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PAW ATOMIC DATA GENERATION

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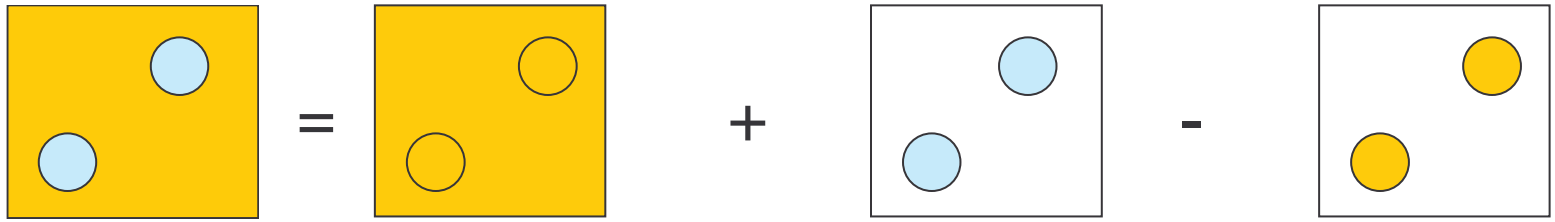
Summary

- ✓ Building atomic data for PAW
- ✓ Atomic data validation
- ✓ PAW atomic data generators for ABINIT
- ✓ Fcc oxygen example
- ✓ Conclusion

Building atomic data for PAW - summary

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

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

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

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

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

Inside circles: atomic data needed

Building atomic data for PAW - summary

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

For each atomic specie

$\{\phi_i^R\}$, $\{\tilde{\phi}_i^R\}$, $\{\tilde{p}_i^R\}$, $V_H[\tilde{n}_{Zc}]$, n_c, $\tilde{n}_c$, D_{ij}^0

- $\{\phi_i^R\}$: *All electron* partial waves
- $\{\tilde{\phi}_i^R\}$: Pseudized soft partial waves
- $\{\tilde{p}_i^R\}$: Projectors (dual of $\tilde{\phi}_i^R$)
- $V_H[\tilde{n}_{Zc}]$: *Hartree* potential due to nuclueus and core electrons (local pot.)
- n_c: Core density
- $\tilde{n}_c$: Pseudized core density
- D_{ij}^0: Frozen part of D_{ij} term

Definitions of radial grids are also needed

Constraints:

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

➢ Have to generate an adapted basis

Building atomic data for PAW I

A 5 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

$$\tilde{\phi}_i \text{ and } \phi_i \text{ join at } r_i$$
$$\tilde{n}_c \text{ and } n_c \text{ join at } r_{core}$$
$$V_{loc} \text{ and } V_{ae} \text{ join at } r_{loc}$$

Building atomic data for PAW II

Step 3 **Projectors**

✓ Calculate (optimized) $\{\tilde{p}_i(r)\}$

Step 4 **Local potential**

✓ Compute $v_H(\tilde{n}_{Zc})$

Step 5 **Additional data**

✓ Compute D_{ij}^0, $\rho_{ij}^{initial}$

The PAW calculation must give the same physical results as a reference *all electrons* calculation

At the atomique level

- ✓ The logarithmic derivatives of wavefunctions must be equal to the ones of a reference calculation (good diffusion properties)

$$\left[-\Delta + V_l(r)\right]\phi_l(\varepsilon, r) = \varepsilon\phi_l(\varepsilon, r) \quad \Rightarrow \quad \left[\phi_l^2(\varepsilon, r)\frac{d}{d\varepsilon}\frac{d}{dr}\ln\phi_l(\varepsilon, r)\right]_R = -\int_0^R \phi_l^2(\varepsilon, r)dr$$

- ✓ The energies of excited configurations must be equal to the *all electron* ones

At the solid state level

- ✓ Physical properties have to be tested: *lattice parameters, bulk modulus,…*

⌦ *Transferability*

Atomic data validation *2-Efficiency*

The plane wave basis must be as small as possible

- ✓ Radius of augmentation regions (spheres).
  Spheres are in principle not allowed to overlap
  In practice a little overlap is allowed
- ✓ Number of partial waves per atom
- ✓ Pseudization scheme
- ✓ Size of radial grids
- ✓ $\tilde{p}_i(g)$ behaviour for large g
  Real Space Optimization
- ✓ Softness of V_{loc} and $\tilde{n}_c$

Good atomic data are always a compromise between accuracy and efficiency

Atomic data generators I

For the ABINIT code, we have chosen to interface two existing codes:

AtomPAW

PAW atomic data generator for "PWPAW"

Written by Natalie Holzwarth and coworkers

Dept. of Physics, Wake Forest University

Launch AtomPAW and a converter separately...

Only one input file

AtomPAW produces 3 files:
Atomic data, densities, potentials

3 files used by ***AtomPAW2Abinit***

Downloadable on abinit.org

USPP

Ultrasoft pseudopotential generator

Written by David Vanderbilt

Department of Physics and Astronomy

Rutgers, The State University of New Jersey

Add a "plugin" into USPP (***USPP2Abinit***)...

Extract "add-on" into USPP's directory and compile...

USPP's behaviour is not changed

Only have to use USPP to produce a file for Abinit

- Fully documented by D. Vanderbilt...
- Set of input files downloadable on D. Vanderbilt's site...

Downloadable on abinit.org

Atomic data generators II

AtomPAW

AtomPAW

- Impose $\varepsilon_i = \varepsilon_n{}^{at}$
- Regular radial grid
- LDA or GGA
- No control on pseudiz. Scheme
- XML format in last version

AtomPAW2Abinit

- Possibility to transfer some data onto a log. radial grid
- Possibility to optimize nonlocal projectors with *King-Smith et al. scheme*
- Compute V_{loc} (Kresse's formulation)

USPP

USPP

- No constraint on ε_i
- Logarithmic radial grid
- LDA or GGA, multiple func.
- Efficient pseudiz. scheme
- Control on pseudiz. scheme

USpp2Abinit

- Possibility to optimize nonlocal projectors with *King-Smith et al. scheme*
- Compute V_{loc} (Kresse's formulation)

fcc oxygen example with USPP I

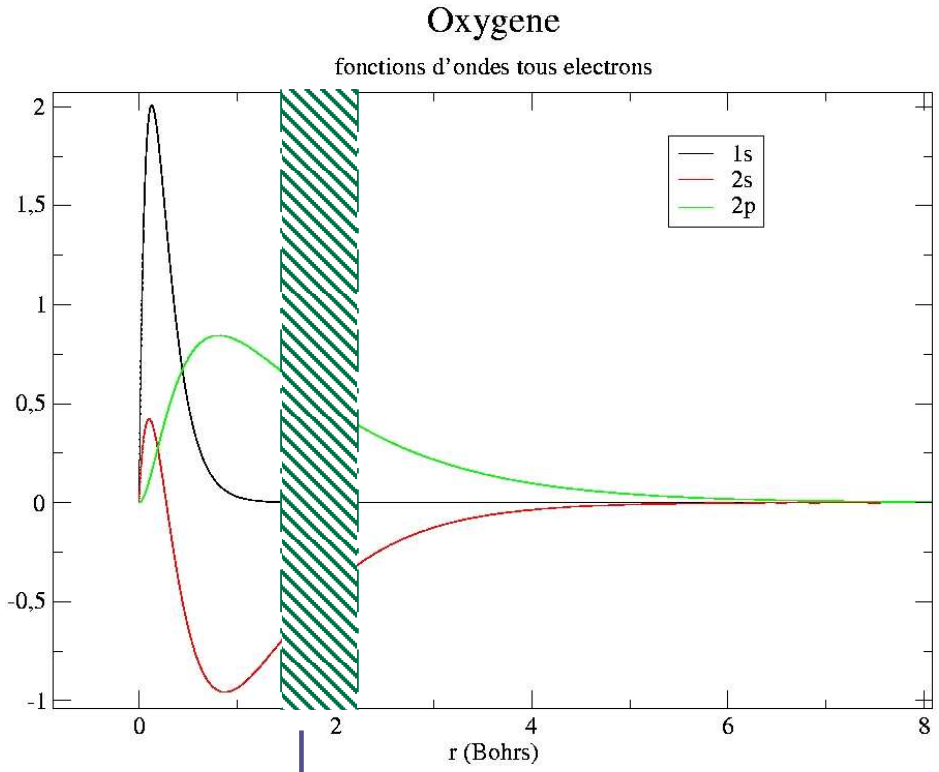
Step 1 **All electrons atomic calculation**

$$[T + V_{AE}(r)]\phi_i = \varepsilon_i \phi_i$$

O : $1s^2 2s^2 2p^4$

E(1s)=-37.51685 Ry
E(2s)=-1.74236 Ry
E(2p)=-0.6766 Ry

Valency choice: $2s^2 2p^4$



Cutoff radius choice:

- Depends of the general context of the study
- Max. radius for non overlaping *fcc* spheres : **2.07 u.a.**

fcc oxygen example with USPP II

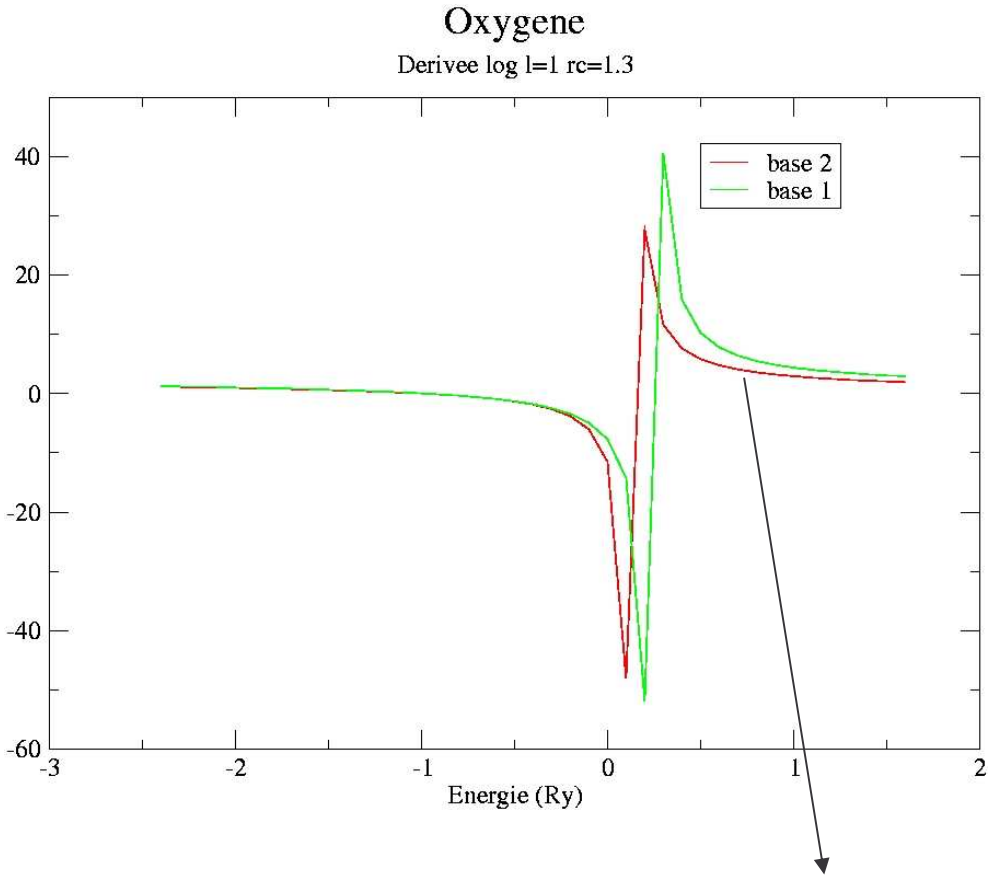
Step 1, cont^{d}

Choice of ref. energies set:

- 2 energies per angular momentum

  s state : ***s*** eigenstate
  p state

  p state : ***s*** state
  p eigenstate



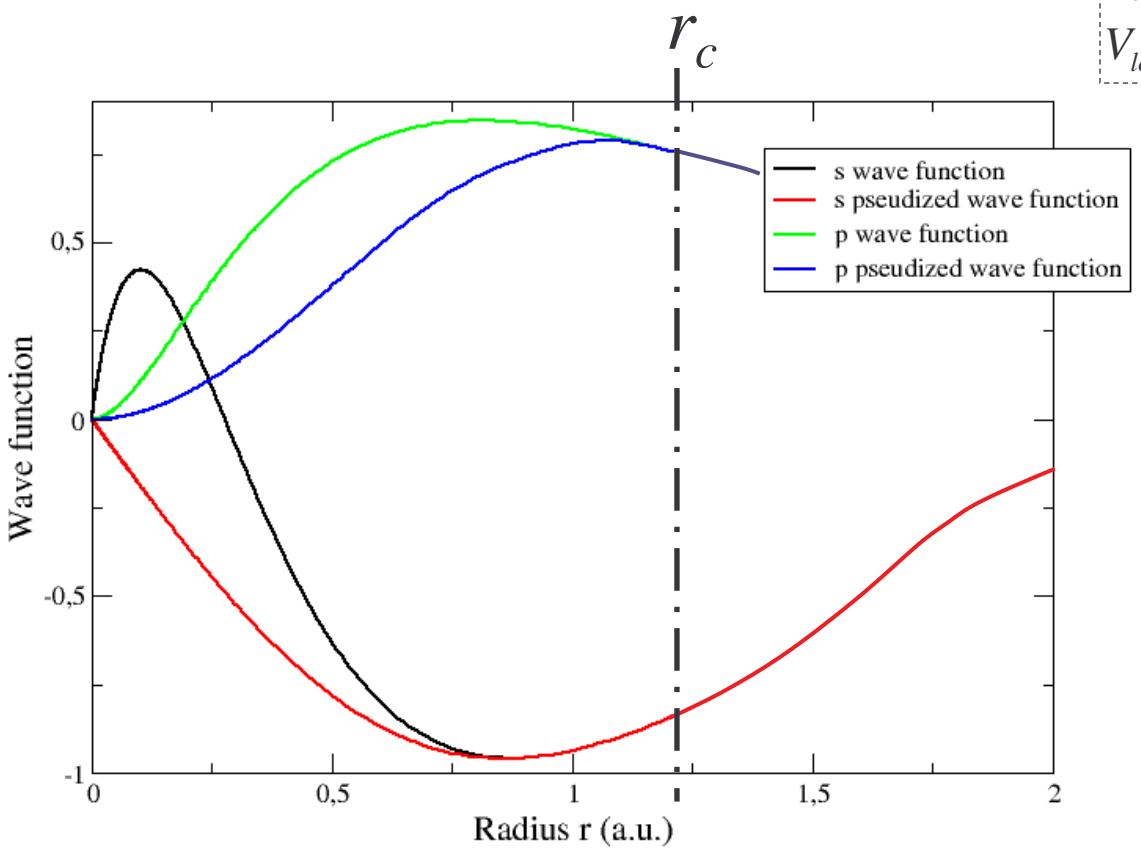
Inverse the Schrödinger equation and get $\{\phi_i(r)\}$

fcc oxygen example with USPP III

Step 2 Pseudofunctions

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}
V_{loc}	and	V_{ae}	join at	r_{loc}



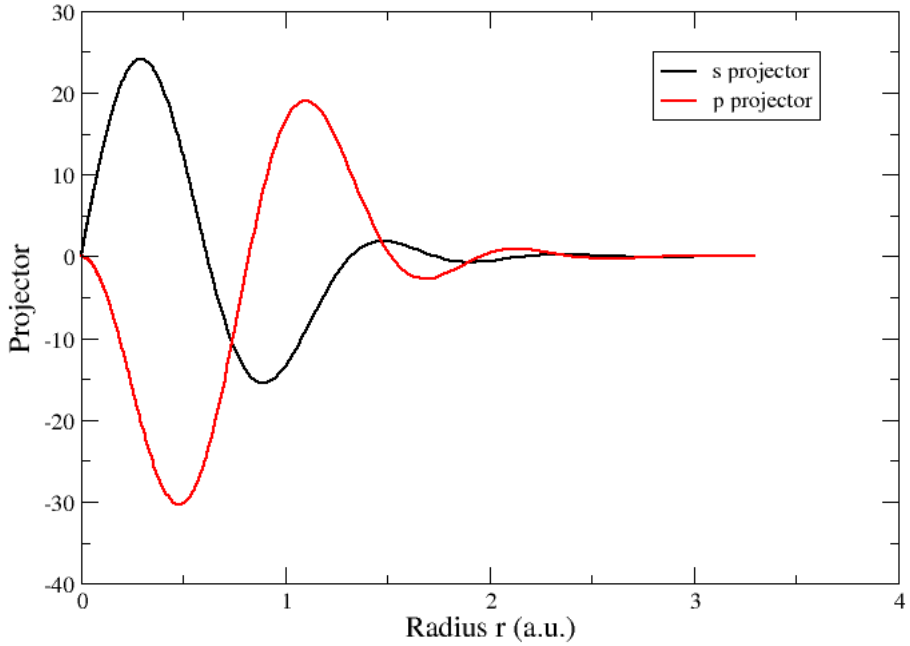
fcc oxygen example with USPP IV

Step 3 Projectors

- ✓ We build $|\chi_i\rangle = (\varepsilon_i - T - V_{loc})\,\tilde{\phi}_i$ that vanish beyond Sup[r_i, r_{loc}]
- ✓ With the matrix $B_{ij} = \langle \tilde{\phi}_i | \chi_j \rangle$, we can calculate the projectors as

$$|\tilde{p}_i\rangle = \sum_j (B)^{-1}_{ij} |\chi_j\rangle \quad \text{and} \quad \langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}$$

- ✓ The projectors are localized by construction



fcc oxygen example with USPP V

Step 4 Compute $v_H[\tilde{n}_{Zc}]$

✓ Apply the following formula that relies Kresse[1] and Blöchl[2] formulations:

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

Other possible formulation: apply a descreening procedure to V_{loc}

Step 5 Compute additional data

✓ Starting guess value for ρ_{ij} : $\rho_{ij}^{initial} = \rho_{ij}^{0}$

✓ Computation of D_{ij}^{0} :

$$D^0_{ij} = \langle \phi_i | -\frac{\Delta}{2} + v_H[n_{Zc}] | \phi_j \rangle - \langle \tilde{\phi}_i | -\frac{\Delta}{2} + v_H[\tilde{n}_{Zc}] | \tilde{\phi}_j \rangle - \sum_{lm} \int_R v_H[\tilde{n}_{Zc}] \hat{Q}^{lm}_{ij} d\mathbf{r}$$

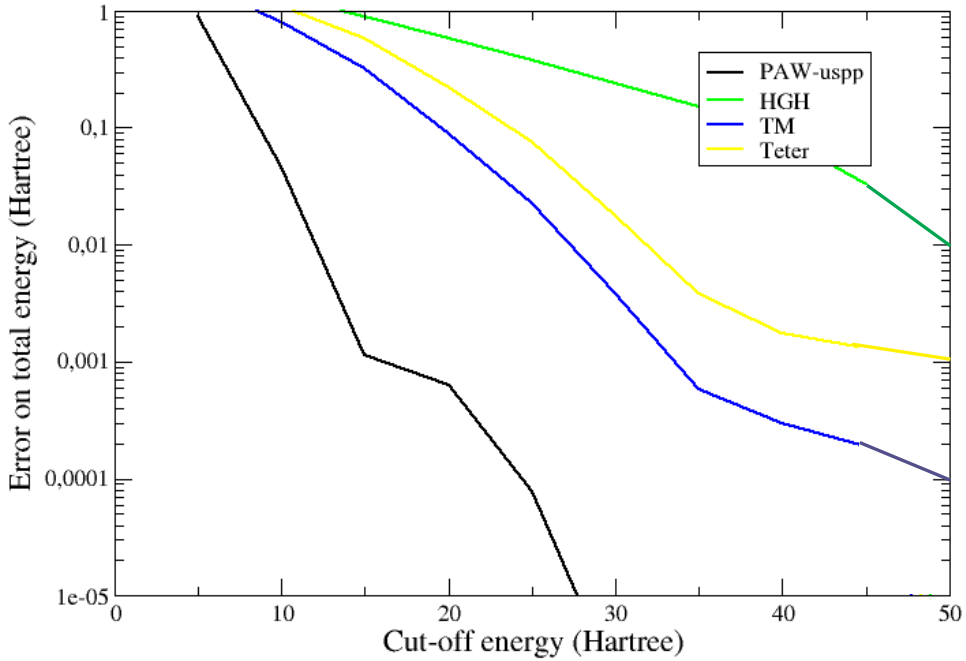
[1] P. Blöchl, Phys. Rev. B **50**, 17953 (1994) [2] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999)

fcc oxygen example - *results*

Accuracy

	NC HGH	NC Teter	PAW AtomPAW	PAW USPP
Cut-off ΔE=1 mHa	60	50	26	15
a_o (Å)	3.11	3.04	3.07	3.06
B_o (GPa)	182	210	194	208
E_{coh} (eV)	2.60		2.89	

Efficiency

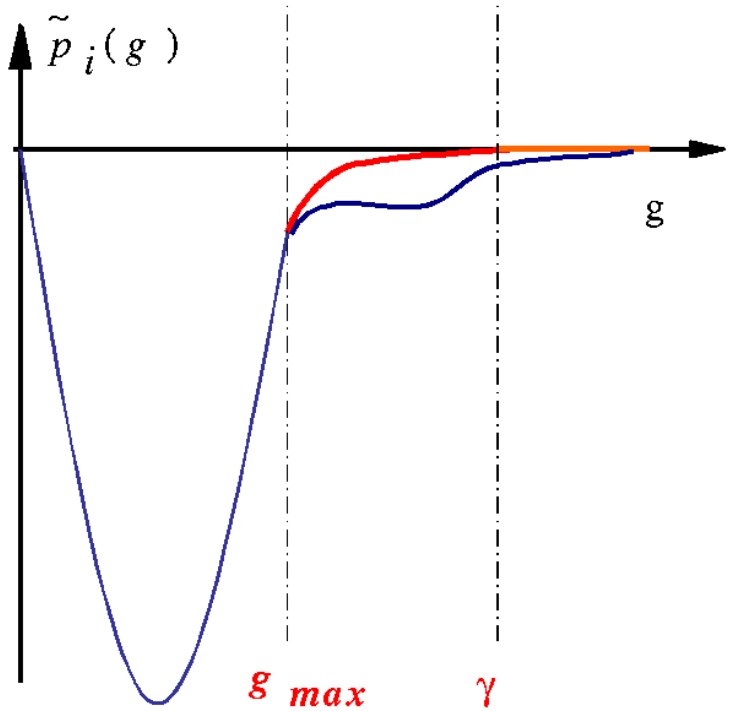


Real Space Optimization I

- *Useful for USPP's atomic data*
- *Available for AtomPAW's atomic data*

Real-space implementation of nonlocal pseudopotentials for 1st-principle total-energy calculations,

R.D. King-Smith, M.C. Payne, J.S. Lin,
Phys. Rev. B 44, 13063 (1991)



- Impose error W_l
- Adjust g_{max} according to E_{cut}
- Choose $2g_{\max} \le \gamma \le 3g_{\max}$
  - Deduce R_o

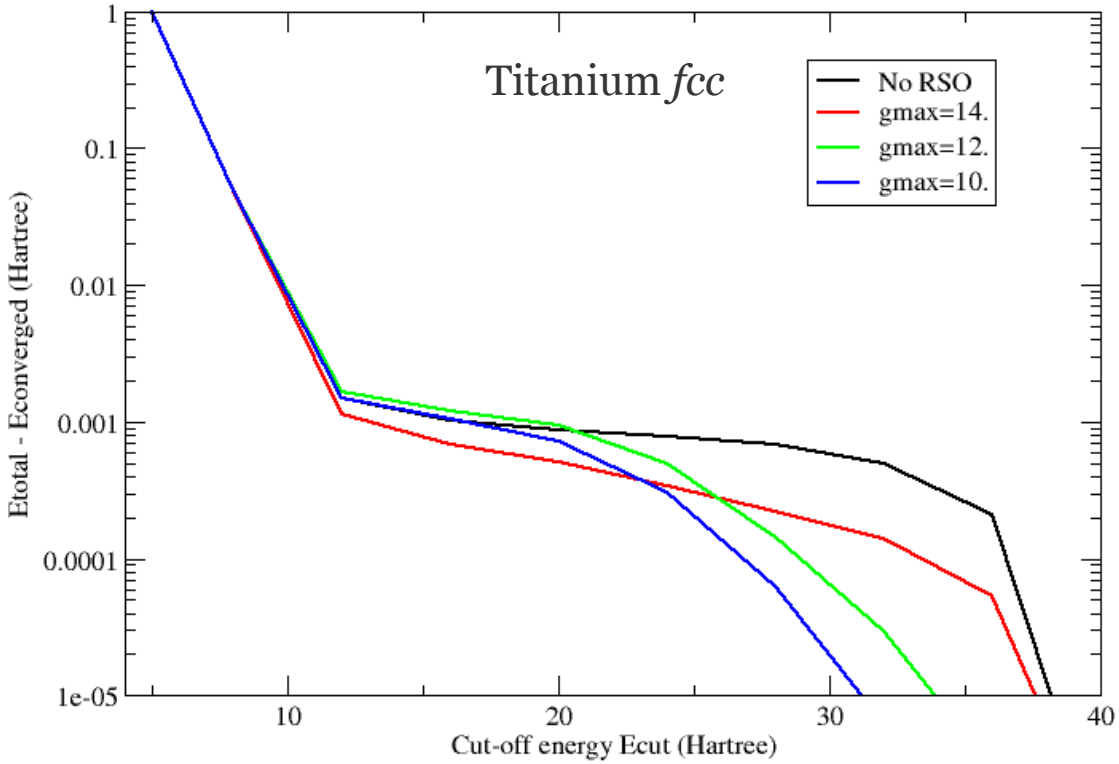
    Choose reasonable R_o

$$\Delta\varepsilon_{n,k}^{nl}(l,m,n) \le W_{l,n} = \max_g \left[\int_{R_0}^{\infty} \tilde{p}_{l,n}(r) j_l(g) r^2 dr \right]$$

Return

Real Space Optimization II

Influence of RSO on convergency



How to choose RSO parameters in practice ?

- $\gamma/g_{max} = 2$ and $0.0001 < W < 0.001$ is a good choice
- g_{max} has to be adjusted
- The lower g_{max} the faster the convergence is;
  but too low g_{max} can produce unphysical results

Where to find generator and prebuild atomic data ?

Why not a small turn on **www.abinit.org** ?

- ✓ **USPP2Abinit** and **AtomPAW2Abinit** downloadable
- ✓ User's guides available
- ✓ A complete tutorial to learn how to use USPP2Abinit
- ✓ A set of prebuild PAW atomic data for ABINIT downloadable from a periodic table

Conclusion

- ✓ PAW atomic data generation needs a **trial-error** type of adjustment
- ✓ Each set of data must be **tested** in the context of each study

- ☑ Two types of atomic data now available
- ☑ ABINIT's user can download/generate atomic data
- ☑ Fully documented on Abinit's web site

To be continued…

- ❑ … Final format ?
- ❑ Evaluate accuracy and performance for elements of the periodic table
- ❑ *XML* "universal" format for PAW atomic data ?
- ❑ An atomic data generator completely written for Abinit ?
- ❑ Spin orbit ?