NCPP, USPP and PAW

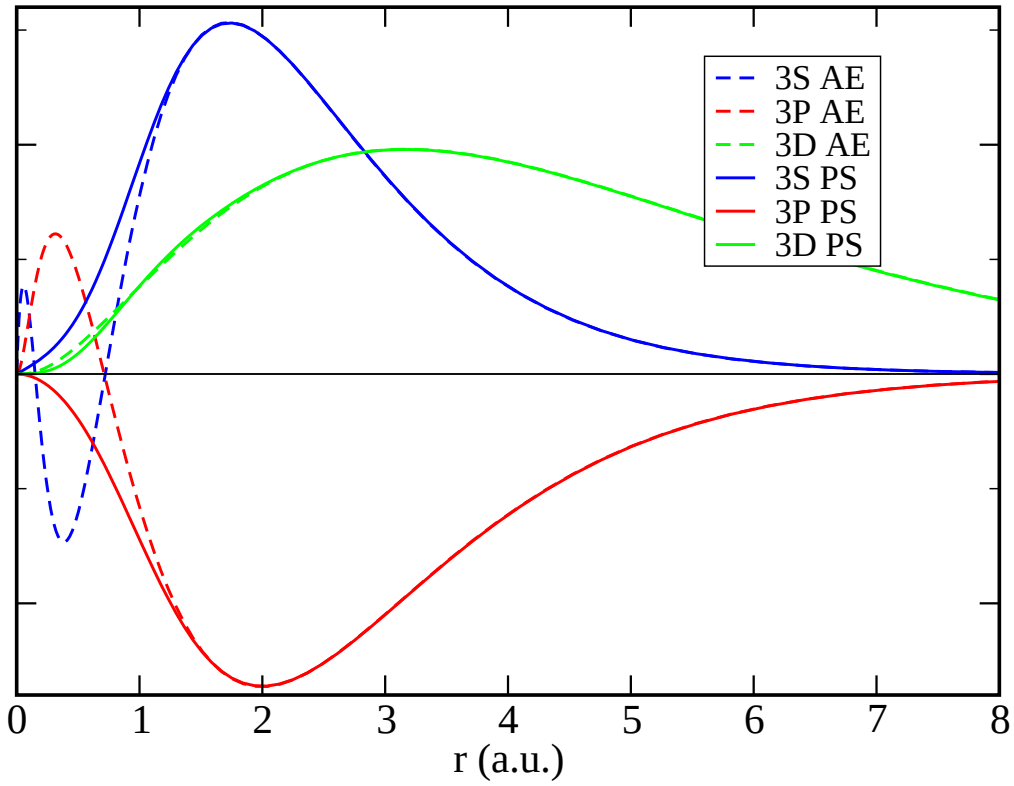
March 25, 2013

An analogy!

- "Dummy cops" used by many 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….

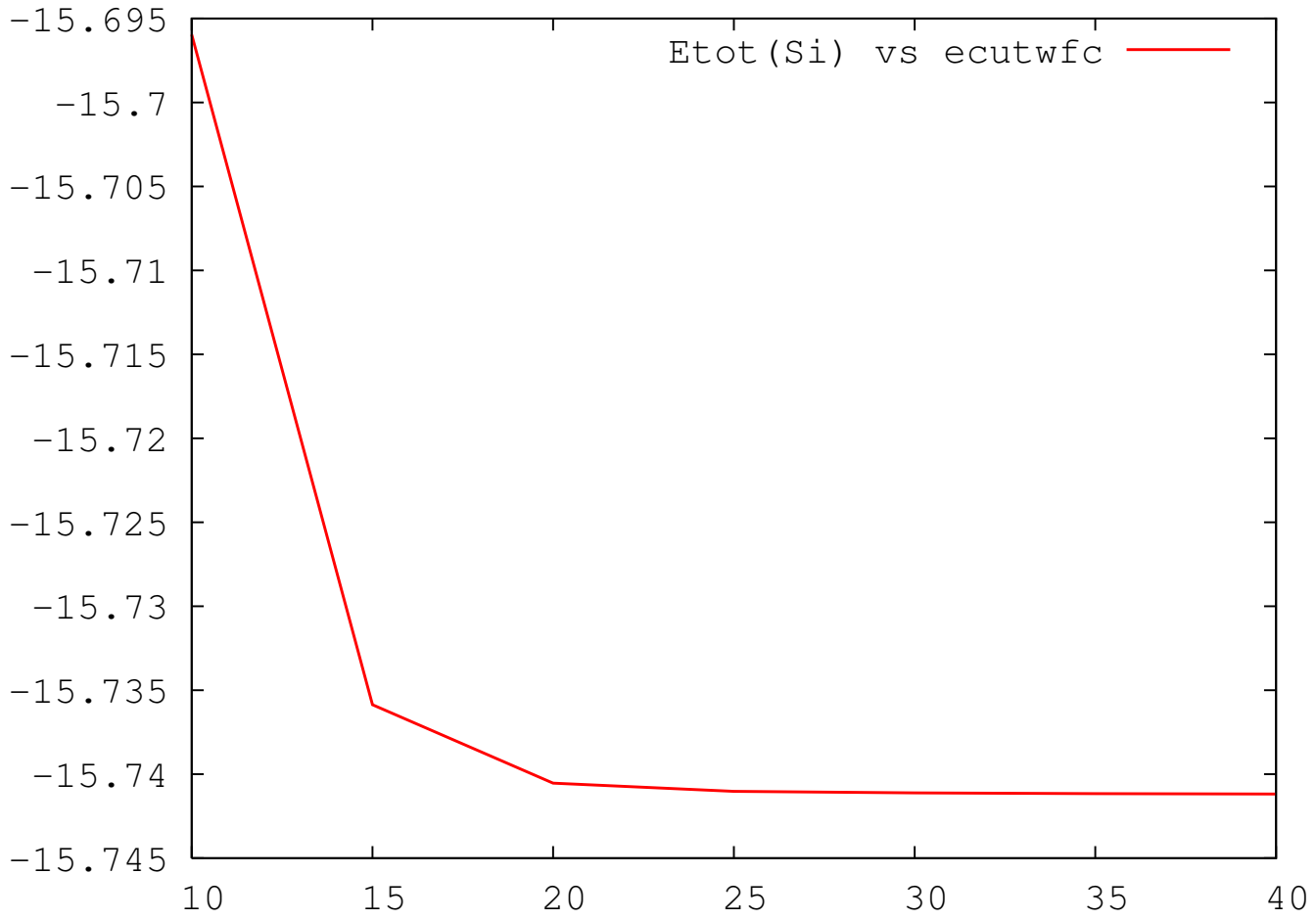
Norm-Conserving Pseudopotentials

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:

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

Matrix elements of the semilocal part between plane waves

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

(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:

$$\langle \mathbf{k}+\mathbf{G}|\hat{V}_{SL}|\mathbf{k}+\mathbf{G}'\rangle = \frac{4\pi}{\Omega}\sum_l(2l+1)P_l(\mathbf{k}_1\cdot\mathbf{k}_2)\int r^2 j_l(k_1r)V_l(r)j_l(k_2r)dr$$

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:

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

$V_l'(r) = V_l(r) - V_0(r)$, $\hat{V}'_{loc} \equiv V_{loc}(r) + V_0(r)$, and $V_0(r)$ an arbitrary function. The $|\phi^{ps}_{lm}\rangle$ 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, $\hat{V}_{KB}|\phi^{ps}_{lm}\rangle = \hat{V}^{ps}|\psi^{ps}_{lm}\rangle$; 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 beware of *ghosts* states .

So why to use a separable form ?

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.

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

(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:

$$\langle \mathbf{k}+\mathbf{G}|\hat{V}_{KB}|\mathbf{k}+\mathbf{G}'\rangle = \frac{(4\pi)^2}{\Omega} \sum_{lm} \frac{1}{\langle \phi_l^{ps}|V_l'|\phi_l^{ps}\rangle} Y_{lm}(\hat{\mathbf{k}}_1) \int r^2 j_l(k_1 r) V_l'(r) \phi_l^{ps}(r) dr$$
$$\times Y^*_{lm}(\hat{\mathbf{k}}_2) \int r^2 j_l(k_2 r) V_l'(r) \phi_l^{ps}(r) dr.$$

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

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*:

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

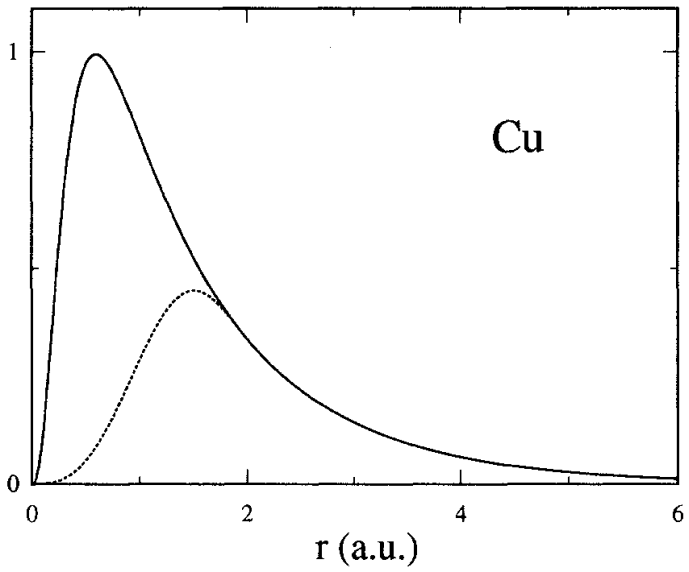
  where $n_c(r)$ is the core charge of the atom (Froyen, Louie, Cohen 1982)

- *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)

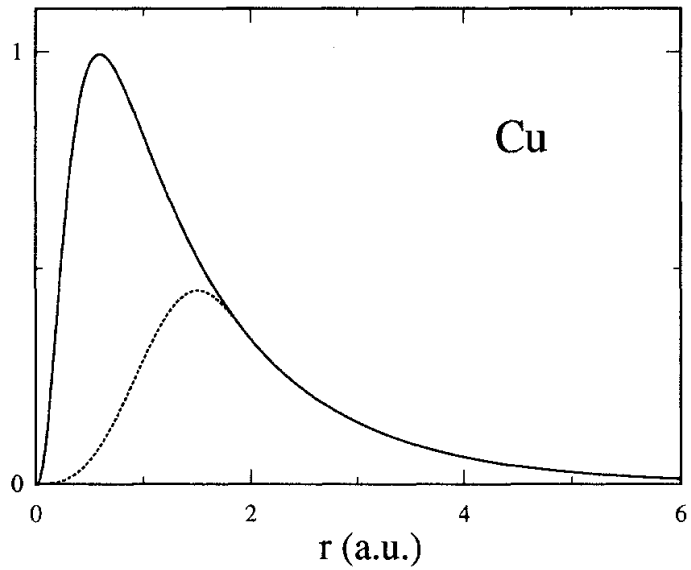
Limitations of norm-conserving pseudopotentials

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))



$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 + \sum_i \sum_{kk'} \langle \psi_i | \beta_k \rangle Q_{kk'}(\mathbf{r}) \langle \beta_{k'} | \psi_i \rangle$$

where the $Q_{kk'}$ ("augmentation charges") are:

$$Q_{kk'}(\mathbf{r}) = \phi_k^*(\mathbf{r})\phi_{k'}(\mathbf{r}) - \widetilde{\phi}_k^*(\mathbf{r})\widetilde{\phi}_{k'}(\mathbf{r}) = \sum_{LM} Q_{kk';LM}(r) Y_{LM}(\mathbf{r})$$

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

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

Ultrasoft pseudopotentials

Generalized eigenvalue problem:

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

with

$$S = 1 + \sum_{kk'} |\beta_k\rangle q_{kk'} \langle \beta_{k'}|$$

where $q_{kk'} = \int Q_{kk'}(\mathbf{r}) d\mathbf{r}$ and

$$\hat{V}_{KS} \equiv V_{loc}(r) + V_{Hxc}(\mathbf{r}) + \sum_{kk'} |\beta_k\rangle D_{kk'} \langle \beta_{k'}|$$

with $D_{kk'} = D^0_{kk'} + \int V_{Hxc}(\mathbf{r}) Q_{kk'}(\mathbf{r}) d\mathbf{r}$

Orthonormality with USPP:

$$\langle \psi_i | S | \psi_j \rangle = \int \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} + \sum_{kk'} \langle \psi_i | \beta_k \rangle q_{kk'} \langle \beta_{k'} | \psi_j \rangle = \delta_{ij}$$

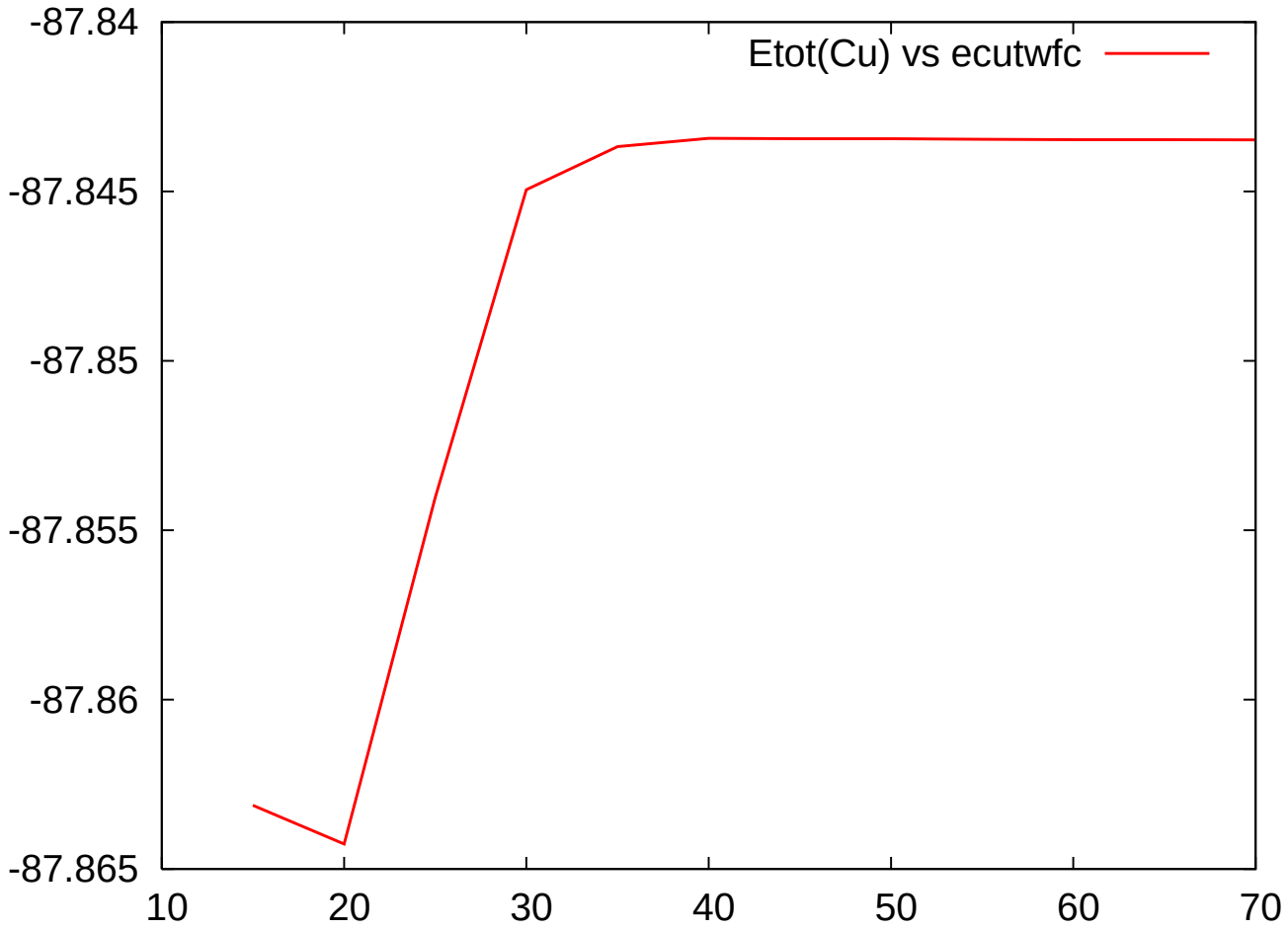
Plane-waves + Ultrasoft pseudopotential calculations

- 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.

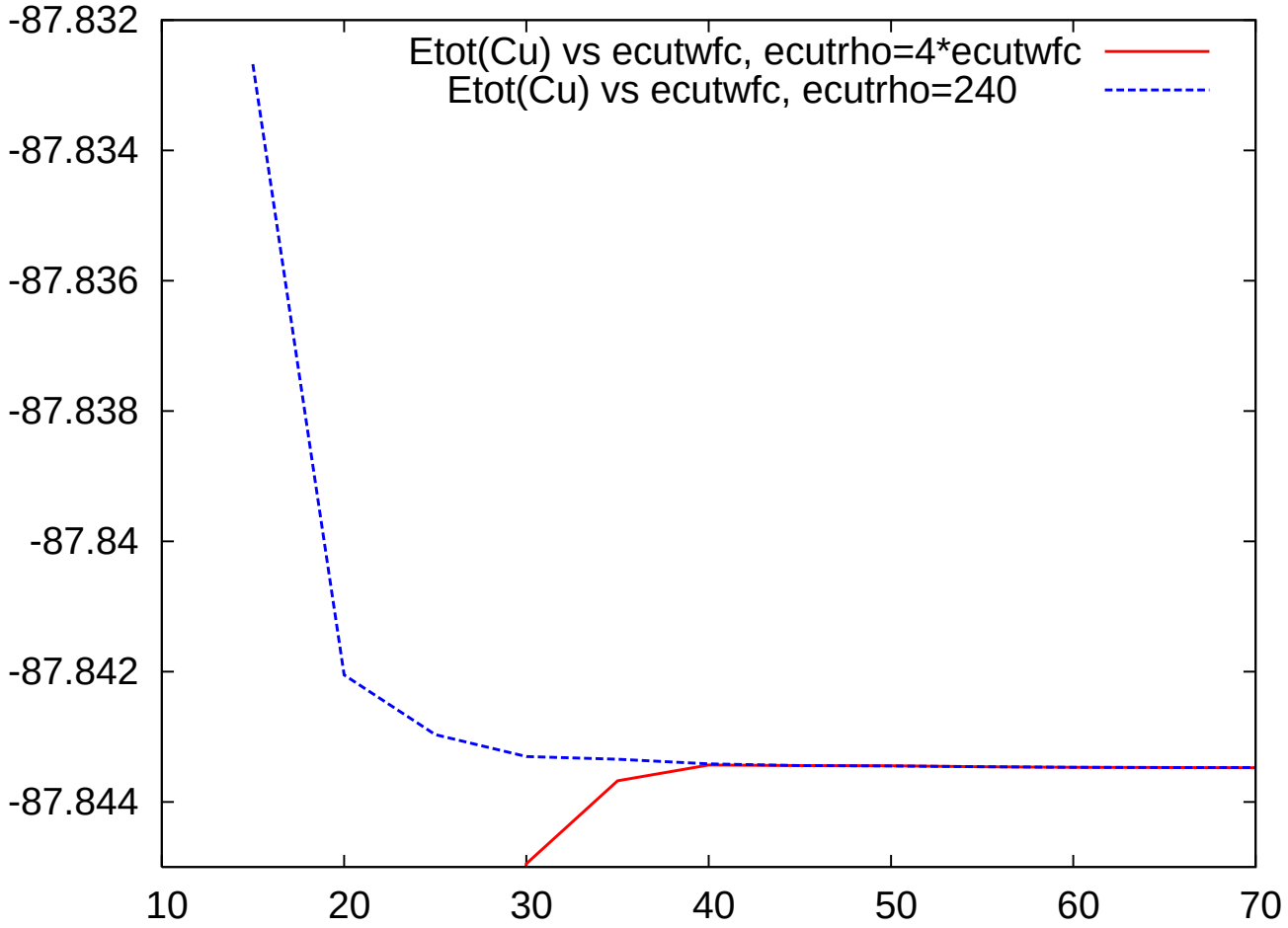
  Input parameter: $ecutrho$ (SYSTEM namelist)

  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.