Approximated Stiffness matrix for non linear operator by a collocation method

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1 Physical context

In electronic structure calculations, one objective is the determination of the ground state of a system composed of atoms, i.e. of K nuclei (positioned in $\mathbf{R}_\alpha$, $\alpha = 1, N$) and $2N$ electrons occupying N_o energy levels. This ground state is determined by solving, in case of Density Functional Theory approximation [1], the following system:

$$\begin{aligned} \mathcal{H}[\rho]\ \psi_i &= \epsilon_i\ \psi_i, \qquad \forall\ i = 1, \ldots, N, & (1)\\ \mathcal{H}[\rho] &= -\frac{1}{2}\Delta + V(\mathbf{r}) + V_C[\rho] + V_{xc}[\rho], & (2) \end{aligned}$$

where the density ρ is related to the orbitals ψ_i in the following way:

$$\rho = 2\ \sum_{i=1}^{N_o} n_i\ |\psi_i|^2, \quad \sum_{i=1}^{N_o} n_i = N, \quad 0 \leqslant n_i \leqslant 1.$$

Theoretically, occupation numbers n_i can be fractional. It occurs when some successive state energies $\epsilon_i = \cdots = \epsilon_{i+k}$ are equal, that is when an energy level is degenerate. For simplicity we will assume here that $n_i = 1$, $\forall i = 1, N_o$, and that the number of occupied energy levels N_o is equal to N. Orbitals satisfy the orthogonality relation $\displaystyle\int_\Omega \psi_i\ \psi_j^*\ d\mathbf{r} = \delta_{i,j}$. Details on the domain $\subset \mathbb{R}^3$ where these equations live will be given later. The different potential terms, expressing the different interactions between electrons and nuclei, write:

$$\begin{aligned} V(\mathbf{r}) &= -\sum_{\alpha=1}^{K} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|},\\ -\Delta V_C &= 4\pi\rho. \end{aligned}$$

One way to solve numerically Poisson equation was presented in [2]. One usually use the Local Density Approximation (LDA) or derivatives to get the exchange-correlation potential V_{xc} in Hamiltonian operator (2). In LDA, the potential $V_{xc}(\mathbf{r})$ is evaluated by knowing the density at this point $\rho(\mathbf{r})$. We thus need the expression of ρ in an interpolating basis.

Assuming orbitals ψ_i are orthonormal, ϵ_i writes:

$$\begin{aligned} \epsilon_i = <\psi_i,\ \mathcal{H}[\rho]\ \psi_i> &= <\psi_i,\ -\frac{1}{2}\Delta\ \psi_i> + <\psi_i,\ (V(\mathbf{r}) + V_C[\rho] + V_{xc}[\rho])\ \psi_i> \\ &= e_{kin} + e_p, & (3) \end{aligned}$$

where e_{kin} is the kinetic energy corresponding to the Laplacian, and e_p is the potential energy. As explained before the potential is expressed in an interpolating basis, and the issue of this paper is the evaluation of e_p by an accurate and efficient method. This leads to look for a method to evaluate the application of an operator - the potential expressed in a collocation basis - to an orbital ψ_i expressed in another basis.

We first present the basis used in this context. Then, a method that approximates the construction of the Stiffness matrix is shown. Finally, some examples illustrate the efficiency and viability of our method. In the next section, we present a multiresolution analysis (MRA) on the three-dimensional unit torus Ω. In physical calculations, we will use a dilatation of this domain by a parameter L, so that functions actually live in $(\mathbb{R}/L\mathbb{Z})^3$.

2 Three-dimensional periodic MRA

Let $\omega = \mathbb{R}/\mathbb{Z}$ be the unit torus on $\mathbb{R}$, and Ω the three-dimensional one $\Omega = (\mathbb{R}/\mathbb{Z})^3$. A periodic MRA $\{\mathbb{V}_J\}$ of $L^2(\Omega)$ is constructed by an isotropic tensor product of one-dimensional MRA $\{V_J\}$:

Def 2.1 (MRA of $L^2(\omega)$) *Let $\{V_J\}$ and $\{\widetilde{V}_J\}$, $j \geqslant 0$ the sequences of two biorthogonal MRA's of $L^2(\omega)$. Each couple of scaling functions $\phi_{J,k}$ and $\widetilde{\phi}_{J,l}$, with indices k, l in $\omega_J = [0, \ldots, 2^J - 1]$ satisfies the biorthogonality relation:*

$$\int_\omega \phi_{J,k}(x)\ \widetilde{\phi}_{J,l}(x)\ dx = \delta_{k,l}, \quad J \in \mathbb{N}, \quad k, l \in \omega_J,$$

where $\delta_{k,l}$ is the Kronecker delta. There is moreover two-scale relations for these functions:

$$\begin{aligned} \phi_{J,k} &= \sum_{\nu \in \omega_J} h_{J+1}(n-2k)\phi_{J+1,n}, \qquad (4) \\ \widetilde{\phi}_{J,k} &= \sum_{\nu \in \omega_J} \widetilde{h}_{J+1}(n-2k)\widetilde{\phi}_{J+1,n}. \end{aligned}$$

where h_J and $\widetilde{h}_J$ are filters coming from the 2^J-periodisation of filters $(h, \tilde{h})$ associated to the scaling functions defined on $\mathbb{R}$.

The basis have compact support, corresponding to a finite length for h and $\widetilde{h}$. Actually, under suitable conditions, ϕ with compact support satisfying (4), and in the Sobolev space $H^m(\omega)$ is of order m. The order m corresponds to the maximal polynomial degree one can locally reproduce on V_J. This order has a decisive impact on approximation of functions in an MRA, as it will be illustrated in the following.

This article is devoted to the evaluation of the Stiffness matrix expanded in scaling function basis, we will not introduce here wavelets. Of course, the second step leading to an adaptive scheme will be the study of such matrices in wavelet basis. The construction of three-dimensional MRA is done as follows:

Def 2.2 (MRA of $L^2(\Omega)$) *Assume the hypothesis of (def 2.1) are fulfilled, we define a couple of biorthogonal MRA $\{\mathbb{V}_J\}$ and $\{\widetilde{\mathbb{V}}_J\}$ of $L^2(\Omega)$ by isotropic tensor product:*

$$\begin{aligned} \mathbb{V}_J &= V_J \otimes V_J \otimes V_J, \\ \widetilde{\mathbb{V}}_J &= \widetilde{V}_J \otimes \widetilde{V}_J \otimes \widetilde{V}_J. \end{aligned}$$

Let $\Omega_J = \omega_J^3$. A scaling function of $\mathbb{V}_J$ centered at $\mathbf{k} = (k_1, k_2, k_3) \in \Omega_J$ writes for each $\mathbf{r} = (x, y, z) \in \Omega$:

$$\Phi_{J,\mathbf{k}}(\mathbf{r}) = \phi_{J,k_1}(x)\ \phi_{J,k_2}(y)\ \phi_{J,k_3}(z).$$

In the following we adopt a vector-type notation for the basis: $\mathcal{F}_J = \{\Phi_{J,\mathbf{k}}\}_{\mathbf{k}\in\Omega_J}$ (the same holds for the dual $\widetilde{\mathcal{F}}_J$). A function f of $\mathbb{V}_J$ with coefficients $C = \{c_{J,\mathbf{k}}\}_{\mathbf{k}\in\Omega_J}$ thus writes:

$$f = C^T \mathcal{F}_J = \sum_{\mathbf{k}\in\Omega_J} < f,\ \widetilde{\Phi}_{J,\mathbf{k}} >\ \Phi_{J,\mathbf{k}}.$$

In next part we introduce some particular families used in our computations.

2.1 Particular MRA used in this context

Algorithm used to solve the system (1) leads to the resolution of an eigenvalue problem at each iterative step [3], which is quickly solved when the system is discretized in an orthogonal basis.

Def 2.3 (Orthogonal MRA of $L^2(\Omega)$) *Let $\{\mathbb{V}_J^{t_1}\}$ be an orthogonal MRA of $L^2(\Omega)$. Scaling functions are called $\Phi_{J,\mathbf{k}}$, and are generated by tensor product of m_1-order scaling functions, with filter h_J.*

In our tests we will use Daubechies families, Symmlets and Coiflets [4]. The potential is expanded in a basis satisfying the interpolation property:

Def 2.4 (Interpolating scaling function) *A scaling function $\Theta_{J,\mathbf{k}}$ of $\mathbb{V}_J^{t_2}$ is interpolating, when it satisfies the condition:*

$$\Theta_{J,\mathbf{k}}(\mathbf{l}/2^{3J}) = \delta_{\mathbf{k},\mathbf{l}}.$$

Such a function is also called Interpolet. In the following, we consider the biorthogonal MRA's $\{\mathbb{V}_J^{t_2}\}$ and $\{\widetilde{\mathbb{V}}_J^{t_2}\}$ where the primal space $\mathbb{V}_J^{t_2}$ is composed of interpolating scaling functions $\Theta_{J,\mathbf{k}}$ of Deslauriers-Dubuc [5] of order m_2. The associated dual scaling function $\widetilde{\Theta}_{J,\mathbf{k}}$ is the Dirac distribution: $\widetilde{\Theta}_{J,\mathbf{k}}(\mathbf{r}) = \delta(\mathbf{k}/2^{3J})$. As explained in section 1, the potential is known at each point $\mathbf{k}/2^{3J}$, $\mathbf{k} \in \Omega_J$. Let P be the set of point values with the appropriate normalization, the potential V writes:

$$V(\mathbf{r}) = P^T \mathcal{T}_J = \sum_{\mathbf{k}\in\Omega_J} < V, \widetilde{\Theta}_{J,\mathbf{k}} > \ \Theta_{J,\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{k}\in\Omega_J} v_{J,\mathbf{k}}\ \Theta_{J,\mathbf{k}}(\mathbf{r}). \tag{5}$$

The objective is to apply the operator V to an orbital ψ_i in an efficient way. The aim is to reduce as far as possible the computational cost, which can become high in three dimensions.

3 Approximated Stiffness matrix by collocation method

Coefficients of the exact potential Stiffness matrix ${}^G\mathbb{B}$ resulting from the Galerkin formulation are:

$$\begin{aligned} {}^G\mathbb{B}_{\mathbf{k},\mathbf{k}'} &= \int_{\Omega_1} \Phi_{J,\mathbf{k}}(\mathbf{r})\ V(\mathbf{r})\ \Phi_{J,\mathbf{k}'}(\mathbf{r})\ d\mathbf{r} = \sum_{\mathbf{m}\in\Omega_J} v_{J,\mathbf{m}} \int_{\Omega} \Phi_{J,\mathbf{k}}(\mathbf{r})\ \Theta_{J,\mathbf{m}}(\mathbf{r})\ \Phi_{J,\mathbf{k}'}(\mathbf{r})\ d\mathbf{r} \\ &= \sum_{\mathbf{m}\in\Omega_J} v_{J,\mathbf{m}}\ \mathbf{T}(\mathbf{k}-\mathbf{m}, \mathbf{k}'-\mathbf{m}), \quad \forall \mathbf{k}, \mathbf{k}' \in \Omega_J. \end{aligned}$$

By a change of variable, thanks to the symmetry around the function $\Theta_{J,\mathbf{m}}$, the calculation of ${}^G\mathbb{B}_{\mathbf{k},\mathbf{k}'}$ leads to a bidimensional convolution of coefficients P by the matrix $\mathbf{T}$. This matrix is a tensor product of three cyclic matrices T, whose coefficients are called connection coefficients [6]:

$$T(k, k') = 2^{J/2} \int_{\omega} \phi(x-k)\ \theta(x)\ \phi(x-k')\ dx.$$

The calculation of T can be found in [6]. For $m_1 = 4$ (Daubechies) and $m_2 = 8$ (Interpolet), T has almost 30 coefficients greater than 10^{-8}. In three dimensions, Table 1 gives the repartition of coefficient modulus. More than 10000 coefficients are greater than 10^{-8}. Important coefficients are situated around the diagonal, that is for $\mathbf{k}$ close to $\mathbf{k}'$.

$\lvert\mathbf{T}(\mathbf{k},\mathbf{k}')\rvert$	$> 10^{-4}$	$> 10^{-8}$	$> 10^{-11}$	$> 10^{-16}$
#	684	9420	14980	12475

Table 1: Number of coefficients of $\mathbf{T}$ located between two magnitudes, with $t_1 = D4$ and $t_2 = I8$. 9420 is the number of coefficients greater in module than 10^{-8}, and smaller than 10^{-4}.

We tried to find good properties for this matrix, to get an almost diagonal approximation of T. But work on this matrix seems not to be a good idea if one want to improve algorithm complexity. That is why we look for other ways to approximate the Stiffness matrix. These methods will be compared with Galerkin formulation by the way of potential energy, which writes here:

$$^{G}\tilde{e}_p = \frac{C^T\ {}^{G}\mathbb{B}\ C}{C^T\ C}.$$

This calculation can easily be done in the specific case of Harmonic Oscillator, where potential and orbital have separability properties. This will be done in section 4. The next of this section is dedicated to new methods to construct approximated Stiffness matrices.

3.1 Transfer operator

Let start with the orbital expanded in the orthogonal basis:

$$\psi_i(\mathbf{r}) = C^T \mathcal{F}_J = \sum_{\mathbf{k}\in\Omega_J} c_{J,\mathbf{k}}\ \Phi_{J,\mathbf{k}}(\mathbf{r}), \tag{6}$$

where $C = \{c_{J,\mathbf{k}}\}_{\mathbf{k}\in\Omega_J}$.

Def 3.1 (Transfer operator) *Let $\mathbb{V}_J^{t_1}$ the 2^{3J}-dimension space associated to an orthogonal MRA of $L^2(\Omega)$, and let $\mathcal{F}_J$ be the scaling function basis of $\mathbb{V}_J^{t_1}$. We also consider two spaces $\mathbb{V}_J^{t_2}$ and $\widetilde{\mathbb{V}}_J^{t_2}$ of two biorthogonal MRA's, with basis $\mathcal{T}_J$ and $\widetilde{\mathcal{T}}_J$.*
We define $X \in \mathcal{M}_{\Omega_J,\Omega_J}(\mathbb{R})$ as the operator associating a set of coefficients C of a function of $f_1 \in \mathbb{V}_J^{t_1}$ to a set of coefficients D of a function $f_2 \in \mathbb{V}_J^{t_2}$:

$$\begin{array}{rccc} X: & \mathcal{M}_{\Omega_J} & \longrightarrow & \mathcal{M}_{\Omega_J}, \\ & C & \longmapsto & D. \end{array}$$

A term of this operator writes:

$$\forall\ \mathbf{k},\mathbf{k}' \in \Omega_J, \quad X(\mathbf{k},\mathbf{k}') = \int_{\Omega_1} \Phi_{J,\mathbf{k}'}\ \widetilde{\Theta}_{J,\mathbf{k}}\ d\mathbf{r}.$$

In the same way, we define the operator Z:

$$\begin{array}{rccc} Z: & \mathcal{M}_{\Omega_J} & \longrightarrow & \mathcal{M}_{\Omega_J} \\ & D & \longmapsto & C, \end{array}$$

associating a function $f_2 \in \mathbb{V}_J^{t_2}$ to $f_1 \in \mathbb{V}_J^{t_1}$. A coefficient of Z writes:

$$\forall\ \mathbf{k},\mathbf{k}' \in \Omega_J,, \quad Z(\mathbf{k},\mathbf{k}') = \int_{\Omega_1} \Theta_{J,\mathbf{k}'}\ \Phi_{J,\mathbf{k}}.$$

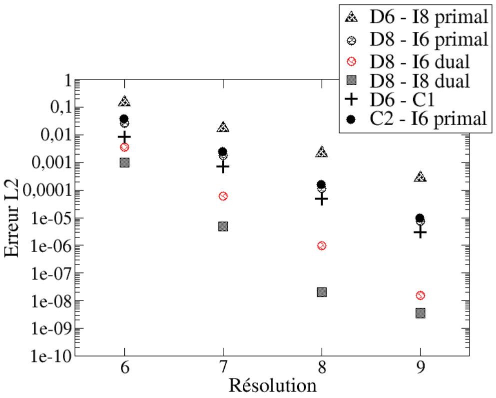

Figure 1: Errors $||D-(ZX)^nD||_{l_2}$ (case primal) and $||D-(X^TZ^T)^nZD||_{l_2}$ (case dual) in function on the resolution J, with $n=10$. The trial function is a Gaussian. t_1 corresponds either to a Daubechies basis of order 3 or 4 (resp. D6, D8), or to a Coiflet basis of order 4 (C2).

We also can define transfer operator from $\mathbb{V}_J^{t_1}$ to $\widetilde{\mathbb{V}}_J^{t_2}$, and from $\widetilde{\mathbb{V}}_J^{t_2}$ to $\mathbb{V}_J^{t_1}$. Actually, these operators are transposes of X and Z: a function f_1 of $\mathbb{V}_J^{t_1}$ with coefficients C, has coefficients $\widetilde{D}=Z^TC$ in $\widetilde{\mathbb{V}}_J^{t_2}$, and from $\widetilde{\mathbb{V}}_J^{t_2}$, one has to apply X^T to get a set of coefficients for the expansion in $\mathbb{V}_J^{t_1}$.

Obviously, we don't have $X=Z^{-1}$. The next example shows, in case of a Gaussian, the behavior of a series of application of operators Z and X.

Example 3.2 *Let f_2 be a Gaussian discretized on an interpolating basis, with coefficients D. Here are presented two kinds of experiments:*

1. *First, express f_2 into $\mathbb{V}_J^{t_1}$: we get $C=ZD$. Do successive passage to $\mathbb{V}_J^{t_2}$ and $\mathbb{V}_J^{t_1}$, by applying the operator ZX. Then evaluate the error $||D-(ZX)^nD||_{l_2}$. As we go here into the primal interpolating space, we denote in figure 1 this case by "primal".*
2. *Second, apply n times X^TZ^T to C, then compute the error $||D-(X^TZ^T)^nZD||_{l_2}$. Here, we express f_2 into the dual interpolating space $\widetilde{\mathbb{V}}_J^{t_2}$, we will then call this "dual".*

Figure 1 shows errors in these two cases "primal" and "dual", for different couples (t_1,t_2). In case "primal", the order m_2 does not increase the error, as it is always at least twice greater than m_1 (D6-C1 is a particular case of quasi-interpolation). The error in this case follows the law 2^{-Jm_1}, that is linear with m_1. In case "dual", there is a dependence not only on m_1, but also on m_2. The order of approximation behaves like $2\min(m_1,m_2)$, that is to say quadratic. In other words, in the second method the successive application of Z^T and X^T is closer to identity.

3.2 Applying Hamiltonian operator to an orbital

There are two different operations in applying Hamiltonian operator defined in (2) to an orbital. Actually, it is linked to the way one evaluates kinetic and potential energies (3). The first one corresponds to the H^1 semi-norm of the function, and is presented in the next subsection. The second one, potential energy, depends on the way one writes the potential Stiffness matrix, and is detailed after.

3.2.1 Kinetic energy

Kinetic energy of an orbital ψ_i (6) is deduced from expression (9), directly using the Stiffness matrix of the Laplacian in $\mathbb{V}_J^{t_1}$:

$$\widetilde{e}_{kin}^J = \frac{(C)^T \ \mathbb{A} \ C}{(C)^T \ C}.$$

The Stiffness matrix $\mathbb{A}$ is obtained in a classical Galerkin way. In the following, let τ_{kin}^J be the relative error: $\tau_{kin}^J = \dfrac{|e_{kin}^J - \widetilde{e}_{kin}^J|}{|e_{kin}^J|}$. The reference energy e_{kin}^J is defined as:

$$e_{kin}^J \sim \frac{L^3}{2^{3J}} \sum_{\mathbf{k}\in\Omega_J} (\nabla \ \psi(x_{J,\mathbf{k}}))^2,$$

where L is a dilatation parameter of the domain Ω (we consider in our tests the torus $(\mathbb{R}/L\mathbb{Z})^3$, rather than Ω, to control the diffusion of test functions inside the domain).

3.2.2 Potential Energy

The potential energy $\widetilde{e}_p$ depends on the construction of the potential Stiffness matrix. We will present here two methods to construct it, starting with the potential V expressed in the collocation basis $\mathcal{T}_J$, with coefficients P (5).

Method 1

In the first method, the Stiffness matrix writes:

$${}^1\mathbb{B} = \ Z \ P \ X.$$

If $D = X \ C$, that is D is the collocation vector of ψ_i on $\mathbb{V}_J^{t_2}$, and $\widetilde{D} = Z^T \ C$, corresponding to the coefficients of ψ_i in the dual interpolating basis, then the potential energy $\widetilde{e}_p$ is approximated by:

$${}^1\widetilde{e}_p^J = \frac{\widetilde{D}^T \ P \ D}{\widetilde{D}^T D}.$$

Method 2

In the second method, ψ_i is expressed in $\widetilde{\mathbb{V}}_J^{t_2}$, and the result of applying potential operator on this orbital is expanded in $\mathbb{V}_J^{t_2}$. One then apply the operator Z to get the expression in $\mathbb{V}_J^{t_1}$:

$${}^2\mathbb{B}^J = Z \ P \ Z^T.$$

Potential energy then writes:

$${}^2\widetilde{e}_p^J = \frac{\widetilde{D}^T \ P \ \widetilde{D}}{\widetilde{D}^T \widetilde{D}}.$$

We will in the next section study the relative error for the potential energy in the three cases: Galerkin, methods 1 and 2. The relative error writes:

$${}^{G,1,2}\tau_p^J = \frac{|{}^{G,1,2}\widetilde{e}_p^J - e_p^J|}{|e_p^J|}, \tag{7}$$

where e_p^J writes:

$$e_p^J \sim \frac{L^3}{2^{3J}} \sum_{\mathbf{k}\in\Omega_J} \ V(x_{J,\mathbf{k}}) \ (\ \psi(x_{J,\mathbf{k}}))^2.$$

4 Approximation order in linear case

We make three-dimensional tests on linear Hamiltonian. In the first case, the Harmonic oscillator, the potential V_o and the solution ψ_o are very regular, so that we get numerically error estimates depending on the basis order. In the second case, the Hydrogen atom, the potential V_h and the orbital ψ_h are both in $\mathcal{C}^0$, and leading to more complicated laws for the error behavior.

In tests presented here, we make a dilatation of the domain Ω, by a change of variable: for all $\mathbf{r} = (X, Y, Z) \in \Omega$, we associate the triplet (x, y, z) so that $X = \frac{x}{L},\ Y = \frac{y}{L},\ Z = \frac{z}{L}$, with $L = 10$. Orbital is expanded in the space $\mathbb{V}_J^{t_2}$ of interpolating scaling functions of order m_2:

$$\psi = 2^{-3J/2} \sum_{\mathbf{k}\in\Omega_J} \psi(x_{J,\mathbf{k}})\ \Theta_{J,\mathbf{k}}. \tag{8}$$

Starting from this expression (8), we evaluate $\widetilde{e}^J_{kin}$ and $\widetilde{e}^J_p$. The coefficients $C = \{c_{J,\mathbf{k}}\}_{\mathbf{k}\in\Omega_J}$ are obtained by applying a change of basis:

$$P_J\ \psi = \sum_{\mathbf{k}\in\Omega_J} c_{J,\mathbf{k}}\ \Phi_{J,\mathbf{k}} = C^T \mathcal{F}_J = (ZD)^T \mathcal{F}_J. \tag{9}$$

4.1 Harmonic oscillator

The model of Harmonic Oscillator is:

$$\mathcal{H} = -\frac{1}{2}\Delta + \frac{1}{2}|\mathbf{r}|^2, \quad \mathbf{r} \in \Omega.$$

A solution $(\mathcal{E}_o,\ \psi_o)$ of the eigenproblem $\mathcal{H}\psi = \mathcal{E}\ \psi$ is known analytically, that is:

$$\begin{aligned} \psi_o(\mathbf{r}) &= C_N\ e^{-|\mathbf{r}|^2/2}, \quad \forall\ \mathbf{r} \in \Omega \\ \mathcal{E}_o &= e_{kin} + e_p, \\ e_{kin} &= \frac{<\psi_o| - \frac{1}{2}\Delta|\psi_o>}{<\psi_o|\psi_o>} = 0.75\ a.u., \\ e_p &= \frac{<\psi_o|\frac{1}{2}|\mathbf{r}|^2|\psi_o>}{<\psi_o|\psi_o>} = 0.75\ a.u.. \end{aligned} \tag{10}$$

C_N is a normalization factor, based on the L^2 norm of ψ_o: $\parallel \psi_o \parallel_2 = 1$. The orbital ψ_o decays rapidly, so no need to have a great L. In this example, orbital ψ_o and potential V_o live in C^∞, so convergence order depends only on MRA orders m_1 and m_2.

4.1.1 Kinetic energy

Figure 2 shows the behavior of relative error τ^J_{kin} in function of 2^J. We used two Interpolet orders, $m_2 = 6$ et $m_2 = 8$, in case of $t_1 = D8$ (order 4). Dependence on m_2 is weak. On log/log scale, we obtain the following behavior for the relative error:

$$\tau^J_{kin} \sim C\ 2^{-2J(m_1-1)}.$$

Below 10^{-9}, the machine precision interferes with values. The results are very similar for a Symmlet and a Daubechies scaling function of same order (the Stiffness matrices of Laplacian are identical). We get the same result with Coiflets (the error is of 10^{-5} with $2^J = 32$), but Daubechies functions have shorter support, and thus are more interesting numerically.

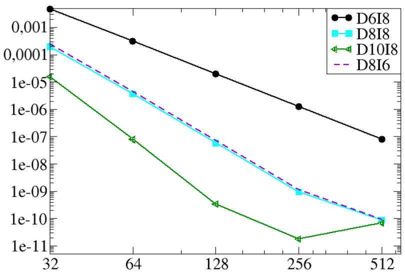

Figure 2: For Harmonic Oscillator, relative error τ_{kin}^J, in function of 2^J. Different order of t_1 and t_2 are showed. The Daubechies indexed by $D8$ is of order 4.

The error between exact and approximated energy is thus quadratic in function of J and m_1. If we want to get an energy with precision ϵ, we need only a precision of $\sqrt{\epsilon}$ on the orbital.

4.1.2 Potential Energy

Galerkin formulation

In case of Harmonic Oscillator, it is easy to evaluate the Galerkin Stiffness matrix, thanks to the separability properties of the operator and the solution:

$$\begin{aligned} V_o(\mathbf{r}) &= \frac{1}{2}(x^2+y^2+z^2) = v(x)+v(y)+v(z), \\ \psi_o(\mathbf{r}) &= C_N\ e^{-|\mathbf{r}|^2/2} = f(x)\ f(y)\ f(z), \\ f(x) &= C_N^{1/3} e^{-x^2/2}. \end{aligned}$$

Let $\omega = [0, L[$, we can express the potential energy in terms of one dimensional quantity:

$$e_p = \int_\Omega \psi_o(\mathbf{r})\ V_o(\mathbf{r})\ \psi_o(\mathbf{r})\ d\mathbf{r} = 3\int_\omega v(x)\ f^2(x)\ dx = 3 \times \frac{1}{4}.$$

	D8I8	D6I8	D6I4
32	0.7500070985	0.750043907	0.75055975
64	0.750000030114	0.75000067514	0.750033937
128	0.750000000058755	0.750000010427	0.750000010427

Table 2: Harmonic Oscillator: potential energy ${}^G\tilde{e}_p^J$ in case of Galerkin formulation.

Table 2 shows potential energies ${}^G\tilde{e}_p^J$ for different couples t_1, t_2. As the solution is extremely regular, the precision directly depends on these two orders. For Daubechies family, $D8$ designs a family of order 4, with support 8. $I8$ corresponds to Interpolet of order 8. Convergence rates are in the three cases 8.5, 6.2 et 4. This suggests an error behavior like:

$${}^G\tau_p^J \sim C\ 2^{-J\ \min(2m_1+\alpha,\ m_2)}, \qquad \alpha \leqslant \frac{1}{2}.$$

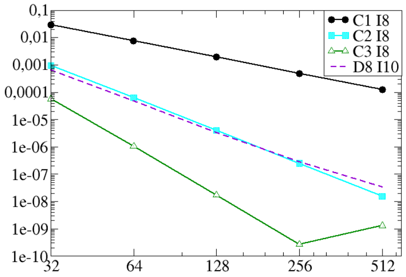

Figure 3: Harmonic Oscillator. Relative error ${}^1\tau_p^J$ in function of the resolution 2^J. In three case, t_1 is a Coiflet family with order respectively 2, 4 and 6. The last case shows that even with a high order, a Daubechies basis does not behave as good as a Coiflet one.

C1 I8	C2 I8	C3 I8	D8e I10	D8s I8
2	4	6	4	4
1.97	4.01	5.87	3.94	4.00

Table 3: Harmonic Oscillator, rates in method 1 for different couples (t_1, t_2). Second line corresponds to m_1. s stands for symmetric, e for extremal.

A reasonable choice is thus an Interpolet order $m_2 \geqslant 2m_1$.

Method 1

Figure 3 shows the evolution of the relative error ${}^1\tau_p^J$ defined in (7) in function of 2^J, for different couples (t_1, t_2). The coefficient rate behaves like:

$$ {}^1\tau_p^J \sim C_1 \; 2^{-J \;\; \min(m_1, m_2)}. \tag{11} $$

Table 3 gives rates corresponding to figure 3. The poor approximation property of a Daubechies scaling function ($D8$, of order 4) is mainly due to the fact it has no vanishing moments.

Method 2

The rates obtained for the relative error in method 2 are relatively high. As observed in figure 4, the error is quadratic:

$$ {}^2\tau_p^J \sim C_2 \; 2^{-J \min(2m_1, m_2)}, \tag{12} $$

factor C_2 depending on $\parallel \psi \parallel_{H^{m_1}}$ and $\parallel \psi \parallel_{H^{m_2}}$. Here, there is not a so big difference between Daubechies and Coiflets. This is certainly due to the fact that orbital is expressed in $\widetilde{\mathbb{V}}_J^{t_2}$, but not in $\mathbb{V}_J^{t_2}$. The quadratic behavior means that if ψ_i is evaluated with error ϵ, then its energy will have an error of ϵ^2. We can therefore conclude that this evaluation of potential energy is optimal.

Energies of method 2 (Table 4) are of same order as those obtained in Galerkin formulation (Table 2). We thus have a method to apply a potential operator with the same approximation order as for the Galerkin formulation, but with a reasonable cost in three dimensions. Indeed, applying operators Z and X is linear with the support of scaling functions, rather than quadratic in case of connection coefficients.

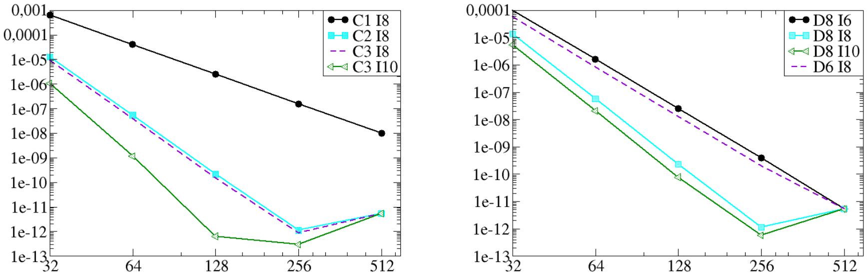

Figure 4: Harmonic Oscillator, ${}^2\tau_p^J$ in function of 2^J, for different orthogonal basis t_1: Coiflets (left) and Daubechies (right). Curves $C3I10$ and $D8I10$ show the influence of m_2, in function of m_1.

J	D6I8	D8I8	C2I8
5	.750043053	.750010176	.7500094682
6	.75000062740	.750000043524	.750000040569
7	.750000009528	.7500000001122	.75000000010048

Table 4: Harmonic Oscillator. ${}^2\tilde{e}_p^J$ for different J (column) and different couples $(t_1,\ t_2)$.

4.2 Hydrogen atom

For Hydrogen atom, Hamiltonian operator writes $\mathcal{H}_e = -\dfrac{1}{2}\Delta + V_h$, with $V_h(\mathbf{r}) = -\frac{1}{|\mathbf{r}|}$. The ground state $(\mathcal{E}_h,\ \psi_h)$ is known analytically:

$$\psi_h(\mathbf{r}) = C_N\ e^{-|\mathbf{r}|},$$

where C_N is a normalization constant. Different energies characterizing the ground states are (in Atomic Unit or Hartree):

- Kinetic energy $e_{kin} = 0.5\ H$.
- Potential Energy $e_p = -1.\ H$.
- Ground state energy $\mathcal{E}_e = e_{cin} + e_p = -0.5\ H$.

4.2.1 Kinetic energy

The evolution of τ_{kin}^J depends on the H^s-regularity of the orbital ψ_e. Indeed, we observe (for instance in figure 5) the following behavior:

$$\tau_{kin}^J \sim C\ 2^{-2J(\min(m_1,s)-1)},$$

prefactor C increasing with m_1. Numerically, Sobolev regularity of the orbital is around 2.4. This value coincide with a theoretical result made by H.-J. Flad (MPI, Leipzig), that should give rise to an article, claiming that Hydrogen orbital has a regularity smaller than $\frac{5}{2}$.

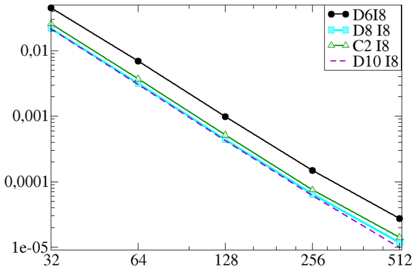

Figure 5: Hydrogen Atom: τ_{kin}^J in function of 2^J, for different couples t_1, t_2.

C1I6		D6I6		C2I6		D8I6		C3I8	
2.06	4.05	3.95	4.14	3.97	4.12	3.93	4.06	4.23	4.06

Table 5: Potential V_h, orbital ψ_o. Convergence rates for the relative errors ${}^1\tau_p^J$ and ${}^2\tau_p^J$.

In figure 5, Daubechies basis is slightly better than Coiflets, certainly due to the fact that the Laplacian Stiffness matrix in Daubechies basis is the same that those with interpolating one. For physical systems, where the potential is more irregular, it is thus not useful to take high order basis.

4.2.2 Potential Energy

The potential V_h is implemented, such that its singularity is located between two discretisation points. Thus it does not appear numerically.

- At first, we evaluate the relative error in case the orbital is a Gaussian (10). Results of convergence are shown in Table 5. As the singularity does not appear numerically, V_h-regularity does not correspond to the reality. Nevertheless, these convergence rates give informations about the quality of the two methods. Actually, it appears in Table 5 that method 2 is in general slightly better that method 1. Values obtained for $t_1 = C1$ are compatible with the behavior like $2^{-J\min(m_1,m_2)}$. The convergence rate is around 4, and certainly represents the numerical regularity of V_h.

- For Hydrogen orbital ψ_h, except for Coiflets of order $m_1 = 2$, we get always a convergence rate between 2.89 and 2.98 for both methods 1 and 2, and for any m_2. As Hydrogen orbital Sobolev regularity is equal to $s_1 = 2.4$, it means that the regularity of V_h, s_2, plays a role in this rate, and we thus can not write estimations like (11) and (12). For each couple (m_1, m_2), the error is of order 10^{-4} for $2^J = 128$.

4.2.3 Influence of pseudo-potential

As in electronic structure calculation, one usually use pseudo-potentials, an example here of results for a particular pseudo-potential is given. Pseudo-potentials have several properties, the main one being to screen nucleus potential (singular) by the first electrons of the atom. The result gives a potential one applies to higher level electronic orbitals.

- In our tests, we use the following one:

  $$V_{loc}(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} erf\left(\frac{|\mathbf{r}|}{\sqrt{2}\ r_{loc}}\right) + e^{-\frac{1}{2}(\frac{|\mathbf{r}|}{r_{loc}})^2}\left(C_1 + C_2(\frac{|\mathbf{r}|}{r_{loc}})^2 + C_3(\frac{|\mathbf{r}|}{r_{loc}})^4 + C_4(\frac{|\mathbf{r}|}{r_{loc}})^6\right),$$

  where erf denotes the error function or repartition of the normal law, and C_i, r_{loc} are coefficients depending on atom characteristics. Numerical values of these parameters can be found in the article [7].

- The second difficulty in atomistic simulation is the long range of potentials, behaving like $1/|\mathbf{r}|$. On the torus Ω, we have to cut it artificially, by applying a window.

The Hamiltonian tested here is thus:

$$\mathcal{H} = -\frac{1}{2}\Delta + \widetilde{V} = -\frac{1}{2}\Delta + \frac{V_{loc}(\mathbf{r})}{1 + e^{\beta\ (|\mathbf{r}| - r_c)}}.$$

The orbital ψ_1 associated to the ground state of the system described by $\mathcal{H}$ is not equal to ψ_e. Nevertheless we will use the couple $(\widetilde{V}, \psi_e)$ in our numerical tests, knowing that $V(\mathbf{r}) \leqslant \widetilde{V}(\mathbf{r}) \quad \forall\ \mathbf{r} \in \Omega$, implying the energy inequality $e_p \leqslant \dfrac{<\psi_e\ ,\ \widetilde{V}\ \ \psi_e>}{<\psi_e,\ \psi_e>}$ (recall that e_p is the theoretical Hydrogen potential energy). The ground state orbital ψ_1 for the potential $\widetilde{V}$ have also to satisfy the same inequality:

$$e_p \leqslant \frac{<\psi_1\ ,\ \widetilde{V}\ \ \psi_1>}{<\psi_1,\ \psi_1>}.$$

Indeed V is deeper than $\widetilde{V}$, meaning that electron is more attracted by V: this implies that kinetic energy $\frac{<\psi_1\ ,\ -\frac{1}{2}\Delta\ \psi_1>}{<\psi_1,\ \psi_1>}$ increases.
Table 6 shows different convergent rates. Figure 6 illustrates observations too. We get the maximal order 2.95 for $m_1 > 4$ and $m_2 > 4$.

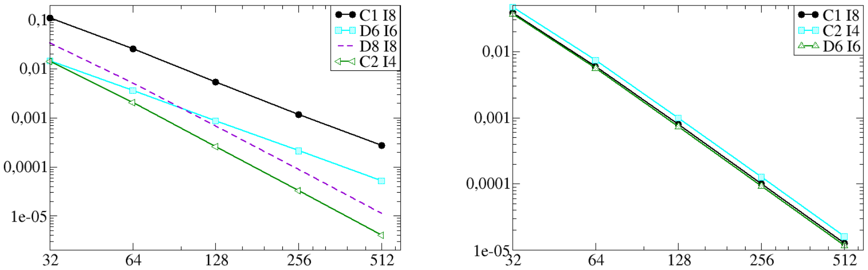

Figure 6: Hydrogen Atom with pseudo-potential. Relative errors (${}^1\tau_p^J$ (left), and ${}^2\tau_p^J$ (right)) in function of 2^J, for several couples (t_1, t_2).

There is not a big difference between $D6I8$ of Table 6 and $D6I6$ of Figure 6. No need to take a high order m_2. Moreover, Daubechies scaling function does not have vanishing moments like Coiflet, as a consequence they are asymmetric, and not centered. This explains the poverty of rate convergences using this family.

(t_1, t_2)	D6I8	C1I8	D8I6	D8I10	C2I4	C2I8	C3I8
m_1, m_2	3,8	2,8	4,6	4,10	4,4	4,8	6,8
rate	1.9	2.2	2.9	2.9	2.95	2.95	2.95

Table 6: Hydrogen Atom with pseudo-potential. Convergence rates of the relative error ${}^1\tau_p^J$, for different couples t_1, t_2.

Conclusion

As a conclusion, we present in this paper approximate methods to construct the Stiffness matrix associated to a potential operator. These methods can be understood as collocation ones, since the potential is developed into an interpolating basis. Their attractivity thus rely one their ability to cope with both orthogonal basis (for orbitals) and collocation one. Method 2 shows in case of regular potential and orbital a precision close to the Galerkin formulation. The difference between methods 1 and 2 are not so clear with loss of regularity, nevertheless they are competitive with Galerkin one, as calculations required in both cases are more efficient than for the classical formulation, for a reasonable error.

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