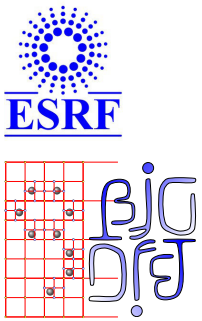


BigDFT project

BigDft Tutorial 19-21 Octobre 2011

CECAM – GRENOBLE

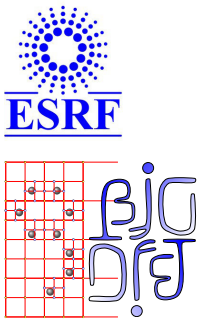
XANES calculation with BigDFT

A. Mirone[1]

[1]ESRF

21 Octobre 2011

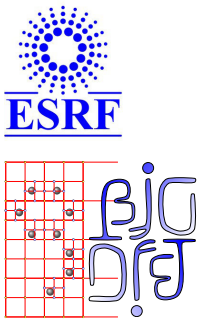
Outline



BigDFT project

1. Basic Formulae
   - Light-Matter Interaction
   - Spectra decomposition
2. from AE to pseudo
   - Introduction
   - $\tilde{\phi}, \tilde{p}$ construction
   - ThePatch
   - Initial state
3. Checks
   - Exact Model
   - Quartz Si K-edge
4. Conclusions

Light-Matter Interaction



BigDFT project

Interaction Hamiltonian

$$H_{int} = \left(\frac{2\pi\hbar c^2}{\omega V}\right)^{1/2} \left(a^{\dagger}_{k,\varepsilon} exp(-i\mathbf{k}\cdot\mathbf{r}) + a_{k,\varepsilon} exp(i\mathbf{k}\cdot\mathbf{r})\right) \frac{e}{mc}\mathbf{p}\cdot\varepsilon$$

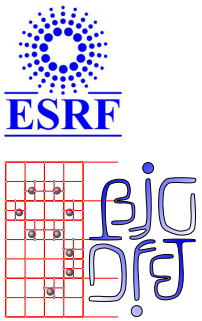
Fermi rule (for absorption)

$$\sigma(\hbar\omega) = (2\pi)^2 \alpha_0 \hbar\omega \sum_n |< n|i >|^2 \delta(\hbar\omega - E_n)$$

Initial state

$$|i >= \mathbf{r}\cdot\varepsilon + i\frac{(\mathbf{k}\cdot\mathbf{r})(\mathbf{r}\cdot\varepsilon)}{2} + \ldots|0>$$

Iterative spectra reconstruction



BigDFT project

From a discrete sum to the moments of spectral function

$$f(E) = \sum_n |< n|i >|^2 \delta(E - E_n)$$

$$\int f(E) E^n dE = \sum_n < i|n > E^n < n|i > = < i|H^n|i >$$

The moment problem

? A distribution is uniquely determined by its moments?

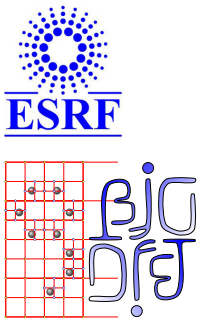
☛ Yes, excepted pathological cases.

- $\sum_{n=0}^{n=\infty} \left(\frac{1}{\mu_{2n}}\right)^{\frac{1}{2n}} = +\infty$: sufficient condition

✘ Possible numerical instability $E^n \to 0$ Or $E^n \to \infty$

☛ Chebyshev Polynomia

Iterative spectra reconstruction



BigDFT project

Numerically stable method: From E^n to $Chebychev_n(E)$

A. Weiss et al. Rev. Mod. Phys. 78, 275 (2006)

Method

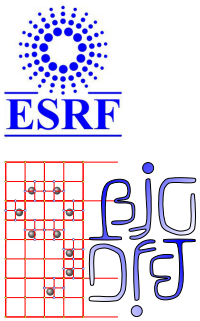
- rescale and shift $H \rightarrow H'$ such that $< n|H'|n > \in]-1,1[$
- $E^n \rightarrow T_n(E) = cos(n * arccos(E))$
- $T_0(E) = 1$; $T_1(E) = E$;
  $T_{m+1}(E) = 2ET_m(E) - T_{m-1}(E)$
- $\mu_n = \int f'(E) T_n(E) =< i|T_n(H')|i > |$
- $T_{m+1}(H')|i >= 2H' T_m(H')|i > - T_{m-1}(H')|i >$

Generalised Eigen-problem

$$\int f(E)E^n dE \quad = \quad \left|< i|S^{1/2}(S^{-1/2}\bar{H}S^{-1/2})^n S^{1/2}|i >\right| \quad =$$

$$\left|< i|S(S^{-1}\bar{H})^n|i >\right|$$

Introduction

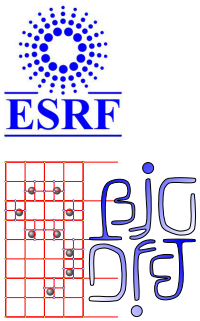


BigDFT project

Goals

- Project the AE initial wf into pseudo-space.
- Stretch the validity domain of the pseudopotential.
- Dont touch valence region.

Introduction



BigDFT project

Ingredients

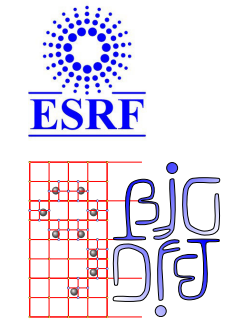
three classes of atomic wavefunction functions :

- the AE atomic ϕ_i
- the corresponding wavefunctions $\tilde{\phi}_i$
- their dual wavefunctions $\tilde{p}_i$.

Functions properties

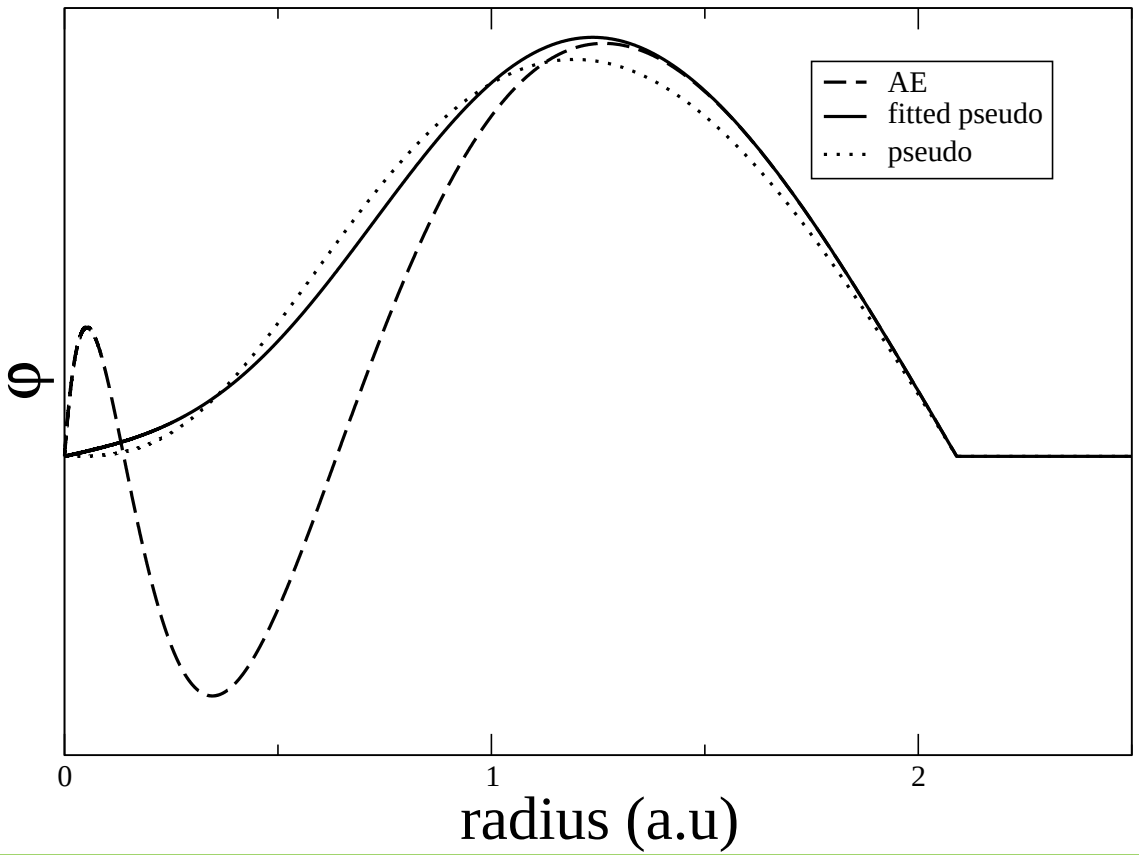
- the wavefunctions $\tilde{\phi}_i$ are identical ϕ_i at the PAW matching radius R and can be arbitrarily chosen inside the matching sphere Ω_R.
- the wavefunctions $\tilde{p}_i$ are zero outside Ω_R and must be duals of the $\tilde{\phi}_i$ wavefunctions : $< \tilde{p}_i | \tilde{\phi}_j >= \delta_{ij}$.

$\tilde{\phi}, \tilde{p}$ construction

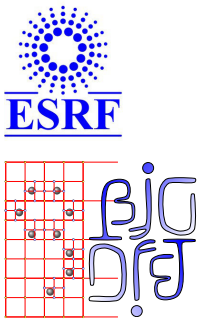


BigDFT project

$\tilde{\phi}_i$ are solved in the pseudopotential plus a gaussian correction term.



The PAW patch



BigDFT project

Generalised Eigen-Problem

$$H_{patched} = H + \sum_{i,j} |\tilde{p}_i\rangle \left(E_i^{ae} \delta_{ij} - \langle \tilde{\phi}_i | H | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j | \quad (1)$$

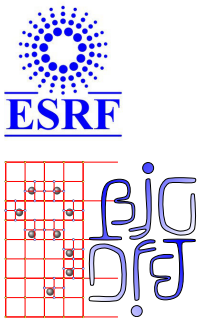
$$S_{patched} = S + \sum_{i,j} |\tilde{p}_i\rangle \left(\delta_{ij} - \langle \tilde{\phi}_i | S | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j | \quad (2)$$

Test

using duality condition

$$\left\langle \tilde{\phi}_k \right| H_{patched} \left| \tilde{\phi}_i \right\rangle = \left\langle \tilde{\phi}_k \right| E_i^{ae} S_{patched} \left| \tilde{\phi}_i \right\rangle \quad (3)$$

Check on the radial grid

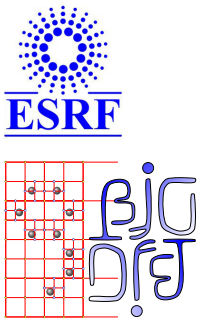


BigDFT project

Table: Comparison between AE and pseudo eigenvalues for a radius R_{match} and different values of n_{paw}

$L = 0$				
AE	$n_{paw} = 6$	$n_{paw} = 4$	$n_{paw} = 2$	$n_{paw} = 0$
-75.953				
-6.291				
0.4116	0.4116	0.4116	0.4112	0.3708
5.990	5.990	5.7111	2.972	2.6091
14.400	14.347	7.9951	7.717	6.4202
25.414	21.252	15.537	13.735	13.726
38.920	26.244	29.269	23.583	23.581
54.858	40.622	37.229	35.943	35.943
73.186	58.728	50.642	50.601	50.602
93.876	72.453	67.530	67.529	67.530

Check on the radial grid

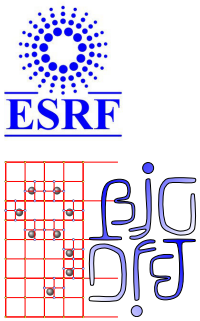


BigDFT project

Table: Comparison between AE and pseudo eigenvalues for a radius R_{match} and different values of n_{paw}

$L = 1$				
AE	$n_{paw} = 6$	$n_{paw} = 4$	$n_{paw} = 2$	$n_{paw} = 0$
-4.536				
0.920	0.920	0.920	0.920	0.869
6.153	6.153	6.133	5.236	4.194
14.013	14.010	13.443	9.839	9.456
24.329	24.267	19.909	18.227	18.222
37.030	35.939	31.673	29.400	29.400
52.085	45.045	42.885	42.882	42.882
69.474	62.377	58.650	58.649	58.649
89.181	76.691	76.690	76.690	76.690
111.19	97.005	97.000	97.001	97.001

Check on the radial grid

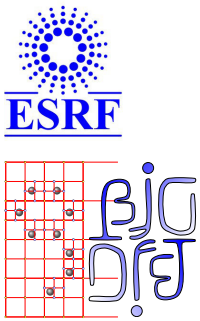


BigDFT project

Table: Comparison between AE and pseudo eigenvalues for a radius $2R_{match}$ and different values of n_{paw}.

$L = 0$				
AE	$n_{paw} = 6$	$n_{paw} = 4$	$n_{paw} = 2$	$n_{paw} = 0$
-75.953				
-6.292				
-0.4746	-0.4701	-0.46943	-0.4751	-0.48020
0.6937	0.69397	0.69424	0.69510	0.67160
2.4371	2.44523	2.45616	2.42955	2.07141
4.8684	4.87480	4.86482	3.09596	3.00667
7.9454	7.92458	6.88421	5.44259	5.12233
11.645	11.5961	8.65917	8.65662	8.03651
15.954	15.9640	12.0805	11.5884	11.4968
20.861	20.7027	16.5836	15.5936	15.5351

Check on the radial grid

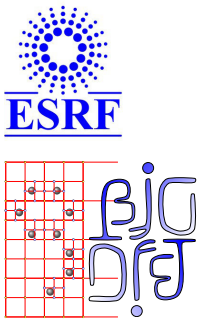


BigDFT project

Table: Comparison between AE and pseudo eigenvalues for a radius $2R_{match}$ and different values of n_{paw}.

$L = 1$				
AE	$n_{paw} = 6$	$n_{paw} = 4$	$n_{paw} = 2$	$n_{paw} = 0$
-4.537				
-0.135	-0.13240	-0.1317	0.1367	-0.1367
0.9327	0.93455	0.9362	-0.9386	0.9128
2.6598	2.66523	2.6763	2.6988	2.4539
5.0337	5.02465	4.9566	4.3418	4.2082
8.0227	7.99939	7.7412	6.5429	6.4885
11.610	11.6710	11.111	9.6590	9.5955
15.785	15.7333	13.591	13.397	13.394
20.541	19.9395	18.383	17.797	17.793
25.873	25.0420	23.609	22.772	22.765

Initial state

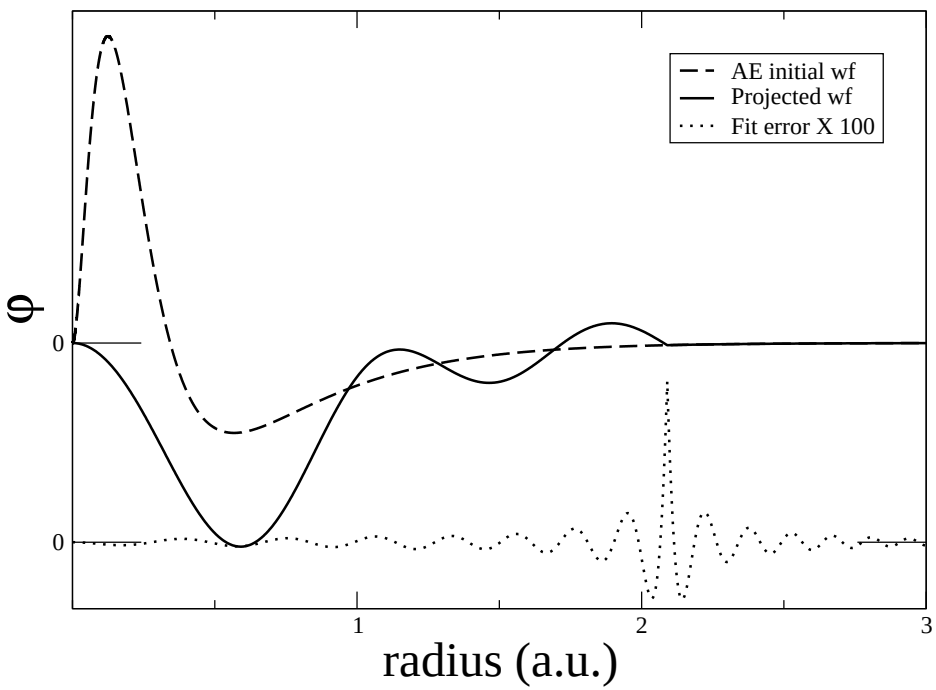


BigDFT project

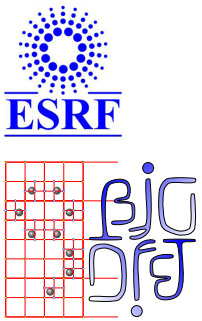
The Projector

- For a localized state ($r < R_{match}$) $P = \sum_i |\tilde{\psi}_i\rangle \langle\psi_i|$
- Is the initial wf localised?

- the core orbitals are not propagated by the Hamiltonian



Exact Model



BigDFT project

The Model

- spherical AE potential $V_{Si}(r)$ plus a perturbation $V(r) = V_{Si}(r) + Y_1^0(\hat{r}) * exp(-(r - r_c)^2/(2\sigma^2)) * h$
- initial wf : dipole operator z times the $1s$ orbital.
- rotational invariance along the z axis

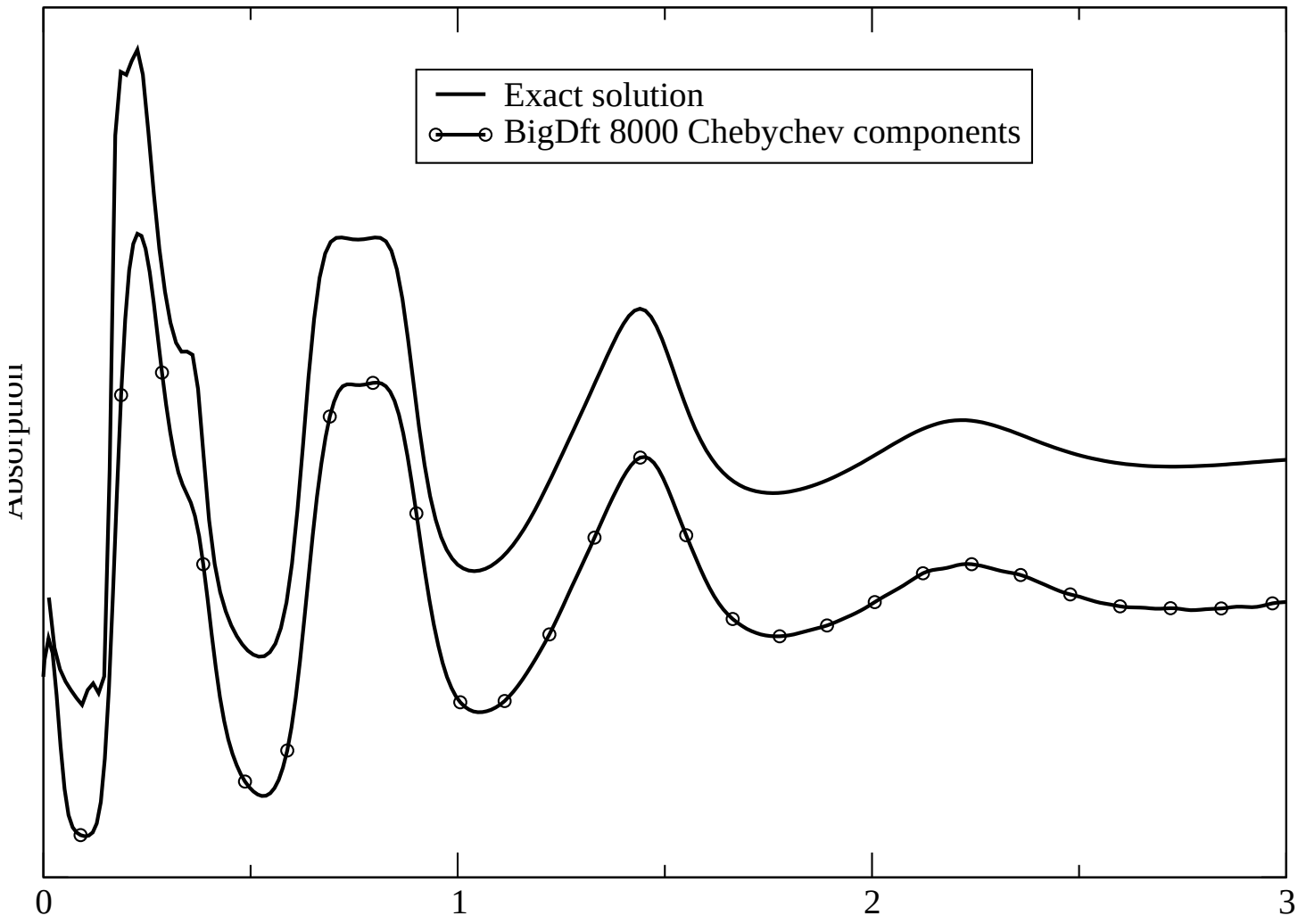
The solution

- $\psi(E, \mathbf{r}) = \sum_l Y_l^0(\hat{r}) c_l(E, r)$
- $-\frac{1}{2}\partial_r^2 c_l(E, r) = (E - V_l(r)) c_l(E, r) + W_{lp}(r) c_p(E, r)$

The Test

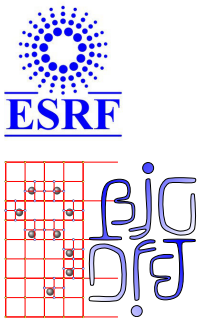
- $r_c = 7.5$ a.u $\qquad h = 3$ Hartree $\qquad \sigma = 0.8$ A.U

Exact Model



BigDFT project

Quartz Si K-edge



BigDFT project

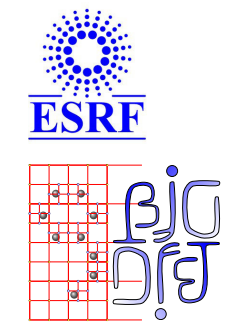
The SCF calculation

- 72 atoms unit cell (18 for the tutorial)
- One ionised Si atom (charged cell)
- Z+1 approximation, Phosphorus
  but **pseudo** already could do Silicon with 1s hole

The spectra calculation

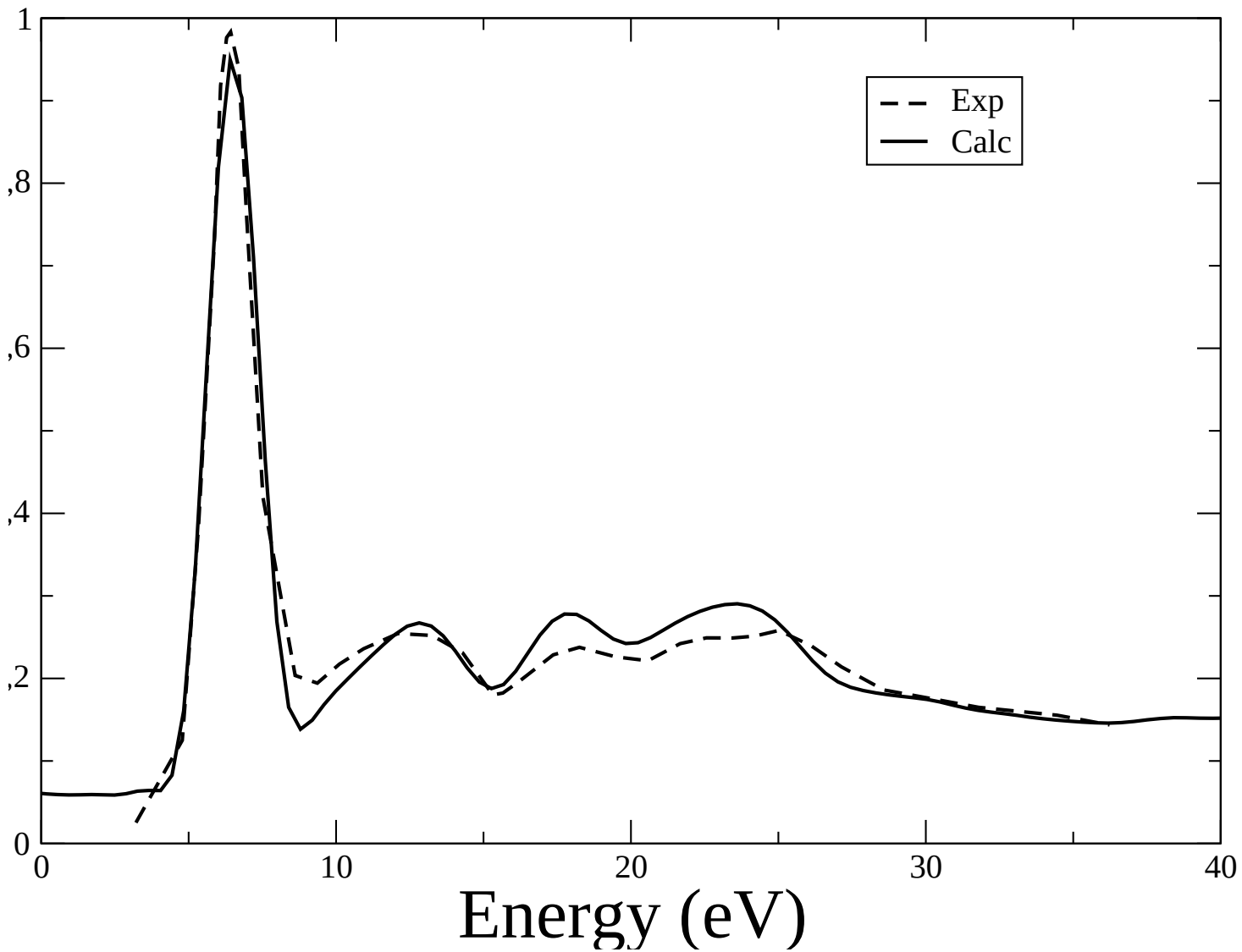
- 72 atoms unit cell plus K-points
- No need for energy dependent convolution (plasmon effect small for quartz)

Quartz Si K-edge

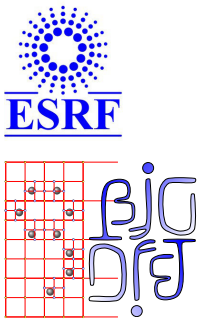


BigDFT project

Bigger cell, kptrlenght=50 a.u.



Conclusions

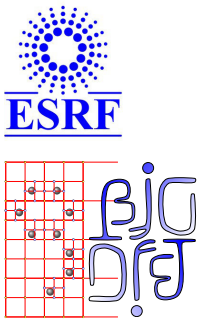


BigDFT project

- new procedure for PAW patch
- large energy range
- neutral on valence wavefunctions
- Subtle tricks for the initial wf.
- Complex gaussians fit.
- Numerically robust implementation: Chebyshev, BigDft
- Exact Model : perfect
- Experiment : good agrement
- A good basis to enter more advanced formalism ..
- To be submitted :

A.Mirone L. Genovese

Xanes calculation with generic pseudopotentials.



BigDFT project

PATCH YOU USB KEY

scp yourloginname@rotule.imag.fr:∼/amirone/* ∼/Desktop