Post-processing techniques in electronic structure calculations with DFTK.jl

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General framework

We seek the ground-state energy and density by solving a constrained minimization problem:

$$E(P) := \underbrace{\mathrm{Tr}\,(H_0 P)}_{\text{linear term}} + \underbrace{E_{\mathrm{nl}}(P)}_{\text{nonlinear term}}$$

- $P \in \mathbb{C}^{N\times N}_{\mathrm{herm}}$ is a trial density matrix;
- N is the dimension of the approximation space (linked to the cut-off energy `Ecut` in `DFTK.jl`);
- $H_0 = -\frac{1}{2}\Delta + V$ is the core Hamiltonian;
- E_{nl} models the electron-electron interaction, depending on the chosen DFT model.

Kohn–Sham equations with LDA

Obtained as the Euler–Lagrange equations of (1):

$$\begin{cases} \underbrace{\left(-\frac{1}{2}\Delta + V_{\mathrm{nuc}}\right)}_{\text{linear term}} \varphi_n + \underbrace{V_{\mathrm{Hxc}}(\rho)}_{\text{nonlinear term}} \varphi_n = \varepsilon_n \varphi_n, \\ \langle \varphi_n, \varphi_m \rangle = \delta_{nm}, \\ \rho = \displaystyle\sum_{n=1}^{N_{\mathrm{el}}} |\varphi_n|^2 . \end{cases}$$

(1)

$$\min_{P \in \mathcal{M}_{N_{\mathrm{el}}}} E(P) = \mathrm{Tr}\,(H_0 P) + E_{\mathrm{nl}}(P),$$

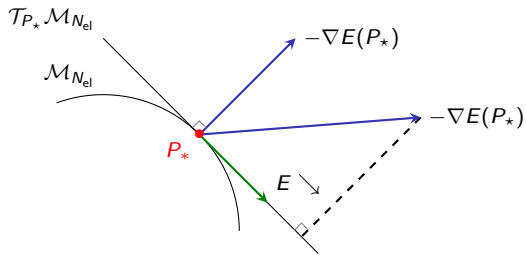
$$\mathcal{M}_{N_{\mathrm{el}}} := \left\{ P \in \mathbb{C}^{N\times N} \;\middle|\; P = P^*,\ \mathrm{Tr}(P) = N_{\mathrm{el}},\ P^2 = P \right\}.$$

Geometrical aspects – First-order condition

$$\min_{P \in \mathcal{M}_{N_{\mathrm{el}}}} E(P) = \mathrm{Tr}\,(H_0 P) + E_{\mathrm{nl}}(P)$$

The first-order optimality condition is $R(P_\star) \coloneqq \nabla_{\mathcal{M}_{N_{\mathrm{el}}}} E(P_\star) = \Pi_{P_\star}(H_\star) = 0$, which gives, with $H_\star = H(P_\star)$,

$$\boxed{P_\star H_\star (1 - P_\star) = (1 - P_\star) H_\star P_\star = 0.}$$



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- $[H_\star, P_\star] = 0 \Rightarrow H_\star$ and $P_\star$ can be codiagonalized;
- if $(\varphi_i)_{1 \le i \le N_{\mathrm{el}}}$ is an o.n.b. of eigenvectors of $H_\star$ ordered by nondecreasing eigenvalues, then $P_\star = \sum_{i \in \mathcal{I}} \varphi_i \varphi_i^*$, with $\mathcal{I}$ the set of occupied orbitals;
- $\mathcal{I} \subset \{1, \dots, N_{\mathrm{el}}\}$ and $|\mathcal{I}| = N_{\mathrm{el}}$:
  - $\mathcal{I} = \{1, \dots, N_{\mathrm{el}}\}$: *Aufbau* principle;
  - $\mathcal{I} = \{1, \dots, N_{\mathrm{el}}\}$ and $\varepsilon_{N_{\mathrm{el}}} < \varepsilon_{N_{\mathrm{el}}+1}$: strong *Aufbau* principle.

In the decomposition $\mathcal{H} = \mathrm{Ran}(P_\star) \oplus \mathrm{Ran}(1 - P_\star)$, assuming the *Aufbau principle*

$$H_\star = \begin{array}{c} \begin{matrix} \leftarrow & \mathcal{I} & \rightarrow & \overline{\mathcal{I}} \end{matrix} \\ \begin{bmatrix} \varepsilon_1 & & & \\ & \ddots & & 0 \\ & & \varepsilon_{N_{\mathrm{el}}} & \\ & 0 & & \ddots \end{bmatrix} \end{array}, \quad P_\star = \begin{array}{c} \begin{matrix} \mathcal{I} & \overline{\mathcal{I}} \end{matrix} \\ \begin{bmatrix} 1_{N_{\mathrm{el}}} & 0 \\ 0 & 0 \end{bmatrix} \end{array}$$

Geometrical aspects – Second-order condition

$$\min_{P \in \mathcal{M}_{N_{\mathrm{el}}}} E(P) = \mathrm{Tr}\,(hP) + E_{\mathrm{nl}}(P)$$

The second-order optimality condition reads (under reasonable assumptions)

$$\forall\, X \in \mathcal{T}_{P_\star}\mathcal{M}_{N_{\mathrm{el}}},\ \left\langle X, [\boldsymbol{D}^2_{\mathcal{M}_{N_{\mathrm{el}}}} E(P_\star)]X \right\rangle_{\mathsf{F}} \geq \eta\, \|X\|_{\mathsf{F}}^2\,, \quad \text{with} \quad \boldsymbol{D}^2_{\mathcal{M}_{N_{\mathrm{el}}}} E(P_\star) = (\boldsymbol{\Omega}_\star + \boldsymbol{K}_\star)$$

- $\boldsymbol{K}_\star = \Pi_{P_\star} \nabla^2 E(P_\star) \Pi_{P_\star}$ is the classical Hessian;
- the operator $\boldsymbol{\Omega}_\star : \mathcal{T}_{P_\star}\mathcal{M}_{N_{\mathrm{el}}} \to \mathcal{T}_{P_\star}\mathcal{M}_{N_{\mathrm{el}}}$ is defined by,

$$\forall\, X \in \mathcal{T}_{P_\star}\mathcal{M}_{N_{\mathrm{el}}}, \quad \boldsymbol{\Omega}_\star(X) \coloneqq -[P_\star, [\nabla E(P_\star), X]].$$

- $\boldsymbol{D}^2_{\mathcal{M}_{N_{\mathrm{el}}}} E(P_\star) = \boldsymbol{\Omega}_\star + \boldsymbol{K}_\star$ can be interpreted as the Hessian of the energy on the manifold, $\boldsymbol{\Omega}_\star$ represents the influence of the curvature. Can also be seen as the Hessian of the Lagrangian.

Structure of $\mathbf{\Omega}_\star$

Let $(\varphi_i, \varepsilon_i)_{1 \le i \le N_{\text{el}}}$ be an eigendecomposition of $H_\star$. Recall, if $\mathcal{H} = \text{Ran}(P_\star) \oplus \text{Ran}(1 - P_\star)$,

$$P_\star = \begin{bmatrix} 1_{N_{\text{el}}} & 0 \\ 0 & 0 \end{bmatrix} \quad \text{and} \quad \mathcal{T}_P \mathcal{M}_{N_{\text{el}}} \coloneqq \left\{ X = \begin{bmatrix} 0 & \times^* \\ \times & 0 \end{bmatrix} \right\}.$$

Then

- for $i \in \mathcal{I}$ and $a \notin \mathcal{I}$
$$(\mathbf{\Omega}_\star X)_{ia} = (\varepsilon_a - \varepsilon_i) X_{ia} \quad \text{and} \quad (\mathbf{\Omega}_\star X)_{ai} = (\varepsilon_a - \varepsilon_i) X_{ai};$$
- the gap $\min_{a \notin \mathcal{I}} \varepsilon_a - \max_{i \in \mathcal{I}} \varepsilon_i$ is the smallest eigenvalue of $\mathbf{\Omega}_\star$.

Remark 1: if the *Aufbau* principle is satisfied, then the gap is $\varepsilon_{N_{\text{el}}+1} - \varepsilon_{N_{\text{el}}}$.

Remark 2: $\mathbf{\Omega}_\star = -\chi_0^{-1}$, the 4pt-independent particle susceptibility operator[1].

[1] used in response calculations in `DFTK.jl`, cf. E. Cancès, Eric, M.F. Herbst, G. Kemlin, A. Levitt, and B. Stamm. *Numerical Stability and Efficiency of Response Property Calculations in Density Functional Theory*. Letters in Mathematical Physics 113(1):21 (2023).

Computational framework

We consider a hierarchy of two discretization spaces with $N \ll N_{\text{ref}}$:

$$\mathcal{V}_N \subset \mathcal{V}_{N_{\text{ref}}}$$

variational approximation space — reference space

The problem becomes:

$$\min_{P \in \mathcal{M}_{N_{\text{el}},N}} \operatorname{Tr}(hP) + E_{\text{nl}}(P), \quad \mathcal{M}_{N_{\text{el}},N} := \left\{ P \in \mathbb{C}^{N \times N} \;\middle|\; P = P^*,\ \operatorname{Tr}(P) = N_{\text{el}},\ P^2 = P \right\}.$$

- For convergence analysis and standard computations (ground-state energy and density, response calculations, ...), we work in $\mathcal{V}_N$.
- For error estimation :
  1. we find a solution $P \in \mathcal{M}_{N_{\text{el}},N} \subset \mathbb{C}^{N \times N} \subset \mathbb{C}^{N_{\text{ref}} \times N_{\text{ref}}}$ in the approximation space $\mathcal{V}_N$ (for instance with a SCF algorithm);
  2. we try to estimate the error w.r.t. $P_\star \in \mathcal{M}_{N_{\text{el}},N_{\text{ref}}} \subset \mathbb{C}^{N_{\text{ref}} \times N_{\text{ref}}}$, the solution in the reference space $\mathcal{V}_{N_{\text{ref}}}$, *for a computational cost at most equivalent as for obtaining* P.

Linearization

Recall that $\boldsymbol{\Omega}_\star + \boldsymbol{K}_\star \in \mathcal{L}(\mathcal{T}_{P_\star}\mathcal{M}_{N_{\mathrm{el}},N_{\mathrm{ref}}})$ is the Jacobian of $P \mapsto R(P) = \Pi_P \nabla E(P)$ at $P_\star$:

$$\Pi_P \nabla E(P) \approx \Pi_{P_\star} \nabla E(P_\star) + (\boldsymbol{\Omega}_\star + \boldsymbol{K}_\star)(P - P_\star) + o(\|P - P_\star\|_{\mathrm{F}}).$$

As $\Pi_{P_\star} \nabla E(P_\star) = 0$, with $R(P)$ the residual, *in the linear regime*,

$$\boxed{\Pi_P(P - P_\star) \approx (\boldsymbol{\Omega}_\star + \boldsymbol{K}_\star)^{-1} R(P)}$$

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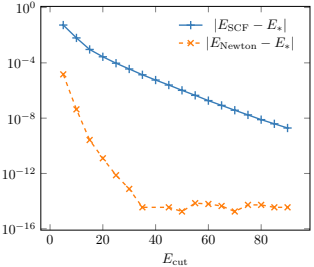
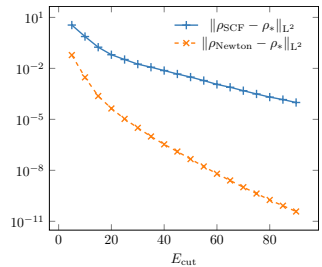
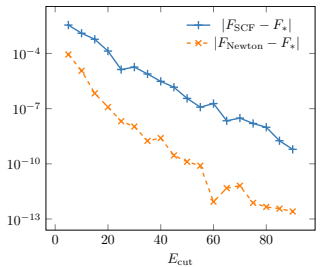
Numerical check: the linear regime is established if $P - (\boldsymbol{\Omega}_\star + \boldsymbol{K}_\star)^{-1} R(P)$ is much closer to $P_\star$.







Interatomic forces (at the discrete level)

Recall $E(P) = \mathrm{Tr}(hP) + E_{\mathrm{nl}}(P)$ with $h = -\frac{1}{2}\Delta + V$: $V = V(X)$ for $X = (X_j) \in \omega^M$ positions of atomic nuclei $\Rightarrow E(P) = E(X, P)$.

Hellmann–Feynman:

$$P_\star = \mathrm{argmin}\left\{ E(X_0, \tilde{P}) \;\middle|\; \tilde{P} \in \mathcal{M}_{N_{\mathrm{el}}, N_{\mathrm{ref}}} \right\};$$

$$F_\star = F(P_\star) = \left[-\nabla_{X_{j\alpha}} E(X_0, P_\star) \right]_{j=1,\dots,M}^{\alpha=1,2,3} = \left[-\,\mathrm{Tr}\left(\partial_{X_{j\alpha}} V(X_0) P_\star \right) \right]_{j=1,\dots,M}^{\alpha=1,2,3}.$$

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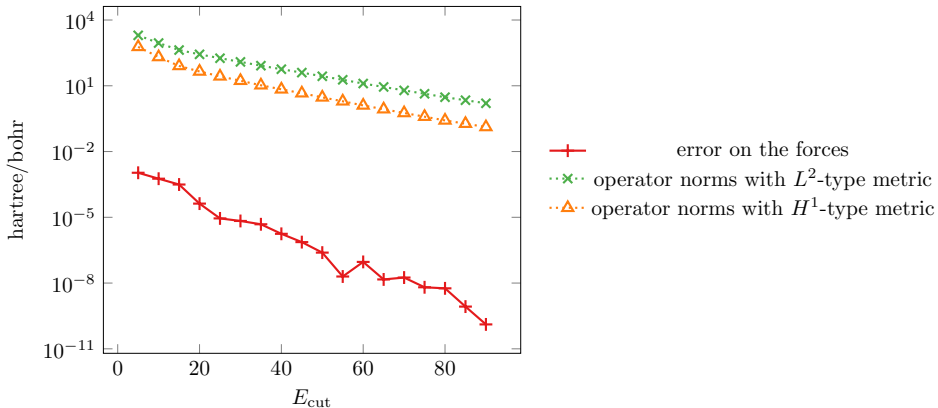
First naive error bound for the interatomic forces $F(P)$:

$$\begin{aligned} |F(P) - F_\star| &\leq \|\mathrm{d}F(P_\star)\|_{\mathrm{op}} \, \|P - P_\star\|_{\mathrm{F}} \\ &\leq \|\mathrm{d}F(P_\star)\|_{\mathrm{op}} \|(\boldsymbol{\Omega}_\star + \boldsymbol{K}_\star)^{-1}\|_{\mathrm{op}} \|R(P)\|_{\mathrm{F}}. \end{aligned}$$

Error on the forces for a silicon crystal.



In the asymptotic regime:

generalization of $\Omega_\star + K_\star$ to $P \neq P_\star$: computable but expensive

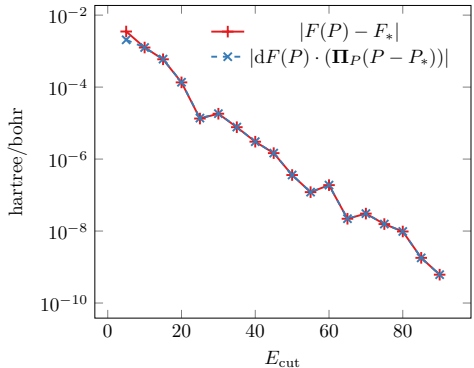
$$P - P_\star \approx (\Omega + K)^{-1} R(P) \approx M^{-1} R(P) \quad \text{in energy norm.}$$

not computable

computable and cheap

Replace the error $F(P) - F_\star$ by $\mathrm{d}F(P) \cdot (\Pi_P(P - P_\star))$.

$\rightsquigarrow$ Good, but not usable in practice ($P_\star$ is unknown).



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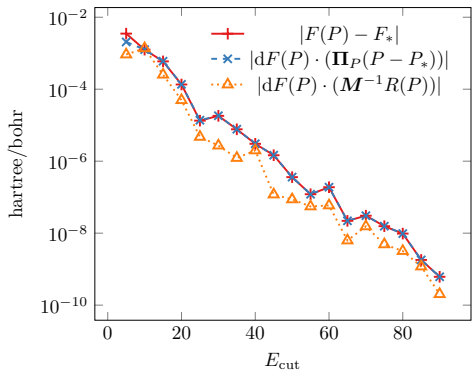
$\rightsquigarrow$ Good, but not usable in practice ($P_\star$ is unknown).

Replace $P - P_\star$ by $M^{-1} R(P)$, with $M \sim -\frac{1}{2}\Delta + 1$.

$\rightsquigarrow$ Better, but still not satisfying.



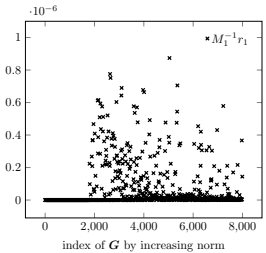
Frequency splitting

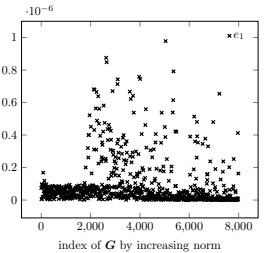
Let $P \in \mathcal{M}_{N_{\text{el}},N_{\text{ref}}}$, then $\mathcal{T}_P\mathcal{M}_{N_{\text{el}},N_{\text{ref}}}$ can be split into low and high frequencies:

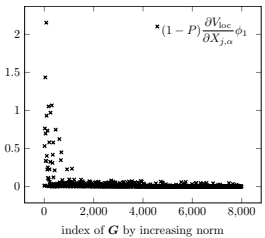
$$\mathcal{T}_P\mathcal{M}_{N_{\text{el}},N_{\text{ref}}} = \Pi_N\mathcal{T}_P\mathcal{M}_{N_{\text{el}},N_{\text{ref}}} \oplus \Pi_N^{\perp}\mathcal{T}_P\mathcal{M}_{N_{\text{el}},N_{\text{ref}}}.$$

low frequencies — high frequencies

If P is a solution of the variational problem in $\mathcal{V}_N$, then $R(P), \boldsymbol{M}^{-1}R(P) \in \Pi_N^{\perp}\mathcal{T}_P\mathcal{M}_{N_{\text{el}},N_{\text{ref}}}$.







$\rightsquigarrow$ $\mathrm{d}F(P)$ is mainly supported on low frequencies.

Enhanced error bounds

We decompose the error/residual relation onto $\Pi_N \mathcal{T}_P \mathcal{M}_{N_{\text{el}}, N_{\text{ref}}} \oplus \Pi_N^{\perp} \mathcal{T}_P \mathcal{M}_{N_{\text{el}}, N_{\text{ref}}}$ to get

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

As the kinetic energy is dominating for high-frequencies, we approximate

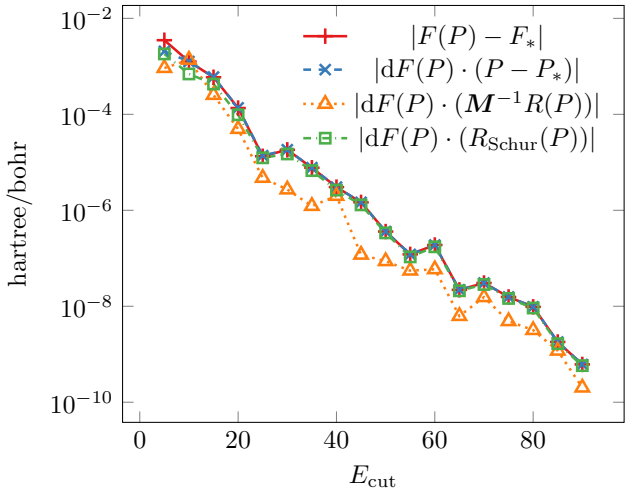
$$(\boldsymbol{\Omega} + \boldsymbol{K})_{21} \approx 0 \quad \text{and} \quad (\boldsymbol{\Omega} + \boldsymbol{K})_{22} \approx \boldsymbol{M}_{22},$$

and thus

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

This yields a new residual, which requires only an inversion on the coarse grid ($\boldsymbol{M}_{22}$ being easy to invert):

$$\boxed{R_{\text{Schur}}(P) = \begin{bmatrix} (\boldsymbol{\Omega} + \boldsymbol{K})_{11}^{-1} \left(R_1 - (\boldsymbol{\Omega} + \boldsymbol{K})_{12} \boldsymbol{M}_{22}^{-1} R_2\right) \\ \boldsymbol{M}_{22}^{-1} R_2 \end{bmatrix}}.$$


10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
hartree/bohr
0
20
40
60
80
E_{cut}
$|F(P) - F_*|$
$|\mathrm{d}F(P) \cdot (P - P_*)|$
$|\mathrm{d}F(P) \cdot (\boldsymbol{M}^{-1} R(P))|$
$|\mathrm{d}F(P) \cdot (R_{\mathrm{Schur}}(P))|$

Conclusion and take-home messages

- With planewaves, the asymptotic regime is quickly established $\Rightarrow$ linearization of KS equations is useful.
- Linearization can be used in a post-processing step:
  1. to estimate the error on QoI: $Q(P) - Q(P_\star) \approx \mathrm{d}Q(P) \cdot R_{\mathrm{Schur}}(P)$ up to higher order terms;
  2. to refine the obtained solution: $Q(P) - \mathrm{d}Q(P) \cdot R_{\mathrm{Schur}}(P)$ is a better approximation of $Q(P_\star)$.
- Implemented by default in `DFTK.jl` in a simplified framework (PR by Bruno Ploumhans). To be released in the next version.

Perspectives and ideas:

- Metallic systems (positive gap assumption does not hold anymore).
- Other quantities of interest than interatomic forces.
- Fully guaranteed bounds (on the energy, taking into account both SCF and discretization errors, cf. poster by Rafael Lainez and me).

`Pluto notebook`

Some references on post-processing techniques:

- E. Cancès, G. Dusson, Y. Maday, B. Stamm, and M. Vohralik. *Post-Processing of the Planewave Approximation of Schrödinger Equations. Part I: Linear Operators.* IMA Journal of Numerical Analysis 41(4):2423-55 (2021).
- G. Dusson. *Post-Processing of the Plane-Wave Approximation of Schrödinger Equations. Part II: Kohn–Sham Models.* IMA Journal of Numerical Analysis 41(4):2456-87 (2021).
- E. Cancès, G. Dusson, G Kemlin, and A. Levitt. *Practical Error Bounds for Properties in Plane-Wave Electronic Structure Calculations.* SIAM Journal on Scientific Computing 44(5):B1312-40 (2022).

Merci!

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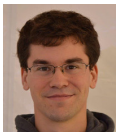

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