# Fully guaranteed and computable error bounds for the energy of Kohn–Sham equations with convex density functionals

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EMC2@Roscoff'24 – 04/07/2024



# Functional setting

- Periodic lattice $\mathcal{R} = \mathbb{Z}\boldsymbol{a}_1 + \mathbb{Z}\boldsymbol{a}_2 + \mathbb{Z}\boldsymbol{a}_3$ for $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$ a basis of $\mathbb{R}^3$.
- Unit cell $\Omega = [0,1)\boldsymbol{a}_1 + [0,1)\boldsymbol{a}_2 + [0,1)\boldsymbol{a}_3$.
- Reciprocal lattice $\mathcal{R}^* = \mathbb{Z}\boldsymbol{b}_1 + \mathbb{Z}\boldsymbol{b}_2 + \mathbb{Z}\boldsymbol{b}_3$ where $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}$.
- Hilbert space $\mathcal{H} = \mathrm{L}^2_{\#}(\Omega)$, with scalar product $\langle \cdot, \cdot \rangle$.
- Orthonormal basis of $\mathcal{H}$ given by Fourier modes:

$$\mathcal{H} := \left\{ u \in \mathrm{L}^2_{\mathrm{loc}}(\mathbb{R}^3),\ u \text{ is } \mathcal{R}\text{-periodic} \right\} = \mathrm{Span}\left\{ r \mapsto e_{\boldsymbol{G}}(\boldsymbol{r}) := \frac{1}{\sqrt{|\Omega|}} \mathrm{e}^{\imath \boldsymbol{G}\cdot\boldsymbol{r}},\ \boldsymbol{G} \in \mathcal{R}^* \right\}$$

- Sobolev spaces:

$$\forall\ s \in \mathbb{R}, \quad \mathrm{H}^s_{\#}(\Omega) := \left\{ u(x) = \sum_{\boldsymbol{G}\in\mathcal{R}^*} \hat{u}_{\boldsymbol{G}} e_{\boldsymbol{G}}(x),\ \sum_{\boldsymbol{G}\in\mathcal{R}^*} \left(1 + \frac{|\boldsymbol{G}|^2}{2}\right)^s |\hat{u}_{\boldsymbol{G}}|^2 < +\infty,\ \hat{u}_{-\boldsymbol{G}} = \hat{u}^*_{\boldsymbol{G}} \right\}$$

# Quantum mechanics of a single electron

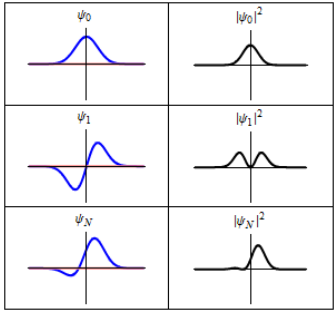
In atomic units, with no spin, we look at the PDE in $\psi(\cdot, t) \in \mathcal{H}$

$$\imath \partial_t \psi(x,t) = \underbrace{-\frac{1}{2}\Delta}_{\text{kinetic operator}} \psi(x,t) + \underbrace{V(x)}_{\substack{\text{potential} \\ \text{(time-independent)}}} \psi(x,t) =: (\underbrace{h}_{\text{Hamiltonian}} \psi)(x,t)$$

- $\|\psi(\cdot, t)\| = 1$.
- Stationary states $\psi(x,t) = \mathrm{e}^{-\imath \varepsilon t} \varphi(x)$ where

$$\begin{cases} h\varphi = \varepsilon \varphi, \\ \|\varphi\| = 1. \end{cases}$$

- Ground-state energy: $E_\star = \min_{\|\varphi\|=1} \langle \varphi, h\varphi \rangle$.
- Ground-state density: $\rho_\star(x) = |\varphi(x)|^2$.



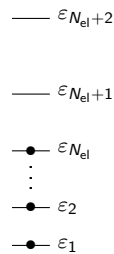

(Wikipedia)

# Quantum mechanics of noninteracting electrons

Consider a system of $N_{\mathrm{el}}$ *noninteracting* electrons:

- Pauli exclusion principle $\rightsquigarrow$ two electrons cannot be in the same quantum state.
- Ground-state $\rightsquigarrow$ electrons fill the $N_{\mathrm{el}}$ lowest energy states (*Aufbau* principle).

$$\begin{cases} h\varphi_i = \varepsilon_i \varphi_i, \quad \varepsilon_1 \leq \cdots \leq \varepsilon_{N_{\mathrm{el}}}, \\ \langle \varphi_i, \varphi_j \rangle = \delta_{ij}, \end{cases} \qquad h := -\frac{1}{2}\Delta + V.$$




- Ground-state energy: $E_\star = \displaystyle\sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_i$.
- Ground-state density: $\rho_\star(x) = \displaystyle\sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i(x)|^2$, with $\displaystyle\int_\Omega \rho_\star(x)\mathrm{d}x = N_{\mathrm{el}}$.

# Density matrices

Orbitals $(\varphi_i)_{1\leq n\leq N_{\mathrm{el}}}$ are not unique (degeneracies) $\rightsquigarrow$ better to work with the *orthogonal projector* onto the space they span :

$$\gamma_\star = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i\rangle\langle\varphi_i|, \quad \mathrm{Ran}(\gamma_\star) = \mathrm{Span}(\varphi_i)_{1\leq n\leq N_{\mathrm{el}}},$$

$$\rho_\star(x) = \gamma_\star(x,x).$$

- $\gamma_\star$ is a rank $N_{\mathrm{el}}$ orthogonal projector (*density matrix*):

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

- The ground-state energy reads

$$E_\star = \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_i = \sum_{i=1}^{N_{\mathrm{el}}} \langle\varphi_i, h\varphi_i\rangle = \sum_{i=1}^{N_{\mathrm{el}}} \mathrm{Tr}(h|\varphi_i\rangle\langle\varphi_i|) = \mathrm{Tr}(h\gamma_\star)$$

and moreover $\mathrm{Tr}(h\gamma_\star) = \min_{\gamma\in\mathcal{M}_{N_{\mathrm{el}}}} \mathrm{Tr}(h\gamma)$.

$$\begin{cases} h\varphi_i = \varepsilon_i\varphi_i, \quad \varepsilon_1 \leq \cdots \leq \varepsilon_{N_{\mathrm{el}}}, \\ \langle\varphi_i,\varphi_j\rangle = \delta_{ij}. \end{cases}$$

## Notations for $\gamma \in \mathcal{M}_{N_{\mathrm{el}}}$

If $\psi \in \mathcal{H} = \mathrm{Ran}(\gamma) \oplus \mathrm{Ran}(1-\gamma)$,

$$\gamma\psi = \sum_{i=1}^{N_{\mathrm{el}}} \langle\varphi_i,\psi\rangle\varphi_i = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i\rangle\langle\varphi_i|\psi\rangle$$

$$\gamma(x,y) = \sum_{i=1}^{N_{\mathrm{el}}} \varphi_i(x)\varphi_i^*(y).$$

# Interacting electrons and DFT

General form of the energy

$$E(\gamma) := \underbrace{\mathrm{Tr}\,(h\gamma)}_{\text{linear term}} + \underbrace{F(\rho_\gamma)}_{\text{nonlinear term}}$$

- $\gamma \in \mathcal{M}_{N_{\mathrm{el}}}$ is a trial density matrix;
- $h = -\frac{1}{2}\Delta + V$ is the core Hamiltonian;
- $F$ models the electron-electron interaction and depends only on the electronic density $\rho_\gamma$.

**General framework:**

$$\min_{\gamma \in \mathcal{M}_{N_{\mathrm{el}}}} \mathrm{Tr}(h\gamma) + F(\rho_\gamma)$$

## Density functional theory (DFT)

$$F(\rho_\gamma) = \frac{1}{2}\mathcal{D}(\rho_\gamma, \rho_\gamma) + E_{\mathrm{xc}}(\rho_\gamma)$$

where $\rho_\gamma(x) = \gamma(x, x)$ and

$$\mathcal{D}(\rho, \rho) = \iint_{\Omega\times\Omega} \frac{\rho(x)\rho(y)}{|x-y|}\mathrm{d}x\mathrm{d}y.$$

# Kohn–Sham equations

## Linearization

For every $\gamma \in \mathcal{M}_{N_{\mathrm{el}}}$, there exists (under reasonable assumptions) $V_{\rho_\gamma} \in L^\infty_\#(\Omega)$ such that

$$\forall\, \hat{\gamma} \in \mathcal{M}_{N_{\mathrm{el}}}, \quad \langle F'(\rho_\gamma), \rho_{\hat{\gamma}} \rangle_{\mathcal{H}',\mathcal{H}} = \mathrm{Tr}(V_{\rho_\gamma} \hat{\gamma}).$$

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## First order optimality conditions

Find $(\varphi_i, \varepsilon_i)_{i=1,\dots,N_{\mathrm{el}}} \in (\mathrm{H}^1_\#(\Omega) \times \mathbb{R})^{N_{\mathrm{el}}}$ such that

Kinetic energy and external potential

$$\begin{cases} H_{\rho_\gamma} \varphi_i := \left(-\frac{1}{2}\Delta + V\right) \varphi_i + V_{\rho_\gamma}\, \varphi_i = \varepsilon_i \varphi_i, \quad \varepsilon_1 \leqslant \varepsilon_2 \leqslant \cdots \leqslant \varepsilon_{N_{\mathrm{el}}}, \\ \langle \varphi_i, \varphi_j \rangle = \delta_{ij}, \\ \gamma = \displaystyle\sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i\rangle\langle\varphi_i|. \end{cases}$$

Nonlinear term coming from the e-e interaction
$V_\rho(x) = V_{\mathrm{H}}[\rho] + V_{\mathrm{xc}}[\rho]$.

## Kohn–Sham Hamiltonian

$$H_{\rho_\gamma} := h + V_{\rho_\gamma}$$

# Discretization

- Finite dimensional subspace of $H^1_{\#}(\Omega)$: for $N \in \mathbb{R}$,

$$\mathcal{V}_N = \mathrm{Span}\,\{e_{\boldsymbol{G}},\ |\boldsymbol{G}| \leq N\}.$$

- Galerkin approximation

$$\boxed{\min\left\{E(\gamma),\ \ \gamma \in \mathcal{M}_{N_{\mathrm{el}}},\ \mathrm{Ran}(\gamma) \subset \mathcal{V}_N\right\}}$$

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## Discrete Kohn–Sham equations

Find $(\varphi_{i,N}, \varepsilon_{i,N})_{i=1,\dots,N_{\mathrm{el}}} \in (\mathcal{V}_N \times \mathbb{R})^{N_{\mathrm{el}}}$ such that

$$\begin{cases} \Pi_N H_{\rho_{\gamma_N}} \Pi_N \varphi_{i,N} = \varepsilon_{i,N} \varphi_{i,N}, \quad \varepsilon_{1,N} \leqslant \varepsilon_{2,N} \leqslant \cdots \leqslant \varepsilon_{N_{\mathrm{el}},N}, \\ \langle \varphi_{i,N}, \varphi_{j,N} \rangle = \delta_{ij}, \\ \gamma_N = \displaystyle\sum_{i=1}^{N_{\mathrm{el}}} |\varphi_{i,N}\rangle\langle\varphi_{i,N}|. \end{cases}$$

# Self-consistent field (SCF) iterations

## SCF iterations

$$\begin{cases} \Pi_N H_{\rho_{\gamma_{N,m}}} \Pi_N \varphi_{i,N,m+1} = \varepsilon_{i,N,m+1} \varphi_{i,N,m+1}, \quad \varepsilon_{1,N,m+1} \leqslant \varepsilon_{2,N,m+1} \leqslant \cdots \leqslant \varepsilon_{N_{\mathrm{el}},N,m+1}, \\ \langle \varphi_{i,N,m+1}, \varphi_{j,N,m+1} \rangle = \delta_{ij}, \\ \gamma_{N,m} = \displaystyle\sum_{i=1}^{N_{\mathrm{el}}} |\varphi_{i,N,m+1}\rangle\langle\varphi_{i,N,m+1}|. \end{cases}$$

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- Does not converge most of the time.
- Lost of tricks should be used: mixing, preconditionning, acceleration, ...
- Arise from a minimization problem $\rightsquigarrow$ more and more applications coming from Riemanian optimization, not considered here.

# Problem formulation and existing results

## Questions

- Can we upper bound $E(\gamma_{N,m}) - E(\gamma)$ by *computable* quantities ? They should depend on $N$ and $m$ and go to 0 as $N, m \to +\infty$.
- Are these bounds satisfactory ? How to use them in practice ?

## Two main difficulties

- Cluster of eigenvalues.
- Nonlinearity of the energy functional.

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- Can we upper bound $E(\gamma_{N,m}) - E(\gamma)$ by *computable* quantities ? They should depend on $N$ and $m$ and go to 0 as $N, m \to +\infty$.
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## Two main difficulties

- Cluster of eigenvalues.
- Nonlinearity of the energy functional.

- Error control for eigenvalues of linear operators is already well established. (Kato–Temple bound, Forsythe (1954), Weinberger (1956), Bazley and Fox (1961), Hu, Huang, Lin and Shen (2014), Larson (2000), Liu (2015))
- Electronic structure. (works by Cancès, Dusson, Maday, Stamm, Vohralik, Levitt, Herbst...)
- Fewer results for nonlinear models. (Gross–Pitaevskii, see Maday and Dusson (2017), see also Chen, He and Zhou (2011))
- Nonguaranteed bounds for nonlinear models and quantities of interest. (Cancès, Dusson, Kemlin, Levitt (2022))
- Dusson and Maday, *An overview of a posteriori error estimation and post-processing methods for nonlinear eigenvalue problems*, JCP 491 (2023).
- Adaptive methods. (Dai, Pan, Yang and Zhou (2021) for linear eigenvalue problems with plane-wave discretization or Liu, Chen, Dusson, Fang and Gao (2022) for a recent application to Kohn–Sham models, see also Hassan, Maday and Wang (2024))

**Lemma**

For any $\mu \in \mathbb{R}$, any $\gamma_1, \gamma_2 \in \mathcal{M}_{N_{\mathrm{el}}}$, it holds

$$E(\gamma_2) - E(\gamma_1) = \mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_2\right) - \mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_1\right) - \left(F(\rho_{\gamma_1}) - F(\rho_{\gamma_2}) - \langle F'(\rho_{\gamma_2}), \rho_{\gamma_1} - \rho_{\gamma_2}\rangle_{\mathcal{H}',\mathcal{H}}\right)$$

**Proof:**

- For any $\mu \in \mathbb{R}$, $\mathrm{Tr}(\mu\gamma_1) = \mu N_{\mathrm{el}} = \mathrm{Tr}(\mu\gamma_2)$.
- $\langle F'(\rho_{\gamma_2}), \rho_{\gamma_1} - \rho_{\gamma_2}\rangle_{\mathcal{H}',\mathcal{H}} = \mathrm{Tr}\left(V_{\rho_{\gamma_2}}(\gamma_1 - \gamma_2)\right)$.

# *A posteriori* analysis

**Assumption**

The nonlinearity $F$ is convex: $\forall\ \gamma_1, \gamma_2 \in \mathcal{M}_{N_{\mathrm{el}}}$,

$$F(\rho_{\gamma_1}) - F(\rho_{\gamma_2}) - \langle F'(\rho_{\gamma_2}), \rho_{\gamma_1} - \rho_{\gamma_2} \rangle_{\mathcal{H}',\mathcal{H}} \leq 0.$$

**Convex models in KS-DFT**

- rHF is convex $F(\rho) = \frac{1}{2}\mathcal{D}(\rho, \rho)$.
- LDA is not $E_{\mathrm{xc}}(\rho) = -c \int_\Omega \rho^{4/3}$.

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**Corollary**

For any $\mu \in \mathbb{R}$, any $\gamma_1, \gamma_2 \in \mathcal{M}_{N_{\mathrm{el}}}$, it holds

$$E(\gamma_2) - E(\gamma_1) \leq \mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_2\right) - \mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_1\right).$$

Moreover, if we choose $\mu \in \mathbb{R}$ such that $\mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_1\right) \geq 0$, then

$$\boxed{E(\gamma_2) - E(\gamma_1) \leq \mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_2\right)}$$

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**Goal:** find $\mu \in \mathbb{R}$ such that $\mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_1\right) \geq 0$.

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**Goal:** find $\mu \in \mathbb{R}$ such that $\mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_1\right) \geq 0$.

**Strategy / Ideas :**

- We aim to apply this bound along SCF iterations, that is $\gamma_2 = \gamma_{N,m}$ and $\gamma_1 = \gamma$, the *exact* ground-state density matrix on $\mathcal{M}_{N_{\mathrm{el}}}$.
- Then, the upper bound does not rely on $\gamma$.
- To derive such a $\mu$, one actually needs to study the linear operator $A = h + V_{\rho_{\gamma_{N,m}}} = H_{\rho_{\gamma_{N,m}}}$.

# Choosing $\mu$

Let $A$ be a general self-adjoint linear operator on $\mathcal{H}$, bounded below and with compact resolvent.

**Infinite dimensional problem**

$$\begin{cases} A\varphi_i = \varepsilon_i \varphi_i, \quad \varepsilon_1 \leqslant \varepsilon_2 \leqslant \cdots \leqslant \varepsilon_{N_{\mathrm{el}}} \\ \langle \varphi_i, \varphi_j \rangle = \delta_{ij}, \\ \gamma^0 = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_i\rangle\langle\varphi_i|, \end{cases}$$

**Variational approximation**

$$\begin{cases} \Pi_N A \Pi_N \varphi_{i,N} = \varepsilon_{i,N} \varphi_{i,N}, \quad \varepsilon_{1,N} \leqslant \varepsilon_{2,N} \leqslant \cdots \leqslant \varepsilon_{N_{\mathrm{el}},N} \\ \langle \varphi_{i,N}, \varphi_{j,N} \rangle = \delta_{ij}, \\ \gamma_N^0 = \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_{i,N}\rangle\langle\varphi_{i,N}|. \end{cases}$$

[1] 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).

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## Theorem[1]

It holds

$$0 \leq \sum_{i=1}^{N_{\mathrm{el}}} (\varepsilon_{i,N} - \varepsilon_i) \leq \eta^2$$

where, for $r_{i,N} = A\varphi_{i,N} - \varepsilon_{i,N}\varphi_{i,N}$,

$$\eta^2 = \sum_{i=1}^{N_{\mathrm{el}}} \langle r_{i,N}, A^{-1} r_{i,N} \rangle + 2\varepsilon_{N_{\mathrm{el}},N} c_N^2 \sum_{i=1}^{N_{\mathrm{el}}} \langle A^{-1} r_{i,N}, A^{-1} r_{i,N} \rangle$$

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- $A > 0$
- Continuous-discrete gap condition

$$\varepsilon_{N_{\mathrm{el}}} \leq \varepsilon_{N_{\mathrm{el}},N} < \underline{\varepsilon_{N_{\mathrm{el}}+1}} \leq \varepsilon_{N_{\mathrm{el}}+1} \leq \varepsilon_{N_{\mathrm{el}}+1,N}$$

- Fully computable constant:

$$c_N \coloneqq \left(1 - \frac{\varepsilon_{N_{\mathrm{el}},N}}{\underline{\varepsilon_{N_{\mathrm{el}}+1}}}\right)^{-1}$$

- Beware of the gap!
- $A > -\frac{1}{2}\Delta + 1$ would not help.

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$$0 \leq \sum_{i=1}^{N_{\mathrm{el}}} (\varepsilon_{i,N} - \varepsilon_i) \leq \eta^2 \quad \Leftrightarrow \quad \mu \coloneqq \frac{1}{N_{\mathrm{el}}} \left( \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_{i,N} - \eta^2 \right) \leq \frac{1}{N_{\mathrm{el}}} \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_i$$

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$$0 \leq \sum_{i=1}^{N_{\mathrm{el}}} (\varepsilon_{i,N} - \varepsilon_i) \leq \eta^2 \quad \Leftrightarrow \quad \mu := \frac{1}{N_{\mathrm{el}}} \left( \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_{i,N} - \eta^2 \right) \leq \frac{1}{N_{\mathrm{el}}} \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_i$$

- $\gamma^0$ minimises $\gamma \mapsto \mathrm{Tr}(A\gamma)$ over $\mathcal{M}_{N_{\mathrm{el}}}$.
- For any $\gamma \in \mathcal{M}_{N_{\mathrm{el}}}$,

$$\mathrm{Tr}\left((A-\mu)\gamma\right) \geq \mathrm{Tr}(A\gamma_0) - \mu N_{\mathrm{el}} \geq \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_i - \sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_i = 0.$$

- Such a $\mu$ therefore satisfies

$$\forall\, \gamma \in \mathcal{M}_{N_{\mathrm{el}}}, \quad \mathrm{Tr}\left((A-\mu)\gamma\right) \geq 0.$$

# Fully guaranteed error bounds on the energy

- Recall $E(\gamma_2) - E(\gamma_1) \leq \mathrm{Tr}\left((h + V_{\rho_{\gamma_2}} - \mu)\gamma_2\right)$ and take $\gamma_2 = \gamma_{N,m}$ and $\gamma_1 = \gamma$.
- Apply the previous strategy to $A = H_{N,m} \coloneqq H_{\rho_{\gamma_{N,m}}}$.
- This gives, with $\mu_{N,m+1} = \dfrac{1}{N_{\mathrm{el}}}\left(\displaystyle\sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_{i,N,m+1} - \eta^2\right)$ computed from the eigendecomposition of $H_{N,m}$:

$$E(\gamma_{N,m}) - E(\gamma) \leq \mathrm{Tr}\left((H_{N,m} - \mu_{N,m+1})\gamma_{N,m}\right)$$

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$$E(\gamma_{N,m}) - E(\gamma) \leq \mathrm{Tr}\left((H_{N,m} - \mu_{N,m+1})\gamma_{N,m}\right)$$

## Theorem

At iteration $m$ of the SCF in $\mathcal{V}_N$, it holds

$$\boxed{E(\gamma_{N,m}) - E(\gamma) \leq \mathtt{err}_{N,m}^{\mathrm{disc}} + \mathtt{err}_{N,m}^{\mathrm{SCF}}}$$

where

$$\mathtt{err}_{N,m}^{\mathrm{disc}} = \mathrm{Tr}\left((H_{N,m} - \mu_{N,m+1})\gamma_{N,m+1}\right) \quad \text{and} \quad \mathtt{err}_{N,m}^{\mathrm{SCF}} = \mathrm{Tr}(H_{N,m}\gamma_{N,m}) - \mathrm{Tr}(H_{N,m}\gamma_{N,m+1})$$

**Note:** $\mathtt{err}_{N,m}^{\mathrm{SCF}} \to 0$ as $m \to +\infty$ and $\mathtt{err}_{N,m}^{\mathrm{disc}} \to 0$ as $N \to +\infty$.

# Computing $\mu$

$$\mu \coloneqq \frac{1}{N_{\mathrm{el}}}\left(\sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_{i,N} - \eta^2\right) \quad \text{with} \quad \eta^2 = \sum_{i=1}^{N_{\mathrm{el}}} \langle r_{i,N}, A^{-1} r_{i,N}\rangle + 2\varepsilon_{N_{\mathrm{el}},N} c_N^2 \sum_{i=1}^{N_{\mathrm{el}}} \langle A^{-1} r_{i,N}, A^{-1} r_{i,N}\rangle$$

- Computing $A^{-1} r_{i,N}$ requires full inversion of the linear operator $A$.
- $\varphi_{i,N} \in \mathcal{V}_N \Rightarrow r_{i,N} = A\varphi_{i,N} - \varepsilon_{i,N}\varphi_{i,N} \in \mathcal{V}_N^\perp$ (*linear* eigenproblems are exactly solved).
- This suggests to decompose $\mathcal{H} = \mathcal{V}_N \oplus \mathcal{V}_N^\perp$ and write

$$A = H_0 + W \coloneqq \begin{bmatrix} \Pi_N h \Pi_N & 0 \\ 0 & \Pi_N^\perp(-\frac{1}{2}\Delta)\Pi_N^\perp \end{bmatrix} + \begin{bmatrix} 0 & \Pi_N V \Pi_N^\perp \\ \Pi_N^\perp V \Pi_N & \Pi_N^\perp V \Pi_N^\perp \end{bmatrix}$$

Thus, assuming $\|H_0^{-1} W\| < 1$, $A^{-1}$ is obtained by a Neumann series, involving only $H_0^{-1}$ = full inversion in $\mathcal{V}_N$ + diagonal inversion in $\mathcal{V}_N^\perp$:

$$A^{-1} = \sum_{n=1}^{+\infty} (-H_0^{-1} W)^n H_0^{-1}$$

# Computing $\mu$

$$\mu := \frac{1}{N_{\mathrm{el}}}\left(\sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_{i,N} - \eta^2\right) \quad \text{with} \quad \eta^2 = \sum_{i=1}^{N_{\mathrm{el}}} \langle r_{i,N}, A^{-1} r_{i,N}\rangle + 2\varepsilon_{N_{\mathrm{el}},N} c_N^2 \sum_{i=1}^{N_{\mathrm{el}}} \langle A^{-1} r_{i,N}, A^{-1} r_{i,N}\rangle$$

Write $A^{-1} = \sum_{n=1}^{+\infty} (-H_0^{-1} W)^n H_0^{-1}$ with $H_0 = \begin{bmatrix} \Pi_N h \Pi_N & 0 \\ 0 & \Pi_N^{\perp}(-\frac{1}{2}\Delta)\Pi_N^{\perp} \end{bmatrix}$ and $W = \begin{bmatrix} 0 & \Pi_N V \Pi_N^{\perp} \\ \Pi_N^{\perp} V \Pi_N & \Pi_N^{\perp} V \Pi_N^{\perp} \end{bmatrix}$

- zeroth order approximation

$$\eta_0^2 = \sum_{i=1}^{N_{\mathrm{el}}} \langle r_{i,N}, H_0^{-1} r_{i,N}\rangle + 2\varepsilon_{N_{\mathrm{el}},N} c_N^2 \sum_{i=1}^{N_{\mathrm{el}}} \langle H_0^{-1} r_{i,N}, H_0^{-1} r_{i,N}\rangle$$

- first order approximation

$$\eta_1^2 = \sum_{i=1}^{N_{\mathrm{el}}} \langle r_{i,N}, H_0^{-1} - H_0^{-1} W H_0^{-1} r_{i,N}\rangle + 2\varepsilon_{N_{\mathrm{el}},N} c_N^2 \sum_{i=1}^{N_{\mathrm{el}}} \langle H_0^{-1} - H_0^{-1} W H_0^{-1} r_{i,N}, H_0^{-1} - H_0^{-1} W H_0^{-1} r_{i,N}\rangle$$

# Computing $\mu$

$$\mu \coloneqq \frac{1}{N_{\mathrm{el}}}\Big(\sum_{i=1}^{N_{\mathrm{el}}} \varepsilon_{i,N} - \eta^2\Big) \quad \text{with} \quad \eta^2 = \sum_{i=1}^{N_{\mathrm{el}}} \langle r_{i,N}, A^{-1} r_{i,N}\rangle + 2\varepsilon_{N_{\mathrm{el}},N} c_N^2 \sum_{i=1}^{N_{\mathrm{el}}} \langle A^{-1} r_{i,N}, A^{-1} r_{i,N}\rangle$$

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$$\eta_0^2 = \sum_{i=1}^{N_{\mathrm{el}}} \langle r_{i,N}, H_0^{-1} r_{i,N}\rangle + 2\varepsilon_{N_{\mathrm{el}},N} c_N^2 \sum_{i=1}^{N_{\mathrm{el}}} \langle H_0^{-1} r_{i,N}, H_0^{-1} r_{i,N}\rangle$$

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$\rightsquigarrow$ Each $\eta$ yields a different bound.
$\rightsquigarrow$ Estimating the remainders of the Neumann series guarantees the bound.

# Overview of the different available bounds

| **Name** | **Notation** | **Fully guaranteed** | **Computational cost** |
|---|---|---|---|
| full inversion | $\eta$ | yes | full inversion of $A$ in $\mathcal{H}$ |
| zeroth order | $\eta_0$ | no | diagonal inversion in $\mathcal{V}_N^\perp$ |
| zeroth order guaranteed | $\eta_{0,\mathrm{g}}$ | yes | diagonal inversion in $\mathcal{V}_N^\perp$ + remainder estimation |
| first order | $\eta_1$ | no | full inversion in $\mathcal{V}_N$ |
| first order guaranteed | $\eta_{1,\mathrm{g}}$ | yes | full inversion in $\mathcal{V}_N$ + remainder estimation |

# Computational framework

- rHF model: $F(\rho) = \frac{1}{2}\mathcal{D}(\rho, \rho)$ (no xc).
- Discretization parameter $\mathrm{E_{cut}} \in \mathbb{R}$ and $N = \sqrt{2\mathrm{E_{cut}}}$:

$$\mathcal{V}_N = \mathrm{Span}\left\{e_{\boldsymbol{G}},\ |\boldsymbol{G}| \leq N\right\} = \mathrm{Span}\left\{e_{\boldsymbol{G}},\ \frac{1}{2}|\boldsymbol{G}|^2 \leq \mathrm{E_{cut}}\right\}.$$

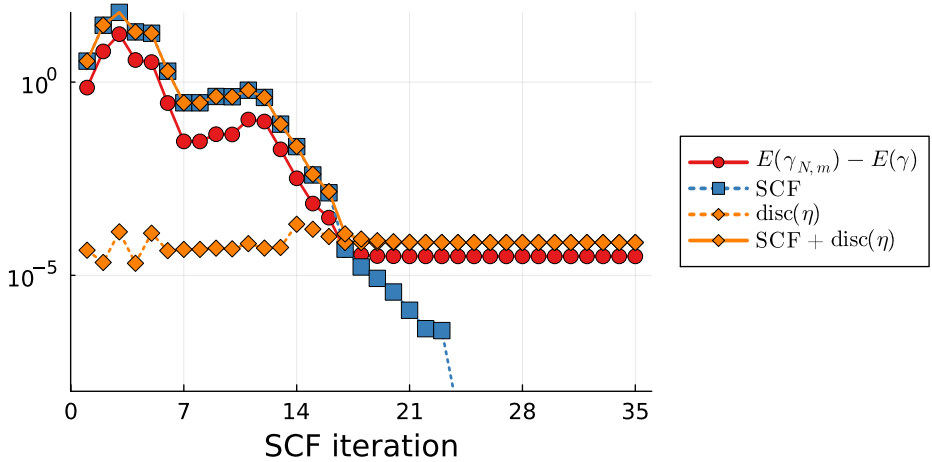
- Hierarchy of subspaces: $\mathcal{V}_N \subset \mathcal{V}_{N_{\mathrm{ref}}}$ and $\mathcal{V}_{N_{\mathrm{ref}}} = \mathcal{V}_N \oplus \mathcal{V}_N^{\perp}$.
  - $\mathcal{V}_N$: approximation space for $\gamma_N$ from SCF iterations and its orbitals $\varphi_{i,N} \in \mathcal{V}_N$;
  - $\mathcal{V}_{N_{\mathrm{ref}}} \approx \mathcal{H}$: reference space for the "true" solution $\gamma$ and the residuals $r_{i,N} \in \mathcal{V}_N^{\perp}$.
- We track

$$E(\gamma_{N,m}) - E(\gamma) \leq \mathtt{err}_{N,m}^{\mathrm{disc}} + \mathtt{err}_{N,m}^{\mathrm{SCF}}$$

  along the SCF iterations: 1D toy system and 3D systems.


# 1D toy model

- $H_\rho = -\frac{1}{2}\Delta + V + V_{\mathrm{H}}[\rho]$, $\forall\ G \in 2\pi\mathbb{Z}$, $\hat{V}_G = \begin{cases} 0 & \text{if } G = 0, \\ \frac{\sin(G)}{|G|^2} & \text{if } G \neq 0. \end{cases}$
- $\mathrm{E_{cut}} = 400$ Ha, $\mathrm{E_{cut,ref}} = 1000$ Ha.



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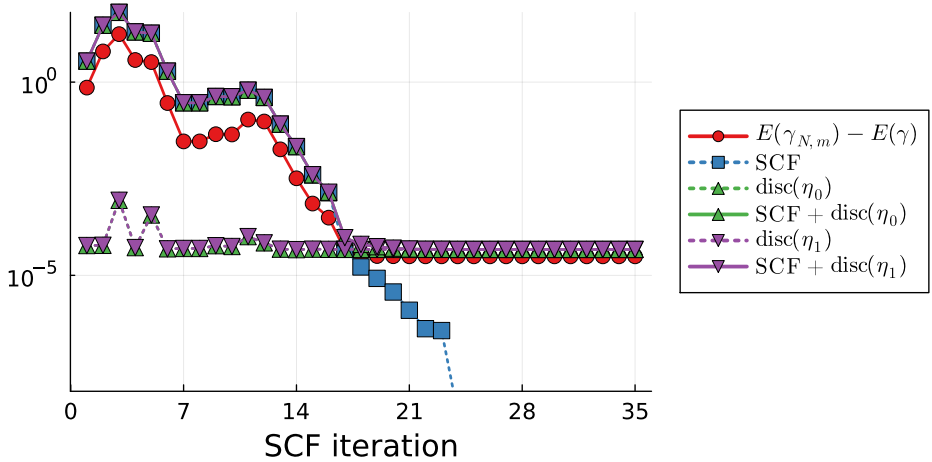

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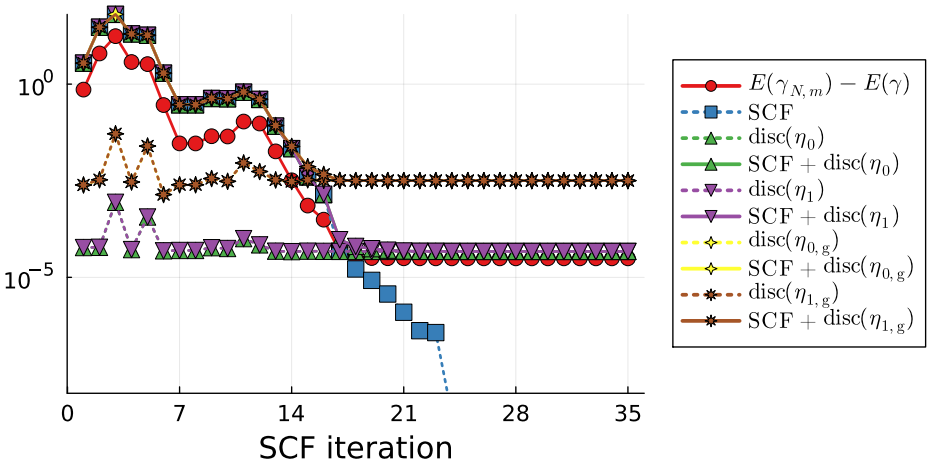

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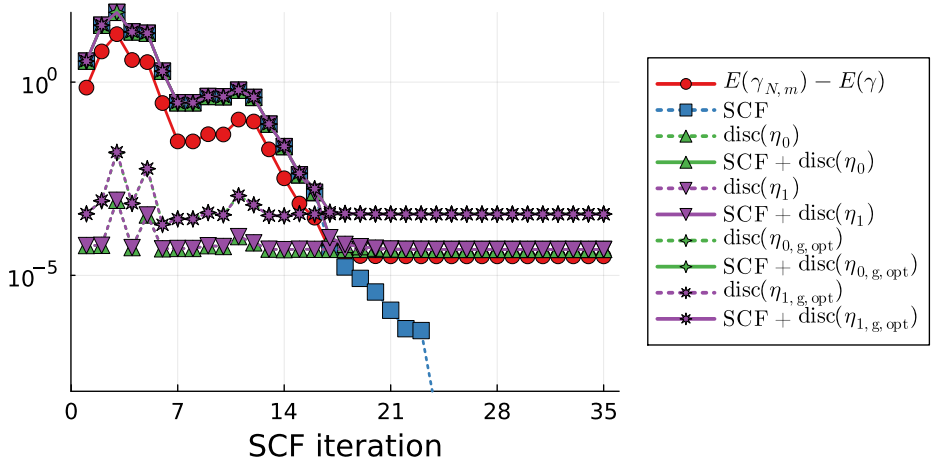


# 3D system and Brillouin zone sampling

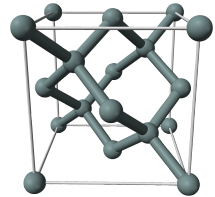
- $H_\rho = -\frac{1}{2}\Delta + V + V_\rho$ with $V \in \mathrm{L}^\infty_\#(\Omega)$: $H_\rho$ is unbounded, self-adjoint operator on $\mathrm{L}^2(\mathbb{R}^3) \Rightarrow$ purely continuous spectrum.
- Bloch transform saves us here[2]: spectral properties of $H_\rho$ can be deduced from those of its Bloch fibers $\{H_{\rho,\boldsymbol{k}}, \boldsymbol{k} \in \mathcal{B}\}$ with $H_{\rho,\boldsymbol{k}} = \frac{1}{2}(-\imath\nabla + \boldsymbol{k})^2 + V + V_\rho$: self-adjoint operators on $\mathrm{L}^2_\#(\Omega)$, bounded below and with compact resolvent $\Rightarrow$ purely discrete spectrum.

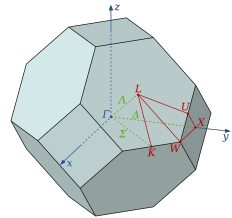
$$\forall\ \boldsymbol{k} \in \mathcal{B}, \quad \begin{cases} H_{\rho,\boldsymbol{k}}\varphi_{i,\boldsymbol{k}} = \varepsilon_{i,\boldsymbol{k}}\varphi_{i,\boldsymbol{k}} \\ \langle \varphi_{i,\boldsymbol{k}}, \varphi_{j,\boldsymbol{k}} \rangle = \delta_{ij} \\ \rho(\boldsymbol{r}) = \fint_{\mathcal{B}} \sum_{i=1}^{N_{\mathrm{el}}} |\varphi_{i,\boldsymbol{k}}(\boldsymbol{r})|^2 \mathrm{d}\boldsymbol{k}. \end{cases}$$

- Everything works the same, with additional (discrete) summation over the Brillouin zone $\mathcal{B}$ and energy

$$E(\gamma) = \underline{\mathrm{Tr}}(h\gamma) + F(\rho) = \fint_{\mathcal{B}} \mathrm{Tr}(h_{\boldsymbol{k}}\gamma_{\boldsymbol{k}})\mathrm{d}\boldsymbol{k} + F(\rho).$$

- Quadrature errors in the Brillouin zone are *not* taken into account.



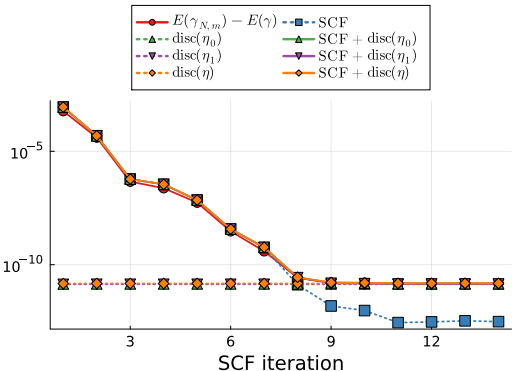



(Wikipedia)

[2] M. Reed and B. Simon, *Methods of modern mathematical physics IV: Analysis of operators* (1978).

# Silicon crystal

- GTH pseudo-potentials.
- $E_{\text{cut}} = 150$ Ha, $E_{\text{cut,ref}} = 400$ Ha.
- $2 \times 2 \times 2$ $\boldsymbol{k}$ grid.

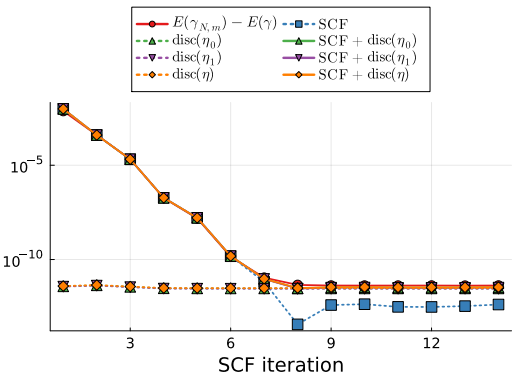



$$1 \leq \frac{\mathbf{err}^{\text{disc}}_{N,m} + \mathbf{err}^{\text{SCF}}_{N,m}}{E(\gamma_{N,m}) - E(\gamma)}$$

| **SCF iteration** | $\eta_0$ | $\eta_1$ | $\eta$ |
|---|---|---|---|
| 1 | 1.49189 | 1.49189 | 1.49189 |
| 2 | 1.19664 | 1.19664 | 1.19664 |
| 3 | 1.2833 | 1.2833 | 1.2833 |
| 4 | 1.47476 | 1.47476 | 1.47477 |
| 5 | 1.29028 | 1.29027 | 1.29029 |
| 6 | 1.24633 | 1.24614 | 1.24653 |
| 7 | 1.48771 | 1.48627 | 1.48924 |
| 8 | 1.03934 | 1.01782 | 1.06222 |
| 9 | 0.969748 | 0.934911 | 1.0068 |
| 10 | 0.958761 | 0.92304 | 0.996747 |
| 11 | 0.964904 | 0.927294 | 1.0049 |
| 12 | 0.969945 | 0.932188 | 1.01009 |
| 13 | 0.970363 | 0.932678 | 1.01044 |
| 14 | 0.970012 | 0.932278 | 1.01014 |

# What about nonconvex models ?

- GTH pseudo-potentials + LDA.
- $E_{\text{cut}} = 200$ Ha and $E_{\text{cut,ref}} = 600$ Ha.
- $2 \times 2 \times 2$ $\boldsymbol{k}$ grid.




$$1 \leq \frac{\mathtt{err}_{N,m}^{\text{disc}} + \mathtt{err}_{N,m}^{\text{SCF}}}{E(\gamma_{N,m}) - E(\gamma)}$$

| SCF iteration | $\eta_0$ | $\eta_1$ | $\eta$ |
|---|---|---|---|
| 1 | 1.3006 | 1.3006 | 1.3006 |
| 2 | **0.99266** | **0.99266** | **0.99266** |
| 3 | **0.992485** | **0.992485** | **0.992485** |
| 4 | 1.0224 | 1.0224 | 1.0224 |
| 5 | 1.06986 | 1.06985 | 1.06986 |
| 6 | 1.07511 | 1.07444 | 1.07581 |
| 7 | 0.863428 | 0.854739 | 0.872515 |
| 8 | 0.659905 | 0.638829 | 0.681944 |
| 9 | 0.79568 | 0.772953 | 0.819459 |
| 10 | 0.806511 | 0.78376 | 0.830315 |
| 11 | 0.779004 | 0.756219 | 0.802843 |
| 12 | 0.774807 | 0.752123 | 0.79854 |
| 13 | 0.79293 | 0.769954 | 0.81697 |
| 14 | 0.79858 | 0.77594 | 0.822268 |

# Conclusion and take-home messages

- Combining estimates for clusters of eigenvalues and convex models, we obtained guaranteed estimates on the energy of solutions to Kohn–Sham equations.
- Computing the full guaranteed is not tractable $\Rightarrow$ approximation by means of Neumann series.
- Best ratio accuracy / computational cost: 0th order approximation of the discretization error.
- General message[3] is to find a good balance between *mathematics* (guaranteed bounds) and *usage* (computable bounds, for a reasonable cost).

**Perspectives and ideas:**

- Adaptive schemes.
- Finite temperature.
- Better control on the remainder terms.
- Extension to nonconvex models.
- Other quantities of interest.

[3] Cancès, Dusson, Kemlin, Levitt, *Practical error bounds for properties in plane-wave electronic structure calculations*, SIAM Journal on Scientific Computing 44 (2022).

Merci!

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(ENPC & Inria)

Eric
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Geneviève
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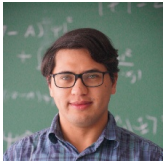

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