**XANES calculation with BigDFT**

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1 ESRF

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Outline

1. Basic Formulae
   - Light-Matter Interaction
   - Spectra decomposition

2. from AE to pseudo
   - Introduction
   - \( \tilde{\phi}, \tilde{\rho} \) construction
   - ThePatch
   - Initial state

3. Checks
   - Exact Model
   - Quartz Si K-edge

4. Conclusions

http://inac.cea.fr/L_Sim/BigDFT
Light-Matter Interaction

Interaction Hamiltonian

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

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

\[ |i> = r \cdot \mathbf{\varepsilon} + i \frac{(\mathbf{k} \cdot \mathbf{r})(\mathbf{r} \cdot \mathbf{\varepsilon})}{2} + ... |0> \]
Iterative spectra reconstruction

From a discrete sum to the moments of spectral function

\[ f(E) = \sum_n |\langle n| i \rangle|^2 \delta(E - E_n) \]

\[ \int f(E) E^n dE = \sum_n \langle i| n \rangle E^n \langle n| i \rangle = \langle i| H^n |i \rangle \]

The moment problem

? A distribution is uniquely determined by its moments?


Yes, excepted pathological cases.


\[ \sum_{n=0}^{\infty} \left( \frac{1}{\mu^{2n}} \right) \frac{1}{2n} = +\infty : \text{sufficient condition} \]


Possible numerical instability \( E^n \to 0 \) Or \( E^n \to \infty \)


Chebyshev Polynomials
Iterative spectra reconstruction

Numerically stable method: From $E^n$ to $\text{Chebychev}_n(E)$


Method

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

Generalised Eigen-problem

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

Goals

- Project the AE initial wf into pseudo-space.
- Stretch the validity domain of the pseudopotential.
- Don't touch valence region.

AE to pseudo

Introduction
- \( \tilde{\phi}, \tilde{p} \) construction
- ThePatch
- Initial wf

Checks
- Exact
- Quartz Si K-edge

Conclusions

http://inac.cea.fr/L_Sim/BigDFT
Ingredients

three classes of atomic wavefunction functions:

- the AE atomic \( \phi_i \)
- the corresponding wavefunctions \( \tilde{\phi}_i \)
- their dual wavefunctions \( \tilde{p}_i \).

Functions properties

- the wavefunctions \( \tilde{\phi}_i \) are identical \( \phi_i \) at the PAW matching radius \( R \) and can be arbitrarily chosen inside the matching sphere \( \Omega_R \).

- the wavefunctions \( \tilde{p}_i \) are zero outside \( \Omega_R \) and must be duals of the \( \tilde{\phi}_i \) wavefunctions: \( \langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij} \).
\( \tilde{\phi}, \tilde{\rho} \) construction

\( \tilde{\phi}_i \) are solved in the pseudopotential plus a gaussian correction term.
The PAW patch

Generalised Eigen-Problem

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

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

Test

using duality condition

\[ \langle \tilde{\phi}_k | H_{\text{patched}} | \tilde{\phi}_i \rangle = \langle \tilde{\phi}_k | E_i^{ae} S_{\text{patched}} | \tilde{\phi}_i \rangle \]
Check on the radial grid

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

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<th>$L = 0$</th>
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Check on the radial grid

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

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http://inac.cea.fr/L_Sim/BigDFT

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ESRF
Initial state

The Projector

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

- the core orbitals are not propagated by the Hamiltonian

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ESRF
The Model

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

The solution

- $\psi(E, r) = \sum_l Y_1^0(\hat{r}) c_l(E, r)$
- $-\frac{1}{2} \partial_r^2 c_l(E, r) = (E - V_l(r)) c_l(E, r) + W_{lp}(r) c_p(E, r)$

The Test

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

![Graph showing absorption spectra comparison between Exact solution and BigDft 8000 Chebychev components.](http://inac.cea.fr/L_Sim/BigDFT)
Quartz Si K-edge

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)

http://inac.cea.fr/L_Sim/BigDFT
Quartz Si K-edge

Bigger cell, kptrlenght=50 a.u.

http://inac.cea.fr/L_Sim/BigDFT
Conclusions

- 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 agreement
- A good basis to enter more advanced formalism ..
- To be submitted :

A.Mirone L. Genovese

Xanes calculation with generic pseudopotentials.

http://inac.cea.fr/L_Sim/BigDFT
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