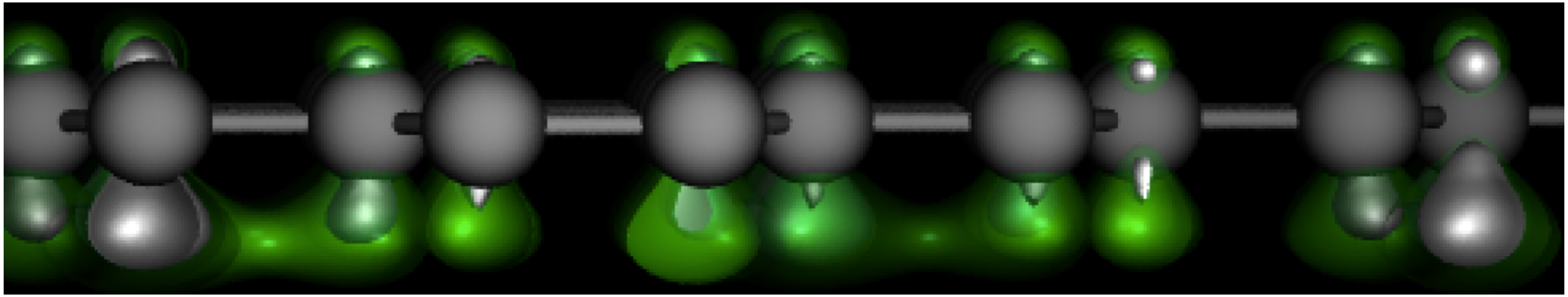
Advanced Workshop on High-Performance & High-Throughput Materials Simulations using Quantum ESPRESSO
ICTP, Trieste, Italy, January 16 to 27, 2017

Plane-Waves, pseudopotentials, k-points, FFTs .... and all that



Ralph Gebauer

slides courtesy of Shobhana Narasimhan

The Abdus Salam
International Centre
for Theoretical Physics

Monday, January 16th, 2017

The Kohn-Sham problem

- Want to solve the Kohn-Sham equations:

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

- 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:

$$\Sigma_\beta \ H_{\alpha\beta} \, c_{i\beta} = \ \varepsilon_i \, c_{i\alpha}$$

Matrix element *Eigenvalue* *Eigenvector*

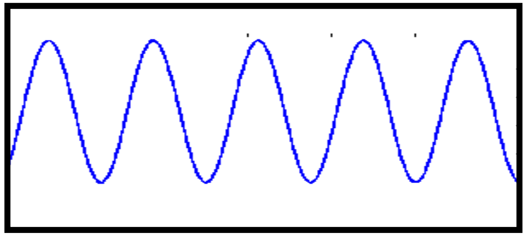
- Solving ⇔ Have to diagonalize a matrix of size N_b x N_b

Size of basis

Some possible basis sets

- Various possible choices of basis:

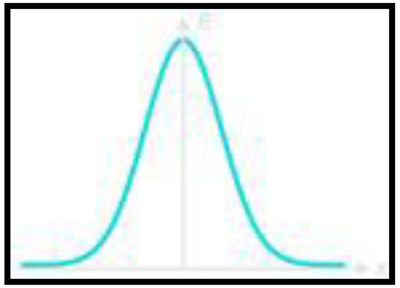
  - Plane waves $e^{iK \bullet r}$



  - 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 $f_{\alpha}(\mathbf{r})$ to be simple?

Advantages of a Plane Wave Basis

- Simple: Easy to take derivatives, etc.⇒ Coding is easy!
- Orthonormal: No overlap integrals.
- Independent of atomic positions ⇒ No "Pulay forces"; easy to calculate forces for structural relaxation & molecular dynamics.

- Unbiased: No assumption about where charge concentrated. (But ∴ 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 ⇔ k-space

Advantages of a Plane Wave Basis

Convenient use of FFTs:

$$\tilde{f}(k) = \sum_{n=0}^{N-1} f_n \, e^{-2\pi i k n/N}$$

Very practical to calculate convolutions, solve Poisson's equation, etc.

$$\begin{aligned} V(\mathbf{r}) &= \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ \tilde{V}(\mathbf{G}) &= 4\pi \, \frac{\tilde{n}(\mathbf{G})}{\mathbf{G}^2} \end{aligned}$$

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! (~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 solution = introduction of artificial supercell or periodic approximat.)

- Sometimes (chemical) interpretation harder.

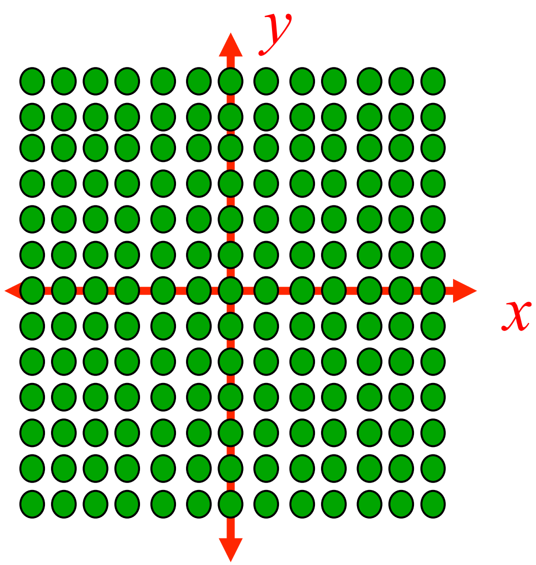
Some popular plane wave codes

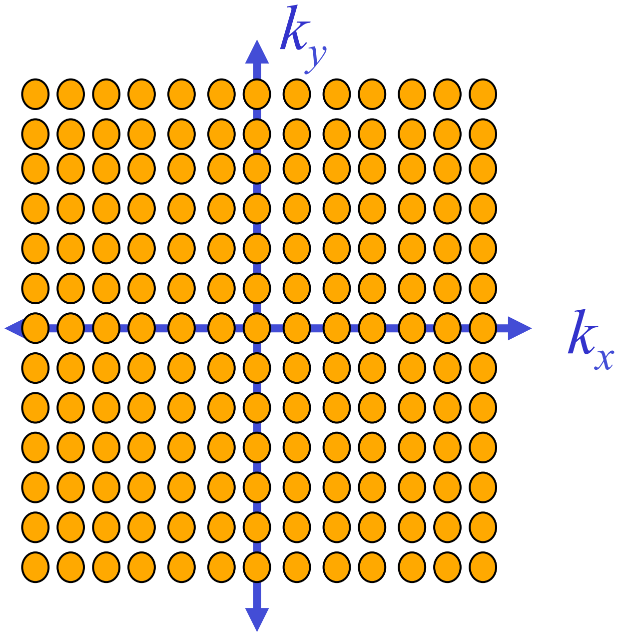
- Quantum ESPRESSO (PWscf)
- VASP
- ABINIT
- CASTEP
- CPMD

(there are others too…)

Periodic Systems

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





- Spacing of **R**'s inversely proportional to spacing of **G**'s

Periodic Systems & Bloch's Theorem

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

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

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

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}),$$

where $\mathbf{R}$ = lattice vector

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

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

where $\mathbf{G}$ = reciprocal lattice vector

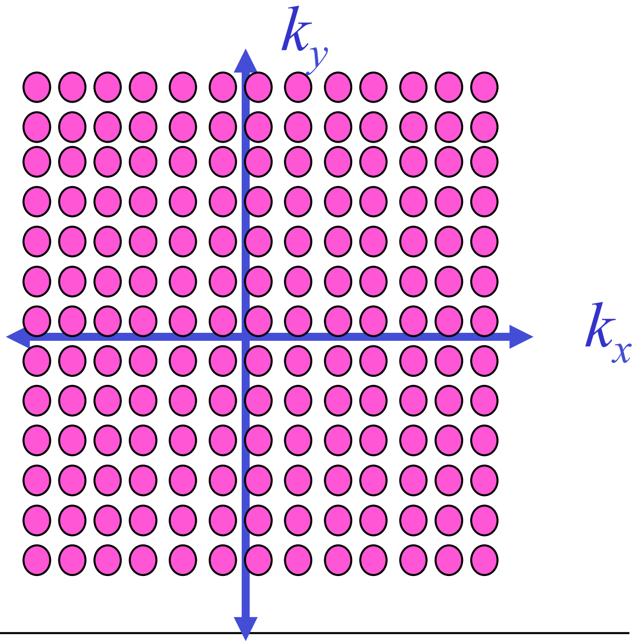
Plane Waves & Periodic Systems

- So, for a periodic system:

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

where **G** = reciprocal lattice vector

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

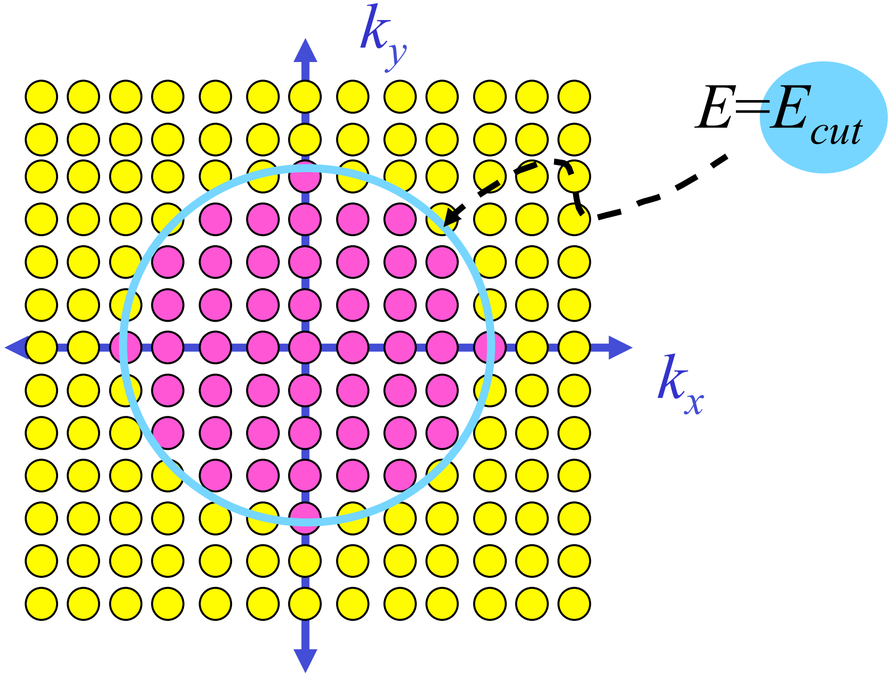


- Only true for periodic systems that grid is discrete.
- In principle, still need infinite number of plane waves.

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:

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



Truncating the Plane Wave Expansion

- Beware: charge density and orbitals have different cutoffs!

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

$$n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\,\psi_i(\mathbf{r})$$

Truncating the Plane Wave Expansion

- Beware: charge density and orbitals have different cutoffs!

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

$$n(\mathbf{r}) = \sum_i \psi_i^*(\mathbf{r})\,\psi_i(\mathbf{r})$$

$$\tilde{n}(\mathbf{G}) = \sum_i \sum_{\mathbf{G}'} \tilde{\psi}_i^*(\mathbf{G}')\,\tilde{\psi}_i(\mathbf{G}-\mathbf{G}')$$

➔ if the orbitals are represented with a cutoff E_{cut}, then the charge density is represented with a cutoff of 4 E_{cut}.

Matrix elements of (non-)local operators

Given a general non-local operator $O(\mathbf{r},\mathbf{r}')$.

Its matrix elements in the plane-wave basis read:

$$\tilde{O}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') = \int d\mathbf{r}\, d\mathbf{r}'\ e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\, O(\mathbf{r},\mathbf{r}')\, e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}'}$$

If $O(\mathbf{r},\mathbf{r}')$ is a local operator, then:

$$O(\mathbf{r},\mathbf{r}') = O(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$$

$$\begin{aligned}\tilde{O}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') &= \int d\mathbf{r}\, d\mathbf{r}'\ e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}\, O(\mathbf{r},\mathbf{r}')\, e^{-i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}'} \\ &= \int d\mathbf{r}\ e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}}\, O(\mathbf{r}) \\ &= \tilde{O}(\mathbf{G}-\mathbf{G}')\end{aligned}$$

Kohn-Sham equations in plane wave basis

- Eigenvalue equation is now:

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

- Matrix elements are:

$$\boxed{\tfrac{1}{2}|\mathbf{k}+\mathbf{G}|^2\delta_{\mathbf{G},\mathbf{G}'} + \mathbf{V}_{\mathrm{ion}}(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}') + \mathbf{V}_{\mathrm{H}}(\mathbf{G}-\mathbf{G}') + \mathbf{V}_{\mathrm{XC}}(\mathbf{G}-\mathbf{G}')}$$

- Nuclear (→ ionic) potential given by:

$$\boxed{V_{ion}(\mathrm{G}) = \sum_\alpha \mathbf{S}_\alpha(\mathrm{G})\mathbf{v}_\alpha(\mathrm{G}); \qquad \mathbf{S}_\alpha(\mathrm{G}) = \sum_{\mathrm{I}} \exp(\mathrm{i}\mathrm{G}\cdot\mathbf{R}_{\mathrm{I}})}$$

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!

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:

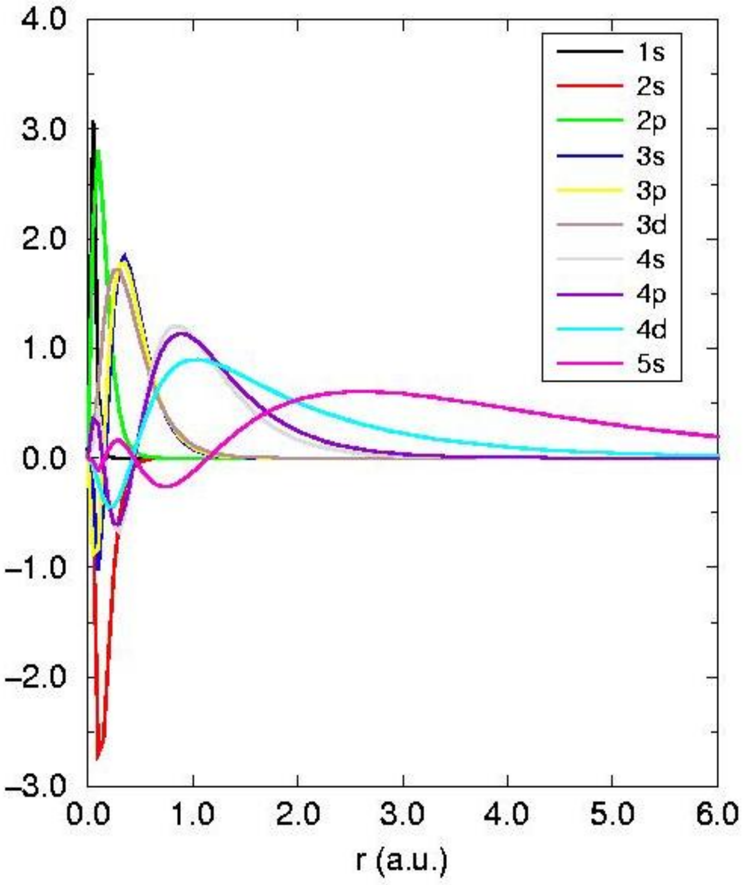
$$\psi_{lm}(\mathbf{r}) = \psi_l(r)Y_{lm}(\theta,\phi) = r^{-1}\phi_l(r)Y_{lm}(\theta,\phi)$$

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

φ(r)



- 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

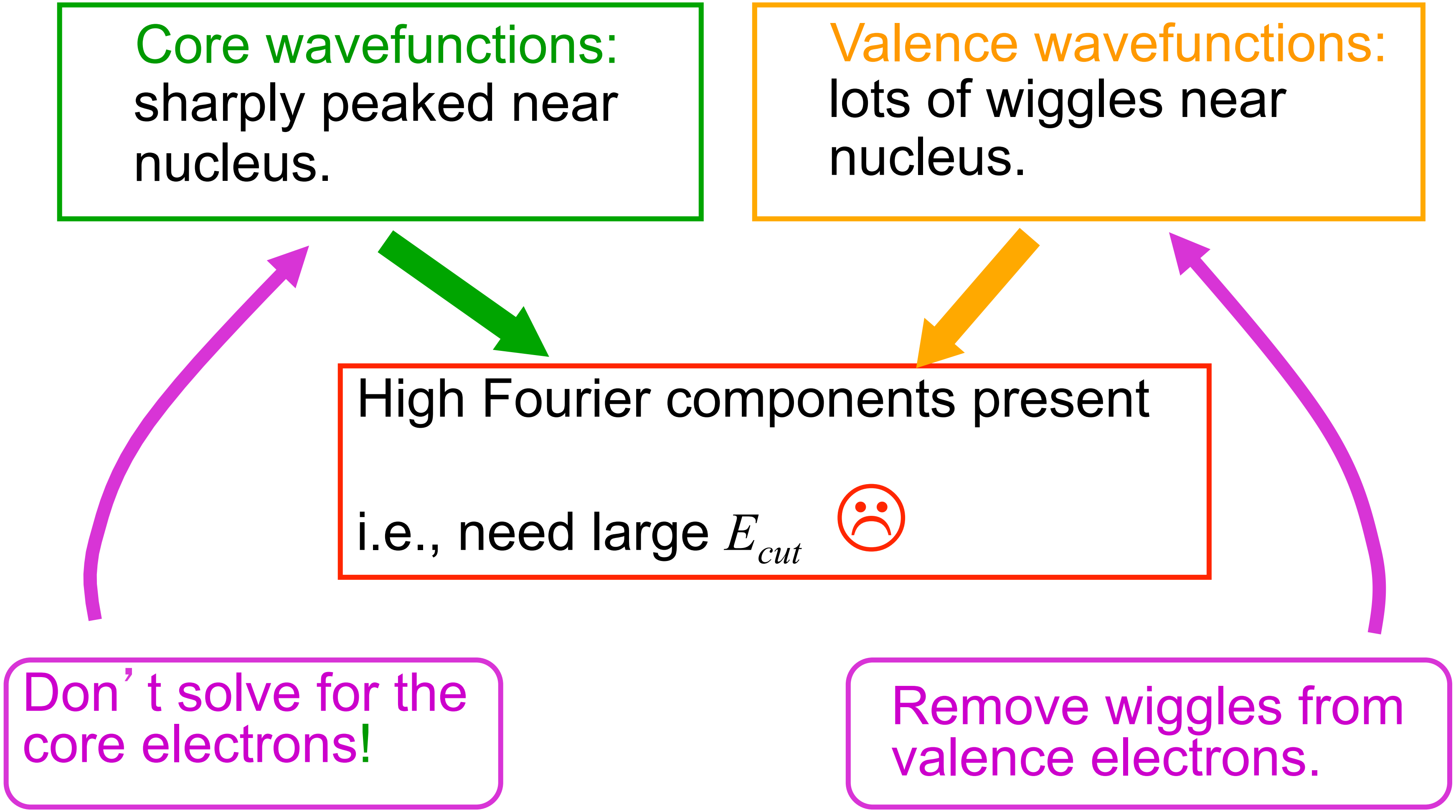
Core wavefunctions: sharply peaked near nucleus.

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 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!)

Generating an *Ab Initio* Pseudopotential

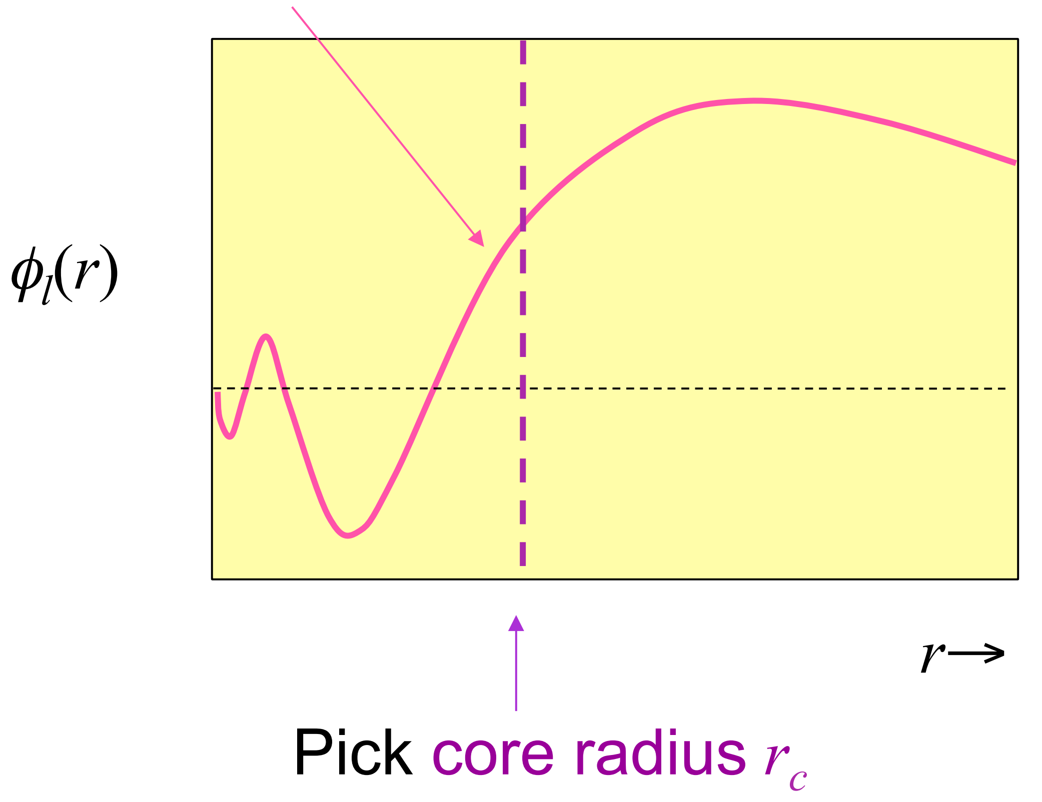
- For the element of interest, pick a reference configuration.

- Perform an “all-electron” calculation for this reference configuration.

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

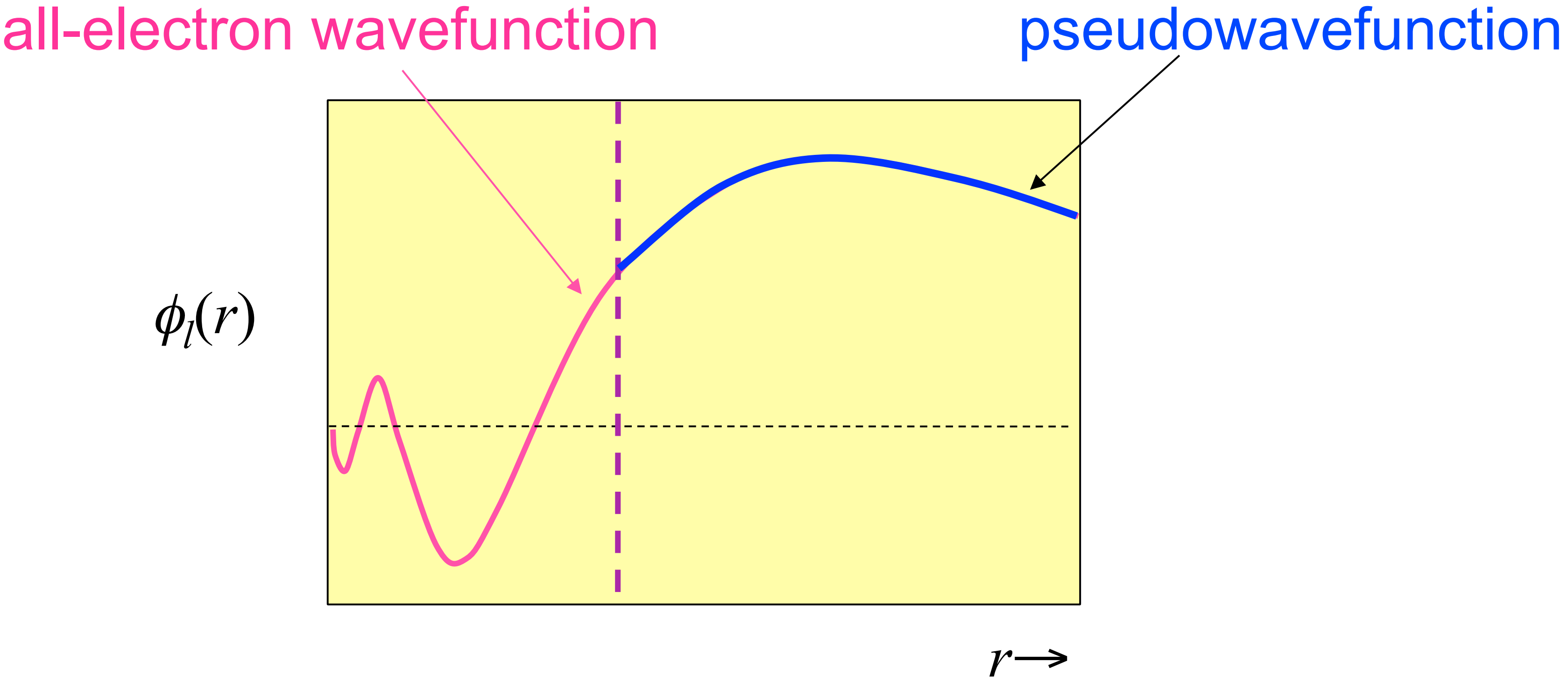
All-Electron Wavefunction

all-electron wavefunction *(for some reference configuration)*



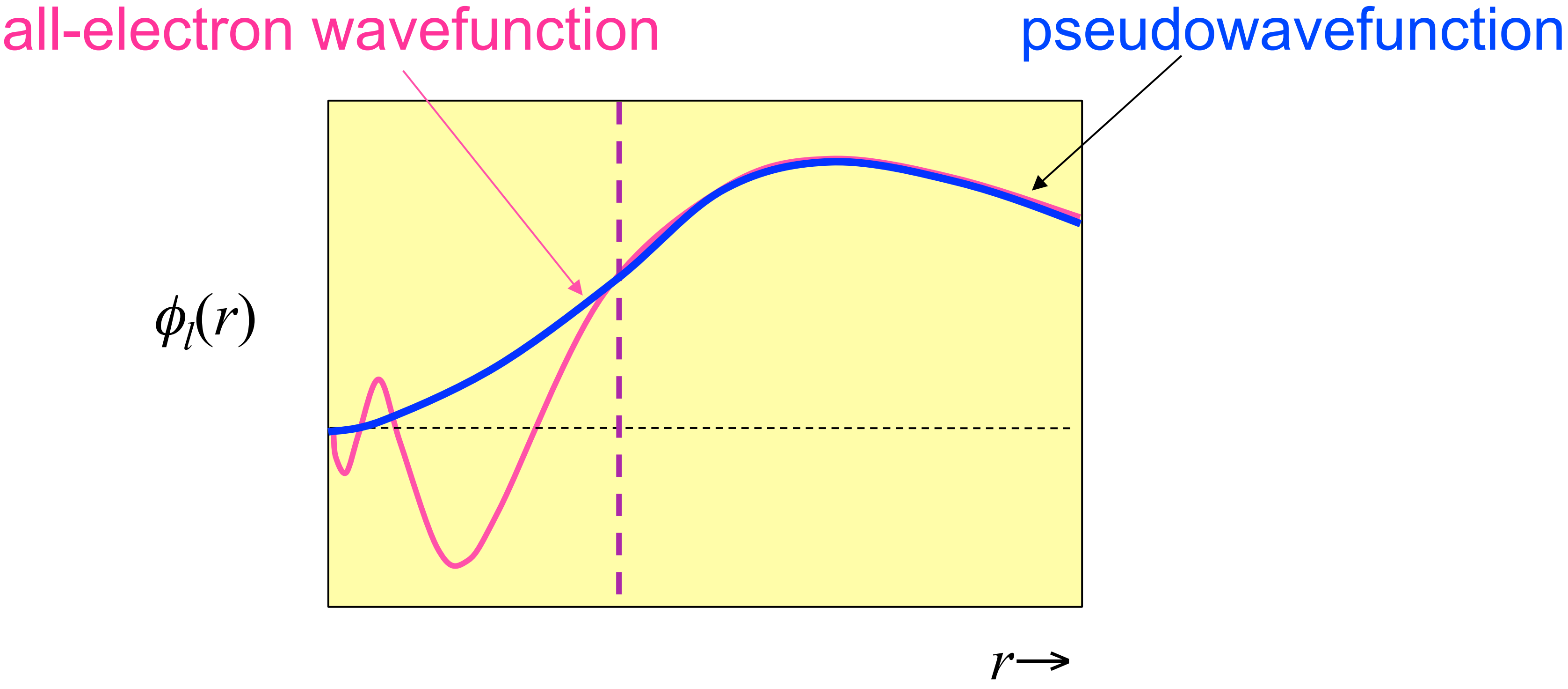
Pick core radius r_c

Pseudowavefunction Outside r_c



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

Pseudowavefunction



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

Choose to get desired properties

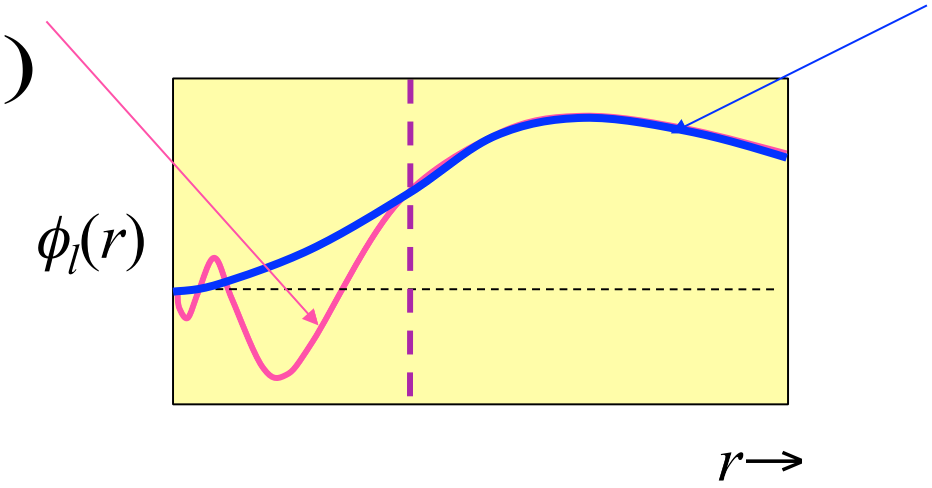
Norm-Conservation

all-electron wavefunction

$\phi_l^{AE}(r)$

pseudowavefunction

$\phi_l^{PS}(r)$



- Norm conservation:

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

- Imposing norm conservation improves transferability!

(Hamann, Schlüter, Chiang, 1979)

Pseudowavefunction → Pseudopotential

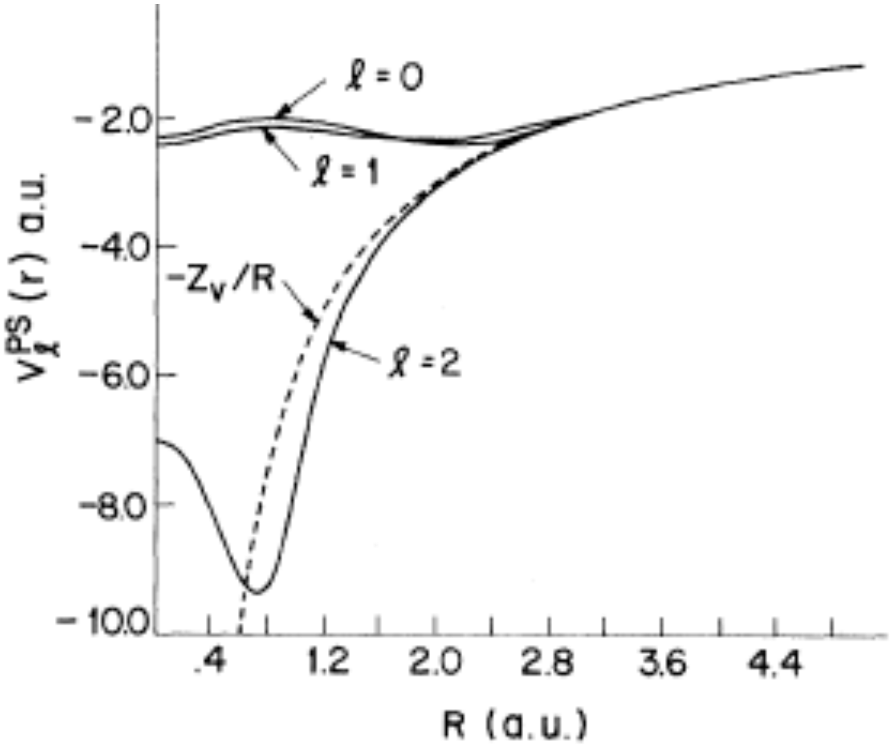
- Invert the radial Schrödinger equation to get a "screened" potential for each l, $V_l^{scr}(r)$

- 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)

Dealing with the non-locality

$$V_{ps} = V_{loc} + \sum_{l} \sum_{m=-l}^{l} |lm\rangle \delta V_l \langle lm|$$

This non-local operator has $(N_{pw})^2$ matrix elements (must be avoided!)

Solution: Kleinman-Bylander representation

$$V_{ps} = V_{loc} + \sum_{lm} \frac{|\delta V_l \psi_{lm}\rangle \langle \psi_{lm} \delta V_l|}{\langle \psi_{lm} | \delta V_l | \psi_{lm}\rangle}$$

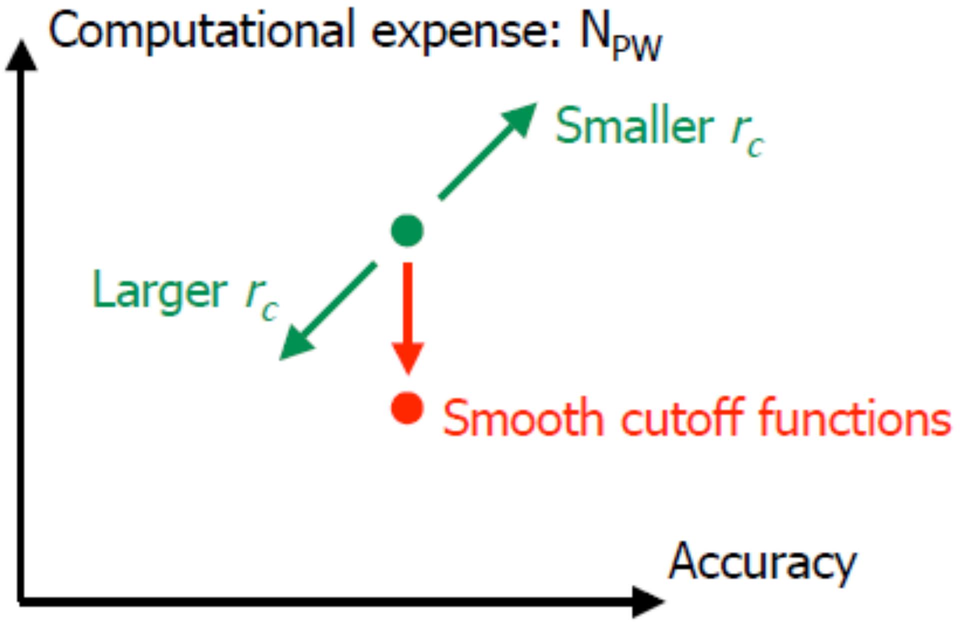
ψ_{lm} is an eigenstate of the pseudo-Hamiltonian, acting as reference state.

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 rc?? Softer, but transferability suffers.



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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, [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

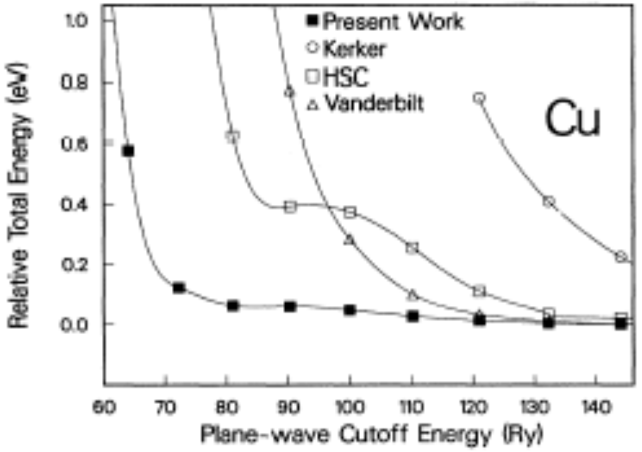


FIG. 8. The calculated total energy of fcc Cu plotted against the cutoff energy of the plane-wave basis set for the four pseudopotentials shown in Fig. 7. The total energy for all four curves are referenced to the total energy calculated at a cutoff energy of 225 Ry. The squares, circles, and triangles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

RRKJ

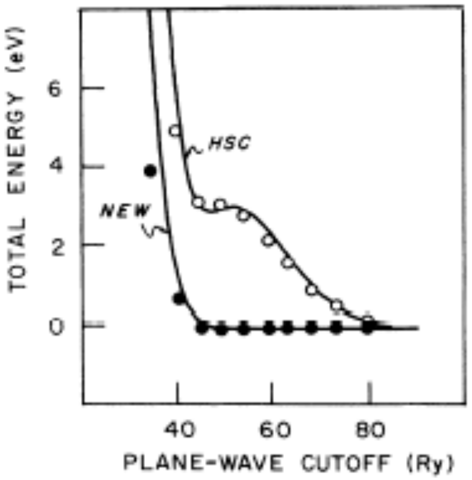


FIG. 3. Atomic (solid lines) and fcc solid (dots) total energies as a function of cutoff energy for copper in the HSC and present approaches. The zero of atomic total energy for each pseudopotential was chosen to be the total atomic energy at a cutoff energy of 324 Ry. The zero of solid total energy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

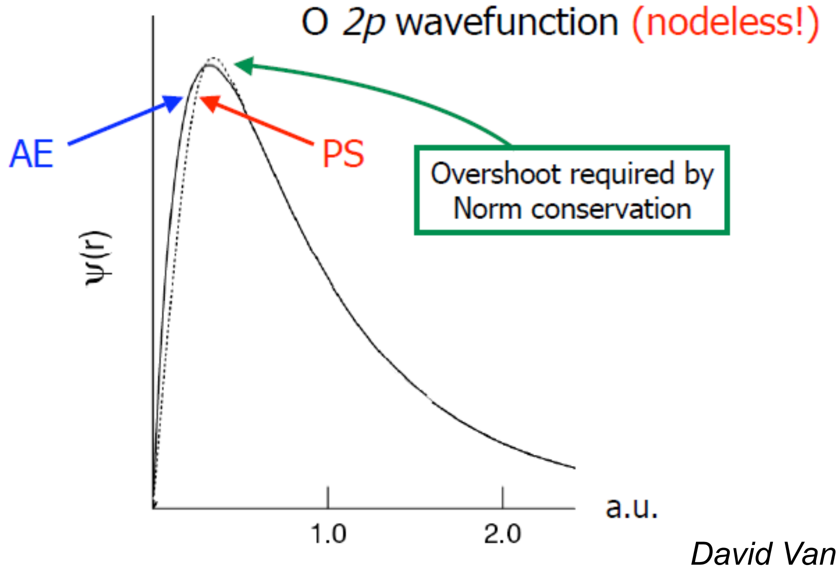
Cut-offs still higher than we would like, especially for

> first row elements (1s, 2p nodeless)

> transition metals (3d nodeless)

> rare-earths (4f nodeless)

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



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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).

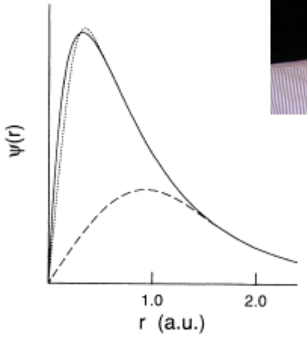


FIG. 1. Oxygen 2*p* radial wave function (solid line), and corresponding pseudo-wave-functions generated using HSC (dotted line) and current (dashed line) methods.

Vanderbilt

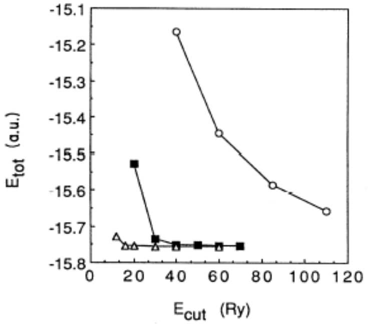


FIG. 1. Total energy of ground-state oxygen atom vs plane-wave cutoff for Bachelet-Hamann-Schlüter pseudopotential (open circles) and for Vanderbilt pseudopotential with $r_c = 1.2$ a.u. (solid squares) and $r_c = 1.8$ a.u. (open triangles).

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: 2,723.
- N. Troullier and JL Martins, “Efficient Pseudopotentials for Plane-Wave Calculations”, Phys. Rev. B, 1991. Times Cited: 9,640.
- AM Rappe, KM Rabe, E Kaxiras and J Joannopoulos, “Optimized Pseudopotentials”, Phys. Rev. B, 1990, Times Cited: 1,011.
- D. Vanderbilt: “Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism”, Phys. Rev. B, 1990. Times Cited: 12,784.

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:

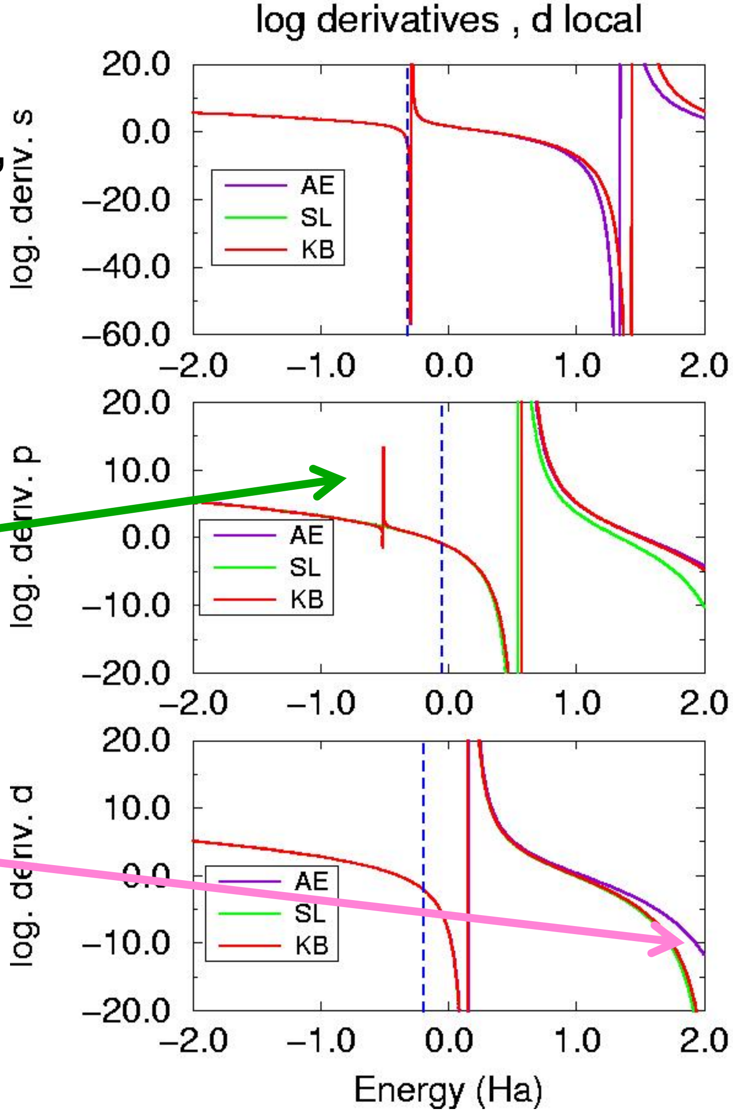
  - do scattering properties of potential change correctly? (Look at log derivatives)

- 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 ☹

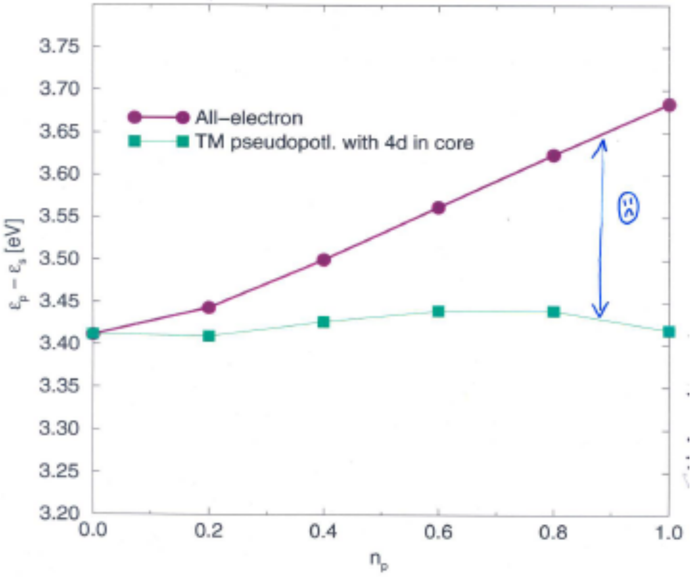
Transferability: Occupation Changes

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 $V_{XC}(\rho^{val}+\rho^{core}) \neq V_{XC}(\rho^{val})+Vxc(\rho^{core})$

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)

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]

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

- 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....

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:

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

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!

Terminology: Local, Semilocal, Separable, etc.

Local PSP

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

Semilocal PSP

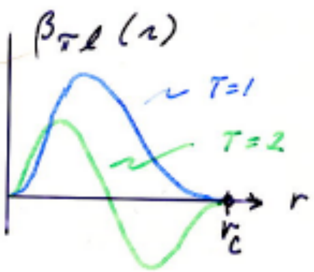
$$\hat{V}_{\rm ps} = \sum_l V_{\rm ps}^{(l)}(r)\, \hat{P}_l \qquad \text{(local in } r\text{, nonlocal in } \theta,\ \phi\text{)}$$

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

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

General nonlocal separable PSP

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



(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 $V_{lj}^{\mathrm{ps}}(r)$
- For "scalar relativistic" target calc., use j-averaged PSPs:

$$V_l^{\mathrm{ps}}(r) = \frac{1}{2l+1}\left[(l+1)\,V^{\mathrm{ps}}_{l,l+\frac{1}{2}} + l\,V^{\mathrm{ps}}_{l,l-\frac{1}{2}}\right]$$

- For spin-orbit interactions, keep also

$$V_l^{\mathrm{so}}(r) = \frac{1}{2l+1}\left[V^{\mathrm{ps}}_{l,l+\frac{1}{2}} - V^{\mathrm{ps}}_{l,l-\frac{1}{2}}\right]$$

and use, schematically speaking,

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