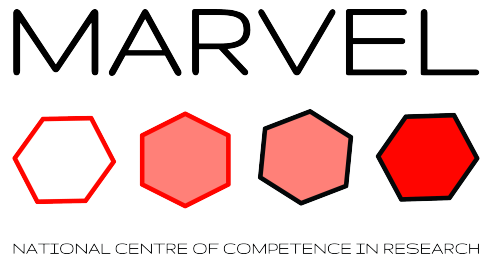
Quantification of Discretization Error in Plane-Wave Density Functional Theory

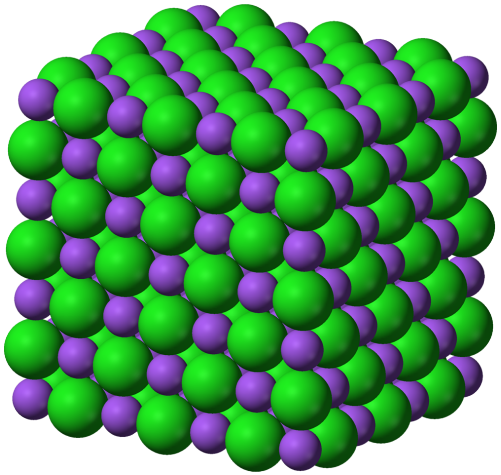
Bruno Ploumhans
MatMat group, EPFL, Switzerland
NCCR MARVEL, EPFL, Switzerland



March 18, 2026

Density functional theory (DFT)

- The most popular first-principles simulation method. Can predict the structure and properties of materials from quantum mechanics.



NaCl (Wikipedia)

$\xrightarrow{\text{DFT}}$

total energy E
energy derivatives
(e.g. forces, elasticity)
...

- Many approximations!

Plane-wave basis leads to discretization error

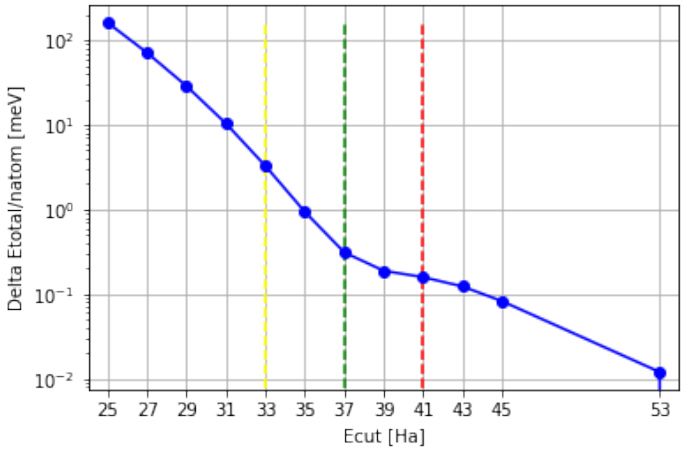
- In materials, Bloch theorem:
  - Periodic lattice, periodic potential.
  - Wavefunctions of the form $\psi_{nk}(x) = u_{nk}(x)e^{ik\cdot x}$ with $u_{nk}(x)$ **periodic**.
- Plane-wave DFT
  - Expand $u_{nk}(x)$ in a Fourier series of plane waves:

$$\psi_{nk}(x) = \sum_G c_{nk}(G)\frac{e^{i(G+k)\cdot x}}{\sqrt{\Omega}}.$$

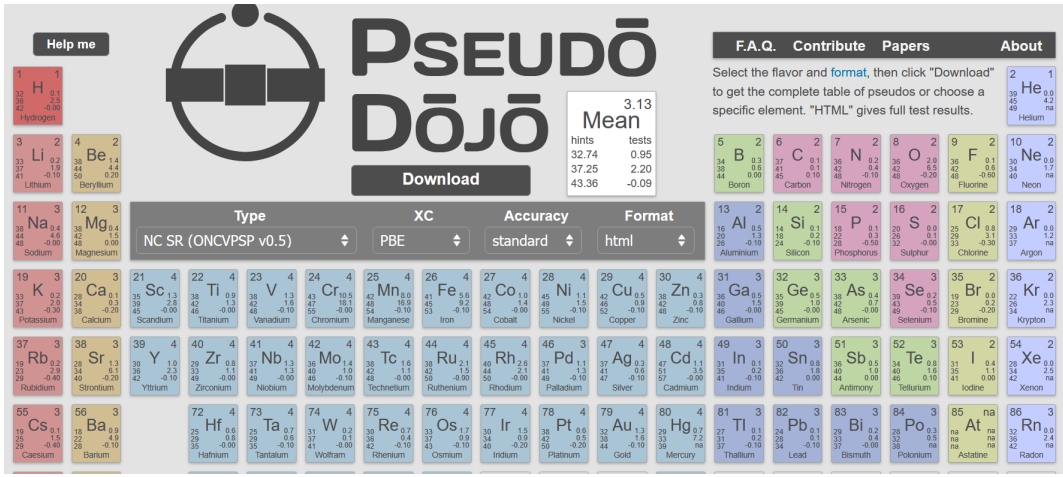
  - Truncate to G such that $\frac{\|G+k\|^2}{2} \leq E_{\text{cut}}$.
  - **Kinetic energy cutoff** E_{cut}: key numerical parameter controlling the basis size.

Common strategies to choose E_{cut}

- Ideal E_{cut} depends on: target accuracy, computed properties, system
- Very dependent on the pseudopotential used to represent the ion-electron interaction
- Common practices:



Convergence studies



Pseudopotential recommendations

Pseudopotential recommendations for E_{cut}

PseudoDojo [van Setten et al. 2018]

- One pseudopotential for most elements in the periodic table
- For each, three recommended cutoff **hints**: *low*, *normal*, *high*
- Simple example: (v0.4.1 NC SR PBE standard)
  - Si: 14, 18, 24 Ha
  - O: 36, 42, 48 Ha
  - Silicon oxide, *high* cutoff: $\max(24, 48) = 48$ Ha
- Easy to use, but be careful!

Discretization error estimates

- What we would like: estimate the discretization error
  - Cheaply
  - Adapting to: system, property of interest
- Follow the strategy from [E. Cancès, G. Dusson, G. Kemlin, A. Levitt 2022]
- Rest of the talk:
  - Part 1: Summary of error estimates
  - Part 2: New developments and benchmarks

Very very short summary of DFT

- Variable: density matrix P (rank-N_{el} orthogonal projector)
- Minimize: total energy $E(P)$
  - Typically using a self-consistent field (SCF) fixed-point method.
  - Residual of the minimization problem:

$$R(P) = [P, [P, \nabla E(P)]]$$

- Forces F: gradient of total energy wrt. atomic positions

Very very short summary of Cancès et al. 2022

- Two basis sets, of sizes controlled by two parameters E_{cut} and $E_{\mathrm{cut,ref}} \gg E_{\mathrm{cut}}$:
  - **Small** plane-wave basis, controlled by E_{cut}. **Minimizer**: P
  - **Large** plane-wave basis, controlled by $E_{\mathrm{cut,ref}}$. **Minimizer**: P_* (expensive, not computed in practice).
  - Transfer from small to large basis: pad with zero Fourier coefficients.
  - $_1$: small basis (low frequencies), $_2$: large basis only (high frequencies).
- Find a $\Delta P \approx P_* - P$:
  1. $\|\Delta P\|$ **estimates** the discretization error $\|P_* - P\|$.
  2. $\mathcal{R}(P + \Delta P)$ is **partially corrected** for the discretization error.

Error estimation strategy [Cancès et al. 2022]

1. Obtain P via an SCF in the small basis of size E_{cut}, transfer it to the large basis of size $E_{\mathrm{cut,ref}}$.
2. Compute ΔP with an **approximate Newton step**:

$$\Delta P = -\underbrace{\begin{pmatrix} (\Omega + K)_{11} & (\Omega + K)_{12} \\ 0 & M_{22} \end{pmatrix}^{-1}}_{\approx \nabla R(P)^{-1}} \cdot R(P)$$

   Equivalently:

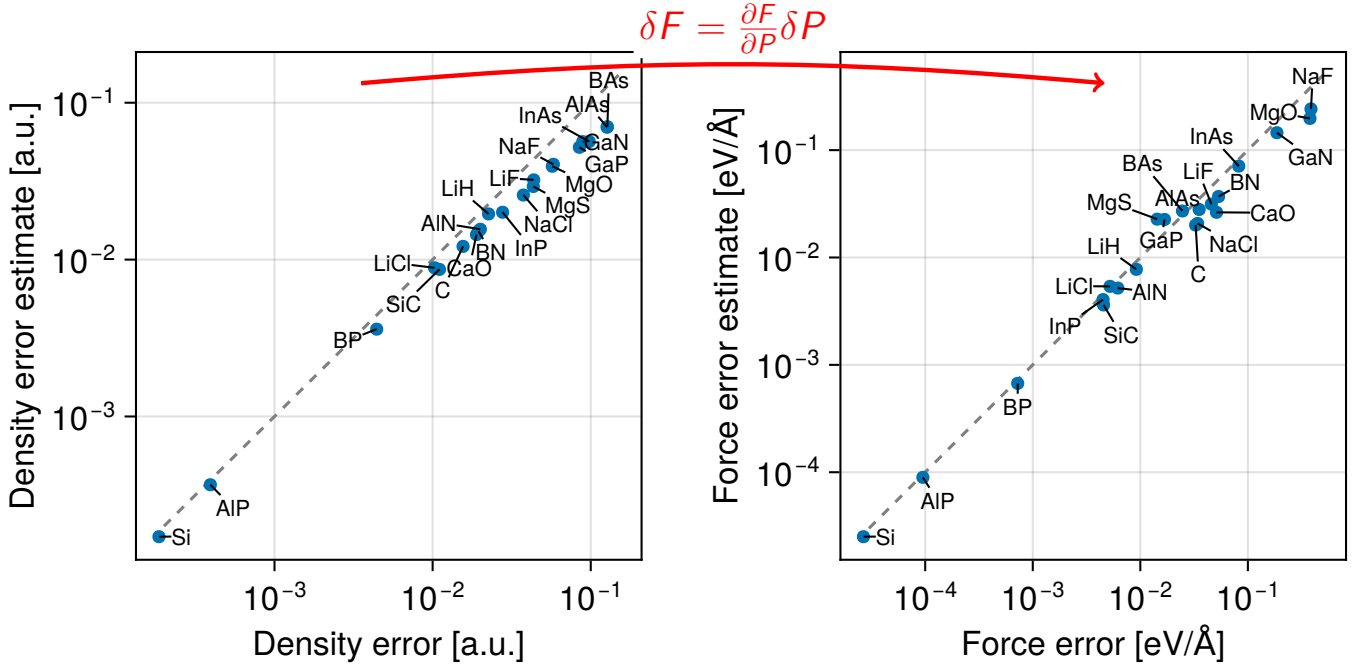
$$\Delta P_2 = -M_{22}^{-1} \cdot R_2,$$
$$\Delta P_1 = -(\Omega + K)_{11}^{-1} \cdot (R_1 - (\Omega + K)_{12} \cdot \Delta P_2).$$

   Dominant cost: $(\Omega + K)_{11}^{-1}$ with CG, happens in the **small** basis.
3. Propagate to property of interest — such as forces $F(P)$:

$$\Delta F = \frac{\partial F}{\partial P} \cdot \Delta P$$

Algorithmic differentiation (AD) to propagate error

- Error estimates applied to 21 common insulators. $E_{\text{cut}} = 20$ Ha for all systems. PseudoDojo pseudopotentials



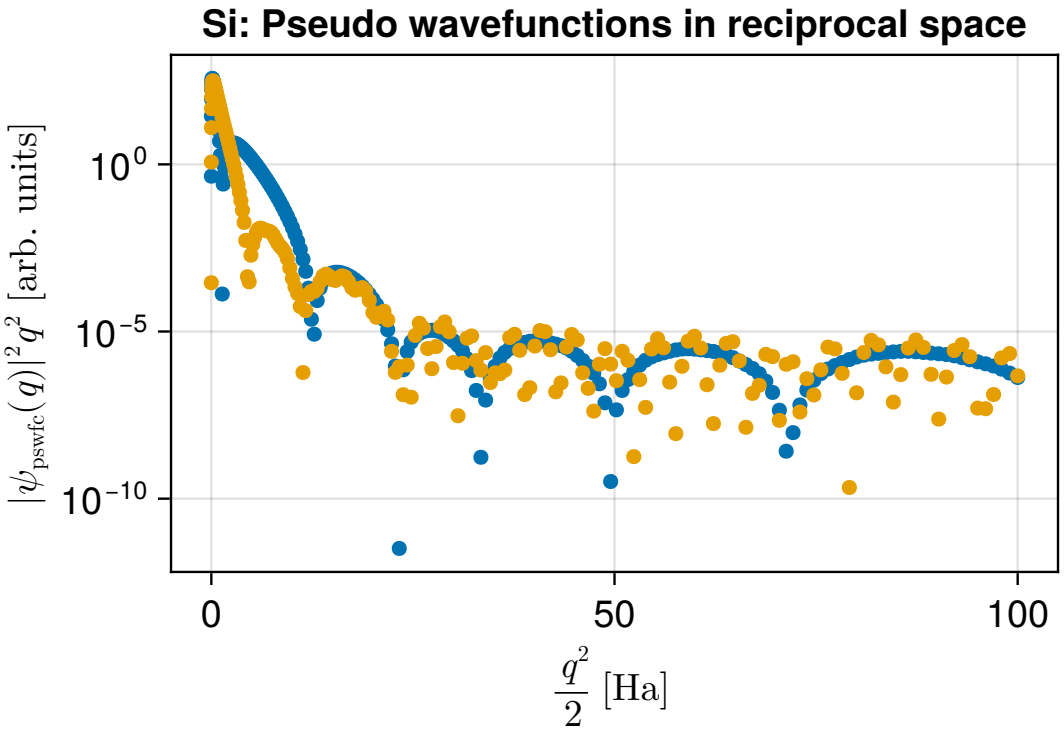
- Fig. 8 from: [Schmitz, **Ploumhans**, Herbst 2026]
- **Excellent agreement** between estimated and reference errors.

Further developments

1. Which $E_{\mathrm{cut,ref}}$ to use?
2. Error propagation to energy and forces
3. (Stopping criterion for the computation of ΔP_1)

Choosing $E_{\mathrm{cut,ref}}$: the problem

- $E_{\mathrm{cut,ref}}$ controls wrt. which reference the error is estimated.
  - Must be sufficiently large to approximate the infinite basis limit.
  - Must be sufficiently small to keep the large basis operations tractable. ($R(P)$ and $(\boldsymbol{\Omega} + \boldsymbol{K})_{12}$)
- Not so easy with numerical pseudopotentials!



Choosing $E_{\mathrm{cut,ref}}$: the strategy

- Strategy: look at the Fourier decay of ΔP_2. Wavefunction representation: $\Delta\psi_{2,n}$
  1. Build an estimate for the discretization error of ΔP_2 compared to an infinite basis:

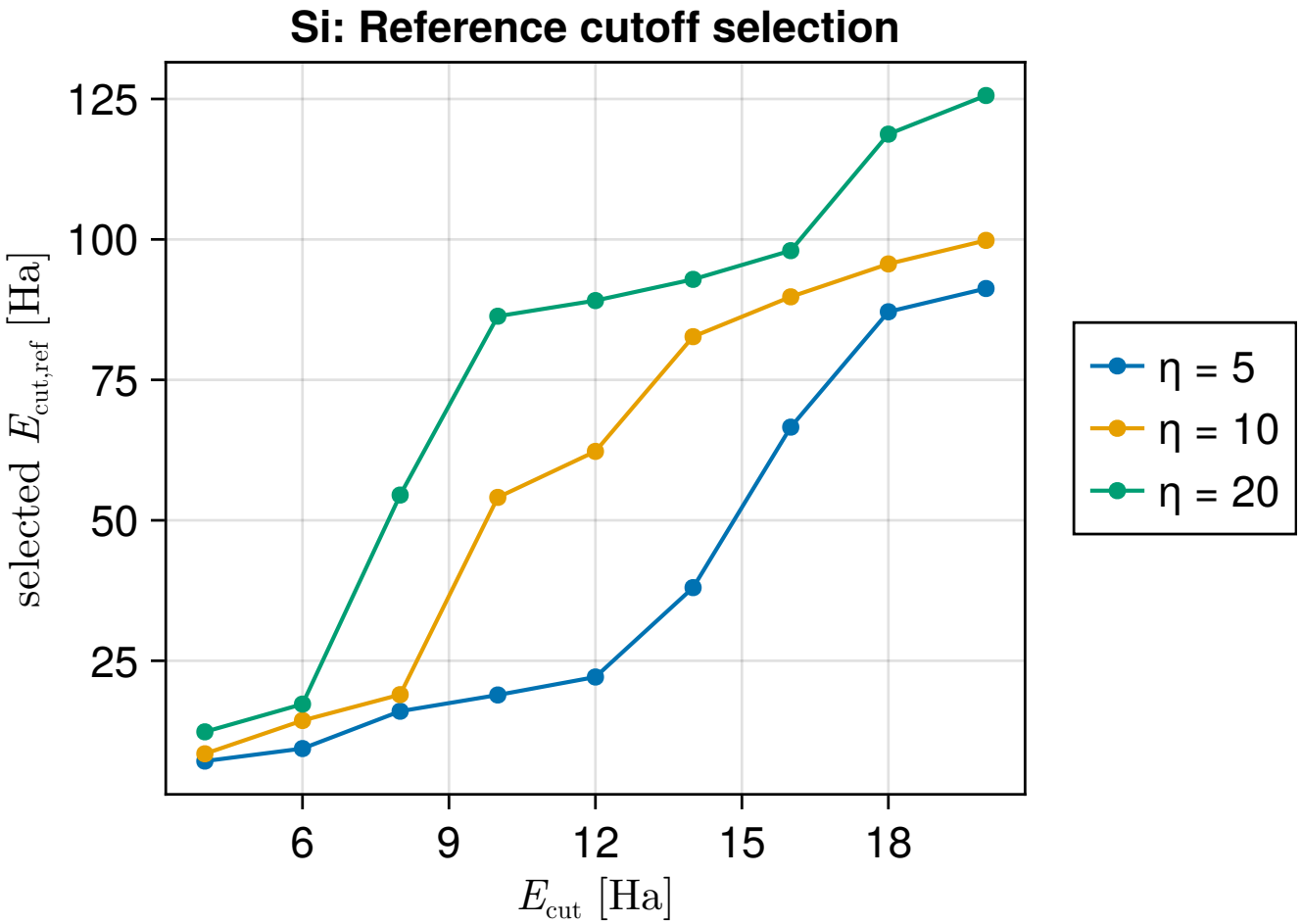
$$E_{\mathrm{disc,approx}}(q_{\mathrm{cut}}) \approx \sqrt{\sum_n \sum_{\|G\|>q_{\mathrm{cut}}} |\Delta\psi_{2,n}(G)|^2}$$

  2. Choose a factor $\eta > 1$ by which this error should be reduced, and select $E_{\mathrm{cut,ref}}$ such that:

$$E_{\mathrm{disc,approx}}(\sqrt{2E_{\mathrm{cut,ref}}}) \leq \frac{1}{\eta} E_{\mathrm{disc,approx}}(\sqrt{2E_{\mathrm{cut}}}).$$

- Approximations: **non-local part of the pseudopotential only**, orthogonal projectors across atoms, replace sum by integral.
- Reasonable η: between 5 and 20.

Choosing $E_{\mathrm{cut,ref}}$: the results



- We successfully capture the slower decay of the pseudopotential past a certain frequency!

Error propagation to total energies

- Given P, ΔP, how to best approximate the total energy $E(P_*)$?
  1. $E(P) + \frac{\partial E}{\partial P} \Delta P$
  2. $E(\mathcal{R}(P + \Delta P))$

Error propagation to total energies

- Given P, ΔP, how to best approximate the total energy $E(P_*)$?
  1. $E(P) + \frac{\partial E}{\partial P}\Delta P$
  2. $E(\mathcal{R}(P + \Delta P))$
- Taylor series expansion of E around P_*:

$$E(P) = E(P_*) + \cancel{\frac{\partial E}{\partial P}(P_*) \cdot (P - P_*)} + \mathcal{O}(\|P - P_*\|^2)$$

Error propagation to total energies

- Given P, ΔP, how to best approximate the total energy $E(P_*)$?
  1. $E(P) + \frac{\partial E}{\partial P}\Delta P$
  2. $E(\mathcal{R}(P + \Delta P))$
- Taylor series expansion of E around P_*:

$$E(P) = E(P_*) + \cancel{\frac{\partial E}{\partial P}(P_*) \cdot (P - P_*)} + \mathcal{O}(\|P - P_*\|^2)$$

- Compared to $E(P_*)$, in terms of $\mathcal{O}(\|P - P_*\|)$:
  1. $E(P)$: order 2
  2. $E(P) + \frac{\partial E}{\partial P}\Delta P$: order 2
  3. $E(\mathcal{R}(P + \Delta P))$: **order 4**!

Error propagation to total energies

- Given P, ΔP, how to best approximate the total energy $E(P_*)$?
  1. $E(P) + \frac{\partial E}{\partial P}\Delta P$
  2. $E(\mathcal{R}(P + \Delta P))$
- Taylor series expansion of E around P_*:

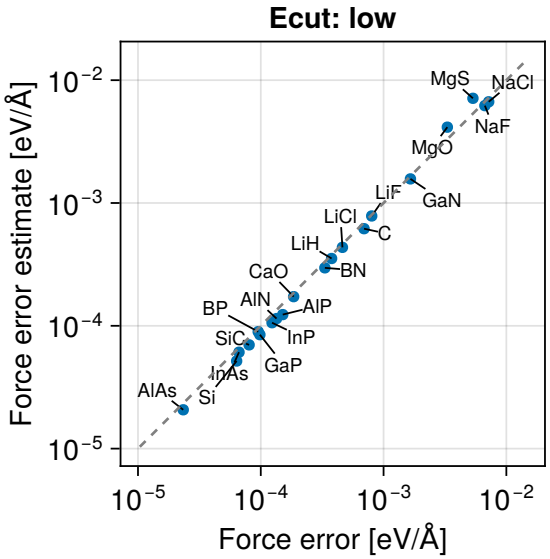
$$E(P) = E(P_*) + \cancel{\frac{\partial E}{\partial P}(P_*) \cdot (P - P_*)} + \mathcal{O}(\|P - P_*\|^2)$$

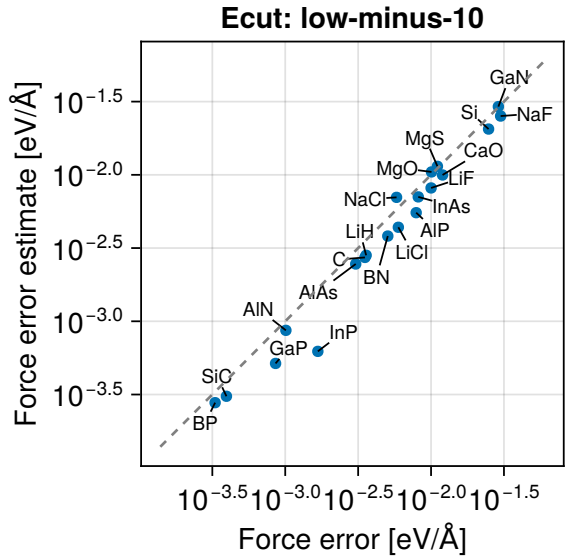
- Compared to $E(P_*)$, in terms of $\mathcal{O}(\|P - P_*\|)$:
  1. $E(P)$: order 2
  2. $E(P) + \frac{\partial E}{\partial P}\Delta P$: order 2
  3. $E(\mathcal{R}(P + \Delta P))$: **order 4**!
- For forces, $F(P)$ is order 1 and the other two are order 2.

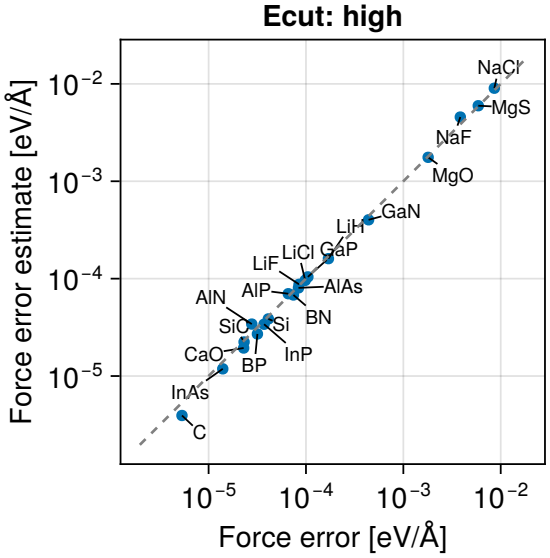
Let's benchmark!

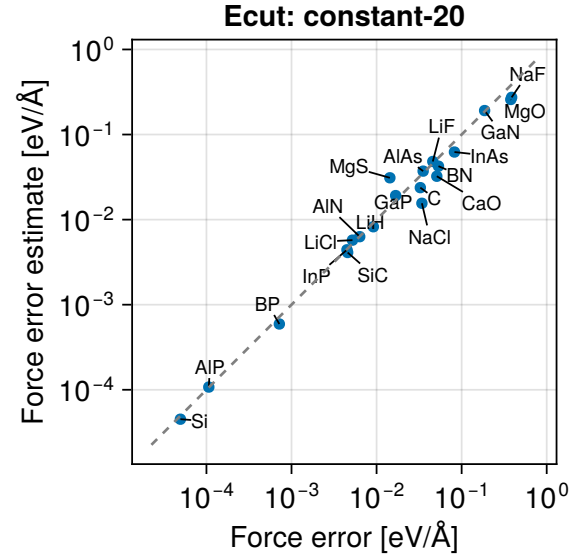
- 21 common insolators
- **Four different E_{cut} values**:
  - low recommendation
  - high recommendation
  - low recommendation -10 Ha
  - constant 20 Ha
- Discretization error estimation:
  1. Choose $E_{\mathrm{cut,ref}}$ with $\eta = 10$.
  2. Propagate to quantity of interest $A(P)$ with $A(\mathcal{R}(P + \Delta P))$.
  3. Use $\tau_{\mathrm{CG}} = 10^{-4}$.
- Compare to (expensive) reference at $E_{\mathrm{cut}} = 150$ Ha.

Forces: estimated vs actual error

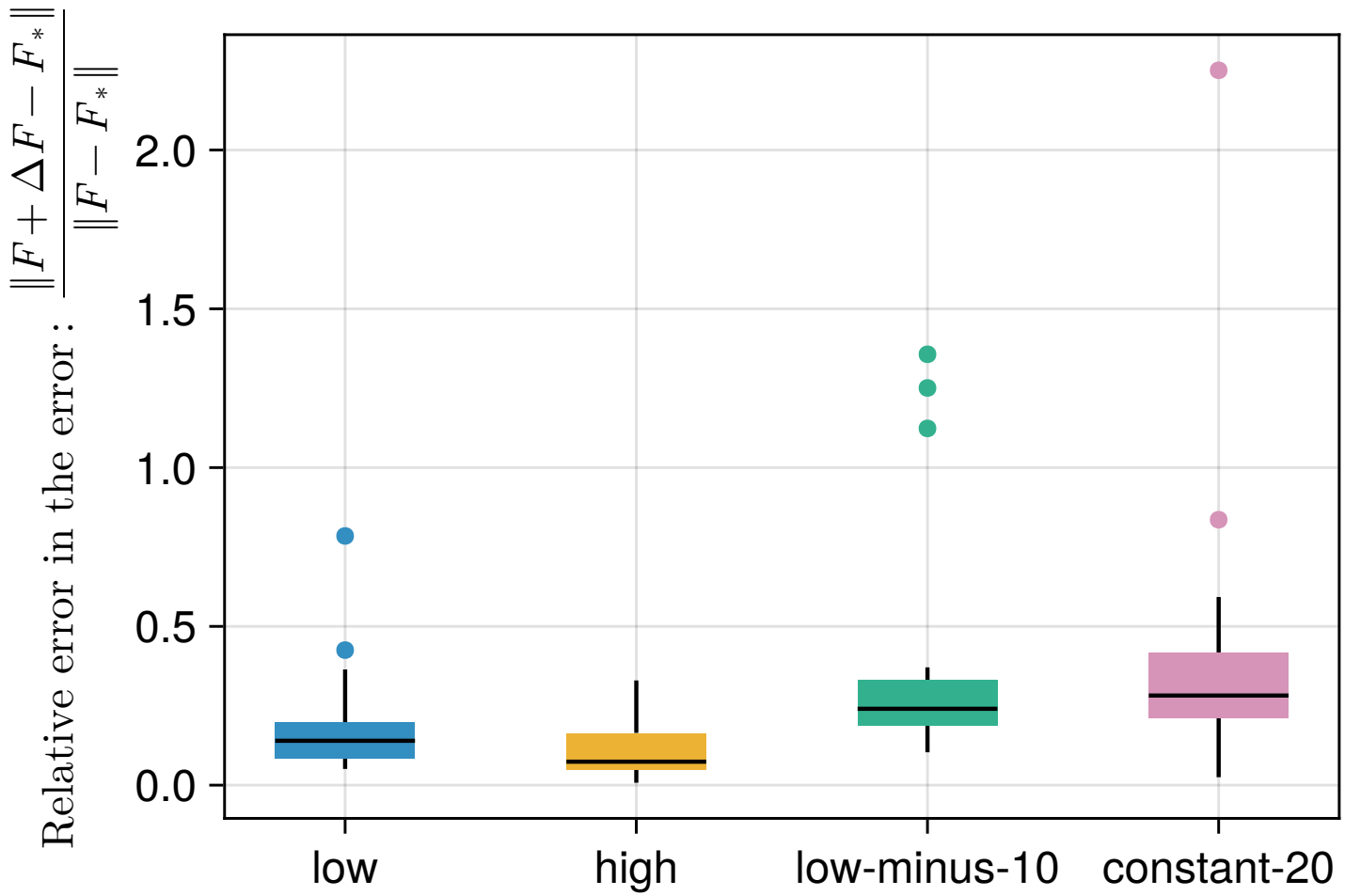




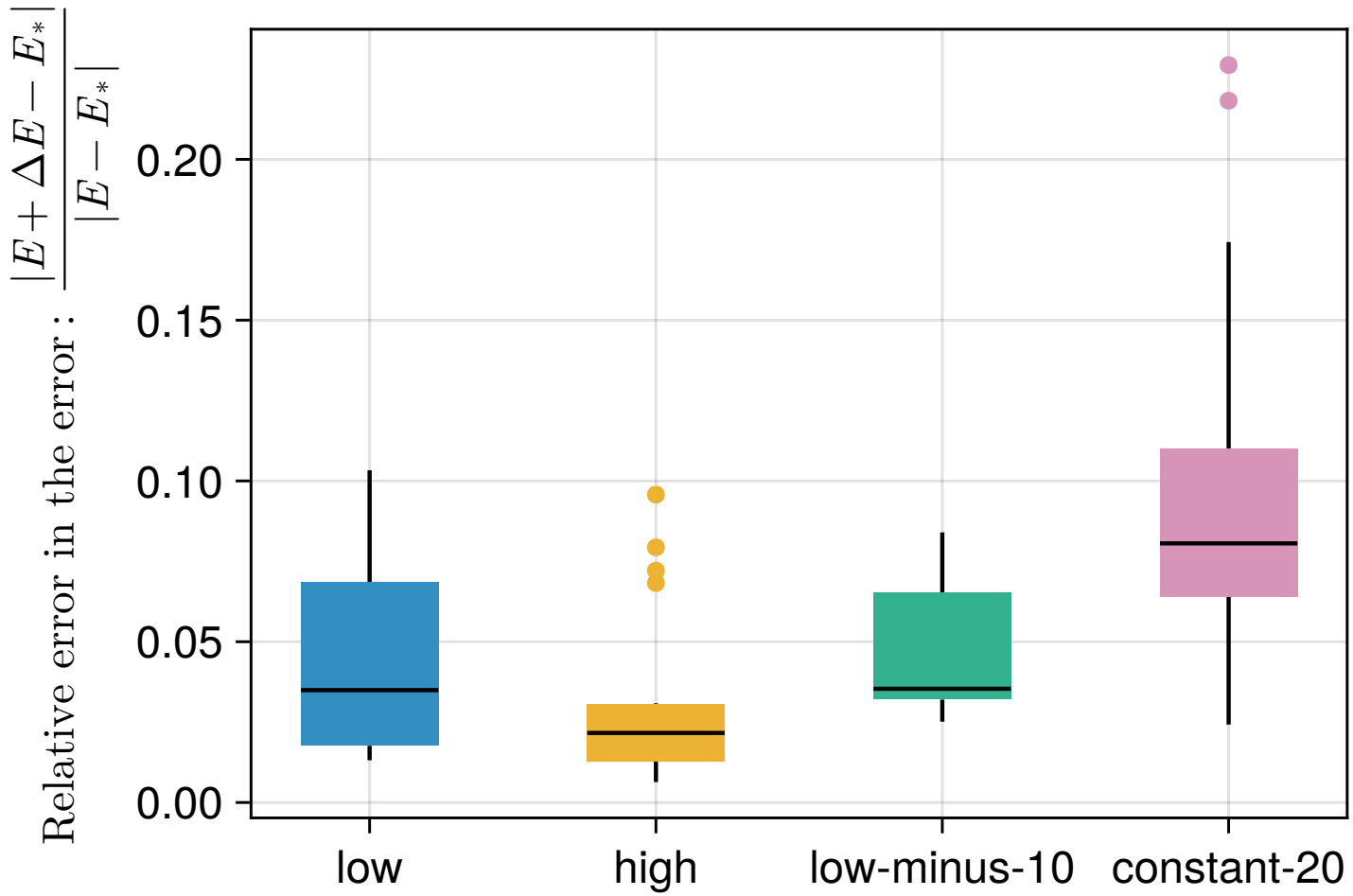




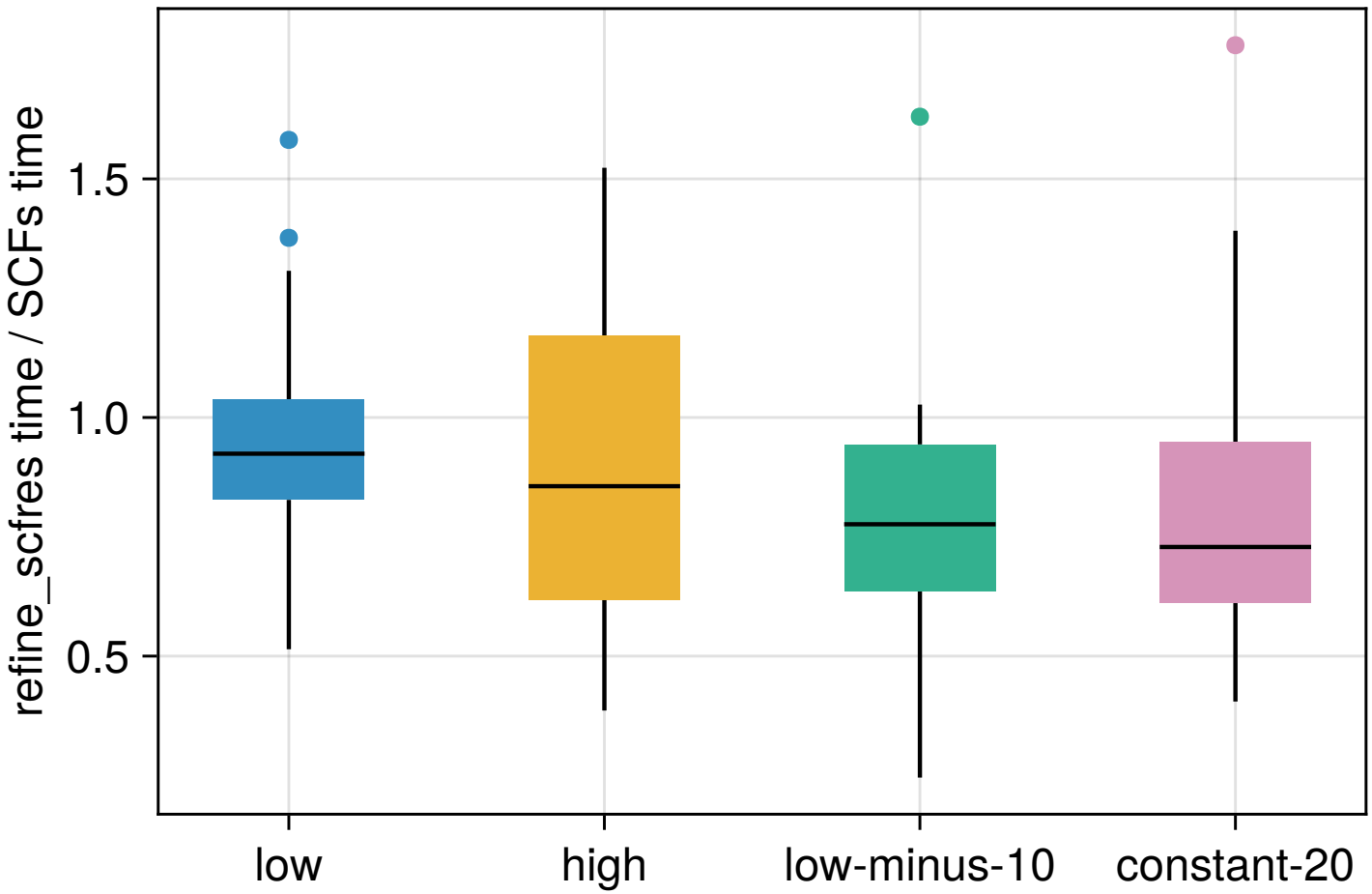
Forces: accuracy of the correction



Energy: accuracy of the correction



Performance: cost of ΔP / cost of P



Take-home messages

- Controlling the discretization error in PW-DFT is important.
  - Be careful with the recommendations of the pseudopotential!

Take-home messages

- Controlling the discretization error in PW-DFT is important.
  - Be careful with the recommendations of the pseudopotential!
- The discretization error can be estimated:
  - Accurately: excellent agreement with reference errors.
  - Efficiently: comparable or slightly cheaper cost than solving the original problem.
  - Automatically: reasonable default parameters.

Take-home messages

- Controlling the discretization error in PW-DFT is important.
  - Be careful with the recommendations of the pseudopotential!
- The discretization error can be estimated:
  - Accurately: excellent agreement with reference errors.
  - Efficiently: comparable or slightly cheaper cost than solving the original problem.
  - Automatically: reasonable default parameters.
- But: what do we do once we know the error?

Thank you!

Thanks to my supervisor Michael F. Herbst

Upcoming paper:
BP, Michael F. Herbst. *In preparation*

Questions?

Appendix

Mathematical framework of discretized PW-DFT

- Number of plane waves: $\mathcal{N} \propto E_{\text{cut}}^{3/2}$
- Density matrices P
  - Rank-N_{el} orthogonal projectors
  - The set of density matrices is the Grassman manifold:

$$\mathcal{M}_{\mathcal{N}} = \{P^2 = P, \operatorname{tr}(P) = N_{\text{el}} \mid P \in \mathbb{C}^{\mathcal{N}\times\mathcal{N}}_{\text{Herm}}\}.$$

  - Link with wavefunctions: $P = \sum_{n=1}^{N_{\text{el}}} \psi_n \psi_n^*$
- Total energy $E(P)$:

$$E(P) = \underbrace{\operatorname{tr}(H_0 P)}_{\text{kinetic and ion-electron}} + \underbrace{E_{\text{Hxc}}(\rho_P)}_{\text{electron-electron}}$$

- Ground state: energy minimization

$$P_* = \operatorname{argmin}_{P\in\mathcal{M}_{\mathcal{N}}} E(P)$$

Mathematical framework of PW-DFT (cont.)

- Hamiltonian:

$$H(P) = \nabla E(P)$$

- Accounting for the geometry of $\mathcal{M}_{\mathcal{N}}$, the residual is

$$R(P) = [P, [P, H(P)]]$$

- First-order optimality condition: $R(P_*) = 0$.
- Usually solved by a fixed-point method: self-consistent field (SCF) method. Direct minimization with gradient-based methods is possible.
- Differentiating the residual:

$$\boldsymbol{\nabla R}(P) \cdot \mathrm{d}P = \underbrace{[\mathrm{d}P, [P, H(P)]]}_{=0 \text{ at } P_*} + \underbrace{[P, [\mathrm{d}P, H(P)]]}_{\boldsymbol{\Omega}(P)\cdot \mathrm{d}P} + \underbrace{[P, [P, \mathrm{d}H(P)]]}_{\boldsymbol{K}(P)\cdot \mathrm{d}P}$$

A "reasonable" expression for $\Delta\psi_{2,n}(G)$

- Let's start from $\Delta P_2 = -\boldsymbol{M}_{22}^{-1} \cdot R_2$
  - In wavefunction representation: $\Delta\psi_{2,n} = -M_{22,n}^{-1} H_{21}(P)\psi_{1,n}$
  - H: kinetic energy + pseudopotential (local and non-local) + Hartree-exchange-correlation potential
- Assumption: Dominant off-diagonal contribution is the non-local part of the pseudopotential

$$V_{\mathrm{nl}} = \sum_{\text{projector index } i} \beta_i d_i \beta_i^*$$

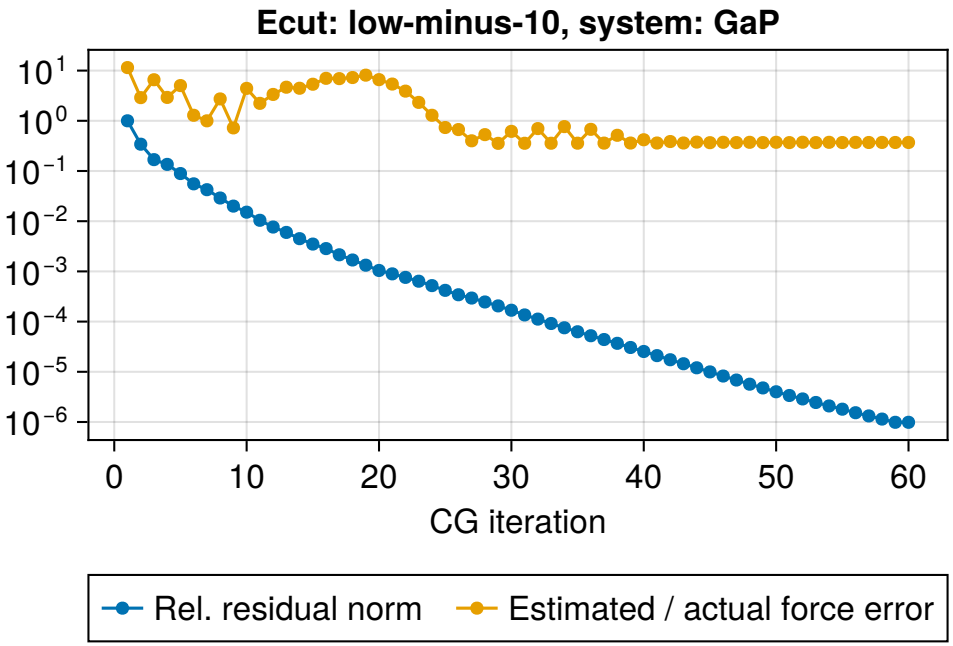
- So

$$\Delta\psi_{2,n}(G) \approx -M_{22,n}^{-1}(G) \sum_i \beta_i(G) d_i \left\langle \beta_i^*, \psi_{1,n} \right\rangle$$

- Direct link between the Fourier decay of the pseudopotential projectors and the Fourier decay of $\psi_{2,n}$.

Performance of ΔP computation

- Dominant cost: $x = A^{-1}b$ with $x = \Delta P_1$ and $A = (\boldsymbol{\Omega} + \boldsymbol{K})_{11}$.
  - Iterative solver: Conjugate Gradient (CG)
  - Cost = Cost per iteration $\times$ Iteration count
- Reduce the iteration count?
  - Usual stopping criterion: $\|Ax_n - b\| \,/\, \|b\| \leq \tau_{\mathrm{CG}}$
  - Relevant quantity: $\|\Delta F\| \,/\, \|F(P) - F(P_*)\|$



- Reasonable stopping criterion: τ_{CG} between 10^{-3} and 10^{-5}

Error propagation to total energies

- (blue) $E(P)$
- (orange) $E(P) + \frac{\partial E}{\partial P}\Delta P$
- (green) $E(\mathcal{R}(P + \Delta P))$
- (reference) $E(P_*)$

Explanation: (green) is 4th order for exact Newton and variational.