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Post-processing of the planewave approximation of Schrödinger equations. Part II: Kohn–Sham models

Geneviève Dusson*
Université Bourgogne Franche-Comté,
Laboratoire de Mathématiques de Besançon,
UMR CNRS 6623, Besançon, France

Abstract

In this article, we provide *a priori* estimates for a perturbation-based post-processing method of the plane-wave approximation of nonlinear Kohn–Sham LDA models with pseudopotentials, relying on [6] for the proofs of such estimates in the case of *linear* Schrödinger equations. As in [5], where these *a priori* results were announced and tested numerically, we use a periodic setting, and the problem is discretized with planewaves (Fourier series). This post-processing method consists of performing a full computation in a coarse planewave basis, and then to compute corrections based on first-order perturbation theory in a fine basis, which numerically only requires the computation of the residuals of the ground-state orbitals in the fine basis. We show that this procedure asymptotically improves the accuracy of two quantities of interest: the ground-state density matrix, *i.e.* the orthogonal projector on the lowest N eigenvectors, and the ground-state energy.

1 Introduction

To determine the electronic ground-state of a system within the Born–Oppenheimer approximation [1], DFT Kohn–Sham models [12] are among the state-of-the-art methods, especially for their good trade-off between accuracy and computational cost. In the context of condensed matter physics and materials science, most simulations of the Kohn–Sham models are performed with periodic boundary conditions, for which a planewave (Fourier) discretization method is particularly suited (see the introduction of [6] for more detail on the physical context). Nevertheless, this method scales cubically with respect to the number of electrons in the system, and becomes expensive for large systems.

In previous works [2, 5, 6], we have proposed a post-processing method to provide cheaper and still accurate results for this problem. This two-grid method consists of computing first a rough approximation of the solution to the Kohn–Sham problem in a coarse planewave basis. This solution is then corrected in a fine basis, based on first-order Rayleigh–Schrödinger perturbation theory, considering the exact Kohn–Sham ground-state as a perturbation of the approximate ground-state computed in the coarse basis. In [5, Section 5], numerical results for this method were presented, showing that in practice, this method leads to a substantial improvement for the ground-state energy, the improvement factor varying between 10 and 100 for small size systems such as the alanine molecule. Besides, the computational extra-cost did not exceed about 3-5% of the total computations, depending on the size of the chosen fine basis.

In this article, we focus on the theoretical improvement of this post-processing method for the Kohn–Sham problem. We provide the proofs of theoretical estimates presented in [5], which partly rely on the proofs for the linear subproblem of the Kohn–Sham model presented in the first part of this contribution [6]. Compared to the procedure proposed in [6], we construct here two different post-processed sets of orbitals

*Corresponding author. Email: genevieve.dusson@math.cnrs.fr

from the ground-state orbitals of the discrete Kohn–Sham problem in the coarse basis. The first one is derived directly from first-order Rayleigh–Schrödinger perturbation theory, but is not *a priori* orthonormal; the second one is orthonormal. From these two sets of orbitals, we define in Definition 4.1 two corresponding density matrices, and two post-processed energies. Note that, since the problem is nonlinear, the corrections given by the perturbative expansion at first-order cannot be computed exactly. However, we derive that the neglected uncomputable contributions are *a priori* small.

The main result of this article is provided in Theorem 5.1. We show that, as in the linear case, the convergence rates of both the post-processed ground-state density matrices and the post-processed ground-state energies are improved within the asymptotic regime where the discretization space is large enough. On top of that, we show that the two versions of the post-processing lead to the same improvement on the density matrix error, but to different improvements on the energy. Indeed, only the post-processed energy computed from the orthonormal post-processed orbitals presents a convergence doubling compared to the density matrix error. These results are valid under the assumption that there is a gap between the highest occupied orbital and the lowest unoccupied orbital, which corresponds to considering insulators. All other assumptions come from the *a priori* analysis for the Kohn–Sham problem and do not differ from [3]. Also, our post-processing method crucially relies on the fact that the Laplace operator, which is the leading part in the Hamiltonian, is diagonal in a planewave basis, so that it commutes with the orthogonal projector on the discretization space.

This article is organized as follows. In Section 2.1, we present the Kohn–Sham model in the periodic setting, and define the main quantities of interest: the ground-state orbitals $(\phi_1^0, \dots, \phi_N^0)$, the density matrix γ_0 and the energy I_0^{KS}. In Section 2.2, we briefly recall the functional setting used in the following sections. In Section 3.1, we present the planewave discretization of this Kohn–Sham problem. In Section 3.2, we recall *a priori* estimates derived in [3]. We also translate these results in terms of density matrix formalism. In Section 4, we describe the post-processing method based on Rayleigh–Schrödinger perturbation theory, and in particular define the corrections. In Section 5.1, we present the main results of this paper, *i.e.* an improved convergence rate on the post-processed ground-state density matrices and energies. The proofs are given in Section 5.2.

List of notation

To help the reader navigate through the paper, we summarize below the principal notation, and refer to the definitions when needed.

To start with, N denotes the number of computed eigenvalues. The quantities related to the choice of discretisation (Section 3.1) are

- E_c: kinetic energy cutoff,
- $N_\mathrm{c} = \sqrt{\frac{E_\mathrm{c}}{2}}\frac{L}{\pi}$: discretisation parameter,
- X_{N_c}: discretisation space.

The quantities related to energies are

- I_0^{KS}: exact ground state energy (2.4),
- $I_{0,N_\mathrm{c}}^{\mathrm{KS}}$: variational approximation of the ground state energy (3.1),
- $\widetilde{\mathcal{E}_{N_\mathrm{c}}}$: perturbed ground state energy (4.11),
- $\widetilde{\widetilde{\mathcal{E}_{N_\mathrm{c}}}}$: orthonormalized perturbed energy (4.12).

The different eigenfunctions, corresponding eigenvalues and Lagrange multiplier matrices defined in this article are

- $\Phi^0 = (\phi_1^0, \cdots, \phi_N^0)^T$ and $(\lambda_1^0, \cdots, \lambda_N^0)$: lowest N eigenfunctions and corresponding eigenvalues of the Hamiltonian. The matrix of Lagrange multipliers Λ^0 is diagonal $\Lambda^0 = \mathrm{diag}(\lambda_1^0, \cdots, \lambda_N^0)$ (Section 2.1).
- $\Phi_{N_\mathrm{c}} := (\phi_{1,N_\mathrm{c}}, \ldots, \phi_{N,N_\mathrm{c}})^T$ and $(\lambda_{1,N_\mathrm{c}}, \ldots, \lambda_{N,N_\mathrm{c}})$: lowest eigenfunctions diagonalizing the Hamiltonian on the discretisation space and corresponding eigenvalues (Section 3.1). The corresponding matrix of Lagrange multiplier is diagonal as well.
- $\Phi_{N_\mathrm{c}}^0 = (\phi_{1,N_\mathrm{c}}^0, \ldots, \phi_{N,N_\mathrm{c}}^0)^T$: eigenfunctions given by a unitary transform of Φ_{N_c} such that $\Phi_{N_\mathrm{c}}^0$ is as much aligned with Φ^0 as possible. The corresponding matrix of Lagrange multipliers $\Lambda_{N_\mathrm{c}}^0 = (\lambda_{ij,N_\mathrm{c}}^0)_{1\le i,j\le N} := (\langle \phi_{i,N_\mathrm{c}}^0 | \mathcal{H} | \phi_{j,N_\mathrm{c}}^0 \rangle)_{1\le i,j\le N} \in \mathbb{R}^{N\times N}$ is not diagonal (Section 3.2).
- $\widetilde{\Phi_{N_\mathrm{c}}} = (\widetilde{\phi_{1,N_\mathrm{c}}}, \ldots, \widetilde{\phi_{N,N_\mathrm{c}}})$ and $(\widetilde{\lambda_{1,N_\mathrm{c}}}, \ldots, \widetilde{\lambda_{N,N_\mathrm{c}}})$: perturbed eigenfunctions and perturbed eigenvalues (4.5).
- $\widetilde{\widetilde{\Phi_{N_\mathrm{c}}}} = (\widetilde{\widetilde{\phi_{1,N_\mathrm{c}}}}, \ldots, \widetilde{\widetilde{\phi_{N,N_\mathrm{c}}}})$: orthonormalized perturbed eigenfunctions (4.6).

The different density matrices involved in the following are:

- γ_0: exact ground state density matrix (2.8),
- γ_{N_c}: approximate density matrix (Section 3.1),
- $\widetilde{\gamma_{N_\mathrm{c}}}$: perturbed density matrix (4.8). Note that this density matrix is not an orthogonal projector, as mentioned in Remark 4.1,
- $\widetilde{\widetilde{\gamma_{N_\mathrm{c}}}}$: orthonormalized perturbed density matrix (4.10).

2 Periodic Kohn–Sham models with pseudopotentials

2.1 Problem setting

In this article, we adopt the system of atomic units, for which $\hbar = 1$, $m_e = 1$, $e = 1$, $4\pi\epsilon_0 = 1$. Thus, the electric charge of the electron is -1, and the charges of the nuclei are positive integers. We consider a periodic setting, therefore the nuclear configuration is supposed to be $\mathcal{R}$-periodic, $\mathcal{R}$ being a periodic lattice with corresponding supercell Ω. To simplify the notation, we consider a cubic lattice $\mathcal{R} = L\mathbb{Z}^3$ $(L > 0)$, which corresponds to a cubic supercell $\Omega = [0, L)^3$. But our arguments also apply in the more general case of any Bravais lattice. For $1 \le p \le \infty$ and $s \in \mathbb{R}_+$, we denote by

$$L^p_\#(\Omega) := \left\{ u \in L^p_{\mathrm{loc}}(\mathbb{R}^3, \mathbb{R}) \mid u \text{ is } \mathcal{R}\text{-periodic} \right\},$$
$$H^s_\#(\Omega) := \left\{ u \in H^s_{\mathrm{loc}}(\mathbb{R}^3, \mathbb{R}) \mid u \text{ is } \mathcal{R}\text{-periodic} \right\},$$

the spaces of real-valued $\mathcal{R}$-periodic L^p and H^s functions.

We consider a spin-restricted LDA Kohn–Sham model [12] with pseudopotentials. This method is typically used for computing condensed phase properties, when the number of atoms in the simulation cell is limited. A detailed presentation of this model employing the same notation can be found in [5, Section 2], see also [3]. We recall here only the main features of the model. Given a system with N valence electron pairs, we are considering the following energy functional

$$\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Psi) = \sum_{i=1}^N \int_\Omega |\nabla \psi_i|^2 + \int_\Omega V_{\mathrm{local}}\, \rho_{[\Psi]} + 2\sum_{i=1}^N \langle \psi_i | V_{\mathrm{nl}} | \psi_i \rangle + \frac{1}{2} D_\Omega(\rho_{[\Psi]}, \rho_{[\Psi]}) + E^c_{\mathrm{xc},\Omega}(\rho_{[\Psi]}), \tag{2.1}$$

where the different terms of the energy are described below. The set of admissible states is

$$\mathcal{M} = \left\{ \Psi = (\psi_1, \ldots, \psi_N)^T \in \left[H^1_\#(\Omega)\right]^N \;\middle|\; \int_\Omega \psi_i \psi_j = \delta_{ij} \right\}. \tag{2.2}$$

The electronic density reads

$$\rho_{[\Psi]}(\mathbf{r}) = 2\sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2. \tag{2.3}$$

The Coulomb energy is defined as

$$D_\Omega(\rho,\rho') = \int_\Omega\int_\Omega G_\Omega(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r})\rho'(\mathbf{r}')d\mathbf{r}d\mathbf{r}' = \int_\Omega \rho(\mathbf{r}')[V_{\mathrm{coul}}(\rho')](\mathbf{r}')d\mathbf{r}',$$

where the Green's function G_Ω and the periodic Coulomb potential $V_{\mathrm{coul}}(\rho')$ are respectively solutions to the following problems

$$\begin{cases} -\Delta G_\Omega = 4\pi\left(\sum_{\mathbf{k}\in\mathcal{R}}\delta_{\mathbf{k}} - \dfrac{1}{|\Omega|}\right) \quad \text{in} \quad \mathbb{R}^3, \\ G_\Omega \quad \mathcal{R}-\text{periodic}, \\ \displaystyle\int_\Omega G_\Omega = 0, \end{cases} \qquad \text{and} \qquad \begin{cases} -\Delta V_{\mathrm{coul}}(\rho') = 4\pi\left(\rho' - \dfrac{1}{|\Omega|}\displaystyle\int_\Omega \rho'\right) \quad \text{in} \quad \mathbb{R}^3, \\ V_{\mathrm{coul}}(\rho') \quad \mathcal{R}-\text{periodic}, \\ \displaystyle\int_\Omega V_{\mathrm{coul}}(\rho') = 0. \end{cases}$$

The pseudopotential, modeling the effects of the nuclei and the core electrons (and some relativistic effects for heavy atoms) consists of two terms: a local component V_{local} (whose associated operator is the multiplication by the $\mathcal{R}$-periodic function V_{local}) and a nonlocal component V_{nl} given by

$$V_{\mathrm{nl}}\psi = \sum_{j=1}^{J}\left(\int_\Omega \xi_j(\mathbf{r})\psi(\mathbf{r})\,d\mathbf{r}\right)\xi_j,$$

where ξ_j are regular enough $\mathcal{R}$-periodic functions and J is an integer depending on the chemical nature of the ions in the unit cell. The exchange-correlation functional based on a local density approximation is given in this periodic setting with pseudopotentials by

$$E^c_{\mathrm{xc},\Omega}(\rho_{[\Psi]}) = \int_\Omega e^{\mathrm{LDA}}_{\mathrm{xc}}(\rho_c(\mathbf{r}) + \rho_{[\Psi]}(\mathbf{r}))\,d\mathbf{r},$$

where $\rho_c \geq 0$ is a nonlinear core correction, and $e^{\mathrm{LDA}}_{\mathrm{xc}}(\overline{\rho})$ is an approximation of the exchange-correlation energy per unit volume in a homogeneous electron gas with density $\overline{\rho}$.

The ground-state energy is then the solution of the following minimization problem:

$$I_0^{KS} = \inf\left\{\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Psi),\ \Psi\in\mathcal{M}\right\}. \tag{2.4}$$

Under some assumptions on $V_{\mathrm{nl}}, V_{\mathrm{local}}$, and $E^c_{\mathrm{xc},\Omega}$ presented in [3] and recalled in Appendix 6.1, (2.4) has a local minimizer $\Phi^0 = (\phi_1^0,\dots,\phi_N^0)\in\mathcal{M}$. Noting that the energy is invariant under a unitary transformation of the orbitals, *i.e.*

$$\forall\Psi\in\mathcal{M},\quad \forall U\in\mathcal{U}(N),\quad U\Psi\in\mathcal{M},\quad \rho_{[U\Psi]} = \rho_{[\Psi]} \quad \text{and} \quad \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(U\Psi) = \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Psi), \tag{2.5}$$

where $\mathcal{U}(N)$ is the group of orthogonal matrices:

$$\mathcal{U}(N) = \left\{U\in\mathbb{R}^{N\times N} \mid U^TU = 1_N\right\}, \tag{2.6}$$

1_N denoting the identity matrix of rank N, any unitary transform of the Kohn–Sham orbitals Φ^0 in the sense of (2.5) is also a minimizer of the Kohn–Sham energy, and (2.4) has an infinity of minimizers. It is therefore possible to diagonalize the matrix of the Lagrange multipliers in the first-order optimality conditions relative to (2.4), and show the existence of a minimizer (still denoted by Φ^0), such that

$$\forall i = 1,\dots,N,\quad \mathcal{H}_0\,\phi_i^0 = \lambda_i^0\phi_i^0, \qquad \text{and} \qquad \forall i,j = 1,\dots,N,\quad \langle\phi_i^0|\phi_j^0\rangle = \delta_{ij},$$

for some $\lambda_1^0 \le \lambda_2^0 \le \cdots \le \lambda_N^0$, where the Hamiltonian $\mathcal{H}_0$ is the self-adjoint operator on $L^2_\#(\Omega)$ with domain $H^2_\#(\Omega)$ defined by

$$\forall u \in H^2_\#(\Omega), \quad \mathcal{H}_0 u = -\frac{1}{2}\Delta u + V_{\text{ion}} u + V_{\text{coul}}(\rho_0) u + V_{\text{xc}}(\rho_0) u,$$

with $\rho_0 = \rho_{[\Phi^0]}$, $V_{\text{ion}} = V_{\text{local}} + V_{\text{nl}}$, and where

$$V_{\text{xc}}(\rho)(\mathbf{r}) = \frac{de_{\text{xc}}^{\text{LDA}}}{d\rho}(\rho_c(\mathbf{r}) + \rho(\mathbf{r})).$$

The matrix of Lagrange multipliers of Φ^0 is then $\Lambda^0 = \text{diag}(\lambda_1^0, \cdots, \lambda_N^0)$.

Let us also define the Kohn–Sham operator for a given density ρ as

$$\mathcal{H}_{[\rho]} = -\frac{1}{2}\Delta + V_{\text{ion}} + V_{\text{coul}}(\rho) + V_{\text{xc}}(\rho), \tag{2.7}$$

so that $\mathcal{H}_0 = \mathcal{H}_{[\rho_0]}$. The potentials V_{local}, $V_{\text{coul}}(\rho)$, and $V_{\text{xc}}(\rho)$ being multiplicative, we use the same notations for the potentials as functions on Ω, and for the corresponding multiplicative operators.

We will suppose in the following that the system under consideration satisfies the *Aufbau* principle, so that $\lambda_1^0 \le \lambda_2^0 \le \cdots \le \lambda_N^0$ are the lowest N eigenvalues of the Kohn–Sham Hamiltonian $\mathcal{H}^0$. Note that, although this property seems to hold in practice for most systems, it has not been proved in general, except for the extended Kohn–Sham model (see [3] for details).

Also, as in the linear case [6], we will make the following assumption:

Assumption 2.1. *There is a gap between the N^{th} and the $(N+1)^{\text{st}}$ eigenvalues of $\mathcal{H}_0$, i.e.*

$$g := \lambda_{N+1}^0 - \lambda_N^0 > 0.$$

In this setting, the Fermi level ϵ_{F} could be defined as any real number in the range $(\lambda_N^0, \lambda_{N+1}^0)$. We define it as $\epsilon_{\text{F}} := \frac{\lambda_N^0 + \lambda_{N+1}^0}{2}$.

The purpose of this problem is to compute two quantities of interest:

1. the ground-state density matrix γ_0 based on the orbitals $\Phi^0 = (\phi_1^0, \dots, \phi_N^0)^T$, defined as

$$\boxed{\gamma_0 := \mathbb{1}_{(-\infty, \epsilon_{\text{F}}]}(\mathcal{H}_0) = \sum_{i=1}^N |\phi_i^0\rangle\langle\phi_i^0|,} \tag{2.8}$$

   which belongs to the Grassmann manifold

$$\Upsilon = \left\{\gamma \in \mathcal{L}(L^2_\#) \;\middle|\; \gamma^* = \gamma,\ \gamma^2 = \gamma,\ \text{Tr}\,(\gamma) = N,\ \text{Tr}\,(-\Delta\gamma) < \infty\right\};$$

2. the ground-state energy defined as

$$\boxed{I_0^{KS} := \mathcal{E}_{0,\Omega}^{\text{KS}}(\Phi^0).}$$

We refer to [6] for the definition of the operator trace Tr.

2.2 Functional setting

In this article, the functional setting is similar to [6]. We denote by $\|\cdot\|$ the operator norm on $\mathcal{L}(L^2_\#)$, the space of bounded linear operators on $L^2_\#(\Omega)$. We also denote by $\mathfrak{S}_1(L^2_\#)$ the Banach space of trace-class operators on $L^2_\#(\Omega)$ endowed with the norm defined by $\|A\|_{\mathfrak{S}_1(L^2_\#)} := \text{Tr}\,(|A|) = \text{Tr}\,(\sqrt{A^*A})$. Also, let the

Hilbert space of Hilbert–Schmidt operators $\mathfrak{S}_2(L^2_\#)$ on $L^2_\#(\Omega)$ be endowed with the inner product defined by $(A,B)_{\mathfrak{S}_2(L^2_\#)} := \mathrm{Tr}\,(A^*B)$. Moreover, let us define for any operator A on $L^2_\#(\Omega)$ with domain $D(A)$,

$$\forall \Psi \in [D(A)]^N, \quad \|A\Psi\|_{L^2_\#} := \left(\sum_{i=1}^N \|A\psi_i\|^2_{L^2_\#} \right)^{1/2},$$

which corresponds to $\|\Psi\|_{L^2_\#}$ when A is the identity operator and $\|\Psi\|_{H^1_\#}$ when $A = (1-\Delta)^{1/2}$.

3 Discretization and resolution of the Kohn–Sham model

3.1 Planewave discretization

In the context of periodic boundary conditions, we discretize the Kohn–Sham problem (2.4) in Fourier modes, also called planewaves. We denote by $\mathcal{R}^* = \frac{2\pi}{L}\mathbb{Z}^3$ the dual lattice of the periodic lattice $\mathcal{R} = L\mathbb{Z}^3$. For $\mathbf{k} \in \mathcal{R}^*$, we denote by $e_\mathbf{k}$ the planewave with wavevector $\mathbf{k}$ and kinetic energy $\frac{1}{2}|\mathbf{k}|^2$, with $|\cdot|$ the Euclidean norm, defined by

$$\begin{aligned} e_\mathbf{k} : \quad & \mathbb{R}^3 \to \mathbb{C} \\ & \mathbf{x} \mapsto |\Omega|^{-1/2} e^{i\mathbf{k}\cdot\mathbf{x}}, \end{aligned}$$

where $|\Omega| = L^3$. The family $(e_\mathbf{k})_{\mathbf{k}\in\mathcal{R}^*}$ forms an orthonormal basis of $L^2_\#(\Omega,\mathbb{C})$ endowed with the scalar product

$$\forall u, v \in L^2_\#(\Omega,\mathbb{C}), \quad \langle u|v\rangle = \int_\Omega \overline{u(\mathbf{r})}\, v(\mathbf{r})\, d\mathbf{r},$$

where $\overline{u(\mathbf{r})}$ denotes the complex conjugate of $u(\mathbf{r})$, and for all $v \in L^2_\#(\Omega,\mathbb{C})$,

$$v(\mathbf{r}) = \sum_{\mathbf{k}\in\mathcal{R}^*} \widehat{v}_\mathbf{k}\, e_\mathbf{k}(\mathbf{r}) \qquad \text{with} \qquad \widehat{v}_\mathbf{k} = \langle e_\mathbf{k}|v\rangle = |\Omega|^{-1/2} \int_\Omega v(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}.$$

To discretize the variational set $\mathcal{M}$, we introduce some energy cutoff $E_\mathrm{c} > 0$ and consider all basis functions with kinetic energy smaller than E_c, *i.e.* $|\mathbf{k}| \leq \sqrt{2E_\mathrm{c}}$. That is, for each cutoff E_c, we set $N_\mathrm{c} = \sqrt{\frac{E_\mathrm{c}}{2}}\frac{L}{\pi}$ and consider the finite-dimensional discretization space

$$X_{N_\mathrm{c}} := \left\{ \sum_{\mathbf{k}\in\mathcal{R}^*, |\mathbf{k}|\leq \frac{2\pi}{L}N_\mathrm{c}} \widehat{v}_\mathbf{k}\, e_\mathbf{k} \;\middle|\; \forall \mathbf{k}, \quad \widehat{v}_{-\mathbf{k}} = \widehat{v}_\mathbf{k}^* \right\} \subset \bigcap_{s\in\mathbb{R}} H^s_\#(\Omega).$$

We denote by Π_{N_c} the orthogonal projector on X_{N_c} for any $H^s_\#(\Omega)$, $s \in \mathbb{R}$, defined as

$$\Pi_{N_\mathrm{c}} v = \sum_{\mathbf{k}\in\mathcal{R}^*, |\mathbf{k}|\leq \frac{2\pi}{L}N_\mathrm{c}} \widehat{v}_\mathbf{k} e_\mathbf{k},$$

and by $\Pi^\perp_{N_\mathrm{c}} = (1 - \Pi_{N_\mathrm{c}})$ the orthogonal projector on $X^\perp_{N_\mathrm{c}}$, the orthogonal complement to X_{N_c}.

Finally, the variational approximation to the ground-state energy in X_{N_c} is defined as

$$I^{\mathrm{KS}}_{0,N_\mathrm{c}} = \inf \left\{ \mathcal{E}^{\mathrm{KS}}_0(\Psi_{N_\mathrm{c}}) \,,\ \Psi_{N_\mathrm{c}} \in \mathcal{M} \cap [X_{N_\mathrm{c}}]^N \right\}. \tag{3.1}$$

Using again the invariance property (2.5), the Euler equations of this minimization problem can be diagonalized and reduced to find the pairs $(\phi_{j,N_\mathrm{c}}, \lambda_{j,N_\mathrm{c}})_{j=1,\ldots,N}$ satisfying

$$\forall j = 1,\ldots,N, \quad \mathcal{H}_{N_\mathrm{c},\mathrm{proj}}\, \phi_{j,N_\mathrm{c}} = \lambda_{j,N_\mathrm{c}}\, \phi_{j,N_\mathrm{c}}, \qquad \text{and} \qquad \forall i,j = 1,\ldots,N, \quad \langle \phi_{i,N_\mathrm{c}} | \phi_{j,N_\mathrm{c}} \rangle = \delta_{ij}, \tag{3.2}$$

$\lambda_{1,N_c} \leq \lambda_{2,N_c} \leq \ldots \leq \lambda_{N,N_c}$, where $\mathcal{H}_{N_c,\mathrm{proj}} : X_{N_c} \to X_{N_c}$ is defined as

$$\mathcal{H}_{N_c,\mathrm{proj}} = \Pi_{N_c} \mathcal{H}_{[\rho_{N_c}]} \Pi_{N_c} = -\frac{1}{2} \Pi_{N_c} \Delta \Pi_{N_c} + \Pi_{N_c} \Big[V_{\mathrm{ion}} + V_{\mathrm{coul}}(\rho_{N_c}) + V_{\mathrm{xc}}(\rho_{N_c}) \Big] \Pi_{N_c}, \tag{3.3}$$

with $\rho_{N_c} = \rho_{[\Phi_{N_c}]}$, $\Phi_{N_c} = (\phi_{1,N_c}, \ldots, \phi_{N,N_c})^T$ and where $\mathcal{H}_{[\rho_{N_c}]}$ is defined by (2.7) for the approximate ground-state density ρ_{N_c}. The corresponding density matrix, which is independent of the chosen orthonormal basis for $\mathrm{Span}(\phi_{1,N_c}, \phi_{2,N_c}, \ldots, \phi_{N,N_c})$, is denoted by $\gamma_{N_c} \in \Upsilon$, and defined as

$$\boxed{\gamma_{N_c} = \sum_{i=1}^{N} |\phi_{i,N_c}\rangle\langle\phi_{i,N_c}|.}$$

Finally, the ground-state energy is defined as

$$\boxed{I_{0,N_c}^{\mathrm{KS}} = \mathcal{E}_0^{\mathrm{KS}}(\Phi_{N_c}).}$$

In order to solve the nonlinear eigenvalue problem (3.2), a Self-Consistent Field (SCF) procedure is employed [15]. It consists of solving a linear eigenvalue problem at each step, at which the Hamiltonian is computed from the density found at the previous step. The details of the algorithm in this setting can be found in [5] and the references therein.

3.2 *A priori* results on the density matrices

The existence of minimizers of problems (2.4) and (3.1) as well as *a priori* error estimates on the convergence of the solutions to the discretized problem (3.1) to those of the continuous problem (2.4) hold under several assumptions presented in [3]. For completeness, these assumptions are recalled in Appendix 6.1.

Moreover, in order to use the *a priori* results of [3] in the proofs of our estimates, we first show that similar *a priori* results hold in the density matrix formalism. To start with, let us define the solution to the discrete problem lying in the space

$$\mathcal{M}^{\Phi^0} := \left\{ \Psi \in \mathcal{M} \;\middle|\; \|\Psi - \Phi^0\|_{L^2_\#} = \min_{U \in \mathcal{U}(N)} \|U\Psi - \Phi^0\|_{L^2_\#} \right\},$$

where $\mathcal{U}(N)$ is defined in (2.6) and $\mathcal{M}$ in (2.2). Therefore we define $\Phi^0_{N_c} = (\phi^0_{1,N_c}, \ldots, \phi^0_{N,N_c})^T \in \mathcal{M}^{\Phi^0}$ such that

$$\|\Phi^0_{N_c} - \Phi^0\|_{L^2_\#} = \min_{U \in U(N)} \|U\Phi_{N_c} - \Phi^0\|_{L^2_\#},$$

where Φ_{N_c} is a solution to (3.2). Moreover, we define the Lagrange multiplier matrix of the orthonormality constraints as

$$\Lambda^0_{N_c} = (\lambda^0_{ij,N_c})_{1 \leq i,j \leq N} := (\langle \phi^0_{i,N_c} | \mathcal{H} | \phi^0_{j,N_c} \rangle)_{1 \leq i,j \leq N} \in \mathbb{R}^{N \times N}.$$

The following lemma exhibits norm equivalences between density matrices and their corresponding orbitals.

Lemma 3.1 ($L^2_\#$ and $H^1_\#$ norm equivalences)**.** *There exist $c, C > 0$ such that for all $\Psi^0 = (\psi^0_1, \ldots, \psi^0_N) \in \mathcal{M}^{\Phi^0}$ with corresponding density matrix $\gamma^0_\Psi = \sum_{i=1}^N |\psi^0_i\rangle\langle\psi^0_i|$, satisfying for all $v \in Span(\phi^0_1, \ldots, \phi^0_N)\backslash\{0\}$, $\|\gamma_{\Psi^0} v\|_{L^2_\#} \neq 0$,*

$$\|\Psi^0 - \Phi^0\|_{L^2_\#} \quad \leq \quad \|\gamma^0_\Psi - \gamma_0\|_{\mathfrak{S}_2(L^2_\#)} \quad \leq \quad \sqrt{2}\|\Psi^0 - \Phi^0\|_{L^2_\#}, \tag{3.4}$$

$$c\|(1-\Delta)^{1/2}(\Psi^0 - \Phi^0)\|_{L^2_\#} \quad \leq \quad \|(1-\Delta)^{1/2}(\gamma^0_\Psi - \gamma_0)\|_{\mathfrak{S}_2(L^2_\#)} \quad \leq \quad C\|(1-\Delta)^{1/2}(\Psi^0 - \Phi^0)\|_{L^2_\#}. \tag{3.5}$$

The proof is given in Appendix 6.2. Note that this lemma is more general than the similar result provided in the linear case [6, Lemma 2.3], as γ^0_Ψ can be any density matrix and not only the discrete density matrix γ_{N_c}.

Based on Lemma 3.1, it is possible to express the results of [3, Theorem 4.2] in terms of density matrices, which we detail in the following Theorem.

Theorem 3.1 (see [3]). *Let Φ^0 be a local minimizer of (2.4). Under Assumption 6.1, there exist $N_c^0 > 0$ and $r_0 > 0$ such that for $N_c \geq N_c^0$, (3.1) has a unique local minimizer $\Phi_{N_c}^0$ in the set*

$$\left\{\Phi_{N_c} \in \mathcal{M}^{\Phi^0} \cap [X_{N_c}]^N \,\middle|\, \|\Phi_{N_c} - \Phi^0\| \leq r_0\right\}.$$

Moreover, if the assumptions of the a priori analysis of [7, Theorem 4.2] recalled in Assumptions 6.1 and 6.2 are satisfied, there exist $c, C > 0$, and $N_c^0 \in \mathbb{N}$ such that for $N_c \geq N_c^0$,

$$c\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|^2_{\mathfrak{S}_2(L^2_\#)} \leq I^{\mathrm{KS}}_{0,N_c} - I_0^{KS} \leq C\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|^2_{\mathfrak{S}_2(L^2_\#)}, \tag{3.6}$$

$$\|(1-\Delta)^{-1/2}(\Phi^0_{N_c} - \Phi^0)\|_{L^2_\#} \leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_{N_c} - \gamma_0)\|_{\mathfrak{S}_2(L^2_\#)}, \tag{3.7}$$

$$\|\gamma_0 - \gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \leq CN_c^{-2}, \tag{3.8}$$

$$\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)} \leq CN_c^{-1}, \tag{3.9}$$

and

$$\|\Lambda^0 - \Lambda^0_{N_c}\|_{\mathrm{F}} \leq C\Big(\|(1-\Delta)^{1/2}(\gamma_{N_c} - \gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} + N_c^{-2}\|(1-\Delta)^{1/2}(\gamma_{N_c} - \gamma_0)\|_{\mathfrak{S}_2(L^2_\#)}\Big), \tag{3.10}$$

where $\|\,.\,\|_{\mathrm{F}}$ denotes the Frobenius norm.

The proof is given in Appendix 6.2.

4 Post-processing of the planewave approximation

Our post-processing method strongly relies on the fact that the Laplace operator is diagonal in planewaves, with explicitly known eigenvalues $|\mathbf{k}|^2, \mathbf{k} \in \mathcal{R}^*$. The smallest eigenvalue of the operator $-\frac{1}{2}\Delta$ on $X_{N_c}^\perp$ being strictly larger than $\frac{1}{2}\left(\frac{2\pi N_c}{L}\right)^2$, if the N^{th} eigenvalue of the operator $\mathcal{H}_{N_c,\mathrm{proj}}$ defined in (3.3) satisfies $\lambda_{N,N_c} < \frac{1}{2}\left(\frac{2\pi N_c}{L}\right)^2$, which holds for N_c large enough, the lowest eigenvalues and eigenvectors of $\mathcal{H}_{N_c,\mathrm{proj}}$ are preserved by addition of the operator $-\frac{1}{2}\Delta$ on $X_{N_c}^\perp$: $(1-\Pi_{N_c})(-\frac{1}{2}\Delta)(1-\Pi_{N_c})$. Therefore, the discrete solution Φ_{N_c} is also the ground-state of the following Kohn-Sham problem

$$\forall j = 1,\ldots,N, \quad \mathcal{H}_{N_c}\,\phi_{j,N_c} = \lambda_{j,N_c}\,\phi_{j,N_c}, \qquad \text{and} \qquad \forall i,j = 1,\ldots,N, \quad \langle \phi_{i,N_c}|\phi_{j,N_c}\rangle = \delta_{ij}, \tag{4.1}$$

$\lambda_{1,N_c} \leq \lambda_{2,N_c} \leq \ldots \leq \lambda_{N,N_c}$, where

$$\mathcal{H}_{N_c} = -\frac{1}{2}\Delta + \Pi_{N_c}\Big[V_{\mathrm{ion}} + V_{\mathrm{coul}}(\rho_{N_c}) + V_{\mathrm{xc}}(\rho_{N_c})\Big]\Pi_{N_c} = \mathcal{H}_{N_c,\mathrm{proj}} + (1-\Pi_{N_c})(-\frac{1}{2}\Delta)(1-\Pi_{N_c}).$$

Replacing $\mathcal{H}_{N_c,\mathrm{proj}}$ by $\mathcal{H}_{N_c}$ in the equations satisfied by Φ_{N_c} will be crucial in our analysis. Conversely, the exact solution $(\phi_j^0, \lambda_j^0)_{j=1,\ldots,N}$ satisfies

$$(\mathcal{H}_{N_c} + \mathcal{V}_{N_c}^\perp + \mathcal{W}_{N_c})\,\phi_j^0 = \lambda_j^0\,\phi_j^0, \qquad \langle \phi_i^0|\phi_j^0\rangle = \delta_{ij}, \tag{4.2}$$

where

$$\mathcal{V}_{N_c}^\perp = [V_{\mathrm{ion}} + V_{\mathrm{coul}}(\rho_{N_c}) + V_{\mathrm{xc}}(\rho_{N_c})] - \Pi_{N_c}\Big[V_{\mathrm{ion}} + V_{\mathrm{coul}}(\rho_{N_c}) + V_{\mathrm{xc}}(\rho_{N_c})\Big]\Pi_{N_c},$$

and

$$\mathcal{W}_{N_c} = [V_{\mathrm{coul}}(\rho_0) + V_{\mathrm{xc}}(\rho_0)] - [V_{\mathrm{coul}}(\rho_{N_c}) + V_{\mathrm{xc}}(\rho_{N_c})].$$

As described in [5, Section 4], we rely on Rayleigh–Schrödinger perturbation method [11] to define improved orbitals $(\widetilde{\phi_{j,N_c}}, \widetilde{\lambda_{j,N_c}})_{j=1,\ldots,N}$, taking (4.2) as the perturbed equation, and (4.1) as the unperturbed one. For non-degenerate eigenvalues, the corrections arising from first-order perturbation theory are

$$\forall\, j = 1,\ldots,N, \quad \phi_j^0 \simeq \phi^0_{j,N_c} + \phi^{(1)}_{j,N_c} + \phi^{(2)}_{j,N_c},$$

where

$$\phi^{(1)}_{j,N_c} = -\left(-\frac{1}{2}\Delta - \lambda_{j,N_c}\right)^{-1} r_j \in X^\perp_{N_c}, \tag{4.3}$$

$r_j \in X^\perp_{N_c}$ being the residual defined by

$$r_j = \left(-\frac{1}{2}\Delta + V_{\rm ion} + V_{\rm coul}(\rho_{N_c}) + V_{\rm xc}(\rho_{N_c}) - \lambda_{j,N_c}\right)\phi_{j,N_c} = \left(\mathcal{H}_{N_c} + \mathcal{V}^\perp_{N_c} - \lambda_{j,N_c}\right)\phi_{j,N_c} = \mathcal{V}^\perp_{N_c}\phi_{j,N_c},$$

and $\phi^{(2)}_{j,N_c}$ being defined by

$$\phi^{(2)}_{j,N_c} = -\left(\mathcal{H}_{N_c} - \lambda_{j,N_c}\right)^{-1}_{|_{(\phi_{j,N_c})^\perp}} \mathcal{W}_{N_c}\phi_{j,N_c}. \tag{4.4}$$

Note that the definition of $\phi^{(1)}_{j,N_c}$ is only consistent because the residuals r_j belong to $X^\perp_{N_c}$ for all $j = 1, \ldots, N$. Moreover, the corrections (4.3) can easily be computed in practice in a very large basis, i.e. introducing a second, very large cutoff, as we will detail in Remark 4.2.

Compared to the linear case [6], the main difference is the presence of the uncomputable potential $\mathcal{W}_{N_c}$, which depends on the exact density ρ_0, and leads to uncomputable corrections (4.4), even projected on a finite basis.

However, we will derive that these uncomputable terms are *a priori* small, and define the post-processed orbitals only from the computable corrections defined in (4.3), which are also well-defined for degenerate eigenvalues. We therefore define the perturbed orbitals, as well as density matrix and energy as follows.

Definition 4.1 (Perturbed eigenvectors, density matrix and energy). *For all $j = 1, \ldots, N$, we define the perturbed eigenvectors as*

$$\widetilde{\phi_{j,N_c}} = \phi_{j,N_c} + \phi^{(1)}_{j,N_c}. \tag{4.5}$$

We also define orthonormal perturbed eigenvectors as an orthonormalization of $(\widetilde{\phi_{j,N_c}})_{j=1,\ldots,N}$. More precisely, for all $j = 1, \ldots, N$, define

$$\widetilde{\widetilde{\Phi_{N_c}}} = {S_{N_c}}^{-1/2}\widetilde{\Phi_{N_c}}, \tag{4.6}$$

where S_{N_c}, the $N \times N$ overlap matrix of $\widetilde{\Phi_{N_c}} = (\widetilde{\phi_{1,N_c}}, \ldots, \widetilde{\phi_{N,N_c}})$, is defined as

$$\forall i,j = 1, \ldots, N, \quad (S_{N_c})_{i,j} = \langle \widetilde{\phi_{i,N_c}} | \widetilde{\phi_{j,N_c}} \rangle. \tag{4.7}$$

We define the perturbed density matrix as

$$\boxed{\widetilde{\gamma_{N_c}} = \sum_{i=1}^{N} |\widetilde{\phi_{j,N_c}}\rangle\langle\widetilde{\phi_{j,N_c}}| = \gamma_{N_c} + \gamma^{(1)}_{N_c} + \sum_{i=1}^{N} |\phi^{(1)}_{j,N_c}\rangle\langle\phi^{(1)}_{j,N_c}|,} \tag{4.8}$$

where

$$\gamma^{(1)}_{N_c} = \sum_{i=1}^{N} |\phi^{(1)}_{j,N_c}\rangle\langle\phi_{j,N_c}| + \sum_{i=1}^{N} |\phi_{j,N_c}\rangle\langle\phi^{(1)}_{j,N_c}|. \tag{4.9}$$

We also define an orthonormalized perturbed density matrix as

$$\boxed{\widetilde{\widetilde{\gamma_{N_c}}} = \sum_{i=1}^{N} |\widetilde{\widetilde{\phi_{i,N_c}}}\rangle\langle\widetilde{\widetilde{\phi_{i,N_c}}}|.} \tag{4.10}$$

We define the perturbed energy as the energy of the perturbed eigenvectors computed with (2.1)

$$\boxed{\widetilde{\mathcal{E}_{N_c}} = \mathcal{E}^{\rm KS}_{0,\Omega}(\widetilde{\Phi_{N_c}}),} \tag{4.11}$$

and the orthonormalized perturbed energy as

$$\boxed{\widetilde{\widetilde{\mathcal{E}_{N_c}}} = \mathcal{E}^{\rm KS}_{0,\Omega}(\widetilde{\widetilde{\Phi_{N_c}}}).} \tag{4.12}$$

Remark 4.1. *Since the post-processed orbitals* (4.5) *are not orthonormal,* $\widetilde{\gamma_{N_c}} \in \Upsilon$ *does not hold in general, although* $\widetilde{\gamma_{N_c}} = \widetilde{\gamma_{N_c}}^*$. *Indeed, a priori,* $\widetilde{\gamma_{N_c}}^2 \neq \widetilde{\gamma_{N_c}}$ *and* $\mathrm{Tr}\,(\widetilde{\gamma_{N_c}}) \neq N$. *On the other hand, the post-processed orbitals* (4.6) *being orthonormal, there holds* $\widetilde{\widetilde{\gamma_{N_c}}} \in \Upsilon$.

Remark 4.2. *Note that the computational cost of the corrections is limited, and similar to the linear case [6]. For all* $j = 1, \ldots, N$, *the operator* $\left(-\frac{1}{2}\Delta - \lambda_{j,N_c}\right)$ *is diagonal in a planewave basis, hence trivial to invert. Each residual* $\mathcal{V}_{N_c}^{\perp}\phi_{j,N_c}$ *can be computed using a very large basis with only two FFT's, hence with a* $O(n_{dof}\log(n_{dof})N)$ *scaling where* n_{dof} *is the number of degrees of freedom in the fine basis. On top of that, to compute the orthonormalized density matrix* (4.10) *and energy* (4.12), *one needs to orthonormalize the post-processed orbitals, with a cost of* $O(n_{dof}N^2)$. *This corresponds to the cost of a QR decomposition of the matrix containing the post-processed orbitals* $\widetilde{\Phi_{N_c}} = (\widetilde{\phi_{1,N_c}}, \ldots, \widetilde{\phi_{N,N_c}})$. *Indeed, as the density matrix* $\widetilde{\widetilde{\gamma_{N_c}}}$ *does not depend on the orbitals themselves but on their span, as well as for the energy* $\widetilde{\widetilde{\mathcal{E}_{N_c}}}$, *we do not need to compute the matrix* ${S_{N_c}}^{-1/2}$ *explicitely in practice.*

We refer to [5, Section 5] for numerical results illustrating the low computational cost of the post-processing, and showing that taking for the second cutoff a few times the planewave cutoff is sufficient. Indeed, taking larger cutoffs for computing the corrections does not change the observed results (see Fig. 1 in [5]).

5 Convergence improvement on the density matrix and the energy

5.1 Theorem

The improvement results on the post-processed density matrices and the energies are collected in the following theorem. Compared to the linear case [6], the results are similar except for the post-processed energy (4.12) based on the orthonormal version of the post-processed density matrix, for which we derive a convergence doubling compared to the density matrix improvement factor of N_c^{-2}.

Theorem 5.1 (Improved convergence for the density matrix and the energy)**.** *Under the gap assumption* (2.1) *and the smoothness assumptions of [3, Theorem 4.2] recalled in Appendix 6.1 and 6.2, there exist* $C \in \mathbb{R}^+$ *and* $N_c^0 \in \mathbb{N}$ *such that for* $N_c \geq N_c^0$,

$$\boxed{\|(1-\Delta)^{1/2}(\gamma_0 - \widetilde{\gamma_{N_c}})\|_{\mathfrak{S}_2(L^2_\#)} \leq C N_c^{-2} \|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)},} \tag{5.1}$$

$$\boxed{\|(1-\Delta)^{1/2}(\gamma_0 - \widetilde{\widetilde{\gamma_{N_c}}})\|_{\mathfrak{S}_2(L^2_\#)} \leq C N_c^{-2} \|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)},} \tag{5.2}$$

$$\boxed{|\widetilde{\mathcal{E}_{N_c}} - I_0^{KS}| \leq C N_c^{-2} |I_{0,N_c}^{\mathrm{KS}} - I_0^{KS}|,} \tag{5.3}$$

and

$$\boxed{|\widetilde{\widetilde{\mathcal{E}_{N_c}}} - I_0^{KS}| \leq C N_c^{-4} |I_{0,N_c}^{\mathrm{KS}} - I_0^{KS}|.} \tag{5.4}$$

Remark 5.1. *The difference of right-hand sides between* (5.3) *and* (5.4) *mainly comes from the property that the orbitals* $\widetilde{\widetilde{\Phi_{N_c}}}$ *are orthonormal whereas the orbitals* $\widetilde{\Phi_{N_c}}$ *are not. Indeed, a priori results lead to a doubling of the convergence rate improvement between* (5.2) *and* (5.4). *But the lack of orthonormality of the postprocessed orbitals* $\widetilde{\Phi_{N_c}}$ *gives rise to an extra error in the energy, which explains the similar convergence rate improvements between the density matrix error* (5.1) *and the energy error* (5.3).

5.2 Proof

In order to prove Theorem 5.1, we first provide in Section 5.2.1 a decomposition of γ_0 based on spectral projection in Lemma 5.1, and then, in Section 5.2.2, we provide four preliminary lemmas. In Section 5.2.3, we decompose the difference $\gamma_0 - \widetilde{\gamma_{N_\mathrm{c}}}$ into six parts in Lemma 5.7, and we then estimate each of these terms in the following lemmas 5.2, 5.8, 5.9, 5.10, and 5.11 in order to prove estimate (5.1). Lemma 5.12 then allows to extend the proof to estimate (5.2). Finally, in Section 5.2.4, we provide a proof for estimates (5.3) and (5.4).

5.2.1 Exact density matrix in terms of approximate density matrix

From [6, Lemma 4.2], whose proof is identical in the nonlinear case, relying on the gap assumption 2.1, there exists a contour Γ and $N_\mathrm{c}^0 \in \mathbb{N}$, such that for all $N_\mathrm{c} \geq N_\mathrm{c}^0$, Γ contains the lowest N eigenvalues of both operators $\mathcal{H}_0$ and $\mathcal{H}_{N_\mathrm{c}}$ and none of the higher ones. Taking such a contour Γ, writing $\mathcal{H}_0 = \mathcal{H}_{N_\mathrm{c}} + \mathcal{V}_{N_\mathrm{c}}^\perp + \mathcal{W}_{N_\mathrm{c}}$, and using the definition of spectral projection, the density matrix defined in (2.8) can be decomposed as

$$\gamma_0 \quad = \quad \frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_0)^{-1}\,dz = \frac{1}{2\pi i}\oint_\Gamma \left(z-\mathcal{H}_{N_\mathrm{c}} - \mathcal{V}_{N_\mathrm{c}}^\perp - \mathcal{W}_{N_\mathrm{c}}\right)^{-1} dz.$$

Then using the Dyson equation twice [10, 13] to decompose the operator $\left(z-\mathcal{H}_{N_\mathrm{c}} - \mathcal{V}_{N_\mathrm{c}}^\perp - \mathcal{W}_{N_\mathrm{c}}\right)^{-1}$, we obtain

$$\begin{aligned}\gamma_0 = &\frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,dz + \frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_{N_\mathrm{c}})^{-1}(\mathcal{V}_{N_\mathrm{c}}^\perp + \mathcal{W}_{N_\mathrm{c}})(z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,dz \\ &+ \frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_0)^{-1}(\mathcal{V}_{N_\mathrm{c}}^\perp + \mathcal{W}_{N_\mathrm{c}})(z-\mathcal{H}_{N_\mathrm{c}})^{-1}(\mathcal{V}_{N_\mathrm{c}}^\perp + \mathcal{W}_{N_\mathrm{c}})(z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,dz. \end{aligned} \tag{5.5}$$

Lemma 5.1 (Decomposition of γ_0)**.** *There holds*

$$\gamma_0 = \gamma_{N_\mathrm{c}} + \gamma_{N_\mathrm{c}}^{(1)} + \gamma_{N_\mathrm{c}}^{(2)} + \widetilde{Q_{N_\mathrm{c}}}, \tag{5.6}$$

where $\gamma_{N_\mathrm{c}}^{(1)}$ *is defined in* (4.9),

$$\gamma_{N_\mathrm{c}}^{(2)} = \frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,\mathcal{W}_{N_\mathrm{c}}\,(z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,dz, \tag{5.7}$$

and

$$\widetilde{Q_{N_\mathrm{c}}} = \frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_0)^{-1}(\mathcal{V}_{N_\mathrm{c}}^\perp + \mathcal{W}_{N_\mathrm{c}})(z-\mathcal{H}_{N_\mathrm{c}})^{-1}(\mathcal{V}_{N_\mathrm{c}}^\perp + \mathcal{W}_{N_\mathrm{c}})(z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,dz. \tag{5.8}$$

Proof. We start from (5.5). By definition of the spectral projection, there holds

$$\gamma_{N_\mathrm{c}} = \frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,dz,$$

i.e. the first term of the right hand side in (5.5). Following the proof of [6, Lemma 4.3], one can show that

$$\gamma_{N_\mathrm{c}}^{(1)} = \frac{1}{2\pi i}\oint_\Gamma (z-\mathcal{H}_{N_\mathrm{c}})^{-1}\,\mathcal{V}_{N_\mathrm{c}}^\perp\,(z-\mathcal{H}_{N_\mathrm{c}})^{-1}.$$

From the definition of $\gamma_{N_\mathrm{c}}^{(2)}$ in (5.7), we get that $\gamma_{N_\mathrm{c}}^{(1)} + \gamma_{N_\mathrm{c}}^{(2)}$ corresponds to the second term of the right hand side in (5.5). Finally, the definition of $\widetilde{Q_{N_\mathrm{c}}}$ in (5.8) allows to conclude the proof of the lemma. ☐

5.2.2 Preliminary lemmas

We collect in a first lemma all results following immediately from [6], relying in particular on the *a priori* estimates of Theorem 3.1.

Lemma 5.2 (see [6])**.** *There exist* $C \in \mathbb{R}^+$ *and* $N_\mathrm{c}^0 \in \mathbb{N}$*, such that for* $N_\mathrm{c} \geq N_\mathrm{c}^0$*,*

$$\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_\mathrm{c}})^2\|_{\mathfrak{S}_2(L^2_\#)} \leq C N_\mathrm{c}^{-2} \|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_\mathrm{c}})\|_{\mathfrak{S}_2(L^2_\#)}, \tag{5.9}$$

$$\|\mathcal{H}_{[\rho_{N_\mathrm{c}}]}(\gamma_{N_\mathrm{c}} - \gamma_0) + \mathcal{H}_0\gamma_0 - \mathcal{H}_{N_\mathrm{c}}\gamma_{N_\mathrm{c}}\|_{\mathfrak{S}_2(L^2_\#)} \leq C N_\mathrm{c}^{-2} \|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_\mathrm{c}})\|_{\mathfrak{S}_2(L^2_\#)}. \tag{5.10}$$

Proof. The proof of (5.9) is identical to [6, proof of Lemma 4.5], given the *a priori* estimate (3.8). The bound (5.10) can be obtained exactly as in the proof of [6, Lemma 4.6] using in particular the *a priori* estimate (3.10). $\square$

We now turn to preliminary results that are specific to the nonlinear case, and will be used to show that the uncomputable terms (4.4) in the perturbative development are small. From [3, (3.19)], there holds for the Coulomb multiplicative potential

$$\forall s \in \mathbb{R}, \quad \forall \rho_1, \rho_2 \in H^s_\#(\Omega), \quad \|V_\mathrm{coul}(\rho_1) - V_\mathrm{coul}(\rho_2)\|_{H^{s+2}_\#} \leq C\|\rho_1 - \rho_2\|_{H^s_\#}, \tag{5.11}$$

from which we deduce in particular with $s = 0$ using Sobolev embeddings that

$$\|V_\mathrm{coul}(\rho_0) - V_\mathrm{coul}(\rho_{N_\mathrm{c}})\|_{L^\infty_\#} + \|\nabla\left(V_\mathrm{coul}(\rho_0) - V_\mathrm{coul}(\rho_{N_\mathrm{c}})\right)\|_{L^3_\#} \leq C\|\rho_0 - \rho_{N_\mathrm{c}}\|_{L^2_\#}, \tag{5.12}$$

which is in particular bounded by a constant independent of N_c. Moreover, under Assumptions 6.1 and 6.2, $V_\mathrm{local} + V_\mathrm{coul}(\rho_{N_\mathrm{c}}) + V_\mathrm{xc}(\rho_{N_\mathrm{c}}) \in H^{3/2+\epsilon}_\#(\Omega)$, for some $\epsilon > 0$, therefore there exist $C \in \mathbb{R}^+$ and $N_\mathrm{c}^0 \in \mathbb{N}$ such that for $N_\mathrm{c} \geq N_\mathrm{c}^0$,

$$\|V_\mathrm{local} + V_\mathrm{coul}(\rho_{N_\mathrm{c}}) + V_\mathrm{xc}(\rho_{N_\mathrm{c}})\|_{L^\infty_\#} + \|\nabla\left(V_\mathrm{local} + V_\mathrm{coul}(\rho_{N_\mathrm{c}}) + V_\mathrm{xc}(\rho_{N_\mathrm{c}})\right)\|_{L^3_\#} \leq C, \tag{5.13}$$

and

$$\|V_\mathrm{xc}(\rho_0) - V_\mathrm{xc}(\rho_{N_\mathrm{c}})\|_{L^\infty_\#} + \|\nabla\left(V_\mathrm{xc}(\rho_0) - V_\mathrm{xc}(\rho_{N_\mathrm{c}})\right)\|_{L^3_\#} \leq C. \tag{5.14}$$

The next lemma deals with the exchange-correlation potential.

Lemma 5.3. *There exist* $C > 0$ *and* $N_\mathrm{c}^0 \in \mathbb{N}$ *such that for* $N_\mathrm{c} \geq N_\mathrm{c}^0$*,*

$$\|V_\mathrm{xc}(\rho_0) - V_\mathrm{xc}(\rho_{N_\mathrm{c}})\|_{H^{-1}_\#} \leq C\|\rho_0 - \rho_{N_\mathrm{c}}\|_{H^{-1}_\#}. \tag{5.15}$$

Proof. Using a Taylor formula with integral remainder, there holds

$$\begin{aligned} \|V_\mathrm{xc}(\rho_0) - V_\mathrm{xc}(\rho_{N_\mathrm{c}})\|_{H^{-1}_\#} &= \left\| \int_0^1 \frac{d^2 e_\mathrm{xc}^\mathrm{LDA}}{d\rho^2}\left(\rho_c + t\rho_0 + (1-t)\rho_{N_c}\right)(\rho_0 - \rho_{N_c}) dt \right\|_{H^{-1}_\#} \\ &\leq \int_0^1 \left\| \frac{d^2 e_\mathrm{xc}^\mathrm{LDA}}{d\rho^2}\left(\rho_c + t\rho_0 + (1-t)\rho_{N_c}\right)(\rho_0 - \rho_{N_c}) \right\|_{H^{-1}_\#} dt. \end{aligned} \tag{5.16}$$

From [3, (4.25)] and the definition of the density (2.3), $\rho_c + t\rho_0 + (1-t)\rho_{N_\mathrm{c}}$ is uniformly bounded in $H^\sigma_\#(\Omega)$ for some $\sigma > 3/2$ uniformly in N_c and t for $N_\mathrm{c} \geq N_\mathrm{c}^0$ and $0 \leq t \leq 1$. As for all $t \in [0,1]$, $\rho_c + t\rho_0 + (1-t)\rho_{N_\mathrm{c}}$ is bounded away from zero uniformly in N_c, and from (6.3) and (6.4), the quantity $\frac{d^2 e_\mathrm{xc}^\mathrm{LDA}}{d\rho^2}\left(\rho_c + t\rho_0 + (1-t)\rho_{N_\mathrm{c}}\right)$ is also uniformly bounded in $H^\sigma_\#(\Omega)$. Note that for $\sigma > 3/2$, there holds

$$\forall f \in H^\sigma_\#(\Omega), \quad \forall g \in H^{-1}_\#(\Omega), \quad fg \in H^{-1}_\#(\Omega) \quad \text{and} \quad \|fg\|_{H^{-1}_\#} \leq C_\sigma \|f\|_{H^\sigma_\#}\|g\|_{H^{-1}_\#}, \tag{5.17}$$

for some constant $C_\sigma \geq 0$ independent of f and g. Indeed,

$$\|fg\|_{H^{-1}_\#} = \sup_{w \in H^1_\#(\Omega), w \neq 0} \frac{\langle fg, w\rangle_{H^{-1}_\#, H^1_\#}}{\|w\|_{H^1_\#}} \leq \sup_{w \in H^1_\#(\Omega), w \neq 0} \frac{\|g\|_{H^{-1}_\#}\|fw\|_{H^1_\#}}{\|w\|_{H^1_\#}}.$$

Noting that $H^\sigma_\#(\Omega)$ is compactly embedded in the space of continuous functions, and using Hölder inequality, we obtain

$$\begin{aligned}
\|fw\|^2_{H^1_\#} &= \|fw\|^2_{L^2_\#} + \|\nabla(fw)\|^2_{L^2_\#} \\
&\leq \|fw\|^2_{L^2_\#} + 2\|f(\nabla w)\|^2_{L^2_\#} + 2\|(\nabla f)w\|^2_{L^2_\#} \\
&\leq C_\sigma \left(\|f\|^2_{L^\infty_\#}\|w\|^2_{L^2_\#} + \|f\|^2_{L^\infty_\#}\|\nabla w\|^2_{L^2_\#} + \|\nabla f\|^2_{L^3_\#}\|w\|^2_{L^6_\#} \right) \\
&\leq C_\sigma \left(\|f\|^2_{H^\sigma_\#}\|w\|^2_{L^2_\#} + \|f\|^2_{H^\sigma_\#}\|w\|^2_{H^1_\#} + \|\nabla f\|^2_{L^3_\#}\|w\|^2_{L^6_\#} \right).
\end{aligned}$$

Finally, using Sobolev embeddings leads to

$$\|fw\|_{H^1_\#} \leq C_\sigma \|f\|_{H^\sigma_\#}\|w\|_{H^1_\#},$$

from which (5.17) follows. Combining (5.16) and (5.17) gives the result. □

Lemma 5.4 (Estimation of $(1-\Delta)^{-1/2}\mathcal{W}_{N_c}$)**.** *There exist $C \in \mathbb{R}^+$ and $N_c^0 \in \mathbb{N}$ such that for $N_c \geq N_c^0$,*

$$\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_0\|_{\mathfrak{S}_2(L^2_\#)} \leq C N_c^{-2} \|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}, \tag{5.18}$$

and

$$\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \leq C N_c^{-2} \|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}. \tag{5.19}$$

Proof. By definition of the Hilbert–Schmidt norm,

$$\begin{aligned}
\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_0\|^2_{\mathfrak{S}_2(L^2_\#)} &= \sum_{i=1}^N \|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\phi_i^0\|^2_{L^2_\#} \\
&= \sum_{i=1}^N \|\mathcal{W}_{N_c}\phi_i^0\|^2_{H^{-1}_\#}.
\end{aligned}$$

As for all $1 \leq i \leq N$, $\phi_i^0 \in H^2_\#(\Omega)$, and for all $N_c \in \mathbb{N}^*$, $\mathcal{W}_{N_c} \in H^{-1}_\#(\Omega)$, we show using (5.17) that there exists $C \in \mathbb{R}^+$ such that for all $N_c \in \mathbb{N}^*$,

$$\|\mathcal{W}_{N_c}\phi_i^0\|_{H^{-1}_\#} \leq C\|\mathcal{W}_{N_c}\|_{H^{-1}_\#}\|\phi_i^0\|_{H^2_\#}.$$

Therefore, as $\sum_{i=1}^N \|\phi_i^0\|^2_{H^2_\#(\Omega)}$ is bounded, there exists $C \in \mathbb{R}^+$ such that for all $N_c \in \mathbb{N}^*$,

$$\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_0\|^2_{\mathfrak{S}_2(L^2_\#)} \leq C\|\mathcal{W}_{N_c}\|^2_{H^{-1}_\#}\sum_{i=1}^N \|\phi_i^0\|^2_{H^2_\#} \leq C\|\mathcal{W}_{N_c}\|^2_{H^{-1}_\#}.$$

From (5.11) with $s = -1$ and (5.15), we derive

$$\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_0\|_{\mathfrak{S}_2(L^2_\#)} \leq C\|\rho_0 - \rho_{N_c}\|_{H^{-1}_\#}. \tag{5.20}$$

Moreover, as shown in [3, (4.85)], there holds

$$\|\rho_0 - \rho_{N_c}\|_{H^{-1}_\#} \leq C\|(1-\Delta)^{-1/2}(\Phi^0 - \Phi^0_{N_c})\|_{L^2_\#}. \tag{5.21}$$

Finally, using (3.7) in (5.21) together with (5.20) allows to prove (5.18).

Since for all $1 \leq i \leq N$, ϕ_{i,N_c} is bounded in $H^2_\#(\Omega)$ independently of N_c, the proof can be easily adapted to show (5.19). □

Lemma 5.5 (Estimation of $(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}$)**.** *There exist $C \in \mathbb{R}^+$ and $N_c^0 \in \mathbb{N}$ such that for $N_c \geq N_c^0$,*

$$\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \leq C\|(1-\Delta)^{1/2}(\gamma_0-\gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}. \tag{5.22}$$

Proof. The proof is similar to the proof of [6, Lemma 4.5]. First,

$$\begin{aligned}\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} &= \left\|(1-\Delta)^{-1/2}(\mathcal{H}_{[\rho_{N_c}]}-\mathcal{H}_{N_c})\gamma_{N_c}\right\|_{\mathfrak{S}_2(L^2_\#)} \\ &= \left\|(1-\Delta)^{-1/2}\left[\mathcal{H}_{[\rho_{N_c}]}(\gamma_{N_c}-\gamma_0)+\mathcal{H}_0\gamma_0-\mathcal{H}_{N_c}\gamma_{N_c}-\mathcal{W}_{N_c}\gamma_0\right]\right\|_{\mathfrak{S}_2(L^2_\#)}.\end{aligned}$$

The result follows by combining (5.10) and (5.18). □

Lemma 5.6 (Estimation of $\|S_{N_c}-1_N\|_{\mathrm{F}}$.)**.** *There exist $C \in \mathbb{R}^+$ and $N_c^0 \in \mathbb{N}$ such that for $N_c \geq N_c^0$,*

$$\|S_{N_c}-1_N\|_{\mathrm{F}} \leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0-\gamma_{N_c})\|^2_{\mathfrak{S}_2(L^2_\#)}. \tag{5.23}$$

Proof. Given the definition of S_{N_c} in (4.7), noting that for all $1 \leq i \leq N$, $\phi_{i,N_c}^{(1)} \in X_{N_c}^{\perp}$, and for all $1 \leq i,j \leq N$, $\langle\phi_{i,N_c}|\phi_{j,N_c}\rangle = \delta_{ij}$, and using the Cauchy–Schwarz inequality, there holds

$$\begin{aligned}\|S_{N_c}-1_N\|_{\mathrm{F}}^2 &= \sum_{i,j=1}^N |\langle\widetilde{\phi_{i,N_c}}|\widetilde{\phi_{j,N_c}}\rangle-\delta_{ij}|^2 \\ &= \sum_{i,j=1}^N |\langle\phi_{i,N_c}|\phi_{j,N_c}\rangle+\langle\phi_{i,N_c}^{(1)}|\phi_{j,N_c}^{(1)}\rangle-\delta_{ij}|^2 \quad \text{(by orthogonality)} \\ &= \sum_{i,j=1}^N |\langle\phi_{i,N_c}^{(1)}|\phi_{j,N_c}^{(1)}\rangle|^2 \\ &\leq \sum_{i,j=1}^N \|\phi_{i,N_c}^{(1)}\|^2_{L^2_\#}\|\phi_{j,N_c}^{(1)}\|^2_{L^2_\#} \\ &= \left(\sum_{j=1}^N \|\phi_{j,N_c}^{(1)}\|^2_{L^2_\#}\right)^2.\end{aligned}$$

Using definition (4.3), and noting that for all $j=1,\dots,N$, the operator $\left(-\frac{1}{2}\Delta-\lambda_{j,N_c}\right)^{-1}$ is diagonal and commute with $\Pi_{N_c}^{\perp}$, we obtain

$$\begin{aligned}\|S_{N_c}-1_N\|_{\mathrm{F}} \leq& \sum_{j=1}^N \|(-\frac{1}{2}\Delta-\lambda_{j,N_c})^{-1}\Pi_{N_c}^{\perp}\mathcal{V}_{N_c}^{\perp}\phi_{j,N_c}\|^2_{L^2_\#} \\ \leq& \|\Pi_{N_c}^{\perp}(1-\Delta)^{-1/2}\|^2 \max_{i=1,\dots,N}\|(1-\Delta)^{1/2}(-\frac{1}{2}\Delta-\lambda_{i,N_c})^{-1}(1-\Delta)^{1/2}\|^2 \\ &\times \sum_{j=1}^N \|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^{\perp}\phi_{j,N_c}\|^2_{L^2_\#}.\end{aligned}$$

There exists $N_c^0 \in \mathbb{N}$ such that for $N_c \geq N_c^0$, the operator $(1-\Delta)^{1/2}(-\frac{1}{2}\Delta-\lambda_{i,N_c})^{-1}(1-\Delta)^{1/2}$ is bounded in $\mathcal{L}(L^2_\#)$ for all $i=1,\dots,N$ independently of N_c. Moreover, there exist $C \in \mathbb{R}^+$ such that $\|\Pi_{N_c}^{\perp}(1-\Delta)^{-1/2}\| \leq$

CN_c^{-1}. Also, $\sum_{j=1}^N \|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^\perp \phi_{j,N_c}\|_{L^2_\#}^2 = \|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^\perp \gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}^2$. Hence, there exist $C \in \mathbb{R}^+$ and $N_c^0 \in \mathbb{N}$ such that for $N_c \geq N_c^0$,

$$\begin{aligned}\|S_{N_c} - 1_N\|_{\mathrm{F}} \leq & CN_c^{-2}\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^\perp \gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}^2 \\ \leq & CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}^2,\end{aligned}$$

from (5.22), which concludes the proof of the lemma. ☐

5.2.3 Proof of estimates (5.1) and (5.2)

Lemma 5.7. *The density matrix difference $\gamma_0 - \widetilde{\gamma_{N_c}}$ can be decomposed as*

$$\gamma_0 - \widetilde{\gamma_{N_c}} = (\gamma_0 - \gamma_{N_c})^2 + \gamma_{N_c}\gamma_{N_c}^{(2)} + \gamma_{N_c}^{(2)}\gamma_{N_c} + \widetilde{Q_{N_c}}\gamma_{N_c} + \gamma_{N_c}\widetilde{Q_{N_c}} - \sum_{j=1}^N |\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|.$$

Proof. Let us first remark, using (5.6), and $\gamma_{N_c}^2 = \gamma_{N_c}$, that

$$\begin{aligned}\gamma_{N_c}\gamma_0 &= \gamma_{N_c} + \gamma_{N_c}\gamma_{N_c}^{(1)} + \gamma_{N_c}\gamma_{N_c}^{(2)} + \gamma_{N_c}\widetilde{Q_{N_c}}, \\ \gamma_0\gamma_{N_c} &= \gamma_{N_c} + \gamma_{N_c}^{(1)}\gamma_{N_c} + \gamma_{N_c}^{(2)}\gamma_{N_c} + \widetilde{Q_{N_c}}\gamma_{N_c}.\end{aligned}$$

Moreover, since for all $i, j = 1, 2, \cdots, N$, ϕ_{i,N_c} is orthogonal to $\phi_{j,N_c}^{(1)}$, one can show as in the proof of [6, Lemma 4.4] that

$$\gamma_{N_c}\gamma_{N_c}^{(1)} + \gamma_{N_c}^{(1)}\gamma_{N_c} = \gamma_{N_c}^{(1)}.$$

Hence

$$\gamma_{N_c}\gamma_0 + \gamma_0\gamma_{N_c} = 2\gamma_{N_c} + \gamma_{N_c}^{(1)} + \gamma_{N_c}\gamma_{N_c}^{(2)} + \gamma_{N_c}^{(2)}\gamma_{N_c} + \gamma_{N_c}\widetilde{Q_{N_c}} + \widetilde{Q_{N_c}}\gamma_{N_c},$$

and thus

$$(\gamma_0 - \gamma_{N_c})^2 = \gamma_0 - \gamma_{N_c} - \gamma_{N_c}^{(1)} - \gamma_{N_c}\gamma_{N_c}^{(2)} - \gamma_{N_c}^{(2)}\gamma_{N_c} - \widetilde{Q_{N_c}}\gamma_{N_c} - \gamma_{N_c}\widetilde{Q_{N_c}},$$

from which we deduce using (4.8) that

$$\gamma_0 - \widetilde{\gamma_{N_c}} = (\gamma_0 - \gamma_{N_c})^2 + \gamma_{N_c}\gamma_{N_c}^{(2)} + \gamma_{N_c}^{(2)}\gamma_{N_c} + \widetilde{Q_{N_c}}\gamma_{N_c} + \gamma_{N_c}\widetilde{Q_{N_c}} - \sum_{j=1}^N |\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|.$$

☐

Lemma 5.8 (Estimation of $(1-\Delta)^{1/2}\widetilde{Q_{N_c}}\gamma_{N_c}$ and $(1-\Delta)^{1/2}\gamma_{N_c}\widetilde{Q_{N_c}}$)**.** *There exist $C \in \mathbb{R}^+$ and $N_c^0 \in \mathbb{N}$ such that for $N_c \geq N_c^0$,*

$$\|(1-\Delta)^{1/2}\widetilde{Q_{N_c}}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}, \tag{5.25}$$

$$\|(1-\Delta)^{1/2}\gamma_{N_c}\widetilde{Q_{N_c}}\|_{\mathfrak{S}_2(L^2_\#)} \leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}. \tag{5.26}$$

Proof. Using the definition of $\widetilde{Q_{N_c}}$ given in (5.8), we have

$$(1-\Delta)^{1/2}\widetilde{Q_{N_c}}\gamma_{N_c} = \frac{1}{2\pi i}\oint_\Gamma (1-\Delta)^{1/2}(z-\mathcal{H}_0)^{-1}(\mathcal{V}_{N_c}^\perp + \mathcal{W}_{N_c})\,(z-\mathcal{H}_{N_c})^{-1}\,(\mathcal{V}_{N_c}^\perp + \mathcal{W}_{N_c})\,(z-\mathcal{H}_{N_c})^{-1}\,\gamma_{N_c}dz.$$

Therefore, using [6, (2.12)] twice, we show that there exists $C \in \mathbb{R}^+$ such that

$$\begin{aligned}\|(1-\Delta)^{1/2}\widetilde{Q_{N_c}}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \leq & C\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z-\mathcal{H}_0)^{-1}(1-\Delta)^{1/2}\| \\ & \times \|(1-\Delta)^{-1/2}(\mathcal{V}_{N_c}^\perp + \mathcal{W}_{N_c})(1-\Delta)^{1/2}\| \\ & \times \max_{z\in\Gamma}\|(1-\Delta)^{-1/2}(z-\mathcal{H}_{N_c})^{-1}(\mathcal{V}_{N_c}^\perp + \mathcal{W}_{N_c})\gamma_{N_c}\,(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)}.\end{aligned}$$

First, $\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z-\mathcal{H}_0)^{-1}(1-\Delta)^{1/2}\|$ is bounded, which is a classical result (see e.g. [4, Lemma 1] for a proof). Second, there exists $C\in\mathbb{R}^+$ such that

$$
\begin{aligned}
\|(1-\Delta)^{-1/2}(\mathcal{V}_{N_c}^{\perp}+\mathcal{W}_{N_c})(1-\Delta)^{1/2}\| &= \|\left[(1-\Delta)^{-1/2}(\mathcal{V}_{N_c}^{\perp}+\mathcal{W}_{N_c})(1-\Delta)^{1/2}\right]^*\| \\
&= \|(1-\Delta)^{1/2}(\mathcal{V}_{N_c}^{\perp}+\mathcal{W}_{N_c})(1-\Delta)^{-1/2}\| \\
&\leq C\left(\|(1-\Delta)^{1/2}\mathcal{V}_{N_c}^{\perp}(1-\Delta)^{-1/2}\|+\|\mathcal{W}_{N_c}\|_{L^\infty}+\|\nabla\mathcal{W}_{N_c}\|_{L^3}\right) \\
&\leq C\Big(\|(1-\Delta)^{1/2}\big(V_{\mathrm{local}}+V_{\mathrm{coul}}(\rho_{N_c})+V_{\mathrm{xc}}(\rho_{N_c})\big)(1-\Delta)^{-1/2}\| \\
&\quad +\|(1-\Delta)^{1/2}V_{\mathrm{nl}}(1-\Delta)^{-1/2}\|+\|\mathcal{W}_{N_c}\|_{L^\infty}+\|\nabla\mathcal{W}_{N_c}\|_{L^3}\Big) \\
&\leq C\Big(\|V_{\mathrm{local}}+V_{\mathrm{coul}}(\rho_{N_c})+V_{\mathrm{xc}}(\rho_{N_c})\|_{L^\infty_\#} \\
&\quad +\|\nabla\left(V_{\mathrm{local}}+V_{\mathrm{coul}}(\rho_{N_c})+V_{\mathrm{xc}}(\rho_{N_c})\right)\|_{L^3_\#} \\
&\quad +\|(1-\Delta)^{1/2}V_{\mathrm{nl}}(1-\Delta)^{-1/2}\| \\
&\quad +\|\mathcal{W}_{N_c}\|_{L^\infty}+\|\nabla\mathcal{W}_{N_c}\|_{L^3}\Big),
\end{aligned}
$$

from [8, Lemma 17], which is bounded from (5.13), (5.12), (5.14), and the inequality $\|(1-\Delta)^{1/2}V_{\mathrm{nl}}(1-\Delta)^{-1/2}\|\leq\sum_{j=1}^J\|\xi_j\|_{L^2_\#}\|\xi_j\|_{H^1_\#}$. Thus, there exists $C\in\mathbb{R}^+$ such that

$$
\|(1-\Delta)^{1/2}\widetilde{Q_{N_c}}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}\leq C\max_{z\in\Gamma}\|(1-\Delta)^{-1/2}(z-\mathcal{H}_{N_c})^{-1}(\mathcal{V}_{N_c}^{\perp}+\mathcal{W}_{N_c})\gamma_{N_c}\,(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)}.
$$

Moreover, $\mathrm{Ran}(\mathcal{V}_{N_c}^{\perp}\gamma_{N_c})\subset X_{N_c}^{\perp}$, and the Laplace operator and the projection $\Pi_{N_c}^{\perp}$ commute. Therefore, noting that $(z-\mathcal{H}_{N_c})^{-1}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}=(z+\frac{1}{2}\Delta)^{-1}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}$, we obtain

$$
\begin{aligned}
\|(1-\Delta)^{1/2}\widetilde{Q_{N_c}}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}\leq C\Big[&\|(1-\Delta)^{-1}\Pi_{N_c}^{\perp}\|\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z+\frac{1}{2}\Delta)^{-1}(1-\Delta)^{1/2}\| \\
&\times\max_{z\in\Gamma}\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)} \\
&+\|(1-\Delta)^{-1}\|\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z-\mathcal{H}_{N_c})^{-1}(1-\Delta)^{1/2}\| \\
&\times\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_{N_c}(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)}\Big].
\end{aligned}
$$

As $\|(1-\Delta)^{-1}\|$ and $\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z+\frac{1}{2}\Delta)^{-1}(1-\Delta)^{1/2}\|$ are bounded, noting that $\|(1-\Delta)^{-1}\Pi_{N_c}^{\perp}\|\leq CN_c^{-2}$, and $\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z-\mathcal{H}_{N_c})^{-1}(1-\Delta)^{1/2}\|$ is bounded independently of N_c, we can proceed as in [6, Lemma 4.6] and show that there exist $C\in\mathbb{R}^+$ and $N_c^0\in\mathbb{N}$ such that for $N_c\geq N_c^0$,

$$
\begin{aligned}
\|(1-\Delta)^{1/2}\widetilde{Q_{N_c}}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}&\leq C\Big(N_c^{-2}\max_{z\in\Gamma}\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)} \\
&\qquad+\max_{z\in\Gamma}\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_{N_c}(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)}\Big) \\
&\leq C\left(N_c^{-2}\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^{\perp}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}+\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}\right).
\end{aligned}
$$

The first estimate (5.25) is finally obtained by using (5.19) and (5.22). The proof for the estimate (5.26) is similar to the proof of [6, Lemma 4.7], relying on (5.25). ☐

Lemma 5.9 (Estimation of $(1-\Delta)^{1/2}\gamma_{N_c}^{(2)}\gamma_{N_c}$)**.** *There exist $C\in\mathbb{R}^+$ and $N_c^0\in\mathbb{N}$, such that for $N_c\geq N_c^0$,*

$$
\|(1-\Delta)^{1/2}\gamma_{N_c}^{(2)}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}\leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0-\gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}.
$$

Proof. First, by definition of $\gamma_{N_c}^{(2)}$ in (5.7),

$$(1-\Delta)^{1/2}\gamma_{N_c}^{(2)}\gamma_{N_c} = \frac{1}{2i\pi}\oint_\Gamma (1-\Delta)^{1/2}(z-\mathcal{H}_{N_c})^{-1}\mathcal{W}_{N_c}(z-\mathcal{H}_{N_c})^{-1}\gamma_{N_c}dz.$$

Hence, using that γ_{N_c} and $(z-\mathcal{H}_{N_c})^{-1}$ commute, that $\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z-\mathcal{H}_{N_c})^{-1}(1-\Delta)^{1/2}\|$ is bounded, we obtain that there exist $C\in\mathbb{R}^+$ and $N_c^0\in\mathbb{N}$ such that for $N_c\geq N_c^0$,

$$\begin{aligned}\|(1-\Delta)^{1/2}\gamma_{N_c}^{(2)}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} &\leq C\max_{z\in\Gamma}\|(1-\Delta)^{1/2}(z-\mathcal{H}_{N_c})^{-1}(1-\Delta)^{1/2}\| \\ &\quad\times\max_{z\in\Gamma}\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_{N_c}(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)} \\ &\leq C\max_{z\in\Gamma}\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_{N_c}(z-\mathcal{H}_{N_c})^{-1}\|_{\mathfrak{S}_2(L^2_\#)} \\ &\leq C\|(1-\Delta)^{-1/2}\mathcal{W}_{N_c}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \\ &\leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0-\gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)},\end{aligned}$$

where we have used (5.19) for this last inequality. This concludes the proof of the lemma. □

Lemma 5.10 (Estimation of $(1-\Delta)^{1/2}\gamma_{N_c}\gamma_{N_c}^{(2)}$)**.** *There exist $C\in\mathbb{R}^+$ and $N_c^0\in\mathbb{N}$, such that for $N_c\geq N_c^0$,*

$$\|(1-\Delta)^{1/2}\gamma_{N_c}\gamma_{N_c}^{(2)}\|_{\mathfrak{S}_2(L^2_\#)} \leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0-\gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}.$$

Proof. Noting that $\gamma_{N_c}^2=\gamma_{N_c}$, and from [6, (2.10)] and [6, (2.12)], we obtain

$$\begin{aligned}\|(1-\Delta)^{1/2}\gamma_{N_c}\gamma_{N_c}^{(2)}\|_{\mathfrak{S}_2(L^2_\#)} &\leq \|(1-\Delta)^{1/2}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}\|\gamma_{N_c}\gamma_{N_c}^{(2)}\|_{\mathfrak{S}_2(L^2_\#)} \\ &= \|(1-\Delta)^{1/2}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}\|\gamma_{N_c}^{(2)}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)},\end{aligned}$$

since γ_{N_c} is an orthogonal projector of finite rank. Moreover, as the orbitals $(\phi_{i,N_c})_{i=1,\cdots,N}$ are bounded in $H^1_\#(\Omega)$ independently of N_c, $\|(1-\Delta)^{1/2}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}$ is bounded. On top of that, using [6, (2.12)],

$$\|\gamma_{N_c}^{(2)}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \leq \|(1-\Delta)^{-1/2}\|\|(1-\Delta)^{1/2}\gamma_{N_c}^{(2)}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)} \leq \|(1-\Delta)^{1/2}\gamma_{N_c}^{(2)}\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}.$$

Therefore, we can use the estimate of Lemma 5.9 to conclude. □

Lemma 5.11 (Estimation of $(1-\Delta)^{1/2}\sum_{j=1}^N|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|$)**.** *There exist $C\in\mathbb{R}^+$ and $N_c^0\in\mathbb{N}$, such that for $N_c\geq N_c^0$,*

$$\|(1-\Delta)^{1/2}\sum_{j=1}^N|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|\|_{\mathfrak{S}_2(L^2_\#)} \leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0-\gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}.$$

Proof. Expanding $\|(1-\Delta)^{1/2}\sum_{j=1}^N|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|\|^2_{\mathfrak{S}_2(L^2_\#)}$, and using the Cauchy–Schwarz inequality twice, we obtain

$$\begin{aligned}
\|(1-\Delta)^{1/2}\sum_{j=1}^{N}|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|\|_{\mathfrak{S}_2(L^2_\#)}^2 =&\mathrm{Tr}\left(\sum_{i,j=1}^{N}|\phi_{i,N_c}^{(1)}\rangle\langle\phi_{i,N_c}^{(1)}|(1-\Delta)|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|\right)\\
=&\sum_{i,j=1}^{N}\langle\phi_{i,N_c}^{(1)}|(1-\Delta)|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|\phi_{i,N_c}^{(1)}\rangle\\
\leq&\sum_{i,j=1}^{N}\|(1-\Delta)^{1/2}\phi_{i,N_c}^{(1)}\|_{L^2_\#}\|(1-\Delta)^{1/2}\phi_{j,N_c}^{(1)}\|_{L^2_\#}\|\phi_{i,N_c}^{(1)}\|_{L^2_\#}\|\phi_{j,N_c}^{(1)}\|_{L^2_\#}\\
\leq&\left(\sum_{i=1}^{N}\|(1-\Delta)^{1/2}\phi_{i,N_c}^{(1)}\|_{L^2_\#}\|\phi_{i,N_c}^{(1)}\|_{L^2_\#}\right)^2.
\end{aligned}$$

Noting that for all $j=1,\dots,N$, $\phi_{j,N_c}^{(1)}\in X_{N_c}^\perp$, so that $\|\phi_{j,N_c}^{(1)}\|_{L^2_\#}\leq CN_c^{-1}\|\phi_{j,N_c}^{(1)}\|_{H^1_\#}$, with $C=\frac{2\sqrt{2}\pi}{L}$, there holds

$$\begin{aligned}
\|(1-\Delta)^{1/2}\sum_{j=1}^{N}|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|\|_{\mathfrak{S}_2(L^2_\#)}\leq& CN_c^{-1}\sum_{j=1}^{N}\|(1-\Delta)^{1/2}\phi_{j,N_c}^{(1)}\|_{L^2_\#}^2\\
\leq& CN_c^{-1}\sum_{j=1}^{N}\|(1-\Delta)^{1/2}(-\frac{1}{2}\Delta-\lambda_{j,N_c})^{-1}(1-\Delta)^{1/2}\|^2\\
&\times\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^\perp\phi_{j,N_c}\|_{L^2_\#}^2.
\end{aligned}$$

Moreover, for all $j=1,\dots,N$, $(1-\Delta)^{1/2}(-\frac{1}{2}\Delta-\lambda_{j,N_c})^{-1}(1-\Delta)^{1/2}$ is a bounded operator. Then using (5.22) and (3.9), we show that there exist $C\in\mathbb{R}^+$ and $N_c^0\in\mathbb{N}$ such that for $N_c\geq N_c^0$,

$$\begin{aligned}
\|(1-\Delta)^{1/2}\sum_{j=1}^{N}|\phi_{j,N_c}^{(1)}\rangle\langle\phi_{j,N_c}^{(1)}|\|_{\mathfrak{S}_2(L^2_\#)} &\leq CN_c^{-1}\sum_{j=1}^{N}\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^\perp\phi_{j,N_c}\|_{L^2_\#}^2\\
&\leq CN_c^{-1}\|(1-\Delta)^{-1/2}\mathcal{V}_{N_c}^\perp\gamma_{N_c}\|_{\mathfrak{S}_2(L^2_\#)}^2\\
&\leq CN_c^{-1}\|(1-\Delta)^{1/2}(\gamma_{N_c}-\gamma_0)\|_{\mathfrak{S}_2(L^2_\#)}^2\\
&\leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_{N_c}-\gamma_0)\|_{\mathfrak{S}_2(L^2_\#)}.
\end{aligned}$$

This conclues the proof. □

Combining the estimations given in Lemmas 5.7, 5.8, 5.9, 5.10, and 5.11 in the density matrix difference decomposition of Lemma 5.7, we easily obtain (5.1).

Lemma 5.12 (Estimation of $(1-\Delta)^{1/2}(\widetilde{\gamma_{N_c}}-\widetilde{\widetilde{\gamma_{N_c}}})$)**.** *There exist $C\in\mathbb{R}^+$ and $N_c^0\in\mathbb{N}$, such that for $N_c\geq N_c^0$,*

$$\|(1-\Delta)^{1/2}(\widetilde{\gamma_{N_c}}-\widetilde{\widetilde{\gamma_{N_c}}})\|_{\mathfrak{S}_2(L^2_\#)}\leq CN_c^{-2}\|(1-\Delta)^{1/2}(\gamma_0-\gamma_{N_c})\|_{\mathfrak{S}_2(L^2_\#)}.$$

Proof. First,

$$
\begin{aligned}
\widetilde{\gamma_{N_\mathrm{c}}} - \widetilde{\widetilde{\gamma_{N_\mathrm{c}}}} &= \sum_{i=1}^{N} |\widetilde{\phi_{i,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{i,N_\mathrm{c}}}| - \sum_{i=1}^{N} |\widetilde{\widetilde{\phi_{i,N_\mathrm{c}}}}\rangle\langle\widetilde{\widetilde{\phi_{i,N_\mathrm{c}}}}| \\
&= \sum_{i=1}^{N} |\widetilde{\phi_{i,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{i,N_\mathrm{c}}}| - \sum_{i=1}^{N} |{S_{N_\mathrm{c}}}^{-1/2}\widetilde{\phi_{i,N_\mathrm{c}}}\rangle\langle {S_{N_\mathrm{c}}}^{-1/2}\widetilde{\phi_{i,N_\mathrm{c}}}| \\
&= \sum_{i=1}^{N} |\widetilde{\phi_{i,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{i,N_\mathrm{c}}}| - \sum_{i=1}^{N}\sum_{k,l=1}^{N} ({S_{N_\mathrm{c}}}^{-1/2})_{i,k} |\widetilde{\phi_{k,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{l,N_\mathrm{c}}}| ({S_{N_\mathrm{c}}}^{-1/2})_{l,i} \\
&= \sum_{i=1}^{N} |\widetilde{\phi_{i,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{i,N_\mathrm{c}}}| - \sum_{k,l=1}^{N} \left(\sum_{i=1}^{N} ({S_{N_\mathrm{c}}}^{-1/2})_{i,k} ({S_{N_\mathrm{c}}}^{-1/2})_{l,i}\right) |\widetilde{\phi_{k,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{l,N_\mathrm{c}}}| \\
&= \sum_{i=1}^{N} |\widetilde{\phi_{i,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{i,N_\mathrm{c}}}| - \sum_{k,l=1}^{N} ({S_{N_\mathrm{c}}}^{-1})_{k,l} |\widetilde{\phi_{k,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{l,N_\mathrm{c}}}| \\
&= \sum_{k,l=1}^{N} (\delta_{k,l} - ({S_{N_\mathrm{c}}}^{-1})_{k,l}) |\widetilde{\phi_{k,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{l,N_\mathrm{c}}}|.
\end{aligned}
$$

Taking the Hilbert–Schmidt norm, we obtain

$$
\begin{aligned}
\|(1-\Delta)^{1/2}(\widetilde{\gamma_{N_\mathrm{c}}} - \widetilde{\widetilde{\gamma_{N_\mathrm{c}}}})\|_{\mathfrak{S}_2(L^2_\#)}^2 &= \mathrm{Tr}\left((\widetilde{\gamma_{N_\mathrm{c}}} - \widetilde{\widetilde{\gamma_{N_\mathrm{c}}}})(1-\Delta)(\widetilde{\gamma_{N_\mathrm{c}}} - \widetilde{\widetilde{\gamma_{N_\mathrm{c}}}})\right) \\
&= \sum_{k,l=1}^{N}\sum_{m,n=1}^{N} (\delta_{k,l} - ({S_{N_\mathrm{c}}}^{-1})_{k,l})(\delta_{m,n} - ({S_{N_\mathrm{c}}}^{-1})_{m,n}) \\
&\quad \times \langle\widetilde{\phi_{l,N_\mathrm{c}}}|(1-\Delta)|\widetilde{\phi_{m,N_\mathrm{c}}}\rangle\langle\widetilde{\phi_{n,N_\mathrm{c}}}|\widetilde{\phi_{k,N_\mathrm{c}}}\rangle \\
&= \sum_{k,l=1}^{N}\sum_{m,n=1}^{N} (\delta_{k,l} - ({S_{N_\mathrm{c}}}^{-1})_{k,l})(\delta_{m,n} - ({S_{N_\mathrm{c}}}^{-1})_{m,n}) \\
&\quad \times \left(\langle\phi_{l,N_\mathrm{c}}|(1-\Delta)|\phi_{m,N_\mathrm{c}}\rangle + \langle\phi_{l,N_\mathrm{c}}^{(1)}|(1-\Delta)|\phi_{m,N_\mathrm{c}}^{(1)}\rangle\right)\left(\delta_{n,k} + \langle\phi_{n,N_\mathrm{c}}^{(1)}|\phi_{l,N_\mathrm{c}}^{(1)}\rangle\right),
\end{aligned}
$$

as for all $i = 1,\dots,N$, $\phi_{i,N_\mathrm{c}} \in X_{N_\mathrm{c}}$ and $\phi_{i,N_\mathrm{c}}^{(1)} \in X_{N_\mathrm{c}}^\perp$, and the Laplace operator commutes with Π_{N_c} and $\Pi_{N_\mathrm{c}}^\perp$. Using the Cauchy–Schwarz inequality and noting that for $i = 1,\dots,N$, ϕ_{i,N_c} and $\phi_{i,N_\mathrm{c}}^{(1)}$ are uniformly bounded in $H^1_\#$-norm independently of N_c, there exists $C \in \mathbb{R}^+$ such that

$$
\begin{aligned}
\|(1-\Delta)^{1/2}(\widetilde{\gamma_{N_\mathrm{c}}} - \widetilde{\widetilde{\gamma_{N_\mathrm{c}}}})\|_{\mathfrak{S}_2(L^2_\#)}^2 &\le C\left(\sum_{k,l=1}^{N} |\delta_{k,l} - ({S_{N_\mathrm{c}}}^{-1})_{k,l}|\right)^2 \\
&\le C\|1_N - ({S_{N_\mathrm{c}}}^{-1})\|_F^2.
\end{aligned}
$$

The matrix S_{N_c} being a perturbation of 1_N, there holds at first order $1_N - {S_{N_\mathrm{c}}}^{-1} = S_{N_\mathrm{c}} - 1_N + h.o.t$, *h.o.t.* standing for higher order terms. Using (5.23), we can therefore conclude in particular that there exist $C \in \mathbb{R}^+$ and $N_\mathrm{c}^0 \in \mathbb{N}$ such that for $N_\mathrm{c} \ge N_\mathrm{c}^0$,

$$
\|(1-\Delta)^{1/2}(\widetilde{\gamma_{N_\mathrm{c}}} - \widetilde{\widetilde{\gamma_{N_\mathrm{c}}}})\|_{\mathfrak{S}_2(L^2_\#)} \le C N_\mathrm{c}^{-2}\|(1-\Delta)^{1/2}(\gamma_0 - \gamma_{N_\mathrm{c}})\|_{\mathfrak{S}_2(L^2_\#)}.
$$

□

Combining (5.1) with the estimation given in Lemma 5.12 allows to prove (5.2).

5.2.4 Proof of estimates (5.3) and (5.4)

We start by proving (5.4). Let us define $\widetilde{\widetilde{\Phi^0_{N_\mathrm{c}}}} \in \mathcal{M}^{\Phi^0}$ by

$$\min_{U\in\mathcal{U}(N)} \|U\widetilde{\widetilde{\Phi_{N_\mathrm{c}}}} - \Phi^0\|_{L^2_\#} = \|\widetilde{\widetilde{\Phi^0_{N_\mathrm{c}}}} - \Phi^0\|_{L^2_\#}.$$

Since $\widetilde{\widetilde{\Phi^0_{N_\mathrm{c}}}} \in \mathcal{M}^{\Phi^0}$, we can combine [3, Lemma 4.7] and [3, (4.47)], and obtain that there exists $C \in \mathbb{R}^+$ and $N^0_\mathrm{c} \in \mathbb{N}$ such that for all $N_\mathrm{c} \geq N^0_\mathrm{c}$,

$$\begin{aligned} \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\widetilde{\Phi^0_{N_\mathrm{c}}}}) - \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Phi^0) &\leq C\|(1-\Delta)^{1/2}(\widetilde{\widetilde{\Phi^0_{N_\mathrm{c}}}} - \Phi^0)\|^2_{L^2_\#} \\ &\leq C\|(1-\Delta)^{1/2}(\widetilde{\widetilde{\gamma_{N_\mathrm{c}}}} - \gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)}, \end{aligned}$$

from (3.5), and noting that the density matrix corresponding to $\widetilde{\widetilde{\Phi^0_{N_\mathrm{c}}}}$ is $\widetilde{\widetilde{\gamma_{N_\mathrm{c}}}}$. Moreover, from the invariance property (2.5), there holds $\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\widetilde{\Phi^0_{N_\mathrm{c}}}}) = \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\widetilde{\Phi_{N_\mathrm{c}}}})$. Using (5.2) and (3.6), we obtain (5.4).

Let us now prove (5.3). The same reasoning cannot be applied as the perturbed eigenvectors $\widetilde{\Phi_{N_\mathrm{c}}}$ do not satisfy the constraint, *i.e.* $\widetilde{\Phi_{N_\mathrm{c}}} \notin \mathcal{M}$. A second-order Taylor expansion on the energy gives

$$\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\Phi_{N_\mathrm{c}}}) - \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Phi^0) = \langle(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})'(\Phi^0), \widetilde{\Phi_{N_\mathrm{c}}} - \Phi^0\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{2}(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})''(\Phi^0)(\widetilde{\Phi_{N_\mathrm{c}}} - \Phi^0, \widetilde{\Phi_{N_\mathrm{c}}} - \Phi^0) + h.o.t.$$

Noting that such a development is also valid for the energy difference $\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\widetilde{\Phi_{N_\mathrm{c}}}}) - \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Phi^0)$, we obtain, still up to second order

$$\begin{aligned} \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\Phi_{N_\mathrm{c}}}) - \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Phi^0) = &\langle(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})'(\Phi^0), \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}} - \Phi^0\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{2}(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})''(\Phi^0)(\widetilde{\widetilde{\Phi_{N_\mathrm{c}}}} - \Phi^0, \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}} - \Phi^0) \\ &+ \langle(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})'(\Phi^0), \widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}}\rangle_{H^{-1}_\#,H^1_\#} \\ &+ \frac{1}{2}(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})''(\Phi^0)(\widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}}, \widetilde{\Phi_{N_\mathrm{c}}} + \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}} - 2\Phi^0) + h.o.t. \\ =&\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\widetilde{\Phi_{N_\mathrm{c}}}}) - \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Phi^0) + \langle(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})'(\Phi^0), \widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}}\rangle_{H^{-1}_\#,H^1_\#} \\ &+ \frac{1}{2}(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})''(\Phi^0)(\widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}}, \widetilde{\Phi_{N_\mathrm{c}}} + \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}} - 2\Phi^0) + h.o.t. \end{aligned}$$

From the continuity of $(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})''(\Phi^0)$ [3, (4.18), (4.47)]), and since $(\mathcal{E}^{\mathrm{KS}}_{0,\Omega})'(\Phi^0)$ is bounded in $H^{-1}_\#$-norm [3, Lemma 4.7], there exist $C \in \mathbb{R}^+$ and $N^0_\mathrm{c} \in \mathbb{N}$ such that for $N_\mathrm{c} \geq N^0_\mathrm{c}$,

$$|\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\Phi_{N_\mathrm{c}}}) - \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\widetilde{\widetilde{\Phi_{N_\mathrm{c}}}})| \leq C\|(1-\Delta)^{1/2}(\widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}})\|_{L^2_\#} + C\|(1-\Delta)^{1/2}(\widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}})\|^2_{L^2_\#}. \tag{5.31}$$

Moreover, developing the expression $\widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}}$, we obtain

$$\|(1-\Delta)^{1/2}(\widetilde{\Phi_{N_\mathrm{c}}} - \widetilde{\widetilde{\Phi_{N_\mathrm{c}}}})\|_{L^2_\#} \leq \|1_N - S_{N_\mathrm{c}}{}^{-1/2}\|_\mathrm{F}\|(1-\Delta)^{1/2}\widetilde{\Phi_{N_\mathrm{c}}}\|_{L^2_\#}. \tag{5.32}$$

Since there exists $N^0_\mathrm{c} \in \mathbb{N}$ such that for $N_\mathrm{c} \geq N^0_\mathrm{c}$, $\|(1-\Delta)^{1/2}\widetilde{\Phi_{N_\mathrm{c}}}\|_{L^2_\#}$ is bounded independently of N_c, there holds at first order

$$\begin{aligned} \|1_N - S_{N_\mathrm{c}}{}^{-1/2}\|_\mathrm{F} &= \frac{1}{2}\|1_N - S_{N_\mathrm{c}}\|_\mathrm{F} + h.o.t. \\ &\leq CN_\mathrm{c}^{-2}\|(1-\Delta)^{1/2}(\gamma_{N_\mathrm{c}} - \gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} \\ &\leq CN_\mathrm{c}^{-2}|\mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Phi_{N_\mathrm{c}}) - \mathcal{E}^{\mathrm{KS}}_{0,\Omega}(\Phi^0)|, \end{aligned} \tag{5.33}$$

where $C \in \mathbb{R}^+$, from (5.23) and (3.6). Combining (5.31), (5.32) and (5.33), we obtain (5.3).

6 Appendix

6.1 Smoothness assumptions

The existence of minimizers of problem (2.4) as well as *a priori* error estimates on the convergence of the solutions to the discretized problem (3.1) to those of the continuous problem (2.4) hold under several assumptions described in [3]. We recall here the main assumptions, under which the proofs of Theorem 5.1 will hold.

Assumption 6.1 (Smoothness assumptions). *There exists $m > 3$ such that the local potential $V_{\rm local}$ satisfies*

$$\exists C \geq 0 \ s.t. \ \forall \mathbf{k} \in \mathcal{R}^*, \ |\widehat{(V_{\rm local})}_{\mathbf{k}}| \leq C|\mathbf{k}|^{-m},$$

and the functions defining the non-local potential $V_{\rm nl}$ are such that

$$\forall 1 \leq j \leq J, \quad \forall \epsilon > 0, \quad \xi_j \in H^{m-3/2-\epsilon}_{\#}(\Omega).$$

Moreover, there holds for the exchange-correlation function

$$\text{the function } \rho \mapsto e_{\rm xc}^{\rm LDA}(\rho) \text{ belongs to } C^1([0,+\infty)) \cap C^3((0,+\infty)), \tag{6.1}$$

$$e_{\rm xc}^{\rm LDA}(0) = 0, \quad \frac{de_{\rm xc}^{\rm LDA}}{d\rho}(0) = 0, \tag{6.2}$$

and there exists $0 < \alpha < 1$ and $C \in \mathbb{R}^+$ such that

$$\forall \rho \in \mathbb{R}^+ \backslash \{0\}, \quad \left| \frac{d^2 e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho) \right| + \left| \rho \frac{d^3 e_{\rm xc}^{\rm LDA}}{d\rho^3}(\rho) \right| \leq C(1 + \rho^{\alpha-1}). \tag{6.3}$$

Finally, there holds for the nonlinear core correction

$$\forall \varepsilon > 0, \quad \rho_c \in H^{m-3/2-\epsilon}_{\#}(\Omega).$$

Note that for example, Troullier-Martins pseudopotentials [14] have Fourier coefficients $\widehat{(V_{\rm local})}_{\mathbf{k}}$ decreasing as $|\mathbf{k}|^{-m}$ with $m = 5$. The assumptions (6.1), (6.2) and (6.3) are satisfied by the Xα exchange-correlation functional with $\alpha = 1/3$ ($e_{\rm xc}^{{\rm X}\alpha}(\rho) = -C_X \rho^{4/3}$, where $C_X > 0$ is a given constant). The exact exchange-correlation functional also verifies these assumptions [9].

The *a priori* results of [3] require some additional assumptions on the exchange-correlation function $e_{\rm xc}^{\rm LDA}$, that we detail below.

Assumption 6.2 (Extra-regularity of the exchange-correlation). *There exists $m > 3$ such that*

$$e_{\rm xc}^{\rm LDA} \in C^{n_m,\alpha_m}((0,+\infty)) \quad \text{where} \quad \left| \begin{array}{l} n_m = [m] + 1 \text{ and } \alpha_m = m - [m] + 1/2 \text{ if } 0 \leq m - [m] \leq 1/2, \\ n_m = [m] + 2 \text{ and } \alpha_m = m - [m] - 1/2 \text{ if } 1/2 < m - [m] \leq 1, \end{array} \right.$$

(where $[m]$ denotes the integer part of m) and

$$e_{\rm xc}^{\rm LDA} \in C^{n_m,\alpha_m}([0,+\infty)) \quad \text{or} \quad \rho_c + \rho^0 > 0 \text{ in } \mathbb{R}^3. \tag{6.4}$$

6.2 Additional proofs

Proof of Lemma 3.1. The proof of (3.4) is identical to the proof of [6, (2.24)], where the condition that for all $v \in {\rm Span}(\phi_1^0, \ldots, \phi_N^0) \backslash \{0\}, \quad \|\gamma_{\Psi^0} v\|_{L^2_\#} \neq 0$, guarantees that the overlap matrix with entries $(\langle \psi_i^0, \phi_j^0 \rangle)_{i,j=1}^N$ is invertible (see [3, Lemma 4.3]). In order to show (3.5), let us recall that the positive operator $|\mathcal{H}_0 - \epsilon_F|$ defined by the functional calculus is $|\mathcal{H}_0 - \epsilon_F| = -\gamma_0(\mathcal{H}_0 - \epsilon_F)\gamma_0 + (1-\gamma_0)(\mathcal{H}_0 - \epsilon_F)(1-\gamma_0)$, where γ_0 is the exact density matrix defined in (2.8). It is known (see e.g. [4]) that, under Assumption 2.1, there exist $0 < c \leq C < \infty$ such that

$$c(1-\Delta) \leq |\mathcal{H}_0 - \epsilon_{\mathrm{F}}| \leq C(1-\Delta).$$

Moreover, as is classical (see e.g. [4, Lemma 1] for a proof) there exists $C \in \mathbb{R}^+$ such that

$$\||\mathcal{H}_0 - \epsilon_F|^{1/2}(1-\Delta)^{-1/2}\| \leq C \quad \text{and} \quad \|(1-\Delta)^{1/2}|\mathcal{H}_0 - \epsilon_F|^{-1/2}\| \leq C. \tag{6.5}$$

To finish the proof, we demonstrate the following lemma. For simplicity, we denote by $A = |\mathcal{H}_0 - \epsilon_F|$ and $\mu_i = |\lambda_i^0 - \epsilon_F|$ for $i \geq 1$.

Lemma 6.1. *Let $\Psi^0 = (\psi_1^0, \dots, \psi_N^0) \in \mathcal{M}^{\Phi^0}$ with corresponding density matrix $\gamma_{\Psi^0} = \sum_{i=1}^N |\psi_i^0\rangle\langle\psi_i^0|$, satisfying for all $v \in Span(\phi_1^0, \dots, \phi_N^0)\backslash\{0\}$, $\|\gamma_{\Psi^0} v\|_{L^2_\#} \neq 0$. There holds*

$$\|A^{1/2}(\Psi^0 - \Phi^0)\|^2_{L^2_\#} \leq \left(1 + N\frac{\max_{k=1,\dots,N}\mu_k}{\min_{i\in\mathbb{N}^*}\mu_i}\right)\|A^{1/2}(\gamma_{\Psi^0} - \gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)}, \tag{6.6}$$

and

$$\|A^{1/2}(\gamma_{\Psi^0} - \gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} \leq \left(1 + 2\frac{\max_{k=1,\dots,N}\mu_k}{\min_{i\in\mathbb{N}^*}\mu_i}\right)\|A^{1/2}(\Psi^0 - \Phi^0)\|^2_{L^2_\#}. \tag{6.7}$$

Proof. On the one hand, using that the $(\phi_i^0)_{i=1,\dots,N}$ are eigenvectors of the operator A with eigenvalues μ_i, and that $(\phi_i^0)_{i=1,\dots,N}$ and $(\psi_i^0)_{i=1,\dots,N}$ are orthonormal, we obtain

$$\begin{aligned}
\|A^{1/2}(\Psi^0 - \Phi^0)\|^2_{L^2_\#} &= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle + \sum_{i=1}^N \langle\phi_i^0|A\phi_i^0\rangle - 2\sum_{i=1}^N \langle\phi_i^0|A\psi_i^0\rangle \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle + \sum_{i=1}^N \mu_i\langle\phi_i^0|\phi_i^0\rangle - 2\sum_{i=1}^N \mu_i\langle\phi_i^0|\psi_i^0\rangle \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle - \sum_{i=1}^N \mu_i + 2\sum_{i=1}^N \mu_i\left(1 - \langle\phi_i^0|\psi_i^0\rangle\right) \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle - \sum_{i=1}^N \mu_i + \sum_{i=1}^N \mu_i\|\phi_i^0 - \psi_i^0\|^2_{L^2_\#}.
\end{aligned}$$

On the other hand, by cyclicity of the trace, noting that A is a self-adjoint operator, then using that $1 - \gamma_{\Psi^0}$ is an orthogonal projector, and that $(1 - \gamma_{\Psi^0})\psi_i^0 = 0$ for $i = 1, \dots, N$, we obtain

$$\begin{aligned}
\|A^{1/2}(\gamma_{\Psi^0} - \gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} &= \mathrm{Tr}\left(\gamma_{\Psi^0}A\gamma_{\Psi^0}\right) + \mathrm{Tr}\left(\gamma_0 A\gamma_0\right) - 2\mathrm{Tr}\left(\gamma_0 A\gamma_{\Psi^0}\right) \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle + \sum_{i=1}^N \langle\phi_i^0|A\phi_i^0\rangle - 2\sum_{i=1}^N \langle\phi_i^0|A\gamma_{\Psi^0}\phi_i^0\rangle \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle + \sum_{i=1}^N \mu_i\langle\phi_i^0|\phi_i^0\rangle - 2\sum_{i=1}^N \mu_i\langle\phi_i^0|\gamma_{\Psi^0}\phi_i^0\rangle \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle - \sum_{i=1}^N \mu_i + 2\sum_{i=1}^N \mu_i\langle\phi_i^0|(1-\gamma_{\Psi^0})\phi_i^0\rangle \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle - \sum_{i=1}^N \mu_i + 2\sum_{i=1}^N \mu_i\|(1-\gamma_{\Psi^0})\phi_i^0\|^2_{L^2_\#} \\
&= \sum_{i=1}^N \langle\psi_i^0|A\psi_i^0\rangle - \sum_{i=1}^N \mu_i + 2\sum_{i=1}^N \mu_i\|(1-\gamma_{\Psi^0})(\phi_i^0 - \psi_i^0)\|^2_{L^2_\#}.
\end{aligned}$$

Therefore, noting again that γ_{Ψ^0} and $1-\gamma_{\Psi^0}$ are orthogonal projectors,

$$\begin{aligned}
\|A^{1/2}(\Psi^0-\Phi^0)\|^2_{L^2_\#} - \|A^{1/2}(\gamma_{\Psi^0}-\gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} &= \sum_{i=1}^N \mu_i \|\phi_i^0-\psi_i^0\|^2_{L^2_\#} \\
&\quad - 2\sum_{i=1}^N \mu_i \|(1-\gamma_{\Psi^0})(\phi_i^0-\psi_i^0)\|^2_{L^2_\#} \qquad (6.8)\\
&\le \sum_{i=1}^N \mu_i \|\phi_i^0-\psi_i^0\|^2_{L^2_\#} - \sum_{i=1}^N \mu_i \|(1-\gamma_{\Psi^0})(\phi_i^0-\psi_i^0)\|^2_{L^2_\#} \\
&= \sum_{i=1}^N \mu_i \|\gamma_{\Psi^0}(\phi_i^0-\psi_i^0)\|^2_{L^2_\#} \\
&\le \max_{k=1,\dots,N} \mu_k \ \sum_{i=1}^N \|\gamma_{\Psi^0}(\phi_i^0-\psi_i^0)\|^2_{L^2_\#} \\
&= \max_{k=1,\dots,N} \mu_k \ \sum_{i,j=1}^N \langle \phi_i^0-\psi_i^0|\psi_j^0\rangle\langle\psi_j^0|\phi_i^0-\psi_i^0\rangle.
\end{aligned}$$

From [3, Lemma 4.3], the overlap matrix with entries $(\langle\psi_i^0|\phi_j^0\rangle)_{i,j=1,\dots,N}$ is symmetric, hence for $i,j=1,\dots,N$, $i\neq j$, noting that $(\psi_i^0)_{i=1,\dots,N}$ and $(\phi_i^0)_{i=1,\dots,N}$ are orthonormal,

$$\langle\psi_j^0|\phi_i^0-\psi_i^0\rangle = \langle\psi_j^0|\phi_i^0\rangle = \langle\psi_i^0|\phi_j^0\rangle = \frac{1}{2}(\langle\psi_j^0|\phi_i^0\rangle + \langle\psi_i^0|\phi_j^0\rangle) = \frac{1}{2}\langle\psi_j^0-\phi_j^0|\phi_i^0-\psi_i^0\rangle.$$

Since for $i=1,\dots,N$, $\langle\psi_i^0|\phi_i^0-\psi_i^0\rangle = -\frac{1}{2}\|\phi_i^0-\psi_i^0\|_{L^2_\#}$, we obtain that for any $i,j=1,\dots,N$,

$$\langle\psi_j^0|\phi_i^0-\psi_i^0\rangle = \frac{1}{2}\langle\psi_j^0-\phi_j^0|\phi_i^0-\psi_i^0\rangle.$$

Hence,

$$\begin{aligned}
\|A^{1/2}(\Psi^0-\Phi^0)\|^2_{L^2_\#} - \|A^{1/2}(\gamma_{\Psi^0}-\gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} &\le \frac{1}{4}\max_{k=1,\dots,N}\mu_k \sum_{i,j=1}^N \|\psi_i^0-\phi_i^0\|^2_{L^2_\#}\|\psi_j^0-\phi_j^0\|^2_{L^2_\#} \\
&= \frac{1}{4}\max_{k=1,\dots,N}\mu_k \left(\sum_{i=1}^N \|\psi_i^0-\phi_i^0\|^2_{L^2_\#}\right)^2 \\
&= \frac{1}{4}\max_{k=1,\dots,N}\mu_k \ \|\Psi^0-\Phi^0\|^4_{L^2_\#} \\
&\le \frac{1}{4}\max_{k=1,\dots,N}\mu_k \ \|\gamma_{\Psi^0}-\gamma_0\|^4_{\mathfrak{S}_2(L^2_\#)},
\end{aligned}$$

where we have used (3.4) for this last line. Finally, noting that the lowest eigenvalue of A is $\min_{i\in\mathbb{N}^*}\mu_i>0$, there holds

$$\|\gamma_{\Psi^0}-\gamma_0\|^2_{\mathfrak{S}_2(L^2_\#)} \le \frac{1}{\min_{i\in\mathbb{N}^*}\mu_i}\|A^{1/2}(\gamma_{\Psi^0}-\gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)}.$$

The estimation (6.6) is obtained by bounding the density matrix error $\|\gamma_{\Psi^0}-\gamma_0\|^2_{\mathfrak{S}_2(L^2_\#)}$ by $4N$. Let us now prove (6.7). Starting from (6.8), using that $1-\gamma_{\Psi^0}$ is an orthogonal projector, hence of operator norm less than 1, and noting that $\min_{i\in\mathbb{N}^*}\mu_i > 0$ is the lowest eigenvalue of A, we obtain

$$
\begin{aligned}
\|A^{1/2}(\gamma_{\Psi^0}-\gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} - \|A^{1/2}(\Psi^0-\Phi^0)\|^2_{L^2_\#} &= 2\sum_{i=1}^N \mu_i \|(1-\gamma_{\Psi^0})(\phi_i^0-\psi_i^0)\|^2_{L^2_\#} - \sum_{i=1}^N \mu_i\|\phi_i^0-\psi_i^0\|^2_{L^2_\#} \\
&\le 2\sum_{i=1}^N \mu_i \|(1-\gamma_{\Psi^0})(\phi_i^0-\psi_i^0)\|^2_{L^2_\#} \\
&\le 2 \max_{k=1,\dots,N}\mu_k \sum_{i=1}^N \|\phi_i^0-\psi_i^0\|^2_{L^2_\#} \\
&= 2 \max_{k=1,\dots,N}\mu_k \, \|\Psi^0-\Phi^0\|^2_{L^2_\#} \\
&\le 2\frac{\max_{k=1,\dots,N}\mu_k}{\min_{i\in\mathbb{N}^*}\mu_i} \, \|A^{1/2}(\Psi^0-\Phi^0)\|^2_{L^2_\#},
\end{aligned}
$$

which proves (6.7).

$\square$

This lemma shows that there exist $c, C > 0$ such that

$$
c\||\mathcal{H}_0-\epsilon_F|^{1/2}(\Psi^0-\Phi^0)\|_{L^2_\#} \quad\le\quad \||\mathcal{H}_0-\epsilon_F|^{1/2}(\gamma_\Psi^0-\gamma_0)\|_{\mathfrak{S}_2(L^2_\#)} \quad\le\quad C\||\mathcal{H}_0-\epsilon_F|^{1/2}(\Psi^0-\Phi^0)\|_{L^2_\#}.
$$

Combining this with (6.5) finishes the proof of Lemma 3.1. $\square$

Remark 6.1. *Lemma 6.1 can more generally be shown to hold for any elliptic self-adjoint positive definite operator A with compact resolvent. Moreover, if* $\mathrm{Tr}\,(\gamma_{\Psi^0}A\gamma_{\Psi^0}) \ge \mathrm{Tr}\,(\gamma_0 A\gamma_0)$*, which is satisfied if γ_{Ψ^0} is the solution of a variational approximation of the linear eigenvalue problem with operator A, we can obtain in this case the improved bound*

$$
\begin{aligned}
\|A^{1/2}(\gamma_{\Psi^0}-\gamma_0)\|^2_{\mathfrak{S}_2(L^2_\#)} &= \mathrm{Tr}\,(\gamma_{\Psi^0}A\gamma_{\Psi^0}) - \mathrm{Tr}\,(\gamma_0A\gamma_0) + 2\sum_{i=1}^N \mu_i\|(1-\gamma_{\Psi^0})(\phi_i^0-\psi_i^0)\|^2_{L^2_\#} \\
&\le 2\left(\mathrm{Tr}\,(\gamma_{\Psi^0}A\gamma_{\Psi^0}) - \mathrm{Tr}\,(\gamma_0A\gamma_0)\right) + 2\sum_{i=1}^N \mu_i\|\phi_i^0-\psi_i^0\|^2_{L^2_\#} \\
&= 2\|A^{1/2}(\Psi^0-\Phi^0)\|^2_{L^2_\#}.
\end{aligned}
$$

Proof of Theorem 3.1. First, Equation (3.6) is obtained by combining [3, (4.27)] with (3.5). To show (3.7), we start from [3, (4.83), $\alpha > 0$] which reads

$$
\begin{aligned}
\|\Phi^0_{N_c}-\Phi^0\|_{L^2_\#} \le C\Big(& N_c^{-1}\|\Phi^0_{N_c}-\Phi^0\|_{H^1_\#} + \|\Phi^0_{N_c}-\Phi^0\|^2_{L^2_\#} + \|\Phi^0_{N_c}-\Phi^0\|^{1+\alpha}_{L^2_\#} \\
&+ \|\Phi^0_{N_c}-\Phi^0\|^{3/2}_{L^2_\#}\|\Phi^0_{N_c}-\Phi^0\|^{3/2}_{H^1_\#} + \|\Lambda^0_{N_c}-\Lambda^0\|_{\mathrm{F}}\|\Phi^0_{N_c}-\Phi^0\|_{L^2_\#}\Big).
\end{aligned}
$$

Noting that $\|\Lambda^0_{N_c}-\Lambda^0\|_{\mathrm{F}}$, $\|\Phi^0_{N_c}-\Phi^0\|_{H^1_\#}$ and $\|\Phi^0_{N_c}-\Phi^0\|_{L^2_\#}$ converge to zero when $N_c\to+\infty$, the last four terms in the right-hand side are of higher order, which leads to

$$
\|\Phi^0_{N_c}-\Phi^0\|_{L^2_\#} \le CN_c^{-1}\|\Phi^0_{N_c}-\Phi^0\|_{H^1_\#}.
$$

Then, from [3, (4.89), $r=-1$] we obtain

$$
\begin{aligned}
\|\Phi^0_{N_c}-\Phi^0\|_{H^{-1}_\#} \le C\Big(& \|\Phi^0_{N_c}-\Phi^0\|^2_{L^2_\#} + N_c^{-2}\|\Phi^0_{N_c}-\Phi^0\|_{H^1_\#} \\
&+ \|\Phi^0_{N_c}-\Phi^0\|_{H^{-1}_\#}\|\Phi^0_{N_c}-\Phi^0\|_{H^2_\#} + \|\Lambda^0_{N_c}-\Lambda^0\|_{\mathrm{F}}\|\Phi^0_{N_c}-\Phi^0\|_{H^{-1}_\#}\Big).
\end{aligned}
$$

Noting that $\|\Lambda^0_{N_c} - \Lambda^0\|_{\mathrm{F}}$ and $\|\Phi^0_{N_c} - \Phi^0\|_{H^2_\#}$ converge to zero when $N_c \to +\infty$, the last two terms in the right-hand side are of higher order, from which we deduce

$$\|\Phi^0_{N_c} - \Phi^0\|_{H^{-1}_\#} \leq C N_c^{-2} \|\Phi^0_{N_c} - \Phi^0\|_{H^1_\#}.$$

Combining this last estimate with (3.5) leads to (3.7).

Equation (3.8) comes from [3, (4.28) with $s = 0$] and (3.4). Equation (3.9) is derived combining [3, (4.28) with $s = 1$] and (3.5). Finally, from [3, (4.86) with $r = -1$], (3.5) and (3.7), we obtain (3.10). ☐

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References

[1] M. Born and R. Oppenheimer, *Zur Quantentheorie der Molekeln*, Annalen der Physik, 389 (1927), pp. 457–484.

[2] E. Cancès, R. Chakir, L. He, and Y. Maday, *Two-grid methods for a class of nonlinear elliptic eigenvalue problems*, IMA J. Numer. Anal., 38 (2018), pp. 605–645.

[3] E. Cancès, R. Chakir, and Y. Maday, *Numerical analysis of the planewave discretization of some orbital-free and Kohn-Sham models*, ESAIM: Mathematical Modelling and Numerical Analysis, 46 (2012), pp. 341–388.

[4] E. Cancès, A. Deleurence, and M. Lewin, *A new approach to the modeling of local defects in crystals: The reduced Hartree-Fock case*, Communications in Mathematical Physics, 281 (2008), pp. 129–177.

[5] E. Cancès, G. Dusson, Y. Maday, B. Stamm, and M. Vohralík, *A perturbation-method-based post-processing for the planewave discretization of Kohn-Sham models*, Journal of Computational Physics, 307 (2016), pp. 446–459.

[6] ——, *Post-processing of the planewave approximation of Schrödinger equations. Part I: linear operators, (submitted).* Available at `https://hal.archives-ouvertes.fr/hal-01908039`, 2020.

[7] E. Cancès, M. Lewin, and G. Stoltz, *The microscopic origin of the macroscopic dielectric permittivity of crystals: a mathematical viewpoint*, Springer, Berlin, Heidelberg, 2012, pp. 87–125.

[8] E. Cancès and G. Stoltz, *A mathematical formulation of the random phase approximation for crystals*, Annales de l'Institut Henri Poincare (C) Non Linear Analysis, 29 (2012), pp. 887–925.

[9] R. M. Dreizler and E. K. U. Gross, *Density functional theory*, Springer Berlin Heidelberg, Berlin, Heidelberg, 1990.

[10] F. J. Dyson, *The S matrix in quantum electrodynamics*, Physical Review, 75 (1949), pp. 1736–1755.

[11] T. Kato, *Perturbation theory for linear operators*, Classics in Mathematics, Springer Berlin Heidelberg, Berlin, Heidelberg, 1976.

[12] W. Kohn and L. J. Sham, *Self-consistent equations including exchange and correlation effects*, Physical Review, 140 (1965), pp. A1133–A1138.

[13] P. L. Taylor, *Quantum approach to the solid state*, N.J., Prentice-Hall, 1970.

[14] N. Troullier and J. Martins, *A straightforward method for generating soft transferable pseudopotentials*, Solid State Communications, 74 (1990), pp. 613–616.

[15] C. Yang, J. C. Meza, B. Lee, and L.-W. Wang, *KSSOLV–a MATLAB toolbox for solving the Kohn-Sham equations*, ACM Transactions on Mathematical Software, 36 (2009), pp. 1–35.