A *posteriori* error estimation for non-linear eigenvalue problems in the context of DFT-methods

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Outline

• Introduction to electronic structure computations
• Introduction to Kohn-Sham DFT-models
• Post-processing based on the perturbation method for LDA Kohn-Sham DFT-models
• A posteriori error estimation for the toy-problem: the Gross–Pitaevskii equation
Introduction
Electronic structure calculations for molecules

Many-body Schrödinger model:
Atomic units:

\[ \hbar = 1, \quad e = 1, \quad m_e = 1, \quad 4\pi\varepsilon_0 = 1, \]

where \( \hbar \) denotes the Planck constant, \( e \) the electrical charge, \( m_e \) the mass of an electron and \( \varepsilon_0 \) is the dielectric permittivity of the void.
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**Born-Oppenheimer approximation:** Let us consider a physical system composed of:

(i) \textit{M nuclei}, that are assumed to be (fixed) classical point charges (localised), whose positions in \( \mathbb{R}^3 \) and electric charges are denoted by \( R_1, \ldots, R_M \) and \( Z_1, \ldots, Z_M \) respectively;

(ii) \textit{N electrons}, considered as quantum particles, and represented by a wave function \( \Psi(x_1, \ldots, x_N) \in \bigotimes_{i=1}^N L^2(\mathbb{R}^3) \approx L^2(\mathbb{R}^{3N}) \), where for all \( 1 \leq i \leq N \), \( x_i \in \mathbb{R}^3 \), such that \( \| \Psi \|_{L^2(\mathbb{R}^{3N})} = 1 \).
Antisymmetry of the wave function

Since electrons are fermionic particles, the Pauli exclusion principle implies that the wavefunction $\Psi$ must be antisymmetric with respect to the exchange of two particles. For any permutation $p$ of the set $\{1, \ldots, N\}$,

$$\Psi(x_{p(1)}, \ldots, x_{p(N)}) = \varepsilon(p) \Psi(x_1, \ldots, x_N), \quad \forall x_1, \ldots, x_N \in \mathbb{R}^3,$$

where $\varepsilon(p)$ is the signature of the permutation $p$. 
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**Notation:** For all $H \subset L^2(\mathbb{R}^3)$ subspace of $L^2(\mathbb{R}^3)$, we will denote by $\bigwedge_{i=1}^N H$ the subspace of antisymmetric functions of $\bigoplus_{i=1}^N H$. In particular,

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\[\textbf{Bra-ket notation:}\] For all \( \phi, \psi \in V \), and self-adjoint operator \( \mathcal{A} \) on \( L^2(\mathbb{R}^{3N}) \) with form domain \( V \), we will denote by

- \( \langle \phi | \psi \rangle \) the \( L^2(\mathbb{R}^{3N}) \)-scalar product of \( \phi \) and \( \psi \);
- \( (\phi, \psi) \in V \times V \mapsto \langle \phi | \mathcal{A} | \psi \rangle \in \mathbb{R} \) the quadratic sesquilinear form associated to \( \mathcal{A} \).
Many-body Schrödinger equation

**Electronic Hamiltonian:** For a fixed configuration of the nuclei, the ground state of the electrons of the molecular system is characterised by: find $\Psi^0 \in V$ such that

$$\Psi^0 = \arg\min_{\Psi \in V, \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1} \langle \Psi | \mathcal{H} | \Psi \rangle,$$

where $\mathcal{H}$ is the self-adjoint operator

$$\mathcal{H} = -\sum_{j=1}^{N} \left( \frac{1}{2} \Delta x_j + \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|R_\alpha - x_j|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}.$$
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The first-order optimality condition writes: find $\Psi^0 \in V$ such that and

$$\mathcal{H}\Psi^0 = E\Psi^0, \quad \text{with} \quad \|\Psi^0\|_{L^2(\mathbb{R}^3)} = 1,$$

where $E$ is the smallest eigenvalue and is indeed the Lagrange-multiplier for the constraint $\|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1.$
Post-processing based on the perturbation method for DFT-models
Kohn-Sham DFT-models

In the Kohn-Sham model, the electronic state of the closed-shell system with an even number $N = 2N$ of electrons is described by $N$ Kohn-Sham orbitals $\Phi = (\phi_1, \cdots, \phi_N)^T \in [H^1(\mathbb{R}^3)]^N$ satisfying the orthonormality conditions

$$\int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}, \quad \forall i, j = 1, \ldots, N.$$
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We therefore define

\[
\mathcal{M} = \left\{ \Phi = (\phi_1, \cdots, \phi_N)^T \in \left[H^1(\Omega)\right]^N \left| \int_{\Omega} \phi_i \phi_j = \delta_{ij} \right. \right\}.
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The associated electronic density

$$\rho[\Phi](x) := 2 \sum_{i=1}^{N} |\phi_i(x)|^2,$$

plays a key-role in DFT.
The Kohn-Sham ground state

The Kohn-Sham ground state is obtained by the following infimum

$$\inf \left\{ \mathcal{E}_{0}^{KS}(\Phi) \mid \Phi \in \mathcal{M} \right\},$$

where the Kohn-Sham energy functional reads

$$\mathcal{E}_{0}^{KS}(\Phi) := \sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla \phi_i|^2 + \int_{\mathbb{R}^3} V_{\text{nuc}} \rho[\Phi] + \frac{1}{2} D(\rho[\Phi], \rho[\Phi]) + E_{\text{xc}}(\rho[\Phi]).$$
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\]

(i) \( V_{\text{nuc}} \) denotes the potential generated by the nuclei:

\[
V_{\text{nuc}} = - \sum_{\alpha=1}^{M} \frac{Z_{\alpha}}{|R_{\alpha} - x_j|}.
\]

(ii) The bilinear form \( D(\cdot, \cdot) \) is in fact the Coulomb energy functional \textit{in vacuo}:

\[
D(\rho, \rho') = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho'(y)}{|x - y|} \, dx \, dy.
\]

(iii) \( E_{\text{xc}}(\cdot) \) is the exchange-correlation functional which collects the errors made in the approximations of the kinetic energy and of the interactions between electrons.
Exchange-correlation functional

**Hohenberg-Kohn theorem:** There exists an *exact* exchange-correlation functional, that is a functional of the electronic density $\rho_{[\Phi]}$ for which solving Kohn-Sham model provides the ground state electronic energy and density of the $\mathcal{N}$-body electronic Schrödinger equation.
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The local density approximation (LDA) consists in approximating the exchange-correlation functional by

$$E_{xc}(\rho_{[\Phi]}) = \int_{\mathbb{R}^3} e_{xc}^{LDA}(\rho_{[\Phi]}(x)) \, dx,$$

where $e_{xc}^{LDA}(\bar{\rho})$ is an approximation of the exchange-correlation energy per unit volume in a uniform electron gas with density $\bar{\rho}$. 
Periodic Kohn-Sham models

In the sequel, we will focus on the periodic versions of Kohn-Sham LDA models.
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**Assumption:** There exists a unit cell, denoted here by $\Omega$, of some periodic lattice $\mathcal{R}$ of $\mathbb{R}^3$. 
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Without loss of generality, assume that we assume that $\Omega = (0, L)^3$.

This is an appropriate setting in many applications in solid state physics and material science.
Periodic Kohn-Sham models

As a consequence, all domain of integrations of the energy-functional are now over $\Omega$ instead of $\mathbb{R}^3$, including the definition of Coulomb energy

$$D_{\Omega}(\rho, \rho') = \int_{\Omega} V_{\text{coul}}(\rho)(x) \rho'(x) \, dx,$$

where the Coulomb potential is now given by

$$V_{\text{coul}}(\rho)(x) = \int_{\Omega} G_{\Omega}(x, y) \rho(y) \, dy,$$

with $G_{\Omega}$ being the Green’s function to the periodic Laplace operator in $\Omega$;
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the exchange-correlation functional

$$E_{\Omega, xc}(\rho) = \int_\Omega e_{\text{xc}}^{\text{LDA}}(\rho(x)) \, dx,$$

and the orthonormality constraint

$$\int_\Omega \phi_i \phi_j = \delta_{ij}.$$
Pseudopotentials

The Kohn-Sham ground state density corresponding to the nuclear potential $V_{\text{nuc}}$ has cusps at the nuclear positions $R_k$.

These singularities reduce the efficiency of the approximation method due to the low regularity of the nuclear potential. In practice, the singular nuclear potential $V_{\text{nuc}}$ is replaced with a smoother potential $V_{\text{ion}}$; this amounts to replacing point nuclei with smeared nuclei.

This is indeed based upon the fact that core electrons (for instance the two 1s electrons) are not affected by the valence electrons.

The resulting model presents the following differences:

(i) $N$ now denotes the number of valence electron pairs only;
(ii) $\Phi$ now denotes the set of the pseudo-orbitals of the valence electrons;
(iii) the nuclear potential $V_{\text{nuc}}$ is replaced by a pseudopotential operator $V_{\text{ion}}$ modeling the Coulomb interaction between the valence electrons and simultaneously the nuclei and the core electrons.
First-order optimality conditions

In this case, the energy-functional is given by

\[ \mathcal{E}_{0,\Omega}^{KS}(\Phi) = \sum_{i=1}^{N} \int_{\Omega} |\nabla \phi_i|^2 + \int_{\Omega} V_{\text{local}} \rho[\Phi] + 2 \sum_{i=1}^{N} \langle \phi_i | V_{\text{nl}} | \phi_i \rangle + \frac{1}{2} D_{\Omega}(\rho[\Phi], \rho[\Phi]) + E_{xc}^{c}(\rho[\Phi]), \]

for some \( \Phi \in \mathcal{M} \).
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for some $\Phi \in \mathcal{M}$.

Take the derivative

$$\frac{d}{d\varepsilon} E_{0,\Omega}^{KS}(\Phi^0 + \varepsilon \Phi')|_{\varepsilon=0} = 0,$$

in order to obtain the nonlinear eigenvalue problem: Find $\Phi^0 \in \mathcal{M}$ and the corresponding eigenvalues $\epsilon_1, \ldots, \epsilon_N$ such that

$$\mathcal{H}^0 \phi_i^0 = \epsilon_i \phi_i^0, \quad i = 1, \ldots, N,$$

where

$$\mathcal{H}^0 = \mathcal{H}_{[\rho^0]} = -\frac{1}{2} \Delta + V_{\text{ion}} + V_{\text{coul}}(\rho^0) + V_{xc}(\rho^0),$$

with $\rho^0 = \rho[\Phi^0]$ and $V_{\text{ion}} = V_{\text{local}} + V_{\text{nl}}$. 
Planewave discretization

Recall: $\Omega = (0, L)^3$ is the computational domain and the unit cell of the lattice $\mathcal{R} = L\mathbb{Z}^3$. 
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These are the Fourier modes with wavevector $k \in \mathcal{R}^*$ and where $\mathcal{R}^* = \frac{2\pi}{L}\mathbb{Z}^3$ denotes the dual lattice of $\mathcal{R}$. 
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We consider all basis functions $e_k$ whose kinetic energy $\frac{1}{2} |k|^2$ is smaller than a cut-off $E_c$ to define the approximation space of real-valued functions

$$X_{N_c} := \left\{ \sum_{k \in \mathcal{R}^*, |k| \leq \frac{2\pi}{L} N_c} \hat{v}_k e_k \mid \hat{v}_{-k} = \hat{v}^*_k, \forall k \right\} \subset L^2_\#(\Omega), \quad \text{with} \quad N_c = \sqrt{\frac{E_c}{2} \frac{L}{\pi}}.$$

Reciprocal space:
Planewave discretization

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We denote by $\Phi_{N_c} = (\phi_{1,N_c}, \ldots, \phi_{N,N_c})^T$ the set of discretised orbitals which are represented by

$$\phi_{i,N_c} = \sum_{k \in \mathcal{R}^*, |k| \leq \frac{2\pi}{L} N_c} (\hat{\phi}_{i,N_c})_k e_k,$$

so that the corresponding density writes

$$\rho[\Phi_{N_c}] = 2 \sum_{i=1}^{N} |\phi_{i,N_c}(x)|^2.$$
1. **Initialization:** Take an initial guess of the orbitals \( \Phi_{N_c}^{(0)} = (\phi_{1,N_c}^{(0)}, \ldots, \phi_{N,N_c}^{(0)})^T \) with associated density \( \rho_{N_c}^{(0)} = \rho_{[\Phi_{N_c}^{(0)}]} \), and a tolerance \( \varepsilon \).
Self-Consistent Field (SCF) iterations

1. **Initialization:** Take an initial guess of the orbitals $\Phi_{Nc}^{(0)} = (\phi_{1,Nc}^{(0)}, \ldots, \phi_{N,Nc}^{(0)})^T$ with associated density $\rho_{Nc}^{(0)} = \rho_{[\Phi_{Nc}^{(0)}]}$, and a tolerance $\varepsilon$.

2. **Iterations:** For $i = 1, 2, \ldots$ until convergence

   (a) Compute the Hamiltonian $\mathcal{H}_{Nc}^{(i-1)} := \Pi_{Nc} \mathcal{H}_{[\rho_{Nc}^{(i-1)}]} \Pi_{Nc}$.

   (b) Solve the linear eigenvalue problem

   $$\mathcal{H}_{Nc}^{(i-1)} \phi_{j,Nc}^{(i)} = \epsilon_{j,Nc}^{(i)} \phi_{j,Nc}^{(i)}$$

   for $j = 1, \ldots, N$ to obtain the set of orbitals $\Phi_{Nc}^{(i)} = (\phi_{1,Nc}^{(i)}, \ldots, \phi_{N,Nc}^{(i)})^T$.

   (c) Compute the new density $\hat{\rho}_{Nc}^{(i)} = \rho_{[\Phi_{Nc}^{(i)}]}$.

   (d) Charge mixing: Replace the charge density $\hat{\rho}_{Nc}^{(i)}$ with a linear combination of $m$ previously computed charge densities, i.e.,

   $$\rho_{Nc}^{(i)} = \alpha_0 \hat{\rho}_{Nc}^{(i)} + \sum_{k=1}^{m} \alpha_k \rho_{Nc}^{(i-k)}$$

   s.t. $\sum_{k=0}^{m} \alpha_k = 1$. 
Solving the linearized eigenvalue problem

Recall the ansatz:

$$\phi_{i,N_c} = \sum_{k \in \mathcal{R}^*, |k| \leq \frac{2\pi}{L} N_c} (\phi_{i,N_c})_k e_k.$$ 

Then, solving

$$\mathcal{H}^{i-1}_{N_c} \phi_{j,N_c}^i = \epsilon_{j,N_c}^i \phi_{j,N_c}^i$$

with $$\mathcal{H}^{i-1}_{N_c} = \Pi_{N_c} \mathcal{H}_{[\rho_{N_c}^{i-1}]} \Pi_{N_c}$$ is equivalent to

$$\langle e_k | \mathcal{H}_{[\rho_{N_c}^{i-1}]} \phi_{j,N_c}^i \rangle = \epsilon_{j,N_c}^i \langle e_k | \phi_{j,N_c}^i \rangle, \quad \forall k \in \mathcal{R}^*, |k| \leq \frac{2\pi}{L} N_c.$$
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Recall the ansatz:
\[ \phi_{i,N_c} = \sum_{k \in \mathcal{R}^*, |k| \leq \frac{2\pi}{L} N_c} (\hat{\phi}_{i,N_c})_k e_k. \]

Then, solving
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with \( \mathcal{H}_{N_c}^{i-1} = \Pi_{N_c} \mathcal{H}_{[\rho_{N_c}^{i-1}]} \Pi_{N_c} \) is equivalent to
\[ \langle e_k | \mathcal{H}_{[\rho_{N_c}^{i-1}]} | \phi_{j,N_c}^i \rangle = \epsilon_{j,N_c}^i \langle e_k | \phi_{j,N_c}^i \rangle, \quad \forall k \in \mathcal{R}^*, |k| \leq \frac{2\pi}{L} N_c. \]
Post-processing: approximate vs. exact solution

Let be given the result of the converged SCF procedure, i.e. given the orthonormal eigenfunctions \( \Phi_{N_c} = (\phi_{1,N_c}, \ldots, \phi_{N,N_c})^T \) and eigenvalues \( (\epsilon_{j,N_c})_{j=1,...,N} \) with density \( \rho_{N_c} \), satisfying

\[
\mathcal{H}_{N_c} \phi_{j,N_c} = \epsilon_{j,N_c} \phi_{j,N_c},
\]

for all \( i, j = 1, \ldots, N \) and where

\[
\mathcal{H}_{N_c} = \Pi_{N_c} \mathcal{H}_{[\Phi_{N_c}]} \Pi_{N_c} = -\frac{1}{2} \Delta + \Pi_{N_c} \left[ V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{\text{xc}}(\rho_{N_c}) \right] \Pi_{N_c}.
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We keep in mind that the exact solution $(\phi_j, \epsilon_j)_{j=1,\ldots,N}$ satisfies

$$(\mathcal{H}_{N_c} + \mathcal{V}_{N_c} + \mathcal{W}_{N_c}) \phi_j = \epsilon_j \phi_j,$$

where

$$\mathcal{V}_{N_c} = \left[ V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{\text{xc}}(\rho_{N_c}) \right] - \Pi_{N_c} \left[ V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{\text{xc}}(\rho_{N_c}) \right] \Pi_{N_c},$$

$$\mathcal{W}_{N_c} = \left[ V_{\text{coul}}(\rho) + V_{\text{xc}}(\rho) \right] - \left[ V_{\text{coul}}(\rho_{N_c}) + V_{\text{xc}}(\rho_{N_c}) \right].$$
Post-processing: Perturbation arguments

The key-observation: \( \mathcal{V}_{N_c} + \mathcal{W}_{N_c} \) is a compact perturbation with respect to the discrete Hamiltonian \( \mathcal{H}_{N_c} \).
Post-processing: Perturbation arguments

The key-observation: \( \mathcal{V}_{N_e} + \mathcal{W}_{N_e} \) is a compact perturbation with respect to the discrete Hamiltonian \( \mathcal{H}_{N_e} \).

Then, define
\[
\mathcal{H}(\nu) = \mathcal{H}_{N_e} + \nu(\mathcal{V}_{N_e} + \mathcal{W}_{N_e}), \quad \nu \in [0, 1],
\]
so that
- \( H(0) = \mathcal{H}_{N_e} \) is the discrete Hamiltonian;
- \( H(1) = \mathcal{H}^0 \) is the exact Hamiltonian.
Post-processing: Perturbation arguments

The key-observation: $\mathcal{V}_{N_c} + \mathcal{W}_{N_c}$ is a compact perturbation with respect to the discrete Hamiltonian $\mathcal{H}_{N_c}$.

Then, define

$$\mathcal{H}(\nu) = \mathcal{H}_{N_c} + \nu (\mathcal{V}_{N_c} + \mathcal{W}_{N_c}), \quad \nu \in [0, 1],$$

so that

- $H(0) = \mathcal{H}_{N_c}$ is the discrete Hamiltonian;
- $H(1) = \mathcal{H}^0$ is the exact Hamiltonian.

Expanding then the orbitals and eigenvalues in terms of powers of the perturbation parameter $\nu$ results in

$$\Phi = \sum_{\ell=0}^{\infty} \nu^\ell \Phi^{(\ell)}_{N_c}, \quad \epsilon_j = \sum_{\ell=0}^{\infty} \nu^\ell \epsilon^{(\ell)}_{j, N_c},$$

with $(\phi^{(0)}_{j, N_c}, \epsilon^{(0)}_{j, N_c}) = (\phi_{j, N_c}, \epsilon_{j, N_c})$ being the solution of the unperturbed ($\nu = 0$) discrete nonlinear eigenvalue problem.
Post-processing: First and second order perturbation

Further, incorporating \textit{a priori} results stating that $\mathcal{W}_{N_c}$ is negligible with respect to $\gamma_{N_c}$ allow to derive the perturbation with respect to $\gamma_{N_c}$ only.
Post-processing: First and second order perturbation

Further, incorporating a priori results stating that \( \mathcal{W}_{N_c} \) is negligible with respect to \( \mathcal{V}_{N_c} \) allow to derive the perturbation with respect to \( \mathcal{V}_{N_c} \) only.

Then, a simple calculation shows that the first order correction to the eigenfunctions \((\phi_{j,N_c})_{j=1,\ldots,N}\) provides

\[
\phi_{j,N_c}^{(1)} = -(-\Delta |_{X^\perp_{N_c}} - \epsilon_{j,N_c})^{-1} r_j \quad \text{for all } j = 1, \ldots, N,
\]

where the residual of the eigenvalue problem

\[
r_j = \mathcal{H}[\rho_{N_c}] \phi_{j,N_c} - \epsilon_{j,N_c} \phi_{j,N_c} = (\mathcal{H}_{N_c} + \mathcal{V}_{N_c}) \phi_{j,N_c} - \epsilon_{j,N_c} \phi_{j,N_c},
\]

is given by

\[
r_j = \left(-\frac{1}{2} \Delta + V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{xc}(\rho_{N_c}) - \epsilon_{j,N_c}\right) \phi_{j,N_c}.
\]
Post-processing: First and second order perturbation

Further, incorporating \textit{a priori} results stating that $\mathcal{W}_{N_c}$ is negligible with respect to $\mathcal{V}_{N_c}$ allow to derive the perturbation with respect to $\mathcal{V}_{N_c}$ only.

Then, a simple calculation shows that the first order correction to the eigenfunctions $(\phi_{j,N_c})_{j=1,...,N}$ provides

$$\phi_{j,N_c}^{(1)} = -(-\Delta|_{X_{N_c}^+} - \epsilon_{j,N_c})^{-1} r_j \quad \text{for all} \quad j = 1, \ldots, N,$$

where the residual of the eigenvalue problem

$$r_j = \mathcal{H}[ho_{N_c}]\phi_{j,N_c} - \epsilon_{j,N_c} \phi_{j,N_c} = (\mathcal{H}_{N_c} + \mathcal{V}_{N_c})\phi_{j,N_c} - \epsilon_{j,N_c} \phi_{j,N_c},$$

is given by

$$r_j = \left(-\frac{1}{2}\Delta + V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{xc}(\rho_{N_c}) - \epsilon_{j,N_c}\right) \phi_{j,N_c}.$$

The first order correction to the eigenvalue vanishes and the second order correction is

$$\epsilon_{j,N_c}^{(2)} = \langle \phi_{j,N_c}^{(1)}, r_j \rangle_{L^2_{\#}} = -\langle r_j | (-\Delta|_{X_{N_c}^+} - \epsilon_{j,N_c})^{-1} | r_j \rangle.$$
Post-processing: theoretical result

We then collect the perturbation terms to assemble the post-processed solution in

\[ \tilde{\phi}_{j, N_c} = \phi_{j, N_c} + \phi_{j, N_c}^{(1)} \quad \text{and} \quad \tilde{\epsilon}_{j, N_c} = \epsilon_{j, N_c} + \epsilon_{j, N_c}^{(2)}, \]

as well as the electron density

\[ \tilde{\rho}_{N_c} = \rho_{[\tilde{\Phi}_{N_c}]}, \]

with \( \tilde{\Phi}_{N_c} = (\tilde{\phi}_{1, N_c}, \ldots, \tilde{\phi}_{N, N_c})^T \). Therefore, the post-processed energy can be provided by \( \mathcal{E}_{0, \Omega}^{KS}(\tilde{\Phi}_{N_c}) \) and we can state the following result.
Post-processing: theoretical result

We then collect the perturbation terms to assemble the post-processed solution in

\[
\tilde{\phi}_{j,N_c} = \phi_{j,N_c} + \phi_{j,N_c}^{(1)} \quad \text{and} \quad \tilde{\epsilon}_{j,N_c} = \epsilon_{j,N_c} + \epsilon_{j,N_c}^{(2)},
\]
as well as the electron density

\[
\tilde{\rho}_{N_c} = \rho_{[\Phi_{N_c}]},
\]
with \( \Phi_{N_c} = (\tilde{\phi}_{1,N_c}, \ldots, \tilde{\phi}_{N,N_c})^T \). Therefore, the post-processed energy can be provided by \( \mathcal{E}_{0,\Omega}^{KS}(\Phi_{N_c}) \) and we can state the following result.

**Theorem:** Consider the same regularity assumptions on the potentials than for the *a priori* analysis (not detailed here). Let \( \Phi \) denote the exact ground-state, \( \Phi_{N_c} \) the planewave approximation and \( \Phi_{N_c} \) the post-processed approximation given above. Then, there exists a constant \( C > 0 \), independent of \( N_c \) and the regularity of the potentials \( V_{\text{local}}, V_{\text{nl}}, V_{\text{xc}} \), such that

\[
\left| \mathcal{E}_{0,\Omega}^{KS}(\Phi) - \mathcal{E}_{0,\Omega}^{KS}(\Phi_{N_c}) \right| \leq C N_c^{-2} \left| \mathcal{E}_{0,\Omega}^{KS}(\Phi) - \mathcal{E}_{0,\Omega}^{KS}(\Phi_{N_c}) \right|.
\]
Post-processing: theoretical result

We then collect the perturbation terms to assemble the post-processed solution in

\[ \widetilde{\phi}_{j,Nc} = \phi_{j,Nc} + \phi_{j,Nc}^{(1)} \quad \text{and} \quad \widetilde{e}_{j,Nc} = \epsilon_{j,Nc} + \epsilon_{j,Nc}^{(2)}, \]

as well as the electron density

\[ \widetilde{\rho}_{Nc} = \rho_{[\tilde{\Phi}_{Nc}]}, \]

with \( \tilde{\Phi}_{Nc} = (\tilde{\phi}_{1,Nc}, \ldots, \tilde{\phi}_{N,Nc})^T \). Therefore, the post-processed energy can be provided by \( E_{KS_0}(\tilde{\rho}_{Nc}) \) and we can state the following result.

**Theorem:** Consider the same regularity assumptions on the potentials than for the \textit{a priori} analysis (not detailed here). Let \( \Phi \) denote the exact ground-state, \( \Phi_{Nc} \) the planewave approximation and \( \tilde{\Phi}_{Nc} \) the post-processed approximation given above. Then, there exists a constant \( C > 0 \), independent of \( N_c \) and the regularity of the potentials \( V_{\text{local}}, V_{\text{nl}}, V_{\text{xc}} \), such that

\[ \left| E_{0,\Omega}^{KS}(\Phi) - E_{0,\Omega}^{KS}(\tilde{\Phi}_{Nc}) \right| \leq C N_c^{-2} \left| E_{0,\Omega}^{KS}(\Phi) - E_{0,\Omega}^{KS}(\Phi_{Nc}) \right|. \]

**In consequence:** Gain of a factor 2 in the convergence rate with respect to \( N_c \) in the asymptotic regime. Little computational overhead (next slide).
Some practical aspects

**Note:** The residual

\[ r_j = \left( -\frac{1}{2} \Delta + V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{xc}(\rho_{N_c}) - \epsilon_{j,N_c} \right) \phi_{j,N_c} \]

is an infinite-dimensional object belonging to \( \Pi_{N_c}^1 \).
Some practical aspects

Note: The residual

\[
r_j = \left(-\frac{1}{2}\Delta + V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{xc}(\rho_{N_c}) - \epsilon_{j,N_c}\right)\phi_{j,N_c}
\]

is an infinite-dimensional object belonging to $\Pi_{N_c}$. We represent $r_j$ in the discrete space $X_{N_c,\text{res}}$ based on some $E_{c,\text{res}} \geq E_c$ which, in turn, corresponds to a certain $N_{c,\text{res}} \geq N_c$. 

Some practical aspects

**Note:** The residual

\[ r_j = \left( -\frac{1}{2} \Delta + V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{xc}(\rho_{N_c}) - \epsilon_{j,N_c} \right) \phi_{j,N_c} \]

is an infinite-dimensional object belonging to \( \Pi_{\frac{1}{N_c}} \).

We represent \( r_j \) in the discrete space \( X_{N_{c,\text{res}}} \) based on some \( E_{c,\text{res}} \geq E_c \) which, in turn, corresponds to a certain \( N_{c,\text{res}} \geq N_c \).

Then, applying the Hamiltonian \( \mathcal{H}_{[\rho_{N_c}]} \) to the orbitals \( \phi_{j,N_c} \) in order to compute the residual \( r_j \) requires two additional FFT’s on the fine grid based on \( E_{c,\text{res}} \) for each orbital.
Some practical aspects

**Note:** The residual

\[ r_j = \left( -\frac{1}{2} \Delta + V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{xc}(\rho_{N_c}) - \epsilon_{j,N_c} \right) \phi_{j,N_c} \]

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Then, applying the Hamiltonian $\mathcal{H}_{[\rho_{N_c}]}$ to the orbitals $\phi_{j,N_c}$ in order to compute the residual $r_j$ requires two additional FFT’s on the fine grid based on $E_{c,\text{res}}$ for each orbital.

**Remark:** Neglecting $W_{N_c}$ allows us to consider

\[ r_j = \left( -\frac{1}{2} \Delta + V_{\text{ion}} + V_{\text{coul}}(\rho_{N_c}) + V_{xc}(\rho_{N_c}) - \epsilon_{j,N_c} \right) \phi_{j,N_c} \]

instead of

\[ \left( -\frac{1}{2} \Delta + V_{\text{ion}} + V_{\text{coul}}(\rho) + V_{xc}(\rho) - \epsilon_{j,N_c} \right) \phi_{j,N_c}, \]

which is not computable.
Numerical results

\[ E_{c,\text{res}} = \lambda E_c \]

- **Molecule:** CO₂
- **Pseudo-potential:** Troullier-Martins
- **LDA:** Perdew-Zunger (PZ81) functional
- **Code:** KSSolve (Matlab)
- **# of valence orbitals:** 8
- **Energy Error:** Hartree (au)

Energy Error vs. \( \lambda \):

- **Without perturbation:** \( E_c = 50 \)
- **With perturbation:**

[Graph showing energy error vs. \( \lambda \)]

[Graph showing time ratio vs. \( \lambda \) for with and without perturbation]
Numerical results

\[ E_{c,\text{res}} = \lambda E_c \]

Molecule: \( \text{CO}_2 \)
Pseudo-potential: Troullier-Martins
LDA: Perdew-Zunger (PZ81) functional
Code: KSSolve (Matlab)
# of valence orbitals: 8
Energy Error: Hartree (au)

\[ \lambda = 5 \]

\begin{align*}
\text{Energy error} & \quad \text{Ecut} \\
\text{Time [sec]} & \quad \text{Ecut}
\end{align*}
Numerical results

\[ E_{c,\text{res}} = \lambda E_c \]

Molecule: \( \text{CO}_2 \)
Pseudo-potential: Troullier-Martins
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\[ E_{\text{c, res}} = \lambda E_c \]

Molecule: CO₂
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Code: KSSolve (Matlab)
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Energy Error: Hartree (au)
A posteriori error estimation for the toy-problem: the Gross–Pitaevskii equation
The periodic Gross–Pitaevskii model reads
\[
\inf \left\{ E_{GP}(v), \, v \in H^1_\#(\Omega), \, \|v\|_{L^2_\#} = 1 \right\},
\]
where the Gross–Pitaevskii functional is given, in absence of an external magnetic field, by
\[
E_{GP}(v) := \int_\Omega |\nabla v|^2 + \int_\Omega V|v|^2 + \frac{\mu}{2} \int_\Omega |v|^4,
\]
where \(V\) is a real-valued periodic potential belonging to \(H^s_\#(\Omega)\) for some \(s > d/2\), and \(\mu \in \mathbb{R}\).
Gross-Pitaevskii equation (scalar case)

The periodic Gross–Pitaevskii model reads

$$\inf \left\{ E_{\text{GP}}(v), \ v \in H^1_\#(\Omega), \ \|v\|_{L^2_\#} = 1 \right\},$$

where the Gross–Pitaevskii functional is given, in absence of an external magnetic field, by

$$E_{\text{GP}}(v) := \int_{\Omega} |v|^2 + \int_{\Omega} V|v|^2 + \frac{\mu}{2} \int_{\Omega} |v|^4,$$

where $V$ is a real-valued periodic potential belonging to $H^s_\#(\Omega)$ for some $s>d/2$, and $\mu \in \mathbb{R}$.

The minimizing function $u$ satisfies the Euler–Lagrange equation

$$-\Delta u + Vu + \mu u^3 = \lambda u, \quad \|u\|_{L^2_\#} = 1,$$

where $\lambda$, the Lagrange multiplier of the constraint $\|v\|_{L^2_\#} = 1$, is in fact the lowest eigenvalue of the mean-field operator $H_u := -\Delta + V + \mu u^2$. 
Gross-Pitaevskii equation: planewave discretization

The variational approximation in the discretization space $X_N$ gives rise to the finite-dimensional constrained optimization problem

$$\inf \left\{ E_{GP}(v_N), \ v_N \in X_N, \ ||v_N||_{L^2} = 1 \right\}.$$
Gross-Pitaevskii equation: planewave discretization

The variational approximation in the discretization space $X_N$ gives rise to the finite-dimensional constrained optimization problem

$$\inf \left\{ E_{GP}(v_N), \ v_N \in X_N, \ |v_N|_{L^2} = 1 \right\}.$$ 

The minimizer $\lambda_N$ satisfies

$$-\Delta u_N + \Pi_N \left[ (V + |u_N|^2)u_N \right] = \lambda_N u_N, \quad |u_N|_{L^2} = 1,$$

where $\lambda_N$ is the Lagrange multiplier associated with the constraint $|v_N|_{L^2} = 1.$
SCF-iterations and adaptive refinement

Adaptive algorithm based on the Roothaan procedure: Find the lowest eigenvalue $\lambda^{(i)}$ and $u^{(i)} \in X_{N_i}$ such that

$$-\Delta u^{(i)} + \Pi_{N_i} \left[(V + \mu |u^{(i-1)}|^2)u^{(i)}\right] \Pi_{N_i} = \lambda^{(i)} u^{(i)}, \quad \|u^{(i)}\|_{L_2^\#} = 1,$$

where $u^{(0)} \in X_{N_0}$ is a given initial guess, and where $(N_i)_{i \in \mathbb{N}}$ is a non-decreasing sequence of integers.
SCF-iterations and adaptive refinement

Adaptive algorithm based on the Roothaan procedure: Find the lowest eigenvalue \( \lambda^{(i)} \) and \( u^{(i)} \in X_{N_i} \) such that

\[
-\Delta u^{(i)} + \Pi_{N_i} \left[ (V + \mu |u^{(i-1)}|^2)u^{(i)} \right] \Pi_{N_i} = \lambda^{(i)} u^{(i)}, \quad \|u^{(i)}\|_{L^2_\#} = 1,
\]

where \( u^{(0)} \in X_{N_0} \) is a given initial guess, and where \((N_i)_{i \in \mathbb{N}}\) is a non-decreasing sequence of integers.

**Goal:** Automatically construct \((N_i)_{i \in \mathbb{N}}\) using an adaptivity criterion based on a posteriori estimates.
SCF-iterations and adaptive refinement

Adaptive algorithm based on the Roothaan procedure: Find the lowest eigenvalue $\lambda^{(i)}$ and $u^{(i)} \in X_{N_i}$ such that

$$-\Delta u^{(i)} + \Pi_{N_i} \left[ (V + \mu |u^{(i-1)}|^2) u^{(i)} \right] \Pi_{N_i} = \lambda^{(i)} u^{(i)}, \quad \|u^{(i)}\|_{L^2} = 1,$$

where $u^{(0)} \in X_{N_0}$ is a given initial guess, and where $(N_i)_{i \in \mathbb{N}}$ is a non-decreasing sequence of integers.

**Goal:** Automatically construct $(N_i)_{i \in \mathbb{N}}$ using an adaptivity criterion based on a posteriori estimates.

The a posteriori estimator of the error between $u^{(i)}$ and $u$ can be decomposed into two contributions:

i) a contribution $\eta^{(i)}_{\text{scf}}$ measuring the error at step $i$ due to the fact that the SCF procedure has not converged;

ii) a contribution $\eta^{(i)}_{\text{dis}}$ measuring the error at step $i$ due to the fact that $u^{(i)}$ is a finite-dimensional approximation of $u$ in $X_{N_i}$. 
A posteriori estimate

**Measure of error:** A common choice for nonlinear problems is the energy difference $E_{GP}(u^{(i)}) - E_{GP}(u)$.

We take here the augmented energy difference $J_u(u^{(i)})$ where

$$J_u(v) = E_{GP}(v) - E_{GP}(u) + \frac{\mu}{2} \int_{\Omega} (|u|^2 - |v|^2)^2.$$
A posteriori estimate

**Measure of error:** A common choice for nonlinear problems is the energy difference  
\[ E_{GP}(u^{(i)}) - E_{GP}(u) \].

We take here the augmented energy difference  
\[ J_u(u^{(i)}) \]  
where
\[
J_u(v) = E_{GP}(v) - E_{GP}(u) + \frac{\mu}{2} \int_{\Omega} (|u|^2 - |v|^2)^2.
\]

**Theorem.** Let \( u \) be the exact solution and \( u^{(i)} \in X_{N_i} \) the numerical approximation of \( u \) generated by the iterative procedure at step \( i \). Then
\[
J_u(u^{(i)}) \leq \eta_{\text{tot}}^{(i)} := \left( \lambda^{(i)} - \lambda^{(i+1)}_{1b} + \int_{\Omega} [(u^{(i)})^2 - (u^{(i-1)})^2](u^{(i)})^2 \right),
\]
where \( \lambda^{(i+1)}_{1b} \) is a lower bound of the exact ground state eigenvalue \( \lambda^{(i+1)}_\infty \) of \( H_{u^{(i)}} \).

In addition, the error bound \( \eta_{\text{tot}}^{(i)} \) can be decomposed as \( \eta_{\text{tot}}^{(i)} = \eta_{\text{scf}}^{(i)} + \eta_{\text{dis}}^{(i)} \) where
\[
\eta_{\text{dis}}^{(i)} = \left( \lambda^{(i+1)}_{N_i} - \lambda^{(i+1)}_{1b} \right) \geq 0, \quad \eta_{\text{scf}}^{(i)} = \left( \int_{\Omega} [(u^{(i)})^2 - (u^{(i-1)})^2](u^{(i)})^2 + \lambda^{(i)} - \lambda^{(i+1)}_{N_i} \right) \geq 0,
\]
where \( \lambda^{(i+1)}_{N_i} \) is the variational approximation of \( \lambda^{(i+1)}_\infty \) in \( X_{N_i} \).
A posteriori estimate

**Measure of error:** A common choice for nonlinear problems is the energy difference $E_{GP}(u^{(i)}) - E_{GP}(u)$.

We take here the augmented energy difference $J_u(u^{(i)})$ where

$$J_u(v) = E_{GP}(v) - E_{GP}(u) + \frac{\mu}{2} \int_{\Omega} (|u|^2 - |v|^2)^2.$$

**Theorem.** Let $u$ be the exact solution and $u^{(i)} \in X_{N_i}$ the numerical approximation of $u$ generated by the iterative procedure at step $i$. Then

$$J_u(u^{(i)}) \leq \eta_{\text{tot}}^{(i)} := \left( \lambda^{(i)} - \lambda_{1b}^{(i+1)} + \int_{\Omega} [(u^{(i)})^2 - (u^{(i-1)})^2](u^{(i)})^2 \right),$$

where $\lambda_{1b}^{(i+1)}$ is a lower bound of the exact ground state eigenvalue $\lambda_{\infty}^{(i+1)}$ of $H_{u^{(i)}}$. In addition, the error bound $\eta_{\text{tot}}^{(i)}$ can be decomposed as $\eta_{\text{tot}}^{(i)} = \eta_{\text{scf}}^{(i)} + \eta_{\text{dis}}^{(i)}$ where

$$\eta_{\text{dis}}^{(i)} = \left( \lambda_{N_i}^{(i+1)} - \lambda_{1b}^{(i+1)} \right) \geq 0, \quad \eta_{\text{scf}}^{(i)} = \left( \int_{\Omega} [(u^{(i)})^2 - (u^{(i-1)})^2](u^{(i)})^2 + \lambda^{(i)} - \lambda_{N_i}^{(i+1)} \right) \geq 0,$$

where $\lambda_{N_i}^{(i+1)}$ is the variational approximation of $\lambda_{\infty}^{(i+1)}$ in $X_{N_i}$.

We can use the perturbed approximation.
Numerical results

Confirmation of perturbation results for eigenvectors

Illustration of error splitting for N=50

References


Numerical results

Confirmation of perturbation results for eigenvectors

Illustration of error splitting for $N=50$

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- $E_{GP}(u^j) - E_{GP}(u)$
- $J_u(u^j)$
- $\eta_{tot}$
- $\eta_{dis}$
- $\eta_{scf}$
Conclusions

• Kohn-Sham DFT-models: Improved accuracy with little additional computational overhead due to perturbation arguments in asymptotic regime (theoretical) and in pre-asymptotic regime (numerical test).

• Sharp *a posteriori* result for the Gross-Pitaevskii equation

• Future work:
  • More numerical tests to confirm initial results
  • Adapt *a posteriori* results and adaptive refinement strategy to Kohn-Sham DFT-models
  • Implementation in *abinit*

Thank you!