A posteriori error estimates in DFT calculations

Gaspard Kemlin

LAMFA, UMR CNRS 7352, UPJV, Amiens, France

https://gkemlin.pages.math.cnrs.fr/   gaspard.kemlin@u-picardie.fr

Joint works with Andrea Bordignon, Eric Cancès, Geneviève Dusson, Rafael Antonio Lainez Reyes and Benjamin Stamm.

A posteriori error estimation for linear models

For A self-adjoint, bounded-below and with compact resolvent, we consider the following infinite dimensional eigenvalue problem and its Galerkin approximation in the finite dimensional space $\mathcal{V}_N$ (*e.g.* planewaves, FE, LCAO...):

$$\begin{cases} Au = \lambda u, \\ \|u\| = 1, \end{cases} \quad \text{and} \quad \begin{cases} \Pi_N A \Pi_N u_N = \lambda_N u_N, \\ \|u_N\| = 1. \end{cases}$$

Residual analysis

$$\mathrm{res}(u_N, \lambda_N) = Au_N - \lambda_N u_N$$

$N \in \mathbb{R}_+$ is the discretization parameter:

- Exact solution: $\mathrm{res}(u, \lambda) = Au - \lambda u = 0$.
- Approximate solution: $\mathrm{res}(u_N, \lambda_N) \neq 0$.

Goals:

- Guaranteed (upper bound on the error $|\lambda - \lambda_N|$).
- Efficient (close to the error).
- Cheap (no more than the cost to get λ_N).
- Adaptive (highlights different contributions).

Existing bounds for linear problems:

- Bauer–Fike (60's): $|\lambda - \lambda_N| \leq \|\mathrm{res}(u_N, \lambda_N)\|$.
- Kato–Temple (50's): $|\lambda - \lambda_N| \leq \frac{\|\mathrm{res}(u_N,\lambda_N)\|^2}{\mathrm{gap}}$.
- More recently (2020)[a], fully guaranteed bound:

$$|\lambda - \lambda_N| \leq \overbrace{\|A^{-1/2}\mathrm{res}(u_N, \lambda_N)\|^2}^{= \langle \mathrm{res}(u_N,\lambda_N), A^{-1}\mathrm{res}(u_N,\lambda_N)\rangle =: \text{ dual norm}} + 2\lambda_N C_N^{-1} \|A^{-1}\mathrm{res}(u_N, \lambda_N)\|^2, \tag{1}$$

with C_N a *computable*, gap dependent, constant.

[a]E. Cancès, G. Dusson, Y. Maday, B. Stamm, and M. Vohralik. Guaranteed a posteriori bounds for eigenvalues and eigenvectors: Multiplicities and clusters, Mathematics of Computation (2020).

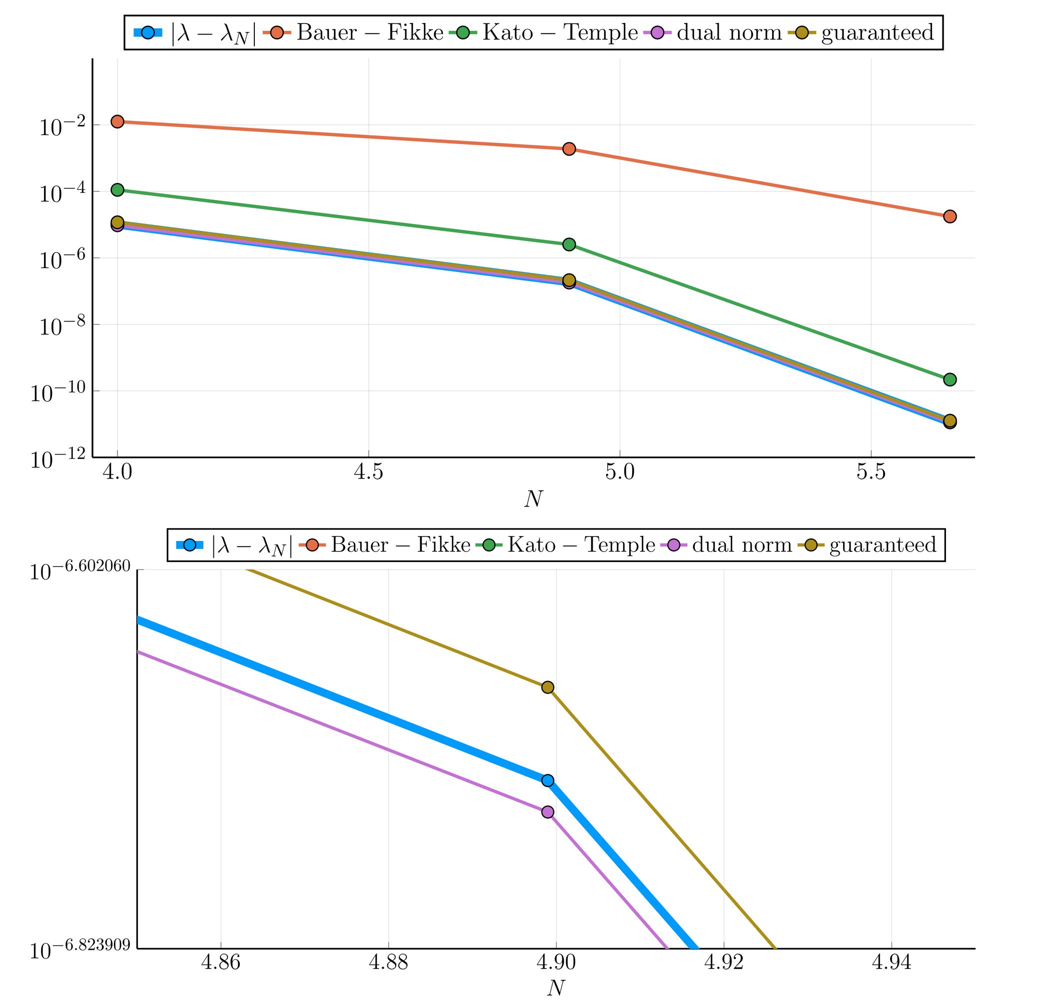

Figure 1: Example for $A = -\frac{1}{2}\Delta + V$. (Top) Only the fully guaranteed one and the dual norm are satisfying. (Bottom) Zoom: the dual norm is *not* an upper bound.

Error estimates for nonlinear models

Generic DFT model: $\min_{\gamma \in \mathcal{M}_{N_{\mathrm{el}}}} E(\gamma) := \mathrm{Tr}(h\gamma) + F(\rho_\gamma)$ where

$$\mathcal{M}_{N_{\mathrm{el}}} := \left\{ \gamma \in \mathcal{S}(L^2_\#(\Omega)),\ \mathrm{Ran}(\gamma) \subset H^1_\#(\Omega),\ \gamma^* = \gamma = \gamma^2,\ \mathrm{Tr}(\gamma) = N_{\mathrm{el}} \right\},$$

$$\gamma = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i\rangle\langle\varphi_i|, \text{ and } \rho_\gamma(x) = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i(x)|^2.$$

Euler–Lagrange/Kohn–Sham equations $\rightsquigarrow$ *nonlinear* eigenvalue problem:

$$\begin{cases} H_{\rho_\gamma}\varphi_i = \varepsilon_i \varphi_i \\ \langle \varphi_i, \varphi_j \rangle = \delta_{ij} \\ \gamma = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i\rangle\langle\varphi_i| \end{cases} \xrightarrow[\text{discretization}]{\text{SCF algorithm}} \begin{cases} \left(\Pi_N H_{\rho_{\gamma_{N,m}}} \Pi_N\right) \varphi_{i,N,m} = \varepsilon_{i,N,m}\varphi_{i,N,m} \\ \langle \varphi_{i,N,m}, \varphi_{j,N,m} \rangle = \delta_{ij} \\ \gamma_{N,m+1} = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_{i,N,m}\rangle\langle\varphi_{i,N,m}| \end{cases}$$

Here, $H_\rho = h + V_\rho$ with $h = -\frac{1}{2}\Delta + V$ and $V_\rho = \frac{\delta F(\rho)}{\delta\rho}$ (= Hartree + xc).

Theorem

At iteration m of the SCF in $\mathcal{V}_N$, it holds, for $\gamma_\star$ a minimizer and under a gap condition (= insulator or semi-conductor):

$$E(\gamma_{N,m}) - E(\gamma_\star) \leq \mathtt{err}^{\mathrm{disc}}_{N,m} + \mathtt{err}^{\mathrm{SCF}}_{N,m}$$
$$\mathtt{err}^{\mathrm{disc}}_{N,m} = \mathrm{Tr}\left(\left(H_{\rho_{\gamma_{N,m}}} - \mu_{N,m+1}\right)\gamma_{N,m+1}\right)$$
$$\mathtt{err}^{\mathrm{SCF}}_{N,m} = \mathrm{Tr}\left(H_{\rho_{\gamma_{N,m}}}\gamma_{N,m}\right) - \mathrm{Tr}\left(H_{\rho_{\gamma_{N,m}}}\gamma_{N,m+1}\right)$$

with $\mu_{N,m+1}$ a *computable* constant, that depends on the gap and the dual norm of the residuals.

Difficulties:

- Nonlinearity of the energy functional: the theorem is valid under the condition that F is *convex*.
- Cluster of eigenvalues: residual is the sum of the individual residuals.
- $\mu_{N,m+1}$ is obtained by applying a (1)-like formula for clusters of eigenvalues applied to $A = H_{\rho_{\gamma_{N,m}}}$ $\rightsquigarrow$ dual norms require to solve linear systems at *every step* of the SCF ! In practice, inexact solve of these linear systems still gives satisfactory (but nonguaranteed) results.

Comments:

- $\mathtt{err}^{\mathrm{disc}}_{N,m} \to 0$ as $N \to +\infty$ provided that the discretization is well chosen.
- $\mathtt{err}^{\mathrm{SCF}}_{N,m} \to 0$ as $m \to +\infty$ provided that the SCF algorithm converges.

Application to 3D materials with `DFTK.jl`

- Silicon cristal, **k**-grid $2 \times 2 \times 2$.
- $\mathcal{V}_N = \mathrm{Span}\left\{ e_{\mathbf{G}},\ |\mathbf{G}| \leq N \right\}$ with $e_{\mathbf{G}}$ Fourier modes (= planewaves).
- $E_{\mathrm{cut}} = 150$ Ha, $E_{\mathrm{cut,ref}} = 400$ Ha.
- $N = \sqrt{2E_{\mathrm{cut}}}$: $\mathcal{V}_{N_{\mathrm{ref}}} = \mathcal{V}_N \oplus \mathcal{V}_N^\perp$ and residuals $\in \mathcal{V}_N^\perp$ (high frequencies).

DFTK

https://dftk.org

- Convex model: rHF, with $F(\rho) = \frac{1}{2}\iint_{\Omega\times\Omega} \frac{\rho(x)\rho(y)}{|x-y|}dxdy$ (no xc).
- Dual norms are computed by approximating $A^{-1} \approx \left(-\frac{1}{2}\Delta + c\right)^{-1}$: (i) cheap to inverse in planewaves (diagonal) and (ii) only high frequencies needed when acting on the residual, where the Laplacian dominates. Results are not guaranteed anymore but still gives very satisfying bounds.
- We can track the error on the energy, with a splitting between discretization error and SCF error: the transition from a SCF-dominating error to a discretization-dominating error clearly appears.
- Very good results for LDA and PBE functionals (even though nonconvex).

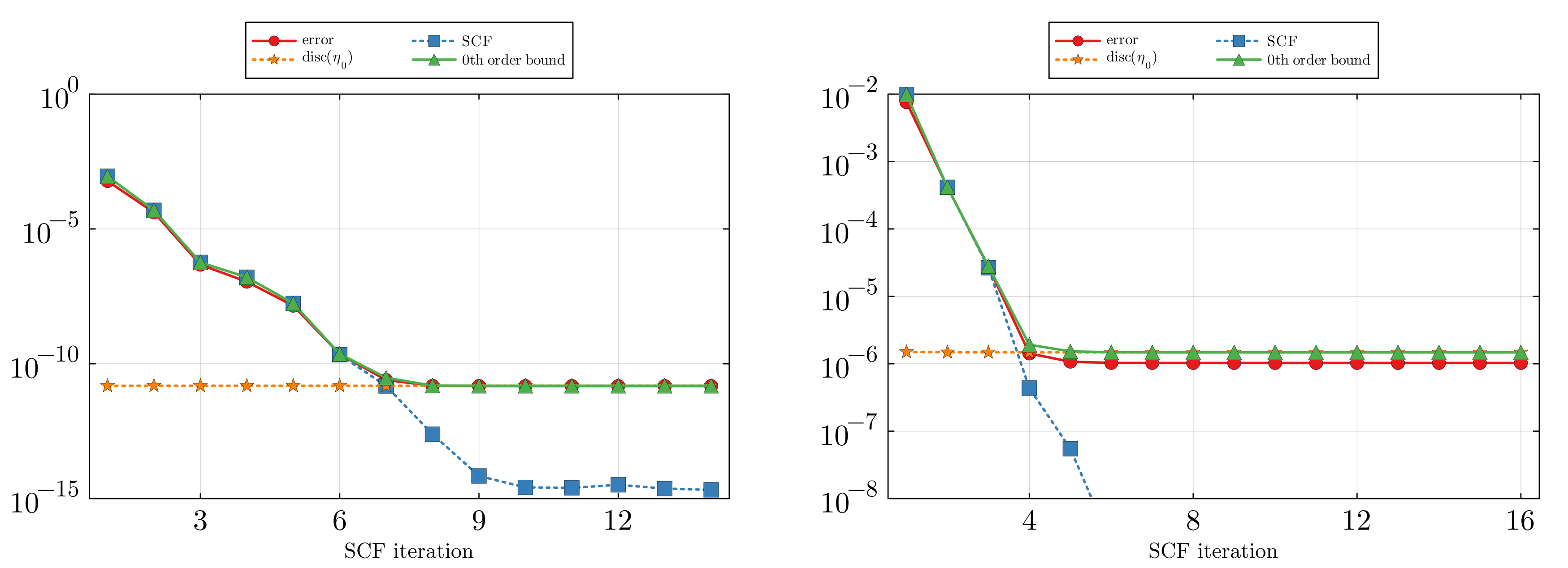

Figure 2: Error control on the energy along the SCF iterations for the rHF model (left, convex F) and the LDA model (right, nonconvex F).

Perspectives and references

- Metallic systems (no gap).
- Error on the density.
- Adaptive schemes.
- Nonconvex models.
- Other discretizations than planewaves.

All details (proofs, definition of $\mu_{N,m+1}$, code) available online:

A. Bordignon, E. Cancès, G. Dusson, G. Kemlin, R.A. Lainez Reyes, B. Stamm. Fully guaranteed and computable error bounds on the energy for periodic Kohn-Sham equations with convex density functionals (2024). arXiv:2409.11769