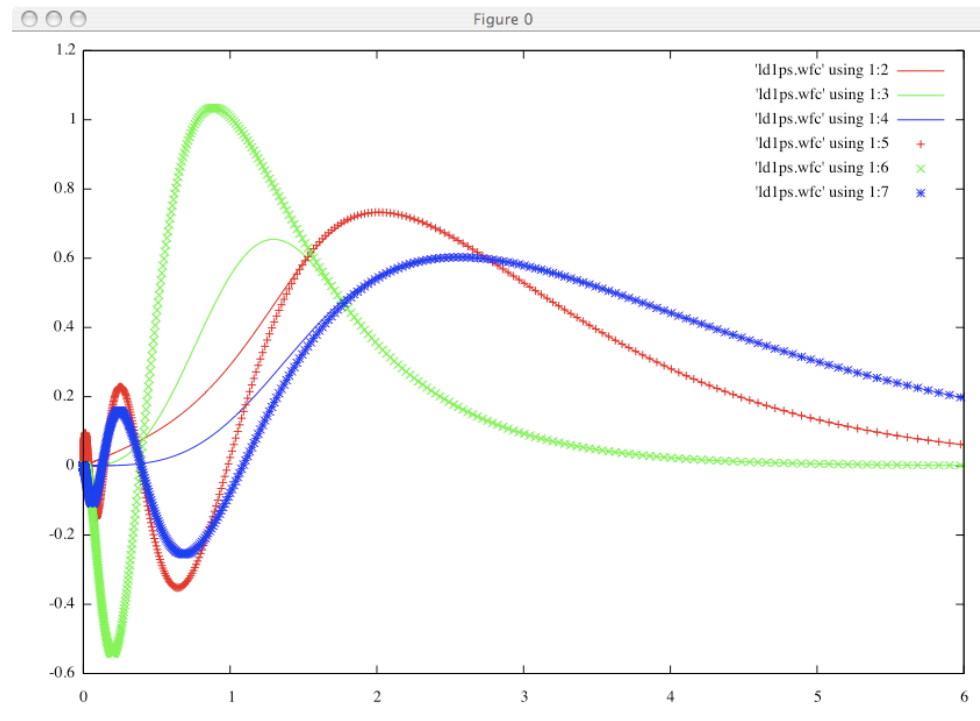


An Introduction to Pseudopotentials

CECAM GIPAW-NMR Tutorial, 23 Sep. 2009



Norm-Conserving Pseudopotentials

Electron-ionic core interactions are typically represented by a nonlocal *Norm-Conserving Pseudopotential* (NCPP): a soft potential for valence electrons only (core electrons disappear from the calculation) having pseudo-wavefunctions containing no “orthonormality wiggles”

In many systems, NCPP's allow accurate calculations with moderate-size ($E_c \sim 10 - 20Ry$) plane-wave basis sets

Empirical Pseudopotentials

Early *empirical* PPs: fitted to some known experimental data (band gaps, ionization potentials, etc.). A classical example: Cohen-Bergstresser PPs for diamond and zincblende semiconductors.

Cohen-Bergstresser PPs are given as a few Fourier components $V(G)$ of the crystal potential for the fcc lattice. The band structure is obtained by diagonalizing $H = T + V$ on a small PW basis set:

$$\langle \mathbf{k} + \mathbf{G} | T + V | \mathbf{k} + \mathbf{G}' \rangle = \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G})^2 \delta_{\mathbf{G}\mathbf{G}'} + \sum_{\mu} S_{\mu}(\mathbf{G} - \mathbf{G}') V_{\mu}(\mathbf{G} - \mathbf{G}')$$

Simple and useful but little more than a parameterization of the band structure.

Atomic Pseudopotentials

Early *atomic*, *transferrable PPs* for self-consistent calculations:

$$V(r) = -e^2 \int \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + (v_1 + v_2 r^2) e^{-\alpha r^2}$$

Appelbaum and Hamann (1973) Silicon, where:

$$n_0(\mathbf{r}) = Z_v \left(\frac{\alpha}{\pi} \right)^{\frac{3}{2}} e^{-\alpha r^2}$$

is assumed to be the ionic electron (pseudo) charge-density distribution ($Z_v =$ number of valence electrons). May also be written as

$$V(r) = -Z_v e^2 \frac{\text{erf}(\sqrt{\alpha} r)}{r} + (v_1 + v_2 r^2) e^{-\alpha r^2}$$

Able to reproduce the band structure of crystalline Si, but also useful in other calculations. Still lacking a first-principle derivation.

Fourier transform for Appelbaum-Hamann PP:

$$V(G) = \frac{1}{\Omega} \int e^{-i\mathbf{G}\cdot\mathbf{r}} V(r) d\mathbf{r} = -\frac{4\pi Z_v e^2}{\Omega G^2} e^{-\frac{G^2}{4\alpha}} + \frac{1}{\Omega} \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} \left[v_1 + \frac{v_2}{\alpha} \left(\frac{3}{2} - \frac{G^2}{4\alpha}\right) \right] e^{-\frac{G^2}{4\alpha}}$$

The $G = 0$ term is divergent, but its divergence is compensated by the divergence in the Hartree term:

$$\langle \mathbf{k} + \mathbf{G} | V_H | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{N\Omega} \int e^{-i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} V_H(\mathbf{r}) d\mathbf{r} = 4\pi e^2 \frac{n(\mathbf{G})}{G^2}$$

where $n(\mathbf{r})$ is the self-consistent charge,

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'.$$

Note that $n(\mathbf{G} = 0) = (\sum Z_v)/\Omega$. Consider the case of one atom per unit cell for simplicity:

$$\lim_{G \rightarrow 0} \left(\frac{4\pi Z_v e^2}{\Omega G^2} + V(G) \right) = \frac{\pi e^2 Z_v}{\Omega \alpha} + \frac{1}{\Omega} \left(\frac{\pi}{\alpha}\right)^{\frac{3}{2}} \left(v_1 + \frac{3}{2} \frac{v_2}{\alpha} \right).$$

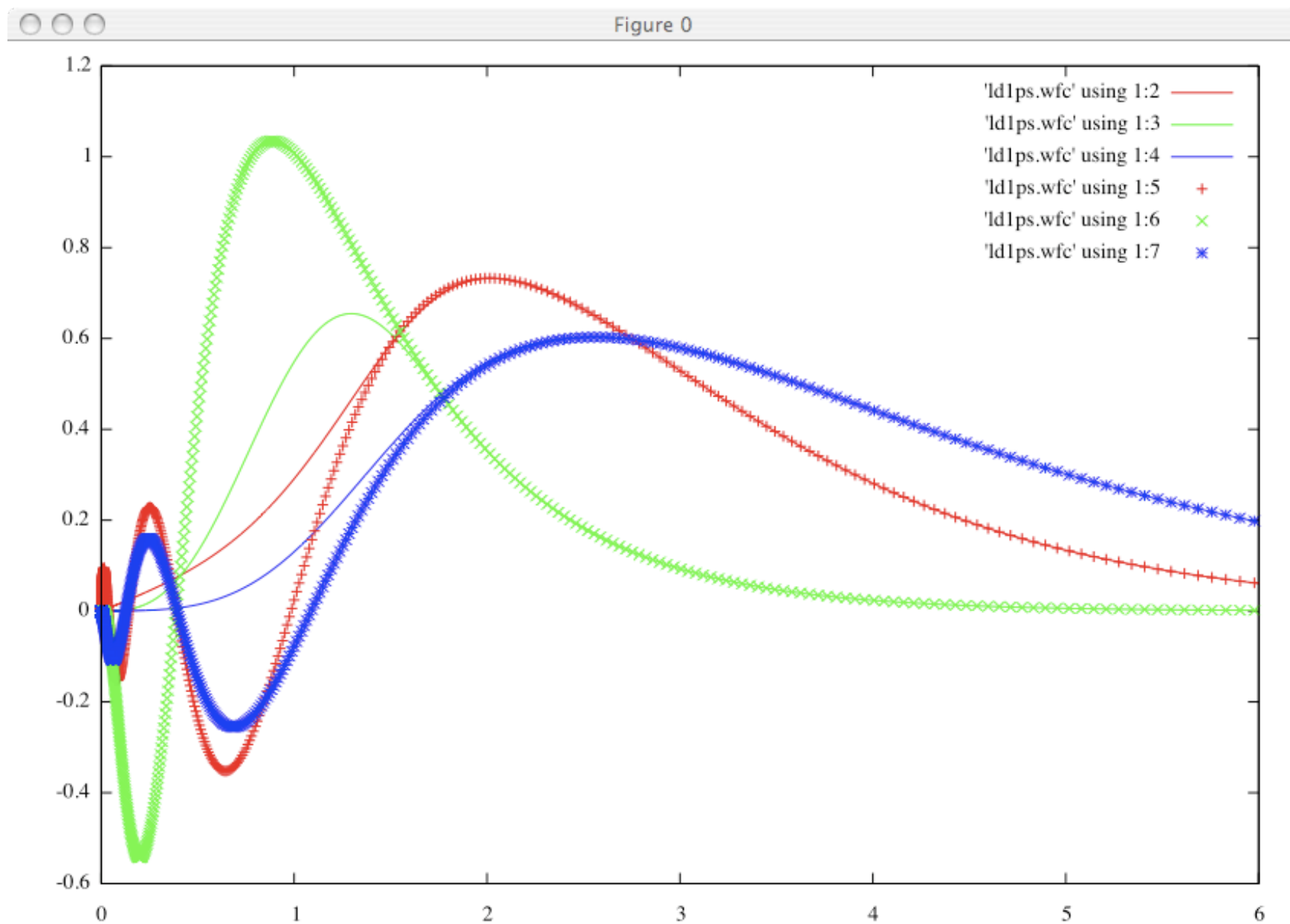
Norm-Conserving Pseudopotentials:

Norm-Conserving, DFT-based PPs were introduced by Hamann, Schlüter, Chiang in 1979. For a given reference atomic configuration, they must meet the following conditions:

- $\epsilon_l^{ps} = \epsilon_l^{ae}$
- $\phi_l^{ps}(r)$ is nodeless
- $\phi_l^{ps}(r) = \phi_l^{ae}(r)$ for $r > r_c$
- $\int_{r < r_c} |\phi_l^{ps}(r)|^2 r^2 dr = \int_{r < r_c} |\phi_l^{ae}(r)|^2 r^2 dr$

where $\phi_l^{ae}(r)$ is the radial part of the atomic valence wavefunction with l angular momentum, ϵ_l^{ae} its orbital energy. The *core radius* r_c is approximately at the outermost maximum of the wavefunction.

All-electron vs Pseudowavefunctions:



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Features of Norm-conserving Pseudopotentials:

+ *transferrable*: their construction ensures that they reproduce the logarithmic derivatives, i.e., the *scattering properties*, of the true potential in a wide range of energies. See the identity

$$-2\pi \left[(r\phi(r))^2 \frac{d}{d\epsilon} \left(\frac{d}{dr} \ln \phi(r) \right) \right]_{r_c} = 4\pi \int_0^{r_c} |\phi(r)|^2 r^2 dr$$

valid for any regular solution of the Schrödinger equation at energy ϵ .

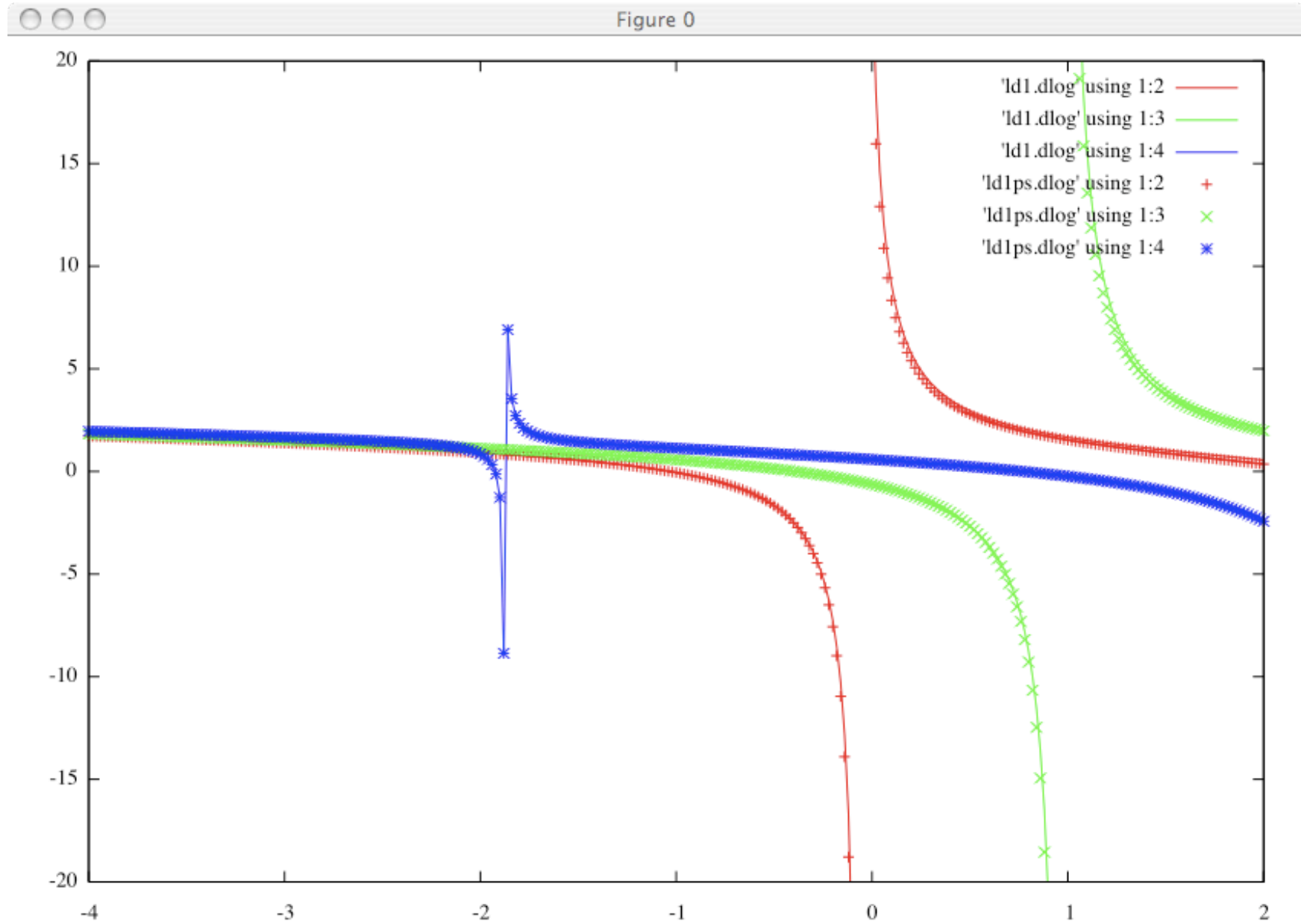
– *non local*: there is one potential per angular momentum:

$$V^{ps}(\mathbf{r}) = \sum_l V_l(r) |l\rangle \langle l|.$$

Traditionally PPs are split into a *local* part, long-ranged and behaving like $-Z_v e^2/r$ for $r \rightarrow \infty$, and a short-ranged *semilocal* term:

$$\hat{V}^{ps} = \hat{V}_{loc} + \hat{V}_{SL}, \quad \hat{V}_{loc} \equiv V_{loc}(r), \quad \hat{V}_{SL} \equiv \sum_{lm} V_l(r) \delta(r-r') Y_{lm}(\hat{\mathbf{r}}) Y_{lm}^*(\hat{\mathbf{r}}'),$$

All-electron vs Pseudo logarithmic derivatives:



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Generation of norm-conserving Pseudopotentials:

1. From an all-electron self-consistent DFT calculation in an atom with a given reference configuration, calculate ϕ_l^{at} and ϵ_l^{at} , by solving the radial Kohn-Sham equation. In the non relativistic case:

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi_l(r)}{dr^2} + \left(\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} + V(r) - \epsilon_l \right) \phi_l(r) = 0 \quad (1)$$

2. Generate ϕ_l^{ps} for valence states that obey norm-conservation conditions, and invert the Kohn-Sham equation at ϵ_l^{ps} to get $V_l(r)$ (or, generate a $V_l(r)$ in such a way that ϕ_l^{ps} and ϵ_l^{ps} obey norm-conservation conditions)

3. *Unscreen* $V_l(r)$ by removing valence contribution to Hartree and exchange-correlation potentials:

$$V_l^{ps}(r) = V_l(r) - V_H(n^{ps}(r)) - V_{xc}(n^{ps}(r))$$

where $n^{ps}(r)$ is the atomic valence charge density (assumed to be spherical):

$$n^{ps}(r) = \frac{1}{4\pi} \sum_l f_l |\phi_l^{ps}(r)|^2$$

(f_l is the occupancy of state with angular momentum l).

Desirable characteristics of a Pseudopotential:

- *Transferability*: can be estimated from atomic calculations on different configurations. In many cases simple unscreening produces an unacceptable loss of transferability. May require the *nonlinear core correction*:

$$V_l^{ps}(r) = V_l(r) - V_H(n^{ps}(r)) - V_{xc}(n_c(r) + n^{ps}(r))$$

where $n_c(r)$ is the core charge of the atom (Froyen, Louie, Cohen 1982)

- *Softness*: atoms with strongly oscillating pseudo-wavefunctions (first-row elements, elements with $3d$ and $4f$ valence electrons) will produce *hard* PPs requiring many PWs in calculations. Larger core radius means better softness but worse transferability. Various recipes to get optimal smoothness without compromising transferability: Troullier and Martins (1990), Rappe Rabe Kaxiras Joannopoulos (1990)

- *Computational efficiency:* NCPP's in the semilocal form are not ideal from this point of view. Calculation of $\hat{V}_{SL}\psi$ in plane waves:

$$(\hat{V}_{SL}\psi)(\mathbf{G}) = \sum_{\mathbf{G}'} \langle \mathbf{k} + \mathbf{G} | \hat{V}_{SL} | \mathbf{k} + \mathbf{G}' \rangle \psi(\mathbf{G}')$$

requires $\mathcal{O}(N^2)$ floating point operations per band, plus $\mathcal{O}(N^2)$ storage, where N is the number of plane waves.

Matrix elements of the semilocal part between plane waves

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}_{SL} | \mathbf{k} + \mathbf{G}' \rangle = \frac{1}{\Omega} \sum_{lm} \int e^{-i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} Y_{lm}(\hat{\mathbf{r}}) V_l(r) Y_{lm}^*(\hat{\mathbf{r}}') \delta(r - r') e^{i(\mathbf{k} + \mathbf{G}') \cdot \mathbf{r}'} d\mathbf{r} d\mathbf{r}'$$

(for one atom at $\mathbf{r} = 0$). Using the expansion of plane waves into spherical Bessel functions j_l :

$$e^{i\mathbf{q} \cdot \mathbf{r}} = 4\pi \sum_l i^l j_l(qr) \sum_m Y_{lm}^*(\hat{\mathbf{q}}) Y_{lm}(\hat{\mathbf{r}})$$

one gets:

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}_{SL} | \mathbf{k} + \mathbf{G}' \rangle = \frac{4\pi}{\Omega} \sum_l (2l + 1) P_l(\mathbf{k}_1 \cdot \mathbf{k}_2) \int r^2 j_l(k_1 r) V_l(r) j_l(k_2 r) dr$$

where $\mathbf{k}_1 = \mathbf{k} + \mathbf{G}$, $\mathbf{k}_2 = \mathbf{k} + \mathbf{G}'$, $P_l(x) =$ Legendre polynomials.

Separable (Kleinman-Bylander) form of pseudopotentials

It is very convenient to recast NCPP's into a *separable*, fully nonlocal form:

$$\hat{V} \equiv V_{loc}(r) + \sum_{nm} |\beta_n\rangle D_{nm} \langle \beta_m|$$

Introduce the following transformation, proposed by Kleinman and Bylander (KB):

$$\hat{V}^{ps} \rightarrow \hat{V}_{KB} = \hat{V}'_{loc} + \hat{V}_{NL}$$

where:

$$\hat{V}_{NL} = \sum_{lm} \frac{|V'_l \phi_{lm}^{ps}\rangle \langle V'_l \phi_{lm}^{ps}|}{\langle \phi_{lm}^{ps} | V'_l | \phi_{lm}^{ps} \rangle} \equiv \sum_{lm} v_l |\beta_{lm}\rangle \langle \beta_{lm}|,$$

$V'_l(r) = V_l(r) - V_0(r)$, $\hat{V}'_{loc} \equiv V_{loc}(r) + V_0(r)$, and $V_0(r)$ an arbitrary function. The $|\phi_{lm}^{ps}\rangle$ are the atomic pseudo-wavefunction (including angular term) for the reference state.

The separable form is an *approximation* if applied to a NCPP generated using the Hamann-Schlüter-Chiang procedure: on the reference state, $\hat{V}_{KB}|\phi_{lm}^{ps}\rangle = \hat{V}^{ps}|\psi_{lm}^{ps}\rangle$; on states not too far from the reference state, $\hat{V}_{KB}|\phi_{lm}\rangle \simeq \hat{V}^{ps}|\psi_l\rangle$.

Why the separable form?

The separable form usually yields good results, but may **badly fail** in some cases due to the appearance of *ghosts*: states with a wrong number of nodes.

Separable pseudopotentials are computationally much more efficient than the conventional (semilocal) form. The calculation of $\hat{V}_{NL}\psi$ in plane waves:

$$(\hat{V}_{NL}\psi)(\mathbf{G}) = \sum_{\mathbf{G}'} \langle \mathbf{k} + \mathbf{G} | \hat{V}_{NL} | \mathbf{k} + \mathbf{G}' \rangle \psi(\mathbf{G}') = \sum_{i=1}^p v_i \beta_i(\mathbf{G}') \sum_{\mathbf{G}'} \beta_i^*(\mathbf{G}') \psi(\mathbf{G}')$$

requires only $\mathcal{O}(pN)$ floating point operations per band and $\mathcal{O}(pN)$ storage, where p is the number of projectors in the system.

$$\begin{aligned} \langle \mathbf{k} + \mathbf{G} | \hat{V}_{KB} | \mathbf{k} + \mathbf{G}' \rangle &= \frac{1}{\Omega} \sum_{lm} \frac{1}{\langle \phi_l^{ps} | V_l' | \phi_l^{ps} \rangle} \int e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} V_l'(r) \phi_l^{ps}(r) Y_{lm}(\hat{\mathbf{r}}) d\mathbf{r} \\ &\quad \times \int e^{i(\mathbf{k}+\mathbf{G}')\cdot\mathbf{r}'} V_l'(r') \phi_l^{ps}(r') Y_{lm}^*(\hat{\mathbf{r}}') d\mathbf{r}' \end{aligned}$$

(for one atom at $\mathbf{r} = 0$).

Using the expansion of plane waves into spherical Bessel functions one gets:

$$\langle \mathbf{k} + \mathbf{G} | \hat{V}_{KB} | \mathbf{k} + \mathbf{G}' \rangle = \frac{4\pi}{\Omega} \sum_{lm} \frac{1}{\langle \phi_l^{ps} | V_l' | \phi_l^{ps} \rangle} Y_{lm}(\hat{\mathbf{k}}_1) \int r^2 j_l(k_1 r) V_l'(r) \phi_l^{ps}(r) dr$$

$$\times Y_{lm}^*(\hat{\mathbf{k}}_2) \int r^2 j_l(k_2 r) V_l'(r) \phi_l^{ps}(r) dr.$$

where $\mathbf{k}_1 = \mathbf{k} + \mathbf{G}$, $\mathbf{k}_2 = \mathbf{k} + \mathbf{G}'$.

Direct generation of norm-conserving pseudopotentials in separable form

Pseudopotentials can be *directly* produced in separable form (Vanderbilt 1991).

- generate a *local potential* $V_{loc}(r)$ such that $V_{loc}(r) = V(r)$ for $r > r_L$; $V_{loc}(r)$ for $r < r_L$ can be any smooth regular function
- generate *atomic waves* $|\phi_i\rangle$: regular solutions of the KS equations, not necessarily bound, at a given energy ϵ_i . There may be more than one such waves per angular momentum: this increases the transferability.
- generate the corresponding *pseudowaves* $|\tilde{\phi}_i\rangle$, such that $\tilde{\phi}_i(r) = \phi_i(r)$ for $r > r_{c,i}$
- generate the corresponding functions $|\chi_i\rangle$ (vanishing for $r > r_{c,i}$):

$$|\chi_i\rangle = (\epsilon_i - T - V_{loc})|\tilde{\phi}_i\rangle;$$

– generate the projectors $|\beta_j\rangle$:

$$|\beta_i\rangle = \sum_j (B^{-1})_{ij} |\chi_j\rangle.$$

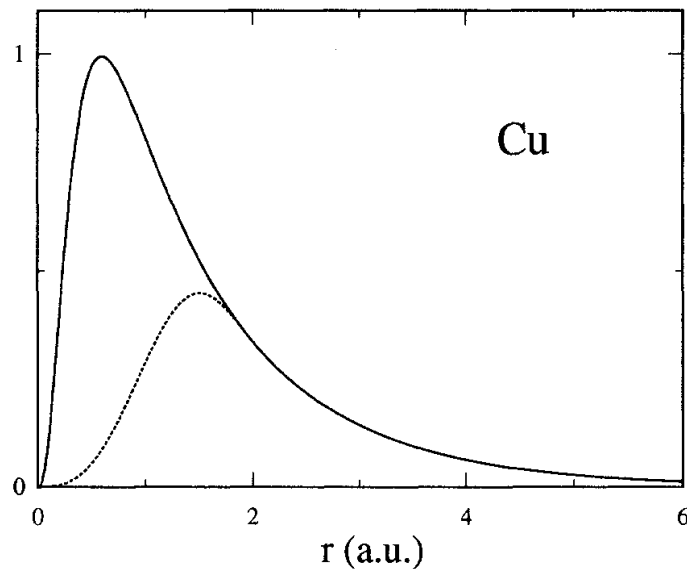
where $B_{ij} = \langle \tilde{\phi}_i | \chi_j \rangle$ and $|\beta_j\rangle$ satisfy $\langle \beta_i | \tilde{\phi}_j \rangle = \delta_{ij}$.

PP's generated in this way are equivalent to Hamann-Schlüter-Chiang NCPP's with KB transformation, if there is only one projector per l , generated using the bound state $\tilde{\phi}_i \equiv \phi_l^{ps}$.

Limitations of norm-conserving pseudopotentials

NCPP's are still "hard" and require a large plane-wave basis sets ($E_c > 70Ry$) for first-row elements (in particular N, O, F) and for transition metals, in particular the 3d row: Cr, Mn, Fe, Co, Ni, ...

Even if just one atom is "hard", a high cutoff is required. This translates into large CPU and RAM requirements. *Ultrasoft (Vanderbilt) pseudopotentials (USPP)* are devised to overcome such a problem:



3d pseudo- and all-electron orbitals for Cu (Laasonen et al, Phys. Rev. B 47, 10142 (1993))

Ultrasoft pseudopotentials

$$\hat{V}_{US} \equiv V_{loc}(r) + \sum_{lm} D_{lm} |\beta_l\rangle \langle \beta_m|$$

Charge density with USPP:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 + \sum_i \sum_{lm} \langle \psi_i | \beta_l \rangle Q_{lm}(\mathbf{r}) \langle \beta_m | \psi_i \rangle$$

where the Q_{lm} (“augmentation charges”) are:

$$Q_{lm}(\mathbf{r}) = \phi_l^*(\mathbf{r})\phi_m(\mathbf{r}) - \tilde{\phi}_l^*(\mathbf{r})\tilde{\phi}_m(\mathbf{r})$$

$|\beta_l\rangle$ are “projectors”

$|\phi_l\rangle$ are atomic states (not necessarily bound)

$|\tilde{\phi}_l\rangle$ are pseudo-waves (coinciding with $|\phi_l\rangle$ beyond some “core radius”)

In practical USPP, the $Q_{lm}(\mathbf{r})$ are *pseudized*. The matching radii r_c may be set to larger values than for NCPP without loss of transferability.

Orthonormality with USPP:

$$\langle \psi_i | S | \psi_j \rangle = \int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} + \sum_{lm} \langle \psi_i | \beta_l \rangle q_{lm} \langle \beta_m | \psi_j \rangle = \delta_{ij}$$

where $q_{lm} = \int Q_{lm}(\mathbf{r}) d\mathbf{r}$

Ultrasoft pseudopotentials and PAW

Projector Augmented Waves (PAW) method: P. E. Blöchl, PRB **50**, 17953 (1994)

A linear transformation \hat{T} connects “true” orbitals $|\psi_i\rangle$ to “pseudo” orbitals $|\tilde{\psi}_i\rangle$:

$$|\psi_i\rangle = \hat{T}|\tilde{\psi}_i\rangle = |\tilde{\psi}_i\rangle + \sum_l \left(|\phi_l\rangle - |\tilde{\phi}_l\rangle \right) \langle \beta_l | \tilde{\psi}_i \rangle$$

where $|\phi_l\rangle =$ “true” atomic states, $|\tilde{\phi}_l\rangle =$ pseudo-waves and

$$\langle \beta_l | \tilde{\phi}_m \rangle = \delta_{lm} \Rightarrow \hat{T}|\tilde{\phi}_l\rangle = |\phi_l\rangle.$$

The pseudo-orbitals are the variational parameters of the calculation.

Assuming that in the core region:

$$|\tilde{\psi}_i\rangle \simeq \sum_l |\tilde{\phi}_l\rangle \langle \beta_l | \tilde{\psi}_i \rangle$$

we recover the USPP expression for the charge density $n(\mathbf{r})$.

The PAW procedure can be used to *reconstruct* all-electron orbitals from pseudo-orbitals

Ultrasoft pseudopotential generation:

- generate a *local potential* $V_{loc}(r)$ such that $V_{loc}(r) = V(r)$ for $r > r_L$
- generate the pseudowaves $|\tilde{\phi}_i\rangle$ such that $\tilde{\phi}_i(r) = \phi_i(r)$ for $r > r_{c,i}$
- generate a set of functions $|\chi_i\rangle$ (vanishing for $r > r_{c,i}$):

$$|\chi_i\rangle = (\epsilon_i - T - V_{loc})|\tilde{\phi}_i\rangle$$

- generate the projectors $|\beta_j\rangle$:

$$|\beta_i\rangle = \sum_j (B^{-1})_{ij} |\chi_j\rangle.$$

where $B_{ij} = \langle \tilde{\phi}_i | \chi_j \rangle$ and $|\beta_j\rangle$ satisfy $\langle \beta_i | \tilde{\phi}_j \rangle = \delta_{ij}$

- define (pseudized) augmentation functions Q_{jk} :

$$Q_{jk}(\mathbf{r}) = \phi_j^*(\mathbf{r})\phi_k(\mathbf{r}) - \tilde{\phi}_j^*(\mathbf{r})\tilde{\phi}_k(\mathbf{r})$$

– define $D_{ij} = B_{ij} + \epsilon_j Q_{ij}$, where

$$Q_{ij} = \int_{r < r_{c,i}} \left(\phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) - \tilde{\phi}_i^*(\mathbf{r}) \tilde{\phi}_j(\mathbf{r}) \right) d\mathbf{r}$$

– “unscreen” D_{ij} and V_{loc} :

$$D_{ij}^0 = D_{ij} - \int Q_{jk}(\mathbf{r}) V_{loc}(\mathbf{r}) d\mathbf{r}, \quad V_{loc}^{ion}(\mathbf{r}) = V_{loc}(\mathbf{r}) - \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - V_{xc}(\mathbf{r}),$$

The pseudo-potential is finally given by

$$V_{US} = V_{loc}^{ion} + \sum_{ij} D_{ij}^{(0)} |\beta_i\rangle \langle \beta_j|,$$

the charge density by

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 + \sum_{jk} Q_{jk}(\mathbf{r}) \langle \phi_i | \beta_j \rangle \langle \beta_k | \phi_i \rangle.$$

Plane-waves + Ultrasoft pseudopotential calculations

- there are additional terms in the charge density and in the forces
- electronic states are orthonormal with an *overlap matrix* S : $\langle \psi_i | S | \psi_j \rangle = \delta_{ij}$
- if the "augmentation charges" are evaluated in **G**-space, a different (larger) cutoff for them may be required

Various tricks: "box grids", **r**-space evaluation, allow to minimize the CPU time required by additional USPP-specific terms