



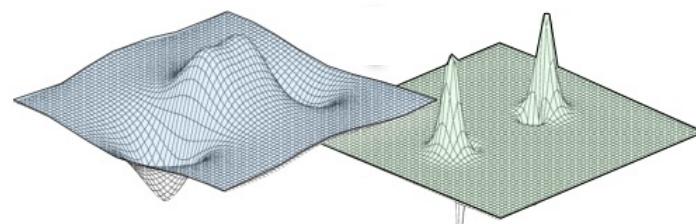
ABINIT School 2026  
*Learning electronic structure calculations using ABINIT*  
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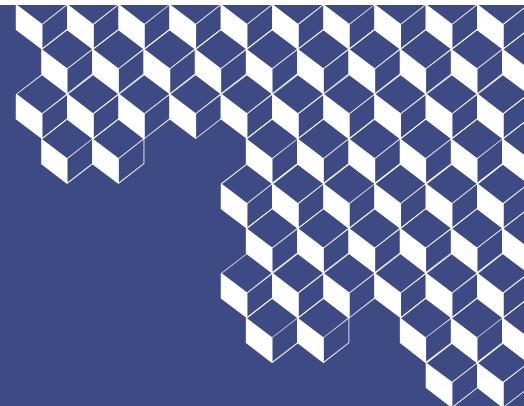


# Pseudopotentials and Projector Augmented-Wave method

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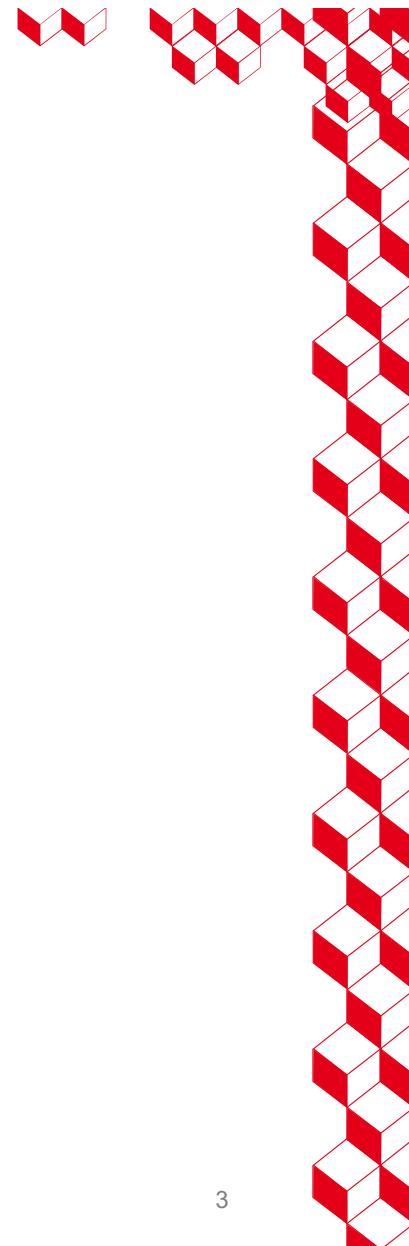


“

**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, Physical Review B 50, 17953 (1994)*

# Outline



## Pseudopotentials

A bit of history

Pseudopotentials, « all-electrons », basis, ...

How to combine the best of each world?

## Projector Augmented-Wave approach

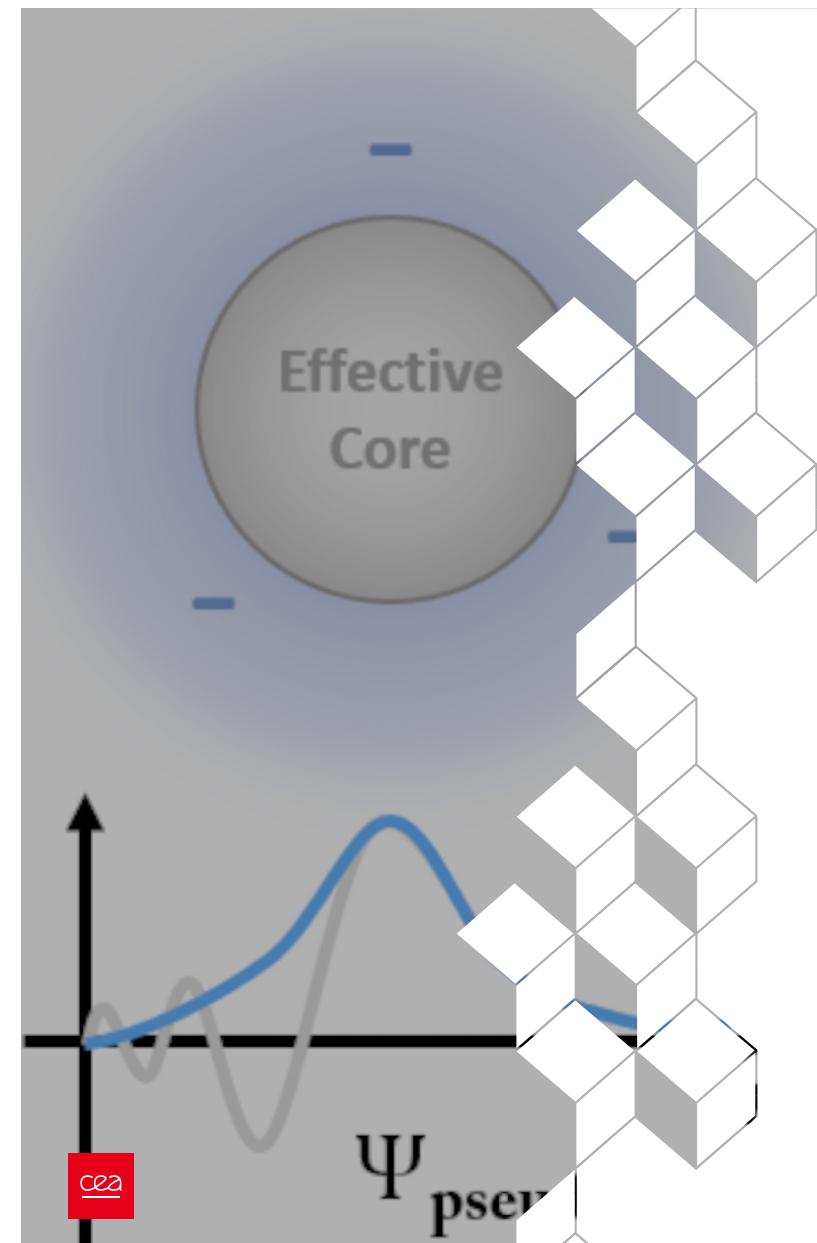
The PAW approach

The PAW linear transformation

Charge density, Hamiltonian, Energy, ...

Approximations, advantages, ...

## How to use PAW in ABINIT



# Plane-wave DFT and Pseudopotentials



# Performing a DFT calculation

## A self-consistent set of equations

$\rho(\mathbf{r}) = \sum_n f_n |\psi_n(\mathbf{r})|^2$ , where  $|\psi_n\rangle$  satisfies

$$\left( -\frac{1}{2} \nabla^2 + V_H[\rho] + V_{xc}[\rho] + V_{ext} + V_{pseudo} \right) |\psi_n\rangle = \varepsilon_n |\psi_n\rangle$$

To solve these *Kohn-Sham* equations, need

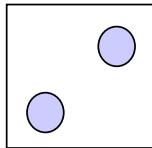
- An exchange-correlation functional
- A basis set for expressing the wave-functions  $|\psi_n\rangle$
- An (iterative) algorithm for finding the wave-functions



# Basis sets

The wave functions are developed on a basis which can be...

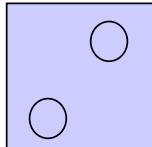
## Localized



Spherical harmonics,  
Gaussians,  
Atomic orbitals, ...

- Few functions (per atom) in the basis
- All the electron wave-functions can be represented, even highly localized ones
- Accurate results, but heavy calculations
- Difficult to manipulate:  
The basis moves with atoms

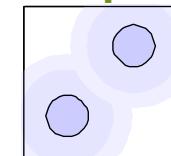
## Delocalized



Plane waves, ...

- Many functions in the basis especially to represent localized wave-functions
- Easy to converge (systematic)
- More adapted to periodic systems

## Adaptive



Wavelets, ...

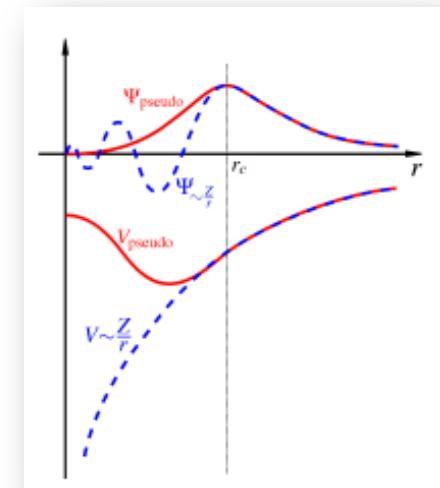


# Pseudopotentials

**Assumption: for chemical properties only valence electrons are relevant...**

*Replace the potential due to the nucleus and the core electrons by a smooth potential*

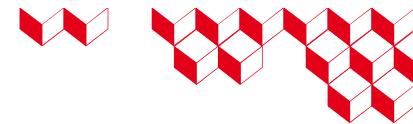
- Eliminate (from the bond) the chemically inactive core electrons
- Reduce the number of electron orbitals to compute explicitly
- Eliminate the rapid variations of the potential in the core region
- Manipulate a smooth pseudo-wavefunction for each valence electron



$$V_{\text{ext}}(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0} \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|}$$

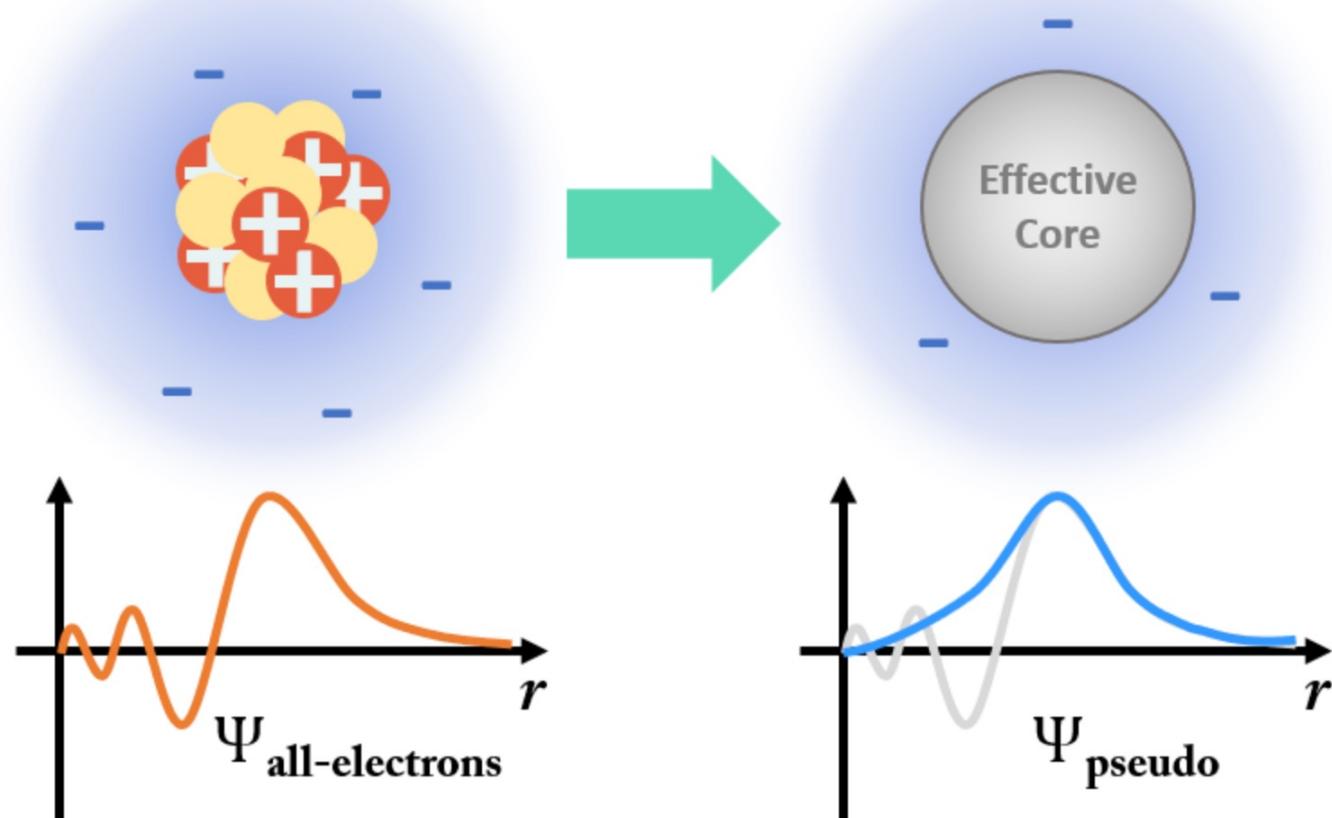
**FROZEN-CORE + PSEUDOPOTENTIAL**

A reasonable approximation...  
... but not perfect



# Pseudopotentials

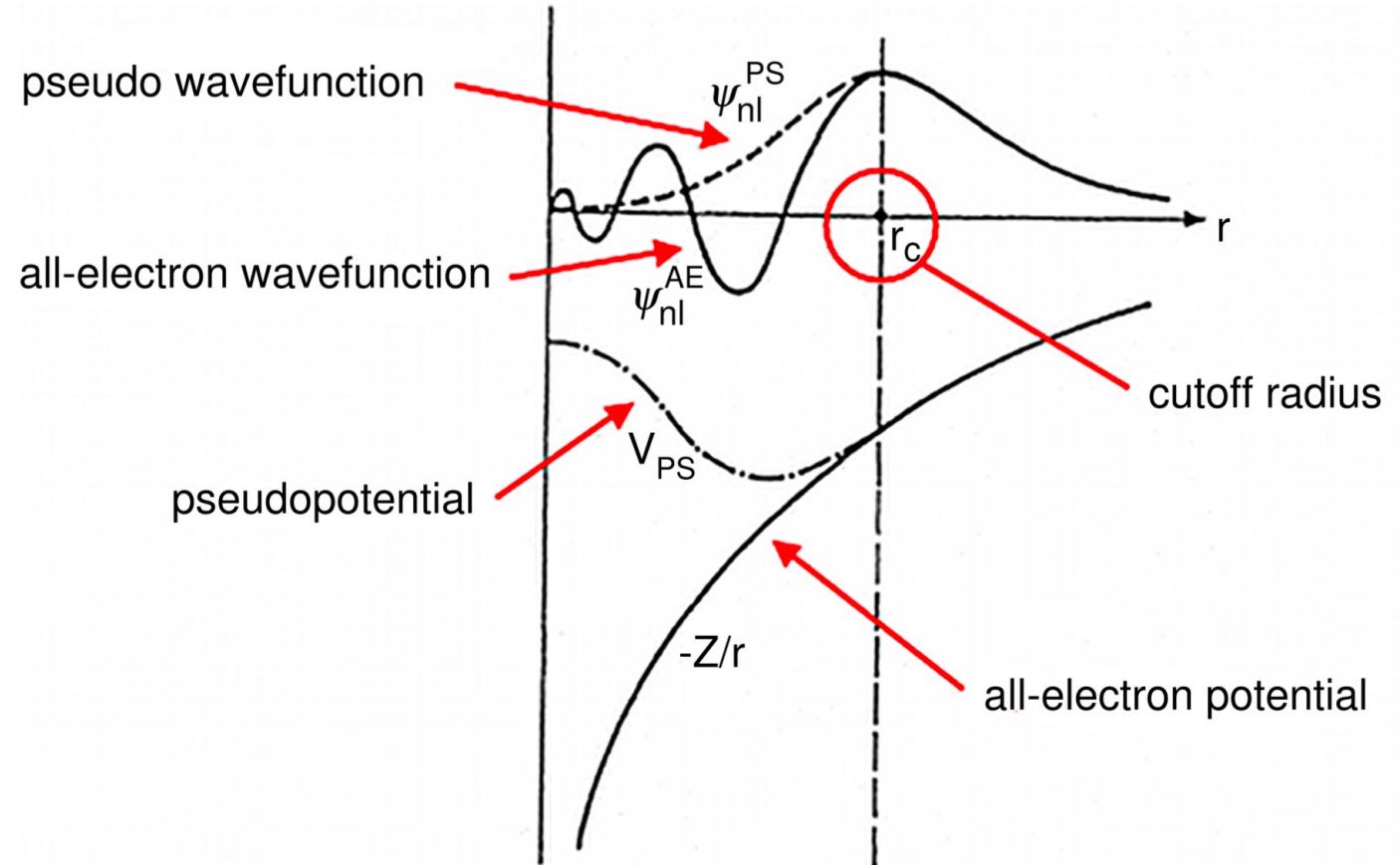
## Schematically





# Pseudopotentials

## Schematically





# Pseudopotentials

## Terminology

- *transferability* : ability to describe the valence electrons in different environments.
- *softness* : the need for the number of plane waves.
- *inclusion of semicore states*

Example : Ti with large core  $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6}_{\text{core}} 4s^2 3d^2$

Ti with semicore  $\underbrace{1s^2 2s^2 2p^6}_{\text{core}} 3s^2 3p^6 4s^2 3d^2$

- *locality* : all  $\ell$ -channel ( $s, p, d$ ) electrons feel the same potential

*Efficiency → a compromise between accuracy and computational cost*



# Pseudopotentials

## A bit of history

- 1979-1982: BHS pseudopotentials  
(Bachelet, Hamann, Schlüter)
- 1982: Separable pseudopotentials  
(Kleinman, Bylander)
- 1990: efficient pseudopotentials  
(Martins, Troullier)
- 1991: ultrasoft pseudopotentials  
(Vanderbilt)

*Norm conserving, non local*

*Norm conserving, non local*  
*Numerically efficient*

*Norm conserving, non local*  
*Psp deduced from pseudo WF*

*No norm constraint, non local*  
*High efficiency, few plane waves*



# Pseudopotentials

Final separable form for modern pseudopotentials

$$V^{PP}(\mathbf{r}, \mathbf{r}') = \underbrace{V_{loc}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')}_{\text{local part}} + \underbrace{\sum_{n,l,m} |\phi_{nlm}(\mathbf{r})\rangle E_{nl}^{KB} \langle \phi_{nlm}(\mathbf{r}')|}_{\text{non-local}}$$

KB energies  
(constants)

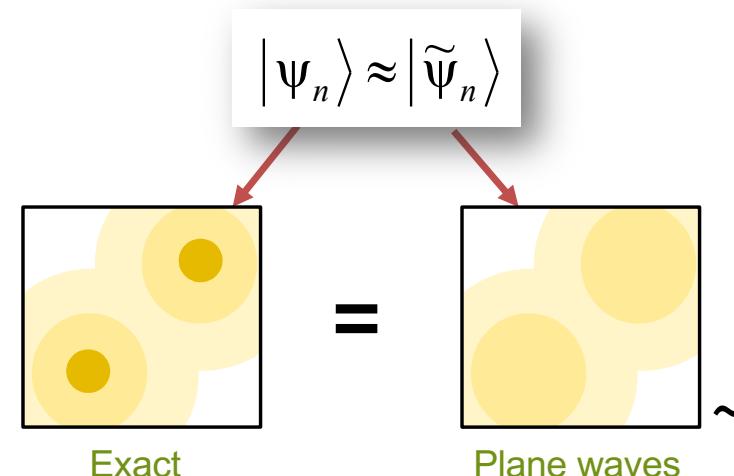
where  $|\phi_{nlm}\rangle$  is a projector (pseudo-wavefunction)  
 $l, m, n$  are quantum numbers.

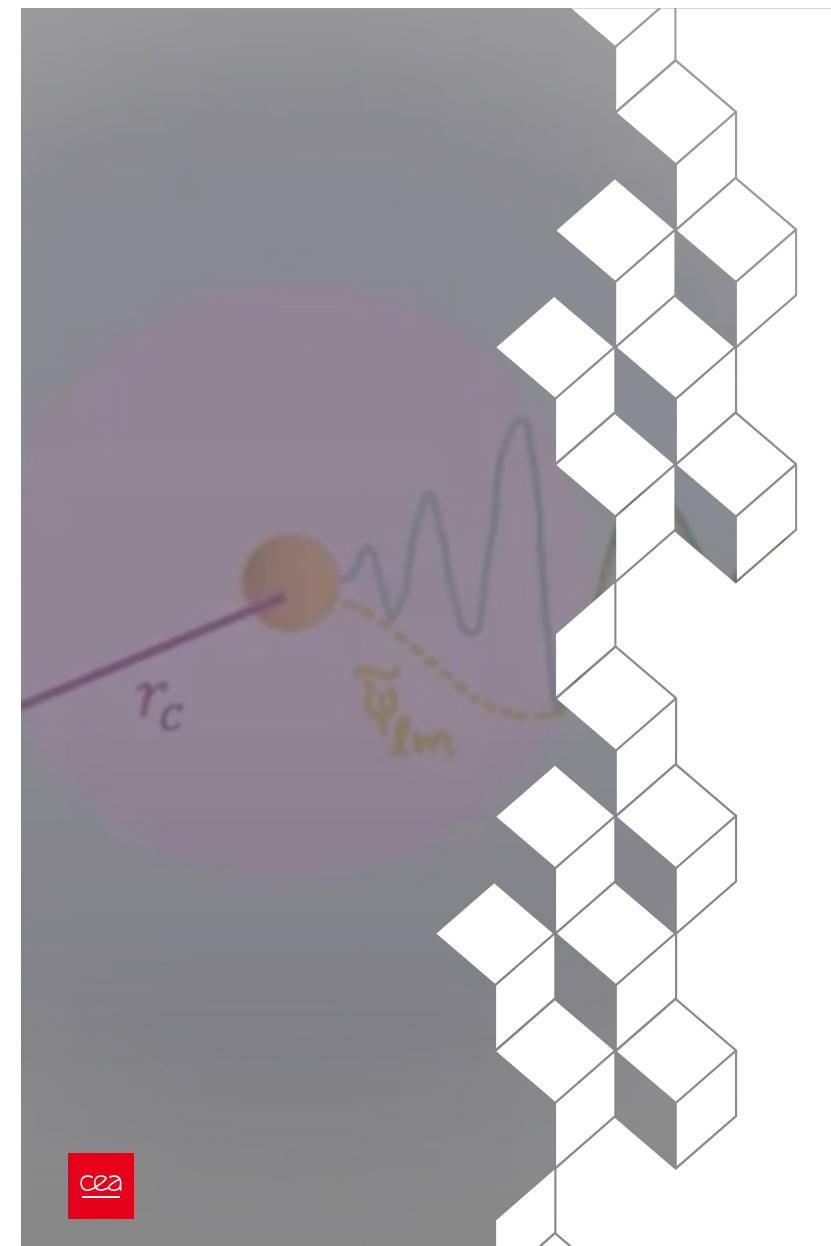
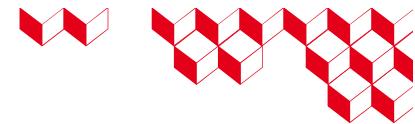


# Pseudopotentials and plane waves

With pseudopotentials, the smoothed potential can be expressed on a (relatively) small plane wave basis...

- $(V^{\text{nucleus}} + V^{\text{core electrons}})$  replaced by  $\tilde{V}^{\text{PP}}$
- Solve:  $\tilde{\mathbf{H}} |\tilde{\Psi}_n\rangle = \epsilon_n |\tilde{\Psi}_n\rangle$  with:  $\tilde{\mathbf{H}} = -\frac{1}{2}\Delta + V_{\text{Hartree}} + V_{\text{XC}} + V_{\text{eff}} + \tilde{V}^{\text{PP}}$
- Take  $|\tilde{\Psi}_n\rangle$  as a reasonable approximation for  $|\Psi_n\rangle$





## PAW basics

***The Projector Augmented-Wave approach***



# Going beyond pseudopotentials?

What do we want to keep from pseudopotential scheme...

- The frozen core electrons → *Avoid expensive computation*
- The use of auxiliary smooth quantities (*potential, wave functions*) – As smooth as possible → *Use plane waves Limit basis size*

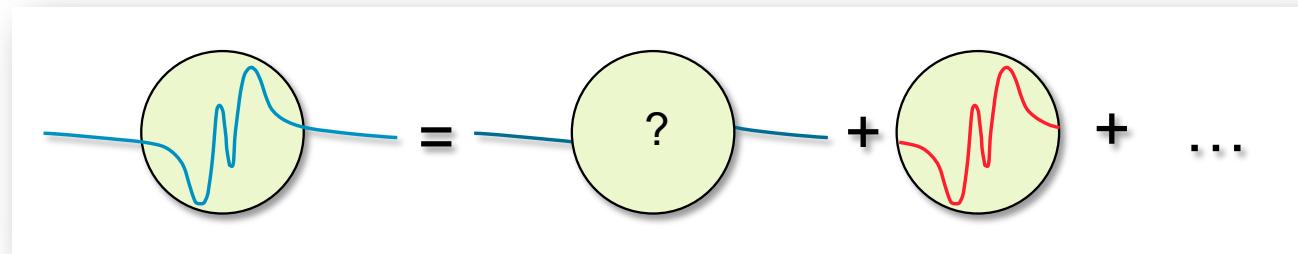
We want also:

- To be able to represent the nodal structure of “exact” wave-functions around the nucleus → *Reach accuracy even near nuclei*
- To use a basis as convenient as possible:  
Adapted to charge density and easy to use → *Take advantage of plane waves and localized basis*

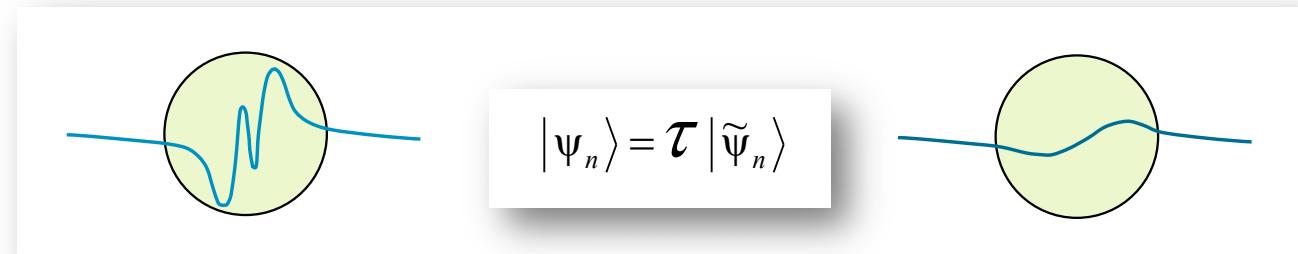


# The best of each world

- Treat both rapid oscillations and smooth sections of the wave functions  
*Use two basis (augmented wave)*



- Find a connection between the smooth auxilliary wave function and the exact one





# Projector Augmented-Wave méthode

## Key features

*Peter Blöchl, Physical Review B 50, 17953 (1994)*

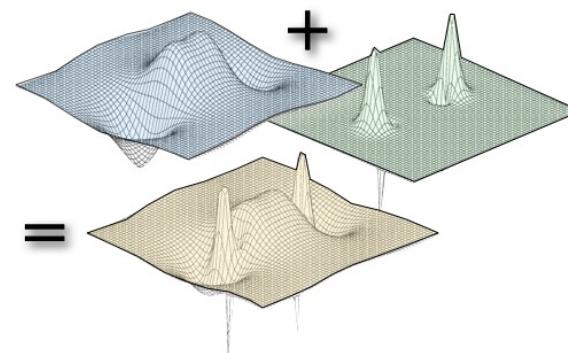
- Frozen core approximation:  
only valence electrons are taken into account in the calculation
- The interaction between valence electrons and the ionic core is taken into account within a pseudopotential without norm constraint
- Several basis are mixed:  
planes waves and local (atomic) orbitals



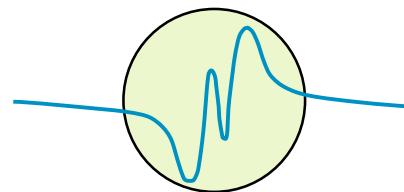
# PAW linear transformation

In search of a linear (and invertible) transformation  $\tau$

- Use two basis (augmented waves)

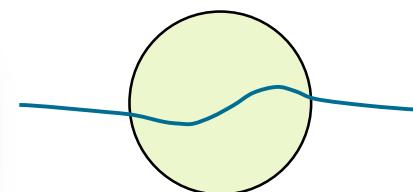


- Find a connection between the smooth auxiliary wave function and the exact one



*Used to compute  
accurate properties*

$$|\Psi_n\rangle = \tau |\tilde{\Psi}_n\rangle$$



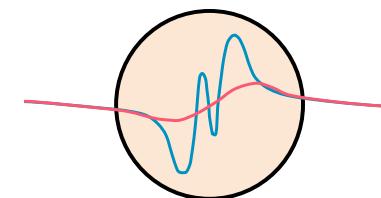
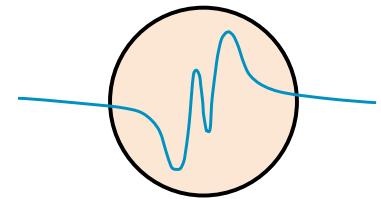
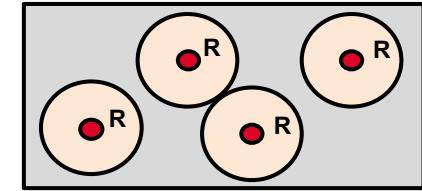
*Manipulated by the DFT code  
Developed on plane waves in ABINIT*



# PAW linear transformation

## Details

- Define non-overlapping spherical regions around atoms R (augmentation regions)
- In each augmentation region, define a partial wave basis  $|\phi_i^R\rangle$
- For each partial wave, define a « soft » pseudo partial wave basis  $|\tilde{\phi}_i^R\rangle$
- Define the  $|\tilde{p}_i^R\rangle$  as duals of  $|\tilde{\phi}_i^R\rangle$



$$\langle \tilde{p}_i^R | \tilde{\phi}_j^{R'} \rangle = \delta_{RR'} \delta_{ij} \quad I = \sum_i |\tilde{\phi}_i^R \rangle \langle \tilde{p}_i^R |$$

$|\tilde{p}_i^R\rangle = 0$  outside the augmentation region



# PAW linear transformation

## Final expression

$$|\psi_n\rangle = \tau |\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i,R} |\phi_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle$$



# PAW linear transformation

## Proof

In search of  $\tau$  as a sum of local transformations :  $\tau = \mathbf{I} + \sum_{\mathbf{R}} S_{\mathbf{R}}$

Expression of  $\tau$  applied to  $|\tilde{\phi}_i^R\rangle$ :

$$|\phi_i^R\rangle = \tau|\tilde{\phi}_i^R\rangle = \left(\mathbf{I} + \sum_{\mathbf{R}} S_{\mathbf{R}}\right)|\tilde{\phi}_i^R\rangle = |\tilde{\phi}_i^R\rangle + (|\phi_i^R\rangle - |\tilde{\phi}_i^R\rangle)$$

If the  $|\tilde{\phi}_i^R\rangle$  are a complete basis:

$$|\tilde{\psi}_n\rangle = \sum_i |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle \quad S_{\mathbf{R}}|\tilde{\psi}_n\rangle = \sum_i S_{\mathbf{R}}|\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle = \sum_i (|\phi_i^R\rangle - |\tilde{\phi}_i^R\rangle) \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle$$

Finally get the expression of the transformation  $\tau$ :

$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i,R} (|\phi_i^R\rangle - |\tilde{\phi}_i^R\rangle) \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle$$

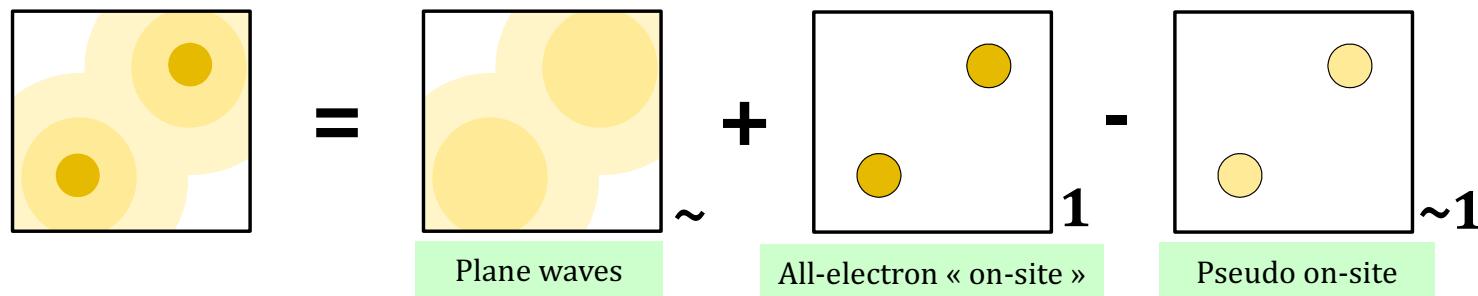
$$\tau = \mathbf{I} + \sum_{i,R} (|\phi_i^R\rangle - |\tilde{\phi}_i^R\rangle) \langle \tilde{p}_i^R | \quad i = (R, l, m, n)$$



# PAW linear transformation

## Final expression

$$|\psi_n\rangle = \tau |\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i,R} |\phi_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle \quad (1)$$





# PAW linear transformation

## For operators

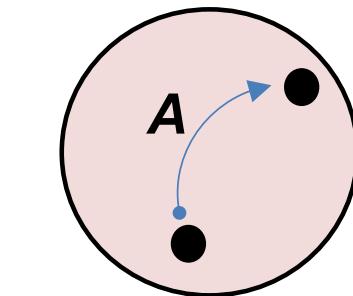
*Expectation value of an operator*

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

*For a “quasi-local” operator*

$$\langle A \rangle = \langle \tilde{A} \rangle + \sum_R \left( \langle A \rangle_1^R - \langle \tilde{A} \rangle_1^R \right) \quad (2)$$

PAW « on-site » contributions



*Completeness assumed !*

*Applicable to...*

- Density operator  $|r\rangle\langle r|$  → charge density
- Kinetic operator  $-\frac{1}{2}\Delta$  → kinetic energy
- Hartree potential  $V_{XC}$  → Hartree energy
- XC potential  $V_H$  → XC energy



# PAW - Charge density

Starting from density operator  $|r\rangle\langle r|$  and applying (2) , we get:

$$n(r) = f_n \langle \tilde{\psi}_n | r \rangle \langle r | \tilde{\psi}_n \rangle + \sum_{i,j,R} f_n \langle \tilde{\psi}_n | \tilde{p}_i^R \rangle \langle \phi_i^R | r \rangle \langle r | \phi_j^R \rangle \langle \tilde{p}_j^R | \tilde{\psi}_n \rangle - \sum_{i,j,R} f_n \langle \tilde{\psi}_n | \tilde{p}_i^R \rangle \langle \tilde{\phi}_i^R | r \rangle \langle r | \tilde{\phi}_j^R \rangle \langle \tilde{p}_j^R | \tilde{\psi}_n \rangle$$

Can be rewritten as:

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_R (n_1^R(\mathbf{r}) - \tilde{n}_1^R(\mathbf{r}))$$

With

$$\begin{aligned} \tilde{n} &= \sum_n f_n \cdot \tilde{\psi}_n^*(\mathbf{r}) \cdot \tilde{\psi}_n(\mathbf{r}) \\ n_1^R(\mathbf{r}) &= \sum_{i,j} \rho_{ij}^R \cdot \phi_i^*(\mathbf{r}) \cdot \phi_j(\mathbf{r}) \\ \tilde{n}_1^R(\mathbf{r}) &= \sum_{i,j} \rho_{ij}^R \cdot \tilde{\phi}_i^*(\mathbf{r}) \cdot \tilde{\phi}_j(\mathbf{r}) \end{aligned} \quad \left. \begin{array}{l} \text{Smooth part evaluated on} \\ \text{plane wave grid} \\ \text{One-site contributions} \\ \text{evaluated on radial grid} \end{array} \right\}$$

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

**On-site density matrix**  
Governs the "on-site" parts

$n$  can be expressed as a function of  $|\tilde{\psi}_n\rangle$



# PAW - Energy

Starting from kinetic operator  $-\frac{1}{2}\Delta$  and applying (2) , we get:

$$E^{kin} = f_n \langle \tilde{\psi}_n | -\frac{1}{2}\Delta | \tilde{\psi}_n \rangle + \sum_{i,j,R} f_n \langle \tilde{\psi}_n | \tilde{p}_i^R \rangle \langle \phi_i^R | -\frac{1}{2}\Delta | \phi_i^R \rangle \langle \tilde{p}_j^R | \tilde{\psi}_n \rangle - \sum_{i,j,R} f_n \langle \tilde{\psi}_n | \tilde{p}_i^R \rangle \langle \tilde{\phi}_j^R | -\frac{1}{2}\Delta | \tilde{\phi}_j^R \rangle \langle \tilde{p}_j^R | \tilde{\psi}_n \rangle$$

Can be rewritten as:

$$E^{kin} = \tilde{E}^{kin} + \sum_R (E_1^{kin R} - \tilde{E}_1^{kin R})$$

With  $\tilde{E}^{kin} = f_n \langle \tilde{\psi}_n | -\frac{1}{2}\Delta | \tilde{\psi}_n \rangle$

Smooth part

$$\left. \begin{aligned} E_i^{kin R} &= \sum_{i,j} \rho_{ij}^R \cdot \langle \phi_i^R | -\frac{1}{2}\Delta | \phi_i^R \rangle \\ \tilde{E}_i^{kin R} &= \sum_{i,j} \rho_{ij}^R \cdot \langle \tilde{\phi}_j^R | -\frac{1}{2}\Delta | \tilde{\phi}_j^R \rangle \end{aligned} \right\}$$

One-site contributions

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

*The same for Hartree energy and XC energy*



# PAW - Energy

$$E = E^{kin} + E_{Hartree} + E_{xc}$$

$$E = \tilde{E} + \sum_R \left( E_1^R - \tilde{E}_1^R \right)$$

Smooth part evaluated on plane wave grid

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

One-site contributions evaluated on radial grid

$$\begin{aligned} E_1^R = & \sum_{ij} \rho_{ij}^R \left\langle \phi_i \left| -\frac{\Delta}{2} \right| \phi_i \right\rangle + E_{xc} [n_1^R + n_c^R] + E_H [n_1^R] + \int_R v_H [\tilde{n}_{Zc}^R] [n_1^R] dr \\ \tilde{E}_1^R = & \sum_{ij} \rho_{ij}^R \left\langle \tilde{\phi}_i \left| -\frac{\Delta}{2} \right| \tilde{\phi}_j \right\rangle + E_{xc} [\tilde{n}_1^R + \tilde{n}_c^R] + E_H [\tilde{n}_1^R + \hat{n}_R^R] + \int_R v_H [\tilde{n}_{Zc}^R] [\tilde{n}_1^R + \hat{n}_R] dr \end{aligned}$$



# PAW - Hamiltonian

$$\tilde{H} = \frac{dE}{d\tilde{\rho}} = \underbrace{\frac{\partial E}{\partial \tilde{\rho}}}_{-\frac{1}{2}\Delta} + \underbrace{\int \frac{\delta E}{\delta \tilde{n}} \frac{\partial \tilde{n}(\mathbf{r})}{\partial \tilde{\rho}} d\mathbf{r}}_{\tilde{v}_{Hxc}(\mathbf{r})} + \sum_{R,ij} \underbrace{\frac{\partial E}{\partial \rho_{ij}^R}}_{D_{ij}^R} \underbrace{\frac{\partial \rho_{ij}^R}{\partial \tilde{\rho}}}_{|\tilde{p}_i^R\rangle\langle\tilde{p}_j^R|}$$

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

Local + Hartree + XC potential

Non-local separable potential

- Similar to Hamiltonian in the pseudo-potential formalism
- Non-local has a varying intensity which is different from an atom to another (depending on atom environment)
- Non-local potential intensity is non-diagonal



# PAW – Wave equation

In order to compute

$$\left\{ \begin{array}{l} n(\mathbf{r}) = \sum_n f_n |\tilde{\psi}_n(\mathbf{r})|^2 + \sum_{R,ij} \rho_{ij}^R (\phi_i(\mathbf{r})\phi_j(\mathbf{r}) - \tilde{\phi}_i(\mathbf{r})\tilde{\phi}_j(\mathbf{r})) \\ \rho_{ij}^R = \sum_n f_n \langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle \end{array} \right.$$

we need  $|\tilde{\psi}_n\rangle$

$$H|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$

$$\langle \psi_n | \psi_m \rangle = \delta_{nm}$$

$$|\psi_n\rangle = \tau |\tilde{\psi}_n\rangle$$

$$\tau = I + \sum_{i,R} (|\phi_i^R\rangle - |\tilde{\phi}_i^R\rangle) \langle \tilde{p}_i^R |$$



# PAW linear transformation

- The wave equation  $H|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$

becomes:

$$\tilde{H}|\tilde{\psi}_n\rangle = \varepsilon_n S |\tilde{\psi}_n\rangle$$

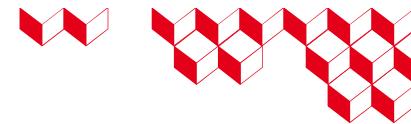
- The orthogonality conditions  $\langle\psi_n|\psi_m\rangle = \delta_{nm}$

become:

$$\langle\tilde{\psi}_n|S|\tilde{\psi}_n\rangle = \delta_{nm}$$

with

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



# PAW - Outline

## At a glance

### What do we need

- A basis suitable to develop “smooth” auxiliary wave-functions
- A set of atomic orbitals
- A basis of pseudo-orbitals and the associated projectors
- A pseudo-potential

*Plane waves*

### Approximations

- The core electrons are frozen (“frozen-core”) *controlled*
- The plane-wave basis is truncated *controlled*
- The partial-wave basis is truncated *controlled*

*Note : radius of augmentation regions is not an approximation*

*At basis completeness, results are independent of it*





# PAW - Outline

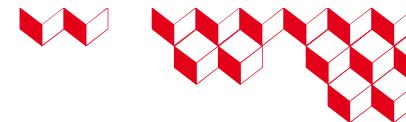
Advantages  
Drawbacks

## Pro

- The “exact” density is computed; we have access to the “nodal” wave functions
  - high transferability (especially for magnetic systems)
  - properties depending on the density near the nucleus are accessible (ex. NMR)
- The size of the plane-wave basis is equivalent to “ultra-soft” pseudo-potentials (no norm constraint)
- The PAW method is as accurate as an “all-electron” method;  
Convergence can be easily controlled
- We have access to a local information around atoms  
(a “local PAW approximation” can be used ; see later)

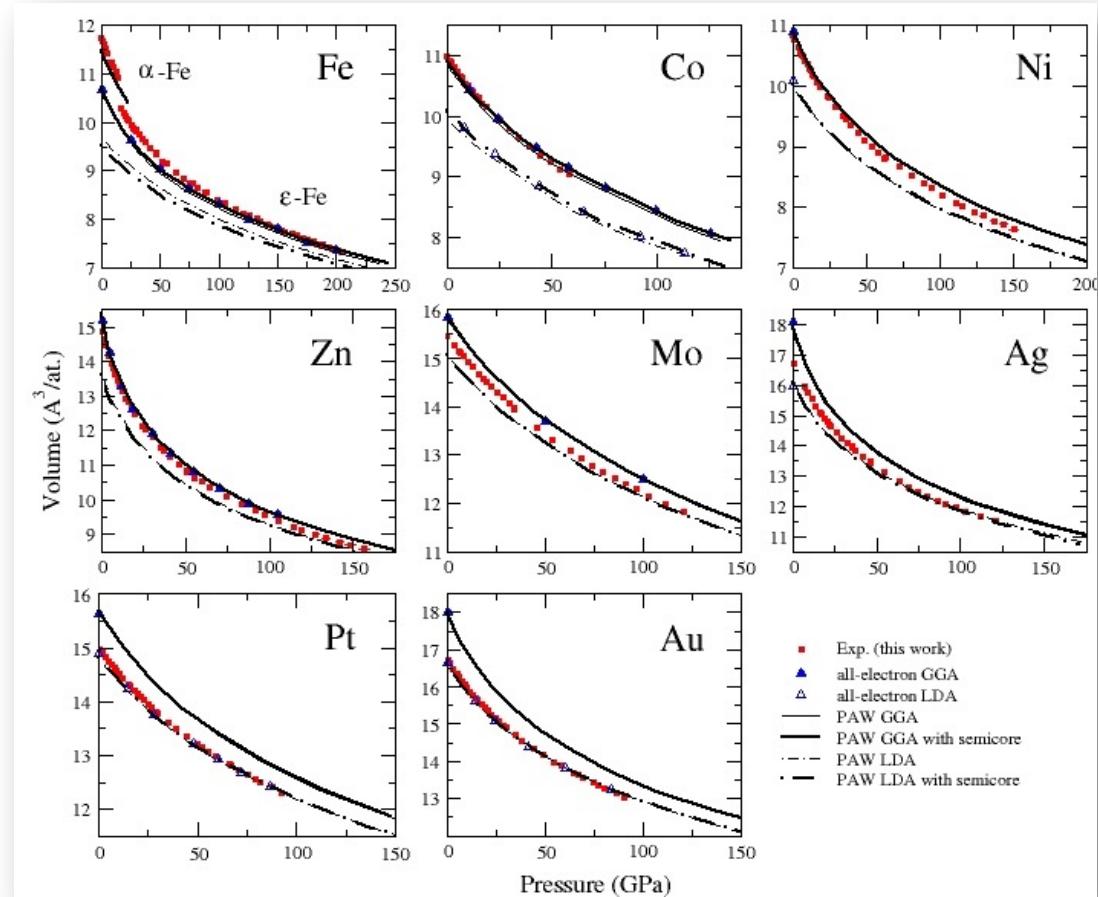
## Con

- Need more developments comparing to “pure” pseudo-potential formalism



# PAW - Example

## Transition metals

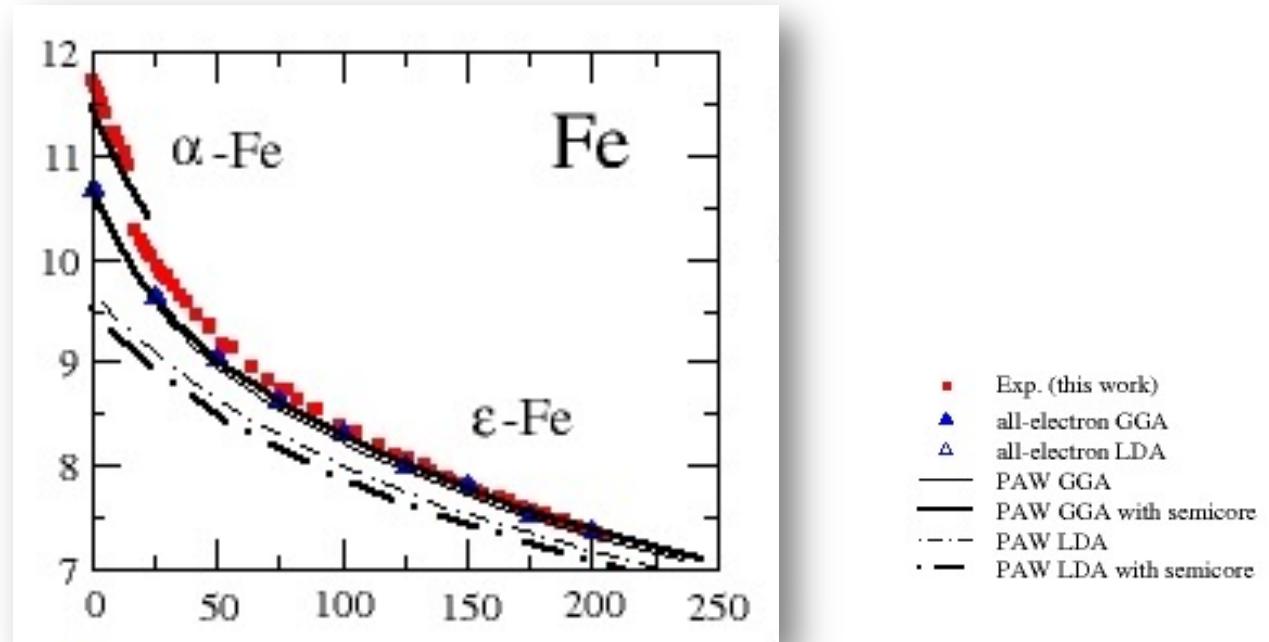


Dewaele, Torrent, Loubeyre, Mezouar, PRB 78, 104102 (2008)



# PAW - Example

## Iron



Dewaele, Torrent, Loubeyre, Mezouar, PRB 78, 104102 (2008)



# PAW – Advanced application

## An example needing the accuracy of PAW

### Electric field Gradient

$$V_{\alpha\beta}(\mathbf{R}, n) = \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \int \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}|} d\mathbf{r}$$

$$\begin{aligned} n(\mathbf{r}) &= n_Z(\mathbf{r}) + n_c(\mathbf{r}) + \tilde{n}(\mathbf{r}) \\ &+ \sum_R (n_1^R(\mathbf{r}) - \tilde{n}_1^R(\mathbf{r})) \end{aligned}$$

$$\begin{aligned} V_{\alpha\beta}(\mathbf{R}, n) &= V_{\alpha\beta}(\mathbf{R}, n_Z + n_c) + V_{\alpha\beta}(\mathbf{R}, \tilde{n}) \\ &+ \sum_R (V_{\alpha\beta}(\mathbf{R}, n_1^R - \tilde{n}_1^R)) \end{aligned}$$

*Mandatory to get correct results*

Zwanziger, Torrent, Appl. Magn.  
Reson. 33, 447 (2008)

**Table 1.** Quadrupole couplings and asymmetries for a variety of structures, obtained by ab initio calculations and comparison with experiment (see references for experimental details).

| Sample                            | Nucleus          | $C_Q$ (MHz) | $\eta$ | $C_{Q\text{exp}}$ (MHz) | $\eta_{\text{exp}}$ |
|-----------------------------------|------------------|-------------|--------|-------------------------|---------------------|
| Ti metal                          | $^{47}\text{Ti}$ | 9.375       | 0.0    | 11.46 [18]              | 0.0                 |
| Zn metal                          | $^{67}\text{Zn}$ | 12.514      | 0.0    | 12.34 [19]              | 0.0                 |
| $\text{CdI}_2$                    | $^{127}\text{I}$ | 91.656      | 0.0    | 97.6 [20]               | 0.0                 |
| $\text{LiNbO}_3$                  | $^7\text{Li}$    | 0.060       | 0.0    |                         |                     |
|                                   | $^{17}\text{O}$  | 1.669       | 0.81   |                         |                     |
|                                   | $^{93}\text{Nb}$ | 20.175      | 0.0    | 22.1 [21]               |                     |
| $\text{SiO}_2$ (quartz)           | $^{17}\text{O}$  | 5.278       | 0.210  | 5.19 [5]                | 0.19                |
| $\text{SiO}_2$ (stishovite)       |                  | 6.511       | 0.119  | $6.5 \pm 0.1$ [22]      | $0.13 \pm 0.05$     |
| $\text{SiO}_2$ (low cristobalite) |                  | 5.235       | 0.147  | $5.3 \pm 0.1$ [22]      | $0.125 \pm 0.005$   |

**Table 2.** EFGs in atomic units for atomic ions in the presence of an imposed external quadrupole electric field of 0.008 atomic units. The EFGs were computed with DFT using the PBE exchange and correlation functional [12] using the Sadlej pVTZ basis.

| Ion              | $V_{zz}$ (atomic units) | Error, rigid core (%) | Core-valence gap (atomic units) |
|------------------|-------------------------|-----------------------|---------------------------------|
| $\text{F}^-$     | -0.430                  |                       | 23.2                            |
| $\text{F}^{7+}$  | 0.000                   | 0.00%                 | 6.29                            |
| $\text{Cl}^-$    | -1.867                  |                       | 1.77                            |
| $\text{Cl}^{7+}$ | 0.000                   | 0.00%                 | 1.33                            |
| $\text{Br}$      | -3.681                  |                       |                                 |
| $\text{Br}^{7+}$ | -0.055                  | 1.49%                 |                                 |
| $\text{I}^-$     | -10.921                 |                       |                                 |
| $\text{I}^{7+}$  | -0.142                  | 1.20%                 |                                 |

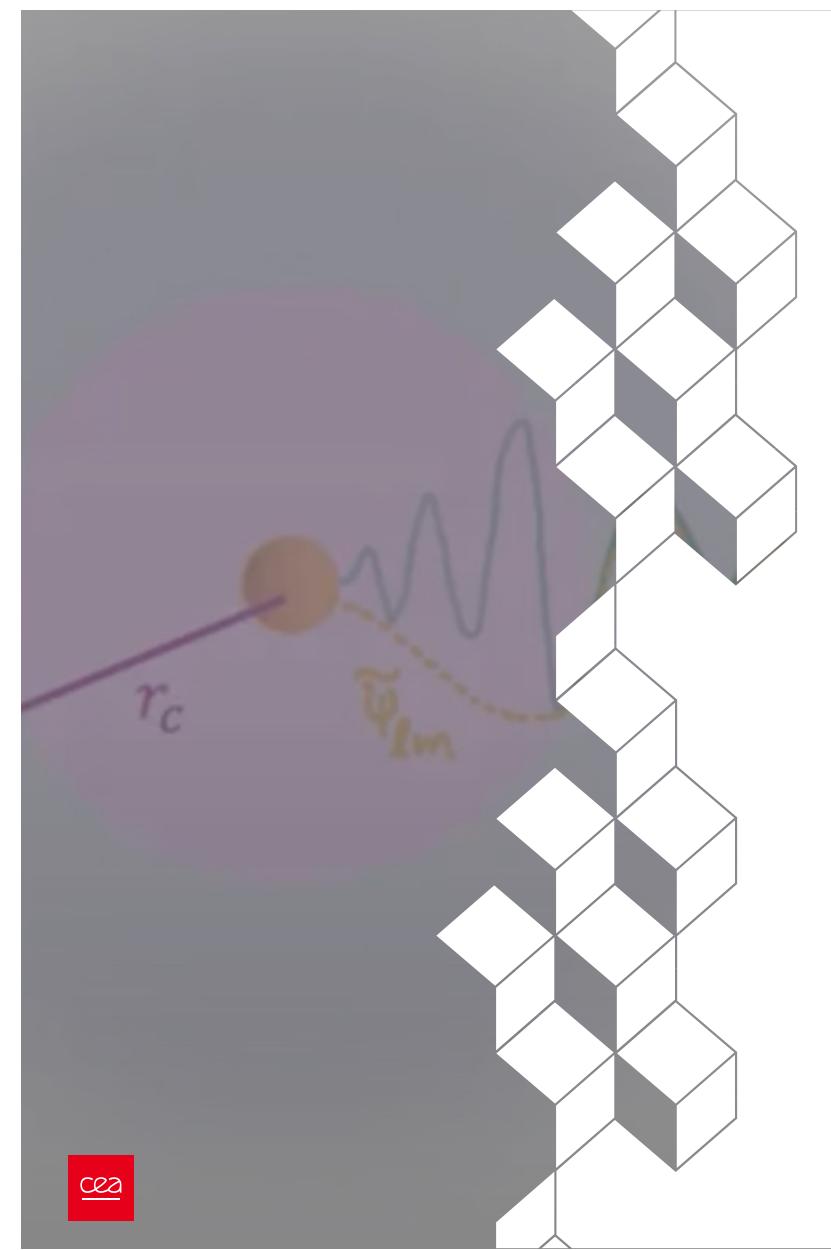


# PAW in ABINIT

## How to

- Use a “PAW atomic dataset” file as “pseudopotential” file.
- Decrease value of plane-wave cut-off energy (wrt norm-conserving psp)
- Give a value for the plane-wave cut-off of the “double grid”  
*(see later)*
- PAW datasets can be downloaded from ABINIT web-site  
for (almost) the whole periodic table
- PAW datasets can be generated “on-demand” with **ATOMPAW** tool

*ABINIT keyword*  
**pawecutdg**



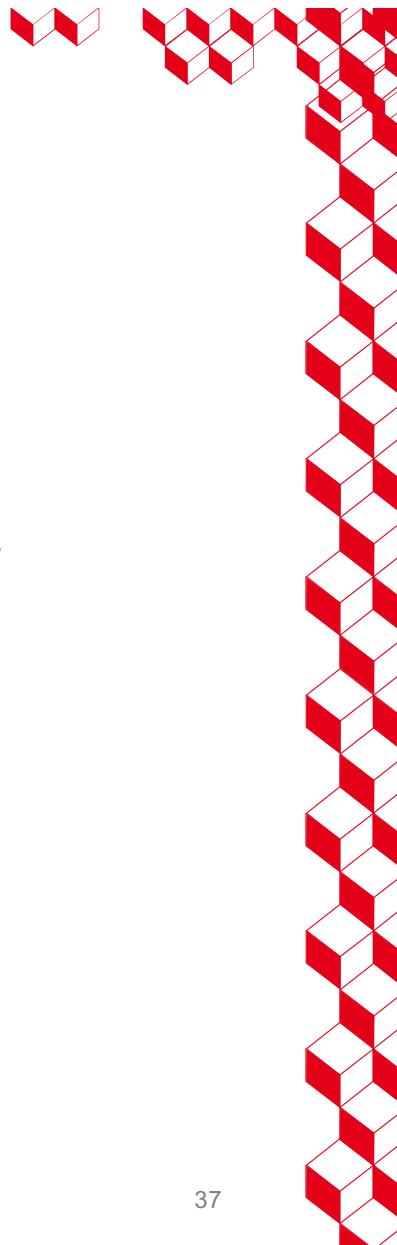
# PAW

*In deep*

*Advanced concepts*

*More about*

# Outline



## About partial waves basis

- Basis completeness
- PAW datasets

## Advanced concepts

- Hartree energy, charge compensation density
- Details on PAW Hamiltonian
- Double grid technique
- PAW, ultrasoft PP, norm-conserving PP

## More about PAW

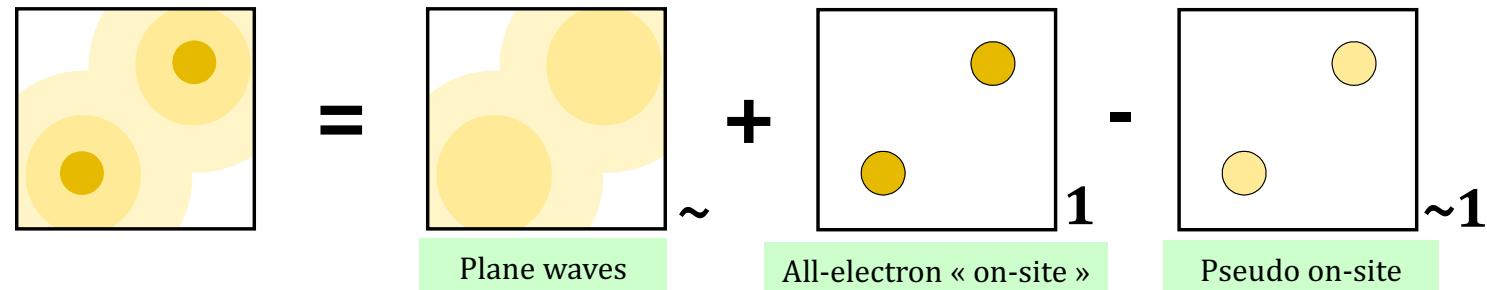
- Derivatives of energy, DFPT
- Local PAW transformation and applications
- Advanced application



# PAW linear transformation

Again

$$|\psi_n\rangle = \tau |\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i,R} |\phi_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle \quad (1)$$

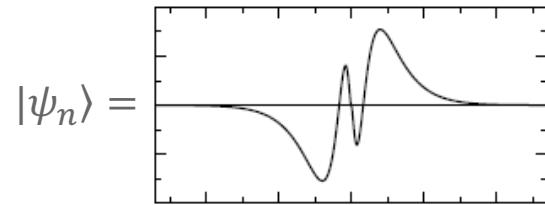




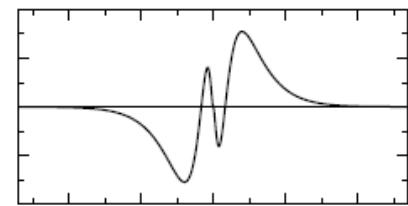
# PAW linear transformation

## How does it operate

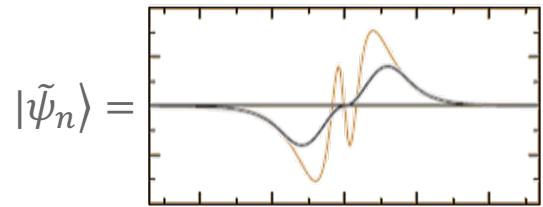
The « exact » wave function is



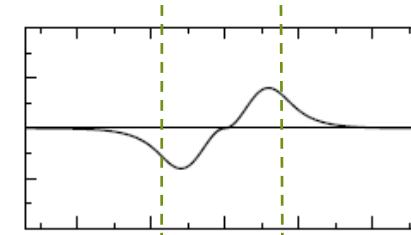
We define an « augmentation region »



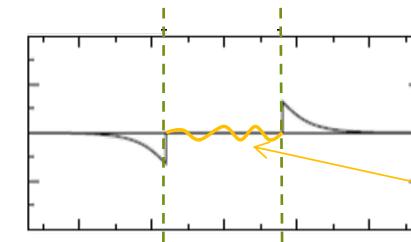
We handle a pseudo wave function



$$|\tilde{\psi}_n\rangle =$$

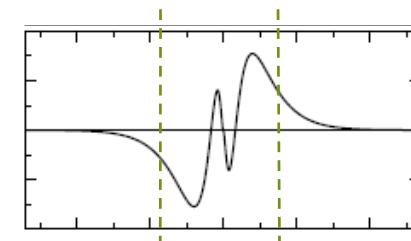


$$|\tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle =$$



If completeness is not perfect

$$|\tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle + \sum_{i,R} |\phi_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n \rangle =$$





# PAW atomic datasets

Stored in a file – See JTH table

A “PAW atomic dataset” contains  $|\phi_i^R\rangle, |\tilde{\phi}_i^R\rangle, |\tilde{p}_i^R\rangle$

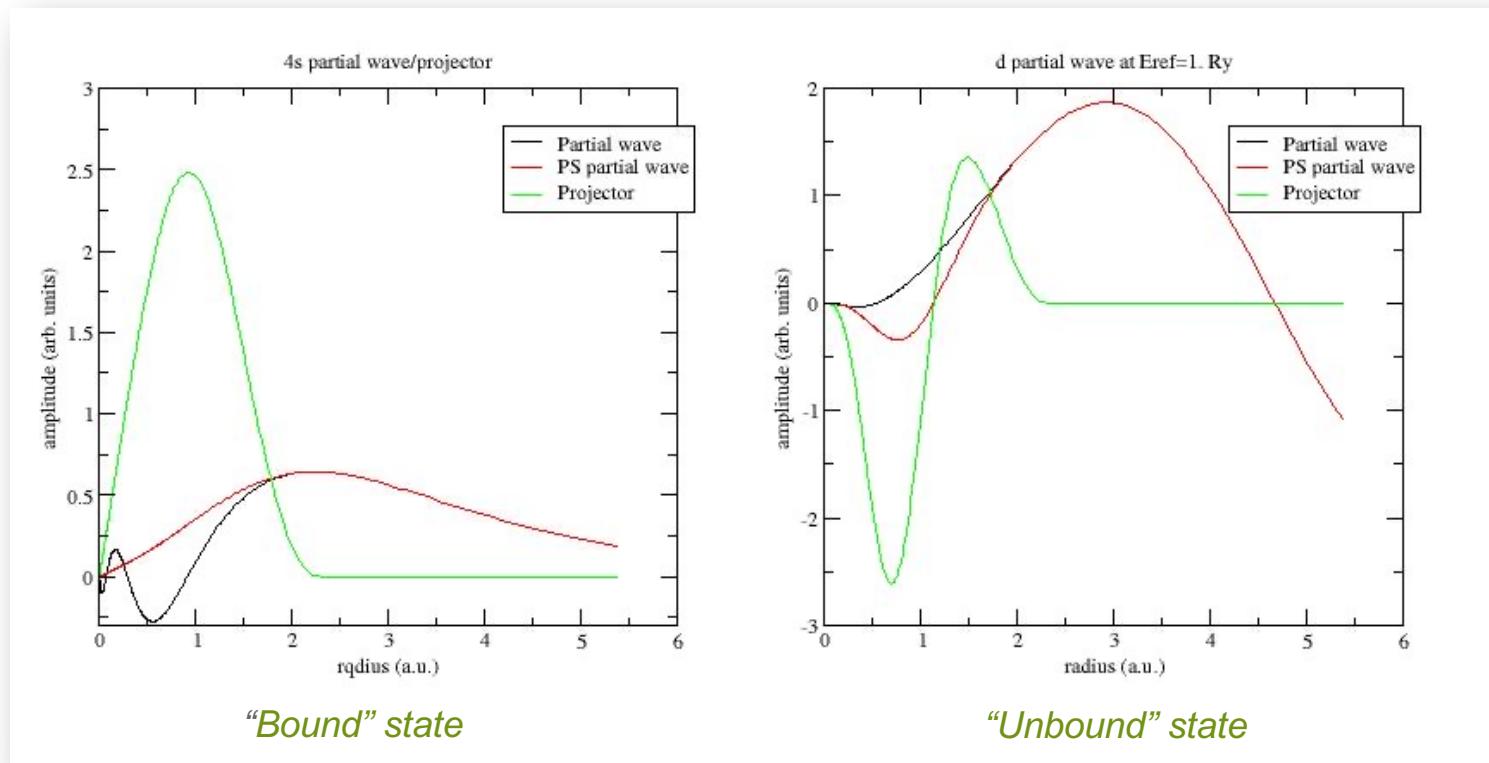
- All useful data concerning the atomic species  
The partial wave basis (atomic orbitals, pseudo-orbitals,  
projectors)  
Used to define the PAW linear transformation
- With PAW atomic datasets, accuracy can be controlled
- With PAW atomic datasets, efficiency can be controlled



# PAW atomic datasets

Partial waves, pseudo partial waves and projectors...

Nickel  $[1s^2 2s^2 2p^6 3s^2 3p^6] 3d^8 4s^2$





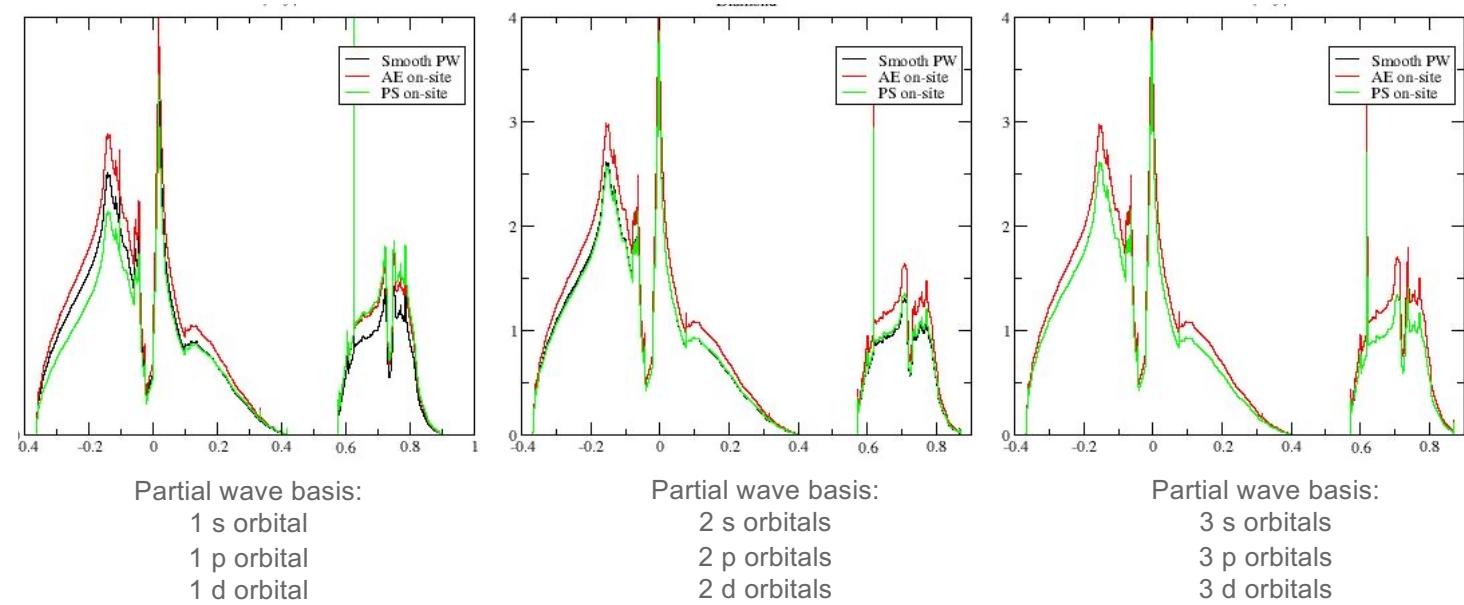
# PAW atomic datasets

## About basis completeness

Evolution of the different contributions to the Density of States (DoS) with respect to the size of the partial wave basis...

$$|\tilde{\psi}_n\rangle = \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle + \sum_{i,R} |\phi_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle$$

*fcc Nickel*





# Compensation charge density

## Norm conservation

- Because of the **loss of norm** during pseudization process, the pseudo-densities  $\tilde{n}$  and  $\tilde{n}_1$  do not have the correct multipoles to allow a correct treatment of long-range electrostatic interaction.

$$V_{Hartree}(\tilde{n}(\mathbf{r})) \not\propto Z/r, \text{ where } Z = \int n(\mathbf{r}) d\mathbf{r}$$

- The computation of the electrostatic potential as sum of 2 terms cannot be achieved easily and converges slowly:

$$V_{Hartree}(\mathbf{r}) = V_{Hartree}(\tilde{n}(\mathbf{r})) + V_{Hartree}(n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}))$$

$\downarrow$   $\downarrow$

*Plane waves: easy* *Slow convergence*



# Compensation charge density

One introduces  $\hat{n}(\mathbf{r})$ , located inside augmentation regions, so that:

- The pseudo density has the same multipoles as the exact density,  
*Doing this, we recover the norm*
- The “on\_site” electrostatic potential vanishes.

$$n(\mathbf{r}) = (\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})) + \sum_R n_1^R(\mathbf{r}) - \underbrace{\left( \sum_R \tilde{n}_1^R(\mathbf{r}) + \hat{n}(\mathbf{r}) \right)}_{V_{Hartree}=0}$$

$\hat{n}(\mathbf{r})$  has to fulfil the multi-pole moment condition:

$$\int_R \hat{n}(\mathbf{r}) \cdot |\mathbf{r} - R| \cdot Y_L(\mathbf{r} - R) \cdot d\mathbf{r} = \int_R (n_1^R - \tilde{n}_1^R)(\mathbf{r}) \cdot |\mathbf{r} - R| \cdot Y_L(\mathbf{r} - R) \cdot d\mathbf{r} = 0$$

and we recover  $V_{Hartree}(\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})) \rightarrow Z/r$



# Compensation charge density

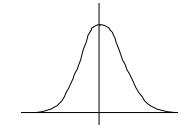
We define:

$$\hat{n}(\mathbf{r}) = \sum_{(i,j),R,L} \rho_{ij}^R \underbrace{q_{ij}^L Y_L(\mathbf{r}-\mathbf{R}) g_L(|\mathbf{r}-\mathbf{R}|)}_{\hat{Q}_{ij}^L(\mathbf{r})}$$

*Norm recovery*

$$q_{ij}^L = \int_R \underbrace{\left[ \phi_i(\mathbf{r})\phi_j(\mathbf{r}) - \tilde{\phi}_i(\mathbf{r})\tilde{\phi}_j(\mathbf{r}) \right]}_{Loss\ of\ norm} |\mathbf{r}-\mathbf{R}|^l \cdot Y_L(\mathbf{r}-\mathbf{R}) \cdot d\mathbf{r}$$

*g : analytical “shape” function*



$$\int_R g_L(r) r^l r^2 dr = 1$$



# **PAW Hartree Energy**

$$n_T = (\tilde{n} + \hat{n}) + (n_1) - (\tilde{n}_1 + \hat{n}) = \tilde{n}_T + n_{T1} - \tilde{n}_{T1} \quad n_1 = \sum_R n_1^R \quad \tilde{n}_1 = \sum_R \tilde{n}_1^R$$

Approximation: in (2),  $\tilde{n}_T$  is replaced by  $\tilde{n}_{T1}$       (*basis completeness is assumed*)

Hartree energy becomes:  $E^H = \frac{1}{2}(\tilde{n}_T)(\tilde{n}_T) - \frac{1}{2}(\tilde{n}_{T1})(\tilde{n}_{T1}) + \frac{1}{2}(n_{T1})(n_{T1})$

$$E^H = \tilde{E}^H - \tilde{E}_1^H + E_1^H = \tilde{E}^H(\tilde{n} + \hat{n}) + \sum_R \left( -\tilde{E}_1^H(\tilde{n}_1^R + \hat{n}) + E_1^H(n_1^R) \right)$$



# PAW Hamiltonian Details

$$\tilde{H} = \frac{dE}{d\tilde{\rho}} = -\frac{1}{2}\Delta + \tilde{v}_{Hxc} + \sum_{i,j} \left| \tilde{p}_i^R \right\rangle D_{ij}^R \left\langle \tilde{p}_j^R \right|$$

$D_{ij}^R$  is the expression of  $\mathbf{H}$  in the partial wave basis:

$$D_{ij}^R = \langle \phi_i^R | -\frac{1}{2}\Delta + v_{Hxc}(n_1^R; n_c) | \phi_i^R \rangle - \langle \tilde{\phi}_j^R | -\frac{1}{2}\Delta + \tilde{v}_{Hxc}(\tilde{n}_1^R; \tilde{n}_c) | \tilde{\phi}_j^R \rangle$$

Example of a formal calculation:

$$\begin{aligned}
 \langle \phi_i | v_H(n^1) | \phi_j \rangle &= \iint_R \phi_i^*(r) \frac{n^1(r)}{|r-r'|} \phi_j(r') dr dr' \\
 &= \iint_R \frac{\phi_i(r)}{r} S_{l_i m_i}(\hat{r}) \left( \sum_{i' j'} \rho_{i' j'} \frac{\phi_{i'}(r')}{r'} S_{l_{i'} m_{i'}}(\hat{r}') \frac{\phi_{j'}(r')}{r'} S_{l_{j'} m_{j'}}(\hat{r}') \right) \left( \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} S_{lm}(\hat{r}) S_{lm}(\hat{r}') \right) \frac{\phi_j(r)}{r} S_{l_j m_j}(\hat{r}) r^2 dr d\Omega r'^2 dr' d\Omega' \\
 &= \sum_l \sum_m \sum_{i' j'} \rho_{i' j'} R G_{l_i m_i, l_{i'} m_{i'}}^{lm} R G_{l_{i'} m_{i'}, l_{j'} m_{j'}}^{lm} V_{l_i, l_{i'}, l_{j'}}^l
 \end{aligned}$$

Spherical harmonics

Gaunt coefficient

with  $V_{l_i, l_{i'}, l_{j'}}^l = \int_0^R \int_0^R \frac{4\pi}{2l+1} \phi_{l_i}(r) \phi_{l_{i'}}(r') \phi_{l_{j'}}(r') \frac{r_{<}^l}{r_{>}^{l+1}} dr dr'$



# PAW Hamiltonian Details

This leads to:

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

|        |         |                      |                     |
|--------|---------|----------------------|---------------------|
| atomic | Hartree | Exchange-correlation | Charge compensation |
|--------|---------|----------------------|---------------------|

$\tilde{v}_{eff}(\mathbf{r})$  is a "local" potential:

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

|                          |                  |
|--------------------------|------------------|
| <i>Nucleus+electrons</i> | <i>Electrons</i> |
|--------------------------|------------------|

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





# PAW Hamiltonian XC potential

All on-site quantities, including potentials,

can be expanded over "real spherical harmonics":  $n_1(r, \theta, \varphi) = \sum_{LM} n_{LM}(r) S_{LM}(\theta, \varphi)$

In the case of the XC potential, it is possible to use a Taylor series around the spherical density:

*This is a very good approximation  
This is computationally efficient*

$$v_{xc}(r, \theta, \varphi) = \sum_{LM} v_{LM}^{xc}(r) Y_{LM}(\theta, \varphi) = v_{xc}[n_0(\vec{r})] + [n(\vec{r}) - n_0(\vec{r})] \frac{dv_{xc}}{dn}[n_0] + \frac{[n(\vec{r}) - n_0(\vec{r})]^2}{2} \frac{d^2v_{xc}}{dn^2}[n_0]$$

↓  
*Direct computation  
on spherical grid*

*Accurate  
CPU expensive*

OR

↓  
*Development in moments*

*Approximated*

*ABINIT keyword  
pawxcdev*



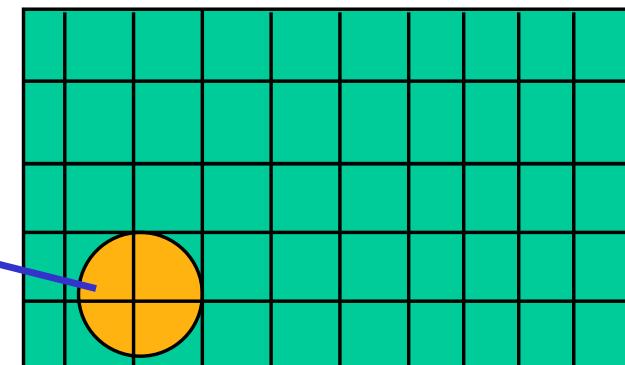
*ABINIT keyword  
pawecutdg*

# Double grid technique

## Interpolation

- A « coarse » FFT grid is used to represent PS wave-functions
- The compensation charge is needed on the FFT grid (regular grid) and on the grid used to describe augmentation regions (radial grid)
- For accuracy, an auxiliary fine FFT grid is used to compute densities and potentials

*If only the « coarse » FFT grid is used, not enough points are in augmentation regions*



« Double FFT » technique used to transfer densities/potentials between grids:

$$\tilde{n}_{coarse}(\vec{r}) \xrightarrow{\text{FFT}} \tilde{n}_{coarse}(\vec{G}) \longrightarrow \tilde{n}_{fine}(\vec{G}) \xrightarrow{\text{FFT}} \tilde{n}_{fine}(\vec{r})$$



# PAW vs pseudopotentials

$$\tilde{H} = \frac{dE}{d\tilde{\rho}} = -\frac{1}{2}\Delta + \tilde{v}_{eff} + \sum_{i,j} \left| \tilde{p}_i^R \right\rangle D_{ij}^R \left\langle \tilde{p}_j^R \right| \quad D_{ij} = D_{ij}^0 + \sum_{kl} \rho_{kl} E_{ijkl} + D_{ij}^{xc} + \sum_L \int \tilde{v}_{eff}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}$$

## From PAW to *ultrasoft* pseudo-potentials

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

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

## From PAW to *norm-conserving* pseudo-potentials

The norm of partial waves is equal to the norm of pseudo partial waves  $\hat{Q}_{i,j}^L(\mathbf{r}) = 0$

$$D_{ij} = D_{ij}^{0,KB}$$

*Norm-conserving pseudopotential formulation*



# PAW – Derivatives of the energy

## Forces, stress tensor

*Hellmann-Feynman theorem*

*First derivative of energy*

$$\frac{dE}{d\lambda} = \sum_n f_n \langle \psi_n | \frac{\partial \tilde{H}}{\partial \lambda} \Big|_{V_{Hxc}^{(0)}} | \psi_n \rangle$$

$$E = \tilde{E} + \sum_R \left( E_1^R - \tilde{E}_1^R \right)$$

- In this term, the non-local contribution is self-consistent (depends on  $V_{Hxc}$ )
- These terms are new, *but they are attached to the atomic sites*



# PAW – Derivatives of the energy

## Forces, stress tensor

In grey:  
norm-conserving psp terms

$$\begin{aligned} F_R = & - \int (\tilde{n} + \hat{n})(r) \frac{\partial v_H(\tilde{n}_{Zc})}{\partial R} dr - \int v_{xc} [\tilde{n} + \tilde{n}_c] \frac{\partial \tilde{n}_c}{\partial R} dr \\ & - \sum_{R,i,j,L} \rho_{ij}^R \int \tilde{v}_{eff}(r) \frac{\partial \hat{Q}_{ij}^L}{\partial R} dr - \sum_{R,i,j} \sum_n \langle \tilde{\psi}_n | \frac{\partial (D_{ij}^R - \epsilon_n S_{ij}^R)}{\partial R} | \tilde{\psi}_n \rangle \end{aligned}$$

$$\begin{aligned} \sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{\partial E}{\partial \epsilon_{\alpha\beta}} = & \sigma^{Kin} + \sigma^{Ewald} + \sigma^{Hxc}(\tilde{n} + \hat{n}; \tilde{n}_c) + \frac{1}{\Omega} \int (\tilde{n} + \hat{n})(r) \frac{\partial v_H(\tilde{n}_{Zc})}{\partial \epsilon_{\alpha\beta}} dr \\ & + \frac{1}{\Omega} \delta_{\alpha\beta} \int v_{xc} [\tilde{n} + \tilde{n}_c] \tilde{n}_c dr + \frac{1}{\Omega} \int v_{xc} [\tilde{n} + \tilde{n}_c] \frac{\partial \tilde{n}_c}{\partial \epsilon_{\alpha\beta}} dr \\ & + \frac{1}{\Omega} \delta_{\alpha\beta} \int \tilde{v}_{eff}(r) \hat{n}(r) dr + \frac{1}{\Omega} \sum_{R,i,j,L} \rho_{ij}^R \int \tilde{v}_{eff}(r) \frac{\partial \hat{Q}_{ij}^L}{\partial \epsilon_{\alpha\beta}} dr \\ & + \frac{1}{\Omega} \sum_{R,i,j} \sum_n \langle \tilde{\psi}_n | \frac{\partial (D_{ij}^R - \epsilon_n S_{ij}^R)}{\partial \epsilon_{\alpha\beta}} | \tilde{\psi}_n \rangle \end{aligned}$$

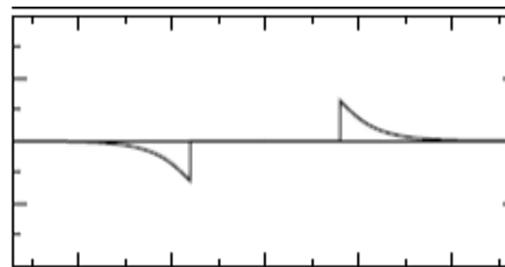


# PAW – Local transformation

## APPROXIMATION 1

The plane-wave and the partial wave basis are complete

$$|\tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle =$$



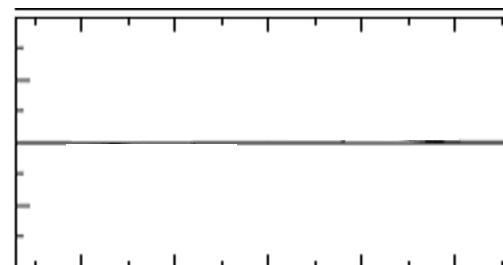
= zero

*inside* augmentation regions

## APPROXIMATION 2

The main part of the density is contained inside PAW augmentation regions

$$|\tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle =$$



= zero

*outside* augmentation regions



# PAW – Local transformation

If the two previous approximations are valid,  
the PAW transformation

$$|\psi_n\rangle = \tau |\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle + \sum_{i,R} |\phi_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle - \sum_{i,R} |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle$$

Reduces to

$$|\psi_n\rangle = \tau |\tilde{\psi}_n\rangle \approx \sum_{i,R} |\phi_i^R\rangle \langle \tilde{p}_i^R | \tilde{\psi}_n\rangle$$

« Local PAW transformation »



# PAW – Local PAW transformation

## ■ When is it valid ?

- When the plane-wave cut-off energy is large enough
- When the partial wave basis contains enough elements
- When the radius of augmentation regions is large enough
- When the electronic density is localized around the nuclei

## ■ Typical application

- Any properties applying to “correlated electrons”
- Used in ABINIT for LDA+U, for local hybrid XC functionals, ...



# PAW – Local PAW transformation

## Application to DFT+U method

- When the local PAW transformation is valid, any new contribution to the Hamiltonian applies only in “on-site” contributions:

$$\tilde{H} = -\frac{1}{2}\Delta + \tilde{\nu}_{eff} + \sum_{i,j} \left| \tilde{p}_i^R \right\rangle \left( D_{ij} + \Delta D_{ij} \right) \left\langle \tilde{p}_j^R \right|$$
$$D_{ij}^U = \left\langle \phi_i^R \right| \Delta H^U \left| \phi_i^R \right\rangle$$

- Easy to implement !  
No need of specific “PAW datasets”



# PAW in ABINIT – try it!

