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PROJECTOR AUGMENTED-WAVE (PAW) METHOD
IN ELECTRONIC STRUCTURE CALCULATIONS

M. Torrent

Commissariat à l'Energie Atomique
Centre d'Etudes de Bruyères le Châtel

Francois Jollet
Gilles Zerah
Francois Bottin

Summary

- ✓ Introduction:
  DFT formalism - Historical context
- ✓ A linear transformation
- ✓ Calculation of energy/Hamiltonian
- ✓ Building atomic data
- ✓ Examples
- ✓ Remarks/Conclusion

DFT formalism I

Many-Body problem: interacting electrons in an external potential

$$H\Psi = \varepsilon\Psi \qquad H = \frac{dE}{d\rho} = -\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|r_i - r_j|} + H_{nucl}^{kin} + H_{nucl}^{Hartree}$$

Ground state density $n_0(r)$ minimize energy $E[n]$

Honenberg - Kohn

Replaced by…

Independant electrons problem:

$$H\Psi_i = \varepsilon_i\Psi_i \qquad H = \frac{dE}{d\rho} = -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V_{ext}(r) + V_{Hartree}(r) + V_{xc}(r)}_{V_{eff}(r)}$$

Approx.

$$n_0(r) = \sum_i |\Psi_i(r)|^2 \qquad \frac{\delta E}{\delta \Psi_i^*} = 0 \qquad (\Psi_i, \Psi_j) = \delta_{ij}$$

Kohn - Sham

DFT formalism II

Solving *Kohn-Sham* equations:

$$V_{eff}(\mathrm{r}) = V_{ext}(\mathrm{r}) + V_{Hartree}(\mathrm{r}) + V_{xc}(\mathrm{r})$$

$$\mathrm{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\mathrm{r})$$

$$\mathrm{H}\Psi_i = \varepsilon_i \Psi_i$$

$$(\Psi_i, \Psi_j) = \delta_{ij}$$

$$n(\mathrm{r}) = \sum_i |\Psi_i(\mathrm{r})|^2$$

$$E = T[n] + E_{xc}[n] + E_{Hartree}[n]$$

Have to express Ψ_i on a convenient basis…

Some notations

Vector/fonction: $\left|\Psi\right\rangle$

$$\left\langle\Psi\right| \quad : \quad \left|\Phi\right\rangle \xrightarrow{\left\langle\Psi\right|} \left\langle\Psi\middle|\Phi\right\rangle = \int \Psi^*(\mathrm{r})\Phi(\mathrm{r})\,d\,\mathrm{r} \quad \cdots\cdots \quad (\Psi,\Phi)$$

Scalar product

Particular case: $\left|\mathrm{r}\right\rangle \quad : \quad \mathrm{r}' \xrightarrow{\left|\mathrm{r}\right\rangle} \delta(\mathrm{r}-\mathrm{r}')$

$$\left\langle \mathrm{r}\middle|\Psi\right\rangle = \Psi(\mathrm{r})$$

Operator: H $\quad \mathrm{H}\left|\Psi\right\rangle \quad \cdots\cdots \quad \mathrm{H}\,\Psi$

$$\left\langle\Psi_1\middle|\mathrm{H}\middle|\Psi_2\right\rangle \quad \cdots\cdots \quad (\Psi_1,\mathrm{H}\,\Psi_2)$$

Linear operator: $\mathbf{O}_{lin} = \left|\Phi\right\rangle\left\langle\Psi\right|$ *(projection operator)*

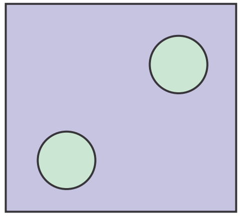
$$\left|\mathrm{r}\right\rangle\left\langle\mathrm{r}\right| \quad : \quad \left\langle\Psi\middle|\mathrm{r}\right\rangle\left\langle\mathrm{r}\middle|\Phi\right\rangle = \Psi(\mathrm{r})\Phi(\mathrm{r})$$

Historical context I

Wave-functions ψ are (generally) developped on a basis which is…

All electrons approach

Localized



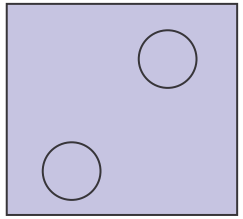
Spherical harmonics + special functions, Gaussian functions,…

All electrons are taken into account

Pb: - The atomic basis is moving with atoms

Pseudopotential approach

Delocalized



Plane waves, …

Only valence electrons are taken into account: core electrons are frozen with nuclueus and represented by a potential

Pseudopotential

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

Historical context II

Pseudopotential approach...

•1979-1982: BHS pseudopotentials (Bachelet,Hamann, Schlüter)

Norm of atomic WF is conserved...

•1982: KB pseudopotentials (Kleinman ,Bylander)

Separable: $V^{PS} = V^{loc}(r) + \sum_l |p_l\rangle E^{KB} \langle p_l|$

•1990: MT pseudopotentials (Martins, Troullier)

Efficient pseudization...

•1991: Ultrasoft pseudopotentials (Vanderbilt)

No more constraint on norm...

•1994: PAW method (Blöchl)

Unified approach...

Historical context: PAW

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

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

- *Develop the solutions of the Kohn-Sham equations on a (plane wave) basis of a minimal size.*
- *Take into regions around atoms where the wave functions vary strongly*
- *Have access to the "true" wave functions and density (not only pseudized ones)*

A linear transformation I

☺ One look for a linear (and inversible) transformation τ so that :

Strong oscillations near the nucleus

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

No oscillation near the nucleus

« True » wave function (all electrons)

Auxilliary wave function (soft pseudofunction)

A linear transformation II

☺ Non-overlapping atomic spheres are defined around atoms ***R*** and one look for:

$$\tau = \mathrm{I} + \sum_R S_R$$

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

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

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

$$S_R\left|\tilde{\phi}_i^R\right\rangle = \left|\phi_i^R\right\rangle - \left|\tilde{\phi}_i^R\right\rangle$$

A linear transformation III

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

$$\left|\tilde{\Psi}_n\right\rangle = \sum_i \left|\tilde{\phi}_i^R\right\rangle \cdot c_i^R \quad \text{in each sphere}$$

$\left\{\left|\tilde{\phi}_i^R\right\rangle\right\}$ *is a non-orthogonal basis*

τ linear implies: c_i^R linear transformation of $\left|\tilde{\Psi}_n\right\rangle$

☺ We define $\left|\tilde{p}_i^R\right\rangle$, named projectors, as duals of the auxiliary functions

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

$$\mathrm{I} = \sum_{R,i} \left|\tilde{\phi}_i^R\right\rangle\left\langle \tilde{p}_i^R\right|$$

It comes:

$$\left|\tilde{\Psi}_n\right\rangle = \sum_{R,i} \left|\tilde{\phi}_i^R\right\rangle \left\langle \tilde{p}_i^R \middle| \tilde{\Psi}_n \right\rangle \qquad \left\langle \tilde{p}_i^R \middle| \tilde{\Psi}_n \right\rangle \rightarrow c_i^R$$

$$S_R\left|\tilde{\Psi}_n\right\rangle = \sum_{R,i} S_R\left|\tilde{\phi}_i^R\right\rangle\left\langle \tilde{p}_i^R \middle| \tilde{\Psi}_n \right\rangle = \sum_{R,i}\left(\left|\tilde{\phi}_i^R\right\rangle - \left|\phi_i^R\right\rangle\right)\left\langle \tilde{p}_i^R \middle| \tilde{\Psi}_n \right\rangle$$

Finally,

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

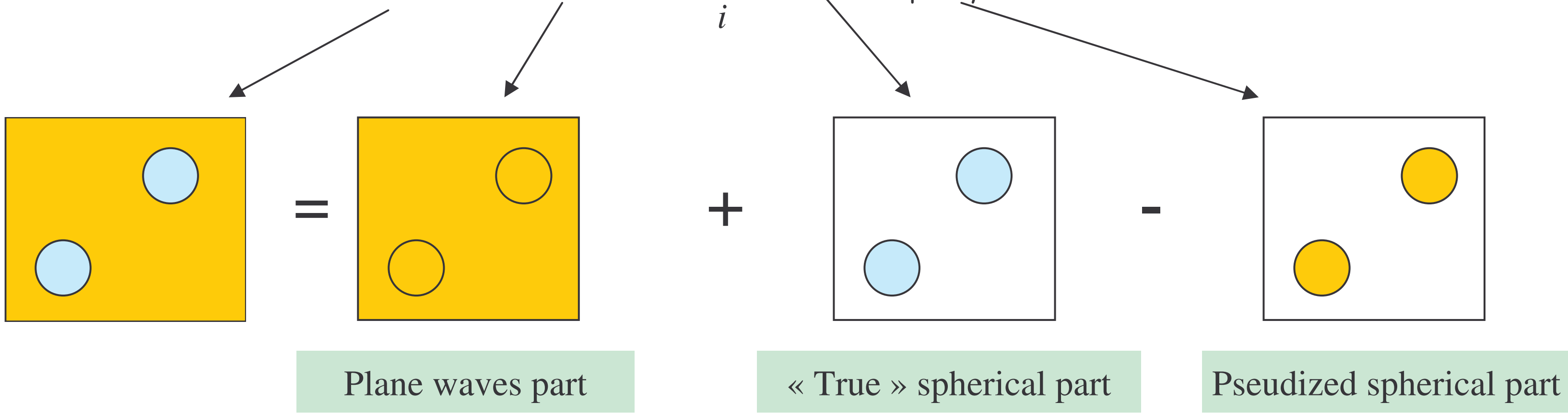
$$\tau = \mathrm{I} + \sum_i \left(\left|\phi_i\right\rangle - \left|\tilde{\phi}_i\right\rangle\right)\left\langle \tilde{p}_i\right|$$

$$i = (R, l, m, n)$$

The PAW method

Wavefunction:

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



Operators:

$$\left\langle A \right\rangle = \sum_n f_n \left\langle \Psi_n \middle| A \middle| \Psi_n \right\rangle = \sum_n f_n \left\langle \tilde{\Psi}_n \middle| \tau^* A \tau \middle| \tilde{\Psi}_n \right\rangle \quad \textbf{(2)}$$

Density:

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

Energy:

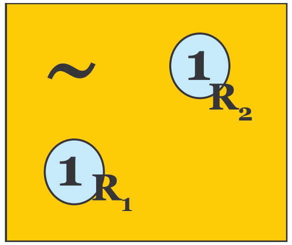
$$E = \tilde{E} + \sum_R \left(E_R^1 - \tilde{E}_R^1 \right)$$

Notations

~ : 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

The general expression of the energy within the DFT formalism is:

$$E = T + E_{Hartree}[n] + E_{xc}[n]$$

Kinetic energy of electrons

$$T = \sum_n f_n \left\langle \Psi_n \middle| -\frac{\Delta}{2} \middle| \Psi_n \right\rangle$$

Hartree energy
(electrostatic)

$$E_{Hartree}[n] = \frac{1}{2} \iint \frac{n(\mathrm{r})n(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|} d\mathrm{r}d\mathrm{r}'$$

Exchange-correlation energy

Approximated: LDA, GGA, …

We have to know density $n(\mathrm{r})$ to determine energy

Calculation of the energy II

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

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_R \left(n_R^1(\mathbf{r}) - \tilde{n}_R^1(\mathbf{r}) \right) \qquad \mathbf{(3)}$$

With

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

Smooth part
evaluated on plane waves grid

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

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

One-center contributions
evaluated on radial grid

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

Governs the spherical part

Using **(2)** and **(3)**, ***E*** can be expressed as a function of $|\tilde{\Psi}_n\rangle$

Calculation of the energy III

Example of the Hartree term

A non linear and non local term

In order to suppress interactions between atoms (expensive to treat)...

Usual trick...

Total density is decomposed as: $n_T = n + n_{Zc} = \underbrace{(\tilde{n} + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}_T} + \underbrace{(n^1 + n_{Zc})}_{n_T^1} - \underbrace{(\tilde{n}^1 + \hat{n} + \tilde{n}_{Zc})}_{\tilde{n}_T^1}$

$\hat{n}(\mathrm{r})$ is **arbitrary density** chosen so that the following multipole moments are zero:

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

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

$$V(\mathrm{r}) = 4\pi \sum_{lm} \frac{M_{lm}(r) Y_{lm}(\hat{r})}{(2l+1) r^{l+1}} = 0, \quad \text{if } r \geq \mathrm{R}$$

As: $Z = \int \underbrace{\tilde{n}(\mathrm{r}) + n^1(\mathrm{r}) - \tilde{n}^1(\mathrm{r})}_{n(r)} \cdot d\,\mathrm{r} = \int \tilde{n}(\mathrm{r}) \cdot d\,\mathrm{r} + \int \hat{n}(\mathrm{r}) \cdot d\,\mathrm{r}$

$\hat{n}(\mathbf{r})$ is called *compensation density*

Calculation of the energy IV

Comment: *Building the compensation density…*

In order to fulfil the multipole moment condition, we define:

$$\hat{n}(\mathrm{r}) = \sum_{ij,lm} \rho_{ij} Q_{ij}^{lm}(\mathrm{r})$$

with

$$Q_{ij}^{lm} = \left\{ \int_R \left[\phi_i^*(\mathrm{r})\phi_j(\mathrm{r}) - \tilde{\phi}_i^*(\mathrm{r})\tilde{\phi}_j(\mathrm{r}) \right] |\mathrm{r}-\mathrm{R}|^l Y_{lm}^*(\mathrm{r}-\mathrm{R}) d\mathrm{r} \right\} \cdot Y_{lm}(\mathrm{r}-\mathrm{R}) \cdot g_l(r-R)$$

$g_l(r)$ localized inside sphere with $\int_R g_l(r) r^l r^2 dr = 1$

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

Calculation of the energy V

Example of the Hartree term –2

$\left(n_T^1 - \tilde{n}_T^1\right)$ only contribute within each augmentation sphere

Goal: no term expressed on two incompatible grids

$$E_{Hartree} = \frac{1}{2}\iint \frac{n_T(\mathbf{r}')n_T(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' d\mathbf{r} = (n_T)(n_T)$$

$$= \underbrace{\frac{1}{2}(\tilde{n}_T)(\tilde{n}_T)}_{(1)} + \underbrace{\left(n_T^1 - \tilde{n}_T^1\right)(\tilde{n}_T)}_{(2)} + \underbrace{\frac{1}{2}\left(n_T^1 - \tilde{n}_T^1\right)\left(n_T^1 - \tilde{n}_T^1\right)}_{(3)}$$

(1) → *On plane waves grid only*

(2) → *Inside spheres only:*
- because of multipole moment condition
- because of little approx.: replace $\tilde{n}_T$ by $\tilde{n}_T^1$

On spherical grid only

(3) → *Inside spheres only*

On spherical grid only

Calculation of the energy VI

Adding the kinetic, lectrostatic and the XC terms:

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

$$\tilde{E} = \sum_n f_n \left\langle \tilde{\Psi}_n \left| -\frac{\Delta}{2} \right| \tilde{\Psi}_n \right\rangle + \tilde{E}_H + \tilde{E}_{xc}$$

$$E_R^1 = \sum_{ij} \rho_{ij}^R \left\langle \phi_i \left| -\frac{\Delta}{2} \right| \phi_i \right\rangle + E_H^1 + E_{\mathrm{xc}}^1$$

$$\tilde{E}_R^1 = \sum_{ij} \rho_{ij}^R \left\langle \tilde{\phi}_i \left| -\frac{\Delta}{2} \right| \tilde{\phi}_i \right\rangle + \tilde{E}_H^1 + \tilde{E}_{\mathrm{xc}}^1$$

Smooth part
evaluated on plane waves grid

One-center contributions
evaluated on radial grid

Calculation of the Hamiltonian I

In order to compute $n(\mathbf{r}) = \sum_n f_n \left|\tilde{\Psi}_n(\mathbf{r})\right|^2 + \sum_{R,ij} \rho_{ij}^R \left(\phi_i(\mathbf{r})\phi_j(\mathbf{r}) - \tilde{\phi}_i(\mathbf{r})\tilde{\phi}_j(\mathbf{r})\right)$

and $\rho_{ij}^R = \sum_n f_n \left\langle \tilde{\Psi}_n \middle| \tilde{p}_i \right\rangle \left\langle \tilde{p}_j \middle| \tilde{\Psi}_n \right\rangle$

we need $\left\{ \left| \tilde{\Psi}_n \right\rangle \right\}$

from

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

$$\mathrm{H}\Psi_n = \varepsilon_n \Psi_n$$

$$\left\langle \Psi_n \middle| \Psi_m \right\rangle = \delta_{nm}$$

$$\tau = \mathrm{I} + \sum_i \left(\left|\phi_i\right\rangle - \left|\tilde{\phi}_i\right\rangle \right) \left\langle \tilde{p}_i \right|$$

Calculation of the Hamiltonian II

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

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

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

$\{ | \tilde{\Psi}_n \rangle \}$ *are variational parameters*

$\tau^* \tau$

We have therefore to solve:

$$\tilde{H} \tilde{\Psi}_n = \varepsilon_n S \tilde{\Psi}_n$$

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

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

Calculation of the Hamiltonian III

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

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

$$D_{ij} = \langle \phi_i | -\frac{\Delta}{2} + v_H[\cdot] + v_{xc}[\cdot] | \phi_j \rangle - \langle \tilde{\phi}_i | -\frac{\Delta}{2} + v_H[\tilde{\cdot}] + v_{xc}[\tilde{\cdot}] | \tilde{\phi}_j \rangle$$
$$+ \sum_L \int \tilde{v}_{eff}(\mathrm{r}) Q_{ij}^L(\mathrm{r}) d\mathrm{r} - \sum_L \int \tilde{v}_{eff}^1(\mathrm{r}) \hat{Q}_{ij}^L(\mathrm{r}) d\mathrm{r}$$

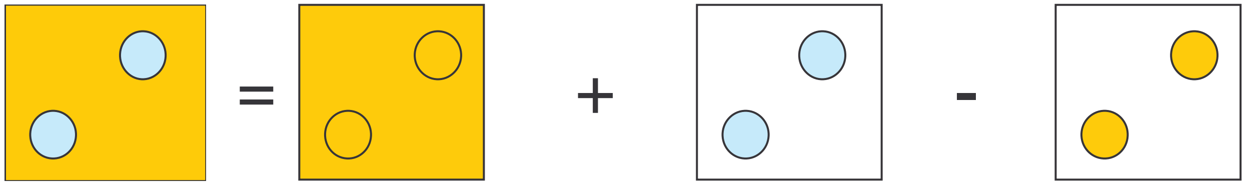
$\tilde{v}_{eff}(\mathrm{r})$ is a local potential

D_{ij} can be written as:

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

Building atomic data for PAW I

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



Hamiltonian: $\tilde{H}\tilde{\psi}_n = \varepsilon_n S\tilde{\psi}_n$

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

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

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

Inside circles: atomic data = frozen quantities during calculation

Building atomic data for PAW II

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

For each atomic specie

$$\left\{\phi_i^R\right\}, \quad \left\{\tilde{\phi}_i^R\right\}, \quad \left\{\tilde{p}_i^R\right\}, \quad n_c, \quad \tilde{n}_c, \quad \tilde{n}_{Zc}, \quad D_{ij}^0$$

- $\left\{\phi_i^R\right\}$ → *All electrons* partial waves
- $\left\{\tilde{\phi}_i^R\right\}$ → Pseudized soft partial waves
- $\left\{\tilde{p}_i^R\right\}$ → Projectors (dual of $\tilde{\phi}_i^R$)
- n_c → Density of core electrons
- $\tilde{n}_c$ → Pseudized density of core electrons
- $\tilde{n}_{Zc}$ → Pseudized density of core electrons + nucleus
- D_{ij}^0 → Frozen part of D_{ij} term

Constraints:

- Precision of the calculation
- Speed of convergence (number of plane waves)

➢ Have to generate an adapted basis

Building atomic data for PAW III

A 4 steps procedure...

Step 1

All electrons atomic calculation

- ✓ Solve atomic Schrödinger equation

  Get $n_c(r), V_{ae}(r)$

- ✓ Choose an energy set $\{\varepsilon_i\}$ an radii $\{r_i\}$ and invert the Schrödinger equation

  Get $\{\phi_i(r)\}$

Step 2

Pseudo functions

- ✓ Apply a soft pseudization scheme:

$\tilde{\phi}_i$	and	ϕ_i	join at	r_i
$\tilde{n}_c$	and	n_c	join at	r_{core}
$\tilde{V}_{loc}$	and	V_{ae}	join at	r_{loc}

Step 3

Projectors

- ✓ Calculate $\{\tilde{p}_i(r)\}$ as duals of $\{\tilde{\phi}_i(r)\}$

Step 4

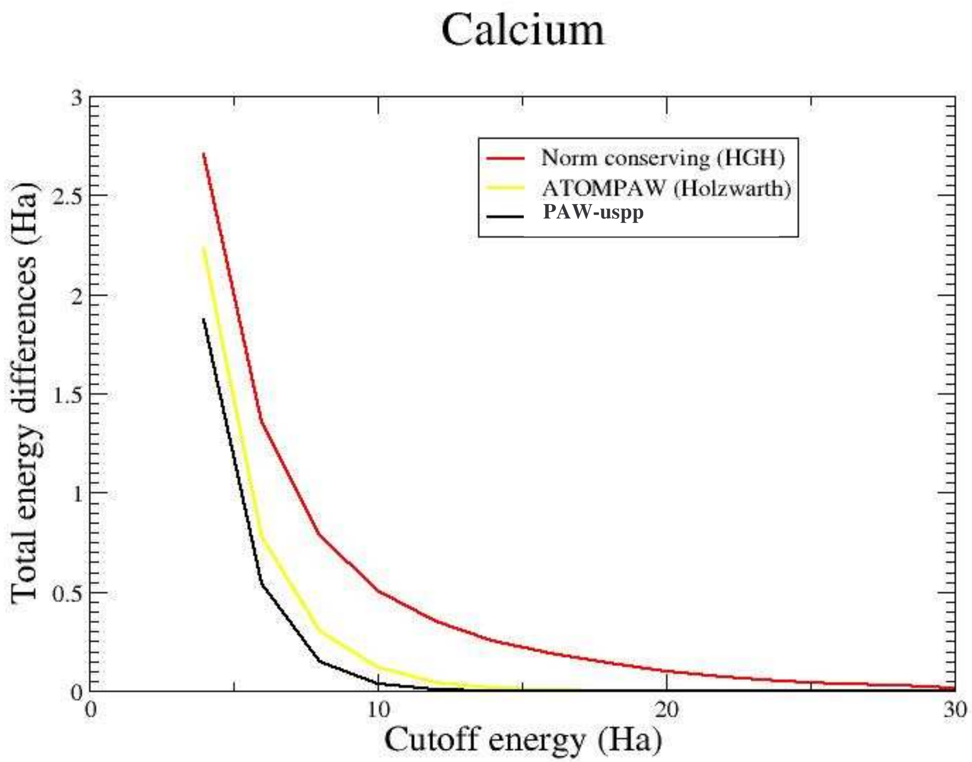
Additional data

- ✓ Compute $\tilde{n}_{Zc}$, D_{ij}^0

Example of *fcc* Ca

Atomic data used:

- Norm-conserving psp HGH
- PAW 1 and PAW 2



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

Basis size required:

- Norm-conserving psp : 5000 plane waves
- PAW : 1000 plane waves

Results (size of crystal):

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

Example of *BaTiO3*

Atomic data used:

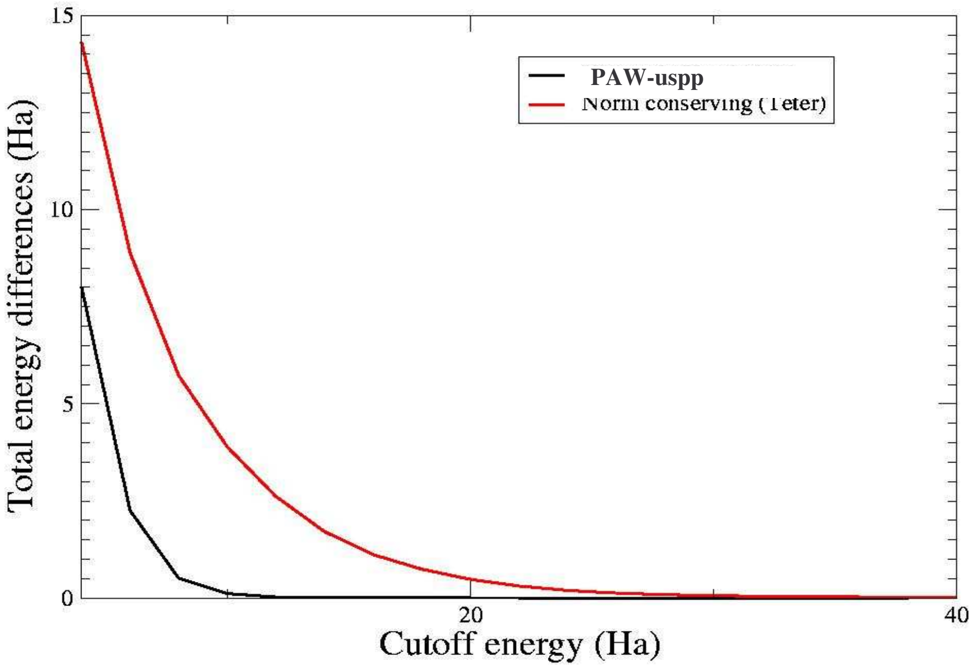
- Norm-conserving psp Teter
- PAW

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

Basis size required:

- Norm-conserving psp : 8400 plane waves
- PAW : 2200 plane waves

Barium Titanate



CPU on a PC-BiXeon- 2.4Ghz:

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

Results (size of crystal):

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

The PAW method - overview

APPROXIMATIONS:

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

ADVANTAGES:

All advantages of « all electrons » and « pseudopotential » methods

- ✓ "True" density of the system is computed ➢ no transferability problem
- ✓ Size of plane waves basis 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 pseudopotential methods are approximations of the PAW method

Approximations: ultrasoft and norm-conserving

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

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

1- From PAW to ultrasoft pseudopotentials

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

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

2- From PAW to norm-conserving pseudopotentials

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

$S = I$

Conclusion

- 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 several codes (in chronological order)...

CP-PAW (www.pt.tu-clausthal.de/~paw) - IBM license - *Fortran*

PWPAW (pwpaw.wfu.edu) – Non-profit use license - *Fortran*

VASP (cms.mpi.univie.ac.at/vasp) – Commercial - Fortran

ABINIT (www.abinit.org) - GNU-GPL - *Fortran*

GridCode (wiki.fysik.dtu.dk/gridcode) – Open source – *Python* + *C*

Socorro (dft.sandia.gov/Socorro) – GNU-GPL – *Python* + *C*

...

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]