

Plane Waves + Pseudopotentials

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The Kohn-Sham problem

- Want to solve the Kohn-Sham equations:

$$\left[-\frac{1}{2} \nabla^2 + V_{nuc}(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{XC}[n(\mathbf{r})] \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

H

- Note that **self-consistent solution** necessary, as H depends on solution:

$$\{\psi_i\} \rightarrow n(r) \rightarrow H$$

- Convention (most of the time, in this talk):

$$e = \hbar = m_e = 1$$

Kohn-Sham Equations in a Basis

- Can choose to expand wavefunctions in a **basis set**:

$$\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{N_b} c_{i\alpha} f_{\alpha}(\mathbf{r})$$

- Now obtain a matrix equation:

$$\sum_{\beta} H_{\alpha\beta} c_{i\beta} = \epsilon_i c_{i\alpha}$$

Matrix element *Eigenvalue* *Eigenvector*

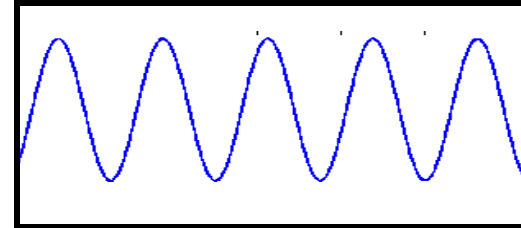
- Solving \Leftrightarrow Have to diagonalize a matrix of size $N_b \times N_b$

Size of basis

Some possible basis sets

- Various possible choices of basis:

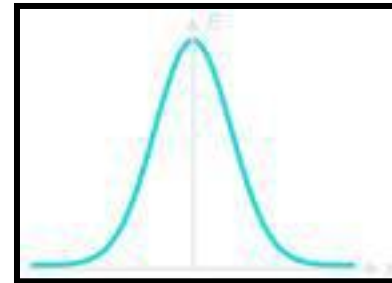
- Plane waves $e^{i\mathbf{K}\cdot\mathbf{r}}$



- Localized sets:

- e.g., Gaussians

- e.g., atomic orbitals



- Mixed basis

- Augmented basis

- Choose so that calculation is fast, accurate, convenient.
- Would like N_b to be small (within reason)?
- Would like form of $\mathbf{f}_\alpha(\mathbf{r})$ to be simple?

Advantages of a Plane Wave Basis

- **Simple**: Easy to take derivatives, etc. \Rightarrow Coding is easy!
- **Orthonormal**: No overlap integrals.
- **Independent of atomic positions** \Rightarrow No “Pulay forces”; easy to calculate forces for structural relaxation & molecular dynamics.
- **Unbiased**: No assumption about where charge concentrated. (But \therefore also wasteful?)
- **Easy to control convergence** w.r.t. size of basis: only one parameter E_{cut} . (energy cut-off for planewaves)
- Can easily take advantage of FFT's : r-space \leftrightarrow k-space



Disadvantages of a Plane Wave Basis

- Often need a HUGE number of plane waves to get an adequate expansion, i.e., N_b can be very large! ($\sim 10^5$ per atom)
(Will discuss... solution = introduction of **pseudopotentials**.)
- The set of plane waves is discrete only if the system is periodic!
(Will discuss tomorrow...solution = introduction of artificial supercell or periodic approximant.)
- Sometimes (chemical) interpretation harder.



Some popular plane wave codes

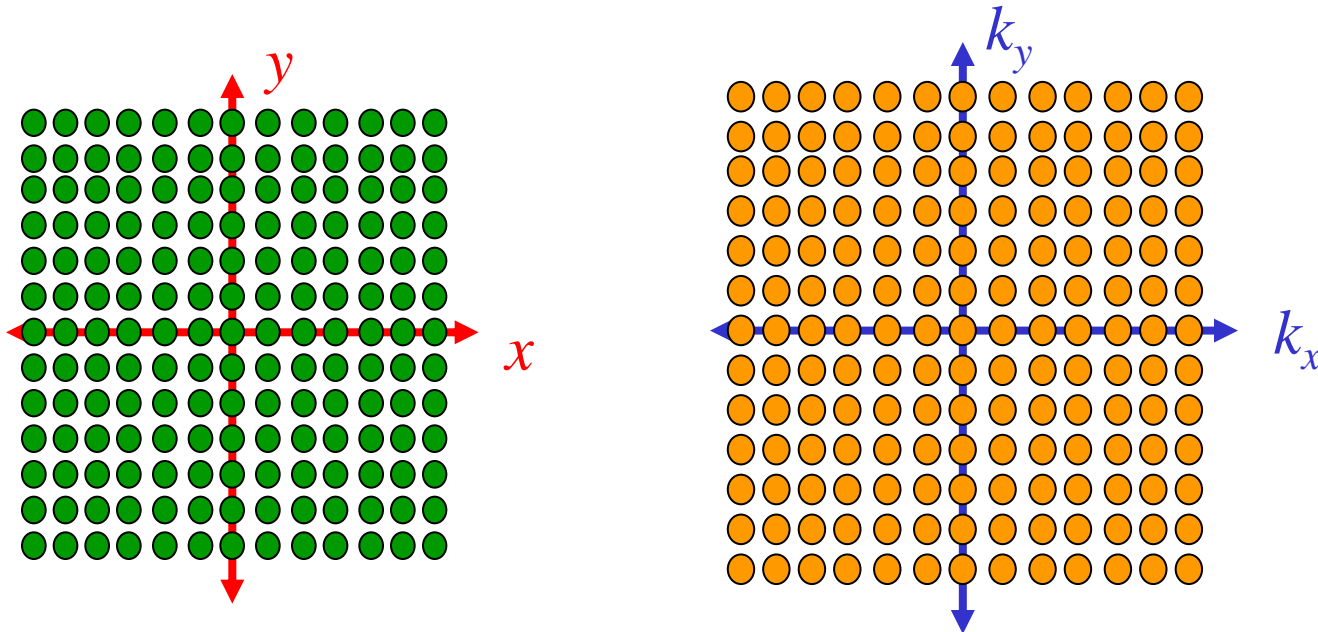


- Quantum ESPRESSO (PWscf)
- VASP
- ABINIT
- CASTEP
- CPMD

(there are others too...)

Periodic Systems

- Periodic systems are characterized by a lattice of
 - lattice vectors \mathbf{R} in real (r-) space
 - reciprocal lattice vectors \mathbf{G} in reciprocal (k-) space



- Spacing of \mathbf{R} 's inversely proportional to spacing of \mathbf{G} 's

Periodic Systems & Bloch's Theorem

- For a periodic system, recall Bloch's Theorem:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

- $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the system, i.e.,

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}), \quad \text{where } \mathbf{R} = \text{lattice vector}$$

- As for all lattice-periodic functions, only certain plane waves will appear in the Fourier expansion of $u_{\mathbf{k}}(\mathbf{r})$:

$$u_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} \quad \text{where } \mathbf{G} = \text{reciprocal lattice vector}$$

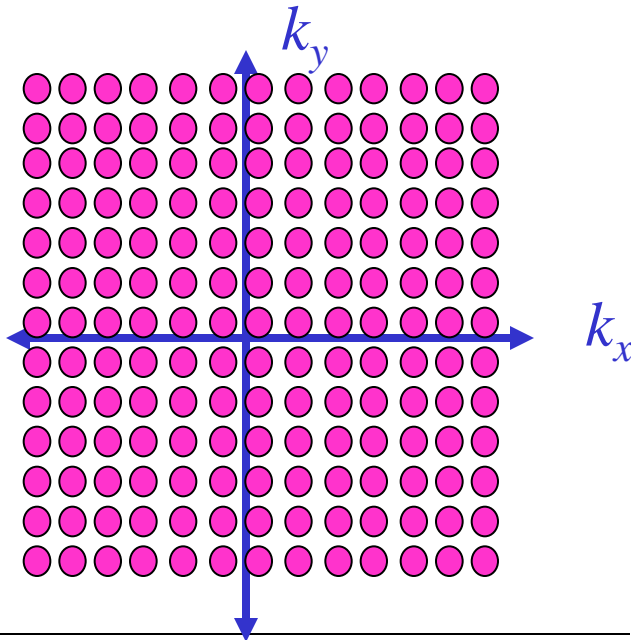
Plane Waves & Periodic Systems

- So, for a periodic system:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

where \mathbf{G} = reciprocal lattice vector

- The **plane waves** that appear in this expansion can be represented as a grid in k-space:

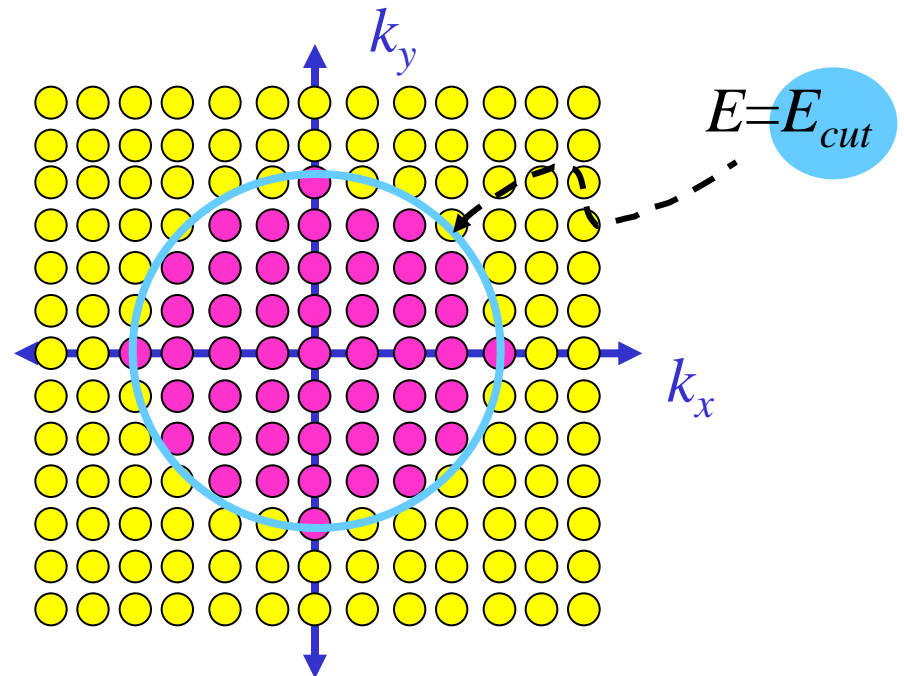


- Only true for periodic systems that grid is discrete.
- In principle, still need **infinite number of plane waves.**

Truncating the Plane Wave Expansion

- In practice, the contribution from higher Fourier components (large $|\mathbf{k}+\mathbf{G}|$) is small.
- So truncate the expansion at some value of $|\mathbf{k}+\mathbf{G}|$.
- Traditional to express this cut-off in energy units:

$$\frac{\hbar^2 |\mathbf{k} + \mathbf{G}|^2}{2m_e} \leq E_{cut}$$



Kohn-Sham equations in plane wave basis

- Eigenvalue equation is now:

$$\sum_{\mathbf{G}'} H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} c_{i,\mathbf{k}+\mathbf{G}'} = \epsilon_i c_{i,\mathbf{k}+\mathbf{G}}$$

- Matrix elements are:

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + V_{\text{ion}}(\mathbf{k} + \mathbf{G}, \mathbf{k} + \mathbf{G}') + V_{\text{H}}(\mathbf{G} - \mathbf{G}') + V_{\text{XC}}(\mathbf{G} - \mathbf{G}')$$

- Nuclear (\rightarrow ionic) potential given by:

$$V_{\text{ion}}(\mathbf{G}) = \sum_{\alpha} \mathbf{S}_{\alpha}(\mathbf{G}) v_{\alpha}(\mathbf{G}); \quad \mathbf{S}_{\alpha}(\mathbf{G}) = \sum_{\mathbf{I}} \exp(i\mathbf{G} \cdot \mathbf{R}_{\mathbf{I}})$$

Nuclear Potential

- Electrons experience a **Coulomb potential** due to the nuclei.
- This has a known and simple form:

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

- But this leads to computational problems!

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]

Atomic Wavefunctions

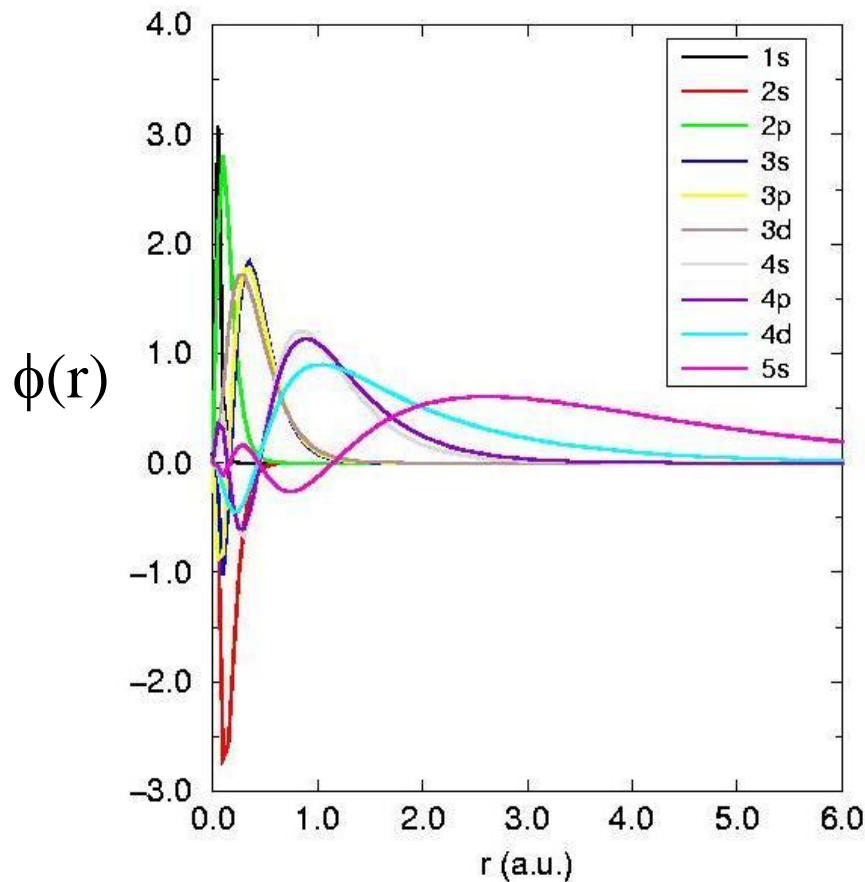
- For hydrogenic atoms, recall:

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

- **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: $[\text{Kr}], 4d^{10}, 5s^1, 5p^0, 5d^0$



- Core wavefunctions sharply peaked near nucleus.
- Valence wavefunctions peaked far away from nucleus, lots of wiggles near nucleus.
- 1s, 2p, 3d, 4f, ... nodeless.
- Not immediately clear whether 4d should be considered 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.
- e.g., when Ag is a constituent of a solid, the wavefunction may also acquire some **5p** or **5d** character?
- **Wavefunctions of core electrons** change only slightly when the bond is formed.

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} ☹️

Solutions 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} ☹️

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

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

- 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 some law-enforcement agencies!
- 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....



Wish List for a Good Pseudopotential

For accuracy:

- Should reproduce scattering properties of true potential.
- **Transferable**: Nice to have one pseudopotential 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!)

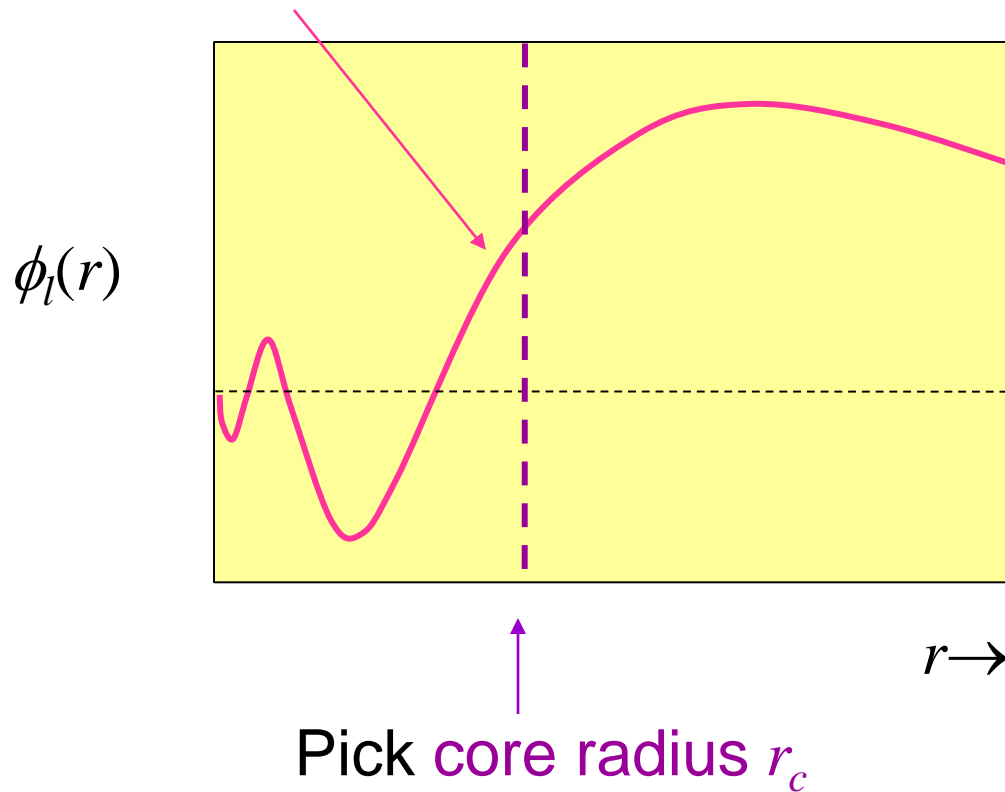
Generating an *Ab Initio* Pseudopotential

- For the element of interest, pick a reference configuration.
- Perform an “all-electron” calculation for this reference configuration.

→ $\phi_{nl}^{AE}(\mathbf{r}), \epsilon_{nl}^{AE}$

All-Electron Wavefunction

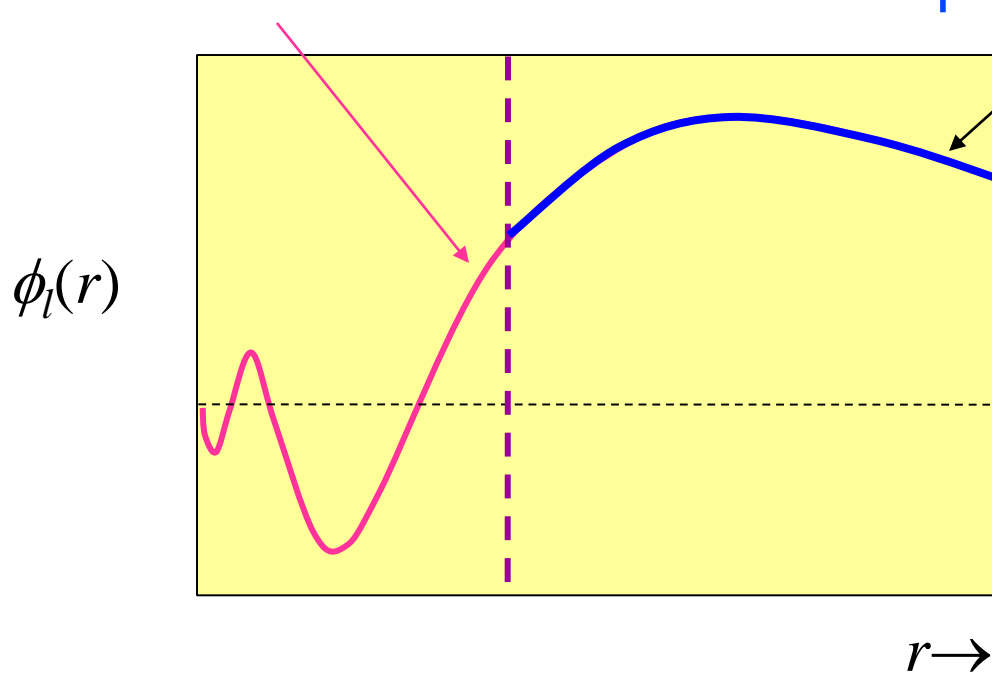
all-electron wavefunction (for some reference configuration)



Pseudowavefunction Outside r_c

all-electron wavefunction

pseudowavefunction

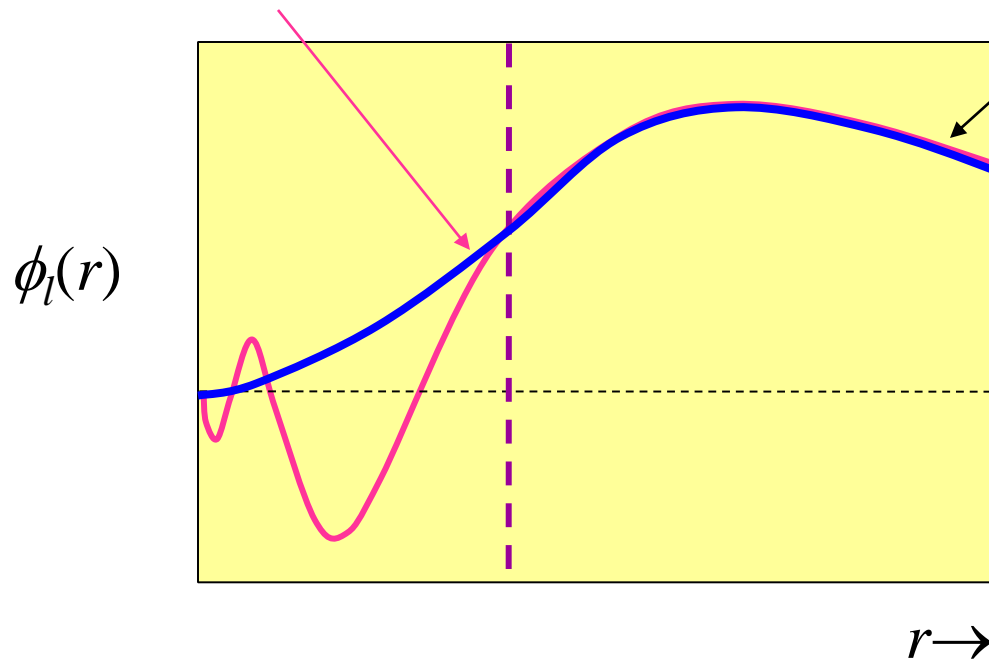


- Pseudowavefunction & all-electron wavefunction are identical outside cut-off radius r_c $\phi_{l,ref}^{AE}(r) = \phi_{l,ref}^{PS}(r) \quad r \geq r_c$

Pseudowavefunction

all-electron wavefunction

pseudowavefunction



- Inside r_c , $\phi_l^{PS}(r) = f(r)$

Choose to get desired properties

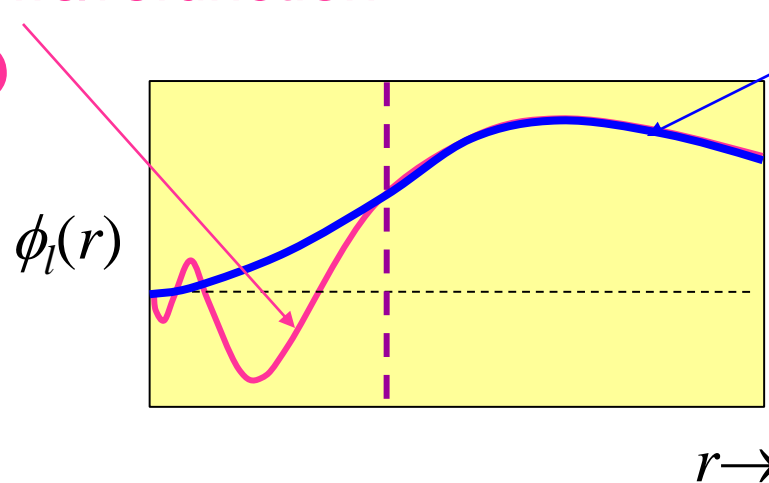
Norm-Conservation

all-electron wavefunction

$$\phi_l^{AE}(r)$$

pseudowavefunction

$$\phi_l^{PS}(r)$$



- Norm conservation:

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

- Imposing **norm conservation** improves **transferability!**
(Hamann, Schlüter, Chiang, 1979)

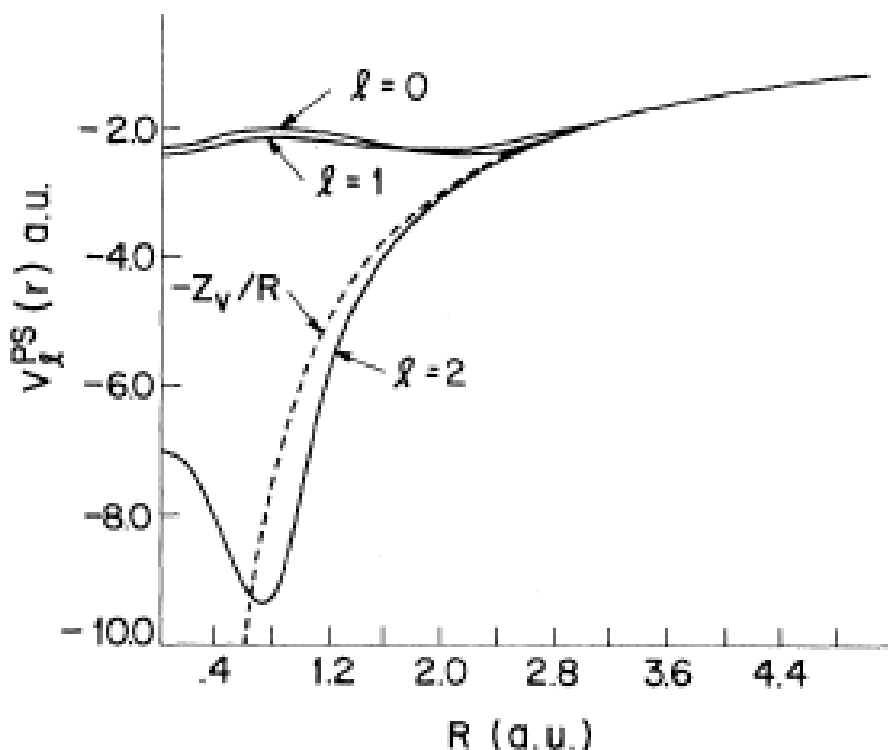
Pseudowavefunction → Pseudopotential

- Invert the radial Schrödinger equation to get a “screened” potential for each l , $V_l^{scr}(r)$
- This “screened” potential includes Hartree and XC contributions; “unscreen” to get pseudopotential.

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

What does a pseudopotential look like?

Example for Mo:



Hamann, Schluter & Chiang, 1979.

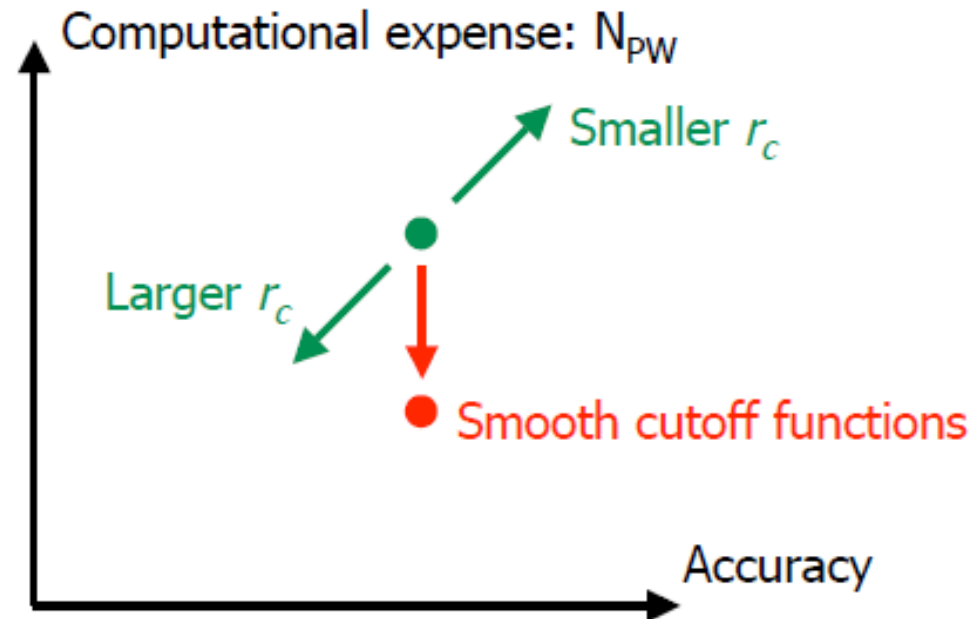
- Weaker than full Coulomb potential
- No singularity at $r=0$
- Different pseudopotential for each l (example of semilocal pseudopotential)
- Will be V_{ion} (replacing nuclear potential)

Some Popular Pseudopotentials: BHS

- 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.

How to Make Softer?

- Increase radial cut-off r_c ?? Softer, but transferability suffers.



David Vanderbilt

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, [RRKJ] 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)

Need lower E_{cut} with soft pseudopotentials

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

Troullier-Martins

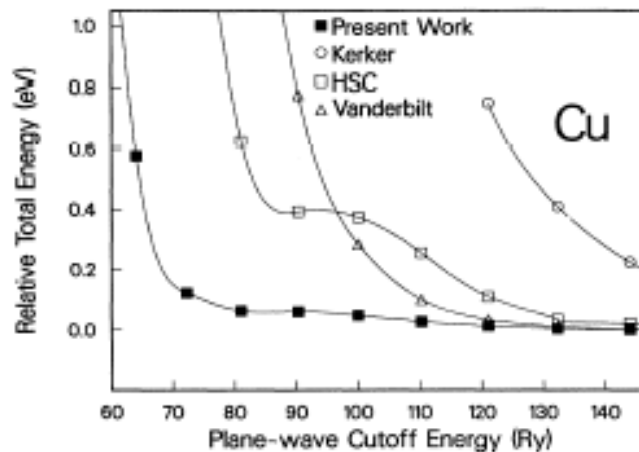


FIG. 8. The calculated total energy of fcc Cu plotted against the cutoff energy of the plane-wave basis set for the four pseudopotentials shown in Fig. 7. The total energy for all four curves are referenced to the total energy calculated at a cutoff energy of 225 Ry. The squares, circles, and triangles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

RRKJ

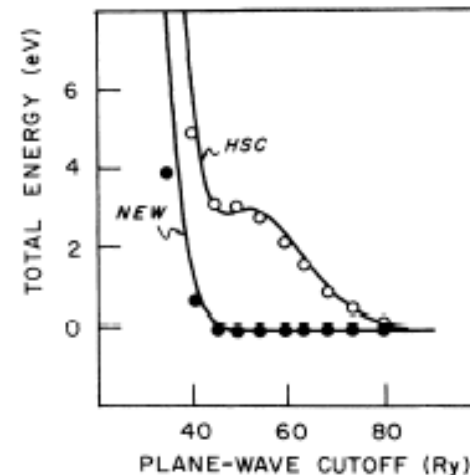


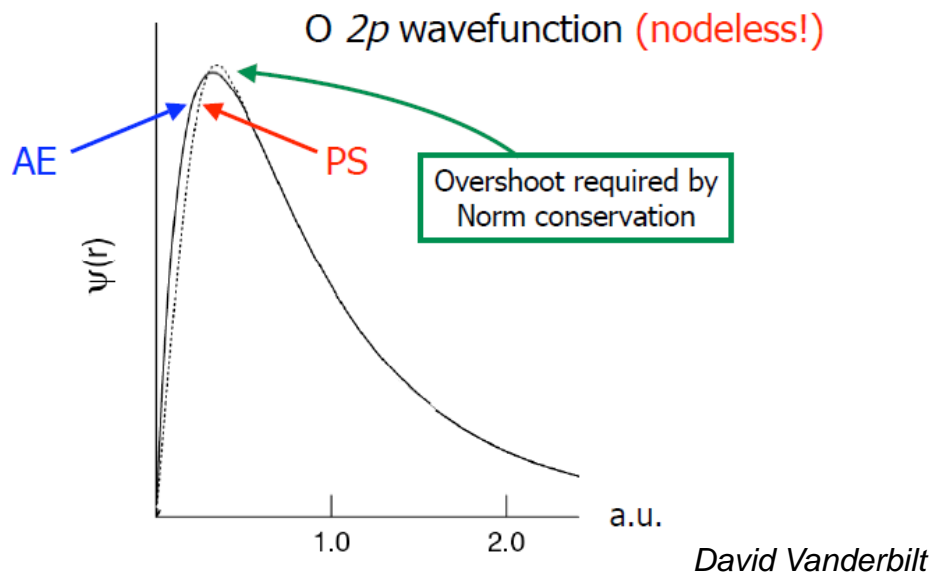
FIG. 3. Atomic (solid lines) and fcc solid (dots) total energies as a function of cutoff energy for copper in the HSC and present approaches. The zero of atomic total energy for each pseudopotential was chosen to be the total atomic energy at a cutoff energy of 324 Ry. The zero of solid total energy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

Nodeless Wavefunctions & Norm Conservation

Cut-offs still higher than we would like, especially for

- > first row elements (1s, 2p nodeless)
- > transition metals (3d nodeless)
- > rare-earths (4f nodeless)

This is because of the constraint of norm conservation...



Ultrasoft Pseudopotentials



- David 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).

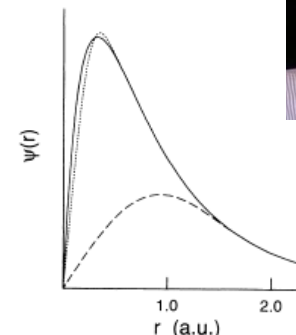


FIG. 1. Oxygen 2p radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Vanderbilt

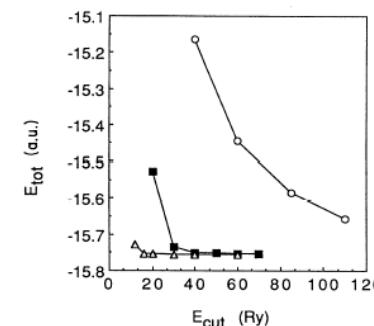


FIG. 1. Total energy of ground-state oxygen atom vs plane-wave cutoff for Bachelet-Hamann-Schlüter pseudopotential (open circles) and for Vanderbilt pseudopotential with $r_c = 1.2$ a.u. (solid squares) and $r_c = 1.8$ a.u. (open triangles).

Laasonen, Car, Lee & Vanderbilt

POPULAR Pseudopotentials!

- GB Bachelet, DR Hamann and M. Schluter, “Pseudopotentials that Work- From H to Pu”, Phys. Rev. B, 1982. Times Cited: 2,536.
- N. Troullier and JL Martins, “Efficient Pseudopotentials for Plane-Wave Calculations”, Phys. Rev. B, 1991. Times Cited: 6,347
- AM Rappe, KM Rabe, E Kaxiras and J Joannopoulos, “Optimized Pseudopotentials”, Phys. Rev. B, 1990, Times Cited: 592.
- D. Vanderbilt: “Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism”, Phys. Rev. B, 1990. Times Cited: 8,355.

Transferability

- Condition that pseudoatom reproduces behavior of all-electron atom in wide variety of chemical environments.
- Recall, pseudopotential derived for reference config. (atom with given occ of levels), using ref 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?

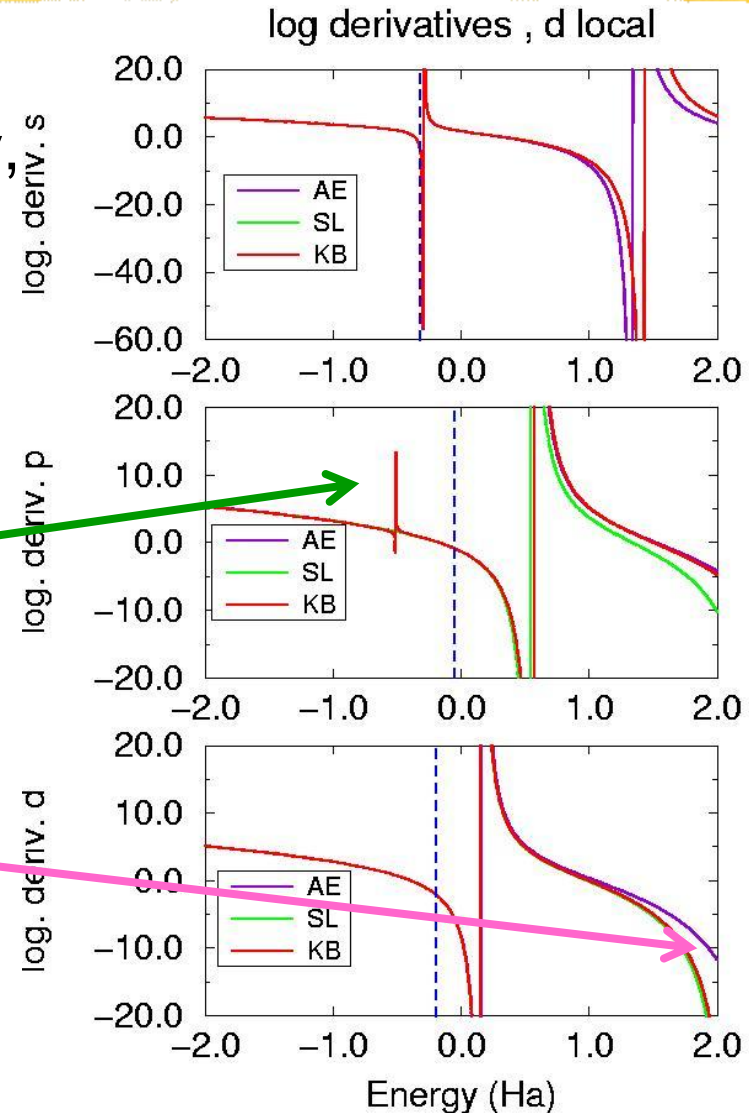
Transferability: log derivatives

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

Ag

Has ghost ☹️

Log derivatives don't match ☹️



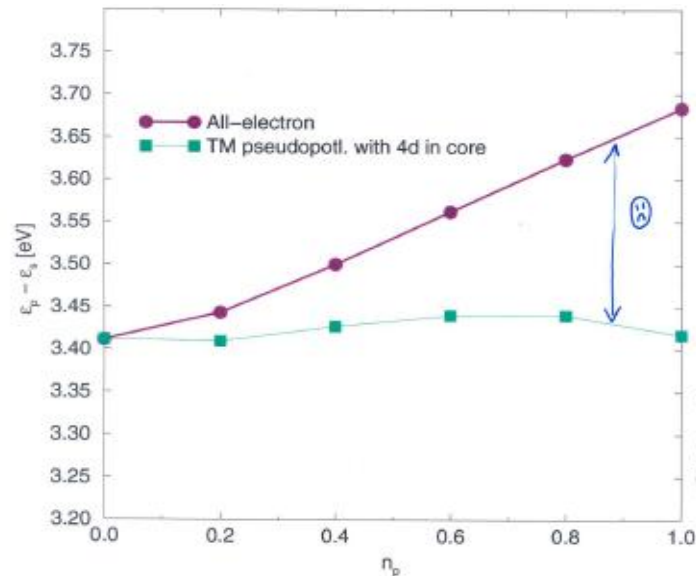
Transferability: Occupation Changes

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'** $N_i = \int_{r_c}^{\infty} |\phi_i|^2 dr$ 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 $V_{XC}(\rho^{val} + \rho^{core}) \neq V_{XC}(\rho^{val}) + V_{XC}(\rho^{core})$

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

<http://www.physics.rutgers.edu/~dhv/talks/bangalore-july06.pdf>

<http://opium.sourceforge.net/>

... and references therein

Extra Stuff: 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]

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

- 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....

Extra Stuff: Norm Conservation & Transferability

- By construction, log derivatives satisfy:

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

- In addition, if we impose **norm conservation**:

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

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

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

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!

Terminology: Local, Semilocal, Separable, etc.

Local PSP

$$\hat{V}_{\text{ps}} = V_{\text{ps}}(r) \quad (\text{local in } r, \theta, \phi)$$

Semilocal PSP

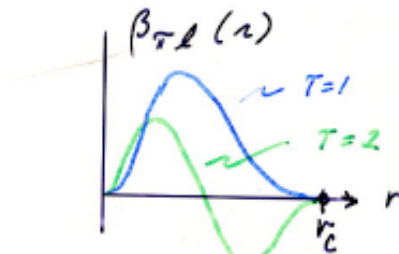
$$\hat{V}_{\text{ps}} = \sum_l V_{\text{ps}}^{(l)}(r) \hat{P}_l \quad (\text{local in } r, \text{ nonlocal in } \theta, \phi)$$

Nonlocal separable PSP (e.g., Kleinman-Bylander)

$$\hat{V}_{\text{ps}} = V_{\text{ps}}^{\text{loc}}(r) + \sum_{lm} D_l |\beta_{lm}\rangle \langle \beta_{lm}|$$

General nonlocal separable PSP

$$\hat{V}_{\text{ps}} = V_{\text{ps}}^{\text{loc}}(r) + \sum_{\tau\tau'} \sum_{lm} D_{\tau\tau'l} |\beta_{\tau lm}\rangle \langle \beta_{\tau' l}|$$



(Note: All are spherically symmetric.)

Extra Stuff: Relativistic Pseudopotentials

- Do all-electron calculation on free atom using Dirac equation
- Obtain $\psi_{nlj}(r)$ for $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$
- Invert **Schrödinger equation** to get $V_{lj}^{\text{PS}}(r)$
- For “scalar relativistic” target calc., use j -averaged PSPs:

$$V_l^{\text{PS}}(r) = \frac{1}{2l+1} \left[(l+1) V_{l,l+\frac{1}{2}}^{\text{PS}} + l V_{l,l-\frac{1}{2}}^{\text{PS}} \right]$$

- For spin-orbit interactions, keep also

$$V_l^{\text{SO}}(r) = \frac{1}{2l+1} \left[V_{l,l+\frac{1}{2}}^{\text{PS}} - V_{l,l-\frac{1}{2}}^{\text{PS}} \right]$$

and use, schematically speaking,

$$\hat{V}_{\text{ps}} = \sum_l |l\rangle \left[V_l^{\text{PS}}(r) + V_l^{\text{SO}}(r) \mathbf{L} \cdot \mathbf{S} \right] \langle l|$$