MULTISCALE METHODS IN ELECTRONIC STRUCTURE CALCULATION: A SOLVER FOR KOHN-SHAM EQUATIONS

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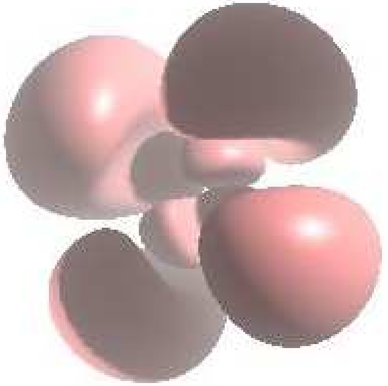


IHP Project
Breaking Complexity

Plan

Mathematical formulation of DFT
Algorithm

- Kohn Sham Equations
- Existing methods
- Use of wavelets
- Potential determination
- Self-consistent algorithm

3D periodic biorthogonal Multi-Resolution Analysis

Solving the self-consistent model

Numerical experiments

KOHN SHAM EQUATIONS

- Let M nuclei $\{Z_\alpha,\ R_\alpha\}_{1\leqslant\alpha\leqslant M}$ supposed to be fixed.
- Let occ be the number of occupied states. Then the behaviour of the $2N$ electrons is determined by the electronic density *(HK 64, KS 65)*:

$$\rho(\mathbf{r}) = 2\sum_{i=1}^{occ} n_i|\Psi_i(\mathbf{r})|^2, \quad \int_{\mathbb{R}^3}\rho(\mathbf{r})d\mathbf{r} = 2N, \quad \sum_{i=1}^{occ} n_i = N,$$

with $\Psi_i \in H^1(\mathbb{R}^3)$, $<\Psi_i|\Psi_j>_{L^2} = \delta_{i,j}$, $\rho \in L^q(\mathbb{R}^3)\cap L^2(\mathbb{R}^3)$, with $1 \leqslant q \leqslant \frac{3}{2}$

- The aim is the minimisation of the following energy:

$$\mathcal{E}[\rho] = 2\sum_{i=1}^{occ} n_i\,\varepsilon_i - \frac{1}{2}\int_{\mathbb{R}^3} V_c[\rho](\mathbf{r})\,\rho(\mathbf{r})d\mathbf{r} - \int_{\mathbb{R}^3} V_{xc}[\rho](\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \mathcal{E}_{xc}[\rho]$$

Mathematical formulation of DFT - Algorithm

KOHN SHAM EQUATIONS

V is the potential between nuclei and electrons: $V(\mathbf{r}) = -\sum_{\alpha=1}^{M} \frac{Z_\alpha}{|R_\alpha - \mathbf{r}|}$

V_c is the Coulomb potential or *Hartree* potential: $V_c[\rho](\mathbf{r}) = \int_{\mathbb{R}^3} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$

$\mathcal{E}_{xc}[\rho]$ is the *exchange-correlation* energy.

The potential V_{xc} derives from this energy: $V_{xc}[\rho] = \frac{\partial \mathcal{E}_{xc}[\rho]}{\partial \rho}$

$(\mathcal{M})$ *Find* $\{\Psi_i\}_{i=1,occ} \in \left(H^1(\mathbb{R}^3)\right)^{occ}$ *such that for all* $v \in H^1(\mathbb{R}^3)$ *:*

$$h_\rho(\Psi_i, v) = \frac{1}{2}\int_{\mathbb{R}^3} \nabla\Psi_i \nabla v \, d\mathbf{r} + \int_{\mathbb{R}^3} V_{ks}[\rho](\mathbf{r})\Psi_i(\mathbf{r})v(\mathbf{r})d\mathbf{r} = \varepsilon_i \int_{\mathbb{R}^3} \Psi_i(\mathbf{r})v(\mathbf{r})d\mathbf{r}$$

with $\varepsilon_1 \leqslant \varepsilon_2 \cdots \leqslant \varepsilon_{occ} < 0$

EXISTING METHODS

- Slater and Gaussian-type orbitals (GAUSSIAN, *DF 86, S 93*):
  $\chi^G_{L,\alpha}(\mathbf{r}) = C\, x^\ell y^m z^n\, e^{-\alpha|\mathbf{r}|^2},\ L = \ell + m + n$

  GTO: Describe the good symetries, but redundantly. Wrong behaviour at $|\mathbf{r}| \to 0$ and $|\mathbf{r}| \to +\infty$.

  STO: Good behaviour at $|\mathbf{r}| \to 0$ and $|\mathbf{r}| \to +\infty$, but complex calculus.

- Plane waves - Fourier transforms (CPMD, ab-init, VASP):
  For any kind of systems; plane waves are eigenvectors of the Laplacien, but a high resolution is needed for a high precision

  $\Rightarrow$ Introduction of pseudopotentials. Need of adaptativity.

- Mixed basis: Gaussians + Plane waves (WIEN)

  Domain decomposition method: LMTO, LAPW,.... Heavy code.

USE OF WAVELETS BASIS

- Fischer and Desfranceschi (1993): radial equation. Continuous and discrete wavelet transforms (Daubechies, BCR).
- Wei and Chou (1996), Tymcak and Wang (1997): Daubechies in DFT
- Cho, Arias and al. (1993). Lippert, Arias and al. (1998): Interpolating wavelets in DFT, for 1s states.
- Flad, Hackbush and al. (2003-2004): Hyperbolic wavelets in Hartree-Fock approximation.
- Harrison, Fann and al. (2003-2004): multiwavelets to solve a problem expressed in term of integral operators.

⇒ Need a basis adapted to the interpolating problem. Linear scaling to apply hamiltonien operator. Adaptive strategy.

POTENTIAL CALCULATION

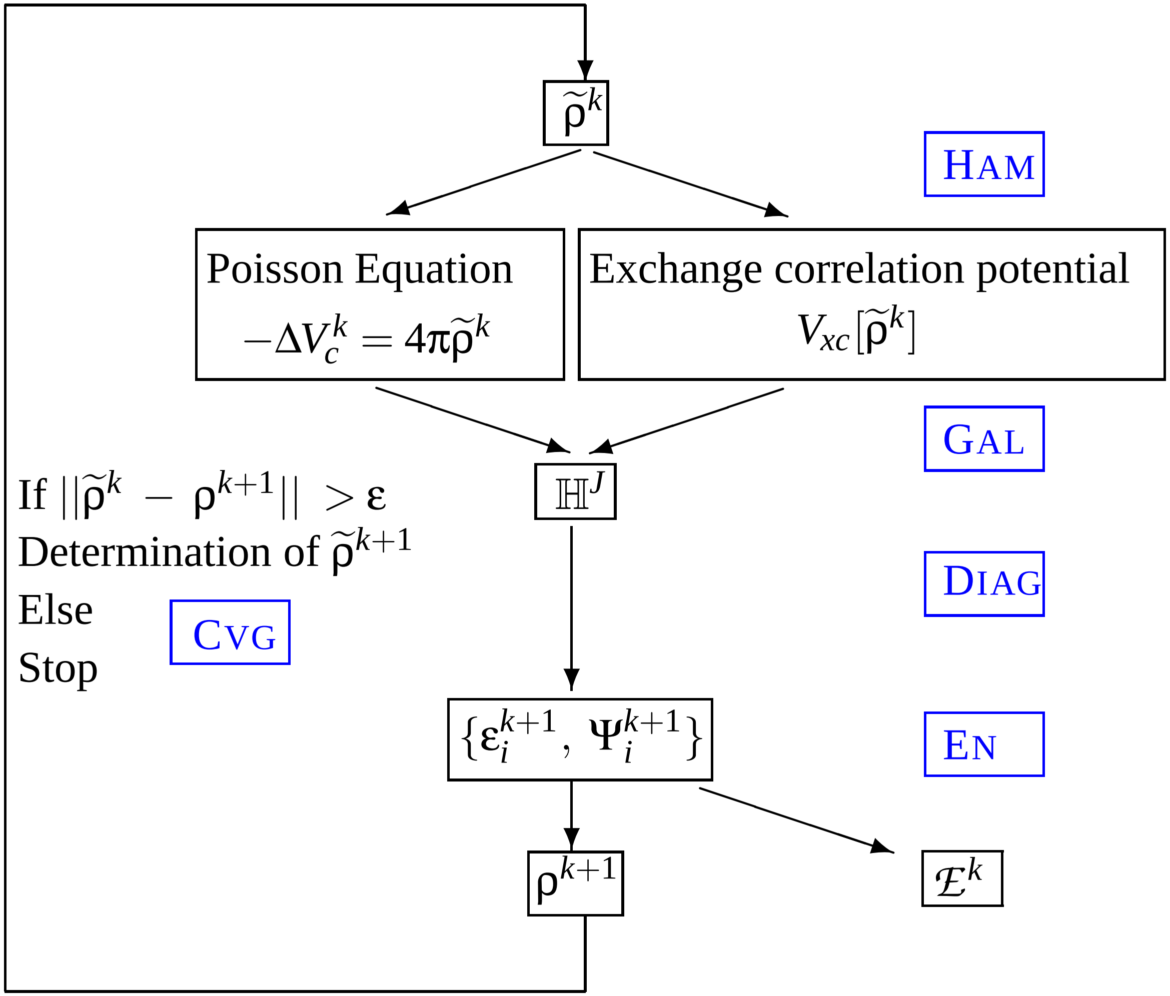
We have chosen to use the following potential forms in our implementation:

- An atomic potential will be given by a *local pseudopotential* (*GM 92*):
  $$V(\mathbf{r}) = -\frac{Z_\alpha}{|\mathbf{r}|} erf\left(\frac{|\mathbf{r}|}{\sqrt{2}\, r_{loc}}\right) +$$
  $$e^{-\frac{1}{2}(\frac{|\mathbf{r}|}{r_{loc}})^2}\left(C_1 + C_2\left(\frac{|\mathbf{r}|}{r_{loc}}\right)^2 + C_3\left(\frac{|\mathbf{r}|}{r_{loc}}\right)^4 + C_4\left(\frac{|\mathbf{r}|}{r_{loc}}\right)^6\right)$$
- **Local Density Approximation**: $\mathcal{E}_{xc}$ comes from the energy of a particle in uniform electron gas (**S 51**):
  $$\mathcal{E}_{xc} = \int_{\mathbb{R}^3} \varepsilon_{xc}[\rho](\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad \varepsilon_{xc}[\rho] = -\frac{a_0 + a_1\, r_s + a_2\, {r_s}^2 + a_3\, {r^3}_s}{b_1\, r_s + b_2\, {r^2}_s + b_3\, r_s^3 + b_4\, r_s^4}$$
  with $r_s = (\frac{3}{4\pi})^{1/3}\rho^{-1/3}$.
- Hartree potential is also the solution of a Poisson equation:

$$-\Delta V_c = 4\pi\, \rho$$

Mathematical formulation of DFT - Algorithm

SELF-CONSISTENT ALGORITHM



$\widetilde{\rho}^k$

HAM

Poisson Equation

$-\Delta V_c^k = 4\pi\widetilde{\rho}^k$

Exchange correlation potential

$V_{xc}[\widetilde{\rho}^k]$

GAL

$\mathbb{H}^J$

If $||\widetilde{\rho}^k \; - \; \rho^{k+1}|| \; > \varepsilon$

Determination of $\widetilde{\rho}^{k+1}$

Else

Stop

CVG

DIAG

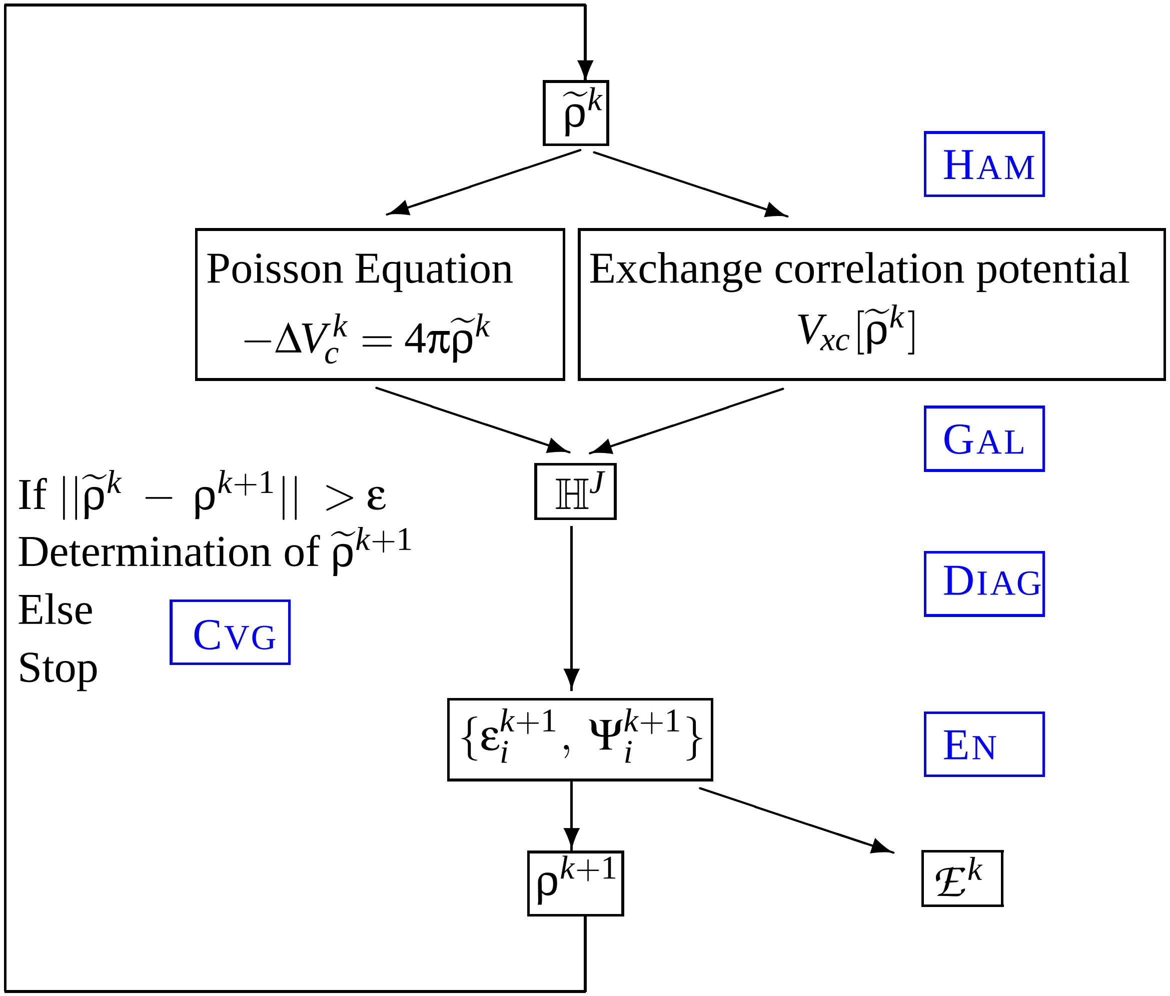
$\{\varepsilon_i^{k+1}, \Psi_i^{k+1}\}$

EN

ρ^{k+1}

$\mathcal{E}^k$

SELF-CONSISTENT ALGORITHM



$\boxed{\widetilde{\rho}^k}$

HAM

Poisson Equation

$-\Delta V_c^k = 4\pi\widetilde{\rho}^k$

Exchange correlation potential

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If $||\widetilde{\rho}^k - \rho^{k+1}|| > \varepsilon$

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Else

Stop

CVG

DIAG

$\boxed{\{\varepsilon_i^{k+1}, \Psi_i^{k+1}\}}$

EN

$\boxed{\rho^{k+1}}$

$\boxed{\mathcal{E}^k}$

$\Longrightarrow$ Discretisation of the problem by means of Galerkin and Petrov Galerkin formulations (for Poisson and for Schrödinger) into wavelets basis.

Plan

Mathematical formulation of DFT

Algorithm

3D periodic biorthogonal Multi-Resolution Analysis

- Biorthogonal MRA of $L^2(\mathbb{R})$
- Interpolating wavelets and lifting scheme
- Biorthogonal MRA of $L^2(\mathbb{R}\backslash\mathbb{Z})$
- Extension in three dimensions
- Examples

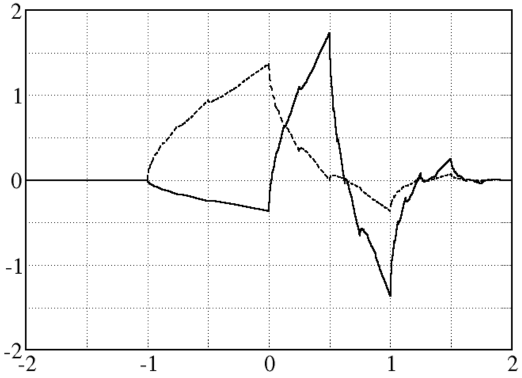
Solving the self-consistent model

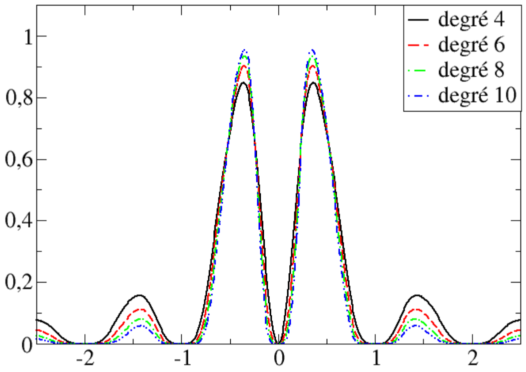
Numerical experiments

BIORTHOGONAL MRA OF $L^2(\mathbb{R})$

- The sequences $V_j = span\{\phi_{j,k} = 2^{j/2}\,\phi(2^j. - k)\}_{k\in\mathbb{Z}}$ (resp. $\widetilde{V}_j$), $j \in \mathbb{Z}$ generate a biorthogonal MRA of $L^2(\mathbb{R})$.
- V_j is completed with W_j so that $V_{j+1} = V_j \oplus W_j$. $W_j = span\{\psi_{j,k}\}_{k\in\mathbb{Z}}$ (resp. $\widetilde{W}_j = span\{\widetilde{\psi}_{j,k}\}_{k\in\mathbb{Z}}$).
- Linear approximation: if $f \in H^s$ then $\varepsilon_j = O(2^{-sj})$.
- Non-linear approximation: if $f \in C^s$, and $F \in \ell_\tau$ then

$$\sigma_N(F) = O(N^{-2/\tau}), \text{ with } \frac{1}{\tau} = s + \frac{1}{2}$$

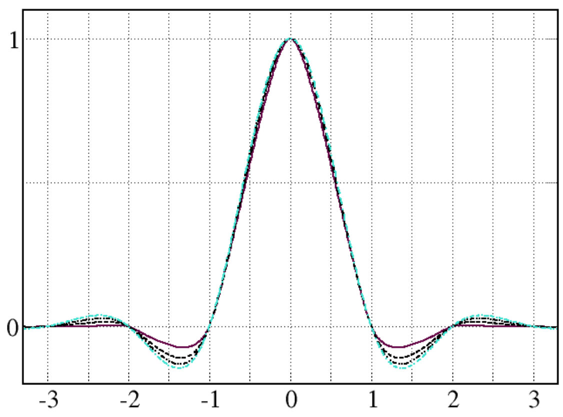




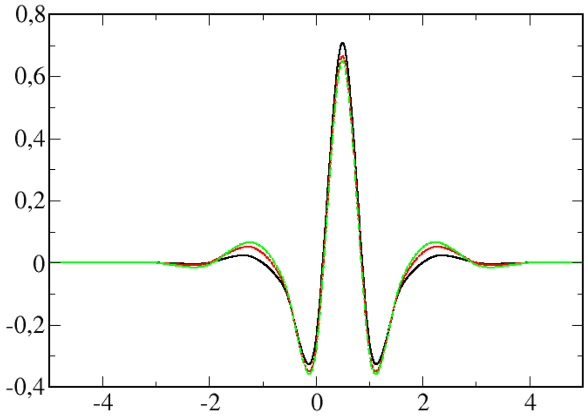
4th-order Daubechies scaling function and wavelet, and Fourier transform of wavelets of different supports.

INTERPOLATING WAVELETS AND LIFTING SCHEME

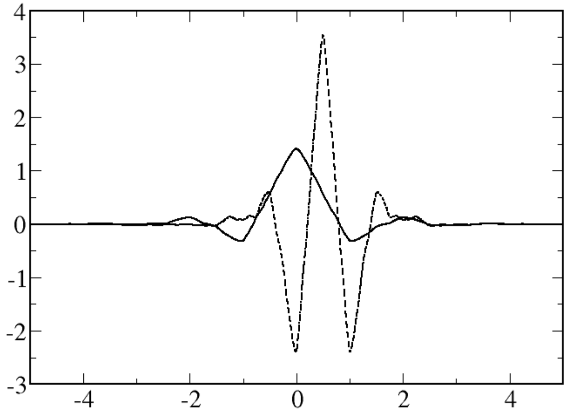
Interpolating scaling functions



Lifted primal wavelets



(6,6) lifted dual basis



Let θ be the Deslauriers-Dubuc interpolating scaling function generating T_0.

- When $\widetilde{\theta}_{0,k} = \delta_k$, then we get a collocation method:

$$\forall f \in T_0, \quad f = \sum_{k\in\mathbb{Z}} t_{j,k}\theta_{j,k} = \sum_{k\in\mathbb{Z}} f(k/2^j)\ \theta^{\sharp}_{j,k}$$

- We can also use the Lifting Scheme (**S 96**) to improve the number of vanishing moments of ζ.

BIORTHOGONAL MRA OF $L^2(\mathbb{R}\backslash\mathbb{Z})$

Definition Periodic MRA on $T = \mathbb{R}\backslash\mathbb{Z}$

Defining the 1-periodization of $u \in L^2(\mathbb{R})$*:*

$$\check{u} = \sum_{l\in\mathbb{Z}} u(.+l)$$

Then we get a biorthogonal MRA $\{\check{V}_j, \check{\tilde{V}}_j\}$ *of* $L^2(T)$ *spanned by* $\{\check{\phi}_{j,k}\}_{k=0,2^j-1}, \{\check{\tilde{\phi}}_{j,k}\}_{k=0,2^j-1}$ *. We can also define* $\{\check{\psi}_{j,k}, \check{\tilde{\psi}}_{j,k}\}_{k=0,2^j-1}$ *, and get biorthogonal properties.*

$\Rightarrow$ No more dilatation invariance. $V_0 = cst$ and

$$dim\,\check{V}_j = dim\,\check{\tilde{V}}_j = dim\,\check{W}_j = dim\,\check{\tilde{W}}_j = 2^j.$$

$\Rightarrow$ The wavelet transform consists in periodic convolutions.

EXTENSION TO THREE DIMENSIONS

Definition Periodic MRA on $\mathbb{T} = (\mathbb{R}\backslash\mathbb{Z})^3$

We define an isotropic tensor product of the biorthogonal MRA $\{\check{V}_j, \check{\tilde{V}}_j\} \in L^2(T)$

$$\mathbb{V}_j(\mathbb{T}) = V_j \otimes V_j \otimes V_j, \quad \tilde{\mathbb{V}}_j(\mathbb{T}) = \tilde{V}_j \otimes \tilde{V}_j \otimes \tilde{V}_j,$$

Let $\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3)$, *with* $\varepsilon_i \in \{0,1\}$. *Taking* $W_j^0 = V_j$ *and* $W_j^1 = W_j$, *we introduce the wavelet isotropic space:*

$$\mathbb{W}_j(\mathbb{T}) = \oplus_{\varepsilon=\{0,1\}^3\backslash\{(0,0,0)\}} \otimes_{m=1}^{3} W_j^{\varepsilon_m}$$

Thus, the scaling function spanning $\mathbb{V}_J$ *is written:*

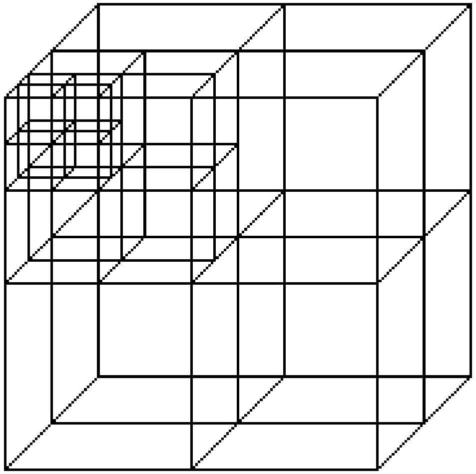
$$\Phi_{j,\mathbf{k}}(\mathbf{r}) = \check{\phi}_{j,k_1}(x)\ \check{\phi}_{j,k_2}(y)\ \check{\phi}_{j,k_3}(z),$$

and one get seven generating wavelets

$$\varepsilon = \{0,1\}^3\backslash\{(0,0,0)\}, \quad \Psi_{j,\mathbf{k}}^{(\varepsilon)}(\mathbf{r}) = \psi_{j,k_1}^{(\varepsilon_1)}(x)\ \psi_{j,k_2}^{(\varepsilon_2)}(y)\ \psi_{j,k_3}^{(\varepsilon_3)}(z)$$

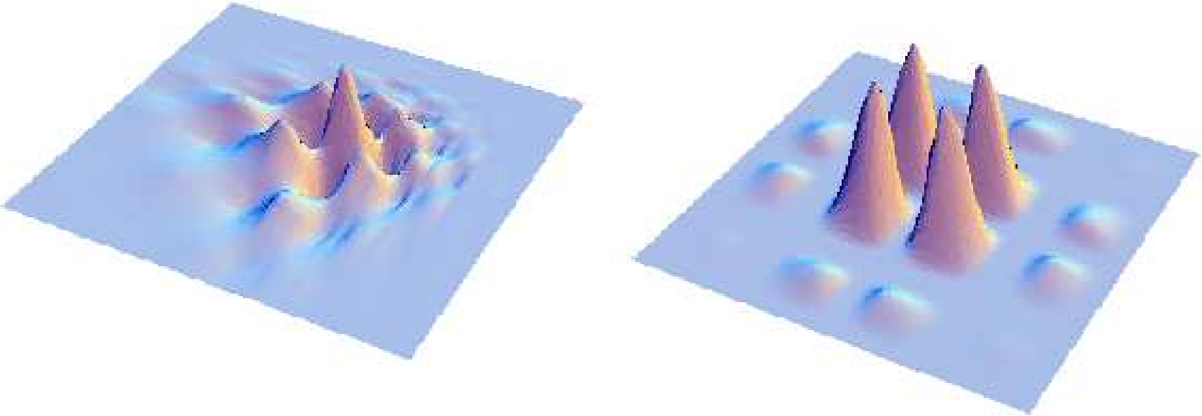
A FAST WAVELET TRANSFORM

j	$I4$	$I4L2$	$I4L4$	$I8$
5	$2.9\ 10^{-3}$	$4.2\ 10^{-3}$	$6.\ 10^{-3}$	$3.7\ 10^{-3}$
6	$7.48\ 10^{-2}$	$8.82\ 10^{-2}$	.109	$8.81\ 10^{-2}$
7	.728	.8791	1.0998	.8747
8	6.48	7.71	9.6	7.82

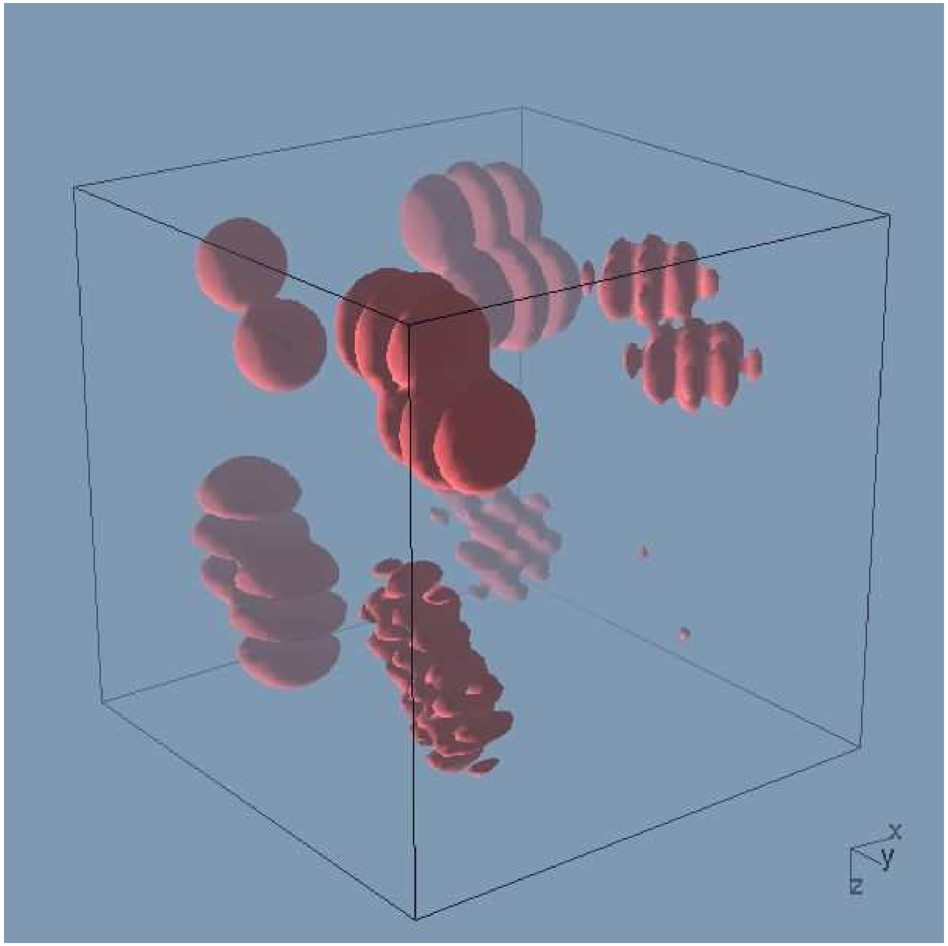


Mean time (sec) for a forward+backward wavelet transform, on a Pentium III 1.39 GHz.

Cut on $z = .5$ of the 4-order Daubechies wavelet $\Psi^{(1,1,1)}_{5,16}$, and the $z = 0$ cut of its discrete Fourier transform.



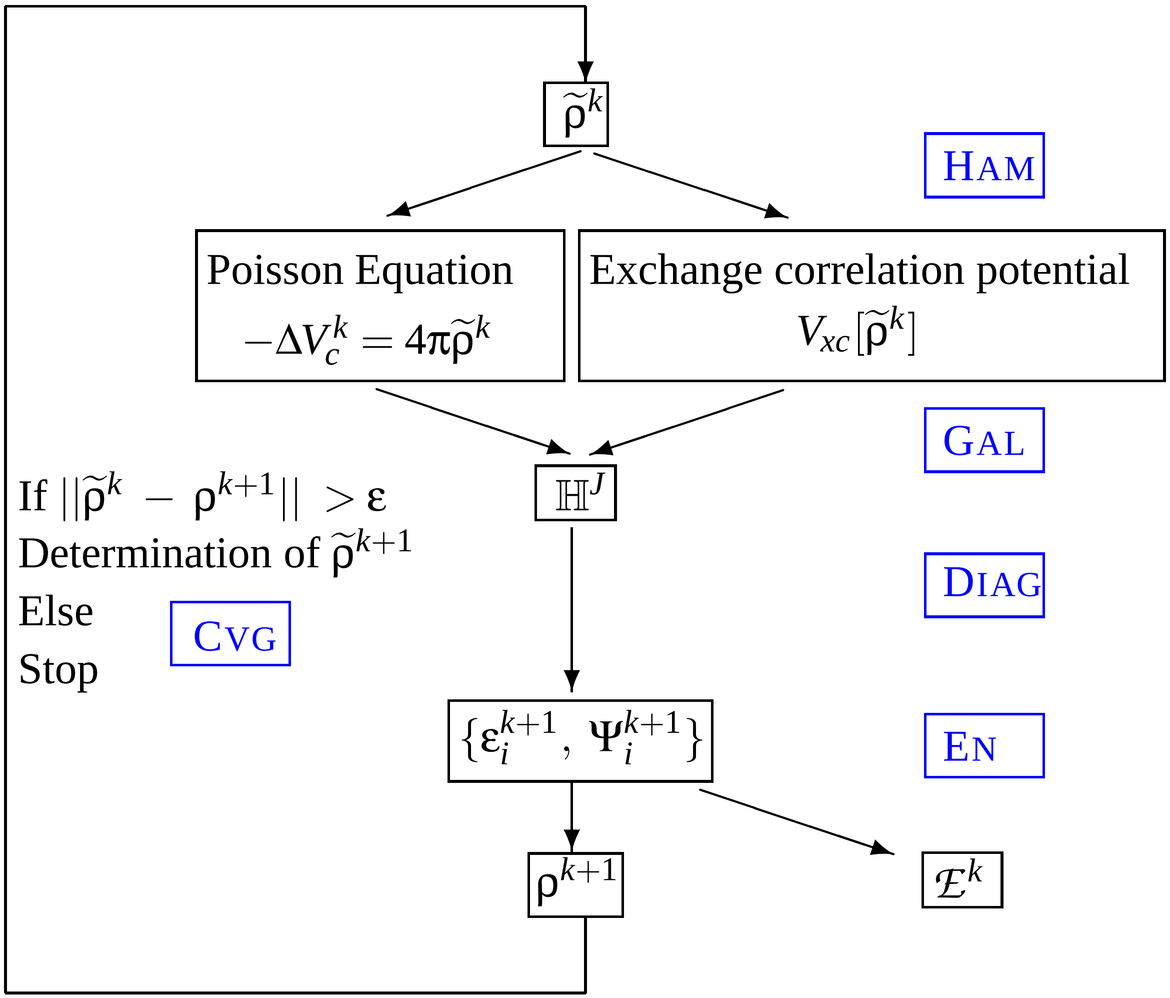
EXEMPLE OF A DECOMPOSITION IN A WAVELET BASIS



A step of the forward wavelet transform applied to the $H2$ density. Isosurface 4.810^{-2} $a.u.$.

Solving the Self-Consistent Model

ALGORITHM



$\widetilde{\rho}^k$

Poisson Equation

$-\Delta V_c^k = 4\pi\widetilde{\rho}^k$

Exchange correlation potential

$V_{xc}[\widetilde{\rho}^k]$

$\mathbb{H}^J$

$\{\varepsilon_i^{k+1}, \Psi_i^{k+1}\}$

ρ^{k+1}

$\mathcal{E}^k$

If $||\widetilde{\rho}^k - \rho^{k+1}|| > \varepsilon$

Determination of $\widetilde{\rho}^{k+1}$

Else

Stop

HAM

GAL

DIAG

EN

CVG

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3D periodic biorthogonal Multi-Resolution Analysis

Solving the self-consistent model

- Hamiltonian construction
- Galerkin formulation
- Diagonalisation procedure
- Evaluation of energies
- Convergence

Numerical experiments

INTRODUCTION

- The system is composed by the M nuclei $\{Z_I,\ R_I\}_{1\leqslant I\leqslant M}$ of a *molecule*: potentials and orbitals decay at infinity, and there are zero outside an open $\Omega =]0,L[^3$.
- Let $(\mathbb{R}\backslash L\mathbb{Z})^3$ be a torus of $\mathbb{R}^3$; we consider functions L-periodic in the three dimensions. We thus define:

$$\forall X,Y,Z \in (\mathbb{R}\backslash L\mathbb{Z})^3,\ f(X,Y,Z) = f(Lx,Ly,Lz) = {}^L f(x,y,z),\ \ x,y,z \in \mathbb{T}$$

- We use two projections of ${}^L f \in L^2(\mathbb{T})$ on MRA:
  - The first t_1, is orthogonal; we note it $\left\{\Phi_{J,\mathbf{k}}, \widetilde{\Phi}_{J,\mathbf{k}}\right\}_{\mathbf{k}\in\Omega_J}$.
  - The second one t_2, is biorthogonal, interpolating (or lifted); we note it $\left\{\theta_{J,\mathbf{k}}, \widetilde{\theta}_{J,\mathbf{k}}\right\}_{\mathbf{k}\in\Omega_J}$. The collocation basis is noted $\Theta_J^\sharp = \left\{\theta_{J,\mathbf{k}}^\sharp\right\}_{\mathbf{k}\in\Omega_J}$.

Solving the Self-Consistent Model

HAM HAMILTONIAN CONSTRUCTION

- *Start:* ${}^L\widetilde{\rho}^k$ is given, projected on $\Theta_J^\sharp$

$\Longrightarrow$ We get ${}^LV^{t_2}$, ${}^LV_{xc}^{t_2}$ with there analytic forms.

$\Longrightarrow$ The resolution of Poisson equation to determine ${}^LV_c^{t_2}$ is made by a collocation method, or a Petrov-Galerkin method. In (**GC 2003**), we use either the preconditionning property of the lifted stiffness matrix, or a solver combining wavelets and multigrid.

$\Longrightarrow$ At the end of this step, we thus get:

$$\forall \mathbf{r} \in \mathbb{T}, \quad {}^LV_{ks}^{t_2}(\mathbf{r}) = \sum_{\mathbf{k}\in\Omega_J} {}^LV_{ks}(\mathbf{k}/2^J)\, \theta_{J,\mathbf{k}}^\sharp(\mathbf{r})$$

$$\text{and} \qquad \mathcal{H}[\,{}^L\widetilde{\rho}^k] = -\frac{1}{2L^2}\Delta + {}^LV_{ks}^{t_2}(\mathbf{r})$$

GAL GALERKIN FORMULATION I

- Let ${}^{L}\psi_i^J = \sum_{\mathbf{k}\in\Omega_J} c^i_{J,\mathbf{k}}\,\Phi_{J,\mathbf{k}}$ for $i = 1, occ$, and $C^i_J = \{c^i_{J,\mathbf{k}}\}_{\mathbf{k}\in\Omega_J}$. At iteration k, the linear system is thus:

$$\mathbb{H}^k_J\, C^i_J = \varepsilon_i\, C^i_J \ ,$$

$$\left[\mathbb{A}^J \ + \mathbb{B}^{k,J}\right] C^i_J = \varepsilon_i\, C^i_J \ ,$$

$$\mathbb{A}^J_{\mathbf{k},\mathbf{k}'} = \frac{1}{2L^2} \int_{\Omega_1} \nabla\Phi_{J,\mathbf{k}}(\mathbf{r})\nabla\Phi_{J,\mathbf{k}'}(\mathbf{r})\; d\mathbf{r}$$

$$\mathbb{B}^{k,J}_{\mathbf{k},\mathbf{k}'} = L^3 \int_{\Omega_1} \Phi_{J,\mathbf{k}}(\mathbf{r})\ {}^{L}V^{t_2}_{ks}(\mathbf{r})\ \Phi_{J,\mathbf{k}'}(\mathbf{r})\; d\mathbf{r}$$

$$= L^3 \sum_{\mathbf{k}\in\Omega_J}^{L} V_{ks}(\mathbf{k}/2^J)\ \underbrace{\int_{\Omega_1} \Phi_{J,\mathbf{k}}(\mathbf{r})\ \theta^{\sharp}_{J,\mathbf{k}}\ \Phi_{J,\mathbf{k}'}(\mathbf{r})\; d\mathbf{r}}_{Connection\quad coefficient} \ ,$$

$\Longrightarrow$ **(B 92, SP 94, DM 93)**, **(F 97 2000, M 96)**

Solving the Self-Consistent Model

GAL GALERKIN FORMULATION II

1. From $\mathbb{V}_J^{t_1}$ to $\mathbb{V}_J^{t_2}$ and then from $\mathbb{V}_J^{t_2}$ to $\mathbb{V}_J^{t_1}$

$$
\begin{aligned}
{}^L V_{ks}^{t_2}\ {}^L\Psi_i^J &= \sum_{\mathbf{k}\in\Omega_J} {}^L V_{ks}(\mathbf{k}/2^J)\ {}^L\Psi_i^J(\mathbf{k}/2^J)\ \theta^{\sharp}_{J,\mathbf{k}}, \\
< {}^L V_{ks}^{t_2}\ {}^L\Psi_i^J \,|\, \Phi_{J,\mathbf{k}'} > &= 2^{-3J/2} \sum_{\mathbf{k}\in\Omega_J} {}^L V_{ks}(\mathbf{k}/2^J)\ {}^L\Psi_i^J(\mathbf{k}/2^J) \int_{\Omega_1} \theta_{J,\mathbf{k}'}\ \Phi_{J,\mathbf{k}}
\end{aligned}
$$

So $\mathbb{B}^{k,J}$ is approximated by the operator:

$$\mathbb{B}^{k,J} = L^3 D_J^{-1}\, Z\ {}^L V_{ks}^{t_2}\ D_J\ X$$

where $D_J = 2^{3J/2}\, I$ and thus the application of $\mathbb{B}^{k,J}$ to C_J^i costs $(2d+d')\times 2^{3J}$ operations.

2. From $\mathbb{V}_J^{t_1}$ to $\widetilde{\mathbb{V}}_J^{t_2}$ and then from $\widetilde{\mathbb{V}}_J^{t_2}$ to $\mathbb{V}_J^{t_1}$

The operator $\mathbb{B}^{k,J}$ is approximated by:

$$\mathbb{B}^{k,J} = L^3 D_J\ X^T\ {}^L V_{ks}^{t_2}\ D_J^{-1}\ Z^T$$

Solving the Self-Consistent Model

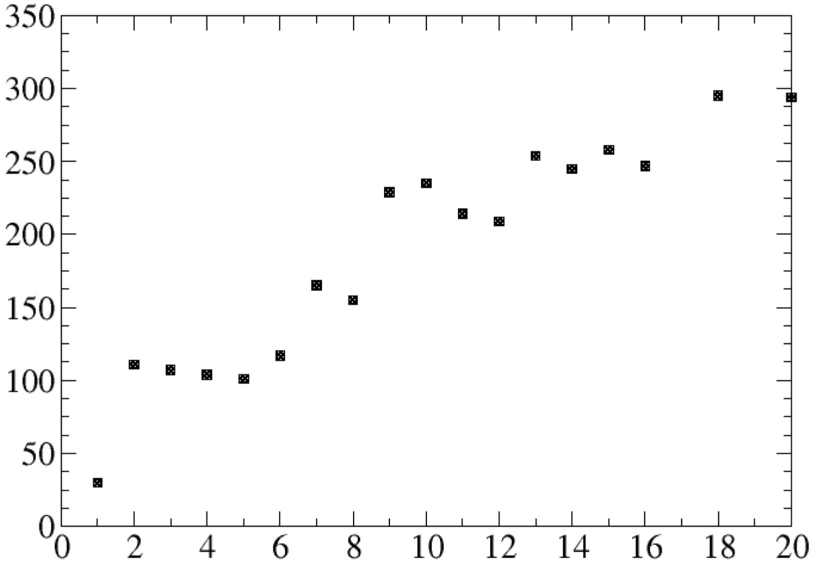
DIAG DIAGONALISATION PROCEDURE

- *Implicit Restart Arnoldi Method* (**S 92, S 96, LSY 97**). ARPACK library.

$\Longrightarrow$ Lanczos method in case of symmetric matrice.

We calculate not only occ occupied Ritz values, but also nv additionnal eigenvalues, and the corresponding virtual orbitals:

$$\rho = 2\sum_{i=1}^{occ} n_i|\Psi_i|^2 \text{ or } \rho = 2\sum_{i=1}^{occ+nv} n_i|\Psi_i|^2 \text{, with } n_i = 0, \quad i = occ+1, nv$$



Matrix/vector product vs number of eigenvalues, for a given Hamiltonien.

For the helium pseudopotential, $occ = 1$, $k = 1$. nv vs matrix vector product. Krylov space dimension is 50, resolution is 128^3. t_1 is Daubechies 6, and t_2 is 8-supported interpolating family.

EN EVALUATION OF ENERGIES

- An eigenvalue should be calculated as follows:

  $$\varepsilon_i^{k+1} = \frac{1}{2L^2}\int_{\Omega_1} |\nabla\, {}^L\psi_i^{k+1}|^2 + L^3 \int_{\Omega_1} {}^L V_{ks}^{t_2}(\mathbf{r})\,|\,{}^L\psi_i^{k+1}|^2(\mathbf{r})d\mathbf{r}$$

  $\Longrightarrow$ Evaluation of one-orbital density on t_2, and then we get directly the potential energy. (costs $(d+2)2^{3J}$ operations.)

  $\Longrightarrow$ A finer resolution should be used to make the square of ${}^L\psi_i^{k+1}$.

  This involves a scheme like: $\mathbb{V}_J^{t_1} \longrightarrow \mathbb{V}_{J+\ell}^{t_2}$

  $\Longrightarrow$ In the next part, numerical tests for this evaluation.

- Let recall the total energy:

$$\mathcal{E}[\,{}^L\widetilde{\rho}^k] =$$

$$2\sum_{i=1}^{occ} n_i\,\varepsilon_i^{k+1} - \frac{L^3}{2}\int_{\Omega_1} {}^L V_c[\,{}^L\widetilde{\rho}^k]\,\rho^{k+1} - L^3\int_{\Omega_1} {}^L V_{xc}[\,{}^L\widetilde{\rho}^k]\rho^{k+1} + \mathcal{E}_{xc}[\,{}^L\widetilde{\rho}^k]$$

Once we get ${}^L\psi_i^{k+1}$ on t_2, we get ρ^{k+1} on t_2. This step costs $(occ\times d+1)2^{3J}$ operations. The calculation of $\mathcal{E}$ is thus linear.

CVG CONVERGENCE

From an input $\widetilde{\rho}^k$ at iteration k, we get a new density ρ^{k+1}.

- The output ρ^{k+1} is contructed with the $\{\psi_i^{k+1}\}$ by following the Aufbau principle.
- If $||\rho^{k+1} - \widetilde{\rho}^k||_{\ell_2} \leqslant \tau$, then the algorithm has converged.
- Else, the simplest construction of a new input $\widetilde{\rho}^{k+1}$ is to take the last output, i.e. $\widetilde{\rho}^{k+1} = \rho^{k+1}$. This algorithm, called the Roothaan algorithm, is the simplest way to minimize the total energy.
- It was proved that Roothaan's algorithm gives not always a unique fixed-point. In DIIS, or ODA, one can construct a new input density $\widetilde{\rho}^{k+1}$ so that the global energy $\mathcal{E}_{KS}$ is minimized along the sequence of $\widetilde{\rho}^k$.

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Numerical experiments

- Hydrogen atom
- Hydrogen in LDA
- Small atoms
- Occupied and unoccupied orbitals
- Compressibility of orbitals

HYDROGEN ATOM

- Linear Hamiltonian $\mathcal{H} = -\frac{1}{2}\Delta - \frac{1}{|\mathbf{r}|}$

J	C2 I8	D6 I8	D8 I8	D8 I6
32	2.410^{-2}	$4.4.10^{-2}$	$2.2.10^{-2}$	$1.8.10^{-2}$
64	$3.6.10^{-3}$	$6.8.10^{-3}$	3.10^{-3}	$2.6.10^{-3}$
128	4.10^{-4}	8.10^{-4}	4.10^{-4}	2.10^{-4}

Cinetic energy for the hydrogen wave function. J is the resolution, $C2I8$ means $t_1 = C2$ and $t_2 = I8$, that is $2-$-order Coiflet and $4-$order interpolet. $L = 10Bohr$.

	C2I8	D6I8	D8I8	D8I6
32	$1.4.10^{-3}$	$6.4.10^{-3}$	$1.4.10^{-2}$	$1.5.10^{-2}$
64	1.10^{-2}	8.10^{-3}	4.10^{-3}	8.10^{-3}

Error in the evaluation of ground state of Hydrogen, by IRAM procedure. $L = 10Bohr$.

HYDROGEN ATOM

1. From $\mathbb{V}_J^{t_1}$ to $\mathbb{V}_J^{t_2}$ $\{c_{J,\mathbf{k}}\}_{\mathbf{k}\in\Omega_J} \longrightarrow \{r_{J,p}\}_{p\in\Omega_J} \longrightarrow E_p^J = \sum_{p\in\Omega_J} r_{J,p}^2 \, V(p)$

J	C2 I8	D6 I8	D8 I8	D8 I6
32	$2.87\ 10^{-2}$	$1.34\ 10^{-2}$	$7.24\ 10^{-3}$	$6.24\ 10^{-3}$
64	$1.80\ 10^{-3}$	$2.74\ 10^{-3}$	$1.06\ 10^{-4}$	$4.63\ 10^{-5}$
128	$8.95\ 10^{-5}$	$1.15\ 10^{-3}$	$4.12\ 10^{-5}$	$4.32\ 10^{-5}$

Potential energy approximation with the first method

2. From $\mathbb{V}_J^{t_1}$ to $\mathbb{V}_J^{t_2}$ and to $\widetilde{\mathbb{V}}_J^{t_2}$

$$\begin{tikzcd}
\{c_{J,\mathbf{k}}\}_{\mathbf{k}\in\Omega_J} \arrow[r] \arrow[dr] & \{r_{J,p}\}_{p\in\Omega_J} \arrow[r] & E_p^J = \sum_{p\in\Omega_J} r_{J,p} \, V(p) \, \widetilde{r}_{J,p} \\
& \{\widetilde{r}_{J,p}\}_{p\in\Omega_J} \arrow[ur] &
\end{tikzcd}$$

J	C2 I8	D6 I8	D8 I8	D8 I6
32	$1.81\ 10^{-2}$	$9.87\ 10^{-3}$	$7.24\ 10^{-3}$	$5.86\ 10^{-3}$
64	$1.16\ 10^{-3}$	$1.21\ 10^{-3}$	$3.16\ 10^{-4}$	$2.28\ 10^{-4}$
128	$4.83\ 10^{-5}$	$5.81\ 10^{-4}$	$1.66\ 10^{-5}$	$1.96\ 10^{-4}$

Potential energy approximation with the second method

HYDROGEN IN LDA - COMPARISON WITH CPMD

	D6I6	D8I6	D6I8	D8I8	C2I8
32^3	-0.4711	-0.4703	-0.4856	-0.4773	-0.4731
64^3	-0.5002	-0.5007	-0.5002	-0.5007	-0.5012

Ground state for hydrogen in DFT-LDA approximation, $L = 7a.u.$.

	# ψ	# ρ	$\mathcal{E}_{pw}$	$\mathcal{E}_{lanczos}$
32^3	1052	8188	-0.4759	-0.4773
48^3	2872	23149	-0.4774	-0.4786
64^3	8188	65578	-0.4777	-0.4787
90^3	23149	185147	-0.4777	-0.4789

CPMD

SMALL ATOMS

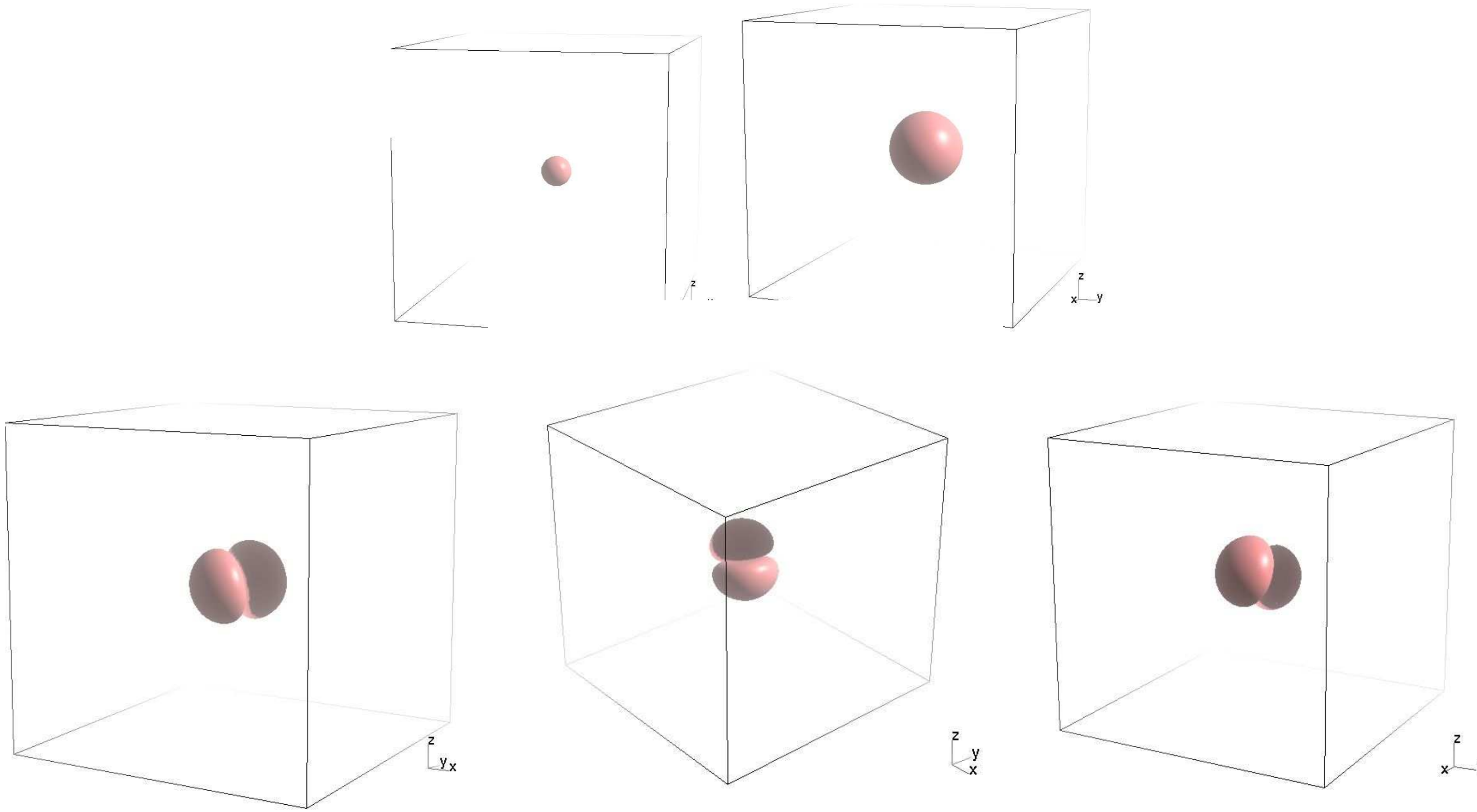
	Hydrogène (H)	Hélium (He)	Lithium (Li)	Néon (Ne)
N	1	2	3	10
n_i	(1/2,0)	(1,0)	(1,1/2)	(1,1,3)
$\mathcal{E}$ (H)	-.5	-2.90	-7.48	-128.94

Experimental values for some atoms, en $Hartree$.

Élement	Résolution	Occupation	L	E_{tot}
Hélium	128^3	(1,0)	9	-4.78
Lithium	64^3	(1,1/2)	10	-11.85
Bérylium	128^3	(1,1)	15	-22.49
Néon	64^3	(1,1,1,1,1)	20	-143.00

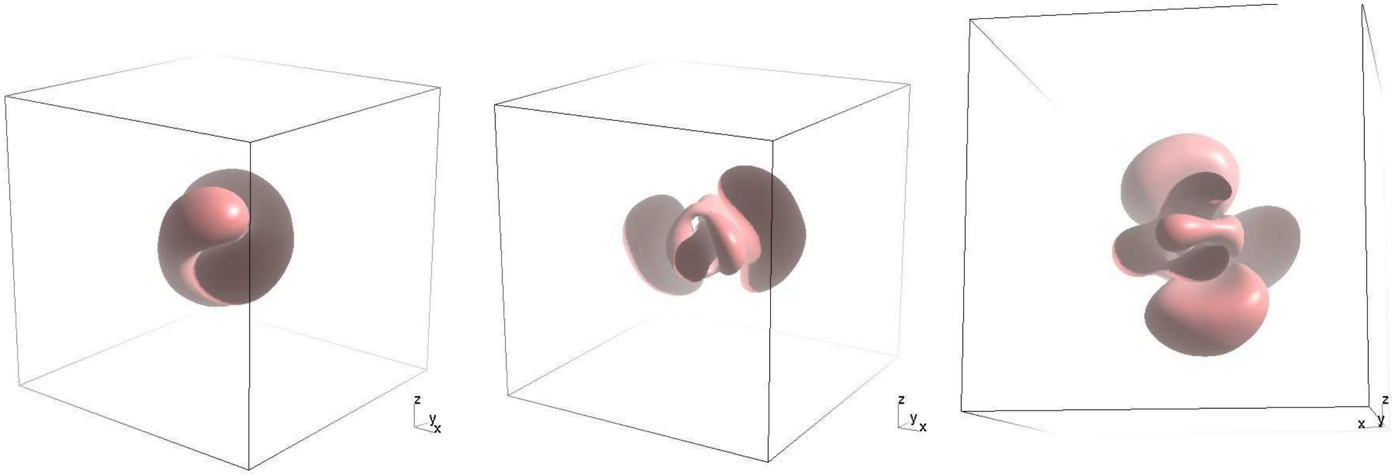
Our evaluations

OCCUPIED AND UNOCCUPIED ORBITALS



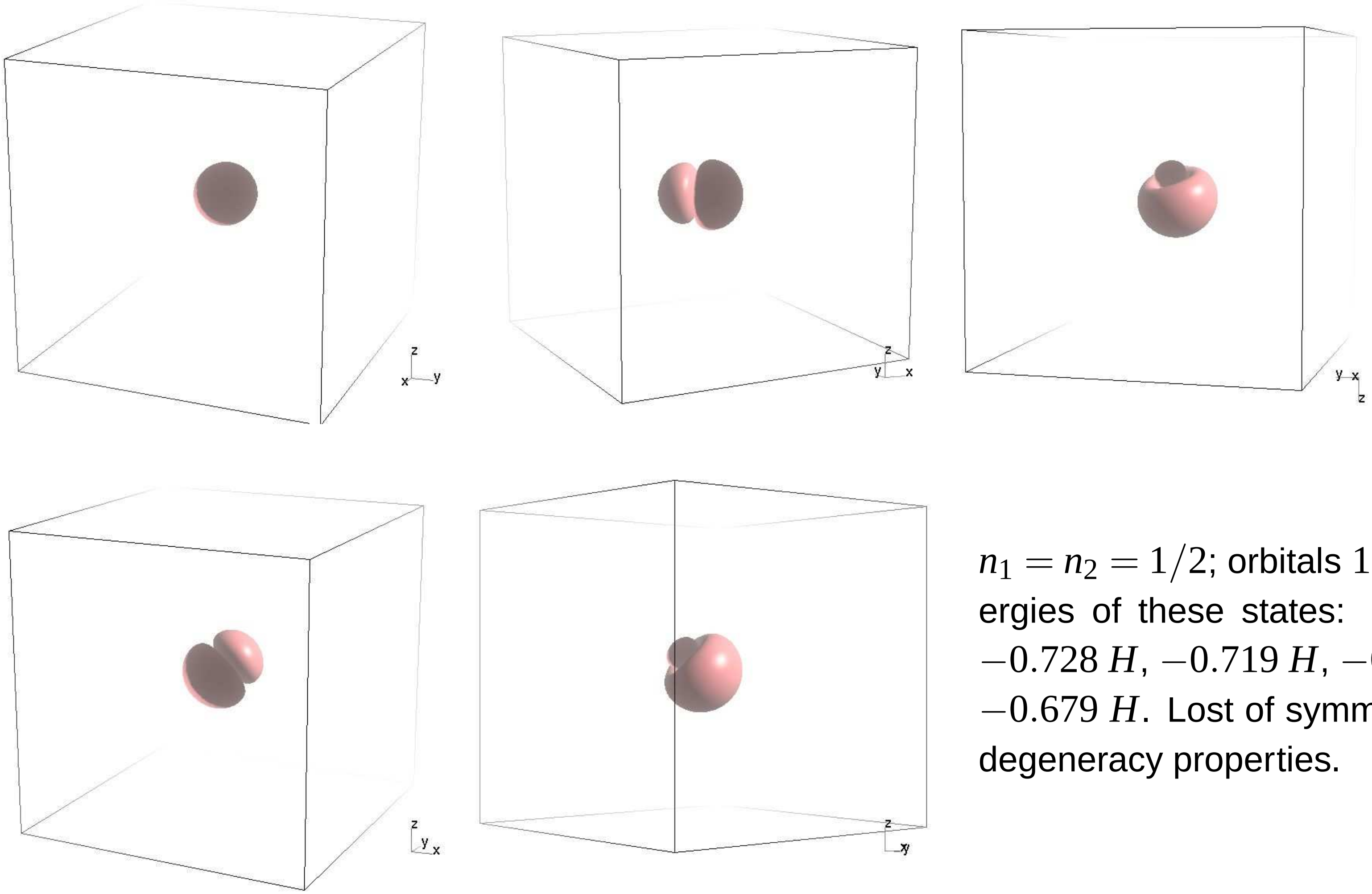
For Helium pseudopotential; $Z = 2,\ n_1 = 1,\ occ = 1,\ nv = 29,\ J = 7, L = 30\ Bohr$. The first orbitals appear in the good order, degeneracy and symmetries. Orbitales are almost antisymmetric.

OCCUPIED AND UNOCCUPIED ORBITALS



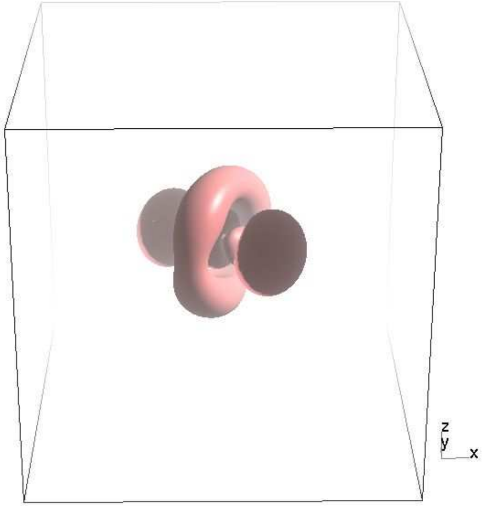
For Helium pseudopotential; $Z = 2,\ n_1 = 1,\ occ = 1,\ nv = 29,\ J = 7$. Higher energy orbitals do not have the symmetries expected. Here are the 11, 16 and 27 orbitals.

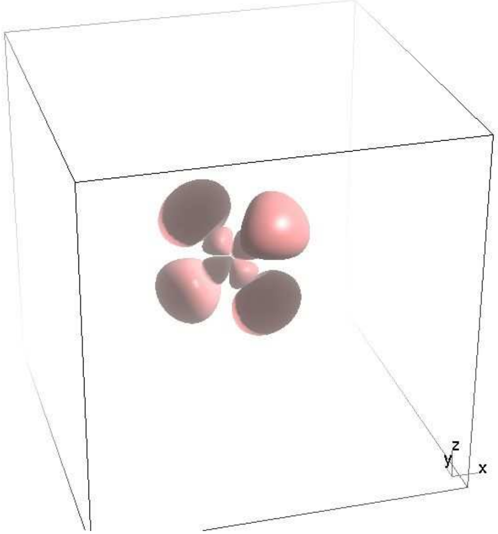
OCCUPIED AND UNOCCUPIED ORBITALS

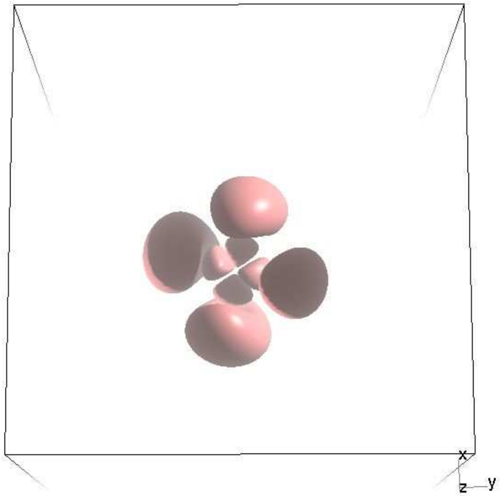


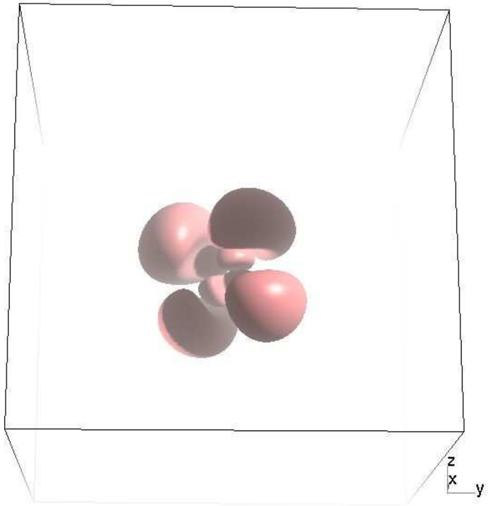
$n_1 = n_2 = 1/2$; orbitals $1-6$. Energies of these states: $-2.1\ H$, $-0.728\ H$, $-0.719\ H$, $-0.704\ H$, $-0.679\ H$. Lost of symmetry and degeneracy properties.

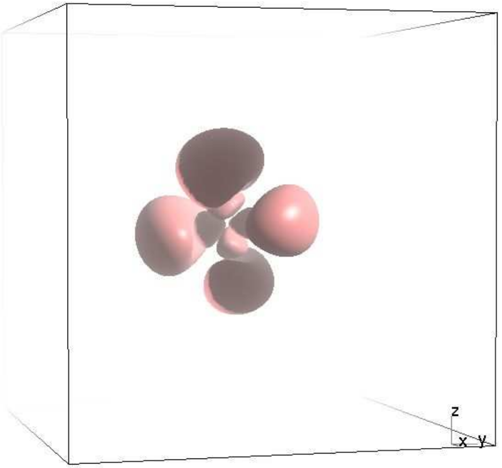
OCCUPIED AND UNOCCUPIED ORBITALS











$n_1 = n_2 = 1/2$, helium pseudopotential. Isosurface of $\pm 0.002 a.u.$. Energies of these states, respectively -0.203, -0.202, -0.200, -0.191, -0.191 H. The first orbitals have not symetries. But higher energy orbitals satisfy degeneracy order and symetries of a real state. Here is the example of the $22-26th$ orbitals, corresponding to $4d$-orbitals.

COMPRESSIBILITY OF ORBITALS

- When the program converges, we get $\{\, \varepsilon_i^f \,,\ {}^L\psi_i^f \,\}_{i=1,\dots,occ}$,

Applying a wavelet transform:

$$\mathbb{P}_J^{t_1}\ {}^L\psi_i^f = {}^L\ \psi_i^J = \sum_{\mathbf{k}\in\Omega_{j_0}} c_{j_0,\ \mathbf{k}}^i\ \Phi_{J,\mathbf{k}} + \sum_{\varepsilon\in\{0,1\}^3\setminus\{(\mathbf{0})\}} \sum_{j=j_0}^{J-1} \sum_{\mathbf{k}\in\Omega_j} d_{j,\mathbf{k}}^{i,\varepsilon} \Psi_{j,\mathbf{k}}^{(\varepsilon)}$$

and defining new sets $\widetilde{\Omega}_j$, $j_0 < j < J$ with thresholding τ:

$$\widetilde{\Omega}_j = \left\{ \mathbf{k} \in \Omega_j,\ \ |d_{j,\mathbf{k}}^{\varepsilon}| \geqslant \tau \right\}$$

We then make an inverse wavelet transform of the compressed function. We get a behaviour like $\parallel \psi_i^J - \widetilde{\psi}_i^\tau \parallel_2 \sim CN^{-\alpha}$

	1	2	3	4	5
64^3	-2	-1.36	-1.36	-1.36	-1.55
128^3	-1.74	-1.43	-1.36	-1.36	-1.36

Coefficient α for the five first virtual orbitals of Helium atom.

COMPRESSIBILITY OF ORBITALS

τ	compression	$\#\Psi_i$	e_c	e_p
1.210^{-7}	86%	36700	0.210^{-7}	0.310^{-8}
6.6210^{-6}	97%	7864	0.610^{-5}	0.810^{-7}
1.4610^{-4}	99%	2621	0.610^{-3}	0.310^{-4}

$J = 6$. Compressibility of the first orbital of Helium, and impact on Kinetic and Potential energies

Behaviour of the different energies:
$|e_c(\psi_1^J) - e_c(\widetilde{\psi}_1^\tau)|_r \sim CN^{-\beta}$,
$|e_p(\psi_1^J) - e_p(\widetilde{\psi}_1^\tau)|_r \sim CN^{-\beta'}$,
Idem for e_{xc}, v_{xc} and $e_{cou\ell}$ γ, γ' and ν.

Cinetic and Potential Energy Slopes for the helium orbital. SCF resolution with $J = 7$, and $t_1 = D8$, $t_2 = I8$.

i	1	2	3	4	5
β	-2.86	-2.38	-1.98	-1.92	-2.05
β'	-3.86	-2.81	-2.61	-2.68	-2.65

COMPRESSIBILITY OF ORBITALS: IMPACT ON ENERGIES

		e_c	e_p	$\mathcal{E}_{xc}$	E_{xc}	$e_{cou\ell}$
	t_1	β	β'	γ	γ'	ν
64^3	d6	-1.93	-2.51	-2.19	-2.18	-2.91
64^3	d8	-2.55	-2.96	-1.7	-1.7	-2.4
64^3	d10	-2.9	-3.35	-1.5	-1.5	-2.5
128^3	d6	-1.45	-2.18	-2.18	-2.18	-2.18
128^3	d8	-2.12	-2.90	-1.91	-1.91	-2.15
128^3	d10	-2.62	-3.33	-2.26	-2.26	-2.52

Slopes of the lines on log/log scales (#ρ vs relative error of energy), for different Daubechies's orders. SCF calculation for the hydrogen atom in LDA approximation. $J = 7, L = 7, t_2 = I8$.

RESULTS - FORECASTS

- A mathematical formulation of the Density-Functional Theory
- A method for the interpolation problem.
- Two methods to solve Poisson equation.
- A solver for Kohn-Sham equations in LDA-approximation.

$\Longrightarrow$ Perform this solver on a regular basis to describe more precisely physical experiments (pseudopotential - exchange-correlation term).

$\Longrightarrow$ Functionnal analysis in DFT: proof of existence of discrete eigenvalues for the linearized hamiltonien, and criteria on V_{xc} for self-consistent convergence (in progress).

$\Longrightarrow$ Towards an adaptive method: analysis of the potential operator compressibility, a first solver with orbitals in wavelet basis.