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PROJECTOR AUGMENTED-WAVE (PAW) BASICS

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Summary

- ✓ Historical context
- ✓ A linear transformation
- ✓ Calculation of the energy
- ✓ Calculation of the hamiltonian
- ✓ Examples
- ✓ Conclusions

Historical context

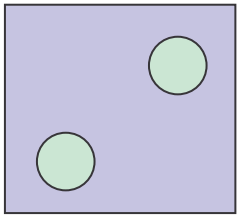
- We want to develop the solutions of the Schrödinger equation on a basis (plane waves) of a minimal size.
- Only valence electrons are taken into account in the calculation.
- The interaction between valence electrons and the ionic core is taken into account within a pseudopotential

- 1979-1982: pseudos BHS (Bachelet,Hamann, Schlüter)
- 1982: pseudos KB (Kleinman ,Bylander)
- 1990: pseudos MT (Martins, Troullier)
- 1991: ultrasoft pseudos (Vanderbilt)
- 1994: PAW method (Blöchl)

Historical context

Wavefunctions are developped on a basis which is…

Localized



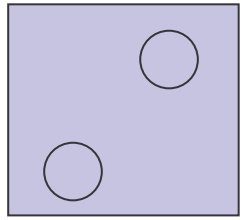
Spherical harmonics + special functions

All electrons are taken into account

Pb: - The atomic basis is moving with atoms

Delocalized

Plane waves



Only valence electrons are taken into account

Pseudopotentials

Pb: - Use of pseudos wavefunctions
- Big size of the plane wave basis

PAW

« The Projector Augmented-Wave method is an extension of augmented wave methods and the pseudopotential approach, which combine their traditions into a unified electronic structure method »

Peter Blöchl

References

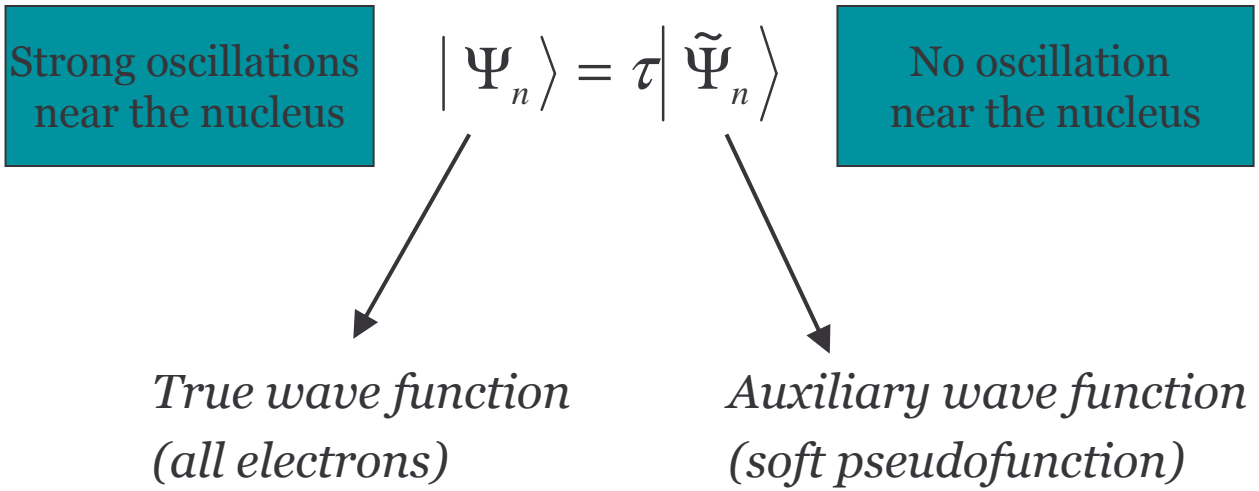
- « *Projector augmented wave method* », P. Blöchl, Phys. Rev. B **50**, 17953 (1994) [Ref 1]

- « *Comparison of the projector augmented-wave, pseudopotential, and linearized augmented-wave plane-wave formalisms for density-functional calculations of solids* », N. Holzwarth et al., Phys. Rev. B **55**, 2005 (1997) [Ref 2]

- « *From ultrasoft pseudopotentials to the projector augmented-wave method* », G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999) [Ref 3]

A linear transformation I

☺ One look for a linear transformation τ so that :



A linear transformation II

☺ Non-overlapping atomic spheres are defined around atoms $\boldsymbol{R}$ and one look for:

$$\tau = 1 + \sum_R S_R$$

☺ In each sphere, a partial wave basis $|\phi_i\rangle$ is built, solution of the Schrödinger equation for the isolated atom

☺ For each partial wave , an auxiliary partial wave $|\tilde{\phi}_i\rangle$ is chosen, that matches to $|\phi_i\rangle$ at the sphere boundaries.

As $|\phi_i\rangle = |\tilde{\phi}_i\rangle + |\phi_i\rangle - |\tilde{\phi}_i\rangle$ one can then define :

$$S_R |\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle$$

A linear transformation III

☺ If the partial wave basis were complete, one would have:

$$|\tilde{\psi}_n\rangle = \sum_i |\tilde{\phi}_i\rangle \cdot c_i \quad \text{in each sphere}$$

☺ If $|\tilde{p}_i\rangle$, named projectors, are defined as dual functions $\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{i,j}$ of the auxiliary functions, it comes:

$$|\tilde{\psi}_n\rangle = \sum_i |\tilde{\phi}_i\rangle\langle \tilde{p}_i | \tilde{\Psi}_n \rangle$$

and $$S_R|\tilde{\psi}_n\rangle = \sum_i S_R|\tilde{\phi}_i\rangle\langle \tilde{p}_i | \tilde{\Psi}_n \rangle = \sum_i \left(|\tilde{\phi}_i\rangle - |\phi_i\rangle\right)\langle \tilde{p}_i | \tilde{\Psi}_n \rangle$$

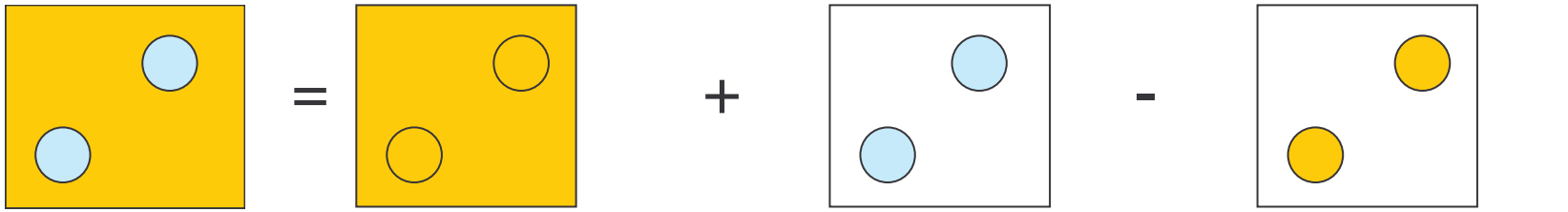
Finally,

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle\right)\langle \tilde{p}_i | \tilde{\Psi}_n \rangle$$

The PAW method

Wavefunction:

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i \left(|\phi_i\rangle - |\tilde{\phi}_i\rangle\right)\langle \tilde{p}_i | \tilde{\psi}_n\rangle = \tau |\tilde{\psi}_n\rangle \quad (1)$$



Plane wave part | All electron spherical part | Pseudized spherical part

Operators:

$$\langle A \rangle = \sum_n f_n \langle \Psi_n | A | \Psi_n \rangle = \sum_n f_n \langle \tilde{\Psi}_n | \tau^* A \tau | \tilde{\Psi}_n \rangle$$

Density:

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_R \left(n_R^1(\mathbf{r}) - \tilde{n}_R^1(\mathbf{r})\right)$$

Energy:

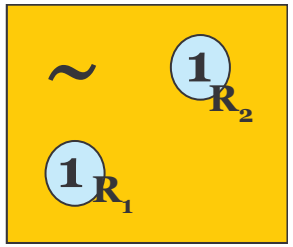
$$E = \tilde{E} + \sum_R \left(E_R^1 - \tilde{E}_R^1\right)$$

Notations

$\tilde{}$: used to represent soft objects obtained by pseudization

1 : used to represent objects inside spheres

Evaluated on a radial grid



R : atoms indices

i, j : quantum numbers ***i=(l,m,n)***

Indices of atomic partial waves

Example:

$$E = \tilde{E} + \sum_R \left(E_R^1 - \tilde{E}_R^1 \right)$$

Calculation of the energy I

It can be shown that, starting from the operator $|r\rangle\langle r|$:

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_R \left(n_R^1(\mathbf{r}) - \tilde{n}_R^1(\mathbf{r}) \right) \qquad \textbf{(2)}$$

with

$$\tilde{n}(\mathbf{r}) = \sum_n f_n \langle \tilde{\psi}_n | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\psi}_n \rangle$$

$$n_R^1(\mathbf{r}) = \sum_{i,j} \rho_{ij}^R \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle$$

$$\tilde{n}_R^1(\mathbf{r}) = \sum_{i,j} \rho_{ij}^R \langle \tilde{\phi}_i | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_j \rangle$$

$$\rho_{ij}^R = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle$$

Governs the spherical part

The general expression of the energy is: $E = T + E_{Hartree} + E_{xc}$

Using **(1)** and **(2)**, ***E*** can be expressed as a function of $|\tilde{\psi}_n\rangle$

Calculation of the energy II

Example of the Hartree term (see [ref 3]):

$$n_T = n + n_{Zc} = \underbrace{(\tilde{n} + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}_T} + \underbrace{(n^1 + n_{Zc})}_{n_T^1} - \underbrace{(\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}_T^1}$$

The compensation charge density $\hat{n}(\mathbf{r})$ is chosen so that the multipole moments:

$$\int_R (n^1(\mathrm{r}) - \tilde{n}^1(\mathrm{r}) - \hat{n}(\mathrm{r})) \cdot |\mathrm{r} - \mathrm{R}|^l \cdot Y_{lm}^*(\mathrm{r} - \mathrm{R}) \cdot d\mathrm{r} = 0$$

With this choice, the electrostatic potential created by $n_R^1 - \tilde{n}_R^1 - \hat{n}_R$ is zero outside the sphere R.

$$V(\mathbf{r}) = 4\pi \sum_{lm} \frac{M_{lm} Y_{lm}(\hat{r})}{(2l+1) r^{l+1}}$$

Calculation of the energy III

$$E_{Hartree} = \frac{1}{2}\iint \frac{n_T(\mathrm{r})n_T(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|}d\mathrm{r}d\mathrm{r}' = \frac{1}{2}(n_T)(n_T) = \frac{1}{2}\underbrace{(\tilde{n}_T)(\tilde{n}_T)}_{(1)} + \underbrace{(n_T^1 - \tilde{n}_T^1)(\tilde{n}_T)}_{(2)} + \frac{1}{2}\underbrace{(n_T^1 - \tilde{n}_T^1)(n_T^1 - \tilde{n}_T^1)}_{(3)}$$

In **(2)** and **(3)**, $(n_T^1 - \tilde{n}_T^1)$ only contribute within each augmentation sphere

Approximation

In (2), $\tilde{n}_T$ is replaced by $\tilde{n}_T^1$

→ **(2)** only contributes within sphere

It is then possible to show that:

$$\begin{aligned} E_{Hartree} &= E_H[\tilde{n}+\hat{n}] + \int v_H[\tilde{n}_{Zc}][\tilde{n}+\hat{n}]d\mathrm{r} + U(\mathrm{R}, Z_{ion}) \\ &+ E_H[n^1] + \int_R v_H[n_{Zc}][n^1]d\mathrm{r} - E_H[\tilde{n}^1+\hat{n}] - \int_R v_H[\tilde{n}_{Zc}][\tilde{n}^1+\hat{n}]d\mathrm{r} \end{aligned}$$

Calculation of the energy IV

Finally, adding the kinetic and the XC terms:

$$E = \tilde{E} + \sum_R \left(E_R^1 - \tilde{E}_R^1 \right)$$

with

$$\tilde{E} = \sum_n f_n \left\langle \tilde{\Psi}_n \left| -\frac{\Delta}{2} \right| \tilde{\Psi}_n \right\rangle + E_{xc}\left[\tilde{n} + \hat{n} + \tilde{n}_c\right] + E_H\left[\tilde{n} + \hat{n}\right] + \int v_H\left[\tilde{n}_{Zc}\right]\left[\tilde{n} + \hat{n}\right] d\mathbf{r} + U(\mathbf{R}, Z_{ion})$$

$$\tilde{E}_R^1 = \sum_{ij} \rho_{ij}^R \left\langle \tilde{\phi}_i \left| \frac{-\Delta}{2} \right| \tilde{\phi}_i \right\rangle + E_{xc}\left[\tilde{n}_R^1 + \hat{n}_R + \tilde{n}_c^R\right] + E_H\left[\tilde{n}_R^1 + \hat{n}_R\right] + \int_R v_H\left[\tilde{n}_{Zc}^R\right]\left[\tilde{n}_R^1 + \hat{n}_R\right] d\mathbf{r}$$

$$E_R^1 = \sum_{ij} \rho_{ij}^R \left\langle \phi_i \left| \frac{-\Delta}{2} \right| \phi_i \right\rangle + E_{xc}\left[n_R^1 + n_c^R\right] + E_H\left[n_R^1\right] + \int_R v_H\left[\tilde{n}_{Zc}^R\right]\left[n_R^1\right] d\mathbf{r}$$

Calculation of the energy V

Comment n°1:

In order to fulfil the multipole moment condition, we define: $\hat{n}(\mathbf{r}) = \sum_{(i,j),L} \rho_{ij} Q_{ij}^{L}(\mathbf{r})$

with $Q_{ij}^{L}(\mathbf{r}) = q_{ij}^{L} g_l(|\mathbf{r}-\mathbf{R}|) Y_L(\mathbf{r}-\mathbf{R})$

$$q_{ij}^{L} = \int_R \left[\phi_i^*(\mathbf{r})\phi_j(\mathbf{r}) - \tilde{\phi}_i^*(\mathbf{r})\tilde{\phi}_j(\mathbf{r})\right] |\mathbf{r}-\mathbf{R}|^l Y_L^*(\mathbf{r}-\mathbf{R}) d\mathbf{r} \qquad \int_R g_l(r) r^l r^2 dr = 1$$

Comment n°2:

The quantity $v_H[\tilde{n}_{Zc}]$ is analogous to a local potential.
This term is introduced in [Ref 3] by Kresse and Joubert.

It can be connected to the formulation of Blöchl in [Ref 1], provided:

$$v_H[\tilde{n}_{Zc}] = \bar{v} + v_H(n_{Zc}^K)$$

with $\tilde{n}_{Zc}^K = \frac{g_0(r)}{4\pi}\left[\int_R (n_c - \tilde{n}_c) d\mathbf{r} - Z_{ion}\right] + \tilde{n}_c$

$\bar{v}$ is an arbitrary localized potential introduced by Blöchl

Calculation of the Hamiltonian I

The orthogonality conditions: $\langle \Psi_n | \Psi_m \rangle = \delta_{nm}$

become: $\langle \tilde{\Psi}_n | S | \tilde{\Psi}_m \rangle = \delta_{nm}$

with $S = 1 + \sum_{R,ij} | \tilde{p}_i^R \rangle \left(\langle \phi_i^R | \phi_j^R \rangle - \langle \tilde{\phi}_i^R | \tilde{\phi}_j^R \rangle \right) \langle \tilde{p}_j^R |$

We have therefore to solve: $\tilde{H} \tilde{\Psi}_n = \varepsilon_n S \tilde{\Psi}_n$

with $\tilde{H} = \frac{dE}{d\tilde{n}} = -\frac{1}{2}\Delta + \tilde{v}_{eff} + \sum_{i,j} | \tilde{p}_i \rangle D_{ij} \langle \tilde{p}_j |$

Calculation of the Hamiltonian II

$$\tilde{H} = \frac{dE}{d\tilde{n}} = -\frac{1}{2}\Delta + \tilde{v}_{eff} + \sum_{i,j} |\tilde{p}_i\rangle D_{ij} \langle \tilde{p}_j|$$

where $\tilde{v}_{eff} = v_H\left[\tilde{n} + \hat{n} + \tilde{n}_{Zc}\right] + v_{xc}\left[\tilde{n} + \hat{n} + \tilde{n}_c\right]$

$$D_{ij} = \sum_L \int \tilde{v}_{eff}(\mathbf{r}) Q_{ij}^L(\mathbf{r}) d\mathbf{r}$$

$$+ \left\langle \phi_i \middle| -\frac{\Delta}{2} + v_H\left[n^1 + n_{Zc}\right] + v_{xc}\left[n^1 + n_c\right] \middle| \phi_j \right\rangle$$

$$- \left\langle \tilde{\phi}_i \middle| -\frac{\Delta}{2} + v_H\left[\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc}\right] + v_{xc}\left[\tilde{n}^1 + \hat{n} + \tilde{n}_c\right] \middle| \tilde{\phi}_j \right\rangle - \sum_L \int \tilde{v}_{eff}^1(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}$$

D_{ij} can be rewritten as:

$$D_{ij} = D_{ij}^0 + \sum_{kl} \rho_{kl} E_{ijkl} + D_{ij}^{xc} + \sum_L \int \tilde{v}_{eff}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}$$

The PAW method - overview

APPROXIMATIONS:

- ✓ Frozen core approximation
- ✓ The partial wave basis is truncated
- ✓ The plane wave basis is truncated

ADVANTAGES:

- ✓ Total density of the system is computed ➢ no transferability problem
- ✓ Plane wave cutoff equivalent to ultra-soft pseudopotentials (no norm-conserving constraint)
- ✓ The PAW method is as accurate as an *all electron* method. Convergency can be controlled.
- ✓ It can be shown that *ultrasoft* and *norm-conserving* methods are approximations of the PAW method.

The PAW method – atomic data

In order to perform a PAW calculation, following atomic data are needed:

For each atom specie

$\{\phi_i^R\}$, $\{\tilde{\phi}_i^R\}$, $\{\tilde{p}_i^R\}$, $V_H[\tilde{n}_{Zc}]$, n_c, $\tilde{n}_c$

- $\{\phi_i^R\}$: *All electron* partial waves
- $\{\tilde{\phi}_i^R\}$: Pseudized soft partial waves
- $\{\tilde{p}_i^R\}$: Projectors (dual of $\tilde{\phi}_i^R$)
- $V_H[\tilde{n}_{Zc}]$: *Hartree* potential due to nuclueus and core electrons (local pot.)
- n_c: Core density
- $\tilde{n}_c$: Pseudized core density

See lesson on PAW atomic data generator

Approximations: ultrasoft and norm-conserving

$$\tilde{H} = \frac{dE}{d\tilde{n}} = -\frac{1}{2}\Delta + \tilde{v}_{eff} + \sum_{i,j} |\tilde{p}_i\rangle D_{ij} \langle \tilde{p}_j|$$

$$D_{ij} = D_{ij}^0 + \sum_{kl} \rho_{kl} E_{ijkl} + D_{ij}^{xc} + \sum_L \int \tilde{v}_{eff}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}$$

1- From PAW to ultrasoft pseudopotentials

Linearisation of ρ_{ij} around atomic occupations in the spheres in the total energy expression leads to:

- $D_{ij} = D_{ij}^{0,US} + \sum_L \int \tilde{v}_{eff}(\mathrm{r}) \hat{Q}_{i,j}^L(\mathrm{r}) d\mathrm{r}$ *Ultrasoft pseudopotential formulation*

2- From PAW to norm-conserving pseudopotentials

$\hat{Q}_{i,j}^L(r) = 0$ ➤ $D_{ij} = D_{ij}^{0,KB}$ *Norm-conserving pseudopotential formulation*

$S=I$

Example of *fcc* Ca

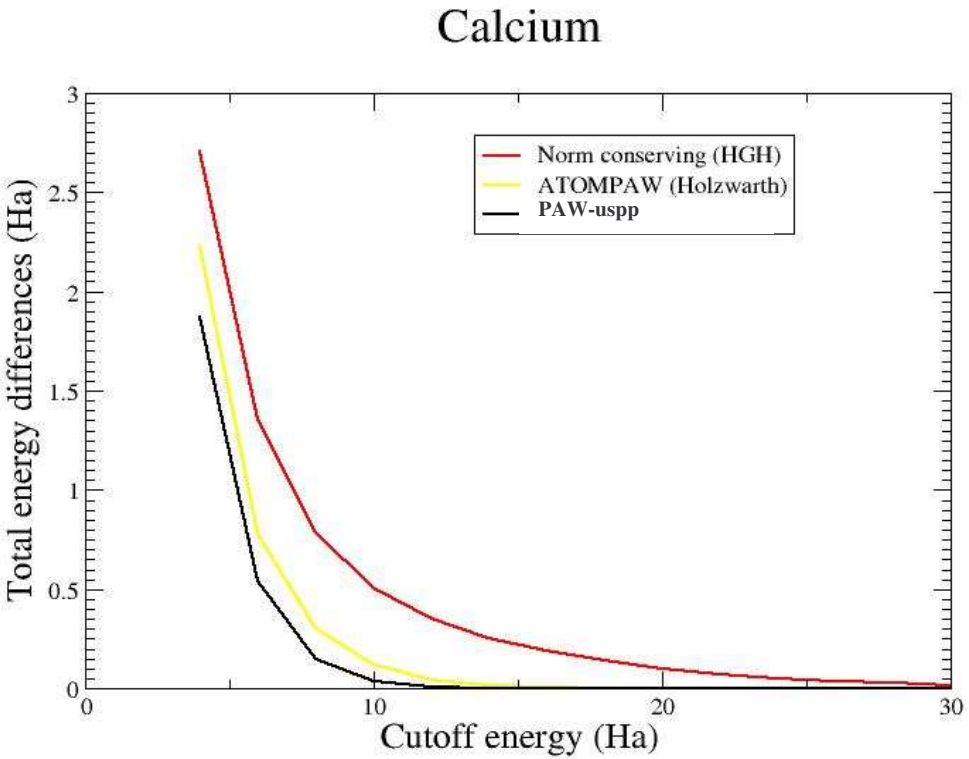
Atomic data used:

- Norm-conserving psp HGH
- PAW from USPP
- PAW from AtomPAW

Convergence criteria: $\Delta(E^{total}) < 1$ mHa

Cutoff energies required:

- HGH : > 40 Ha
- PAW-USPP : 20 Ha
- PAW-AtomPAW : 20 Ha



Results:

- HGH : a_o = 10.3 a.u.
- PAW-USPP : a_o = 10.2 a.u.

Example of *fcc* oxygen

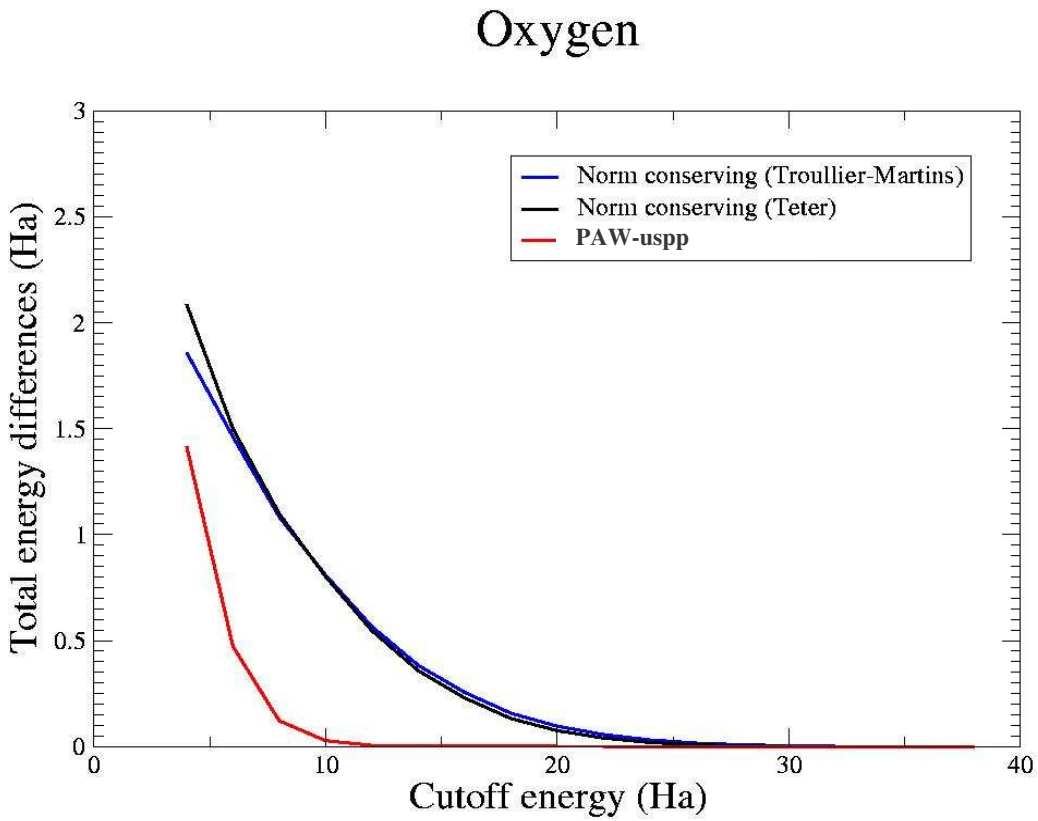
Atomic data used:

- Norm-conserving psp Teter
- Norm-conserving psp TM
- PAW from USPP

Convergence criteria: $\Delta(E^{total}) < 1$ mHa

Cutoff energies required:

- Teter : 30 Ha
- TM : 33 Ha
- PAW-USPP : 15 Ha



Results:

- Teter : a_o = 5.76 a.u.
  B_o = 210 GPa
- PAW-USPP : a_o = 5.80 a.u.
  B_o = 208 GPa

Example of $BaTiO_3$

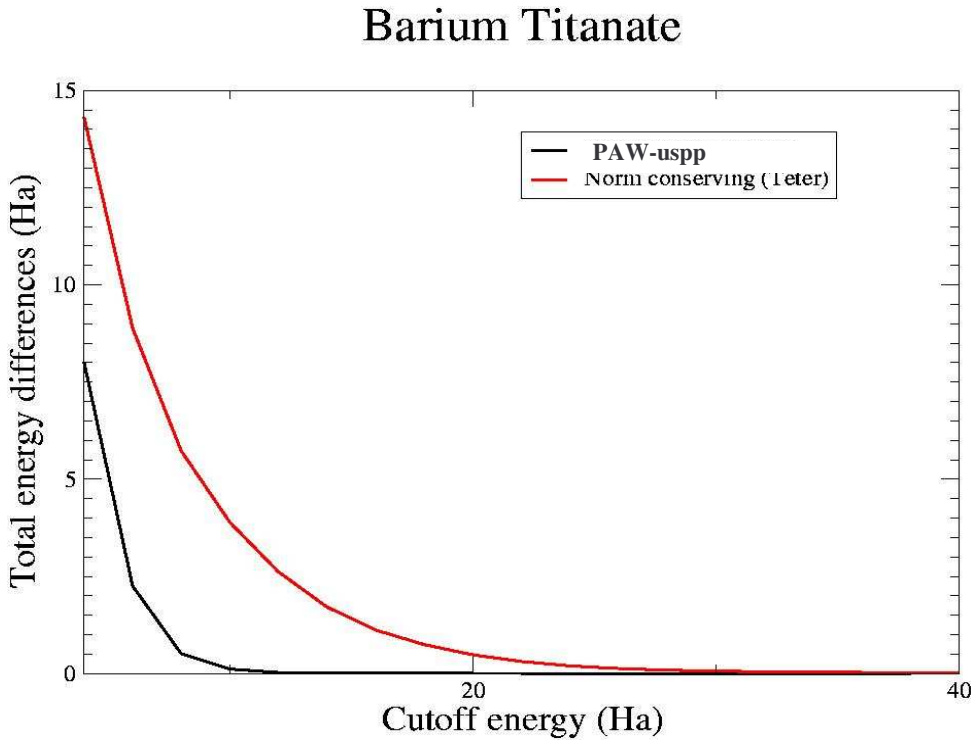
Atomic data used:

- Norm-conserving psp Teter
- PAW from USPP

Convergence criteria: $\Delta(E^{total}) < 1$ mHa

Cutoff energies required:

- Teter : 56 Ha
- PAW-USPP : 23 Ha



CPU on a PC-BiXeon:

- Teter : *CPU* = 260 s.
- PAW-USPP : *CPU* = 100 s.

Results:

- Teter : a_o = 7.45 a.u.
- PAW-USPP : a_o = 7.48 a.u.

Conclusions

- The PAW method gives access to the « true » wavefunction and electronic density
- Convergency can be controlled
- Accuracy and efficiency are of the same order of ultrasoft pseudopotentials approach

Available in ABINIT v4.6.3+

- Energy, forces, stresses, molecular dynamics in PAW
- Linear response in PAW is coming...