Some mathematical inputs in computational chemistry

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CECAM VB NonorCI

Outline

Problem presentation: the Gross-Pitaevskii equation

Physical problem: Ground state of a system of bosons at very low temperature.

Two ways of seeing the problem: minimization problem – eigenvalue problem

Minimization problem: Energy functional minimization

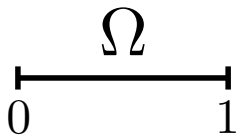
$$I = \inf \left\{ E(v),\ v \in H^1_{\#}(\Omega),\ \int_\Omega v^2 = 1 \right\} \quad \text{with } \Omega = (0,1)$$

$$\text{where} \quad E(v) = \frac{1}{2}\int_\Omega |\nabla v|^2 + \frac{1}{2}\int_\Omega V v^2 + \frac{1}{4}\int_\Omega v^4, \quad V \in L^p, p > 1$$

Nonlinear eigenvalue problem

$$\begin{cases} \forall v \in X, (-\Delta + V + u^2)u = \lambda u \\ \displaystyle\int_\Omega u^2 = 1. \end{cases}$$

Setting: 1-Dimensional, Periodic Setting.



Remark: λ is the smallest eigenvalue and is **simple**.

Resolution method

1- Space discretization: Planewave expansion.

Expansion in Fourier series:

$$u(x) = \sum_k \hat{u_k} e_k(x) \quad \text{where} \quad e_k(x) = e^{2\pi i k.x}$$

Exact space: $X = H^1_{\#}(\Omega)$. Discretized space: $X_N = \text{Span}\{e_k, |k| \leq N, k \in \mathbb{N}\}$.

Discretized problem $\forall v_N \in X_N, \int_\Omega \nabla u_N \cdot \nabla v_N + \int_\Omega V u_N v_N + \int_\Omega u_N^3 v_N - \lambda_N \int_\Omega u_N v_N = 0.$

2- Iterative resolution: Algorithm used to solve the equation on X_N:

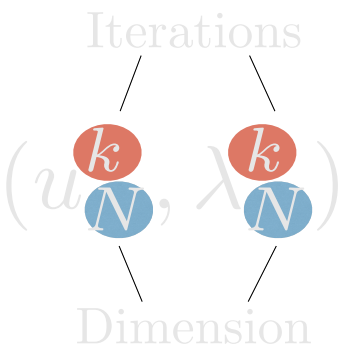
1. **Initialization:** Well-chosen pair (u_N^0, λ_N^0).
2. **Iterations:** Loop until convergence ($\|u_N^k - u_N^{k-1}\|_{H^1}$ small).

   Linear Problem

   $$\Pi_N(-\Delta \widetilde{u_N^k} + V\widetilde{u_N^k} + (u_N^{k-1})^2 \widetilde{u_N^k}) = \lambda_N^{k-1} u_N^{k-1}.$$

   Normalization $u_N^k = \widetilde{u_N^k} / \|\widetilde{u_N^k}\|_{L^2}$.

   Rayleigh Quotient $\lambda_N^k = \int \nabla (u_N^k)^2 + V(u_N^k)^2 + (u_N^k)^4$.
3. **Output:** Approximate eigenfunction and eigenvalue $(u_N^{k_{out}}, \lambda_N^{k_{out}})$.



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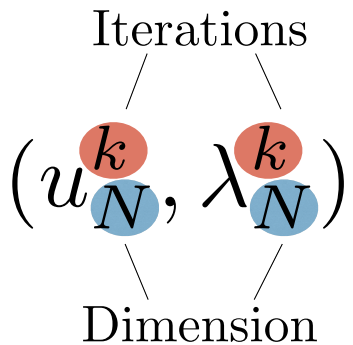

Error balance–Separation of error

Aim

- Analyse the error bound
- Find the origin of the error: space discretization and iterations
- Be able to refine the right parameter at each step
- Get the **best compromise** between space discretization and number of iteration that minimizes the number of computations for a given accuracy.

Two error sources:

- Size of the Fourier space $2N+1$.
- Number of iterations k.

Therefore, we decompose the main residual into **two computable parts**

$$R_{disc} = -\Delta u_N^k + V u_N^k + (u_N^{k-1})^2 u_N^k - \lambda_N^{k-1} u_N^{k-1}$$

$$R_{iter} = (u_N^k)^3 - (u_N^{k-1})^2 u_N^k - \lambda_N^k u_N^k + \lambda_N^{k-1} u_N^{k-1}$$

such that

$$R_N^k = R_{disc} + R_{iter}.$$

Error balance–Estimator

Writing $R_N^k = R_{disc} + R_{iter}$, we find

$$\|u - u_N^k\|_{H^1} \leq \alpha(err_k + err_N)$$

where err_k depends on the number of iterations and

$$\begin{aligned} err_k \quad = \quad & \|R_{iter}\|_{H^{-1}} \quad + \|(V + 3(u_N^k)^2 - \lambda_N^k - 1)_-\|_{L^\infty} \\ & \left[\frac{\|R_{iter}\|_{H^{-1}}}{\beta_N^k} + \frac{2}{\beta_N^k} |\lambda_N^k - \mu_N^1| \|u_N^k - v_N^1\|_{L^2} \right. \\ & \left. + \frac{3}{2} \|u_N^k - v_N^1\|_{L^2}^2 \left(1 + \frac{\|2(u_N^k)^2 v_N^1\|_{H^{-1}}}{\beta_N^k} \right) \right] \end{aligned}$$

and err_N depends on the dimension and

$$err_N = \|R_{disc}\|_{H^{-1}}$$

We note $err_{tot} \leq err_N + err_k$, with $err_{tot} = \|R_N^k\|_{H^{-1}}$

These terms are computable. We use them for adaptative refinement.

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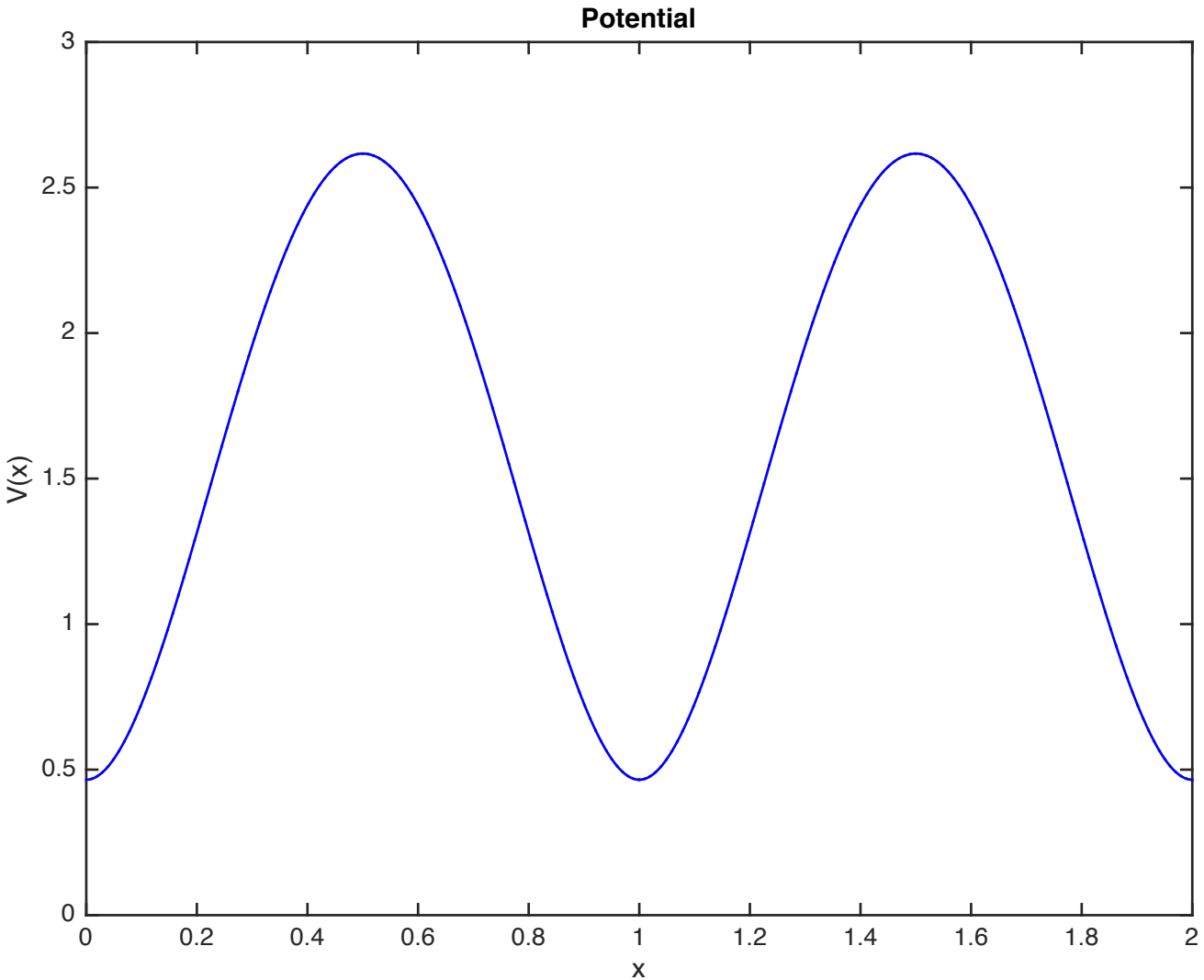
Numerical simulations: Framework

The Fourier coefficients of the potential V are given by $\widehat{V}_k = -\frac{1}{\sqrt{2\pi}} \frac{1}{|k|^4 - \frac{1}{4}}$,



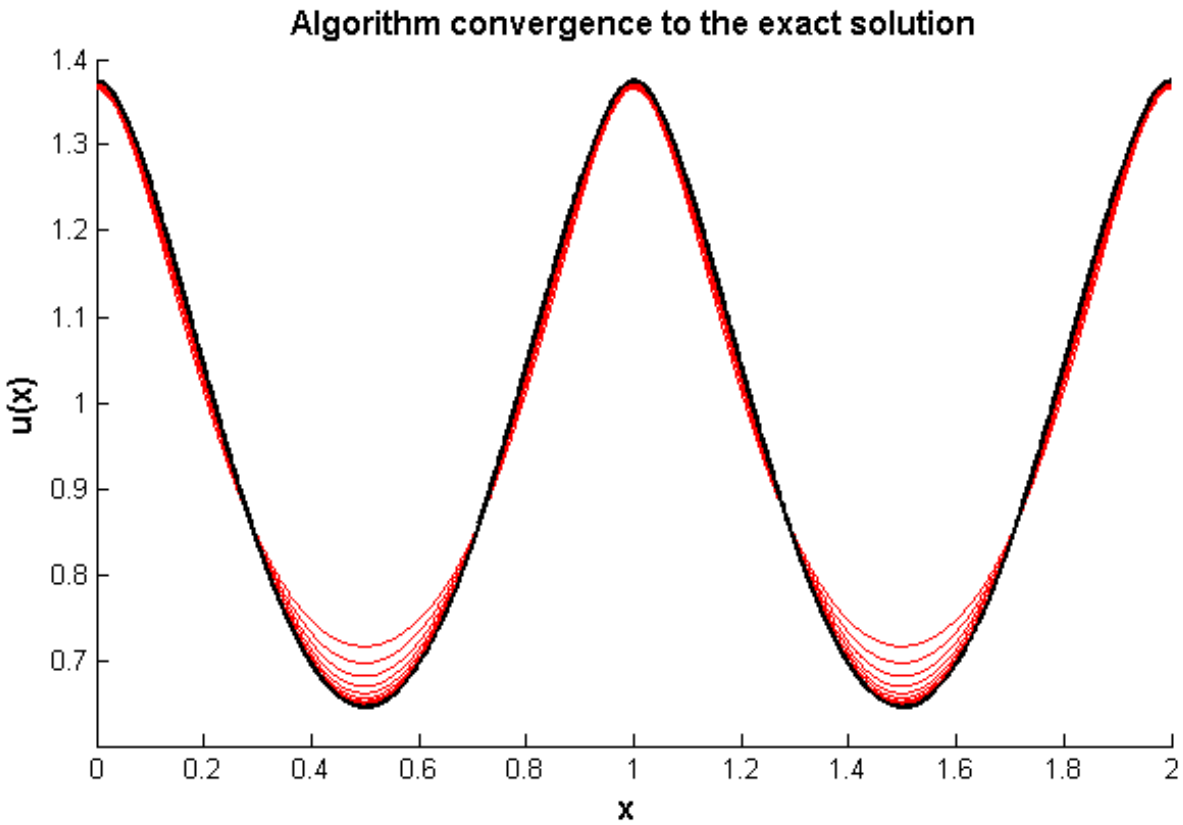
Exact solution

"Exact" solution

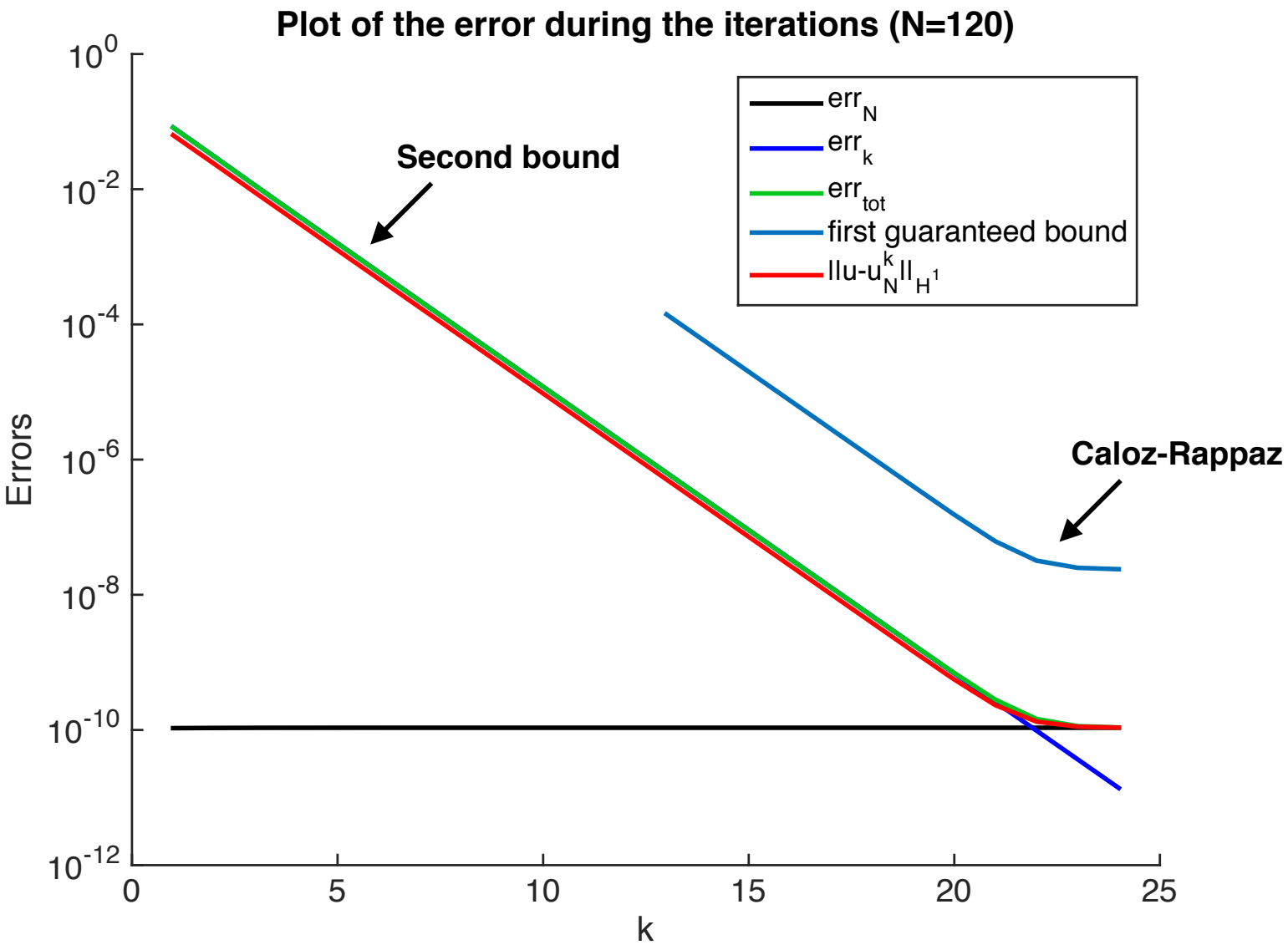
- Calculated in a discrete space with N=500.
- Norm of the residual:

$$\|R_N^k\|_{H^{-1}} = 4.10^{-13}$$

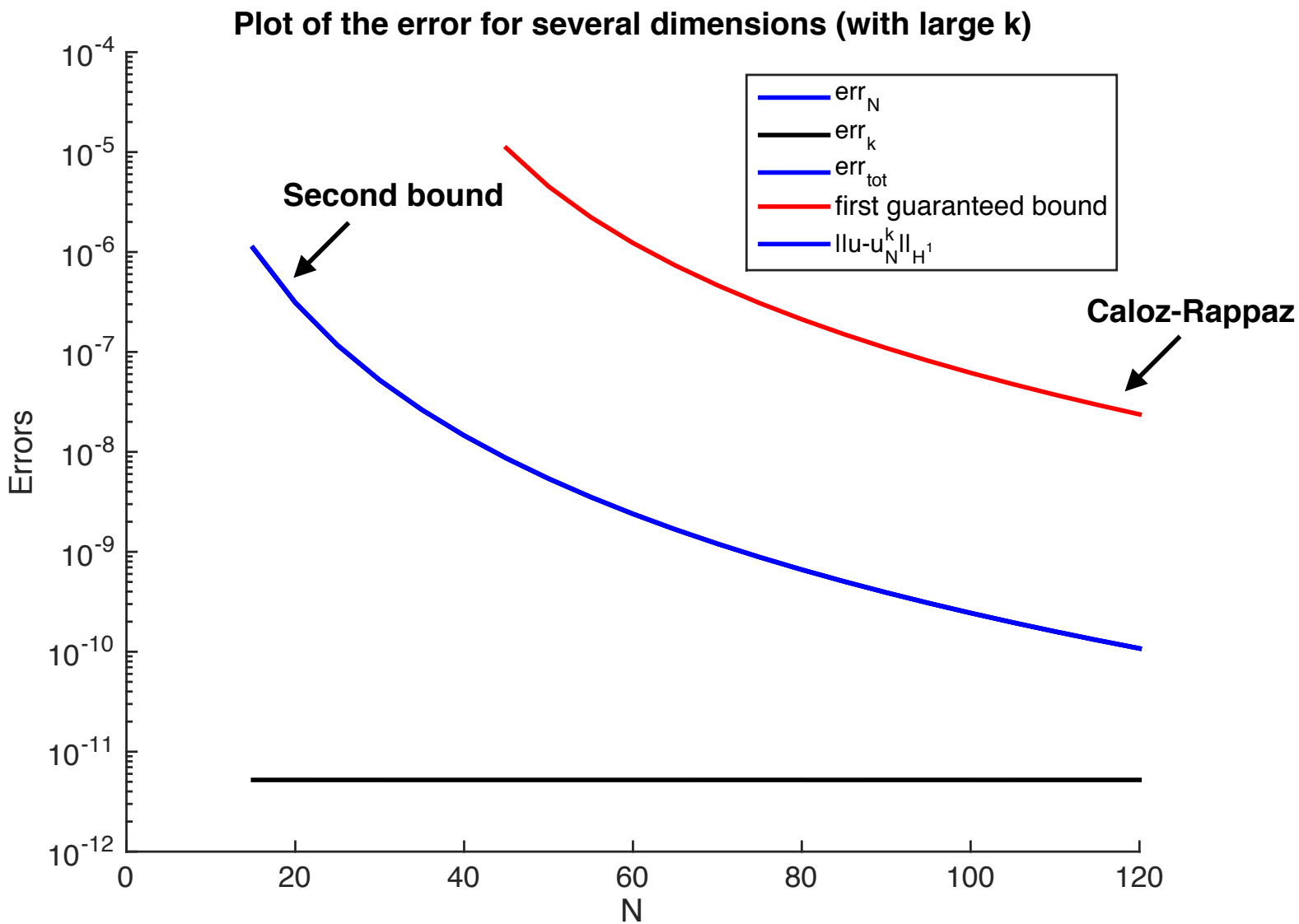
Results no more precise than 10^{-13}



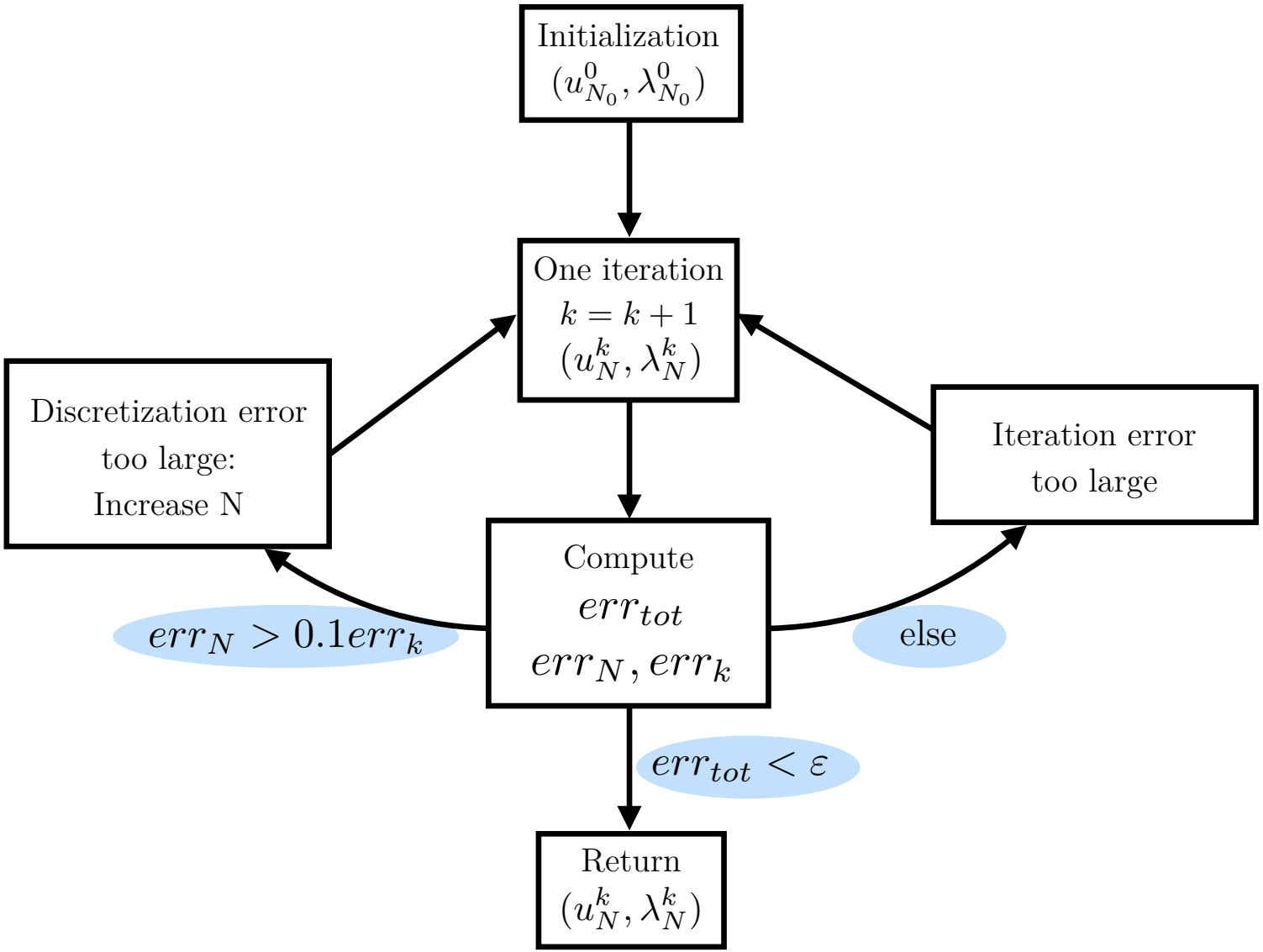
Simulations using a large dimension



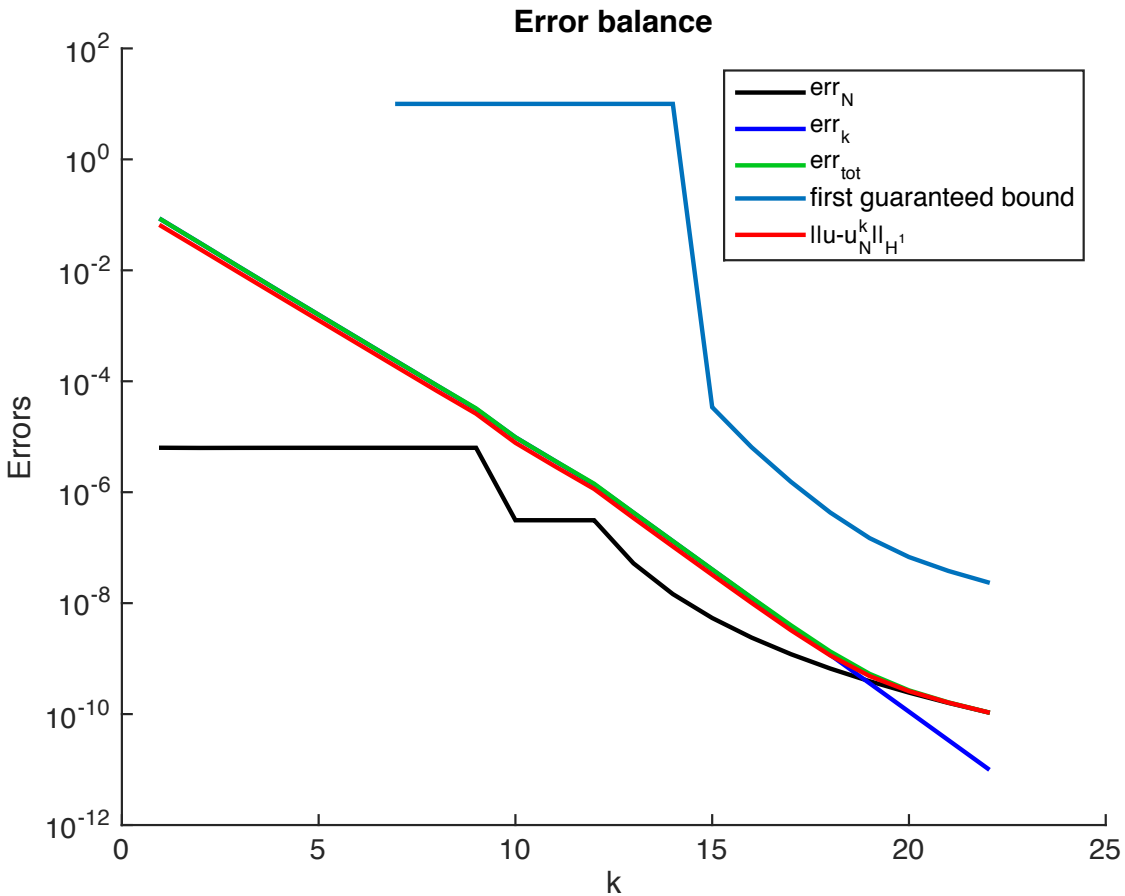
Simulations with a large number of iterations

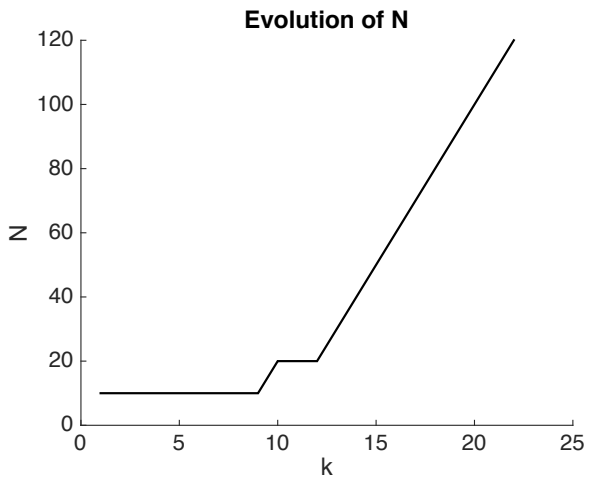


Error balance algorithm



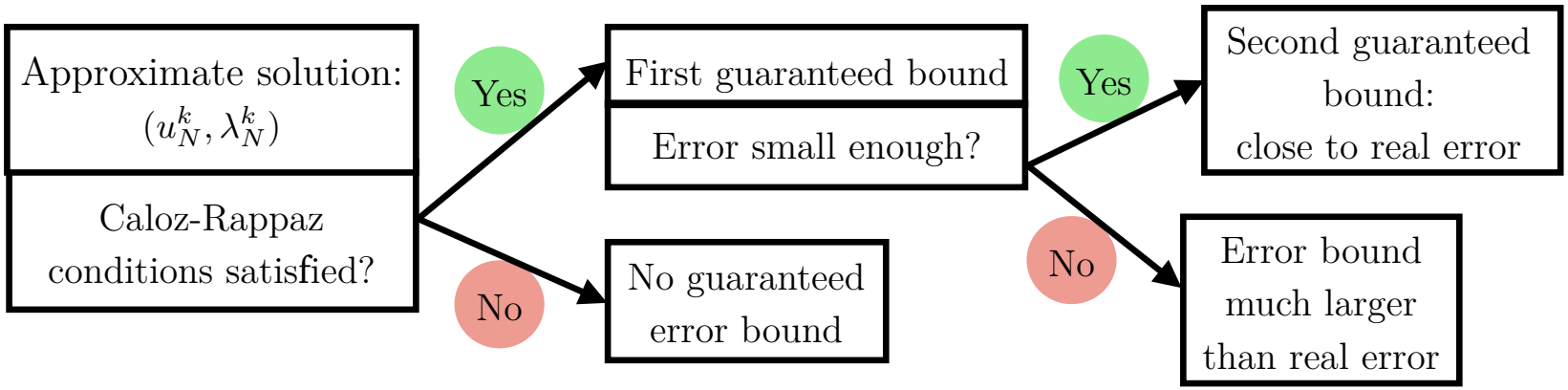
Error balance results





Is the error guaranteed?

Mathematical approach:

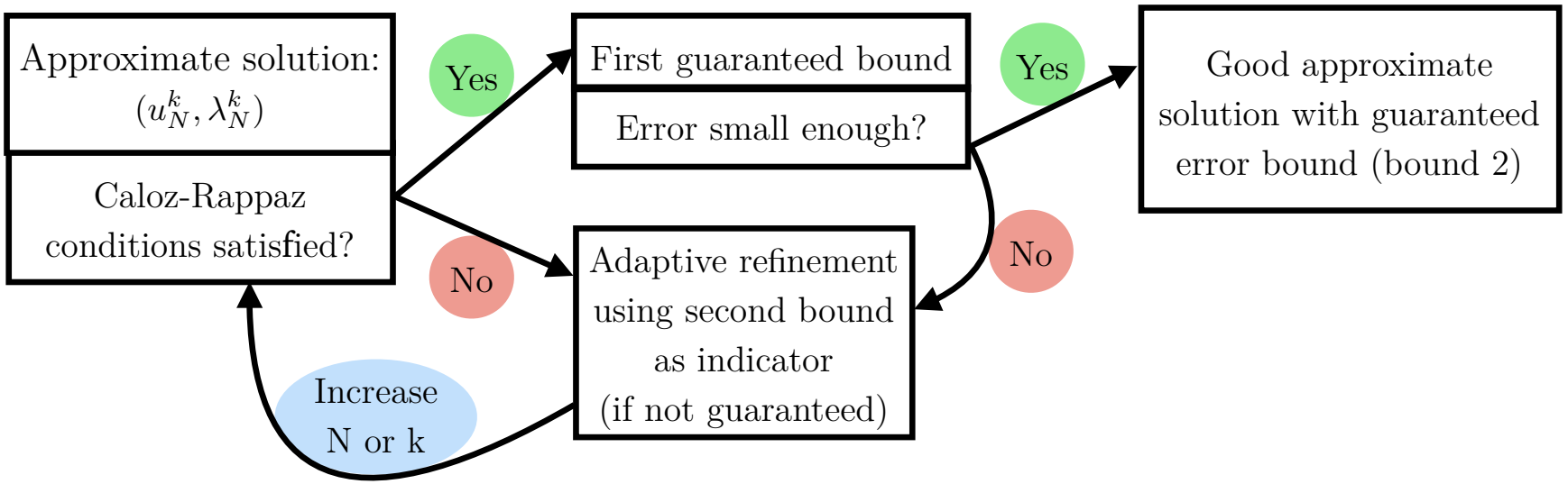


Conclusion:

- Error not guaranteed for too coarse solutions
- Error bound used for adaptive refinement
- Error guaranteed for fine solutions

Is the error guaranteed?

Practical aspects:



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and beyond . . .

We want now to incorporate the error due to the model . . .

Indeed, what is of interest for us is the solution to the full, original, Schrödinger equation. What is the link between Schrödinger and one of the feasible model.

- Kohn Sham, DFT
- Hartree Fock

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- Kohn Sham, DFT — better correlation models
- Hartree Fock — **post Hartree Fock methods**

post Hartree-Fock . . . CI-Full CI

We are using Slatter determinants to minimize the Schrodinger energy . . . leads to the following equation

Find $(\Phi, \lambda) \in Y \times \mathbb{R}^N$ such that, $\forall \psi \in Y$

$$\frac{1}{2}\int_{\mathbb{R}^3} \nabla\varphi_i \nabla\psi_i + \int_{\mathbb{R}^3} V\varphi_i\psi_i + 2\sum_{j=1}^{N}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\varphi_j(y)|^2\varphi_i(x)\psi_i(x)}{|x-y|}\,dx\,dy$$
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We are using Slatter determinants. . .

This has led us to an eigenvalue problem . . . where we have withdrawn **only** the N lowest eigenvalues : the occupied orbitals.

There are $\mathcal{N} - N$ to be used : the excited states.
The basic Hartree Fock determinant is written as

$$\Psi_0(\mathbf{x}) = \frac{1}{\sqrt{N!}} \det(\varphi_i(x_j))_{i,j=1}^{N}$$

and we denote it as

$$\Psi_0 := \Psi[1, 2, \ldots, N]$$

for obvious reasons as it involves the N occupied orbitals.

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$$\Psi_0(\mathbf{x}) = \frac{1}{\sqrt{N!}}\det(\varphi_i(x_j))_{i,j=1}^{N} := \Psi[1,2,\ldots,N].$$

Single excited determinant can then be constructed as

$$\Psi_j^a := \Psi[1,2,\ldots,j-1,a,j+1,\ldots,N]$$

where the occupied orbital j is replaced by the unoccupied orbital a. Analogously, doubly excited determinants are constructed as

$$\Psi_{j,k}^{a,b} := \Psi[1,2,\ldots,j-1,a,j+1,\ldots,k-1,b,k+1,\ldots,N]$$

Higher excitations involve index

$$\mu = \begin{pmatrix} a_1 & \ldots & a_k \\ \ell_1 & \ldots & \ell_k \end{pmatrix}$$

where a_i designates an index of unoccupied orbital that replaces the occupied one ℓ_i associated to an excitation of order k. Such an excited determinant is denoted as $\Psi_\mu = X_\mu \Psi_0$ where X_μ is a k-order excitation operator.

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The linear combinaison of all these excited determinants represents all the antisymetric functions that can be built . . . Actually, all the excited determinants may not be so useful . . . meaning that the coefficients in front of some of these, in the expansion of the ground state solution to Schrödinger problem, may be VERY small.

Would we know this a priori, we would look for minimization on reduced expansions based on only those that are useful.

This is the spirit of Coupled Cluster approximations

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post Hartree-Fock . . . CC

The *Projected Coupled Cluster Method* consists in the ansatz

$$T = T(\mathbf{t}) = \sum_k T_k = \sum_\mu t_\mu X_\mu$$

e.g. the CCSD method is given by $T = T_1 + T_2 = T(\mathbf{t})$ where the unknowns are the cluster amplitudes t_μ that are determined by the following (nonlinear) equation

$$\forall \mu \in \mathcal{J}_1 \cup \mathcal{J}_2, \qquad 0 =< \Psi_\mu, e^{-T} H e^{T} \Psi_0 >$$

We define the residual $f_\mu(\mathbf{t})$ by

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The natural question is then to understand the link between the norm of $\mathbf{t}$ and the energy norm of the wave function. Following Reinhold Schneider this is provided by the quantity $\|\mathbf{t}\|_V$ defined by

$$\|\mathbf{t}\|_V^2 = \sum_{\mu \in \mathcal{J}} \varepsilon_\mu |t_\mu|^2$$

where $\varepsilon_\mu = \sum_{i=1}^{k} \lambda_{a_i} - \lambda_{\ell_i}$, and the λ's are Hartree Fock eigenvalues in increasing order. This norm is equivalent to the H^1 norm of Ψ. The correct evaluation of the norm of the residual $\mathbf{f}(\tilde{\mathbf{t}}) := (f_\mu(\tilde{\mathbf{t}}))_\mu$ is thus

$$\|\mathbf{f}\|_{V'}^2 = \sum_{\mu \in \mathcal{J}} \varepsilon_\mu^{-1} |f_\mu|^2$$

An adaptive strategy for Coupled Cluster Approximations

Starting from an initial index set $\mathcal{J}_0$ composed say of single excitations. The procedure — as usual in the adaptive process — follows the rule

$$\text{ESTIMATE} \longrightarrow \text{MARK} \longrightarrow \text{REFINE} :$$

at step i, in order to define $\mathcal{J}_{i+1}$ we estimate those $f_\mu(\tilde{\mathbf{t}}_i)$ that may be added in order to improve the accuracy of the computation.

$$\forall \mu \in \mathcal{J}, \quad f_\mu(\mathbf{t}_i) := < \Psi_\mu | e^{-T_i} H e^{T_i} | \Psi_0 > = 0$$

By marking those indices associated with the those that have the largest contribution in the above V' (dual)-norm (i.e. with the relative weight ε_μ^{-1}) we add them in the set $\mathcal{J}_i$ to get a $\mathcal{J}_{i+1}$ (finer) adapted set and we continue recursively by enriching up to a level where the error estimator is small at the required accuracy.

An adaptive strategy for Coupled Cluster Approximations

Starting from an initial index set $\mathcal{J}_0$ composed say of single excitations. The procedure — as usual in the adaptive process — follows the rule

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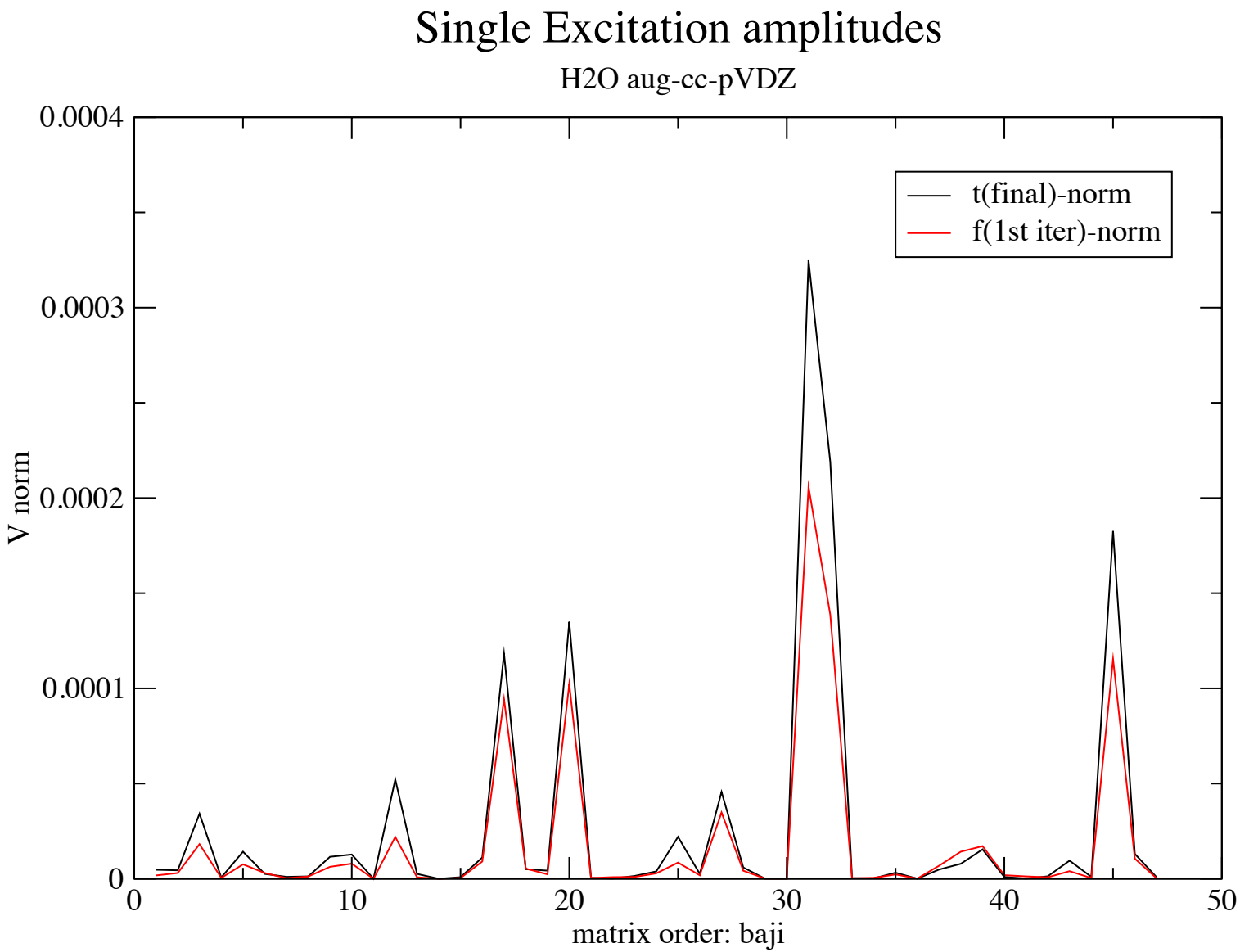
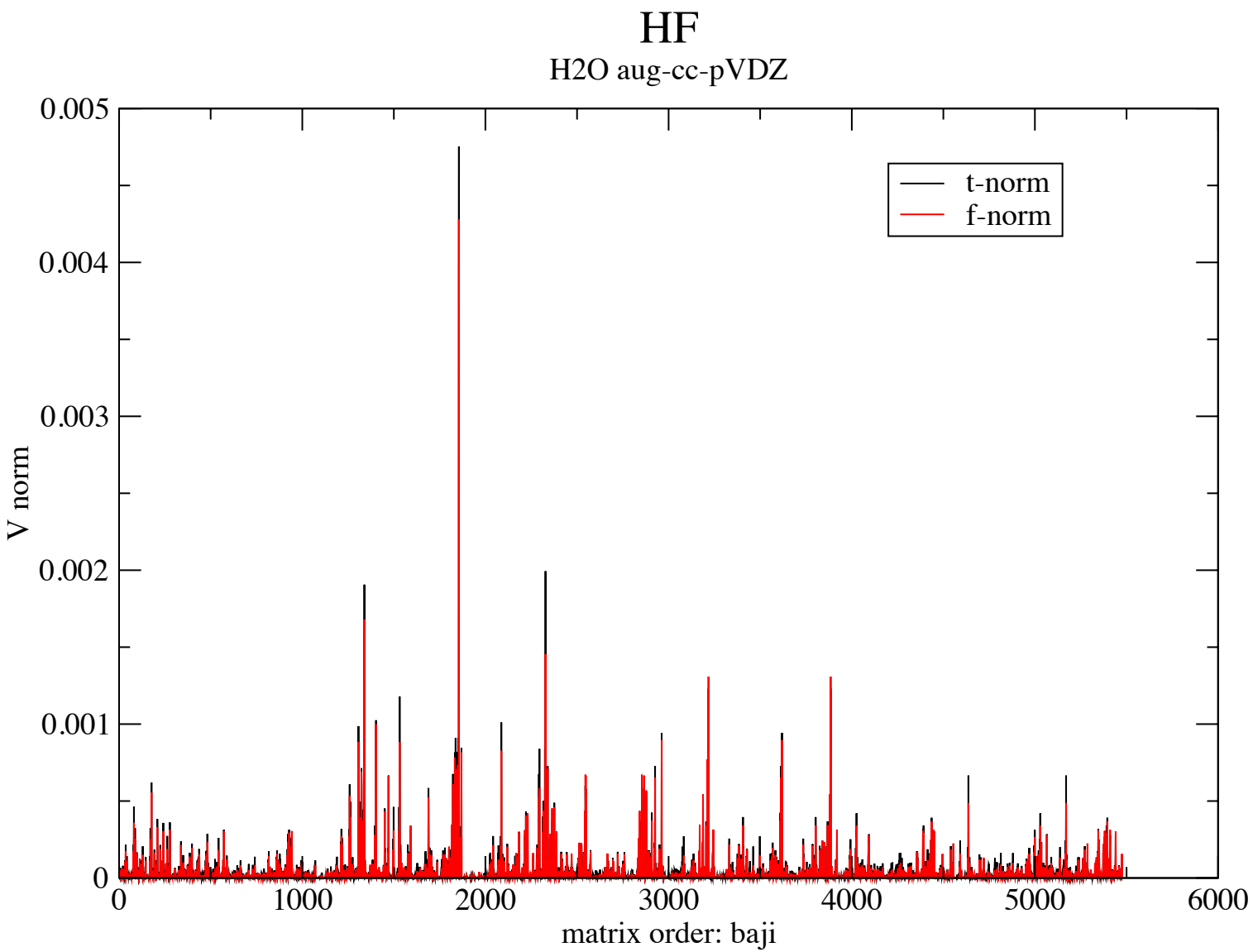


An adaptive strategy for Coupled Cluster Approximations



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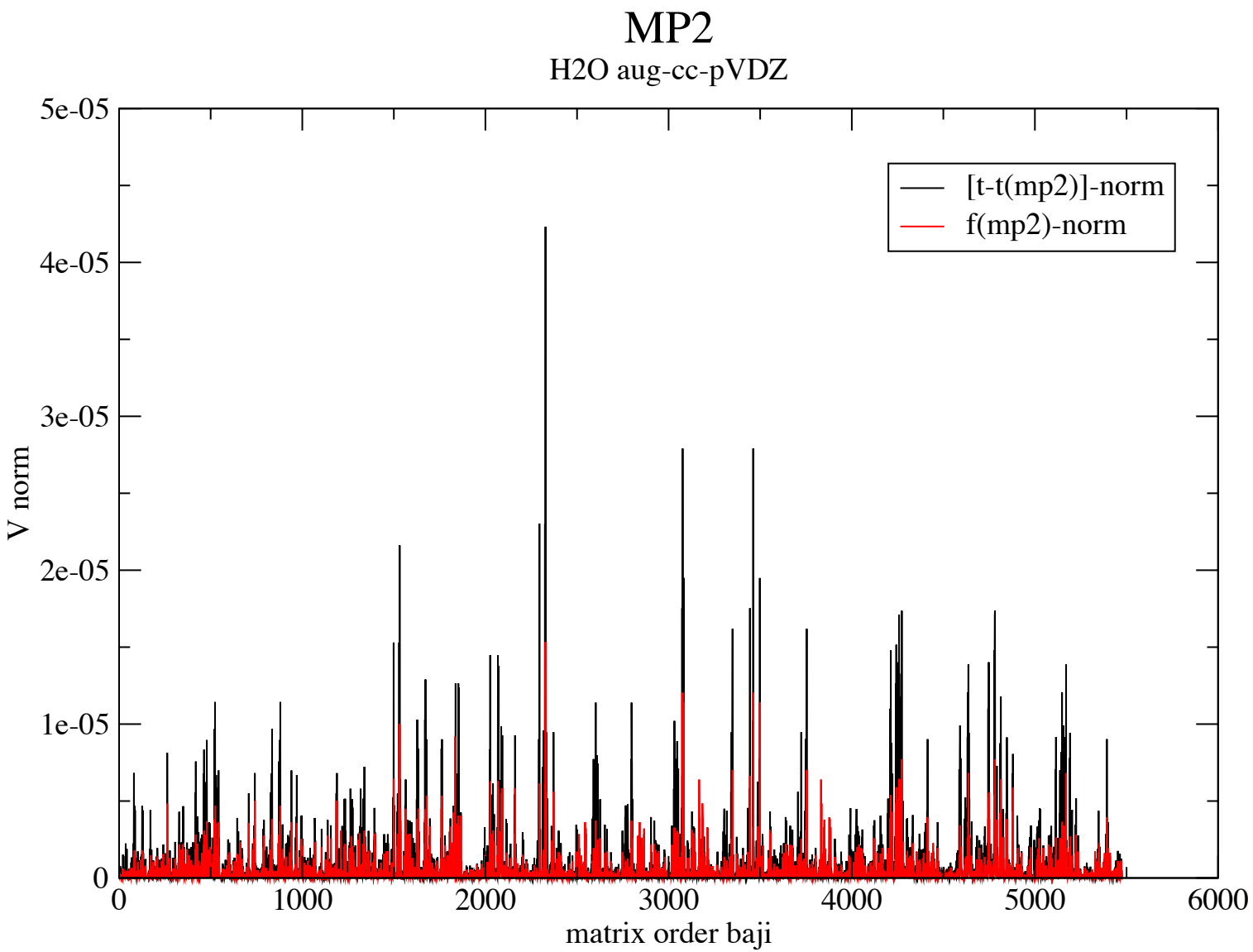

Outline

Conclusion, and perspectives

Conclusion:

- A posteriori Analysis for a nonlinear eigenvalue problem
- A posteriori analysis for the error in the model

Perspectives:

- A posteriori Analysis on the Kohn-Sham model.
- Other discretizations like wavelets, finite elements.

References

A priori results:

- Cancès, E., Chakir, R., & Maday, Y. (2012). *Numerical analysis of the planewave discretization of some orbital-free and Kohn-Sham models.* ESAIM: Mathematical Modelling and Numerical Analysis, 46(02), 341-388.

A posteriori Analysis:

- Dusson, G., & Maday, Y. (2013). *A Posteriori Analysis of a Non-Linear Gross-Pitaevskii type Eigenvalue Problem.*

Model Error:

- in collaboration with Marco Caricato : Gaussian and Filippo Lipparini : Group of Jürgen Gauss at Mainz