Error estimators for Density Functional Theory

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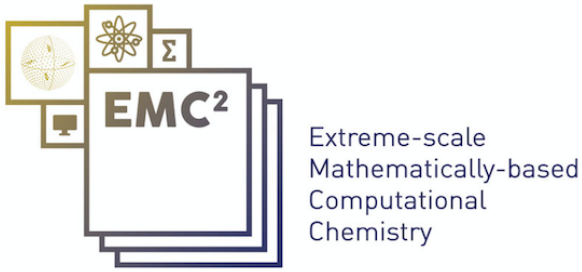
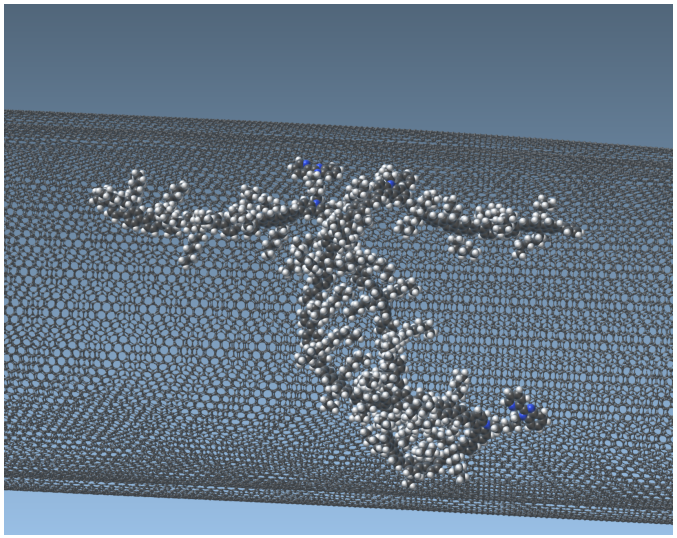


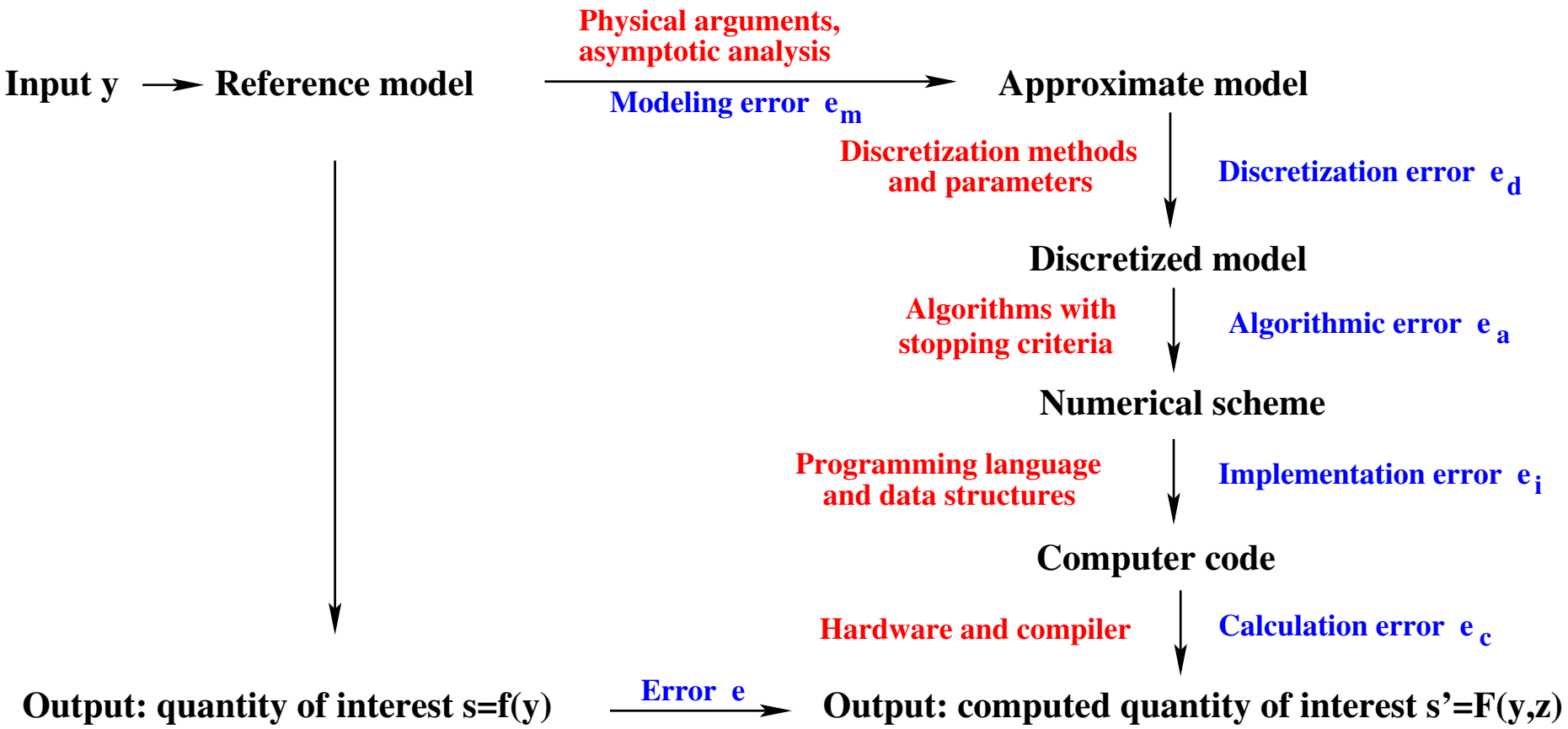
Numerical challenges in DFT

- very large systems with high accuracy
- metallic / heterogeneous systems
- databases for materials and drug discovery and design (machine learning)
  Ex.: open catalyst data set (Chanussot et al. ’20)
  264,890,000 Density Functional Theory (DFT) calculations

Need for fast, reliable, black-box numerical methods with error estimators



Motivation



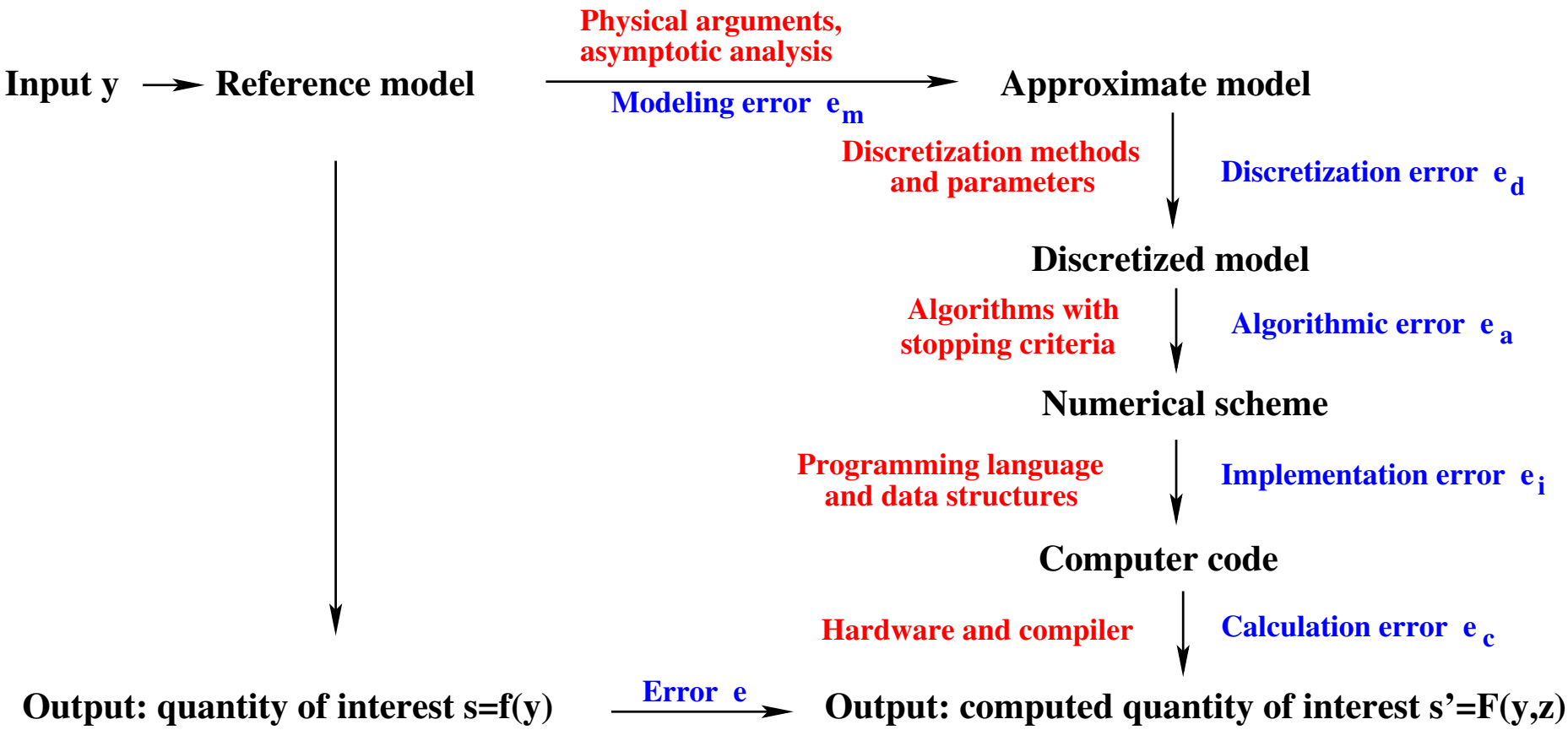
Total error: $\mathbf{e} = \mathbf{e}_{\mathrm{m}} + \mathbf{e}_{\mathrm{d}} + \mathbf{e}_{\mathrm{a}} + \mathbf{e}_{\mathrm{i}} + \mathbf{e}_{\mathrm{c}}$

Example: $s =$ **static polarizability of the CO_2 molecule**

$y = (\#\mathrm{C\ atoms} = 1, \#\mathrm{O\ atoms} = 2, \mathrm{total\ charge} = 0)$

(+ universal parameters: $\hbar, m_{\mathrm{e}}, e, \varepsilon_0$**,** z_X**,** $m_{X^{\mathrm{iso}}}$**)**

Motivation



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Goal 1: provide error estimates (certification)

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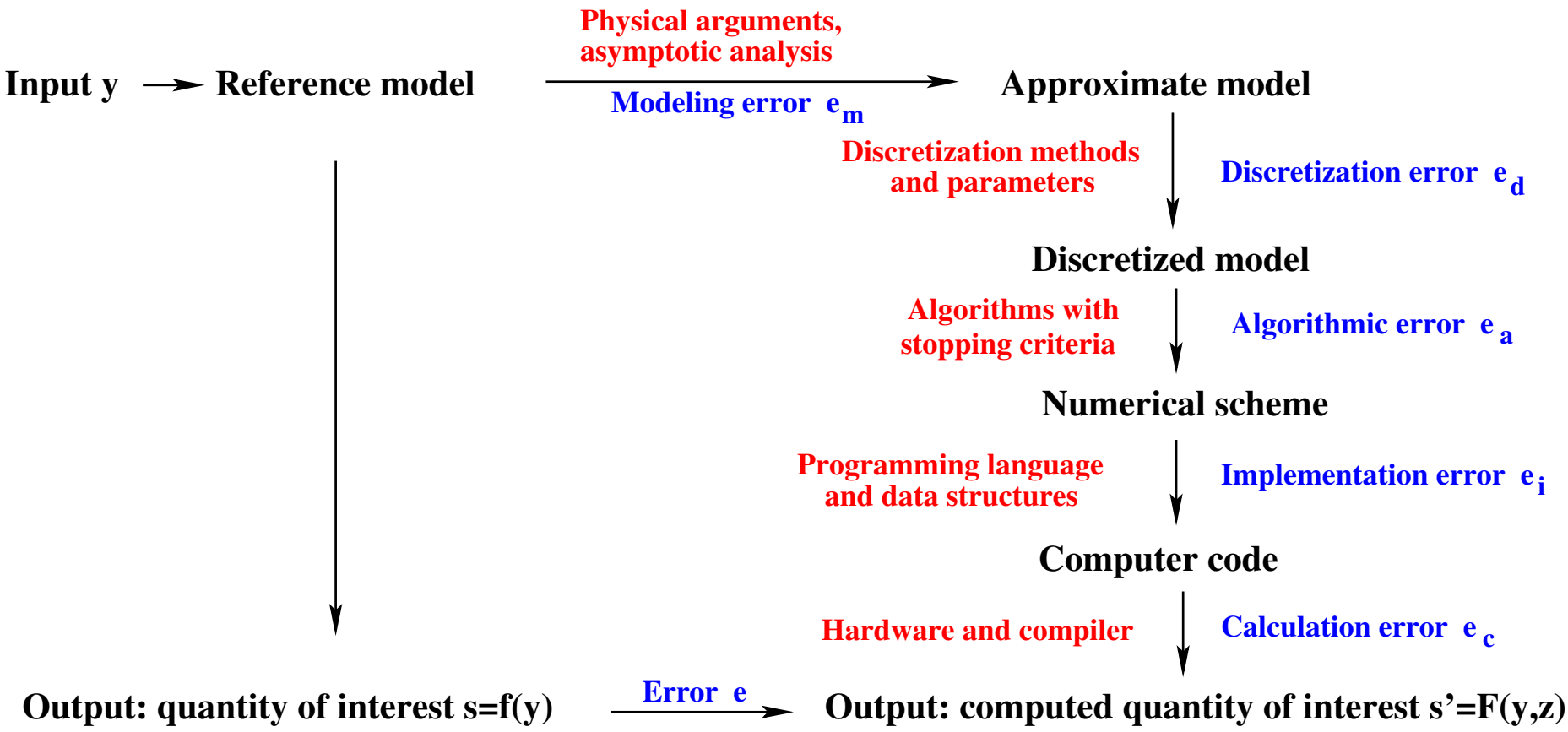


Total error: $\mathrm{e} = \mathrm{e_m} + \mathrm{e_d} + \mathrm{e_a} + \mathrm{e_i} + \mathrm{e_c}$

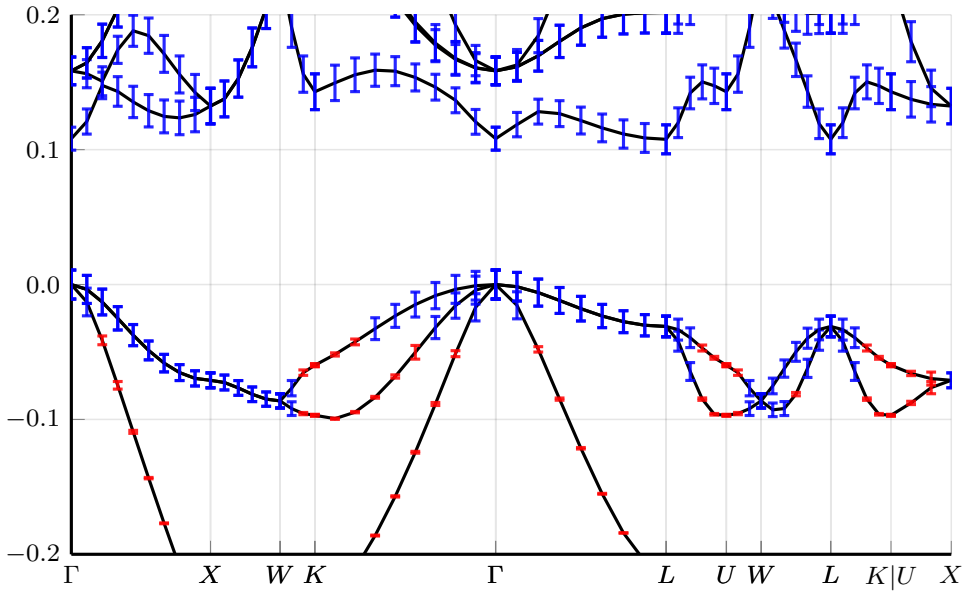
Goal 1: provide error estimates (certification)

Goal 2: optimize dynamically the computational resources (error balancing)
(DFT $\sim$ 15% of CPU time available in HPC centers)

An example of fully guaranteed error bars

Herbst, Levitt, EC, *Faraday discussions* '20

Si band diagram
(*non-self-consistent* DFT-LDA model with GTH pseudopotentials)

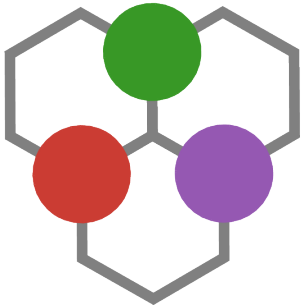
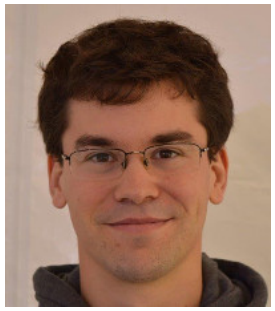


fully guaranteed error bars
accounting for

- **discretization error**
- **algorithmic error**
- **floating-point arithmetics (=implementation error assuming bug-free code)**

Numerical methods implemented in DFTK (Density-Functional ToolKit)

- planewave DFT package in julia (2018-), MIT license
- outcome of the EMC2 ERC Synergy project
- main developers: Michael Herbst (now at EPFL) and Antoine Levitt (now at Paris-Saclay)

- supports mathematical developments (low entrance barrier, ∼7k lines of code) and scale-up to relevant applications (∼ 1,000 electrons)
- fully composable with julia ecosystem
  - arbitrary precision (32bit, 64bit...)
  - algorithmic differentiation
  - interval arithmetic
  - ...

Outline of the talk

1. **Geometrical structure of the Kohn-Sham model**

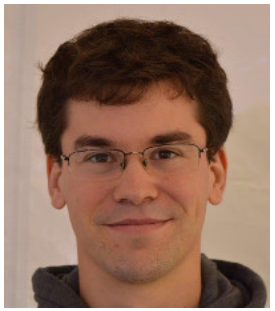
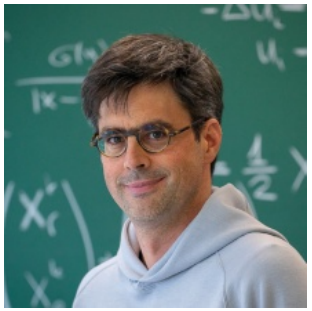
2. **Practical error bounds on interatomic forces in Kohn-Sham DFT**

   EC, G. Dusson, G. Kemlin and A. Levitt, SIAM J. Sci. Comput. '22

3. **Computation of response properties for metals**

   EC, M. Herbst, G. Kemlin, A. Levitt and B. Stamm, Lett. Math. Phys. '23



1 - Geometrical structure of the Kohn-Sham model

Periodic supercell $\Omega = \mathbb{R}^3/\mathbb{L}$, $\quad \mathbb{L}$**: Bravais lattice of** $\mathbb{R}^3$

M **ionic cores, positions** $X := (X_j)_{1 \leq j \leq M} \in \Omega^M$

N **valence electron pairs (spin-unpolarized state)**

Orbital formulation of the continuous Kohn-Sham model

$$\min \left\{ E^{\mathrm{KS}}(X,\Phi) \mid \Phi = (\phi_1, \cdots, \phi_N) \in \left(H^1_{\#}(\Omega;\mathbb{C})\right)^N, \ \int_\Omega \phi_i^* \phi_j = \delta_{ij} \right\}$$

$$E^{\mathrm{KS}}(X,\Phi) = \sum_{i=1}^{N} \int_\Omega |\nabla \phi_i|^2 + \int_\Omega v(X)\rho_\Phi + E_{\mathrm{Hxc}}(\rho_\Phi) \quad \textbf{with} \quad \rho_\Phi(\mathbf{r}) := 2\sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

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Discretization in a planewave basis set

Fourier modes: $e_{\boldsymbol{G}}(\mathbf{r}) := |\Omega|^{-1/2} e^{i\boldsymbol{G}\cdot\boldsymbol{r}}, \quad \mathbf{G} \in \mathbb{L}^*$ **(reciprocal lattice)**

Approximation spaces: $\mathcal{X} = \mathrm{Span}\left(e_{\mathbf{G}}, \ \mathbf{G} \in \mathbb{L}^*, \ \dfrac{|\mathbf{G}|^2}{2} < E_{\mathrm{c}} \right)$

↑

energy cut-off

Orbital formulation of the continuous Kohn-Sham model

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Orbital formulation of the discretized KS model (used in most simulations)

$$\phi_i(\mathbf{r}) = \sum_{\mathbf{G}\in\mathbb{L}^* \mid |\mathbf{G}|<\sqrt{2E_{\mathrm{c}}}} C_{\mathbf{G}i} e_{\mathbf{G}}(\mathbf{r}) \in \mathcal{X}, \qquad N_{\mathrm{c}} := \dim(\mathcal{X})$$

minimization set: $\mathrm{St}(N,N_{\mathrm{c}}) := \left\{ C = [C_{\mathbf{G}i}] \in \mathbb{C}^{N_{\mathrm{c}}\times N} \mid C^*C = I_N \right\}$

drawback: gauge invariance (C and CU have same energy $\forall U \in U(N_{\mathrm{c}})$)

Orbital formulation of the continuous Kohn-Sham model

$$\min\left\{E^{\mathrm{KS}}(X,\Phi)\mid \Phi=(\phi_1,\cdots,\phi_N)\in\left(H^1_{\#}(\Omega;\mathbb{C})\right)^N,\ \int_\Omega \phi_i^*\phi_j=\delta_{ij}\right\}$$

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Density matrix (1-RDM) formulation (math. analysis, linear scaling methods)

$P=CC^*$ **orthogonal proj. on span(columns of** C**)**

minimization set: $\mathrm{Gr}(N,N_{\mathrm{c}}):=\left\{P\in\mathbb{C}^{N_{\mathrm{c}}\times N_{\mathrm{c}}}_{\mathrm{herm}}\mid P^2=P,\ \mathrm{Tr}(P)=N\right\}$

Geometrical properties of the Grassmann manifold

The Frobenius inner product on $\mathbb{C}^{N_c \times N_c}_{\text{herm}}$ induces a Riemannian metric on

$$\mathcal{M} := \mathrm{Gr}(N, N_c) = \{P \in \mathbb{C}^{N_c \times N_c}_{\text{herm}} \mid P^2 = P,\ \mathrm{Tr}(P) = N\}$$

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Remark: we consider a hierarchy of 2 approximation spaces ($E_{\rm calc} \ll E_{\rm ref}$)

$$\underbrace{\mathcal{X}_{\rm calc}}_{\text{variational approximation space}} \subset \underbrace{\mathcal{X}_{\rm ref}}_{\text{error estimation space}}$$

- **to study the convergence of numerical algorithms, we take $E_c = E_{\rm calc}$**

  EC, G. Kemlin and A. Levitt, *Convergence analysis of direct minimization and self-consistent iterations*, SIAM J. Mat. Anal. 42 (2021) 243–274

- **to derive practical error bounds, we take $E_c = E_{\rm ref}$**

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Tangent space

$$\forall P \in \mathcal{M}, \quad T_P\mathcal{M} = \{Q \in \mathbb{C}^{N_c\times N_c}_{\text{herm}} \mid PQP = (I-P)Q(I-P) = 0\}$$

The orthogonal projector $\mathbf{\Pi}_P \in \mathcal{L}(\mathbb{C}^{N_c\times N_c}_{\text{herm}})$ on $T_P\mathcal{M}$ if given by

$$\forall M \in \mathbb{C}^{N_c\times N_c}_{\text{herm}}, \quad \mathbf{\Pi}_P M = [P,[P,M]]$$

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Riemannian gradient and Hessian

Let $\mathcal{E} \in C^1(\mathbb{C}^{N_c\times N_c}_{\rm herm};\mathbb{R})$ **and** $E : \mathcal{M} \ni P \mapsto E(P) := \mathcal{E}(P) \in \mathbb{R}$

- **Gradient of E at $P \in \mathcal{M}$:** $\nabla_{\mathcal{M}} E(P) = \mathbf{\Pi}_P(\nabla\mathcal{E}(P)) \in T_P\mathcal{M}$

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- **Gradient of E at $P \in \mathcal{M}$:** $\nabla_{\mathcal{M}} E(P) = \mathbf{\Pi}_P(\nabla\mathcal{E}(P)) \in T_P\mathcal{M}$
- **Hessian of E at $P \in \mathcal{M}$:** $\boldsymbol{D}^2_{\mathcal{M}} E(P) = \mathbf{\Omega}_P + \boldsymbol{K}_P \in \mathcal{L}(T_P\mathcal{M})$

with $\mathbf{\Omega}_P, \boldsymbol{K}_P : T_P\mathcal{M} \to T_P\mathcal{M}$ given by

$$\mathbf{\Omega}_P = -[P,[\nabla\mathcal{E}(P),\bullet]] \quad \textbf{and} \quad \boldsymbol{K}_P = \mathbf{\Pi}_P\, \boldsymbol{D}^2\mathcal{E}(P)\, \mathbf{\Pi}_P$$

2 - Practical error bounds on interatomic forces

Error bounds on energy and density

- *a priori* **error bounds: EC-Chakir-Maday '12, Zhou et al. '13, EC-Dusson '17...**
- *a posteriori* **error bounds: EC-Dusson-Maday-Stamm-Vohralík '14-'21, Chen-Dai-Gong-He-Zhou '14, Chen-Schneider '15, Kaye-Lin-Yang '15, Herbst-Levitt-EC '20 ...**

This work: error bounds on properties (non-variational)

Interatomic forces (at the discrete level)

- **Manifold of admissible 1-RDM**

$$\mathcal{M} = \mathrm{Gr}(N, N_{\mathrm{ref}}) = \{P \in \mathbb{C}^{N_{\mathrm{ref}} \times N_{\mathrm{ref}}}_{\mathrm{herm}} \mid P^2 = P,\ \mathrm{Tr}(P) = N\}$$

- **Kohn-Sham energy functional** $E^{\mathrm{KS}} : \Omega^M \times \mathcal{M} \to \mathbb{R}$

$$E^{\mathrm{KS}}(X, P) := \mathrm{Tr}\,(TP) + \mathrm{Tr}\,(V(X)P) + E_{\mathrm{Hxc}}(P)$$

- **Kohn-Sham ground state and interatomic forces (Hellmann-Feynman)**

$$P_*(X) = \operatorname*{argmin}_{P \in \mathcal{M}} E(X, P) \qquad F_j(X) := -\mathrm{Tr}\left(\nabla_{X_j} V(X) P_*(X)\right) + F_{\mathrm{ion}}(X)$$

Force component $f_* = [F_{j\alpha}(X_0)]_\alpha$ for a fixed nuclear configuration X_0

$$E(P) := E^{\mathrm{KS}}(X_0, P) \qquad f(P) := -\mathrm{Tr}\left(\partial_{X_{j\alpha}} V(X_0) P\right)$$

$$P_* := \operatorname*{argmin}_{P \in \mathcal{M}} E(P), \qquad f_* = f(P_*)$$

First-order optimality condition

$$\nabla_{\mathcal{M}} E(P_*) = 0$$

Residual associated with an approximate solution P

$$\boxed{R(P) := \nabla_{\mathcal{M}} E(P) = [P, [P, H(P)]]}$$

where $H(P) := T + V(X_0) + \nabla \mathcal{E}_{\mathrm{Hxc}}(P)$ is the Kohn-Sham Hamiltonian, ($\nabla \mathcal{E}_{\mathrm{Hxc}}(P)$ = Frobenius gradient of $\mathbb{C}^{N_{\mathrm{ref}} \times N_{\mathrm{ref}}}_{\mathrm{herm}} \ni P \mapsto \mathcal{E}_{\mathrm{Hxc}}(P) \in \mathbb{R}$)

General principle:

- $\mathcal{M}$ **smooth Riemannian manifold (set of admissible states)**
- $R : \mathcal{M} \ni P \mapsto R(P) \in T_P\mathcal{M}$ **smooth function (residual)**
- $f : \mathcal{M} \to \mathbb{R}$ **smooth function (observable)**

Equilibrium state : $R(P_*) = 0$
Quantity of interest (QoI): $f_* := f(P_*)$

Error estimators: in the linear regime

$$\boxed{P - P_* \approx \boldsymbol{R}'(P)^{-1} R(P) \quad \textbf{and} \quad f(P) - f_* \approx \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{R}'(P)^{-1} R(P) \rangle}$$

Two practical questions: if $P \approx$ DM of the KS ground-state in $\mathcal{X}_{\text{calc}} \subset \mathcal{X}_{\text{ref}}$

1. **are we in the linear regime in usual DFT calculations on real materials?**
2. **if so, how to compute an accurate and computationally efficient bound for $\langle \nabla_{\mathcal{M}} f(P), \boldsymbol{R}'(P)^{-1} R(P) \rangle$?**

Are we in the linear regime in practice?

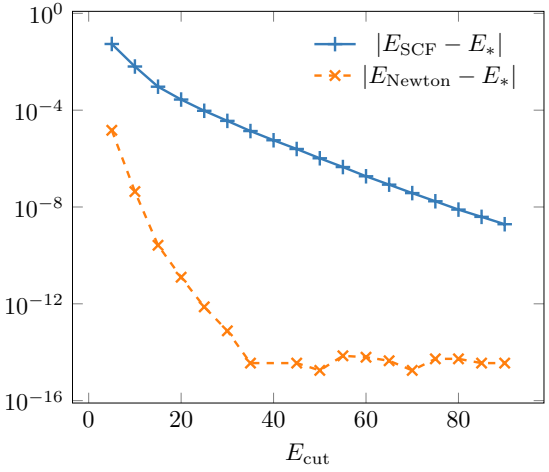
Apparently yes! ... for planewave calculations with nice pseudopotentials

Numerical test: if $P - P_* \approx \boldsymbol{R}'(P)^{-1}R(P)$, then the QoI computed from

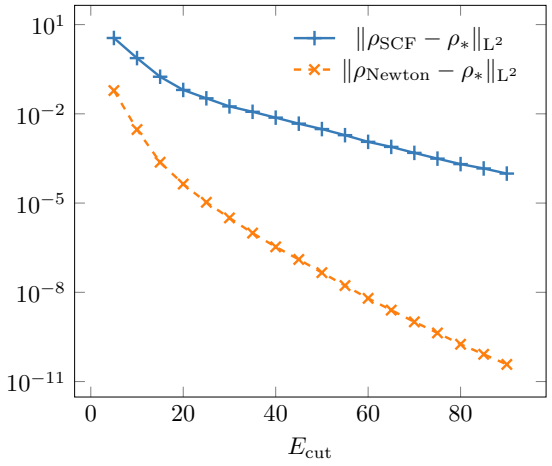
$$P_{\text{Newton}} = \mathfrak{R}\left(P - \boldsymbol{R}'(P)^{-1}R(P)\right) \qquad (\mathfrak{R} \text{ suitable retraction})$$

should be much better than the ones computed from P

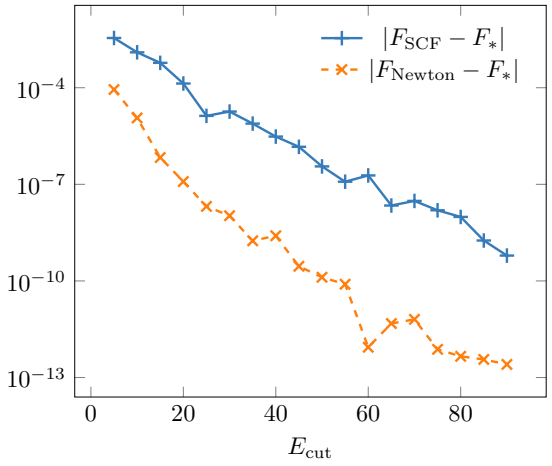
Example: FCC silicon crystal (energies in Hartrees)



Energy



Ground-state density



Interatomic forces

Accurate and efficient approximation of $P - P_*$

Let P be the variational approximation of the KS ground state in $\mathcal{X}_{\text{cal}}$

$$\underbrace{P - P_*}_{\text{not computable}} \approx \underbrace{\boldsymbol{R}'(P)^{-1} R(P)}_{\text{computable but expensive}} \approx \underbrace{\boldsymbol{M}_P^{-1} R(P)}_{\text{computable and cheap}} \quad \textbf{in energy norm}$$

M_P^{-1} very simple operator deduced from mathematical analysis

Equivalence between these three quantities proved in the asymptotic regime

Accurate and efficient approximation of $P - P_*$

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$$P = \sum_{i=1}^{N} \phi_i \phi_i^*, \quad \phi_i \in \mathcal{X}_{\rm cal}, \quad \Pi_{\mathcal{X}_{\rm cal}} H(P) \Pi_{\mathcal{X}_{\rm cal}} \phi_i = \varepsilon_i \phi_i, \quad \phi_i^* \phi_j = \delta_{ij}, \quad \varepsilon_1 \leq \varepsilon_2 \leq \cdots$$

$$P = \sum_{i=1}^{N} \phi_i \phi_i^* \in \mathcal{M} \;\leftrightarrow\; \Phi = (\phi_1 | \cdots | \phi_N) \in \mathrm{St}(N, N_{\rm ref}) \textbf{ s.t. } P = \Phi\Phi^*$$

$$Q = \sum_{i=1}^{N} \phi_i \xi_i^* + \xi_i \phi_i^* \in \mathcal{T}_P\mathcal{M} \;\leftrightarrow\; \Xi = (\xi_1 | \cdots | \xi_N) \in \mathbb{C}^{N_{\rm ref} \times N} \textbf{ s.t. } \Phi^*\Xi = 0$$

$$R(P) = [P, [P, H(P)]] \in \mathcal{T}_P\mathcal{M} \;\leftrightarrow\; R^{\rm MO}(\Phi) = (r_1 | \cdots | r_N) = P^{\perp} H(P) \Phi \in \mathbb{C}^{N_{\rm ref} \times N}$$

$$\boldsymbol{M}_P Q \in \mathcal{T}_P\mathcal{M} \;\leftrightarrow\; \boldsymbol{M}_\Phi^{\rm MO}\Xi := ((-\Delta - t_i)\xi_i)_{1 \leqslant i \leqslant N} \quad t_i := \textstyle\int_\Omega |\nabla \phi_i|^2$$

First (unsuccessful) attempt to compute error bounds on interatomic forces

$$f(P) - f_* \approx \langle \nabla_{\mathcal{M}} f(P), P - P_* \rangle \qquad \textbf{(we are in the linear regime)}$$

$$\overset{?}{\approx} \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{M}_P^{-1} R(P) \rangle \qquad (P - P_* \approx \boldsymbol{M}_P^{-1} R(P) \textbf{ in energy norm})$$

First (unsuccessful) attempt to compute error bounds on interatomic forces

$$f(P) - f_* \approx \langle \nabla_{\mathcal{M}} f(P), P - P_* \rangle$$ **(we are in the linear regime)**

$$\overset{?}{\approx} \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{M}_P^{-1} R(P) \rangle$$ **wrong by several orders of magnitude**

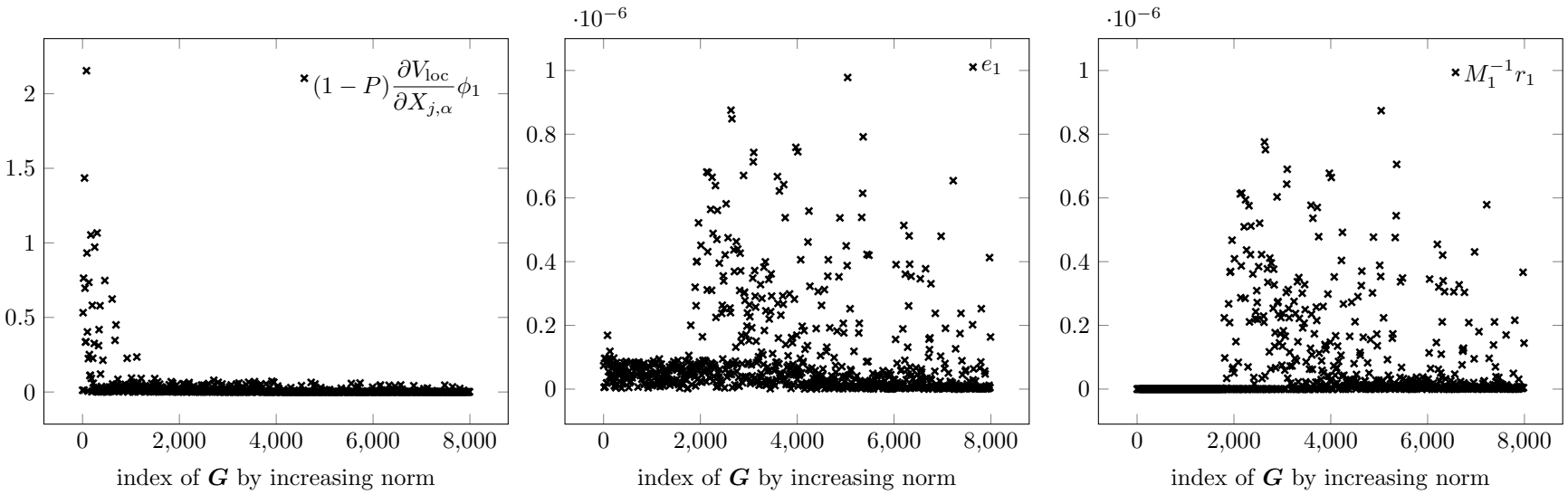
First (unsuccessful) attempt to compute error bounds on interatomic forces

$$f(P) - f_* \approx \langle \nabla_{\mathcal{M}} f(P), P - P_* \rangle$$ **(we are in the linear regime)**

$$\overset{?}{\approx} \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{M}_P^{-1} R(P) \rangle$$ **wrong by several orders of magnitude**

because $\nabla_{\mathcal{M}} f(P)$ and $P - P_*$ are almost orthogonal for nonnegative Sobolev norms

Example: FCC silicon crystal



Fourier coefficients of $\nabla_{\mathcal{M}} f(P)$ (left), $P - P_*$ (center) $\boldsymbol{M}_P^{-1} R(P)$ (right)

Second (successful) attempt to compute error bounds on interatomic forces

$$f(P) - f_* \approx \langle \nabla_{\mathcal{M}} f(P), P - P_* \rangle$$ **(we are in the linear regime)**

$$\overset{?}{\approx} \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{R}'(P)^{-1} R(P) \rangle$$ **yes, but too computationally expensive**

Second (successful) attempt to compute error bounds on interatomic forces

$$f(P) - f_* \approx \langle \nabla_{\mathcal{M}} f(P), P - P_* \rangle \qquad \textbf{(we are in the linear regime)}$$

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A Schur complement approach to solve $\boldsymbol{R}'(P)Q = R(P)$

$$P = \sum_{i=1}^{N} \phi_i \phi_i^* \in \mathcal{M}, \qquad Q = \sum_{i=1}^{N} (\phi_i \xi_i^* + \xi_i \phi_i^*) \in T_P \mathcal{M},$$

$$\mathcal{X}_{\text{ref}} = \mathcal{X}_{\text{calc}} \oplus \mathcal{X}_{\text{calc}}^{\perp}, \qquad \phi_i \in \mathcal{X}_{\text{calc}}, \qquad \xi_i = \underbrace{\xi_{i,1}}_{\in \mathcal{X}_{\text{calc}}} + \underbrace{\xi_{i,2}}_{\mathcal{X}_{\text{calc}}^{\perp}}, \qquad Q = Q_1 + Q_2$$

$$\begin{pmatrix} \boldsymbol{R}'(P)_{11} & \boldsymbol{R}'(P)_{12} \\ \boldsymbol{R}'(P)_{21} & \boldsymbol{R}'(P)_{22} \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} = \begin{pmatrix} R(P)_1 \\ R(P)_2 \end{pmatrix}$$

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Q_1 small (in energy norm) but large impact on the error on interactomic forces
Q_2 large (in energy norm) but smaller impact on the error on interactomic forces
$Q_2 \approx M_P^{-1} R(P)_2$ (in energy norm), $R(P)_1 = 0$ **if P variational solution in $\mathcal{X}_{\text{calc}}$**

Second (successful) attempt to compute error bounds on interatomic forces

$$f(P) - f_* \approx \langle \nabla_{\mathcal{M}} f(P), P - P_* \rangle \qquad \textbf{(we are in the linear regime)}$$

$$\overset{?}{\approx} \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{R}'(P)^{-1} R(P) \rangle \qquad \textbf{yes, but too computationally expensive}$$

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$$\begin{pmatrix} \boldsymbol{R}'(P)_{11} & \boldsymbol{R}'(P)_{12} \\ \mathbf{0} & \boldsymbol{M}_P \end{pmatrix} \begin{pmatrix} Q_1^{\text{app}} \\ Q_2^{\text{app}} \end{pmatrix} = \begin{pmatrix} R(P)_1 \\ R(P)_2 \end{pmatrix}$$

$$\boxed{Q_2^{\text{app}} = \boldsymbol{M}_P^{-1} R(P)_2, \qquad (\boldsymbol{\Omega}_P + \boldsymbol{K}_P)_{11} Q_1^{\text{app}} = R(P)_1 - (\boldsymbol{\Omega}_P + \boldsymbol{K}_P)_{12} \boldsymbol{M}_P^{-1} R(P)_2}$$

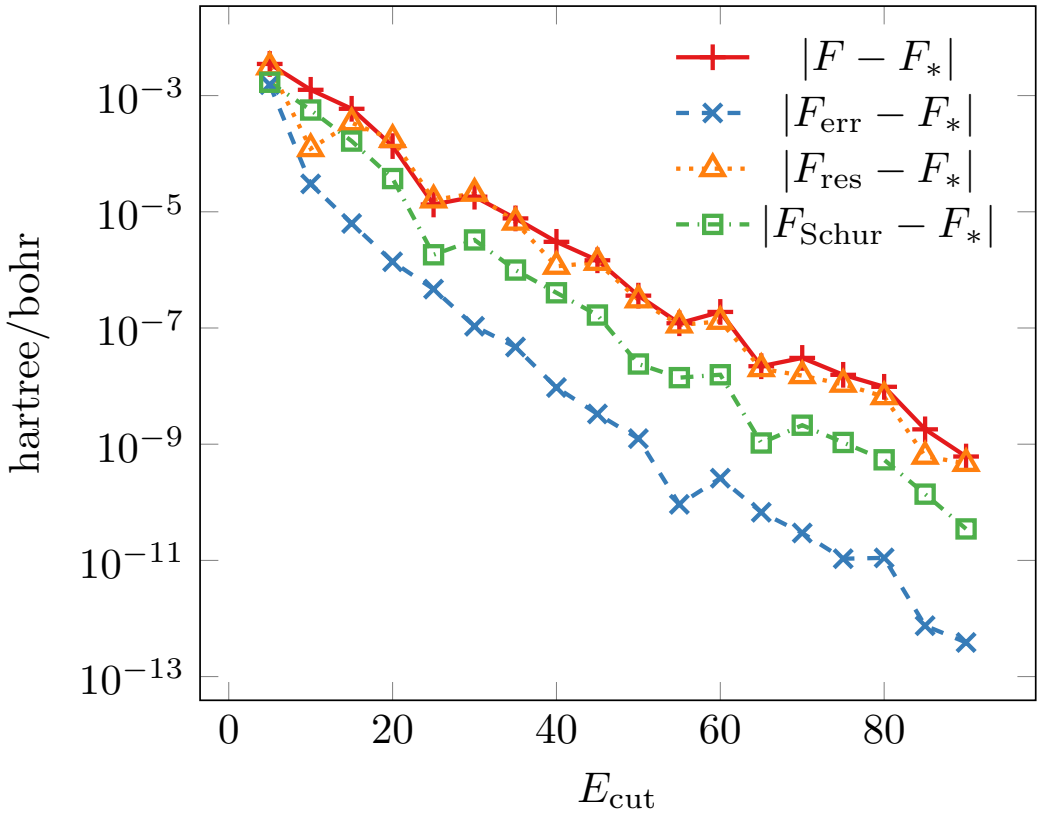
Numerical results: post-processing

$$f - f_* \coloneqq f(P) - f(P_*) \quad \textbf{(red)}$$

$$f_{\textbf{res}} - f_* \coloneqq f(P) - \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{M}^{-1} R(P) \rangle - f(P_*) \quad \textbf{(orange)}$$

$$f_{\textbf{Schur}} - f_* \coloneqq f(P) - \langle \nabla_{\mathcal{M}} f(P), \boldsymbol{R}'_{\text{app}}(P)^{-1} R(P) \rangle - f(P_*) \quad \textbf{(green)}$$

$$f_{\textbf{err}} - f_* \coloneqq f(P) - \langle \nabla_{\mathcal{M}} f(P), P - P_* \rangle - f(P_*) \quad \textbf{(blue)}$$



3 - Response properties for metals

Linear (noninteracting) Schrödinger-like Hamiltonian H
Perturbation δV **of the potential**

$$H \to H + \delta V \quad \Rightarrow \quad \rho \to \rho + \delta\rho + o(\delta V) \quad \textbf{with } \delta\rho \textbf{ linear in } \delta V$$

$$\boxed{\delta\rho = \chi_0 \, \delta V}$$

χ_0 : **non-interacting density-density response function**
independent-particle susceptibility
irreducible polarizability

Goal: compute $\delta\rho := \chi_0 \, \delta V$ **for metals**

Unperturbed Hamiltonian H

$$H\phi_n = \varepsilon_n \phi_n, \qquad \int_\Omega \phi_m^*(\boldsymbol{r})\phi_n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \delta_{mn}, \qquad \varepsilon_1 \leqslant \varepsilon_2 \leqslant \varepsilon_3 \leqslant \cdots,$$

Ground-state density

$$\rho(\boldsymbol{r}) = \sum_{n=1}^{+\infty} f_n \left|\phi_n(\boldsymbol{r})\right|^2 \quad \textbf{with} \quad f_n := f\left(\frac{\varepsilon_n - \varepsilon_\mathrm{F}}{T}\right) \quad \textbf{and} \quad f(x) = \frac{2}{1+e^x}$$

Occupation numbers f_n for $T = 0$ (left) and $T > 0$ (right)

ε_F **(Fermi level) such that** $$\int_\Omega \rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = \sum_{n=1}^{+\infty} f_n = \sum_{n=1}^{+\infty} f\left(\frac{\varepsilon_n - \varepsilon_\mathrm{F}}{T}\right) = N_\mathrm{el}$$

Notation: $$f_n' := \frac{1}{T} f'\left(\frac{\varepsilon_n - \varepsilon_\mathrm{F}}{T}\right) =: \frac{f_n - f_n}{\varepsilon_n - \varepsilon_n}$$

Linear response

$$H \to H + \delta V \quad \Rightarrow \quad \rho \to \rho + \delta\rho + o(\delta V) \quad \textbf{with } \delta\rho \textbf{ linear in } \delta V$$

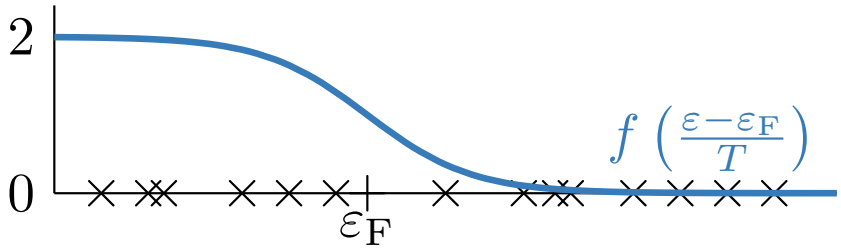
Sum-over-state formula

$$\delta\rho(\boldsymbol{r}) \coloneqq (\chi_0 \delta V)(\boldsymbol{r}) = \sum_{n=1}^{+\infty} \sum_{m=1}^{+\infty} \frac{f_n - f_m}{\varepsilon_n - \varepsilon_m} \left(\delta V_{mn} - \delta\varepsilon_{\mathrm{F}}\, \delta_{mn}\right) \phi_n^*(\boldsymbol{r}) \phi_m(\boldsymbol{r}),$$

with $\delta V_{mn} \coloneqq \langle \phi_m, \delta V \phi_n \rangle$ **and** $\delta\varepsilon_{\mathrm{F}} = \dfrac{\displaystyle\sum_{n=1}^{+\infty} f_n' \delta V_{nn}}{\displaystyle\sum_{n=1}^{+\infty} f_n'}$ **to satisfy** $\displaystyle\int_\Omega \delta\rho(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} = 0$

For periodic Schrödinger-like operators $H = -\frac{1}{2}\Delta + V$ in 3D,

$$\varepsilon_n \underset{n\to\infty}{\sim} Cn^{2/3} \qquad \textbf{(Weyl formula)}$$



In most applications (always except in Warm Dense Matter),

only a number $N \gtrsim N_{\rm el}$ of occupation numbers f_n are non-negligible

$$\rho(\boldsymbol{r}) \simeq \sum_{n=1}^{N} f_n |\phi_n(\boldsymbol{r})|^2$$

$$\delta\rho(\boldsymbol{r}) \simeq \left(\sum_{n=1}^{N}\sum_{m=1}^{+\infty} + \sum_{n=1}^{+\infty}\sum_{m=1}^{N}\right) \frac{f_n - f_m}{\varepsilon_n - \varepsilon_m} \left(\delta V_{mn} - \delta\varepsilon_F \delta_{mn}\right) \phi_n^*(\boldsymbol{r})\phi_m(\boldsymbol{r})$$

but still one infinite sum in the sum-over-state formula

Alternatives to the sum-over-state formula

$$\rho(\boldsymbol{r}) \simeq \sum_{n=1}^{N} f_n \left|\phi_n(\boldsymbol{r})\right|^2 \quad \Rightarrow \quad \delta\rho(\boldsymbol{r}) \simeq \sum_{n=1}^{N} f_n(\phi_n^*(\boldsymbol{r})\delta\phi_n(\boldsymbol{r}) + \delta\phi_n^*(\boldsymbol{r})\phi_n(\boldsymbol{r})) + \delta f_n \left|\phi_n(\boldsymbol{r})\right|^2$$

the $\delta\phi_n$'s and the δf_n's are not unique (gauge invariance)

Let P: orthogonal projector on $\mathrm{Span}(\phi_n)_{1\leq n\leq N}$, and $Q := 1 - P$. We have

$$\delta\phi_n = \underbrace{\delta\phi_n^P}_{\in \mathrm{Ran}(P)} + \underbrace{\delta\phi_n^Q}_{\in \mathrm{Ran}(Q)}$$

and

$$\forall 1 \leqslant n \leqslant N, \quad f_n\delta\phi_n = \sum_{m=1}^{N} \Gamma_{mn}\phi_m + f_n\delta\phi_n^Q \quad \textbf{with} \quad \Gamma_{mn} := f_n \left\langle \phi_m, \delta\phi_n \right\rangle$$

Thus

$$\delta\rho(\boldsymbol{r}) \simeq \sum_{n,m=1}^{N} \left(\Gamma_{mn} + \overline{\Gamma_{nm}}\right) \phi_n^*(\boldsymbol{r})\phi_m(\boldsymbol{r}) + \sum_{n=1}^{N} 2f_n \mathrm{Re}\left(\phi_n^*(\boldsymbol{r})\delta\phi_n^Q(\boldsymbol{r})\right) + \sum_{n=1}^{N} \delta f_n \left|\phi_n(\boldsymbol{r})\right|^2$$

Alternatives to the sum-over-state formula (continued)

$$\delta\rho(\boldsymbol{r}) \simeq \sum_{n,m=1}^{N} \left(\Gamma_{mn} + \overline{\Gamma_{nm}}\right) \phi_n^*(\boldsymbol{r})\phi_m(\boldsymbol{r}) + \sum_{n=1}^{N} 2f_n \mathrm{Re}\left(\phi_n^*(\boldsymbol{r})\delta\phi_n^Q(\boldsymbol{r})\right) + \sum_{n=1}^{N} \delta f_n \left|\phi_n(\boldsymbol{r})\right|^2$$

$$= \left(\sum_{n=1}^{N}\sum_{m=1}^{+\infty} + \sum_{n=1}^{+\infty}\sum_{m=1}^{N}\right) \frac{f_n - f_m}{\varepsilon_n - \varepsilon_m} \left(\delta V_{mn} - \delta\varepsilon_{\mathrm{F}}\,\delta_{mn}\right) \phi_n^*(\boldsymbol{r})\phi_m(\boldsymbol{r})$$

By identification, we get that

1. the Γ_{mn}'s and the δf_n's must satisfy

$$\begin{cases} 2\mathrm{Re}(\Gamma_{nn}) + \delta f_n = f_n'(\delta V_{nn} - \varepsilon_{\mathrm{F}}) & \textbf{for } m = n \\ \Gamma_{mn} + \overline{\Gamma_{nm}} = \Delta_{mn} := \dfrac{f_n - f_m}{\varepsilon_n - \varepsilon_m}\delta V_{mn} & \textbf{for } m \neq n \end{cases} \longrightarrow \textbf{gauge choice needed}$$

2. the $\delta\phi_n^Q$'s must satisfy the Sternheimer equations

$$Q(H - \varepsilon_n)Q\delta\phi_n^Q = b_n := -Q(\delta V \phi_n) \longrightarrow \textbf{possibly ill-conditioned}$$

Gauge choice for the Γ_{mn}'s and the δf_n's

$2\mathrm{Re}(\Gamma_{nn})+\delta f_n = f'_n(\delta V_{nn}-\varepsilon_\mathrm{F})$ **and** $\Gamma_{mn}+\overline{\Gamma_{nm}} = \Delta_{mn}$ **with** $\Delta_{mn} = \overline{\Delta_{nm}}$ **if** $m \neq n$

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Natural (and good!) gauge choice for the Γ_{nn}'s ($m = n$) and the δf_n's

$$\Gamma_{nn} = 0 \quad \textbf{and} \quad \delta f_n = f_n'(\delta V_{nn} - \varepsilon_\mathrm{F})$$

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Possible gauge choices for the Γ_{mn}'s ($m \neq n$)

1. orthonormal gauge: impose $\delta\langle\phi_m, \phi_n\rangle = 0$

$$\Gamma_{mn}^{\mathrm{orth}} = \frac{f_n}{\varepsilon_n - \varepsilon_m}\delta V_{mn}$$ **(natural but very bad as the $\Gamma_{mn}^{\mathrm{orth}}$ may blow up)**

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$2\mathrm{Re}(\Gamma_{nn})+\delta f_n = f'_n(\delta V_{nn}-\varepsilon_\mathrm{F})$ **and** $\Gamma_{mn}+\overline{\Gamma_{nm}} = \Delta_{mn}$ **with** $\Delta_{mn} = \overline{\Delta_{nm}}$ **if** $m \neq n$

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2. gauges used in Abinit and Quantum Espresso

$$\Gamma^{\mathrm{Abinit}}_{mn} = \mathbb{1}_{f_n>f_m}\Delta_{mn}, \qquad \Gamma^{\mathrm{QE}}_{mn} = \frac{\Delta_{mn}}{1+e^{(\varepsilon_n-\varepsilon_m)/T}}$$

Gauge choice for the Γ_{mn}'s and the δf_n's

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3. simple gauge and minimal gauge (used in DFTK)

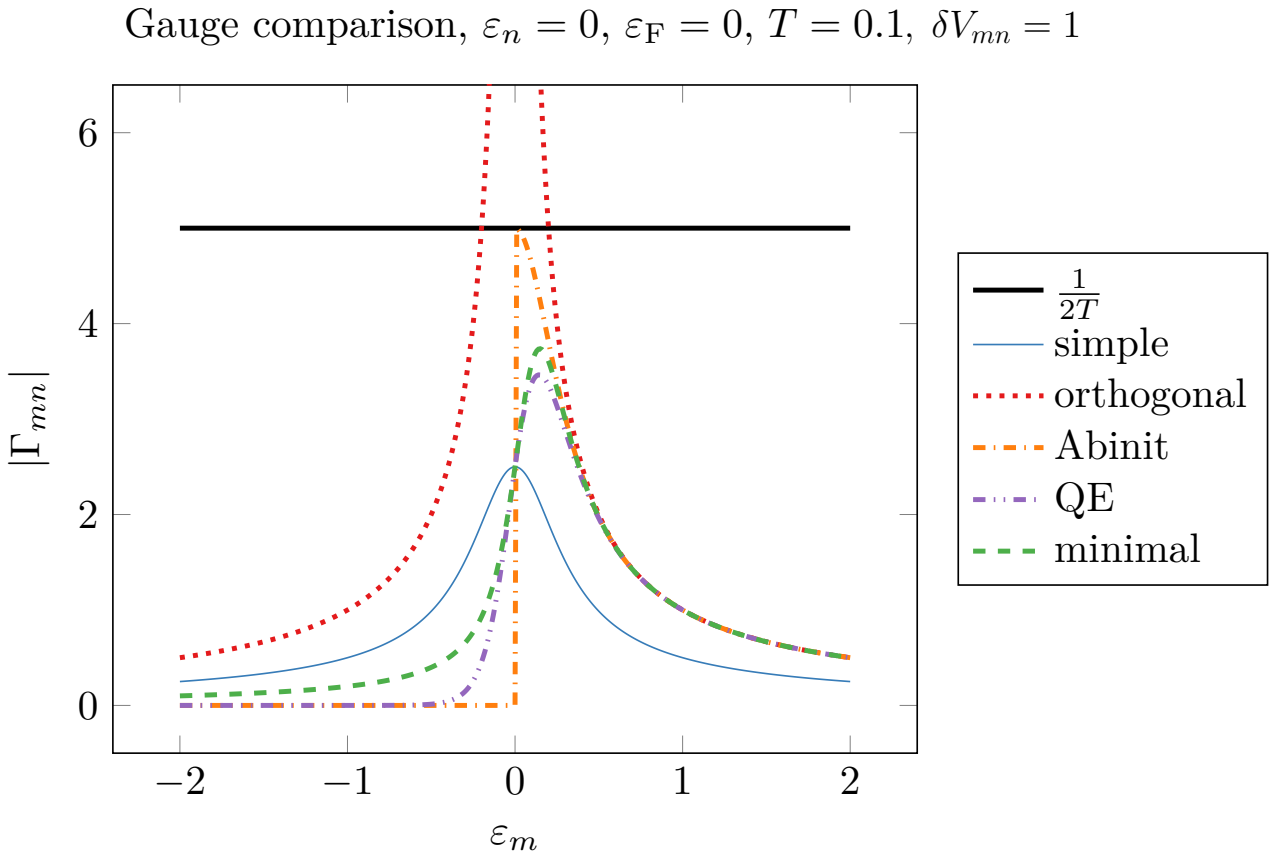
$$\Gamma_{mn}^{\mathrm{simple}} = \frac{1}{2}\Delta_{mn} = \underset{\Gamma_{mn}+\overline{\Gamma_{nm}}=\Delta_{mn}}{\mathrm{argmin}} |\Gamma_{mn}|^2 + \left|\overline{\Gamma_{nm}}\right|^2, \quad \Gamma_{mn}^{\mathrm{min}} = \frac{f_n^2}{f_m^2+f_n^2}\Delta_{mn} = \underset{\Gamma_{mn}+\overline{\Gamma_{nm}}=\Delta_{mn}}{\mathrm{argmin}} \frac{1}{f_n^2}|\Gamma_{mn}|^2 + \frac{1}{f_m^2}\left|\overline{\Gamma_{nm}}\right|^2$$

Gauge choice for the Γ_{mn}'s and the δf_n's

For all these gauge choices but the orthogonal one, we have

$$|\Gamma_{mn}| \leqslant |\Delta_{mn}| \leqslant \max_{x\in\mathbb{R}} \frac{1}{T} |f'(x)| \, |\delta V_{mn}| = \frac{1}{2T} |\delta V_{mn}| \, . \tag{1}$$

If we make an error on δV, it is at most amplified by a factor of $\frac{1}{2T}$



Solving the Sternheimer equation $Q(H-\varepsilon_n)Q\,\delta\phi_n^Q = b_n$

Output of the numerical diagonalization iterative scheme (ex. LOBPCG) used to compute the density

- N **fully converged orthonormal eigenmodes** $(\varepsilon_n, \phi_n)_{1\leq n\leq N}$

  $\Phi := (\phi_1, \cdots, \phi_N)$ **orthonormal basis of** $\mathrm{Ran}(P) = \mathrm{Ker}(Q)$

- N_{ex} **extra, only partially converged, orthonormal eigenvectors**

  $\Phi_{\mathrm{ex}} := (\phi^\ell_{N+1}, \ldots, \phi^\ell_{N+N_{\mathrm{ex}}})$, ℓ : **# of iter. of the diagonalization scheme**

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We can assume without loss of generality that

- $(\Phi, \Phi_{\mathrm{ex}})$ **is an orthonormal family**
- $\Phi^*_{\mathrm{ex}} H_\rho \Phi_{\mathrm{ex}} \in \mathbb{C}^{N_{\mathrm{ex}}\times N_{\mathrm{ex}}}$ **is a diagonal matrix whose elements are labelled** $\varepsilon^\ell_m := \langle \phi^\ell_m, H\phi^\ell_m\rangle$ **for** $N+1 \leqslant m \leqslant N+N_{\mathrm{ex}}$
- $(\phi^\ell_m, \varepsilon^\ell_m) \underset{\ell\to\infty}{\longrightarrow} (\phi_m, \varepsilon_m)$

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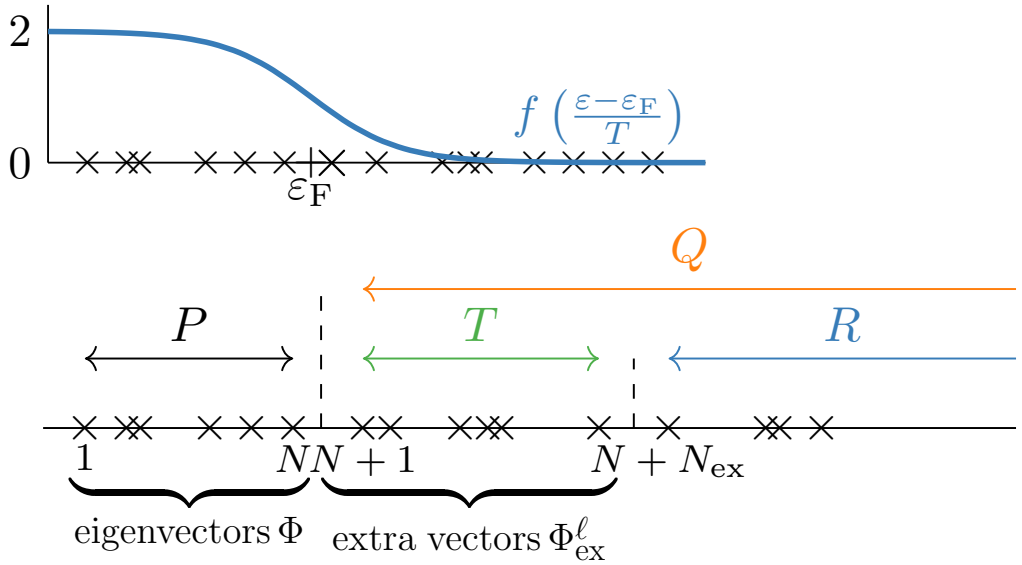
Let's use these extra approximate eigenvectors to improve the computation of response properties!

Solving the Sternheimer equation $Q(H-\varepsilon_n)Q\,\delta\phi_n^Q = b_n$ (continued)

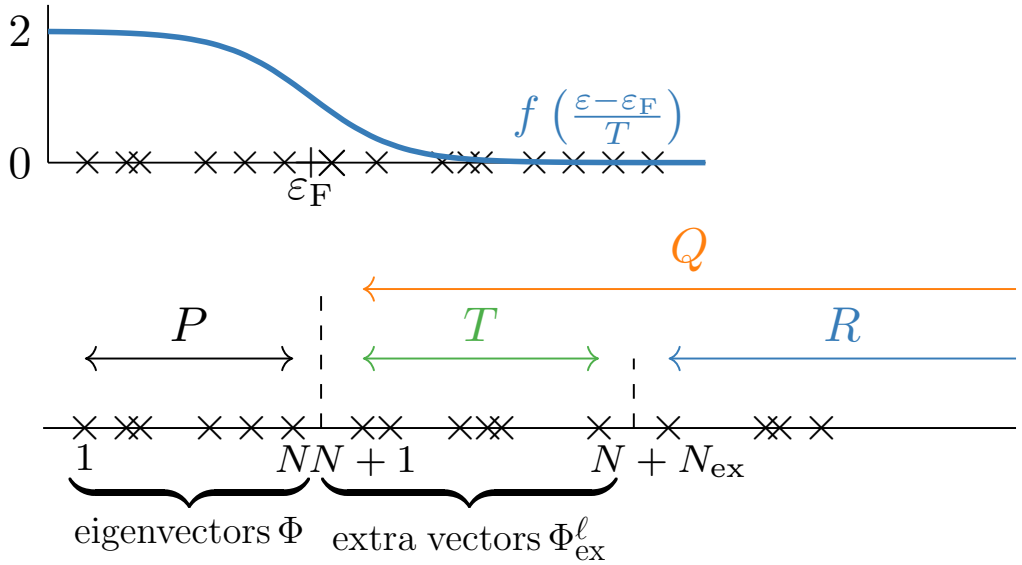


Schur complement method

$$\delta\phi_n^Q = \underbrace{\Phi_{ex}\alpha_n}_{\in \mathrm{Ran}(T)} + \underbrace{\delta\phi_n^R}_{\in \mathrm{Ran}(R)}, \qquad n \le N$$

$$\overbrace{\begin{pmatrix} \Phi_{ex}^*(H-\varepsilon_n)\Phi_{ex} & \Phi_{ex}^* H R \\ R H \Phi_{ex} & \underbrace{R(H-\varepsilon_n)R}_{\text{coercive, large, but well-conditioned}} \end{pmatrix}}^{\text{coercive, ill-conditioned, but small}} \begin{pmatrix} \alpha_n \\ \delta\phi_n^R \end{pmatrix} = \begin{pmatrix} \Phi_{ex}^* b_n \\ R\, b_n \end{pmatrix}$$

Solving the Sternheimer equation $Q(H-\varepsilon_n)Q\,\delta\phi_n^Q = b_n$ (continued)



Schur complement method

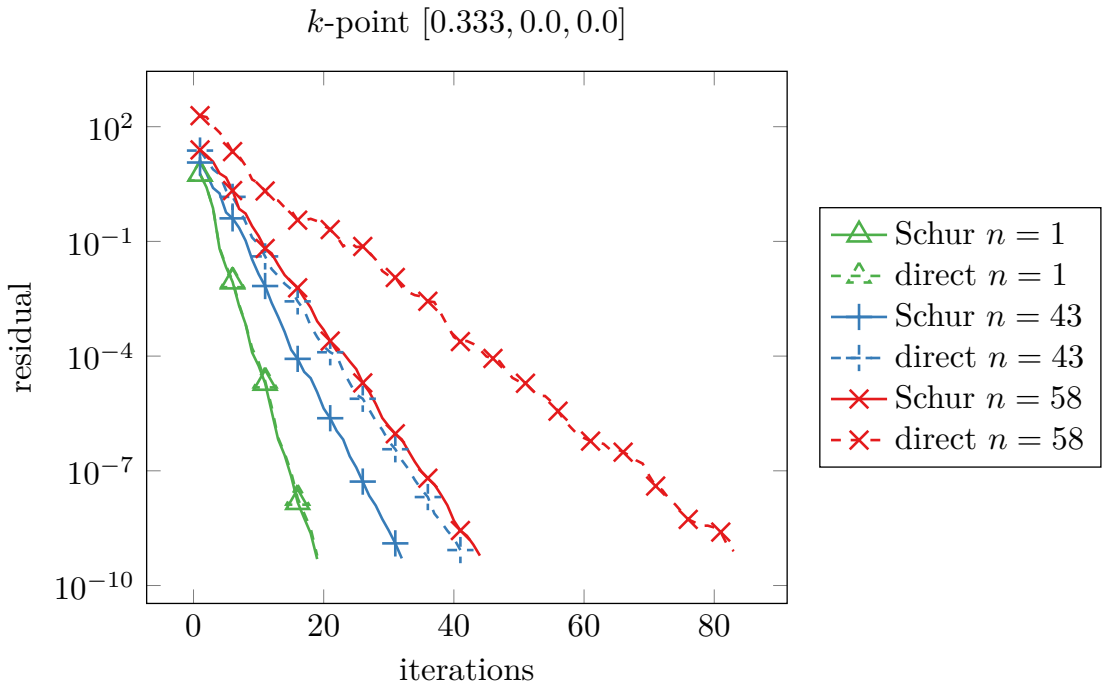
$$\delta\phi_n^Q = \underbrace{\Phi_{ex}\alpha_n}_{\in \mathrm{Ran}(T)} + \underbrace{\delta\phi_n^R}_{\in \mathrm{Ran}(R)}\,, \qquad n \le N$$

$$A_n := \left(\Phi_{ex}^*(H-\varepsilon_n)\Phi_{ex}\right)^{-1}, \quad \alpha_n = A_n\left(\Phi_{ex}^* b_n - \Phi_{ex}^*(H-\varepsilon_n)\delta\phi_n^R\right)$$

$$\left[R(H-\varepsilon_n)\left(1-\Phi_{ex}A_n\Phi_{ex}^*(H-\varepsilon_n)\right)R\right]\,\delta\phi_n^R = Rb_n - R(H-\varepsilon_n)\Phi_{ex}A_n\Phi_{ex}^* b_n$$

Numerical results: convergence of the Sternheimer solver for Al_{40}

k-point – coordinate	$[0, 0, 0]$	$[1/3, 0, 0]$	$[1/3, 1/3, 0]$
N	69	58	67
$\varepsilon_{N+1} - \varepsilon_N$	0.0320	0.0134	0.0217
# CG iterations $n = N$ Schur	48	**44**	41
# CG iterations $n = N$ direct	56	**83**	58



Conclusion

Error bounds for DFT

- guaranteed, optimal, cheap error bounds on the ground-state energy and density for linear Schrödinger equations
- practical (not guaranteed), optimal, cheap error bounds on the ground-state energy and density for DFT
- practical (not guaranteed), quite accurate, not too expensive error bounds for non-variational quantities such as forces for DFT

Error bounds for DFT

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- practical (not guaranteed), quite accurate, not too expensive error bounds for non-variational quantities such as forces for DFT

Response properties

- easy for insulators
- harder for metals
  - gauge choice is important

    we have clarified this point and proposed new, very simple gauges
  - the Sternheimer equation is ill-conditioned

    we have improved its resolution using a Schur complement method

Thank you for your attention