

THE « 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)

FIRST PART

PAW BASICS

Before PAW

A bit of history

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

How to combine the best of each world?

The PAW formalism

The PAW approach

The PAW linear transformation

Charge density, Hamiltonian, Energy, ...

Approximations, advantages, ...

How to use PAW in ABINIT

PAW BASICS

Before PAW

A self-consistent set of equations

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

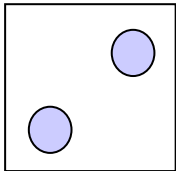
$$\left(-\frac{1}{2}\nabla^2 + V_H[\rho] + V_{xc}[\rho] + V_{ext} + V_{pseudo} \right) |\psi_n\rangle = \epsilon_n |\psi_n\rangle$$

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

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

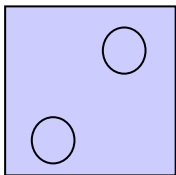
Localized



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

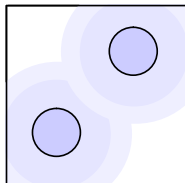
Delocalized



Plane waves, ...

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

Adaptive

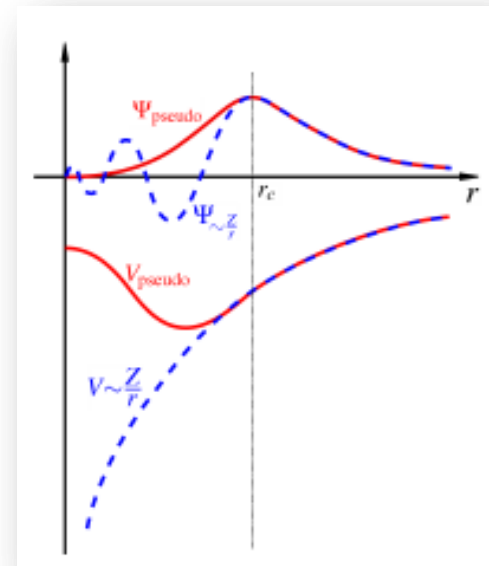


Wavelets, ...

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

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

Separable from...

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

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

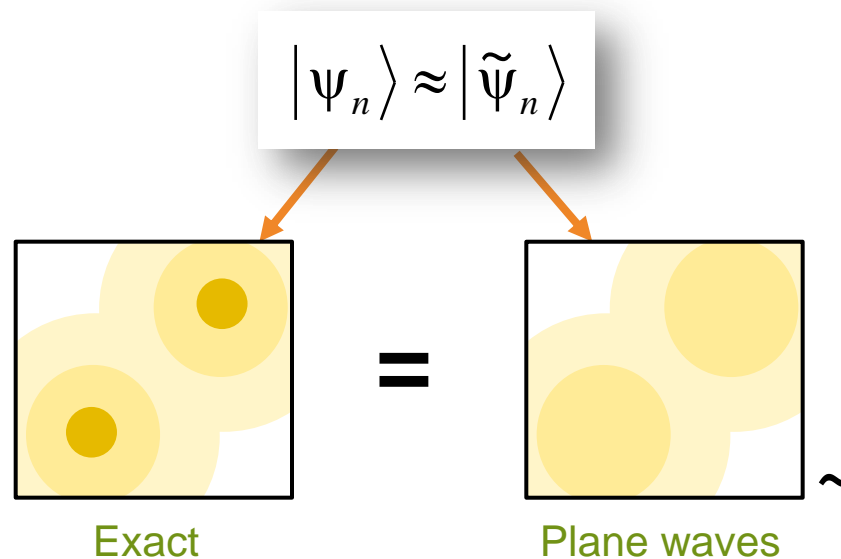
PSEUDOPOTENTIALS AND PLANE WAVES

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

■ $(V^{nucleus} + V^{core\ electrons})$ replaced by \tilde{V}^{PP}

■ Solve: $\tilde{H} |\tilde{\Psi}_n\rangle = \epsilon_n |\tilde{\Psi}_n\rangle$ with: $\tilde{H} = -\frac{1}{2} \Delta + V_{Hartree} + V_{XC} + V_{eff} + \tilde{V}^{PP}$

■ Take $|\tilde{\Psi}_n\rangle$ as a reasonable approximation for $|\Psi_n\rangle$



GOING BEYOND PSEUDOPOTENTIALS ?

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

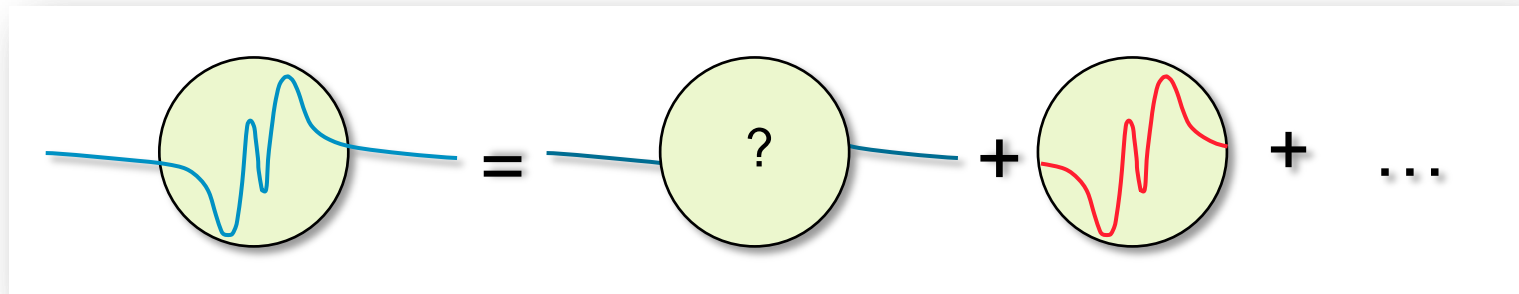
- To use a basis as convenient as possible:
Adapted to charge density and easy to use



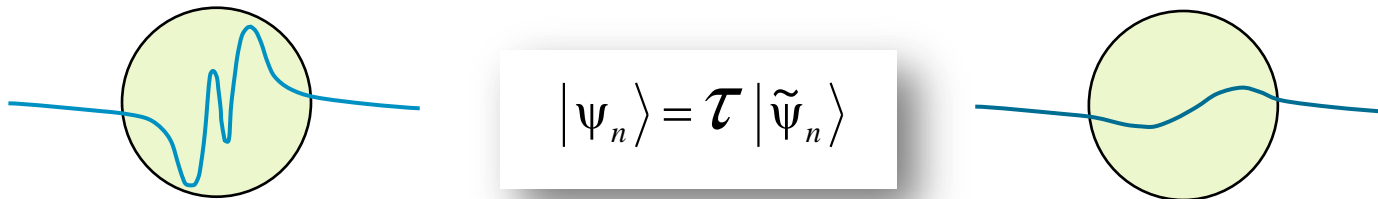
Take advantage of plane waves and localized basis

Treat both rapid oscillations and smooth sections of the wave functions

Use two basis (augmented wave)



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



PAW BASICS

The PAW formalism

Key features of PAW

- 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

THE PAW LINEAR TRANSFORMATION

In search of a linear (and inversible) transformation τ so that

« **Exact** »
wave function

*Strong oscillations
near the nucleus*

*Used to compute
accurate properties*

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

« **Auxilliary** » smooth
wave function

*No oscillation
near the nucleus*

*Manipulated by the DFT code
(SCF cycle)*

Developed on plane waves in ABINIT

- 1- Define non-overlapping spherical regions around atoms **R** (*augmentation regions*)

In search of τ as a sum of local transformations :

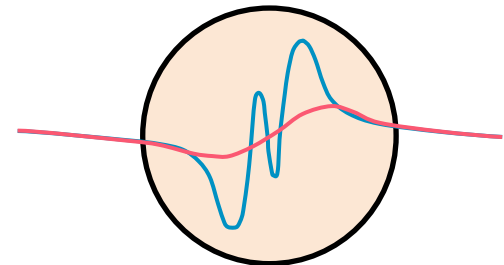
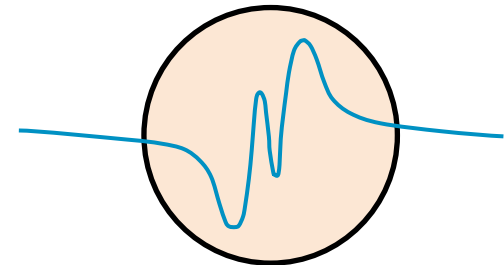
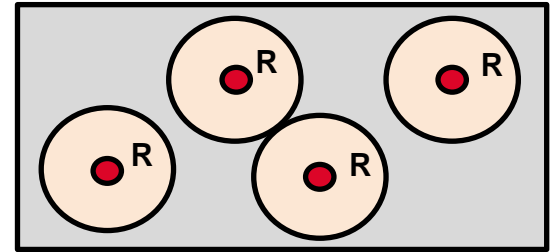
$$\tau = \mathbf{I} + \sum_{\mathbf{R}} S_{\mathbf{R}} \quad |\psi_n\rangle = \tau |\tilde{\psi}_n\rangle = |\tilde{\psi}_n\rangle + \sum_{\mathbf{R}} S_{\mathbf{R}} |\tilde{\psi}_n\rangle$$

- 2- In each augmentation region around **R**, define a partial wave basis $|\phi_i^{\mathbf{R}}\rangle$

A good choice : atomic orbitals
(solutions of atomic Schrödinger equation, in augmentation region)

- 3- For each partial wave, define a « soft » pseudo partial wave basis $|\tilde{\phi}_i^{\mathbf{R}}\rangle$

$|\tilde{\phi}_i^{\mathbf{R}}\rangle$ matches $|\phi_i^{\mathbf{R}}\rangle$ at augmentation region boundary



4- It is easy to obtain an expression of τ applied to $|\tilde{\phi}_i^R\rangle$:

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

$$S_{\mathbf{R}}|\tilde{\phi}_i^R\rangle = (|\phi_i^R\rangle - |\tilde{\phi}_i^R\rangle)$$

5- Let's define the $|\tilde{p}_i^R\rangle$ as duals of $|\tilde{\phi}_i^R\rangle$:

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

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

If the $|\tilde{\phi}_i^R\rangle$ are a complete (non-orthogonal) basis,
the closure relation is:

$$\mathbf{I} = \sum_i |\tilde{\phi}_i^R\rangle \langle \tilde{p}_i^R|$$

6- If the $|\tilde{\phi}_i^R\rangle$ are a complete basis, the wave functions $|\tilde{\psi}_n\rangle$ can be developed as:

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

Then

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

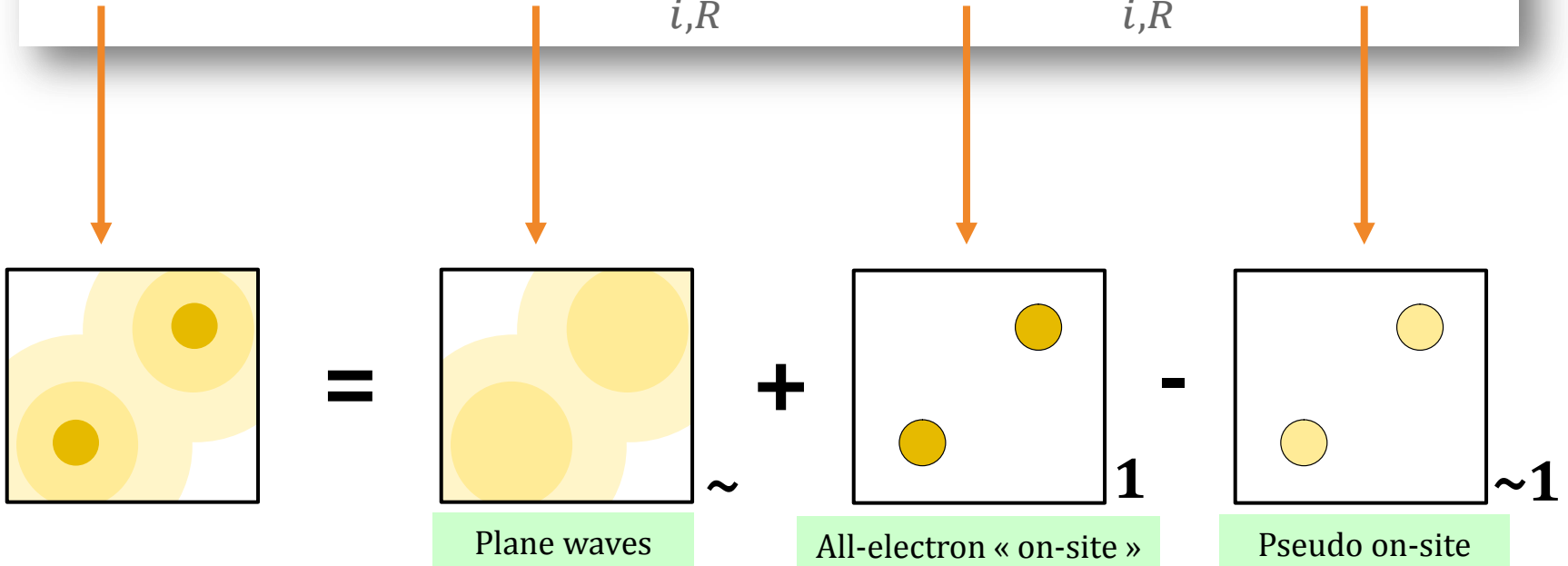
We finally get the expression of the transformation $\boldsymbol{\tau}$:

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

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

THE PAW LINEAR TRANSFORMATION

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



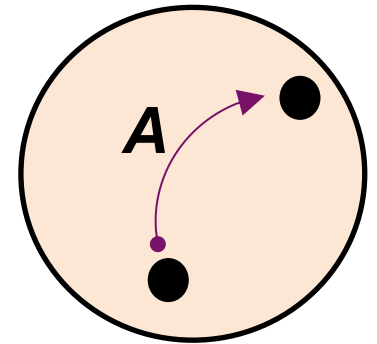
Expectation value of an operator

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

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

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:

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

With
$$\tilde{n} = \sum_n f_n \cdot \tilde{\psi}_n^*(\mathbf{r}) \cdot \tilde{\psi}_n(\mathbf{r})$$

$$n_1^R(\mathbf{r}) = \sum_{i,j} \rho_{ij}^R \cdot \phi_i^*(\mathbf{r}) \cdot \phi_j(\mathbf{r})$$

$$\tilde{n}_1^R(\mathbf{r}) = \sum_{i,j} \rho_{ij}^R \cdot \tilde{\phi}_i^*(\mathbf{r}) \cdot \tilde{\phi}_j(\mathbf{r})$$

Smooth part evaluated on plane wave grid

One-site contributions evaluated on radial grid

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

On-site density matrix

Governs the "on-site" parts

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

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:

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

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

Smooth part

$$E_i^{kin R} = \sum_{i,j} \rho_{ij}^R \cdot \langle \phi_i^R | -\frac{1}{2}\Delta | \phi_i^R \rangle$$

$$\tilde{E}_i^{kin R} = \sum_{i,j} \rho_{ij}^R \cdot \langle \tilde{\phi}_j^R | -\frac{1}{2}\Delta | \tilde{\phi}_j^R \rangle$$

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

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

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

Smooth part evaluated on plane wave grid

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

One-site contributions evaluated on radial grid

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

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

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

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

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

$$\mathbf{H}|\psi_n\rangle = \varepsilon_n|\psi_n\rangle$$

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

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

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

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

becomes:

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

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

become:

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

with

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

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*

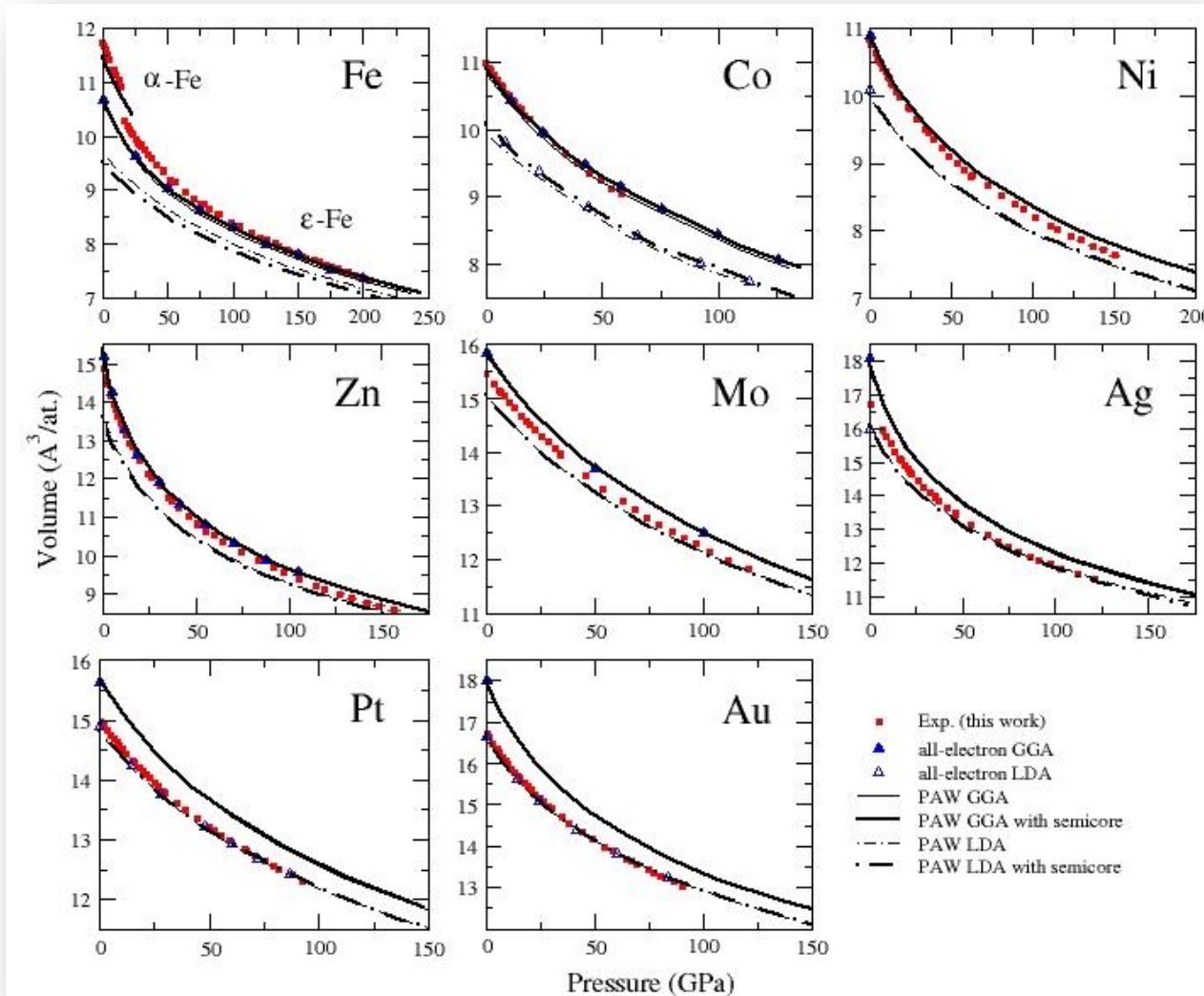
Advantages

- 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)

Drawbacks

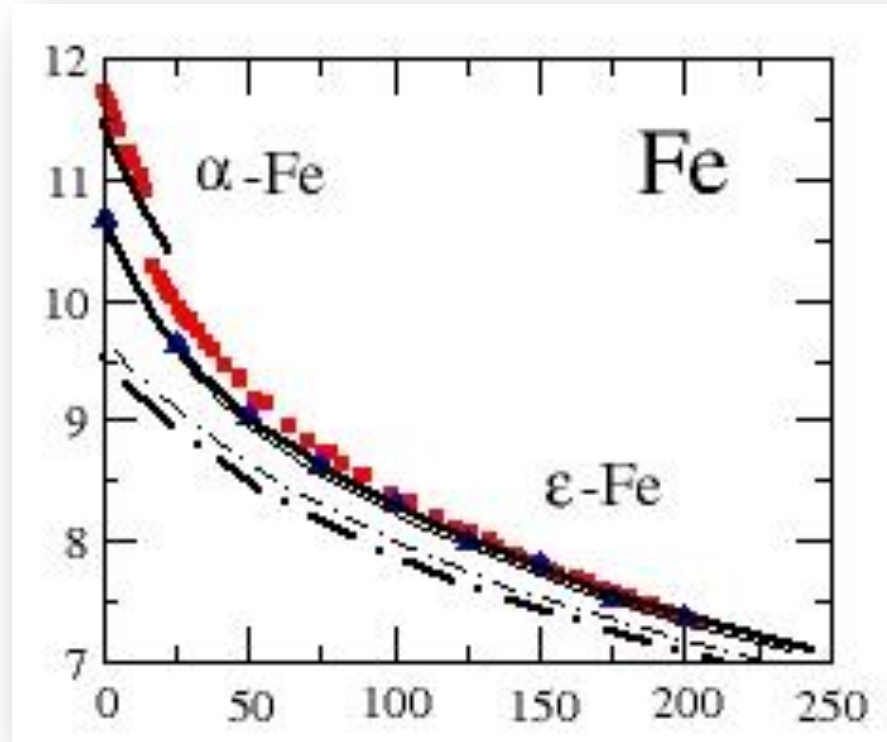
- Need more developments comparing to “pure” pseudo-potential formalism

PAW – RESULTS ON TRANSITION METALS



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

PAW VS ALL-ELECTRON – IRON



- Exp. (this work)
- ▲ all-electron GGA
- △ all-electron LDA
- PAW GGA
- PAW GGA with semicore
- - - PAW LDA
- - - PAW LDA with semicore

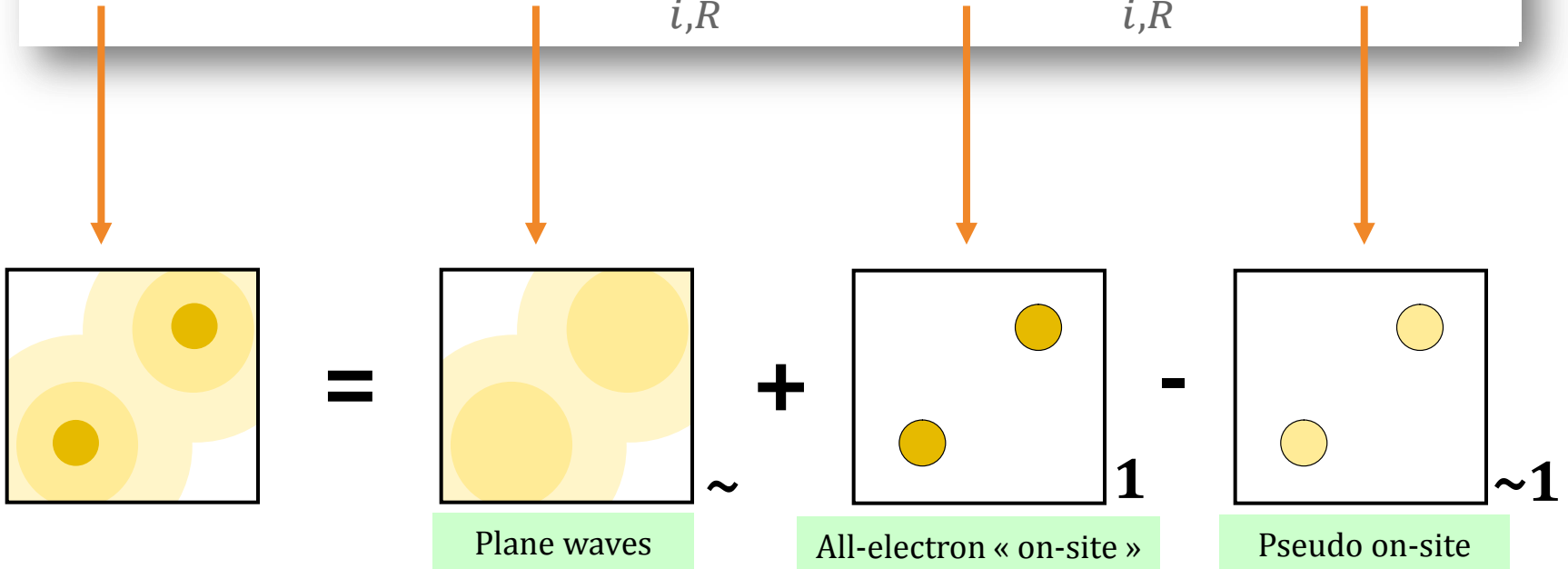
- Use a “PAW atomic dataset” file as “pseudopotential” file.
- Decrease value of plane-wave cut-off energy (wrt norm-conserving psp)
- Give a value for the plane-wave cut-off of the “double grid”
(*see later*)
- PAW datasets can be downloaded from ABINIT web-site for (almost) the whole periodic table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

ABINIT keyword
pawcutdg

SECOND PART

PAW IN DEEP

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



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

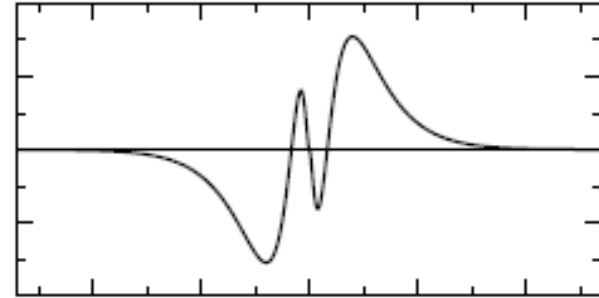
Advanced application

PAW IN DEEP

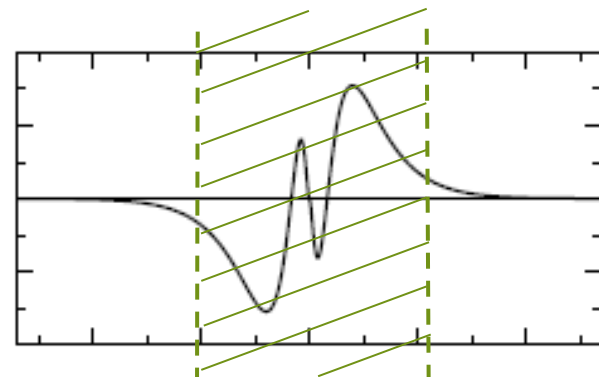
About partial wave basis

The « exact » wave function is

$$|\psi_n\rangle =$$

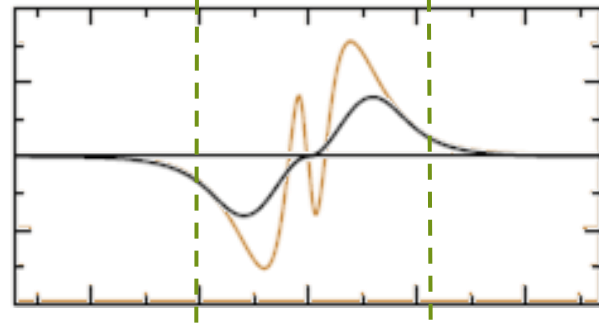


We define an « augmentation region »



In the pseudo-potential formalism, we handle a pseudo wave function

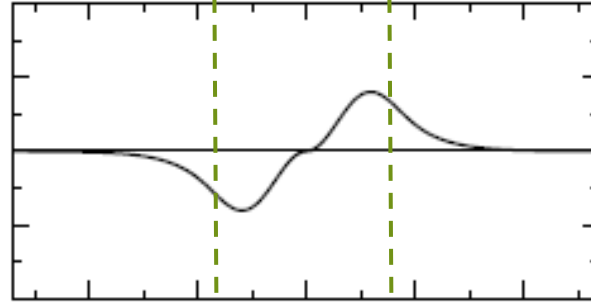
$$|\tilde{\psi}_n\rangle =$$



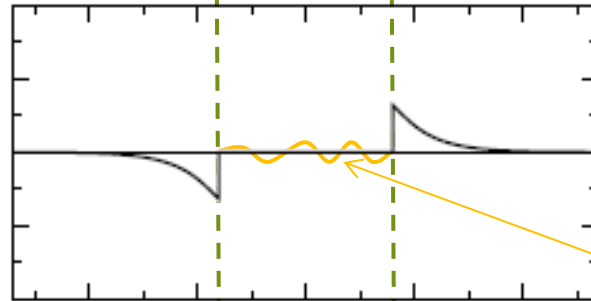
PAW TRANSFORMATION: HOW DOES IT OPERATE ?

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

=



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

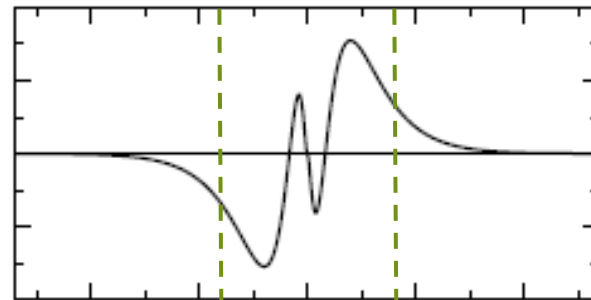


If the partial wave basis and the plane wave basis are complete, $|\tilde{\psi}_n\rangle$ is identical one the two basis inside the augmentation region

If completeness is not perfect

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

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



A “PAW atomic dataset” contains

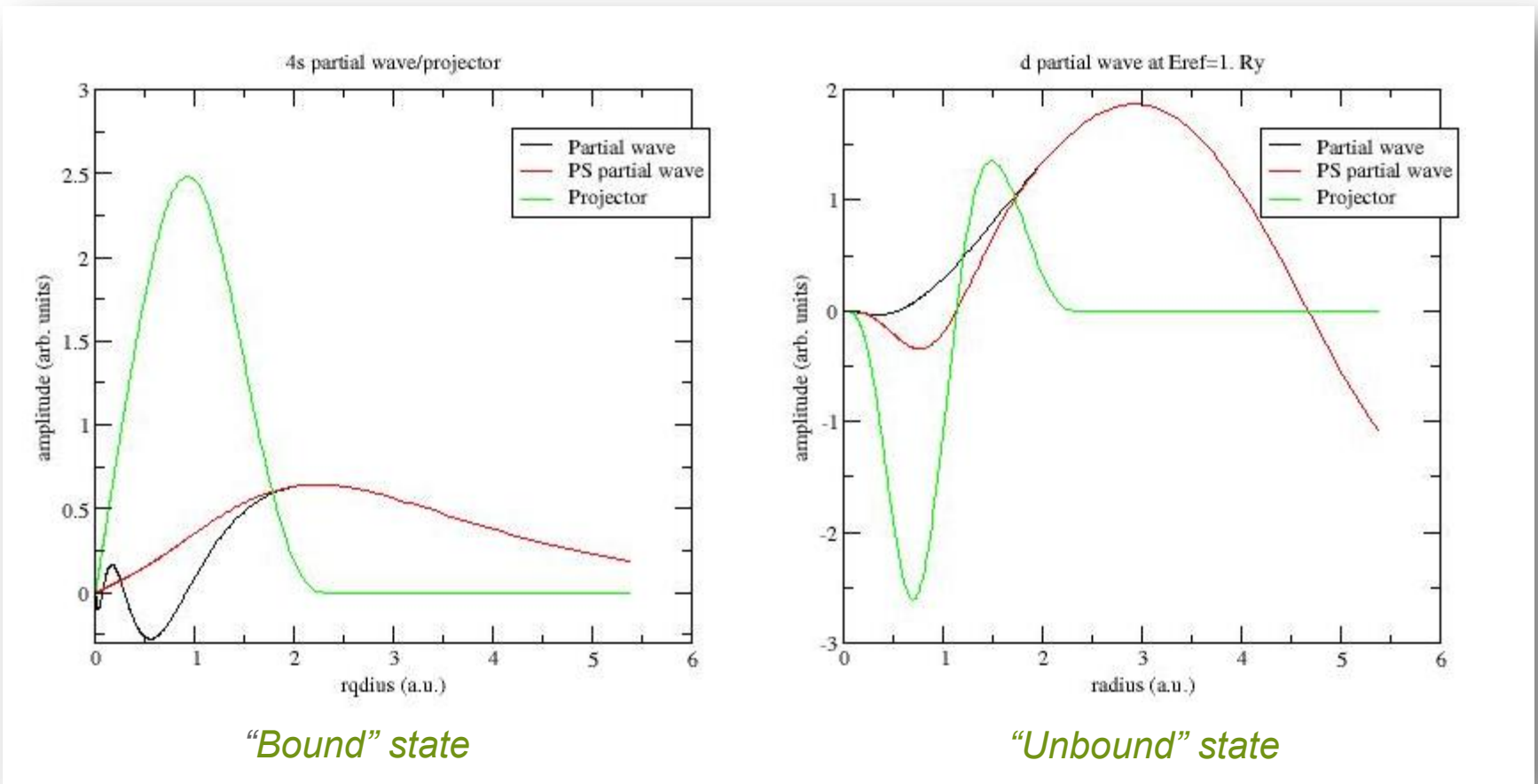
$$|\phi_i^R\rangle, |\tilde{\phi}_i^R\rangle, |\tilde{p}_i^R\rangle$$

- 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

To be developed in the next presentation...

Partial waves, pseudo partial waves and projectors...

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

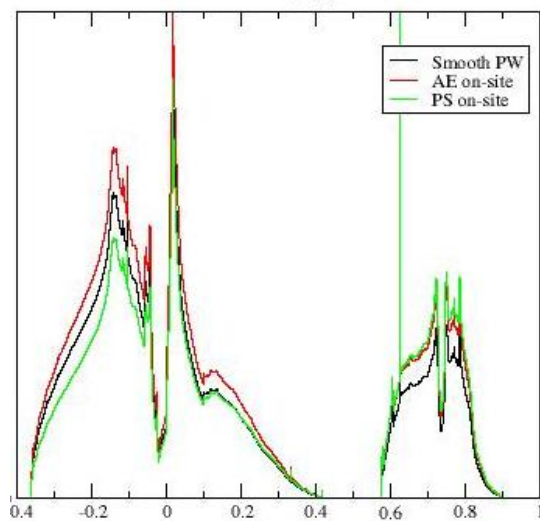


ABOUT THE BASIS COMPLETENESS

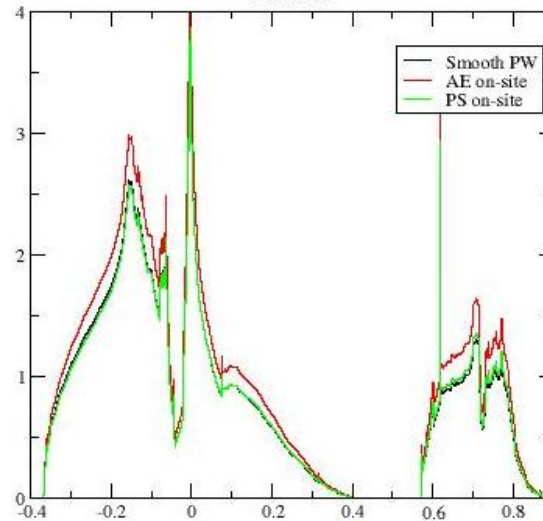
Evolution of the different contributions to the Density of States (DoS) with respect to the size of the partial wave basis...

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

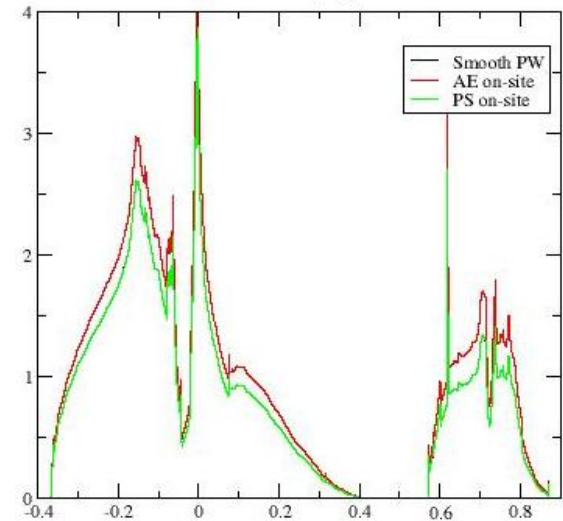
fcc Nickel



Partial wave basis:
1 s orbital
1 p orbital
1 d orbital



Partial wave basis:
2 s orbitals
2 p orbitals
2 d orbitals



Partial wave basis:
3 s orbitals
3 p orbitals
3 d orbitals

PAW IN DEEP

Advanced concepts

12 mai 2014

COMPENSATION CHARGE DENSITY

The electrostatic potential computation faces two difficulties

- 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:

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

↓

Plane waves: easy

↓

Slow convergence

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.

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

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

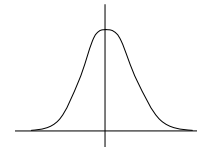
We define:

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

Norm recovery

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

g : analytical “shape” function



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

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

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

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

Example of a formal calculation:

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

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

This leads to:

$$D_{ij} = \underbrace{D_{ij}^0}_{\text{atomic}} + \underbrace{\sum_{kl} \rho_{kl} E_{ijkl}}_{\text{Hartree}} + \underbrace{D_{ij}^{xc}}_{\text{Exchange-correlation}} + \underbrace{\sum_L \int \tilde{v}_{eff}(\mathbf{r}) \hat{Q}_{ij}^L(\mathbf{r}) d\mathbf{r}}_{\text{Charge compensation}}$$

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

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

Nucleus+electrons *Electrons*

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

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

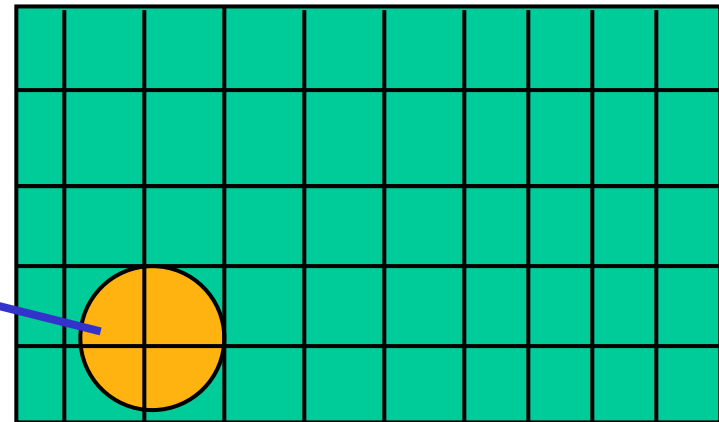
*ABINIT keyword
pawxcdev*

« DOUBLE GRID » TECHNIQUE

ABINIT keyword
pawcutdg

- 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:

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

PAW VS PSEUDOPOTENTIALS

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

■ From PAW to *ultrasoft* pseudo-potentials

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

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

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

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

$$D_{ij} = D_{ij}^{0,KB} \quad \text{Norm-conserving pseudopotential formulation}$$

PAW IN DEEP

More about PAW

DERIVATIVES OF ENERGY

Hellmann-Feynman theorem

First derivative of energy

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

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

- 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*

DERIVATIVES OF E – CHAINS OF DEPENDENCIES

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

Identifying where the WF appear in the energy formula

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

In grey: norm-conserving psp's terms

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

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

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

$$v_{xc}^{ij} = \langle \phi_i | v_{xc} (n_1 + n_c) | \phi_j \rangle$$

$$n_1(\mathbf{r}) = \sum_{i,j} \rho_{ij} \langle \phi_i | \mathbf{r} \rangle \langle \mathbf{r} | \phi_j \rangle$$

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

FORCES AND STRESS TENSOR

$$\mathbf{F}_R = -\int (\tilde{n} + \hat{n})(\mathbf{r}) \frac{\partial v_H(\tilde{n}_{Zc})}{\partial R} d\mathbf{r} - \int v_{xc}[\tilde{n} + \tilde{n}_c] \frac{\partial \tilde{n}_c}{\partial R} d\mathbf{r}$$

$$- \sum_{R,i,j,L} \rho_{ij}^R \int \tilde{v}_{eff}(\mathbf{r}) \frac{\partial \hat{Q}_{ij}^L}{\partial R} d\mathbf{r} - \sum_{R,i,j} \sum_n \langle \tilde{\psi}_n | \frac{\partial (D_{ij}^R - \varepsilon_n S_{ij}^R)}{\partial R} | \tilde{\psi}_n \rangle$$

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \frac{\partial E}{\partial \varepsilon_{\alpha\beta}} = \sigma^{Kin} + \sigma^{Ewald} + \sigma^{Hxc}(\tilde{n} + \hat{n}; \tilde{n}_c) + \frac{1}{\Omega} \int (\tilde{n} + \hat{n})(\mathbf{r}) \frac{\partial v_H(\tilde{n}_{Zc})}{\partial \varepsilon_{\alpha\beta}} d\mathbf{r}$$

$$+ \frac{1}{\Omega} \delta_{\alpha\beta} \int v_{xc}[\tilde{n} + \tilde{n}_c] \tilde{n}_c d\mathbf{r} + \frac{1}{\Omega} \int v_{xc}[\tilde{n} + \tilde{n}_c] \frac{\partial \tilde{n}_c}{\partial \varepsilon_{\alpha\beta}} d\mathbf{r}$$

$$+ \frac{1}{\Omega} \delta_{\alpha\beta} \int \tilde{v}_{eff}(\mathbf{r}) \hat{n}(\mathbf{r}) d\mathbf{r} + \frac{1}{\Omega} \sum_{R,i,j,L} \rho_{ij}^R \int \tilde{v}_{eff}(\mathbf{r}) \frac{\partial \hat{Q}_{ij}^L}{\partial \varepsilon_{\alpha\beta}} d\mathbf{r}$$

$$+ \frac{1}{\Omega} \sum_{R,i,j} \sum_n \langle \tilde{\psi}_n | \frac{\partial (D_{ij}^R - \varepsilon_n S_{ij}^R)}{\partial \varepsilon_{\alpha\beta}} | \tilde{\psi}_n \rangle$$

In grey:
norm-conserving psp terms

We need the Density-Functional Perturbation Theory

$$E^{(i)} = \frac{1}{i!} \left(\frac{d^i}{d\lambda^i} E \right)_{\lambda=0}$$

- 2n+1 theorem (Gonze et al, 1995)

$$E^{(2n+1)} = \left(E \left[\sum_{i=0}^n \lambda^i \psi_m^{(i)}, \lambda \right] \right)^{(2n+1)} \quad \text{Non variational}$$

$$E^{(2n)} = \min_{\psi_{m,trial}^{(n)}} \left(E \left[\sum_{i=0}^{n-1} \lambda^i \psi_m^{(i)} + \lambda^n \psi_{m,trial}^{(n)}, \lambda \right] \right)^{(2n)} \quad \text{Variational}$$

- Sternheimer equation gives first-order wave function
(new terms appear for PAW)

$$P_c^* \left(\tilde{H}^{(0)} - \varepsilon_n^{(0)} S^{(0)} \right) P_c \left| \tilde{\psi}_n^{(1)} \right\rangle = -P_c^* \left(\tilde{H}^{(1)} - \varepsilon_n^{(0)} S^{(1)} \right) \left| \tilde{\psi}_n^{(0)} \right\rangle$$

Just an idea of the complexity of DFPT formula

2nd derivative of non-local energy with respect to displacements of atom \mathbf{a} in α and β directions

$$\chi_{\alpha\beta}^a = \sum_{ij} \left\{ \begin{array}{l} \sum_n (D_{ij}^{KV} - \varepsilon_n s_{ij}) \frac{\partial^2 (\langle \tilde{\psi}_n | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_n \rangle)}{\partial R_\alpha^a \partial R_\beta^a} \\ + \sum_L q_{ij}^L \rho_{ij} \int_{R^3} \left[\tilde{v}_{eff} \frac{\partial^2 (g_L Y_L)}{\partial r_\alpha \partial r_\beta} + \frac{\partial v_H(\tilde{n}_{ZC})}{\partial r_\alpha} \frac{\partial (g_L Y_L)}{\partial r_\beta} + \frac{\partial v_H(\tilde{n}_{ZC})}{\partial r_\beta} \frac{\partial (g_L Y_L)}{\partial r_\alpha} \right] d\mathbf{r} \\ - \sum_L q_{ij}^L \frac{\partial \rho_{ij}}{\partial R_\alpha^a} \int_{R^3} \left[\frac{\partial v_H(\tilde{n}_{ZC})}{\partial r_\beta} g_L Y_L + \tilde{v}_{eff} \frac{\partial (g_L Y_L)}{\partial r_\beta} \right] d\mathbf{r} \\ - \sum_L q_{ij}^L \frac{\partial \rho_{ij}}{\partial R_\beta^a} \int_{R^3} \left[\frac{\partial v_H(\tilde{n}_{ZC})}{\partial r_\alpha} g_L Y_L + \tilde{v}_{eff} \frac{\partial (g_L Y_L)}{\partial r_\alpha} \right] d\mathbf{r} \end{array} \right\}$$

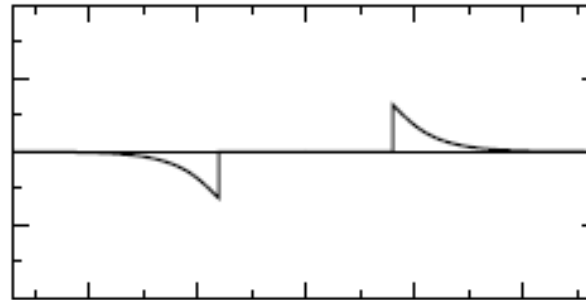
*In grey: norm-conserving
psps terms*

Audouze, Jollet, Torrent, Gonze, Phys. Rev. B **73**, 235101 (2006)
Audouze, Jollet, Torrent, Gonze, Phys. Rev. B **78**, 035105 (2008)

APPROXIMATION 1

The plane-wave and the partial wave basis are complete

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



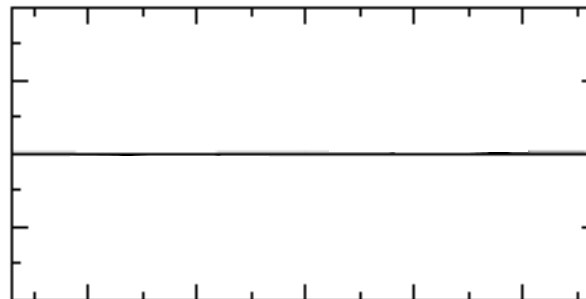
= zero

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

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* »

■ 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, ...

Specific expression for the Hamiltonian

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

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

$$D_{ij}^U = \langle \phi_i^R | \Delta \mathbf{H}^U | \phi_i^R \rangle$$

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

See tomorrow lecture on LDA+U...

An example needing the accuracy of PAW

Electric field Gradient

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

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

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

Mandatory to get correct results

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)	η	$C_{Q\text{exp}}$ (MHz)	η_{exp}
Ti metal	^{47}Ti	9.375	0.0	11.46 [18]	0.0
Zn metal	^{67}Zn	12.514	0.0	12.34 [19]	0.0
CdI_2	^{127}I	91.656	0.0	97.6 [20]	0.0
LiNbO_3	^7Li	0.060	0.0		
	^{17}O	1.669	0.81		
	^{93}Nb	20.175	0.0	22.1 [21]	
SiO_2 (quartz)	^{17}O	5.278	0.210	5.19 [5]	0.19
SiO_2 (stishovite)		6.511	0.119	6.5 ± 0.1 [22]	0.13 ± 0.05
SiO_2 (low cristobalite)		5.235	0.147	5.3 ± 0.1 [22]	0.125 ± 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)
F^-	-0.430		23.2
F^{7+}	0.000	0.00%	
Cl^-	-1.867		6.29
Cl^{7+}	0.000	0.00%	
Br	-3.681		1.77
Br^{7+}	-0.055	1.49%	
I^-	-10.921		1.33
I^{7+}	-0.142	1.20%	



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