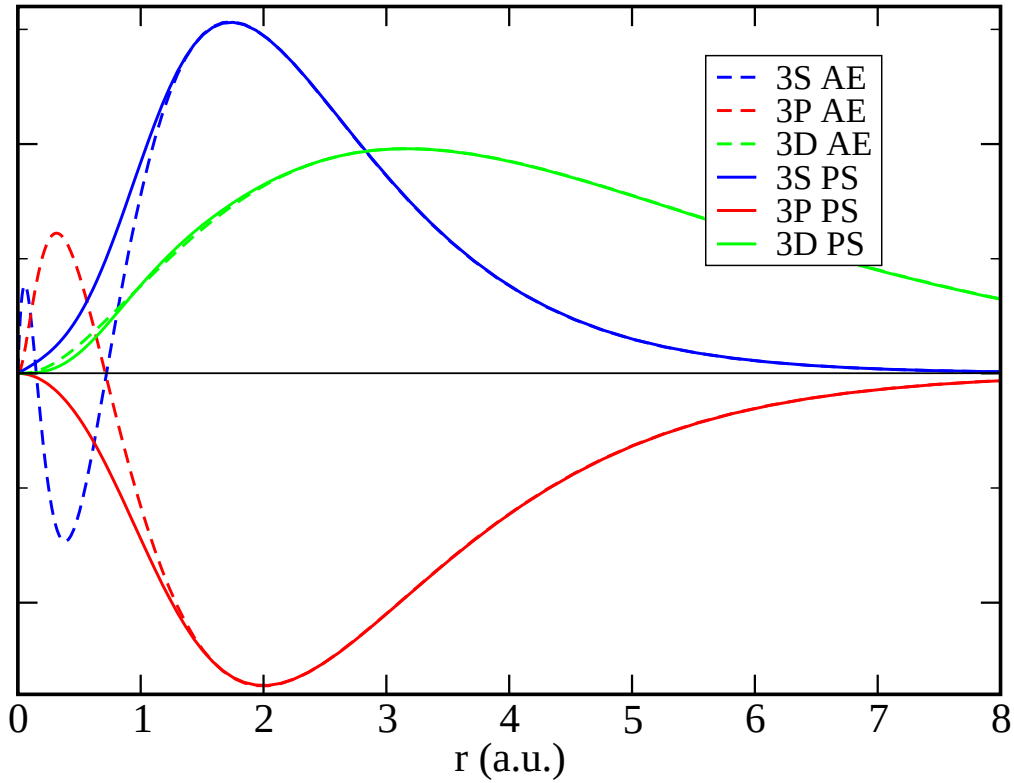
NC and US Pseudopotentials

July 22, 2008

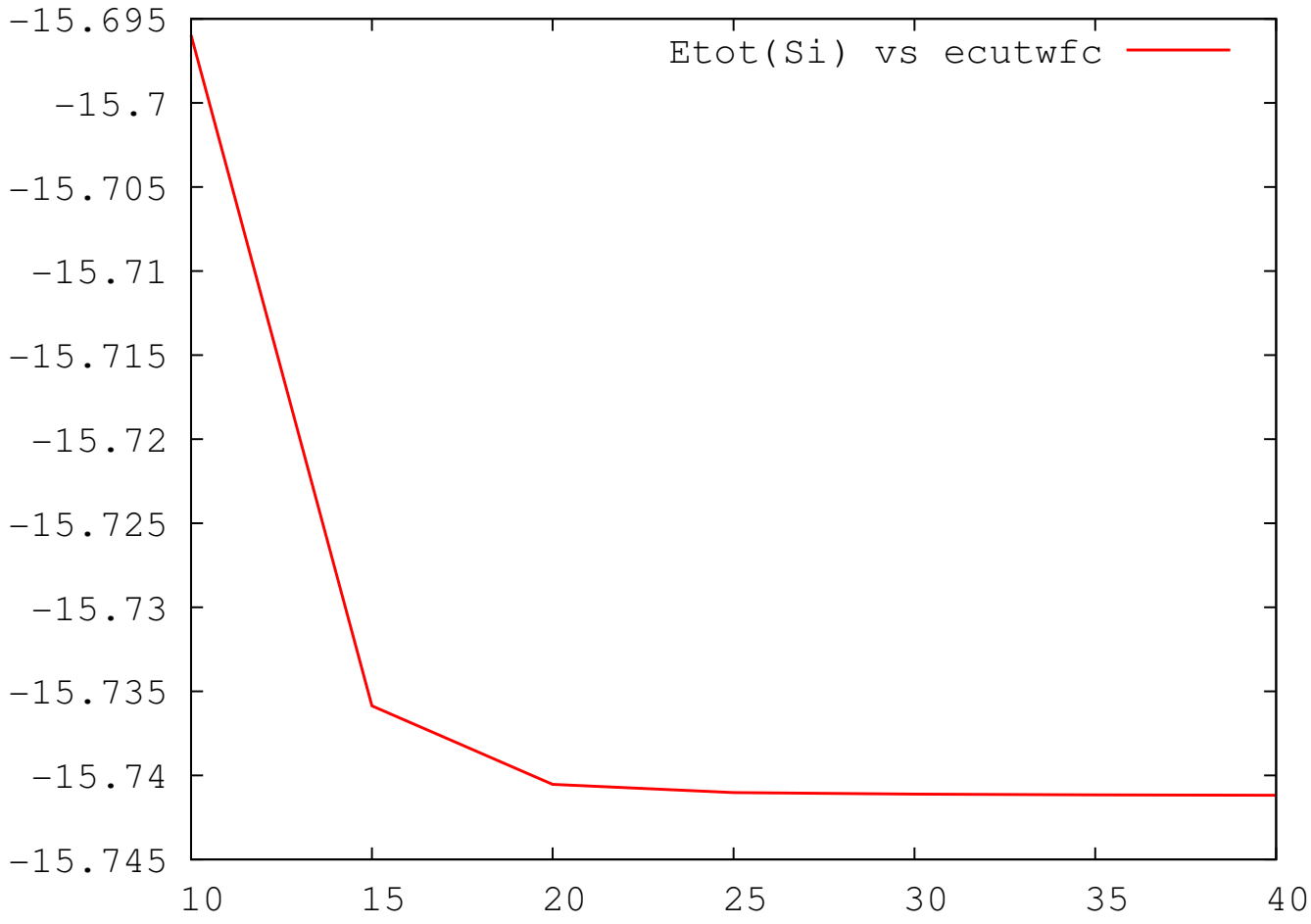
Norm-Conserving Pseudopotentials

Electron-ionic core interactions can be 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"



Norm-Conserving Pseudopotentials

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



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.

Features of Norm-conserving Pseudopotentials:

+ *transferrable*: they reproduce the logarithmic derivatives, i.e., the *scattering properties*, of the true potential in a wide range of energies.

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

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

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

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

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

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

The separable form usually yields good results, but beware of *ghosts* states

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*:

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

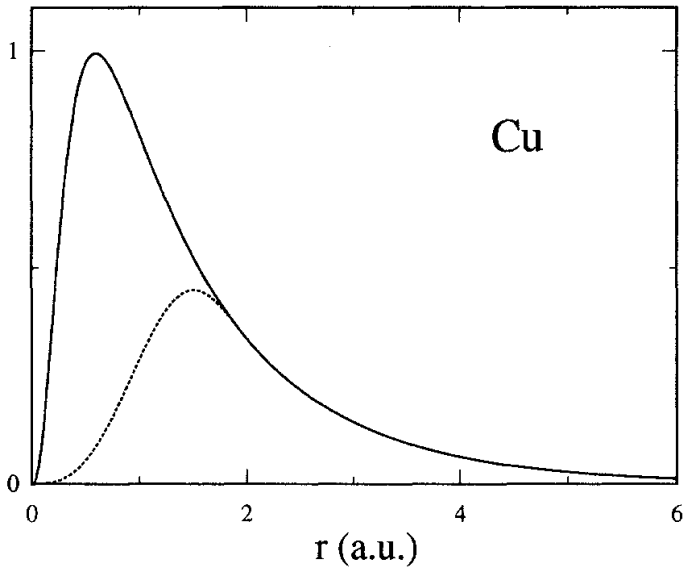
  where $n_c(r)$ is the core charge of the atom (Froyen, Louie, Cohen 1982)

- *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)

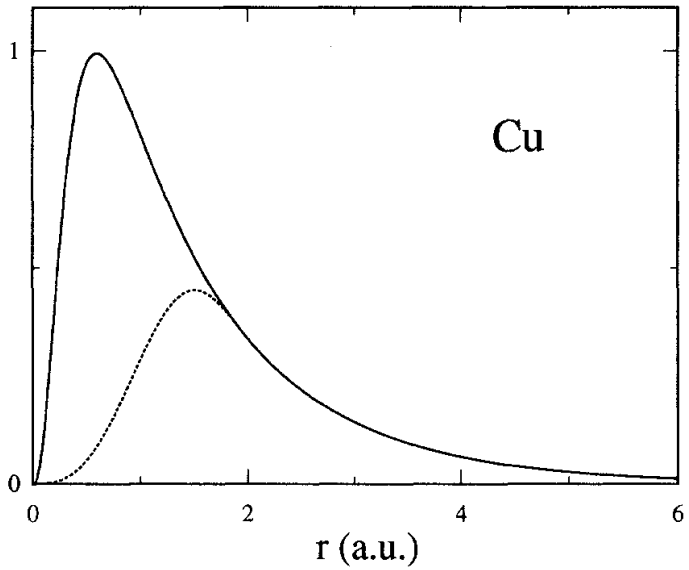
Limitations of norm-conserving pseudopotentials

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: give up norm consevation keeping transferability.



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



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

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

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

$|\beta_l\rangle$ are "projectors"
$|\phi_l\rangle$ are atomic states (not necessarily bound)
$|\widetilde{\phi}_l\rangle$ are pseudo-waves (coinciding with $|\phi_l\rangle$ beyond some "core radius")

In practical USPP, the $Q_{lm}(\mathbf{r})$ are *pseudized*.

Ultrasoft pseudopotentials

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

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

Generalized eigenvalue problem:

$$[H - \varepsilon_i S]\,|\psi_i\rangle = 0$$

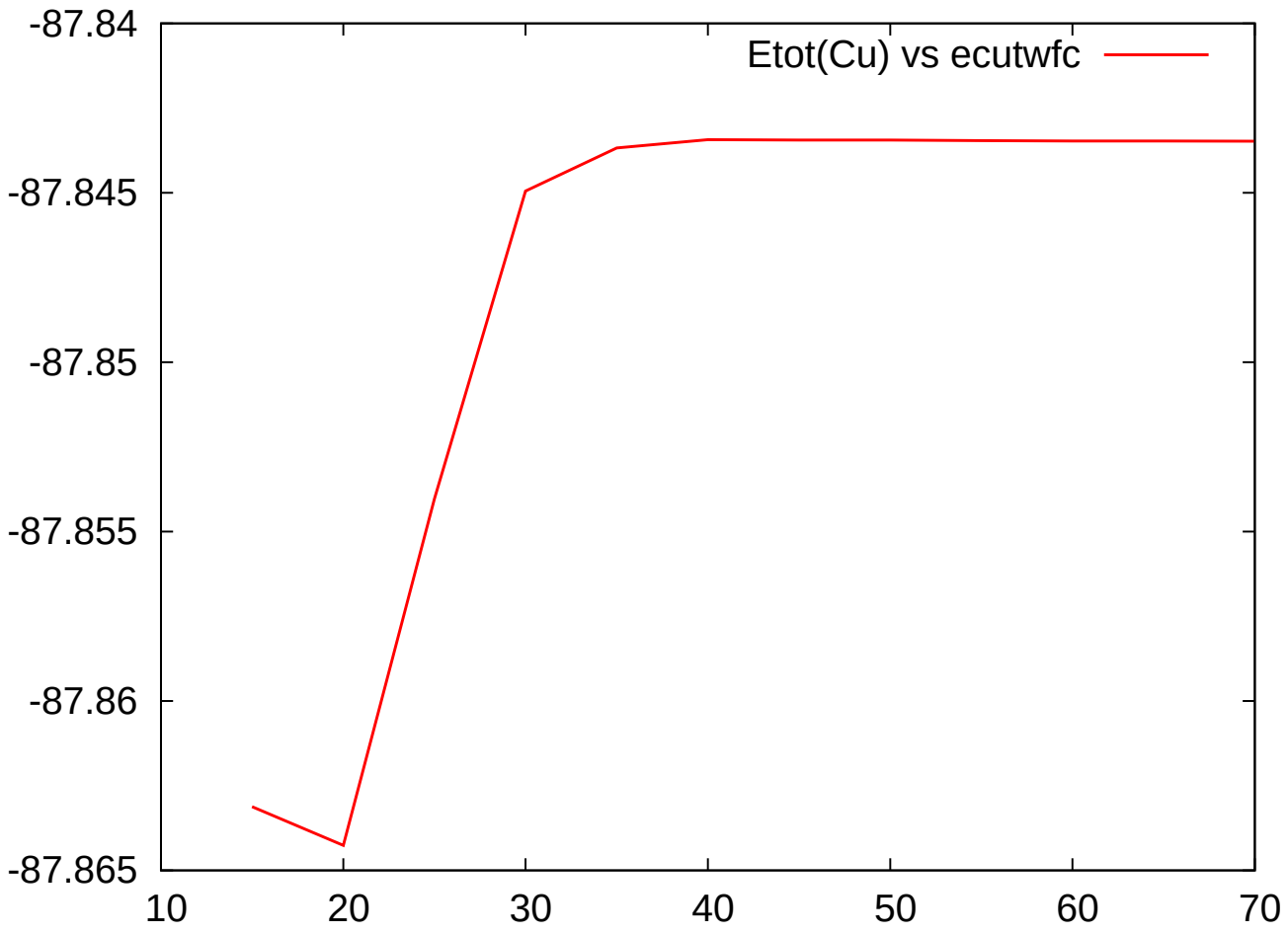
Plane-waves + Ultrasoft pseudopotential calculations

- there are additional terms in the charge density, in the forces ...
- electronic states are orthonormal with an *overlap matrix* S: $\langle\psi_i|S|\psi_j\rangle = \delta_{ij}$
- the "augmentation charges" typically require a larger cutoff for the charge density.

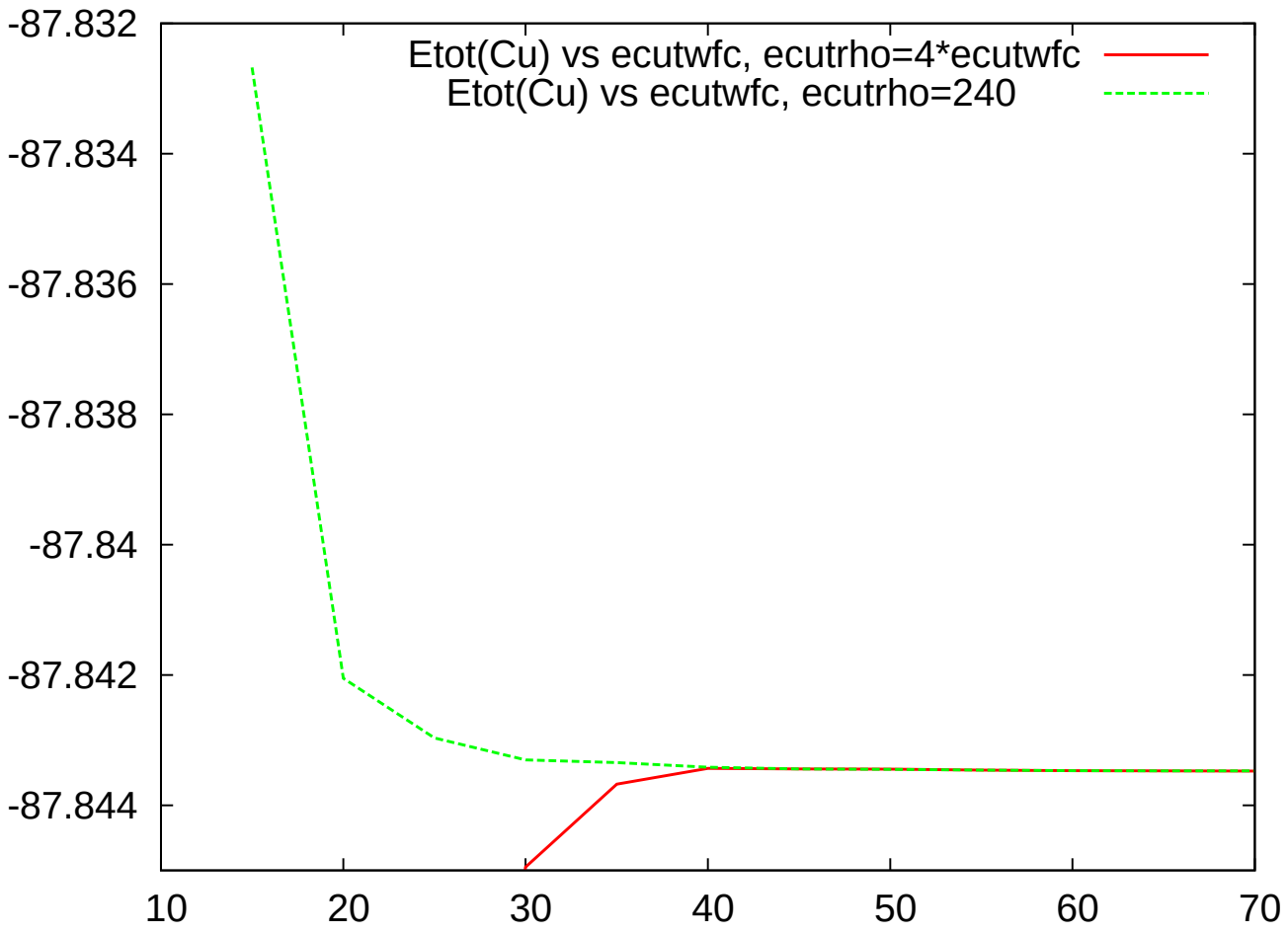
  Input parameter: $ecutrho$ (SYSTEM namelist)

  Default value is $ecutrho = 4 \times ecutwfc$ (OK for NC PP)

  For US PP a larger value $ecutrho \approx 8 \times ecutwfc$ is often needed.



Is it variational ?



With the appropriate $ecutrho$, an $ecutwfc$ of 25-30 Ry is fine.