Error bounds for properties in planewave electronic structure calculations

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May 6, 2022

Computing properties of materials systems

Electronic structure models, such as Density Functional Theory (DFT), offer good compromise between accuracy and computational cost.

Accurate prediction of many properties, such as :

- energies, forces

In practice, approximate solutions and hence approximate quantities of interest.

- How to estimate errors on **quantities of interest** ?
- How the errors on the solutions of a given problem pass on properties computed from these solutions ?

In this talk, focus on the discretization error, i.e. basis set error.

Outline

Density Functional Theory

The ground state problem (Kohn–Sham model, 1965)

Mathematical problem : M **nonlinear eigenvalue** equations in 3D

Find M orthonormal orbitals

$$\Phi^0 = (\phi_1^0, \dots, \phi_M^0) \in X = \left\{ \Phi = (\phi_1, \dots, \phi_M) \in \left[H^1(\Omega)\right]^M \middle| \int_\Omega \phi_i \phi_j = 1 \right\}$$

with corresponding lowest eigenvalues $\lambda_1^0, \dots, \lambda_M^0$, such that

$$\left(-\frac{1}{2}\Delta + V^{KS}_{\{\mathbf{R}_k\},\rho_{[\Phi^0]}}\right)\phi_i^0 = \lambda_i^0 \phi_i^0, \quad i = 1, \dots, M, \quad \text{with} \quad \rho_{[\Phi^0]} = 2\sum_{i=1}^{M} |\phi_i^0|^2.$$

Discretization : planewave, gaussian basis sets, etc.

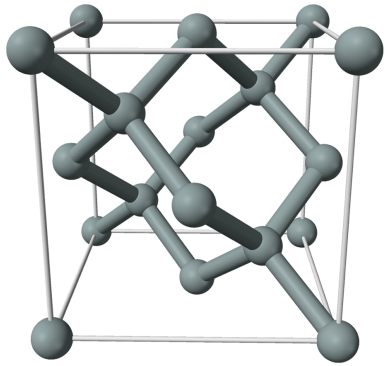
Practical resolution : Iterative procedure (SCF algorithm).

1. Start from initial guess : $(\phi_{i,0}, \lambda_{i,0})$
2. At each iteration, solve eigenvalue problem

$$\left(-\frac{1}{2}\Delta + V^{KS}_{\{\mathbf{R}_k\},\rho_{[\Phi_{j-1}]}}\right)\phi_{i,j} = \lambda_{i,j}\phi_{i,j}, \quad i = 1, \dots, M.$$

3. Stop when two following iterates are close enough

Modelling crystalline systems



$\mathcal{R}$: crystal lattice.

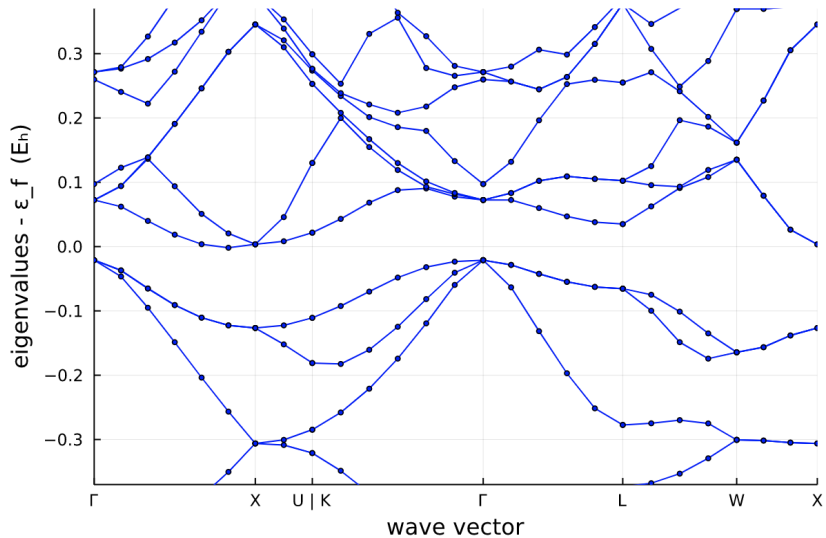
Infinite periodic system with Hamiltonian $-\frac{1}{2}\Delta + V_{\text{per}}$, with V_{per} $\mathcal{R}$-periodic.

Equivalent to study a family of Hamiltonians indexed by $\boldsymbol{k}$ (in the Brillouin zone) in the unit cell :

$$\frac{1}{2}(-i\nabla + \boldsymbol{k})^2 + V_{\text{per}}$$

Properties integrated over the Brillouin zone.
Example : Density of states

$$\sum_{n\in\mathbb{N}} \int_{\boldsymbol{k}} 1(\lambda_{n\mathbf{k}} \leq \varepsilon) d\mathbf{k}$$



Silicon band spectrum (DFTK)

In practice, finite sum over the Brillouin zone

Errors arising in the course of the calculation

- Model error :
  1. Pseudopotentials
  2. Exchange-correlation functional $\rightarrow$ see Francois Gygi's talk
  3. k-point sampling $\rightarrow$ see Xin Xing's talk
- Discretization error $\rightarrow$ this talk
- Algorithmic error, numerical error

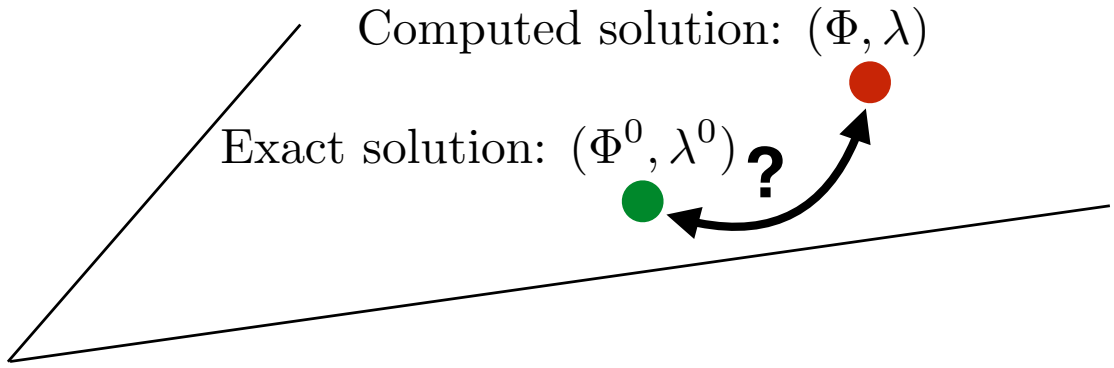
Several approximations of different nature

- **How large is the total error ?**
- **How large is each error component ?**

Usefullness of error bounds

1. **Certify** the precision of the results.
2. **Optimize** the computational ressources : minimize the computational cost to obtain a desired accuracy.

The perfect error bound



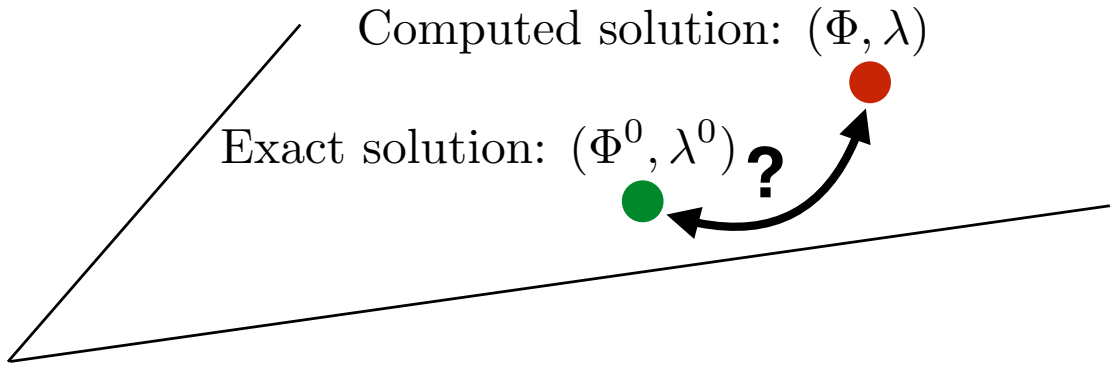
The goal is to derive an inequality of the type :

$$\|(\Phi^0, \lambda^0) - (\Phi, \lambda)\|_? \leq \eta(\textit{disc.}, \textit{algo.}, \ldots) = \text{ Error bound}$$

Wish-list for the error bound :

1. Computable upper bound of the error
2. Guaranteed / valid under checkable assumptions
3. Efficient (close to the error)
4. Cheap to compute
5. Allow adaptivity

The perfect error bound



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Outline

Abstract formulation

Problem : Solve $R(x) = 0$, solution x_*.
Example : $x = (\Phi, \lambda)$, $R(x) = (-\Delta + V)\Phi - \lambda\Phi$.

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Taylor expansion close to a solution x_* :

$$R(x) \simeq DR(x)(x - x_*).$$

Hence,

$$x - x_* \simeq [DR(x)]^{-1} R(x).$$

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Quantity of interest : A

$$A(x) - A(x_*) \simeq [DA(x)][DR(x)]^{-1} R(x).$$

To estimate the error, one needs to estimate $[DA(x)][DR(x)]^{-1} R(x)$.

Possible bound : $\|[DA(x)]\| \|[DR(x)]^{-1}\| \|R(x)\|$.

Guaranteed bounds

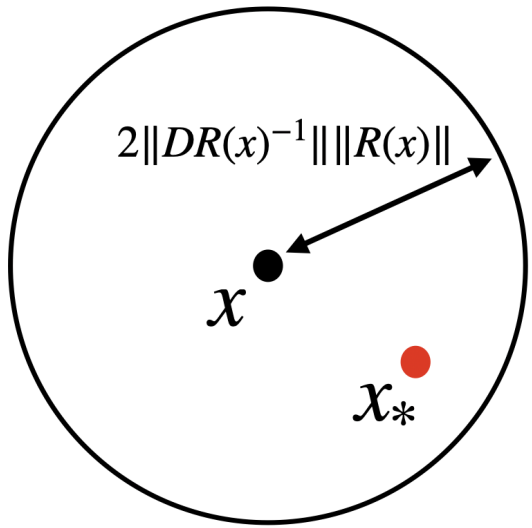
Solve $R(x) = 0$ with $R : Y \to Z$.

Inverse function theorem - Newton–Kantorovitch [1]

Two conditions to be satisfied :

- $DR(x) \in \mathcal{L}(Y; Z)$ is an isomorphism
- $2\|DR(x)^{-1}\|_{Z,Y'} L(2\|DR(x)^{-1}\|_{Z,Y'}\|R(x)\|_{Z'}) \leq 1$

  with $\quad L(\alpha) = \sup_{y \in \bar{B}(x,\alpha)} \|DR(x) - DR(y)\|_{Y,Z'}.$



Then the problem $R(x) = 0$ has a unique solution x_* in the ball $\bar{B}(x, 2\|DR(x)^{-1}\|_{Z,Y'}\|R(x)\|_{Z'})$.

Moreover, $\boxed{\|x - x_*\|_Y \leq 2\|DR(x)^{-1}\|_{Z,Y'}\|R(x)\|_{Z'}.}$

- Possible to obtain guaranteed bounds
- Requires control over first and second order derivatives
- Result on existence of solution

1. Caloz, Rappaz : Numerical analysis for nonlinear and bifurcation problems. Handb. Numer. Anal. 5, 487-637 (1997).

Main difficulties for applications to DFT

- Structure of the problem not too easy to write in this form - constraints and degeneracies
- Computation of the inverse of the Jacobian very costly
- Choice of the norm in

$$\|x - x_*\|_Y \leq 2\|DR(x)^{-1}\|_{Z,Y'}\|R(x)\|_{Z'}.$$

- Inequalities may be suboptimal

$$A(x) - A(x_*) \leq \|[DA(x)]\|\|[DR(x)]^{-1}\|\|R(x)\|$$

In the following, discretization error considered :

- Practical error bounds for DFT problems [2]

2. Cances, D., Kemlin, Levitt : Practical error bounds for properties in plane-wave electronic structure calculations, http ://arxiv.org/abs/2111.01470, (2021)

Outline

Formulation of the DFT ground state problem

Ground state minimization problem :

$$\min\{E(P),\ P \in \mathcal{M}\} \quad \text{where} \quad \mathcal{M} := \left\{ P \in \mathcal{H} \;\middle|\; P^2 = P,\ \mathrm{Tr}(P) = N_{\mathrm{el}} \right\},$$

$$\boxed{E(P) := \mathrm{Tr}(H_0 P) + E_{\mathrm{nl}}(P).}$$

- Unknown : P orthogonal projector of rank N_{el} (number of electrons)

$$P = \sum_{n=1}^{N_{\mathrm{el}}} |\phi_n\rangle \langle\phi_n|$$

- H_0 : linear part of the Hamiltonian
  1. Laplace operator
  2. Local potential
  3. Nonlocal potential
- $E_{\mathrm{nl}}(P)$: nonlinear part of the energy
  1. Hartree
  2. Exchange-correlation
- Hamiltonian of the Kohn–Sham equations :

$$H(P) := \nabla E(P) = H_0 + \nabla E_{\mathrm{nl}}(P)$$

Discretization with planewaves

Discretization parameter E_{cut}.

Discrete problem : $\min\{E(P),\ P \in \mathcal{M},\ \mathrm{Ran}\,(P) \subset \mathcal{X}_{E_{\text{cut}}}\}.$

$$\mathcal{X}_{E_{\text{cut}}} := \mathrm{Span}\left\{ e_G,\ G \in \mathcal{R}^* \;\middle|\; \frac{1}{2}|G|^2 \leqslant E_{\text{cut}} \right\},$$

- G : vector of the reciprocal lattice $\mathcal{R}^*$
- e_G : Fourier mode with wave-vector G :

$$\forall\, x \in \mathbb{R}^3, \quad e_G(x) := \frac{1}{\sqrt{|\Gamma|}} \exp\left(\mathrm{i} G \cdot x\right)$$

- $|\Gamma|$: Lebesgue measure of the unit cell Γ

Reference problem : $\min\{E(P),\ P \in \mathcal{M},\ \mathrm{Ran}\,(P) \subset \mathcal{X}_{E_{\text{cut,ref}}}\}.$

Denote dim $\mathcal{X}_{E_{\text{cut,ref}}}$ by $\mathcal{N}$,

Manifold $\mathcal{M} := \left\{ P \in \mathbb{C}^{\mathcal{N}\times\mathcal{N}} \;\middle|\; P = P^*, \quad P^2 = P, \quad \mathrm{Tr}\ P = N_{\text{el}} \right\}$

First-order optimality conditions :

Gradient of energy orthogonal to the tangent space of $\mathcal{M}$.

$$\mathcal{T}_P\mathcal{M} = \left\{ X \in \mathbb{C}^{\mathcal{N}\times\mathcal{N}} \;\middle|\; PXP = 0, P^\perp X P^\perp = 0 \right\},$$

If $P = \begin{pmatrix} I_{N_{\mathrm{el}}} & 0 \\ 0 & 0 \end{pmatrix}$ then

$$\mathcal{T}_P\mathcal{M} = \left\{ X = \begin{pmatrix} 0 & Y^* \\ Y & 0 \end{pmatrix},\ Y \in \mathbb{C}^{(\mathcal{N}-N_{\mathrm{el}})\times N_{\mathrm{el}}} \right\}.$$

Residual : $R(P) = \mathbf{\Pi}_P H(P) = PH(P)P^\perp + P^\perp H(P)P.$

Optimality conditions :

$$R(P_*) = 0, \quad \text{i.e.} \quad P_* H(P_*) P_*^\perp = 0, \quad P_*^\perp H(P_*) P_* = 0.$$

Corresponding eigenvalue problem (in terms of orbitals) :

$$H(P_*)\phi_{*n} = \lambda_{*n}\phi_{*n}, \quad \langle \phi_{*m}, \phi_{*n} \rangle = \delta_{mn}, \quad P_* = \sum_{n=1}^{N_{\mathrm{el}}} |\phi_{*n}\rangle \langle \phi_{*n}| .$$

Analysis with **orthogonal projectors** / Practice with **orbitals**.

Orthogonal projectors vs orbitals

- Uniqueness of projector solution (upon gap assumption) $P \in \mathbb{C}^{\mathcal{N}\times\mathcal{N}}$.
- Orbitals defined up to unitary transform
- Low storage cost of orbitals : $\Phi = (\phi_1| \cdots |\phi_{N_{\mathrm{el}}}) \in \mathbb{C}^{\mathcal{N}\times N_{\mathrm{el}}}$.
- Well-established correspondence between those objects

$$P = \Phi\Phi^* = \sum_{i=1}^{N_{\mathrm{el}}} |\phi_i\rangle \langle\phi_i|$$

Corresponding optimization problem :

$$\min \left\{ E(\Phi\Phi^*), \Phi \in \mathbb{C}^{\mathcal{N}\times N_{\mathrm{el}}}, \Phi^*\Phi = I_{N_{\mathrm{el}}} \right\}.$$

Tangent space :

$$X \in \mathcal{T}_{\Phi\Phi^*}\mathcal{M} : \; X = \sum_{i=1}^{N_{\mathrm{el}}} |\phi_i\rangle \langle\xi_i| + |\xi_i\rangle \langle\phi_i| = \Phi\Xi^* + \Xi\Phi^*$$

where $\Xi = (\xi_1| \cdots |\xi_{N_{\mathrm{el}}}) \in \mathbb{C}^{\mathcal{N}\times N_{\mathrm{el}}}$ is s.t. $\Phi^*\Xi = 0$.

$$\boxed{\Xi \simeq_\Phi X.}$$

Residual representation : $R(\Phi\Phi^*) \simeq_\Phi H\Phi - \Phi(\Phi^* H\Phi)$.

Second-order geometry

We need first order expansion of the residual, i.e. second-order of the energy

2^{nd}-order expansion (Cances, Kemlin, Levitt : SIAM J. Matrix Anal. Appl. 2021) :
For $P = P_* + X + O\left(\|X\|_{\mathrm{F}}^2\right) \in \mathcal{M}$ with $X \in \mathcal{T}_{P_*}\mathcal{M}$,

$$\boxed{E(P) = E(P_*) + \langle X, \boldsymbol{L}_* X\rangle_{\mathrm{F}} + o\left(\|X\|_{\mathrm{F}}^2\right).}$$

"Super-operator" : $\quad \boldsymbol{L}_* = \boldsymbol{\Omega}_* + \boldsymbol{K}_* \in L(\mathbb{C}^{\mathcal{N}\times\mathcal{N}}), \quad \boldsymbol{L}_* \geqslant 0 \quad$ on $\mathcal{T}_{P_*}\mathcal{M}$.

- Assumption : $\boldsymbol{L}_* \geq \eta > 0$.
- Linear part $\quad \forall\, X \in \mathcal{H}, \quad \boldsymbol{\Omega}_* X = -[P_*, [H(P_*), X]]$

$$\boldsymbol{\Omega}_* = \sum_{i=1}^{N_{\mathrm{el}}} \sum_{a=N_{\mathrm{el}}+1}^{\mathcal{N}} (\lambda_a - \lambda_i)\left(|\phi_{*i} \otimes \phi_{*a}\rangle\langle\phi_{*i} \otimes \phi_{*a}| + |\phi_{*a} \otimes \phi_{*i}\rangle\langle\phi_{*a} \otimes \phi_{*i}|\right),$$

- Nonlinear part $\quad \boldsymbol{K}_* := \boldsymbol{\Pi}_{P_*} \boldsymbol{\nabla}^2 E(P_*) \boldsymbol{\Pi}_{P_*} = \boldsymbol{\Pi}_{P_*} \boldsymbol{\nabla}^2 E_{\mathrm{nl}}(P_*) \boldsymbol{\Pi}_{P_*}.$

Extension of the definition of $\boldsymbol{L}_*$ to $\boldsymbol{L}(P)$ for P near P_*.

Linearization in the asymptotic regime

Residual expansion : $R(P) = \boldsymbol{L}(P)\boldsymbol{\Pi}_P(P - P_*) + O\left(\|P - P_*\|_{\mathrm{F}}^2\right).$

In the asymptotic regime : $P - P_* = \boldsymbol{\Pi}_P(P - P_*) + O\left(\|P - P_*\|_{\mathrm{F}}^2\right).$
First error bound :

$$P - P_* = (\boldsymbol{L}(P))|_{\mathcal{T}_P\mathcal{M}})^{-1}R(P) + O\left(\|P - P_*\|_{\mathrm{F}}^2\right).$$

- Check the approximation numerically : Solve

$$P_{\mathrm{Newton}} = \mathfrak{R}\left(P - (\boldsymbol{L}(P))|_{\mathcal{T}_P\mathcal{M}})^{-1}R(P)\right),$$

  with $\mathfrak{R}$ a suitable retraction on $\mathcal{M}$.

Corresponds to one Newton step to solve the equation $R(P_*) = 0$.

Linearization : Numerical results

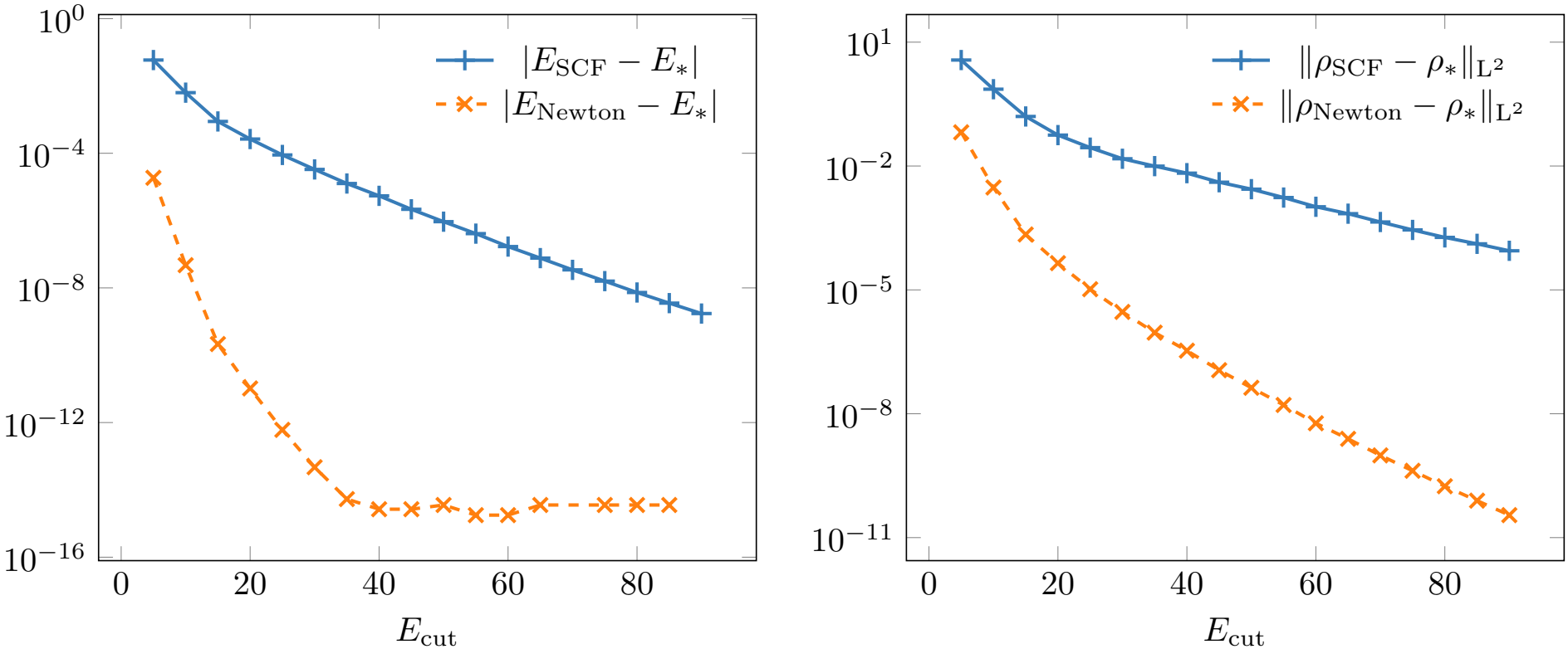


FIGURE – Silicon, low energy cutoff : $E_{\text{cut}} = 5$ Ha.

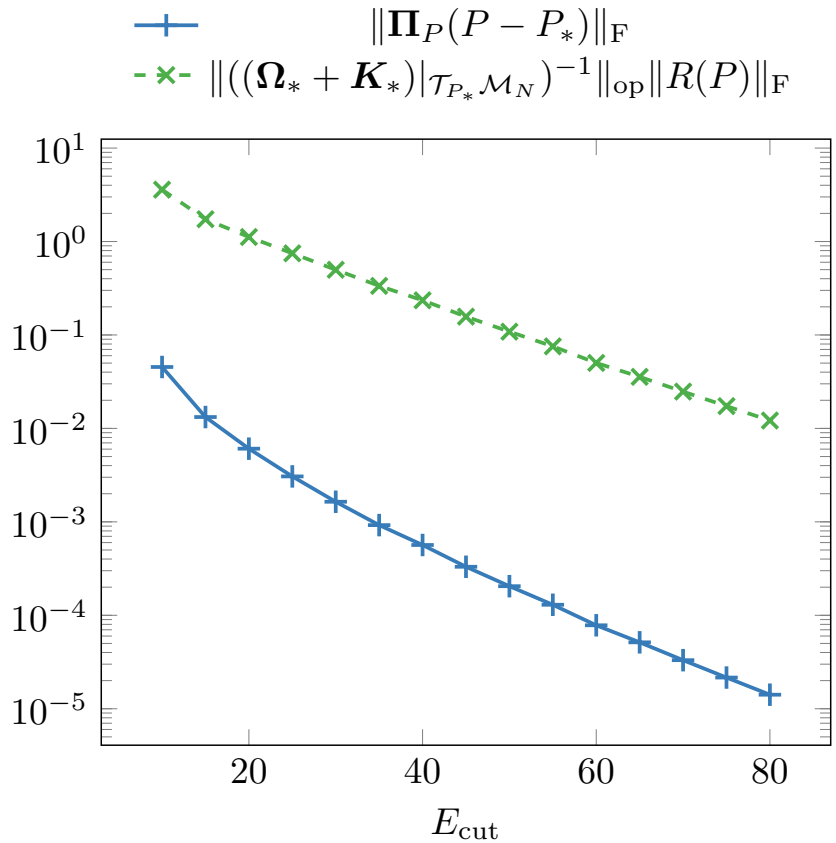
Numerical setup :

- DFTK, Julia code for planewave DFT [Herbst, Levitt]
- LDA approximation, Teter 93 exchange-correlation functional
- a reference solution computed with $E_{\text{cut,ref}} = 125$ Ha
- $2 \times 2 \times 2$ k-point grid
- periodic lattice for the FCC phase of silicon, $a = 10.26$ Bohrs

Error bound based on operator norms

$$\begin{aligned}\|P - P_*\| &\approx \|(\boldsymbol{L}_*|_{\mathcal{T}_{P_*}\mathcal{M}})^{-1} R(P)\| \\ &\leqslant \|(\boldsymbol{L}_*|_{\mathcal{T}_{P_*}\mathcal{M}})^{-1}\|_{\mathrm{op}} \|R(P)\| \quad (+ \text{ h.o.t.}),\end{aligned}$$

where $\|\cdot\|_{\mathrm{op}}$ is the (super-)operator norm associated with the chosen norm $\|\cdot\|$ on $\mathcal{H}$.

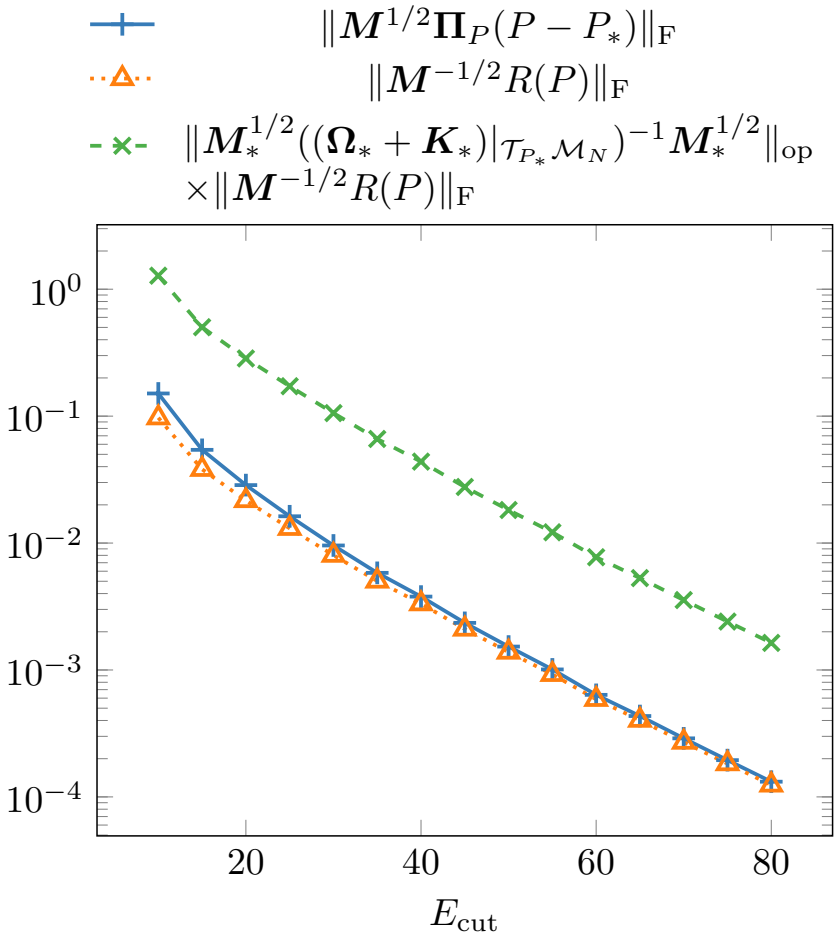


Huge overestimation of the error.

Choosing an adequate norm

Choice of a metric : $\boldsymbol{M} \simeq (1 - \Delta)$

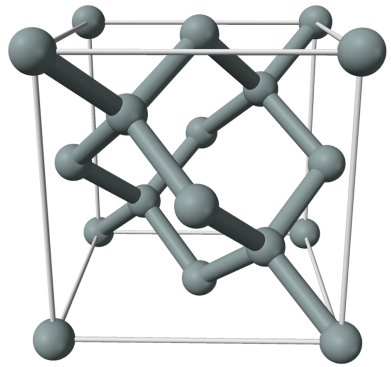
$$\left\| \boldsymbol{M}^{1/2} \boldsymbol{\Pi}_P (P - P_*) \right\|_{\mathrm{F}} \leqslant \| \boldsymbol{M}^{1/2} (\boldsymbol{L}_* |_{\mathcal{T}_{P_*} \mathcal{M}})^{-1} \boldsymbol{M}^{1/2} \|_{\mathrm{op}} \left\| \boldsymbol{M}^{-1/2} R(P) \right\|_{\mathrm{F}} .$$



Error overestimation but asymptotics correct.

A first quantity of interest : the forces

Hamiltonian depends on the atomic positions : $(X_j)_{1 \leqslant j \leqslant N_{\mathrm{at}}}$.



Force acting on atom j :

$$F_j = -\mathrm{Tr}\left((\nabla_{X_j}(V_{\mathrm{loc}} + V_{\mathrm{nloc}}))P_* \right).$$

A first (but important) quantity of interest.

Estimation on the forces

Observable $A : \mathcal{M} \to \mathcal{G}$:

$$A(P) - A(P_*) = \mathrm{d}A(P) \cdot (\mathbf{\Pi}_P(P - P_*)) + \mathrm{h.o.t.},$$

hence the bound

$$\|A(P) - A(P_*)\|_{\mathcal{G}} \leqslant \|\mathrm{d}A(P)\|_{\mathcal{T}_P\mathcal{M}\to\mathcal{G}} \|\mathbf{\Pi}_P(P - P_*)\|_{\mathcal{T}_P\mathcal{M}} \quad (+ \text{ h.o.t.}).$$

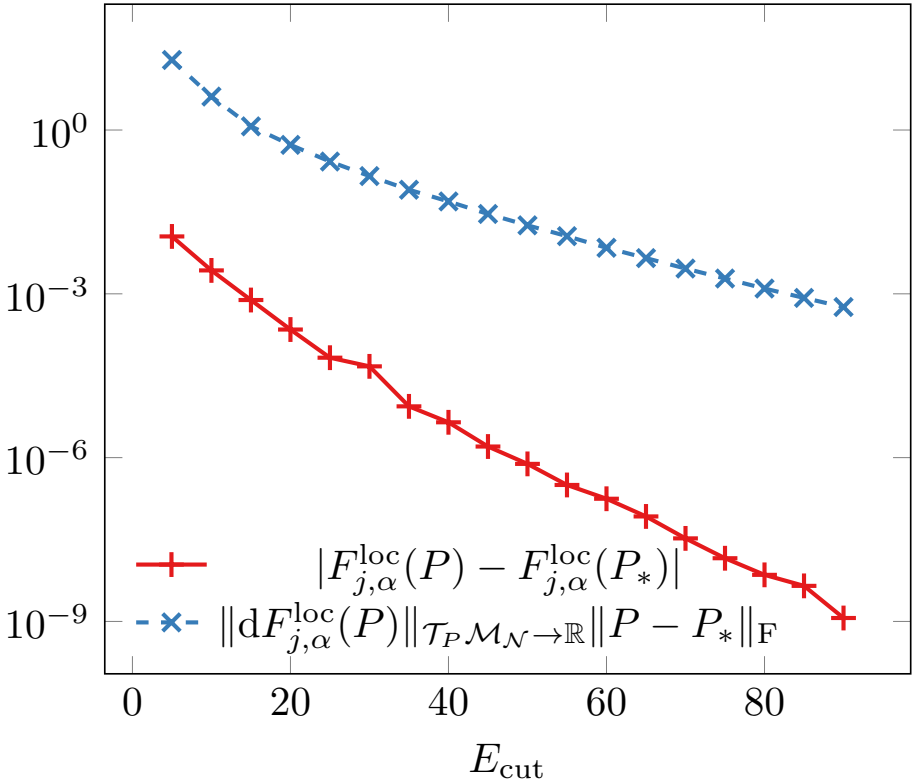
Force on atom j along the direction α due to the local part of the pseudopotential :

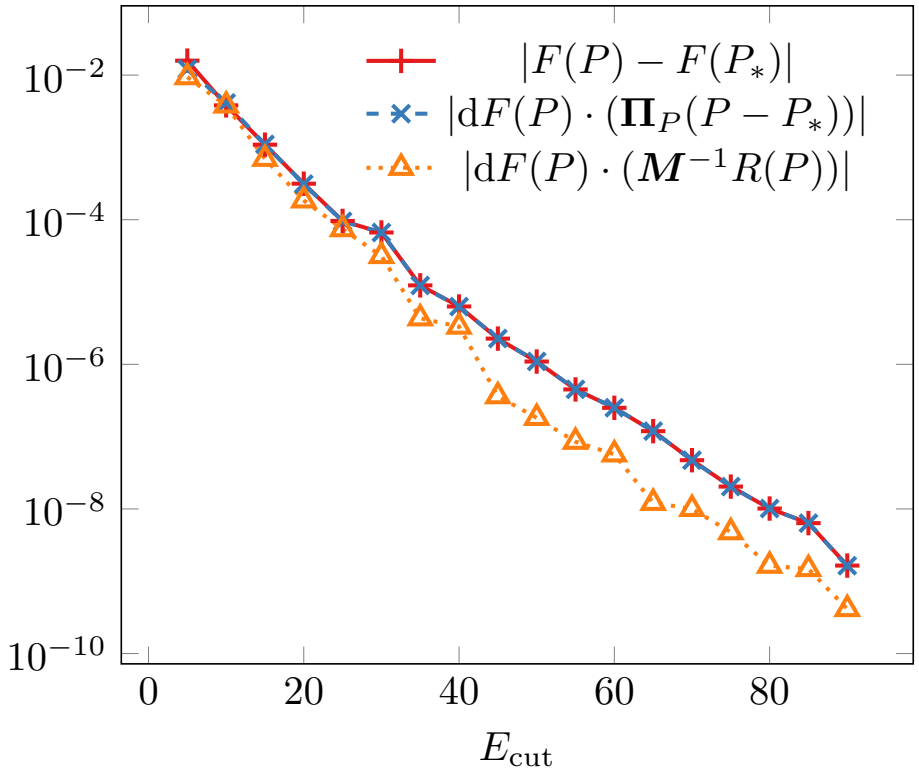
$$F^{\mathrm{loc}}_{j,\alpha}(P) = -\mathrm{Tr}\left(\frac{\partial V_{\mathrm{loc}}}{\partial X_{j,\alpha}} P\right).$$

Thus

$$|F^{\mathrm{loc}}_{j,\alpha}(P) - F^{\mathrm{loc}}_{j,\alpha}(P_*)| \leqslant \left\|\mathbf{\Pi}_P \frac{\partial V_{\mathrm{loc}}}{\partial X_{j,\alpha}}\right\|_{\mathrm{F}} \|\mathbf{\Pi}_P(P - P_*)\|_{\mathrm{F}} \quad (+ \text{ h.o.t.}).$$

Results : Force estimation for Silicon





Estimation does not match asymptotically.

Asymptotically : $P - P_* \approx (-\Delta + 1)^{-1} R(P),$

but $\mathrm{d}F(P)\cdot\mathbf{\Pi}_P(P - P_*) \neq \mathrm{d}F(P)\cdot((-\Delta + 1)^{-1} R(P)).$

Justification : gradients $\nabla F_{j,\alpha}(P)$ are mostly supported on low frequencies.

Next idea : Frequency splitting and postprocessing.

Frequency splitting

Idea : split the space $\boxed{\mathcal{X}_{E_{\text{cut,ref}}} = \mathcal{X}_{E_{\text{cut}}} \oplus \mathcal{X}_{E_{\text{cut}}}^{\perp},}$ with

- $\mathcal{X}_{E_{\text{cut}}} = \text{Span}\left(e_G,\ \frac{|G|^2}{2} \leqslant E_{\text{cut}}\right)$
- $\mathcal{X}_{E_{\text{cut}}}^{\perp} = \text{Span}\left(e_G,\ E_{\text{cut}} < \frac{|G|^2}{2} \leqslant E_{\text{cut,ref}}\right)$

Decomposition of the tangent space $\mathcal{T}_P\mathcal{M} = \mathbf{\Pi}_{E_{\text{cut}}}\mathcal{T}_P\mathcal{M} \oplus \mathbf{\Pi}_{E_{\text{cut}}}^{\perp}\mathcal{T}_P\mathcal{M}$

$$\mathbf{\Pi}_{E_{\text{cut}}}\left(\sum_{i=1}^{N_{\text{el}}} |\phi_i\rangle\langle\xi_i| + |\xi_i\rangle\langle\phi_i|\right) := \sum_{i=1}^{N_{\text{el}}} |\phi_i\rangle\langle\Pi_{\mathcal{X}}\xi_i| + |\Pi_{\mathcal{X}}\xi_i\rangle\langle\phi_i|,$$

$$\mathbf{\Pi}_{E_{\text{cut}}}^{\perp}\left(\sum_{i=1}^{N_{\text{el}}} |\phi_i\rangle\langle\xi_i| + |\xi_i\rangle\langle\phi_i|\right) := \sum_{i=1}^{N_{\text{el}}} |\phi_i\rangle\left\langle\Pi_{\mathcal{X}}^{\perp}\xi_i\right| + \left|\Pi_{\mathcal{X}}^{\perp}\xi_i\right\rangle\langle\phi_i|,$$

Amounts to decompose the ξ_i as

$$\xi_i = \Pi_{\mathcal{X}}\xi_i + \Pi_{\mathcal{X}}^{\perp}\xi_i.$$

Improved error bound

$$P - P_* \approx (\boldsymbol{L}(P)|_{\mathcal{T}_P\mathcal{M}})^{-1} R(P)$$

Postprocessing : splitting between $\boldsymbol{\Pi}_{E_{\mathrm{cut}}}\mathcal{T}_P\mathcal{M}$ and $\boldsymbol{\Pi}^{\perp}_{E_{\mathrm{cut}}}\mathcal{T}_P\mathcal{M}$

$$\begin{bmatrix} \boldsymbol{L}_{11} & \boldsymbol{L}_{12} \\ \boldsymbol{L}_{21} & \boldsymbol{L}_{22} \end{bmatrix} \begin{bmatrix} P_1 - P_{*1} \\ P_2 - P_{*2} \end{bmatrix} = \begin{bmatrix} R_1 \\ R_2 \end{bmatrix}.$$

Improved error bound

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Postprocessing : splitting between $\boldsymbol{\Pi}_{E_{\mathrm{cut}}} \mathcal{T}_P\mathcal{M}$ and $\boldsymbol{\Pi}^{\perp}_{E_{\mathrm{cut}}} \mathcal{T}_P\mathcal{M}$

$$\begin{bmatrix} \boldsymbol{L}_{11} & \boldsymbol{L}_{12} \\ 0 & (-\Delta + 1)_{22} \end{bmatrix} \begin{bmatrix} P_1 - P_{*1} \\ P_2 - P_{*2} \end{bmatrix} = \begin{bmatrix} R_1 \\ R_2 \end{bmatrix}.$$

Hence

$$P_2 - P_{*2} \approx (-\Delta + 1)_{22}^{-1} R_2, \tag{1}$$

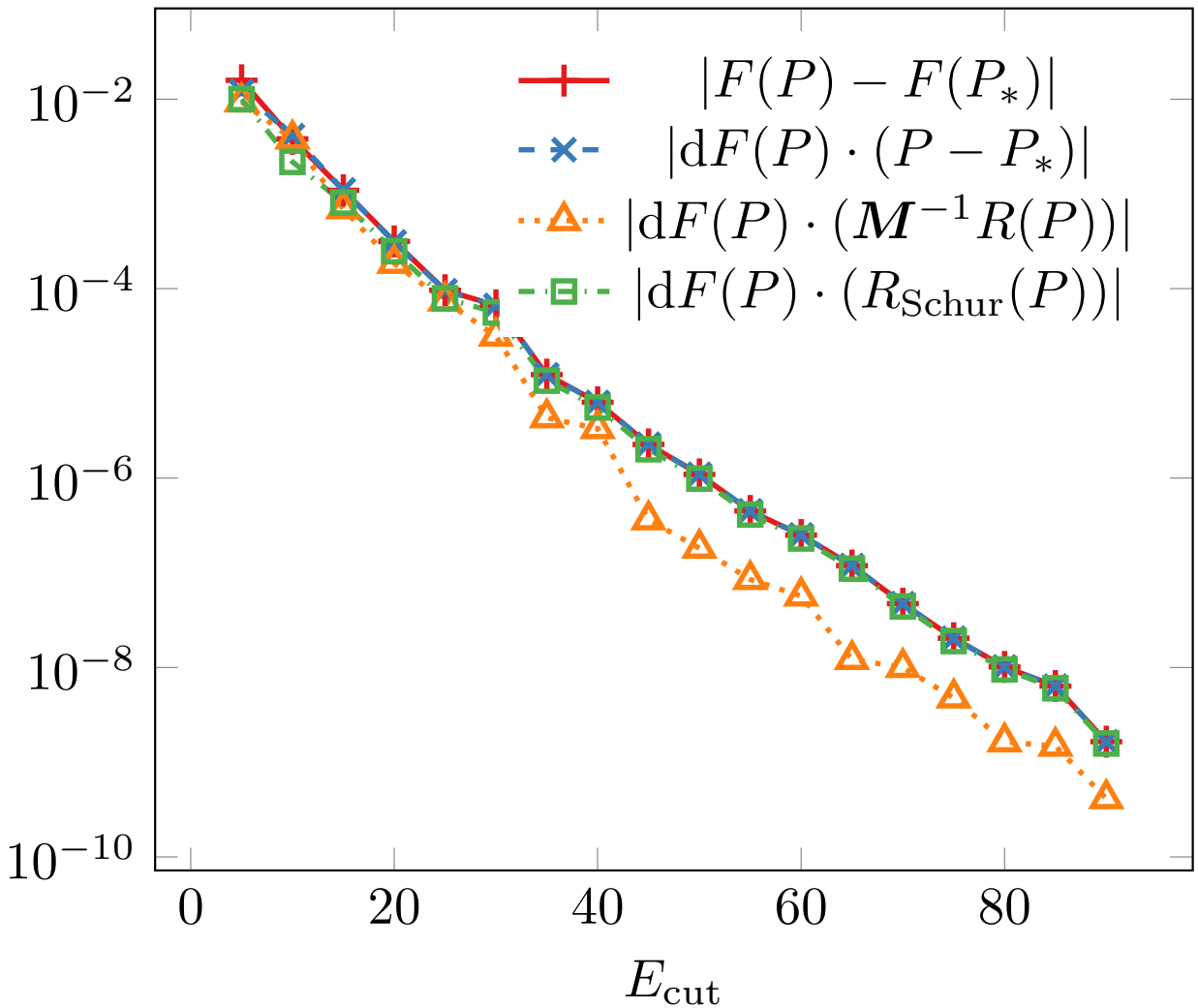
$$P_1 - P_{*1} \approx \boldsymbol{L}_{11}^{-1}(R_1 - \boldsymbol{L}_{12}(-\Delta + 1)_{22}^{-1} R_2). \tag{2}$$

Single inexpensive computation on the fine grid.

New residual :

$$R_{\mathrm{Schur}}(P) = \begin{bmatrix} \boldsymbol{L}_{11}^{-1}(R_1 - \boldsymbol{L}_{12}(-\Delta + 1)_{22}^{-1} R_2) \\ (-\Delta + 1)_{22}^{-1} R_2 \end{bmatrix}.$$

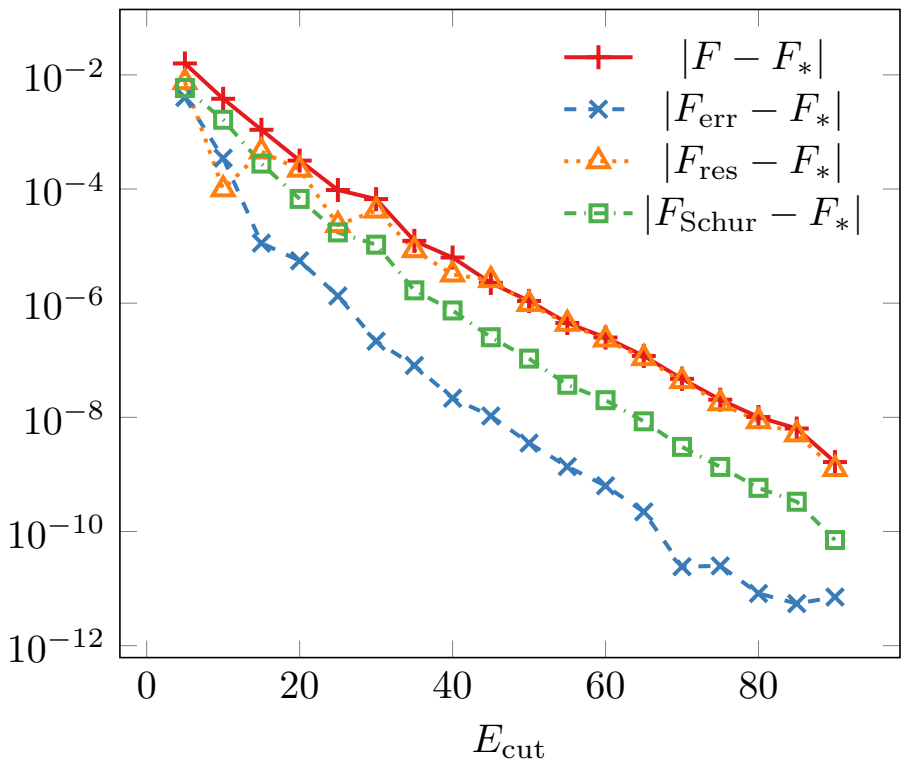
New estimation on the forces



New bound seems satisfactory.

New estimation on the forces

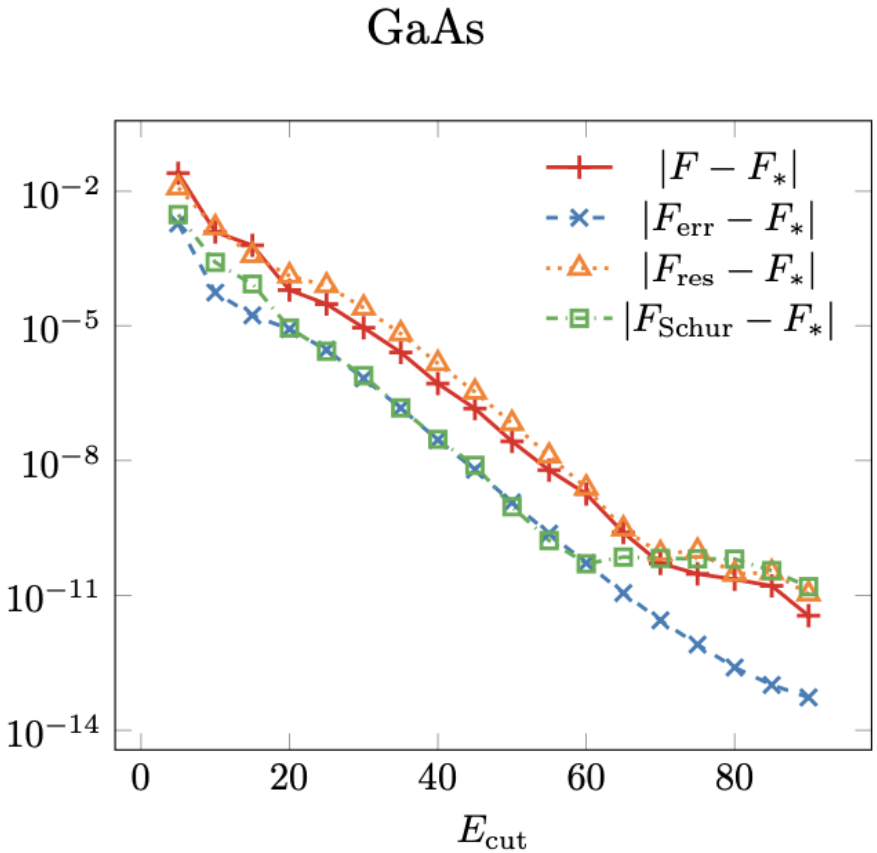
$$F_{\text{err}} - F_* := F(P) - \mathrm{d}F(P) \cdot (\mathbf{\Pi}_P(P - P_*)) - F(P_*),$$
$$F_{\text{res}} - F_* := F(P) - \mathrm{d}F(P) \cdot ((-\Delta + 1)^{-1} R(P)) - F(P_*),$$
$$F_{\text{Schur}} - F_* := F(P) - \mathrm{d}F(P) \cdot (R_{\text{Schur}}(P)) - F(P_*),$$

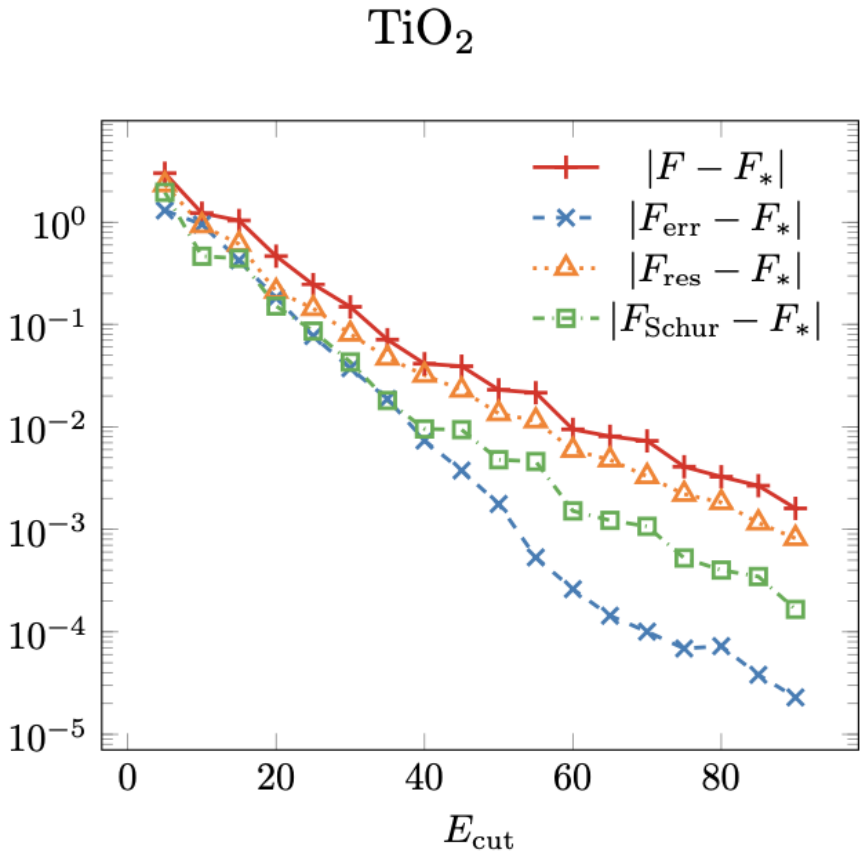


Bound on the force can be used as error bound or improved force.

A few remarks

- Similar results for TiO2 and GaAs





- Bounds not guaranteed but work could be done in this direction
- Forces as simple observable but extension possible

Conclusion

- Error bounds for quantities of interest
- Balance to find between computational cost and accuracy of error bound
- Compromise between postprocessing vs guaranteed bounds

Other perspectives :

- Couple such analysis with SCF error
- Look at metals

Thank you !