Pseudopotential methods for DFT calculations

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Outline – pseudopotential method.

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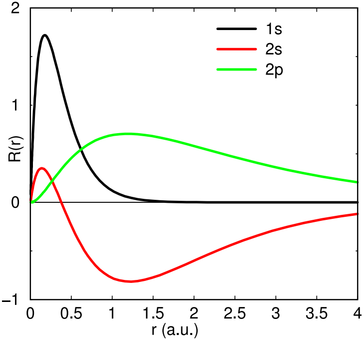
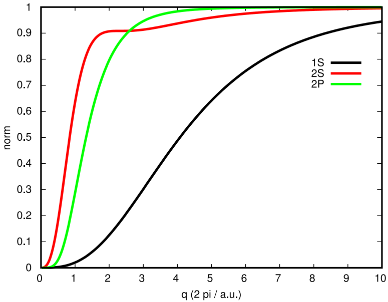
Why do we need pseudopotentials?



- Valence wavefunctions feel the effect of core states both directly and as an orthogonality condition

- Core functions are very localized: they are hard to expand in a plain wave basis set
- They provide little to no contribution to chemical properties



Before Density-Functional Theory

- The idea to use a simplified potential for computationa purposes dates back to the thirties (Fermi, Kleimann)
- Early *empirical* PPs by Cohen-Bergstresser (1966): fitted to some known spectroscopic data (band gaps, ionization potentials, etc.).

  They are little more than band structure parametrization: *they only work for the system on which they are fitted*.
- Early *atomic, transferable PPs* for self-consistent calculations, Appelbaum and Hamann (1973):

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

  Constructed on educated guess, but lacking a first-principle derivation.

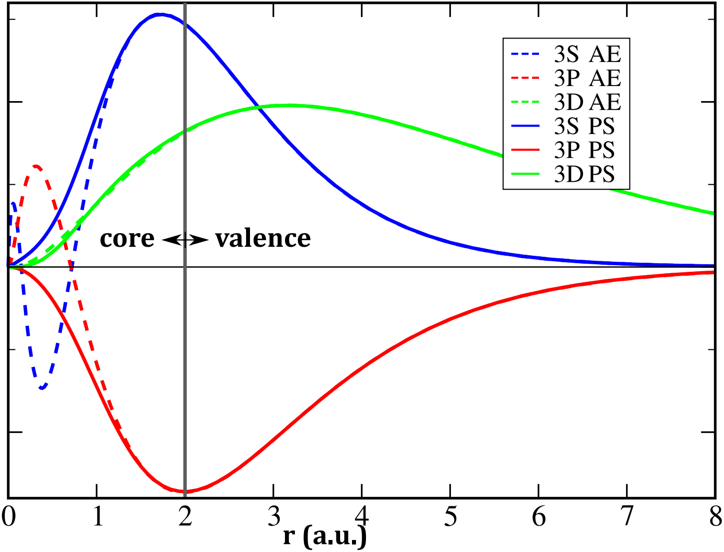
Norm conserving pseudopotentials

DFT-based PPs were introduced by Hamann, Schlüter, Chiang (1979). The potential is built on a given reference atomic configuration, to 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.

Norm conserving pseudopotentials



Non-local NCPPs

Traditionally NCPPs are split into a *local* and a *non-local* part:

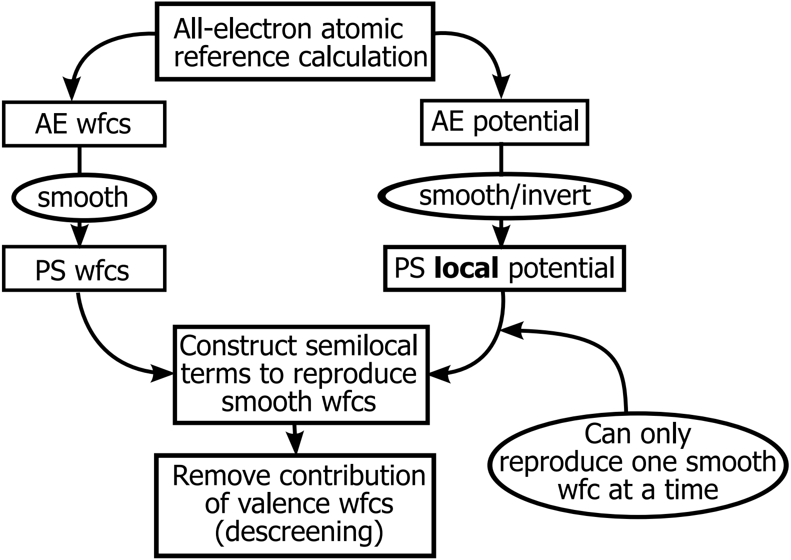
$$\hat{V}^{ps} = \hat{V}_{loc} + \hat{V}_{SL}$$

- local part: locality means $\hat{V}_{loc} \equiv V_{loc}(r)$; long-ranged and absintotically behaving like the electrostatic field generated by the total core+nucleus charge: $-Z_v e^2/r$ for $r \rightarrow \infty$,
- non-local part, there is one short range potential per angular momentum:
  $V^{ps}(\mathbf{r}) = \sum_{l=0,\infty} V_l(r)|l\rangle\langle l|$.

the non-local part is very expensive to compute:

$$\hat{V}_{NL} \equiv \sum_{lm} V_l(r)\delta(r-r')Y_{lm}(\hat{\mathbf{r}})Y^*_{lm}(\hat{\mathbf{r}}')$$

Norm conserving pseudopotentials



All-electron atomic reference calculation

AE wfcs

smooth

PS wfcs

AE potential

smooth/invert

PS **local** potential

Construct semilocal terms to reproduce smooth wfcs

Remove contribution of valence wfcs (descreening)

Can only reproduce one smooth wfc at a time

Fully-separable *semi-local* NCPPs

It is very convenient to recast NCPP's into a *separable*, fully nonlocal form introduced by Kleinman and Bylander (1982):

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

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

where:

$$< \beta_n | \phi_m^{ps} > = \delta_{nm}$$

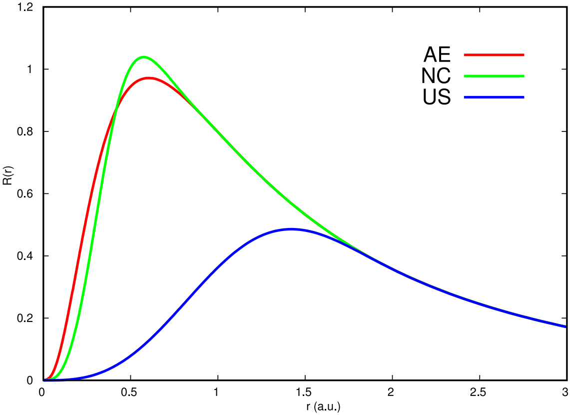
Instead of having one projector per angular momentum you only have a few reference states.

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

Ultrasoft pseudopotentials

- NCPP has little effect on hard nodeless wavefunctions, such as 2P for oxygen, or 3D for copper.
- A much more aggressive softening can be enforced if the norm-conservation condition is relaxed.

David Vanderbilt (1990) – inner charge of valence wavefunctions is rigid thus it needs not be threated self-consistently.



Ultrasoft pseudopotentials – features

USPP allow the use of much smaller plane wave basis in many cases, but...

- there are additional terms in the charge density and in the forces
- electronic states are orthonormal with an *overlap matrix* S: $\langle\psi_i|S|\psi_j\rangle = \delta_{ij}$
- the charge which has been removed has to be put back to compute the density functional ⇒ augmentation charges
- the wavefunctions are smoother, but the charge density is not smoothed at all!

Ultrasoft pseudopotentials – formalism

Charge density:

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 + \sum_i \sum_{lm} \rho_{ij} Q_{ij}(\mathbf{r})$$

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

$$\underbrace{Q_{lm}(\mathbf{r})}_{\text{augmentation charge}} = \underbrace{\phi_l^*(\mathbf{r})\phi_m(\mathbf{r})}_{\text{AE charge}} - \underbrace{\widetilde{\phi}_l^*(\mathbf{r})\widetilde{\phi}_m(\mathbf{r})}_{\text{pseudo charge}}$$

the ρ_{ij} ("channel occupations") are:

$$\rho_{ij} = \sum_{ij} \sum_n f_i f_j \langle \psi_n | \beta_i \rangle \langle \beta_j | \psi_n \rangle$$

The projectors are the same as in the NC case.

Summary of pseudopotential methods

What we have see up to now:

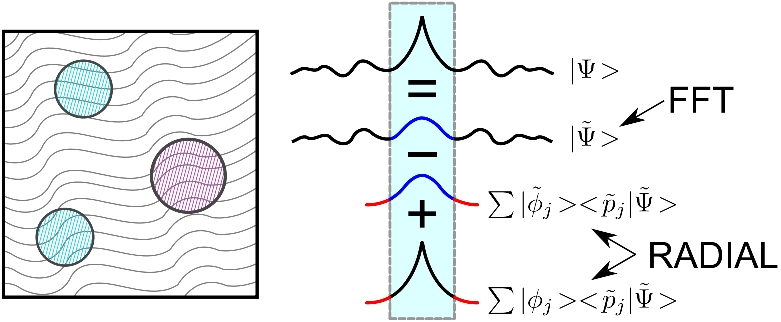
- We want pseudopotentials to make faster calculations
- We introduce NCPP to make them transferable...
- ... semilocal formulation to make them faster ...
- ... Ultrasoft to make them softer (at the price of orthogonality)

As the tricks mass one over each other the theory become more and more complicate, but has worked reliably for three decades!

It is time for a reformulation that comprehend everything in a coherent and more elegant frame.

Projector-augmented wave method

Blöchl (1998) proposed a method to reconstruct all-electron wavefunctions from the pseudo wavefunctions.
The calculation is divided in a plane wave part and several one-center terms.



Compensation charge is introduced to remove interactions between one-center terms

Projector-augmeted Wave method

- Instead of recostructing the all-electron wfcs we can define a linear transform:

$$\begin{aligned} \mathcal{T} &= 1 + \sum_i (|\phi_i> - |\phi_i^{PS}>) < \tilde{\beta}_i| \\ |\psi^{AE}> &= |\psi^{PS}> + \sum_i (|\phi_i^{AE}> - |\phi_i^{PS}>) < \tilde{\beta}_i|\psi^{PS}> \end{aligned}$$

- By applying $\mathcal{T}$ we can, transform any operator to a PS operator, acting on PS wavefunctions!

$$\begin{aligned} \tilde{A} &= \mathcal{T}^\dagger A \mathcal{T} \\ &= A + \sum_{i,j} |\tilde{\beta}_i> \left(<\phi_i|A|\phi_j> - <\tilde{\phi}_i|A|\tilde{\phi}_j> \right) <\tilde{\beta}_j| + \Delta A \end{aligned}$$

The operator itself is split in plane-wave and one-center parts.

PAW and Ultrasoft

Ultrasoft can be considered as a special case of PAW under certain conditions:

- In the Ultrasoft formalism the one-center terms are computed only once in the reference configuration – in PAW they are updated at each iteration (it does not depend on the reference)
- For practical reasons, Ultrasoft pseudopotential is contructed on a norm conserving PP, not on the all-electron charge
- US augmentation charge has to reproduce the real charge, PAW compensation charge only need to respect a few conditions

⇒ PAW can achieve AE precision

Conclusions

- Pseudopotentials are a fundamental part of DFT calculations, they allow calculations that would be prohibitive otherwise
- All of this is already implemented in Quantum-ESPRESSO
- There are some aproximations that must be considered:

→ chemical properties are reproduced correctly, but charge inside the core region is not (not for PAW)

→ cores should not overlap (for PAW too), but a bit of overlap/softness tradeoff is acceptable

→ (USPP) charge density may required an higher cutoff

→ bad pseudopotentials deal bad results (and there is not such a thing as a passable PP)

- What is simpler of computers is not simpler for humans!