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Yvon Maday, Gabriel Turinici

Mathematical Modelling and Numerical Analysis Will be set by the publisher
Modélisation Mathématique et Analyse Numérique

e-mail: maday@ann.jussieu.fr e-mail: turinici@asci.fr

NUMERICAL ANALYSIS OF THE ADIABATIC VARIABLE METHOD FOR THE APPROXIMATION OF THE NUCLEAR HAMILTONIAN

Yvon Maday[1,2] and Gabriel Turinici[1]

Abstract. Many problems in quantum chemistry deal with the computation of fundamental or excited states of molecules and lead to the resolution of eigenvalue problems. One of the major difficulties in these computations lies in the very large dimension of the systems to be solved. Indeed these eigenfunctions depend on $3n$ variables where n stands for the number of particles (electrons and/or nucleari) in the molecule. In order to diminish the size of the systems to be solved, the chemists have proposed many interesting ideas. Among those stands the adiabatic variable method; we present in this paper a mathematical analysis of this approximation and propose, in particular, an a posteriori estimate that might allow for verifying the adiabaticity hypothesis that is done on some variables; numerical simulations that support the a posteriori estimators obtained theoretically are also presented.

Résumé. De nombreux problèmes en chimie quantique portent sur le calcul d'états fondamentaux ou excités de molécules et conduisent à la résolution de problèmes aux valeurs propres. Une des difficultés majeures dans ces calculs est la très grande dimension des systèmes qui sont en présence lors des simulations numériques. En effet les modes propres recherchés sont fonctions de $3n$ variables où n est le nombre de particules (électrons ou noyaux) de la molécule. Afin de réduire la dimension des systèmes à résoudre les chimistes multiplient les idées intéressantes qui permettent d'approcher le système complet. La méthode des variables adiabatiques entre dans ce cadre et nous présentons ici une étude mathématique rigoureuse de cette approximation. En particulier nous proposons un estimateur a posteriori qui pourrait permettre de vérifier l'hypothèse d'adiabaticité faite sur certaines variables ; des simulations numériques qui implémentent cet estimateur sont aussi présentées.

AMS Subject Classification. 65N25, 35P15, 81V55.

The dates will be set by the publisher.

1. Introduction

One problem frequently encountered in computational quantum chemistry (cf. [9]- [14]) consists in the evaluation of the eigenmodes of some Hamiltonian operator corresponding to eigenvalues smaller than some prescribed value E_{MAX}.

Under the Born-Oppenheimer approximation the nuclear Hamiltonian operator can be written as $H = T + V$ where V stands for the potential multiplicative part (assumed to be known by a previous electronic ab-initio computation or by empirical means) and T is the kinetic (Laplace) operator.

The number of independent variables being important any argument leading to the simplification of the behavior of the solution allows to enlarge the class of molecules that can be treated.

Keywords and phrases: a posteriori estimator, adiabatic variable method, computational quantum chemistry, nuclear hamiltonian

[1] ASCI, UPS 9029, bâtiment 506, Université Paris-Sud, 91405 Orsay

[2] Analyse numerique, Université Paris VI, place Jussieu, 75252 Paris cedex 05, France

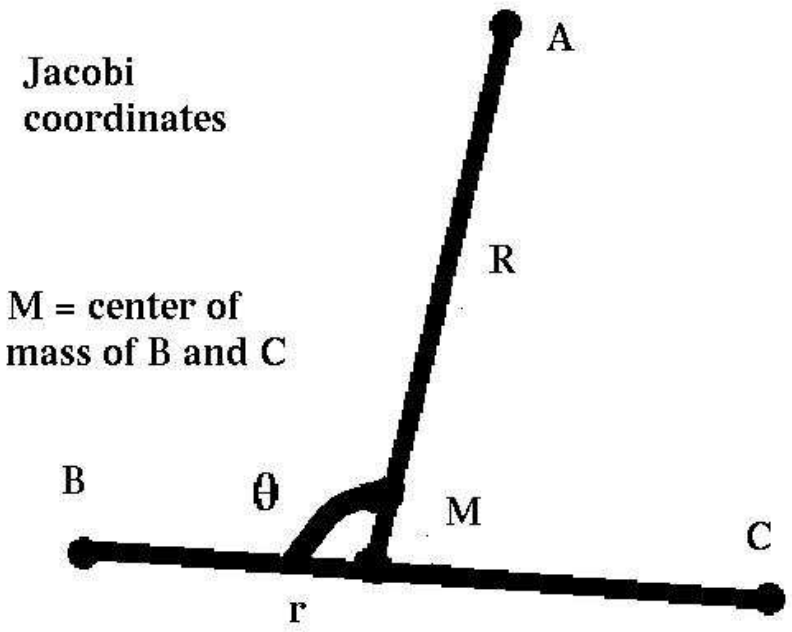

FIGURE 1. Jacobi coordinate system

Firstly it seems natural to introduce the first eigenmodes of the Laplace operator written in the coordinate system and search for the eigenmodes of the Hamiltonian operator in this modal basis. In order to do so we use some Lanczos-type iterative method which relies on the computation of a vector sequence $\{\psi_n\}_n$ defined recursively by:

$$\psi_{n+1} = c_0 H(\psi_n) - c_1 \ \psi_{n-1}. \tag{1}$$

In terms of CPU time the most expensive part is to apply the Hamiltonian operator H to ψ_n. In fact, even if the chosen basis is well adapted for the Laplace operator (such that it is diagonal), the potential operator matrix is full. In general we are interested in determining a large part of the spectrum, the size of the discretization basis (and hence the size of matrices involved) is usually so large that it forbids any computation. We are then lead to search for methods allowing us to further reduce the number of basis functions. The *pseudo-spectral adiabatic variable method* proposed in [9], [10] is one such pertinent discretization tool that seems to give quite good results in practice.

Its principle is presented below for a triatomic molecule.

Let the Laplace operator be written in Jacobi coordinates (R, r, θ) (cf. [9]), and let us assume that we want to find a function ψ on the open brick[1] $\Omega =]-1,1[^2 \times]0,\pi[$ of $\mathbb{R}^3$ such that :

$$\tilde{H}\psi = E\psi, \quad \text{with } \tilde{H} = \tilde{T}_{R,r,\theta} + V = -\partial_{RR} \ - \partial_{rr} - \ \frac{f(R,r)}{\sin\theta}\partial_\theta \sin\theta \partial_\theta \ + \ V, \tag{2}$$

where the function ψ has to satisfy

$$\psi(\pm 1, r, \theta) = \psi(R, \pm 1, \theta) = 0 \ , \|\psi\|_{L^2(\Omega)} = 1. \tag{3}$$

[1]The initial range for R, r is mapped by affine transformations into $]-1,1[$; the coordinates R, r are to be considered henceforth as relative deviations from some equilibrium position; note that the physical meaning of θ is preserved.

Then

1. We identify by a normal-mode analysis around the equilibrium position some special variable for our system named **the adiabatic variable**. Here it will be θ and we write the Hamiltonian using the coordinate transformation $z = \cos\theta$.

$$H = -\partial_{RR} \ - \partial_{rr} - \ f(R,r)\partial_z(1-z^2)\partial_z \ + \ V = T_{R,r,z} \ + \ V. \tag{4}$$

2. We consider the Hamiltonian operator obtained by removing the terms containing derivatives in the adiabatic variable; we call it **reduced Hamiltonian**, here it is

$$H^r := T_{R,r,z} \ - (-f(R,r)\partial_z(1-z^2)\partial_z) + \ V = -\partial_{RR} \ - \partial_{rr} + \ V \tag{5}$$

   and diagonalize it by a **fast** procedure. In fact the 3D problem is reduced to a small number of 2D problems by freezing the values of the adiabatic coordinate. It is here that the physical intuition comes into play, the adiabatic variable being in a certain way the one that allows us to accurately describe the total hamiltonian by its action in a small number of fixed values.
3. Since we are looking for eigenmodes with a corresponding energy smaller than E_{MAX}, we keep among the vectors obtained in step 2 above only those with energy smaller than $(1+\epsilon)E_{MAX}$ (where $\epsilon > 0$).
4. We construct by tensor product of the vectors obtained in step 3 with characteristic functions of the adiabatic variable a reduced basis used to finally diagonalize the full hamiltonian operator H.

In practice this procedure gives good results. However the choice of the adiabatic variable(s) and/or coordinate system affects substantially its efficiency. Therefore it seems interesting to give some a priori estimates to help intuition in the choice of the adiabatic variable for a given system and to complement this analysis by a posteriori estimators so as to decide about its usefulness once the computation is over and also in order to confirm the choice of ϵ used in the truncation[2].

Before proceeding with the different error analysis, it is important to introduce the choice of the values of the adiabatic variable that are being frozen during step 2. These are the Gauss quadrature points for that variable. This choice can be justified by at least two reasons. The first one is that these points are optimal for the evaluation (through quadrature formulas) of integrals involved in the computation of the action of the potential over the vectors required in the Lanczos recurrence. The second argument is that this set of points is optimal for interpolating in the linear space of polynomials spanned by the first eigenmodes of the differential operator $\partial_z(1-z^2)\partial_z$ in the adiabatic variable, i.e. the Legendre polynomials $\{L_n\}_n$. The values we freeze are therefore the Gauss-Legendre points, namely the zeroes $\{\zeta_i\}_{1\le i\le N+1}$ of the Legendre polynomial L_{N+1} of degree $N+1$. It is classical to associate to these points a (localized) basis containing characteristic polynomials of degree $\le N$, $\{h_j\}_{1\le j\le N+1}$ such that $h_j(\zeta_i) = \delta_{i,j}$, $i,j = 1,...N+1$ (Kronecker symbol).

We introduce the interpolation operator $\mathcal{J}_N$ from $\mathcal{C}^0(]-1,1[)$ to $\mathcal{P}_N(]-1,1[)$ on these nodes. This operator has optimal approximation properties (cf. [1] Thm.13.2, p.299), that is for any real $\sigma > \frac{1}{2}$, there exists some constant $c > 0$ such that

$$\forall v \in H^\sigma(]-1,1[), \quad \|v - \mathcal{J}_N v\|_{L^2(]-1,1[)} \le cN^{-\sigma}\|v\|_{H^\sigma(]-1,1[)}. \tag{6}$$

2. A PRIORI ANALYSIS

We propose this analysis for the case of the triatomic system (2) - (3) where for simplicity we set $f(R,r) \equiv 1$. This a priori analysis is not the main purpose of the paper and serves only as preliminary verification of the pertinence of the algorithm. A more detailed analysis is presented in the next section. As we have already seen, the discretization has 2 steps. Firstly we introduce the eigenfunctions of the operator $T_{R,r,z}$ on $L^2(]-1,1[^3)$, here $\varphi_{k,\ell,n}(R,r,z) = \sin(\frac{k\pi}{2}(R+1))\sin(\frac{\ell\pi}{2}(r+1))L_n(z)$ for (k,ℓ,n) in $\mathbb{N}^3$. We propose an initial discretization

[2]This "adiabatic reduction method" has some similarities with the dimension reduction method used in mechanics. See [15] for a presentation of this method and for adapted error estimators. However the method and the analysis technique are different.

space $X_{M,N}$ spanned by $\varphi_{k,\ell,n}$ for $1 \leq k,\ell \leq M$, $0 \leq n \leq N$. In the second step we diagonalize over $X_{M,0}$ the 2D operators $-\partial_{RR} - \partial_{rr} + V(.,.,\zeta_i)$ for each i, $1 \leq i \leq N+1$; we call $\left(\Phi_{p,q,i}\right)_{1\leq p,q\leq M}$ and $\left(\Lambda_{p,q,i}\right)_{1\leq p,q\leq M}$ the L^2 associated normalized eigenvectors and corresponding eigenvalues respectively.

We define some Sobolev-type spaces associated with the kinetic operator $T_{R,r,z}$. More precisely let X_0^s be the closure of $C_0^1(]-1,1[^3) \cap C^\infty(]-1,1[^3)$ in the domain of $(T_{R,r,z})^{s/2}$ endowed with its canonical norm. Theorem 5.6 from [6] and Theorem 2.3 from [5] tome 1 p.19 allow to describe X_0^s. We obtain for instance:

$$X_0^2 = \{u \in H_0^1(]-1,1[^3); \partial_{RR}u, \partial_{rr}u, \partial_{Rr}u, \sqrt{1-z^2}\partial_{Rz}u, \sqrt{1-z^2}\partial_{rz}u, (1-z^2)\partial_{zz}u \in L^2(]-1,1[^3)\}. \quad (7)$$

Next we introduce the linear space $\mathcal{E}_\delta$ spanned by $\Phi_{p,q,i}(R,r)h_i(z)$ (3D functions) that correspond to eigenvalues $\Lambda_{p,q,i} \leq (1+\epsilon)E_{MAX}$. The final approximation of our problem then consists in searching in $\mathcal{E}_\delta$ the eigenfunctions of the operator H_δ defined for all $\psi, \varphi \in X_0^1$ as follows

$$\begin{aligned}(H_\delta\varphi,\psi) = &\int_{]-1,1[^3} \partial_R\psi\partial_R\varphi + \partial_r\psi\partial_r\varphi + (1-z^2)\partial_z\psi\partial_z\varphi dRdrdz \\ &+ \int_{]-1,1[^2} \sum_{i=1}^{N+1} V(R,r,\zeta_i)(\psi\varphi)(R,r,\zeta_i)\rho_i dRdr, \end{aligned} \quad (8)$$

where $\{\rho_i\}_{1\leq i\leq N+1}$ are the weights of the Gauss-Legendre quadrature formula.

Remark 2.1. It is interesting to note that $\Phi_{p,q,j}(R,r)h_j(z)$, $1 \leq p,q \leq M$, $1 \leq j \leq N+1$ are the eigenfunctions on $X_{M,N}$ of the operator H_δ^r defined as follows

$$(H_\delta^r\varphi,\psi) = \int_{]-1,1[^2} \sum_{i=1}^{N+1} \left((\partial_R\psi\partial_R\varphi + \partial_r\psi\partial_r\varphi)(R,r,\zeta_i) + V(R,r,\zeta_i)(\psi\varphi)(R,r,\zeta_i) \right) \rho_i dRdr.$$

This operator is a kind of localized hamiltonian in the points ζ_i (chemists are used to noting it $H(R,r,z=\zeta_i)$,$i=1,N+1$) made up by contributions from each ζ_i point.

Remark 2.2. The method can be readily extended for the case of more than 3 variables by recursively applying the above procedure. In fact we consider some of them as adiabatic until we reach a matrix that can be easily diagonalized. See [12] for an example in the case of 6 variables.

We write our problem in the form:

$$find \;\; u = (\psi,\lambda) \in L^2(]-1,1[^3) \times \mathbb{R} \;\; such\ that\ F(u) = 0, \quad (9)$$

where F is the smooth (C^1) function from $L^2(]-1,1[^3) \times \mathbb{R}$ into the dual $(X_0^2)^* \times \mathbb{R}$ of $X_0^2 \times \mathbb{R}$ given by:

$$\begin{aligned} < F(\psi,\lambda),(\varphi,\mu) >_{(X_0^2)^*\times\mathbb{R},X_0^2\times\mathbb{R}} &= \int_{]-1,1[^3} \psi(H\varphi - \lambda\varphi) + \mu\left(\int_{]-1,1[^3} \psi^2 - 1\right) \\ &= \int_{]-1,1[^3} \psi(T_{R,r,z}\varphi + V\varphi - \lambda\varphi) + \mu\left(\int_{]-1,1[^3} \psi^2 - 1\right). \end{aligned} \quad (10)$$

It is easy to see that $F(\psi,\lambda) = 0$ is equivalent to (2)-(3). Moreover if λ_0 is a simple (i.e. of multiplicity 1) eigenvalue of (2) corresponding to an eigenvector ψ_0 (chosen with L^2-norm equal to 1) and $V \in L^\infty$ (which is never a restriction in practice), then, applying the Fredholm alternative as proven in Appendix A we conclude that $DF(\psi_0,\lambda_0)$ is an isomorphism from $L^2(]-1,1[^3) \times \mathbb{R}$ to $(X_0^2)^* \times \mathbb{R}$. In order to avoid technical difficulties we will suppose, in what follows, that all eigenvalues under consideration are simple and $V \in L^\infty$.

Let Π_δ be the projector to $\mathcal{E}_\delta$ associated with $T_{R,r,z}$ that is for all $v \in X_0^2$, $\Pi_\delta v$ is the element of $\mathcal{E}_\delta$ that verifies

$$\forall\ u_\delta \in \mathcal{E}_\delta\ :\ \int_{]-1,1[^3} T_{R,r,z}(v - \Pi_\delta v)u_\delta = 0. \tag{11}$$

We define functions F_δ from $L^2 \times \mathbb{R}$ into $(X_0^2)^* \times \mathbb{R}$ by the formulas:

$$\begin{aligned} < F_\delta(\psi,\lambda),(\varphi,\mu) >_{(X_0^2)^*\times\mathbb{R},X_0^2\times\mathbb{R}} &= \textstyle\int_{]-1,1[^3} \psi(H_\delta - \lambda)(\Pi_\delta\varphi) \\ &+\mu\left(\textstyle\int_{]-1,1[^3} \psi^2 - 1\right) + \textstyle\int_{]-1,1[^3} \psi T_{R,r,z}(\varphi - \Pi_\delta\varphi). \end{aligned} \tag{12}$$

Proposition 2.3. *The solutions of $F_\delta(\psi_\delta,\lambda_\delta) = 0$ are exactly eigenfunctions of H_δ on $\mathcal{E}_\delta$.*

Proof. Choose first φ orthogonal to $\mathcal{E}_\delta$ with respect to $T_{R,r,z}$ and $\mu = 0$ and obtain $\psi \in \mathcal{E}_\delta$; then choosing $\varphi = 0$ yields $\|\psi\|_{L^2} = 1$ and finally $\varphi \in \mathcal{E}_\delta$ and $\mu = 0$ proves that

$$(H_\delta\psi,\varphi) = (\lambda\psi,\varphi),\ \forall\varphi \in \mathcal{E}_\delta. \tag{13}$$

□

We are now applying Theorem 6.1 ([3] vol. 5 p.530) to show that $\|F_\delta(\psi_0,\lambda_0)\|_{(X_0^2)^*\times\mathbb{R}}$ is an upper bound (modulo some constant) for the error between (ψ_0,λ_0) and $(\psi_\delta,\lambda_\delta)$. More precisely there exists a constant $C > 0$ that does not depend on M,N or E_{MAX} and a neighborhood V of δ_0 (defined as the "limit" value where $F_{\delta_0} = F$) such that for all $\delta \in V\backslash\{\delta_0\}$ and (ψ_0,λ_0) such that $F(\psi_0,\lambda_0) = 0$ there exists $(\psi_\delta,\lambda_\delta)$ solution of $F_\delta(\psi_\delta,\lambda_\delta) = 0$ such that:

$$\|\psi_0 - \psi_\delta\|_{L^2(\Omega)} + |\lambda_0 - \lambda_\delta| \le C\|F_\delta(\psi_0,\lambda_0)\|_{(X_0^2)^*\times\mathbb{R}}. \tag{14}$$

It remains to evaluate the right hand side of (14) in order to obtain the a priori upper bound for the error between the exact and the discrete solution.

Since (ψ_0,λ_0) is a solution to our problem and by the definition (11) of the projector Π_δ we obtain for all $(\varphi,\mu) \in (X_0^2) \times \mathbb{R}$:

$$< F_\delta(\psi_0,\lambda_0),(\varphi,\mu) >_{(X_0^2)^*\times\mathbb{R},X_0^2\times\mathbb{R}} = \int_{]-1,1[^3} \psi_0(H_\delta - H)(\Pi_\delta\varphi)\ + (\psi_0 - \Pi_\delta\psi_0)T_{R,r,z}(\varphi - \Pi_\delta\varphi). \tag{15}$$

Definition. We state that N,M and E_{MAX} are chosen in a coherent manner and denote $N^2 \simeq M^2 \simeq E_{MAX}$ if there exists 3 constants independent of the discretization such that $N^2 \le c_1M^2 \le c_2E_{MAX} \le c_3N^2$.

We will make use in the following of some (optimal) approximation properties of projector Π_δ :

Lemma 2.4. *Assume that $N^2 \simeq M^2 \simeq E_{MAX}$. Then for any $b \ge 1 \ge a \ge 0$ there exists a constant $c(a,b)$ such that:*

$$\forall v \in X_0^b :\ \|v - \Pi_\delta v\|_{X_0^a} \le c(a,b)(\epsilon_\delta)^{b-a}\|v\|_{X_0^b}. \tag{16}$$

where ϵ_δ is $\max\left\{\frac{1}{N},\frac{1}{M},\frac{1}{\sqrt{E_{MAX}}}\right\}$

Proof. See the appendix A. □

Using lemma 2.4 the optimality properties of the interpolation operator $\mathcal{I}_N$ (stated in (6)) we obtain from (14) and (15) the following a priori estimate :

Theorem 2.5. *Let (ψ_0, λ_0) be a simple eigenmode of (2)-(3) and $s \geq 1$, $t > \frac{1}{2}$ such that $\psi_0 \in X_0^s$ and $V\psi_0 \in L^2(]-1,1[^2; H^t(]-1,1[))$. Then there exists a constant $C(s,t) > 0$ such that for each δ there exists a solution of $F_\delta(\psi_\delta, \lambda_\delta) = 0$[3] such that:*

$$\|\psi_0 - \psi_\delta\|_{L^2} + |\lambda_0 - \lambda_\delta| \leq C(s,t) \left((\epsilon_\delta)^s \|(\psi_0, \lambda_0)\|_{X_0^s \times \mathbb{R}} + N^{-t} \|V\psi_0\|_{L^2(]-1,1[^2; H^t(]-1,1[))} \right). \tag{17}$$

Proof. Inserting in (14) the equality (15) and using the definition of the norm in $(X_0^2)^* \times \mathbb{R}$ one obtains

$$\begin{aligned} \|\psi_0 - \psi_\delta\|_{L^2(\Omega)} + |\lambda_0 - \lambda_\delta| &\leq C \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} \psi_0 (H_\delta - H)(\Pi_\delta \varphi) \ + (\psi_0 - \Pi_\delta \psi_0) T_{R,r,z}(\varphi - \Pi_\delta \varphi) \\ &\leq C \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} (V\psi_0 - (Id_{\mathbb{R}^2} \otimes \mathcal{J}_N) V\psi_0) \Pi_\delta \varphi + (\psi_0 - \Pi_\delta \psi_0) T_{R,r,z}(\varphi - \Pi_\delta \varphi) \\ &\leq \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} (V\psi_0 - (Id_{\mathbb{R}^2} \otimes \mathcal{J}_N) V\psi_0) \Pi_\delta \varphi + \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} (\psi_0 - \Pi_\delta \psi_0) T_{R,r,z}(\varphi - \Pi_\delta \varphi) \end{aligned} \tag{18}$$

By the definition of the projector Π_δ the second term in the right hand side of (18) equals

$$\sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} (\psi_0 - \Pi_\delta \psi_0) T_{R,r,z} \varphi, \tag{19}$$

and can be upper bounded by

$$\sup_{\|\varphi\|_{X_0^2}=1} \|\psi_0 - \Pi_\delta \psi_0\|_{L^2} \|T_{R,r,z}(\varphi)\|_{L^2} \leq \|\psi_0 - \Pi_\delta \psi_0\|_{L^2} \leq c(0,s) \epsilon_\delta^s \|\psi_0\|_{X_0^s}. \tag{20}$$

Using (6) and the stability of the projector Π_δ one can now bound the first term in the right hand side of (18) and obtain the conclusion of the theorem. □

Remark 2.6. If V is smooth enough, it is obvious that the norms $\|\psi_0\|_{X_0^p}$, $\|V\psi_0\|_{L^2(]-1,1[^2; H^{2p}(]-1,1[))}$ and $\|V\psi_0\|_{H^{2p}(]-1,1[^2; L^2(]-1,1[))}$ are upper bounded by $c|\lambda_0|^p$ so that for the natural choice $N^2 \simeq M^2 \simeq E_{MAX}$ the convergence rate scales as $c(p) \left(\frac{\lambda_0}{N^2} \right)^p$.

3. A POSTERIORI ANALYSIS OF THE METHOD

Let us still focus on the case of the triatomic system (2) and (3), and let us consider now an *a posteriori* error analysis. The goal of such a tool is to asses the approximation once the computation is done. We are working as before on the formulation $F(u) = 0$ defined in (10).

The result (17) show that for any simple eigenmode $u_0 = (\psi_0, \lambda_0)$ of (2)-(3), there exists an eigenmode $(\psi_\delta, \lambda_\delta)$ which is close enough. To know more precisely how close they are, one uses results derived from [10] which allow to prove that under certain hypothesis, $F(u)$ is an estimator for the error between u_0 and u. We shall make use of this abstract result in the following form:

Theorem 3.1. *Let Z,Y be two Hilbert spaces and $F \in C^1(Z,Y)$. Let u_0 be a solution of $F(u) = 0$ such that $DF(u_0) \in Isom(Z,Y)$ and moreover assume DF satisfies a Lipschitz-type property*

$$\exists \epsilon_{u_0} > 0 : \quad \|[DF(u_0) \ - \ DF(u_0 + tU)] \ U\|_Y \leq \ ct\|U\|_Z^2, \ \forall \ 0 < t < \epsilon_{u_0}, \ \forall \ U \in Z, \ \|U\| < \epsilon_{u_0}. \tag{21}$$

[3] In fact since the eigenmode (ψ_0, λ_0) is simple for δ close enough to δ_0 the problem $F_\delta(\psi_\delta, \lambda_\delta) = 0$ will have only two solutions with corresponding eigenvalues close to λ_0 that is $(\psi_\delta, \lambda_\delta)$ and $(-\psi_\delta, \lambda_\delta)$.

Then there exists some $R > 0$ ($R = min\left\{\frac{1}{2}\|DF(u_0)^{-1}\|^{-1}_{\mathcal{L}(Y,Z)}\ ,\ \|DF(u_0)\|_{\mathcal{L}(Z,Y)}\right\}$) *such that for all* $u \in B(u_0, R)$*:*

$$\frac{1}{2}\|DF(u_0)\|^{-1}_{\mathcal{L}(Z,Y)} \cdot \|F(u)\|_Y \leq \|u - u_0\|_Z \leq 2\|DF(u_0)^{-1}\|_{\mathcal{L}(Y,Z)} \cdot \|F(u)\|_Y. \tag{22}$$

Choose $Z = L^2(]-1,1[^3) \times \mathbb{R}$ and $Y = (X_0^2)^* \times \mathbb{R}$ and note that DF obviously satisfies the hypothesis (21) of Theorem 3.1 ; recalling that $DF(\psi_0, \lambda_0) \in Isom(L^2(]-1,1[^3) \times \mathbb{R}, (X_0^2)^* \times \mathbb{R})$ we obtain from Theorem 3.1 :

$$c\|F(\psi_\delta, \lambda_\delta)\|_Y \leq \|\psi_0 - \psi_\delta\|_{L^2(]-1,1[^3)} + |\lambda_0 - \lambda_\delta| \leq C\|F(\psi_\delta, \lambda_\delta)\|_Y \tag{23}$$

for two positive constants c and C.

We write easily

$$\|F(\psi_\delta, \lambda_\delta)\|_Y = \sup_{(\varphi,\mu)\in X_0^2\times\mathbb{R}} \frac{\int_{]-1,1[^3}(T_{R,r,z}\psi_\delta + V\psi_\delta - \lambda_\delta\psi_\delta)\varphi}{\|(\varphi,\mu)\|_{X_0^2\times\mathbb{R}}}, \tag{24}$$

(note that μ does not enter in this estimate). Define π_M as the L^2-projection operator from $L^2(]-1,1[^3)$ to $X_{M,0}$; we will use the following approximation property of π_M (cf. [16] Ch.9, p.278): for any $\sigma \geq 0$ there exists a constant $c > 0$ depending only of σ such that

$$\forall v \in H^\sigma(]-1,1[^2; L^2(]-1,1[)) \quad \|v - \pi_M v\|_{L^2(]-1,1[^2;L^2(]-1,1[))} \leq cN^{-\sigma}\|v\|_{H^\sigma(]-1,1[^2;L^2(]-1,1[))} \tag{25}$$

By defining φ_{MN} as the L^2 projection of φ on X_{MN} we obtain

$$\begin{aligned}
\|F(\psi_\delta, \lambda_\delta)\|_Y &= \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3}((V\psi_\delta - \pi_M \otimes \mathcal{J}_N(V\psi_\delta))\varphi + (T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi \\
&= \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3}((V\psi_\delta - \pi_M \otimes \mathcal{J}_N(V\psi_\delta))\varphi + (T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN} \\
&\leq \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3}((V\psi_\delta - \pi_M \otimes \mathcal{J}_N(V\psi_\delta))\varphi \\
&+ \sup_{\varphi\in X_0^2, \|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3}(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN},
\end{aligned} \tag{26}$$

where we have used the fact that $T_{R,r,z}\psi_\delta \in X_{MN}$ between the first and second line. The **first contribution** in the right hand side measures the approximation resulting from the reduction of the action of V to X_{MN}. By (6) - (25) it can be bounded as follows

$$\begin{aligned}
&\sup_{\varphi\in X_0^2, \|\varphi\|_{X_0^2}=1} |\int_{]-1,1[^3}(V\psi_\delta - \pi_M \otimes \mathcal{J}_N(V\psi_\delta))\varphi| \\
&\leq c(N^{-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H^s(]-1,1[)} + M^{-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2(]-1,1[))}),
\end{aligned} \tag{27}$$

for all $\sigma \geq 0$ and $s > \frac{1}{2}$ such that

$$V\psi_\delta \in L^2(]-1,1[^2; H^s(]-1,1[)) \cap H^\sigma(]-1,1[^2; L^2(]-1,1[). \tag{28}$$

The **second contribution** in the right hand side of (26) represents the loss of information resulting from neglecting in X_{MN} the eigenmodes $\Phi_{p,q,i}h_i$ having energy larger than $(1+\epsilon)E_{MAX}$. It is *this* contribution that allows us to asses the adiabaticity of the chosen coordinate system since it measures the amount of energy

contained in the projection of $(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)$ on the rejected eigenmodes. Indeed its projection on all other eigenmodes is zero by the definition of ψ_δ . This leads us to

$$\begin{aligned}
&\sup_{\varphi\in X_0^2,\|\varphi\|_{X_0^2}=1}\int_{]-1,1[^3}(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN}\\
&= \sup_{\varphi\in X_0^2,\|\varphi\|_{X_0^2}=1}\int_{]-1,1[^3}(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)(\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN}))\\
&\leq \|T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta\|_{L^2}\sup_{\varphi\in X_0^2,\|\varphi\|_{X_0^2}=1}\|\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN})\|_{L^2}. \qquad (29)
\end{aligned}$$

In these estimates, $\pi_{\mathcal{E}_\delta}$ is the L^2 projection operator over the reduced space $\mathcal{E}_\delta$.

An upper bound for the last term is given by the

Lemma 3.2. *For any element φ_{MN} in $X_{M,N}$ the following estimate is true*

$$\|\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN})\|_{L^2}^2 \leq (\frac{1}{(1+\epsilon)E_{MAX}})^2\Big(\|(-\partial_{RR} - \partial_{rr})\varphi_{MN}\|_{L^2(]-1,1[^3)}^2 + \|V\|_{L^\infty}^2\|\varphi_{MN}\|_{L^2(]-1,1[^3)}^2\Big). \qquad (30)$$

Moreover for any $b \geq 0$ there exists a constant C independent of M,N,E_{MAX} such that

$$\|\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN})\|_{L^2} \leq C\Big(\frac{1}{\sqrt{E_{MAX}}}\Big)^b\|\varphi_{MN}\|_{X_0^b}. \qquad (31)$$

Proof. See the appendix A . □

From now on we suppose ϵ smaller than some fixed constant (usually less than 1). Using the stability of the L^2 projector on eigenmodes we obtain that there exists a constant $c > 0$ such that

$$\|\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN})\|_{L^2} \leq (\frac{c}{E_{MAX}})(1 + \|V\|_{L^\infty})\|\varphi\|_{X_0^2} \leq \frac{c(V)}{E_{MAX}}\|\varphi\|_{X_0^2}. \qquad (32)$$

This allows us to write first

$$\begin{aligned}
&\sup_{\|\varphi\|_{X_0^2}=1}\int_{]-1,1[^3}(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN}\\
&\leq \tfrac{c(V)}{E_{MAX}}\|T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta\|_{L^2(]-1,1[^3)}. \qquad (33)
\end{aligned}$$

Recalling the definition of ψ_δ, we have

$$\pi_{\mathcal{E}_\delta}(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta) = 0. \qquad (34)$$

from the definition of the eigenmodes that span $\mathcal{E}_\delta$, we also have

$$(Id - \pi_{\mathcal{E}_\delta})((-\partial_{RR} - \partial_{rr})\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta) = 0, \qquad (35)$$

hence

$$T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta = (Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta), \qquad (36)$$

so that

$$\sup_{\|\varphi\|_{X_0^2}=1}\int_{]-1,1[^3}(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN} \leq \frac{c(V)}{E_{MAX}}\|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)} \qquad (37)$$

Combining this inequality with (27) allows us to state the following result:

Theorem 3.3. *Let $\sigma \geq 0$, $s > \frac{1}{2}$ be such that $V\psi_\delta \in L^2(]-1,1[^2; H^s(]-1,1[)) \cap H^\sigma(]-1,1[^2; L^2(]-1,1[))$. Then there exists two constants c and $c(V)$ such that*

$$\|\psi_0 - \psi_\delta\|_{L^2(]-1,1[^3)} + |\lambda_0 - \lambda_\delta| \leq \frac{c(V)}{E_{MAX}} \|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)}$$
$$+c(M^{-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2]-1,1[)} + N^{-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H^s]-1,1[)}) \tag{38}$$

and

$$\frac{c}{\sup(M,N)^2} \quad \|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)} \leq \Big(\|\psi_0 - \psi_\delta\|_{L^2(]-1,1[^3)} + |\lambda_0 - \lambda_\delta|\Big)$$
$$+c(M^{-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2]-1,1[)} + N^{-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H^s]-1,1[)}). \tag{39}$$

Proof. Only (38) has been proven, we are going to prove (39) after having noticed that the first term in the right hand side of (38) accounts for the reliability of the adiabatic variable reduction and the second accounts for the choice of the filtering frequency (M,N)[4]. All we have to prove is that the estimator in the right hand side of (38) is not too large. For φ in X_0^2 denote φ_{MN} as its projection on X_{MN} ; then for all $\mu \in \mathbb{R}$

$$\int_{]-1,1[^3} (T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN} = < F(\psi_\delta,\lambda_\delta), (\varphi,\mu) > - \int_{]-1,1[^3} ((V\psi_\delta - \pi_M \otimes \mathcal{J}_N(V\psi_\delta))\varphi,$$

so that

$$\sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} (T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN}$$
$$\leq \sup_{\|\varphi\|_{X_0^2}=1} < F(\psi_\delta,\lambda_\delta), (\varphi,\mu) > + \sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} ((V\psi_\delta - \pi_M \otimes \mathcal{J}_N(V\psi_\delta))\varphi. \tag{40}$$

Using the upper bound in (27) we obtain

$$\sup_{\|\varphi\|_{X_0^2}=1} \int_{]-1,1[^3} (T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)\varphi_{MN}$$
$$\leq \|F(\psi_\delta,\lambda_\delta)\|_{(X_0^2)^* \times \mathbb{R}} + c(N^{-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H^s]-1,1[)} + M^{-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2]-1,1[)}) \tag{41}$$

The term $(T_{R,r,z}\psi_\delta + \pi_M \otimes \mathcal{J}_N(V\psi_\delta) - \lambda_\delta\psi_\delta)$ being in X_{MN} hence in X_0^2, we choose it as φ after proper normalization in the above supremum; recalling for $b=2$, $a=0$ the inverse inequality that is true for elements of X_{MN} ([1] p.256)

$$\forall\ b \geq a \geq 0,\ \forall \psi_{MN} \in X_{M,N} \quad \|\psi_{MN}\|_{X_0^b} \ \leq\ C\ \max(M,N)^{b-a}\|\psi_{MN}\|_{X_0^a}. \tag{42}$$

we obtain trivially from (36) and the first inequality in (23) the second estimate of the theorem. □

Remark 3.4. The estimator can be explicitly computed since it involves L^2 norms of discrete functions ; moreover its computation can be done in a fast manner as it will be seen in section 5, remark 5.1.

[4]When the functions involved are regular enough, the second term in the right hand side of (38) can be considered small enough to be neglected (see also [7,8]); this is the case for instance in formula (38) with $N^2 \simeq M^2 \simeq E_{MAX}$ as soon as the regularity allows to use $\sigma, s > 2$ (and ψ_δ is close enough to the solution).

4. FURTHER RESULTS

4.1. X_0^1 estimate

Although the L^2 norm seems the most natural when studying the convergence of the eigenfunctions, there are some remarkable situations (see below) where another norm, here the X_0^1 norm, is required to measure the error. Our approach lets us the freedom to analyze these cases as well, obtaining thus an estimator for the error expressed as $\|\psi_0 - \psi_\delta\|_{X_0^1} + |\lambda_0 - \lambda_\delta|$.

Indeed, denote by $H_*^s = D(A^{s/2})$ the domain in $L^2(]-1,1[)$ of the $s/2$-th power of the operator $A = \partial_z(1-z^2)\partial_z$ endowed with canonical norm; then, for any $\alpha > 0$ there exists some constant $c_\alpha > 0$ such that the following interpolation property is valid (use (6) and (5.9) p.256, like in Thm. 13.4, p.303 [1]):

$$\forall v \in H_*^\alpha(]-1,1[), \quad \|v - \mathcal{J}_N v\|_{H_*^1} \leq c_\alpha N^{1-\alpha}\|v\|_{H_*^\alpha}. \tag{43}$$

The result reads:

Theorem 4.1. *Let $\sigma \geq 0$, $s > \frac{1}{2}$ be such that $V\psi_\delta \in L^2(]-1,1[^2; H^s(]-1,1[)) \cap H^\sigma(]-1,1[^2; L^2(]-1,1[))$. There exists constants $c, C > 0$ and $c(V) > 0$ such that*

$$\begin{aligned} \|\psi_0 - \psi_\delta\|_{X_0^1} + |\lambda_0 - \lambda_\delta| &\leq \frac{c(V)\max(M,N)}{E_{MAX}} \|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)} \\ + \quad & c(M^{1-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2]-1,1[)} + N^{1-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H_*^s)}) \end{aligned} \tag{44}$$

and

$$\begin{aligned} \frac{C}{\max(M,N)} \quad \|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)} &\leq \left(\|\psi_0 - \psi_\delta\|_{X_0^1} + |\lambda_0 - \lambda_\delta|\right) \\ + c(M^{1-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2]-1,1[)} &+ N^{1-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H_*^s)}). \end{aligned} \tag{45}$$

Proof. We follow the same lines of proof as in Theorem 3.3 making use of the abstract result for $Z = X_0^1 \times \mathbb{R}$, $Y = X_0^{1\,*} \times \mathbb{R}$. For the second part we are making use of (42) for $b = 1$, $a = 0$. □

Remark 4.2. From the a priori estimate (and the common sense) it is natural to choose $N^2 \simeq M^2 \simeq E_{MAX}$. Theorem 2 gives an *optimal* a posteriori estimate to judge on the adiabaticity of the variable.

4.2. Separate estimates for eigenvalues and eigenfunctions

The estimators obtained before do not provide separated indications on the convergence of the eigenvalues and the eigenfunctions alone; moreover they cannot account for well-known phenomena like super-convergence of eigenvalues when compared with the H^1 convergence of eigenfunctions.

It seems therefore legitimate to us to search for such tailored estimators. The framework is the following: suppose as can be hinted from Thm. 3.3 and 4.1 that our discretization of the problem allows for a better convergence of eigenfunctions in the L^2 norm when compared with H^1 norm[5]. Then we recall in what follows that the error for the eigenvalues behaves (asymptotically) like the square of the H^1 error for eigenfunctions. We use this to obtain an estimator for the error in the eigenvalues alone; it is that estimator that we illustrate next in numerical experiments.

[5] this is generally true for most approximation of nuclear structure computations while this may however not be the case for electronic structure when incomplete basis are used

Let $(\psi_\delta, \lambda_\delta)$ be an approximation of the eigenmode (ψ_0, λ_0) (ψ_δ and ψ_0 are L^2-normalized to 1). Then we can write:

$$\begin{aligned}\lambda_\delta - \lambda_0 &= (H\psi_\delta, \psi_\delta) - (H\psi_0, \psi_0) = (H(\psi_\delta - \psi_0), (\psi_\delta - \psi_0)) + 2(H\psi_0, (\psi_\delta - \psi_0)) \\ &= (H(\psi_\delta - \psi_0), (\psi_\delta - \psi_0)) + 2\lambda_0(\psi_0, \psi_\delta - \psi_0) \end{aligned} \quad (46)$$

Using the normalization of ψ_δ and ψ_0 we see that $2\lambda_0(\psi_0, \psi_\delta - \psi_0)$ equals $-\lambda_0 \int (\psi_\delta - \psi_0)^2$. By the definition of the space X_0^1 we obtain:

$$\lambda_\delta - \lambda_0 = \|\psi_\delta - \psi_0\|^2_{X_0^1} + \int (V - \lambda_0)(\psi_\delta - \psi_0)^2. \quad (47)$$

In what follows we need the following

HYPOTHESIS [A]: the $L^2 = X_0^0$ norm of the error for eigenfunctions converges faster than the X_0^1 norm.

Note that this is typically the case (through an Aubin-Nitsche type argument see for instance [1]) for good enough approximations, i.e. assuming we are in the convergence range.

Assuming hypothesis [A] holds, then there exists c_1 and c_2 (close to 1) not depending on the parameter δ such that for δ small enough

$$c_1\|\psi_\delta - \psi_0\|^2_{X_0^1} \leq |\lambda_\delta - \lambda_0| \leq c_2\|\psi_\delta - \psi_0\|^2_{X_0^1}. \quad (48)$$

Let us now assume (to simplify) that $M^2 \simeq N^2 \simeq E_{MAX}$. From the discussion above we know that in the term $\|\psi_0 - \psi_\delta\|_{X_0^1} + |\lambda_0 - \lambda_\delta|$ the leading part is the first one (the second one behaving like the square of the first) so we obtain by Theorem 3 a new error estimator $\frac{c(V)}{\sqrt{E_{MAX}}}\|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)}$ for $\|\psi_0 - \psi_\delta\|_{X_0^1}$ and of course, its square is an estimator for $|\lambda_0 - \lambda_\delta|$. We have therefore proven:

Corollary 4.3. *Under the hypothesis [A] and for the $M^2 \simeq N^2 \simeq E_{MAX}$ there exists two constants $c > 0$, $C > 0$ and $c(V) > 0$ such that*

$$\begin{aligned}\max\{\|\psi_0 - \psi_\delta\|_{X_0^1}, \sqrt{|\lambda_0 - \lambda_\delta|}\} \leq \tfrac{c(V)}{\sqrt{E_{MAX}}}\|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)} + \\ c(M^{1-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2]-1,1[)} + N^{1-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H^s_*)})\end{aligned} \quad (49)$$

and

$$\begin{aligned}\tfrac{C}{\sqrt{E_{MAX}}}\|(Id - \pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)} \leq \min\{\|\psi_0 - \psi_\delta\|_{X_0^1}, \sqrt{|\lambda_0 - \lambda_\delta|}\} \\ c(M^{1-\sigma}\|V\psi_\delta\|_{H^\sigma(]-1,1[^2;L^2]-1,1[)} + N^{1-s}\|V\psi_\delta\|_{L^2(]-1,1[^2;H^s_*)}).\end{aligned} \quad (50)$$

5. NUMERICAL RESULTS AND CONCLUSIONS

In order to prove the efficiency of our error estimator we have considered some numerical experiments. The system of interest is the water molecule : the hydrogen atoms are located in A and C and the oxygen in B ; we are interested in finding the fundamental and the first 8 excited states.

Although the theory described so far was derived (for the sake of simplicity) only for some constant multiplication function $f(R, r) \equiv 1$ in the kinetic operator in the adiabatic variable $f(R, r)\partial_z(1 - z^2)\partial_z$ (see above) it can be easily extended in order to accommodate the most appropriate modelisation

$$f(R, r) = \frac{\mu_1}{R^2} + \frac{\mu_2}{r^2}, \quad r \in]r_{min}, r_{max}[, \ R \in]R_{min}, R_{max}[, \ r_{min}, R_{min} > 0 \quad (51)$$

where μ_1 and μ_2 are structural constants that depend on the system under consideration.

Remark 5.1. The explicit computation of the contribution

$$\|(Id-\pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)} \tag{52}$$

can be done in a "fast" (i.e. less operation than for the evaluation of ψ_δ) manner as follows; let us note

$$\partial_z(1-z^2)\partial_z h_i = \sum_{j=1}^{M} \gamma_i^j\ h_j \quad for\ all\ i=1,...,N \tag{53}$$

$$\Phi_{p,q,i}(R,r) = \sum_{r,s=1}^{M} \alpha_{pqi}^{rs}\varphi_{r,s,0}(R,r). \tag{54}$$

Then we consider the following change of basis

$$\Phi_{p,q,i}(R,r) = \sum_{p',q'=1}^{M} \eta_{pqi}^{p'q'j}\Phi_{p',q',j}(R,r) \quad for\ all\ i,j=1,..,N\ p,q=1,...,M, \tag{55}$$

where, by the orthonormality of all basis involved (i.e. $(\Phi_{p,q,i})_{p,q=1}^{M}$ for every i and $(\varphi_{r,s,0})_{r,s=1}^{M}$), we have:

$$\eta_{pqi}^{p'q'j} = \sum_{r,s=1}^{M} \alpha_{pqi}^{rs}\alpha_{p'q'j}^{rs}, \tag{56}$$

hence

$$\Phi_{p,q,i}(R,r)(\partial_z(1-z^2)\partial_z h_i)(z) = \sum_{p',q'=1}^{M}\sum_{j=1}^{N} \gamma_i^j\eta_{pqi}^{p'q'j}\Phi_{p',q',j}(R,r)h_j(z). \tag{57}$$

From the formula $\psi_\delta = \sum_{p,q,i}\check{\psi}_{pqi}\Phi_{p,q,i}h_i$ given by the solution of the reduced problem we notice

$$A\psi_\delta := [\partial_z(1-z^2)\partial_z]\psi_\delta = \sum_{p',q',j}\left[\sum_{p,q,i}\gamma_i^j\eta_{pqi}^{p'q'j}\check{\psi}_{pqi}\right]\Phi_{p',q',j}(R,r)h_j(z). \tag{58}$$

This gives us the value of the coefficients $A\psi_\delta$ in the orthonormal basis $\Phi_{p',q',j}(R,r)h_j(z)$. By tensorization the computation (58) can be done in $c\max(M,N)^5$ operations, less than the number of operations required by the computation of ψ_δ (for instance, the diagonalization of $2D$ hamiltonians is of higher complexity) [9,10,12].

Indeed, our goal is to compute for $\{(p',q',j);|\Lambda_{p',q',j}|\geq(1+\epsilon)E_{MAX}\}$ the term:

$$\beta_{p',q',j} = \sum_{r,s,p,q,i}\check{\psi}_{pqi}\alpha_{pqi}^{rs}\alpha_{p'q'j}^{rs}\gamma_i^j, \quad p',q'=1,...,M, \quad j=1,...,N. \tag{59}$$

It is easy to check that summing first for p and q we obtain in $c\max(M,N)^5$ operations some coefficients

$$\theta_{rs}^i = \sum_{p,q}\check{\psi}_{pqi}\alpha_{pqi}^{rs}. \tag{60}$$

Next we sum up for the "i" index and note $\chi_{rs}^j = \sum_i\theta_{rs}^i\gamma_i^j$. Our quantity is:

$$\sum_{rs}\chi_{rs}^j\alpha_{p'q'j}^{rs} \tag{61}$$

and it is clear now that we can compute it for all values of $(p'q'j)$ needed in $c\max(M,N)^5$ operations. The L^2 norm of $\|(Id-\pi_{\mathcal{E}_\delta})(\partial_z(1-z^2)\partial_z\psi_\delta)\|_{L^2(]-1,1[^3)}$ is obtained by summing up the square of $\beta_{p',q',j}$ for all indices $\{(p',q',j);|\Lambda_{p',q',j}|<(1+\epsilon)E_{MAX}\}$. Note that only these coefficients have to be computed in (61) and that in (60) the $\check{\psi}_{pqi}$ all vanish for indices $\{(p,q,i);|\Lambda_{p,q,i}|\geq(1+\epsilon)E_{MAX}\}$. Taking this into account leads to a further reduction in CPU time [10].

The results are displayed in the figures 2-11. We choose discretization parameters M and N such that $N^2\simeq M^2\simeq E_{MAX}$. We are plotting the effectivity indexes, i.e. the quotient "true error over estimated error". Of course the ideal case would be "effectivity index = constant", but this never happens for discretization of non linear problems. Due to the intricate nature of the eigenvalue problem we cannot expect that. What we do expect is that our estimator be robust and rather insensitive to different discretization parameters (here E_{MAX}). The quotient " true error over estimated error" was computed with energy expressed in atomic units (Hartree, E_h): $1E_h=219474.63cm^{-1}$; the true error was computed with respect to a solution obtained with a very fine discretization.

The relative error was measured with respect to the first excitation of the system, that is the difference between the first and the second eigenvalue, and was found to be in the range $3\%-0.001\%$, which is typical for this kind of computations. This choice for measuring the relative error is suggested by the fact that the value of zero for the potential (or energy) is defined up to an additive constant, thus only relative variations are relevant. Other procedures for measuring the relative error on the i-th eigenvalue can be proposed (one may consider as basis for computations the difference between the "i"-th and "$i-1$"-th eigenvalues), the present choice was retained for the sake of uniformity. Finally, let us mention that in practice chemists are satisfied when the energies are known up to several cm^{-1} units, $1cm^{-1}=.455\cdot10^{-5}E_h$. The computations presented also comply with this requirement, as e.g. for the first eigenvalue, the error decreases from $24cm^{-1}$ to less than $1cm^{-1}$.

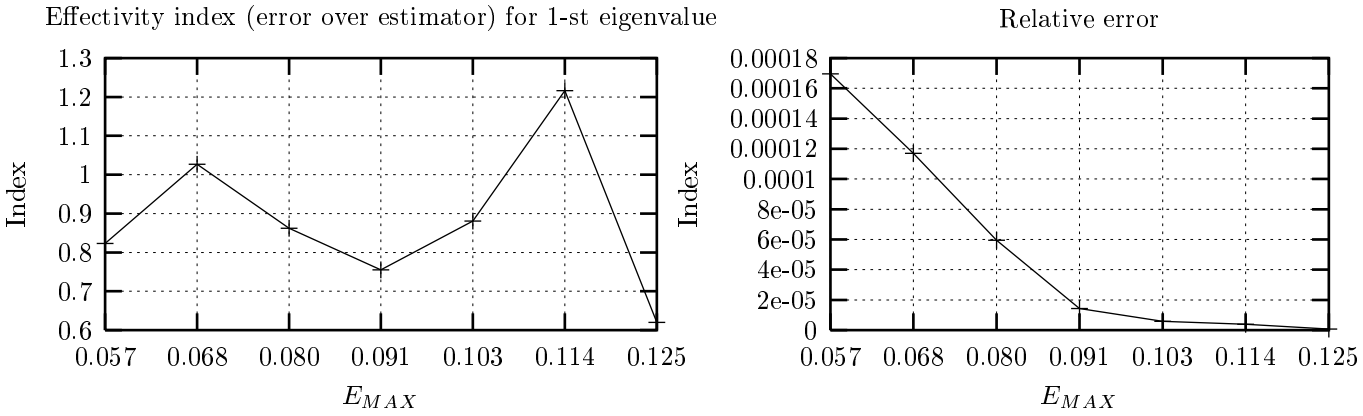

FIGURE 2. First eigenvalue (energy expressed in Hartree (E_h))

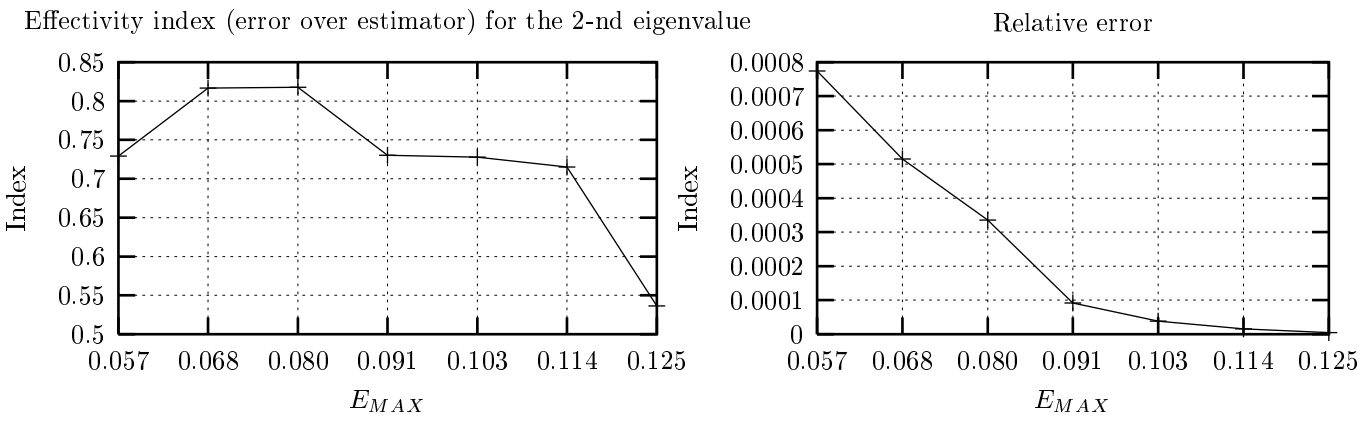

FIGURE 3. Second eigenvalue (energy expressed in Hartree (E_h))

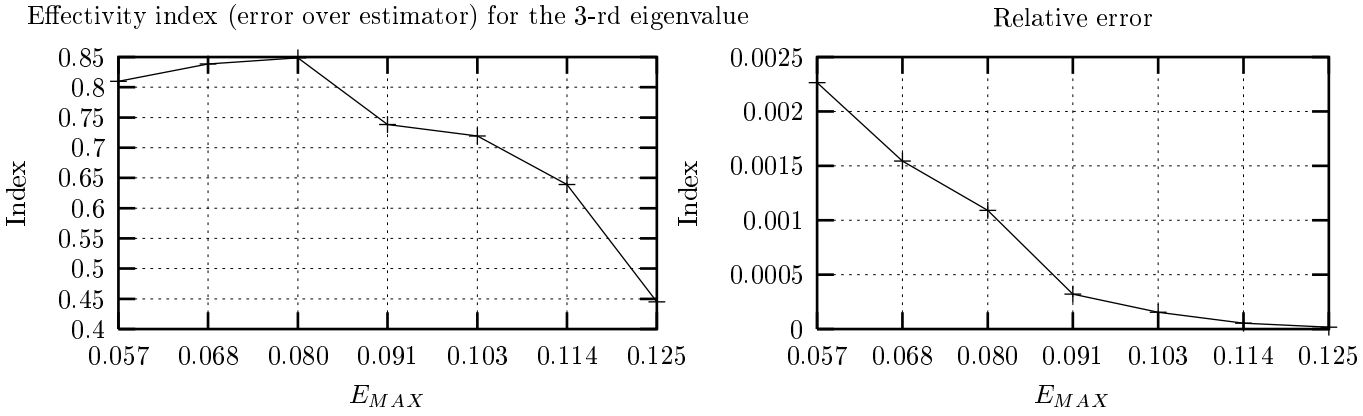

FIGURE 4. Third eigenvalue (energy expressed in Hartree (E_h))

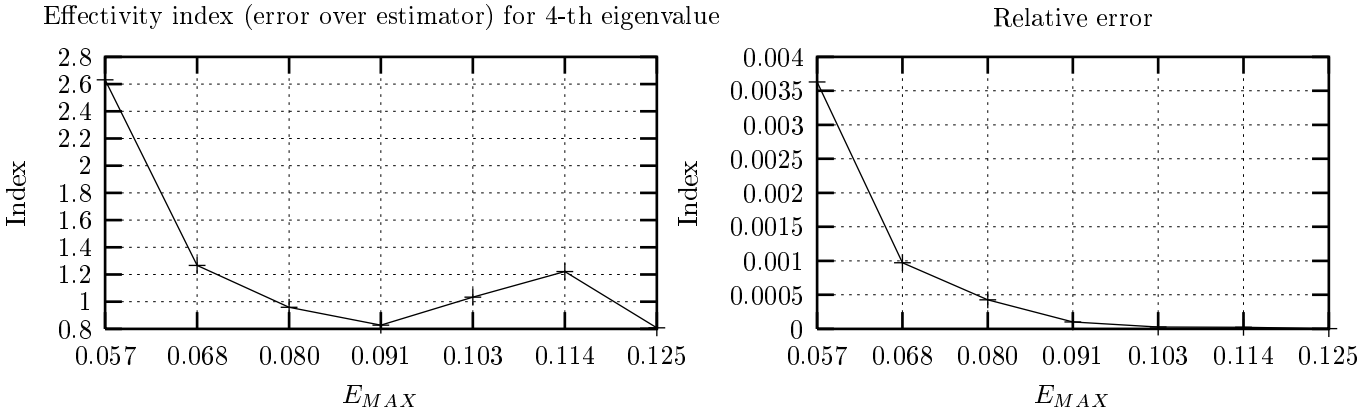

FIGURE 5. Fourth eigenvalue (energy expressed in Hartree (E_h))

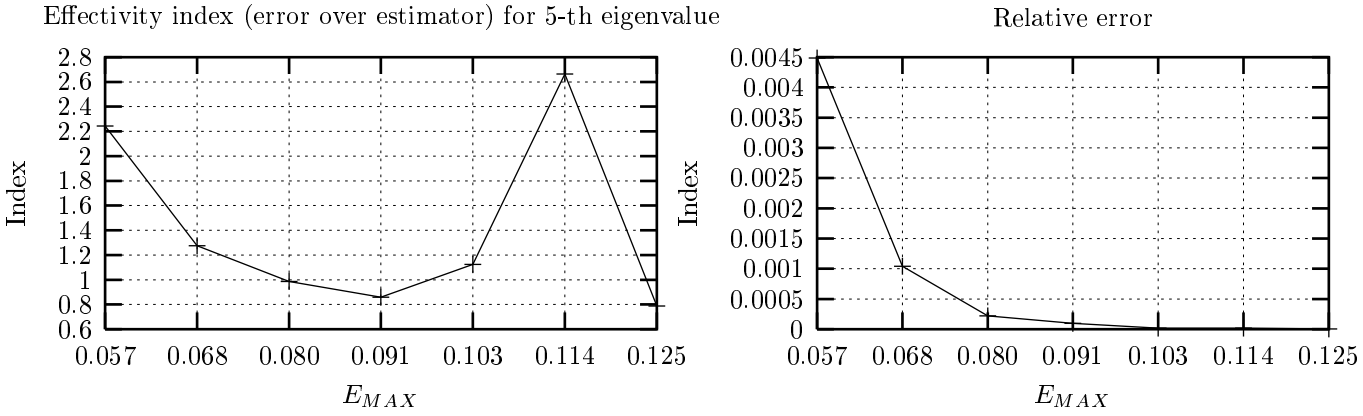

FIGURE 6. Fifth eigenvalue (energy expressed in Hartree (E_h))

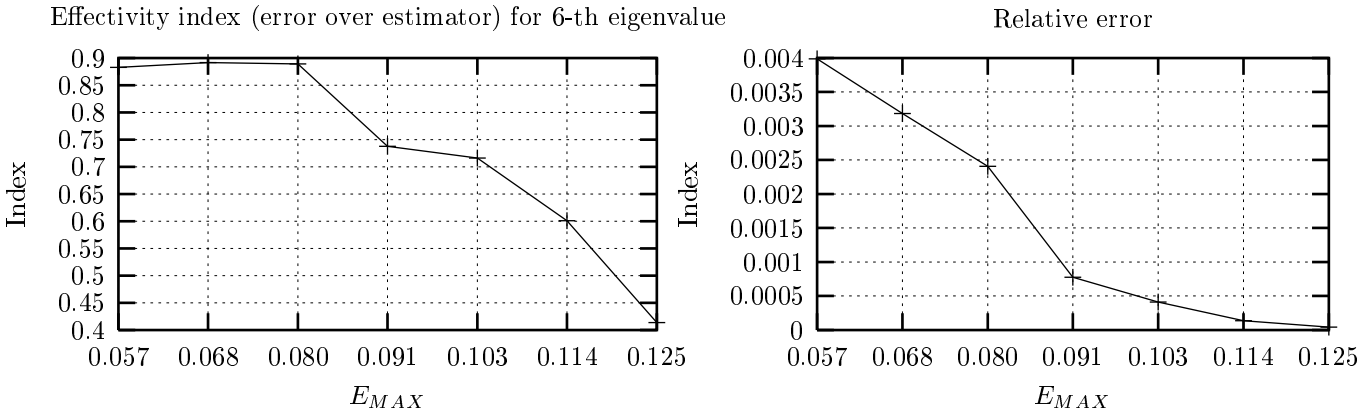

FIGURE 7. Sixth eigenvalue (energy expressed in Hartree (E_h))

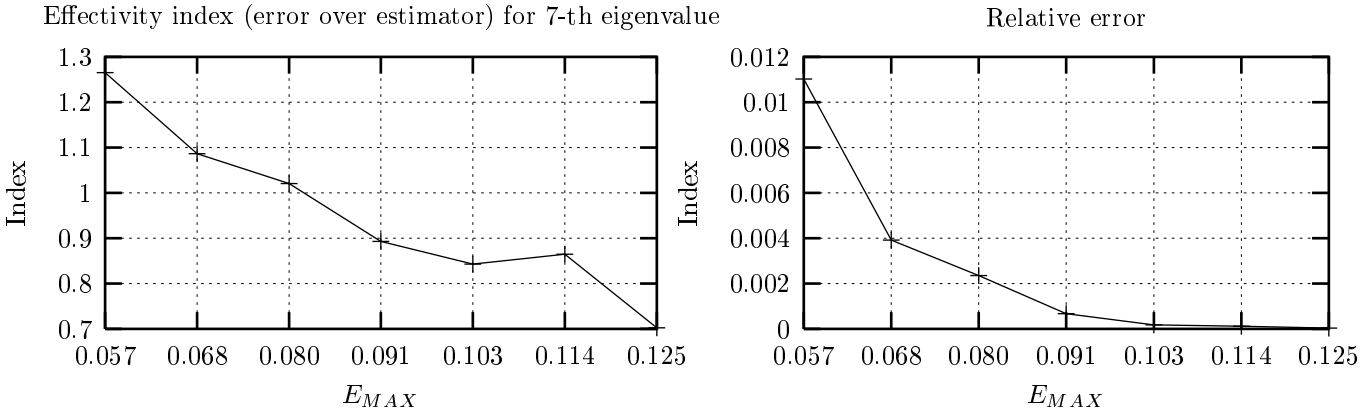

FIGURE 8. Seventh eigenvalue (energy expressed in Hartree (E_h))

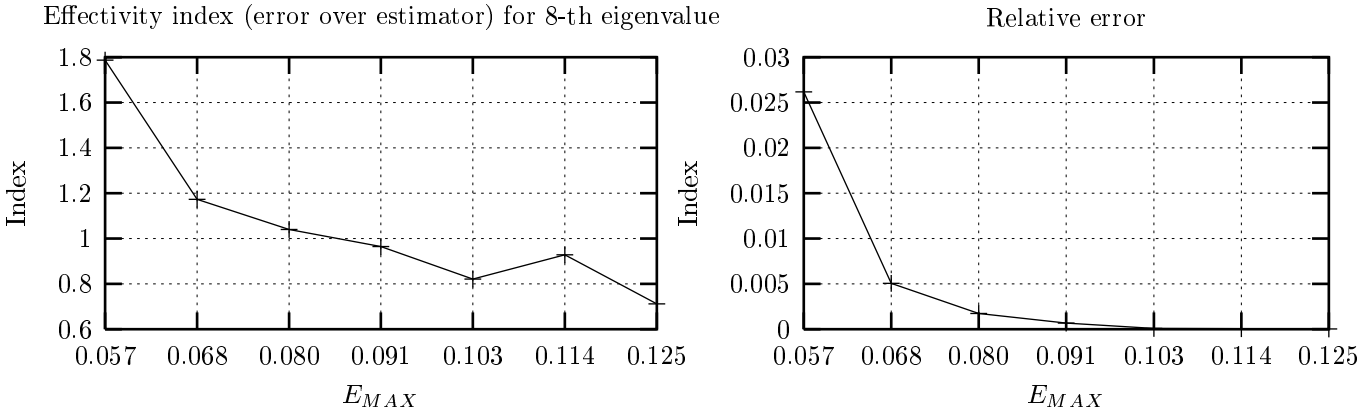

FIGURE 9. Eighth eigenvalue (energy expressed in Hartree (E_h))

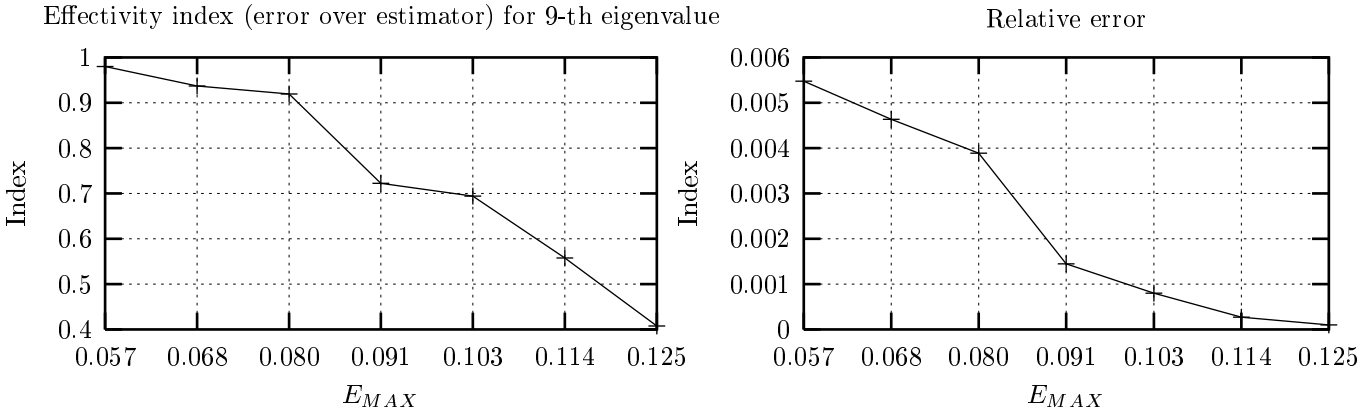

FIGURE 10. Ninth eigenvalue (energy expressed in Hartree (E_h))

We would also want that the estimator **quantitatively** describe the order of magnitude of the error. For the effectivity index this condition requires that the ratio between the extremal values of the effectivity index be no larger than 10. As we can see from the results displayed, all our indexes fulfill this requirement. In fact in our case this ratio is roughly 2 (except for eigenmodes 4,5 and 8 where it is closer to 3).

The index involves the norm of the operator $DF(\psi_0, \lambda_0)$ and its inverse mapping; it is surprising to notice that the range for the effectivity indexes is basically the same, **even for different eigenmodes**, which was not predicted by the theory. It seems that the various norms $DF(\psi_0, \lambda_0)$ vary slowly when calculated in different eigenmodes. The variation of the effectivity index for two values of $E_{MAX} = 0.0797E_h(17500cm^{-1})$ and $E_{MAX} = 0.1253E_h(27500cm^{-1})$ is plotted in figure 11 for all the nine eigenmodes.

Let us finally mention that the form of the estimator is not easy to find intuitively; other empirical combinations of, for instance, powers of E_{MAX} and the L^2 "residual" norm involved display divergence for the effectivity index.

Remark 5.2. It is of course natural to test the estimator on other types of molecules and also on other choices of adiabatic variables that might be less performant. This will allow to investigate the quality of the part of the estimator related to adiabaticity. This study requires more heavy discussions with our colleagues chemists,

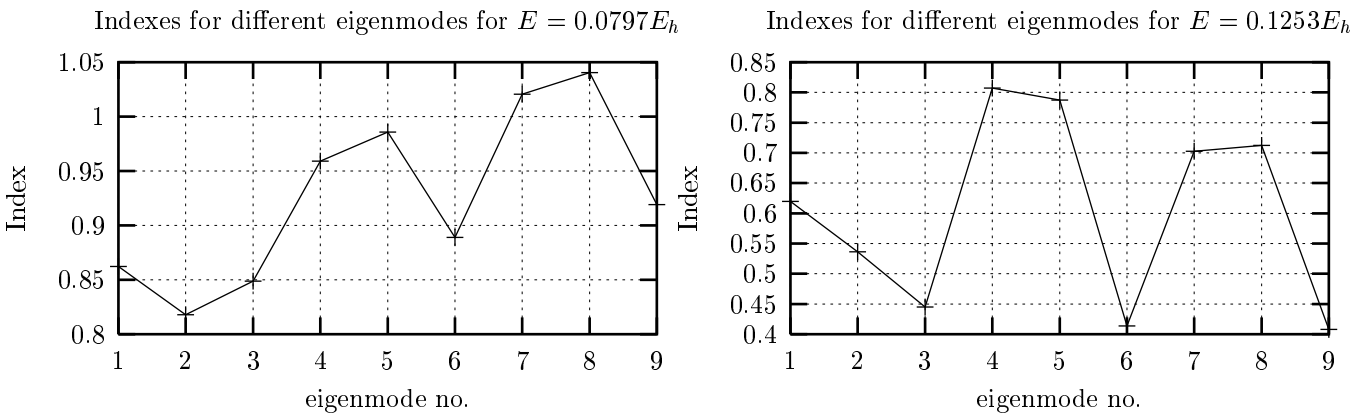

FIGURE 11. Effectivity indexes for different eigenmodes and cut-off E_{MAX} values.

which is planed to be done in a future work. Some preliminary results were already obtained for the water molecule in a different Jacobi system: the hydrogen atoms are located in B and C and the oxygen in A. Due to this change of the coordinate system, the adiabatic variable, still taken as the angle θ (see Figure 1), is different from the one chosen before. As a typical example a plot of the effectivity index and of the relative error for the 5-th eigenvalue is presented in Figure 12. Note that a full scan of the energy ($E_{MAX} > 0.091$) was not possible due to our limited knowlegde of the potential V. In this range of energy the effectivity index variation does not exceed an order of magnitude, but the (relative) error is about 150 times greater than before (compare with Figure 6). It appears that this choice of the adiabatic configuration is less pertinent than the former and our estimator reveals it here.

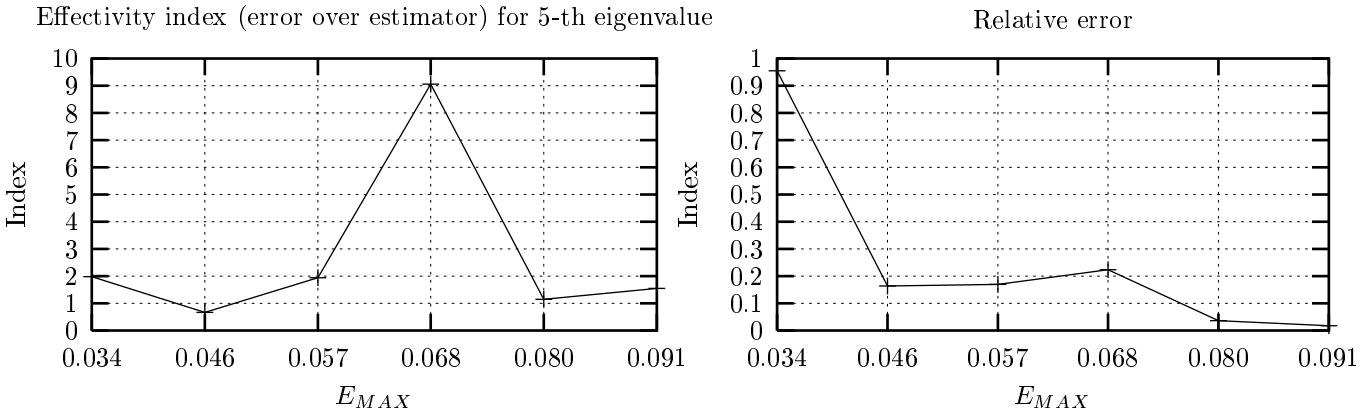

FIGURE 12. The system studied is again the water molecule in the Jacobi coordinates. This time the hydrogen atoms are located in B and C and the oxygen in A. This choice of coordinate system seems to not have good adiabaticity properties as the relative error is much larger than in the case of the initial coordinate system.

The authors wish to thank C. Leforestier from *Laboratoire Structure et Dynamique des Systèmes Moléculaires et Solides, Université de Montpellier 2* for providing his basic code to use with our estimators and for the discussions on the subject.

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Appendix A.

Remark A.1. By the definition of the spaces X_0^s the operator $T_{R,r,z}$ is an isometry between X_0^2 and $X_0^0 = L^2(]-1,1[^3)$; for any $g \in L^2(]-1,1[^3)$ the equation

$$T_{R,r,z} f = g \tag{62}$$

has therefore an unique solution $f \in X_0^2$; moreover the mapping that to g associates the solution f of (62) is a compact mapping from $L^2(]-1,1[^3)$ into $L^2(]-1,1[^3)$ (because of the embedding $H_0^1(]-1,1[^3) \subset L^2(]-1,1[^3)$ which is compact). By the Lax-Milgram lemma, as soon as $V \in L^\infty$, $\alpha \geq \|V\|_{L^\infty}$ the same properties remain true for the equation

$$(H + \alpha Id) f = T_{R,r,z} f + Vf + \alpha f = g \tag{63}$$

Is is essential for the a posteriori analysis of the (2)-(3) to study the properties of the differential $DF(\psi_0, \lambda_0)$ of F in the solution (ψ_0, λ_0) of (2)-(3) ; more precisely, it will be proven that if λ_0 is a simple eigenmode (i.e. of multiplicity 1) of H and $V \in L^\infty$ then $DF(\psi_0, \lambda_0)$ is an isomorphism from $L^2(]-1,1[^3) \times \mathbb{R}$ into $(X_0^2)^* \times \mathbb{R}$.

A straightforward computation gives the following formula for $DF(\psi_0, \lambda_0)$:

$$\begin{aligned} &< DF(\psi_0, \lambda_0)(\psi, \lambda), (\varphi, \mu) > = \int_{]-1,1[^3} H\varphi\psi - \lambda_0\psi\varphi - \lambda\psi_0\varphi + 2\mu \int_{]-1,1[^3} \psi_0\psi \\ &= \int_{]-1,1[^3} (H\varphi - \lambda_0\varphi + 2\mu\psi_0) \cdot \psi - \lambda \int_{]-1,1[^3} \psi_0\varphi = < (\psi, \lambda), DF(\psi_0, \lambda_0)^*(\varphi, \mu) > \end{aligned} \tag{64}$$

where $DF(\psi_0, \lambda_0)^*$ is the adjoint of $DF(\psi_0, \lambda_0)$. To prove the bijectivity of $DF(\psi_0, \lambda_0)$ we check that $DF(\psi_0, \lambda_0)^*$ is bijective. This is equivalent to prove that for any $\beta \in \mathbb{R}$ and $w \in L^2(]-1,1[^3)$ there exists an (unique) couple

(φ, μ) such that :

$$H\varphi + 2\mu\psi_0 - \lambda_0\varphi = w \tag{65}$$

$$\int_{]-1,1[^3} \psi_0\varphi = \beta \tag{66}$$

The equation (65) can be written $(H-\lambda_0)\varphi = w - 2\mu\psi_0$. If we suppose that λ_0 is a simple eigenvalue, then, by the remark A.1 and by the Fredholm alternative[6] (65) has a solution iff $w - 2\mu\psi_0 \perp \psi_0$ that is $\mu = \frac{<w,\psi_0>}{2}$; in this case the set of solutions is $\{\varphi_0 + \gamma\psi_0; \gamma \in \mathbb{R}\}$ where φ_0 is a particular **fixed** solution. By (66) we compute $\gamma = \beta - <\psi_0, \varphi_0>$ and so we have found a couple $(\varphi = \varphi_0 + \gamma\psi_0, \mu)$ that satisfy (65) and (66). It is therefore natural to suppose that $V \in L^\infty$ and that all eigenvalues under study are simples.

A.1. **Proof of lemma 3.2.**

Let us remind that all element φ_{MN} in $X_{M,N}$ can be written as

$$\varphi_{MN}(R,r,z) = \sum_{p,q,i=1}^{N+1} c_{p,q,i}\Phi_{p,q,i}(R,r)h_i(z), \tag{67}$$

with

$$c_{p,q,i} = \int_R \int_r \varphi_{MN}(R,r,\zeta_i)\Phi_{p,q,i}(R,r)dRdr. \tag{68}$$

By the definition of eigenmodes $\Phi_{p,q,i}$ we have also (by use of integration by parts)

$$\begin{aligned} c_{p,q,i} &= \int_R \int_r \varphi_{MN}(R,r,\zeta_i)\tfrac{1}{\Lambda_{p,q,i}}\big((-\partial_{RR} - \partial_{rr} - V(R,r,\zeta_i))\Phi_{p,q,i}\big)dRdr \\ &= \tfrac{1}{\Lambda_{p,q,i}}\int_R \int_r \big((-\partial_{RR} - \partial_{rr} - V(R,r,\zeta_i))\varphi_{MN}\big)(R,r,\zeta_i)\Phi_{p,q,i}(R,r)dRdr. \end{aligned} \tag{69}$$

Moreover by the definition of the projector we have

$$\big(\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN})\big)(R,r,z) = \sum_{(p,q,i);|\Lambda_{p,q,i}|>(1+\epsilon)E_{MAX}} c_{p,q,i}\Phi_{p,q,i}(R,r)h_i(z), \tag{70}$$

so that

$$\begin{aligned} &\|\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN})\|^2_{L^2} \leq \textstyle\sum_{(p,q,i);|\Lambda_{p,q,i}|>(1+\epsilon)E_{MAX}} (c_{p,q,i})^2\rho_i \\ &\leq \textstyle\sum_{(p,q,i);|\Lambda_{p,q,i}|>(1+\epsilon)E_{MAX}} \frac{1}{\Lambda^2_{p,q,i}}\Big(\int_R \int_r \big((-\partial_{RR} - \partial_{rr} - V(R,r,\zeta_i))\varphi_{MN}(R,r,\zeta_i)\big)\Phi_{p,q,i}(R,r)dRdr\Big)^2\rho_i. \end{aligned} \tag{71}$$

By the orthogonality of $\Phi_{p,q,i}$ we have

$$\begin{aligned} \|\varphi_{MN} - \pi_{\mathcal{E}_\delta}(\varphi_{MN})\|^2_{L^2} \quad &\leq (\tfrac{1}{(1+\epsilon)E_{MAX}})^2\Big(\|(-\partial_{RR} - \partial_{rr})\varphi_{MN}\|^2_{L^2(]-1,1[^3)} \\ &\quad + \|\textstyle\sum_i (V(.,.,\zeta_i)\varphi_{MN}(.,.,\zeta_i))^2\rho_i\|^2_{L^2(]-1,1[^2)}\Big) \end{aligned} \tag{72}$$

which concludes the proof of the first part of the lemma.

[6] we write $H - \lambda_0 = (H + \alpha Id) - (\alpha + \lambda_0)Id$ and we use, for α large enough, the Fredholm alternative ([4] p. 39) for the compact operator $(H + \alpha Id)^{-1}$ and the eigenvalue $\frac{1}{\alpha+\lambda_0} \neq 0$.

To prove (31) note that it is trivially true for $b = 0$ and by the argument above for $b = 2$; using once more in (69) the definition of eigenmodes $\Phi_{p,q,i}$ and after one supplementary integration by parts we obtain

$$c_{p,q,i} = \frac{1}{\Lambda^2_{p,q,i}} \int_R \int_r \big((-\partial_{RR} - \partial_{rr} - V(R,r,\zeta_i))^2 \varphi_{MN}\big)(R,r,\zeta_i)\Phi_{p,q,i}(R,r)dRdr \tag{73}$$

so, by the same line of reasoning as above, upper bound (31) is proved for $b = 4$; by continuing the procedure for all even values of b and using classical interpolation arguments the conclusion will follows.

A.2. **Proof of lemma 2.4.**

Let $\Pi_{M,N}$ be the projector to $X_{M,N}$ associated with $T_{R,r,z}$ that is for all $v \in X_0^1$, $\Pi_{M,N}v$ is the element of $X_{M,N}$ that verifies

$$\forall\ u \in X_{M,N}\ :\ \int_{]-1,1[^3} T_{R,r,z}(v - \Pi_{M,N}v)u = 0. \tag{74}$$

Note that $\Pi_\delta \Pi_{M,N} = \Pi_\delta$. It is classical[7] to see that $\Pi_{M,N}$ has optimal approximation properties, that is, for any $b \geq 1 \geq a \geq 0$ there exists a constant c independent of M,N such that

$$\|v - \Pi_{M,N}v\|_{X_0^a} \leq c\Big(\frac{1}{\max(M,N)}\Big)^{b-a} \|v\|_{X_0^b}. \tag{75}$$

Write then :

$$\|v - \Pi_\delta v\|_{X_0^a} \leq \|v - \Pi_{M,N}v\|_{X_0^a} + \|\Pi_{M,N}v - \Pi_\delta \Pi_{M,N}v\|_{X_0^a}. \tag{76}$$

By (75) the first term in (76) is optimal, so only the second term remains to be (optimally) upper bounded. Denote $f = \Pi_{M,N}v$; recall the minimization property of Π_δ :

$$\Pi_\delta v = argmin\{\|v - u\|_{X_0^1};\, u \in \mathcal{E}_\delta\}$$

and write, for $a = 1$:

$$\|f - \Pi_\delta f\|_{X_0^1} \leq \|f - \pi_{\mathcal{E}_\delta} f\|_{X_0^1} \leq C\max(M,N)\|f - \pi_{\mathcal{E}_\delta} f\|_{L^2} \leq C\max(M,N)\Big(\frac{1}{\sqrt{E_{MAX}}}\Big)^b \|f\|_{X_0^b}, \tag{77}$$

which ends the proof of the lemma for $a = 1$; the values of a in $[0,1[$ are treated by the duality technique of Aubin and Nitsche (see for instance [1] p. 274-275).

[7] use for instance the reasoning in [1] p. 262