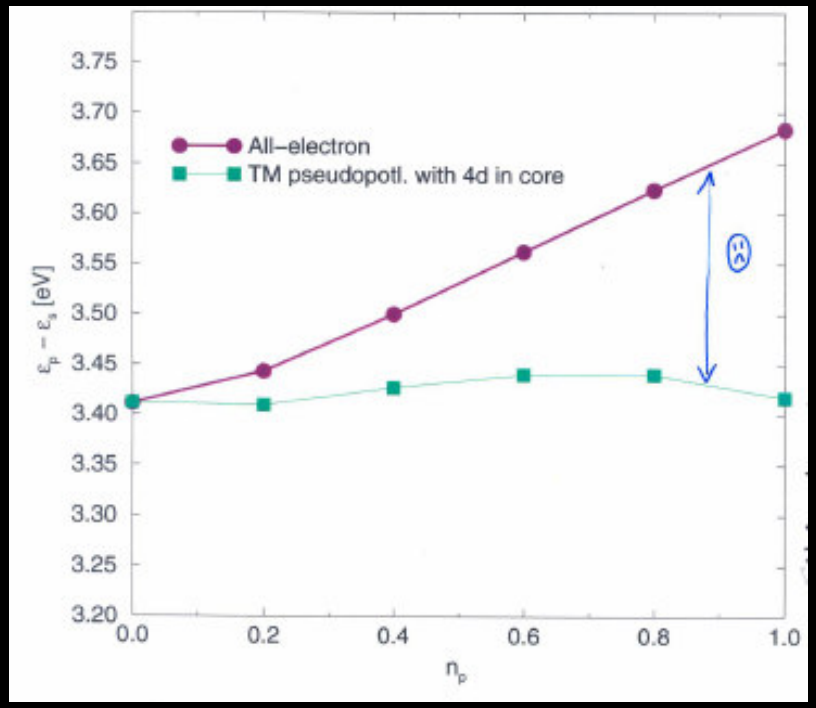


Ag

Transferability: Chemical Hardness

- See how eigenvalues change with occupation
- Chemical Hardness matrix: $\eta_{ij} = \frac{1}{2}\frac{\partial \epsilon_i}{\partial f_j}$ [Teter, 1993] .

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