Numerical analysis of the planewave discretization of some orbital-free and Kohn-Sham models

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Abstract

We provide *a priori* error estimates for the spectral and pseudospectral Fourier (also called planewave) discretizations of the periodic Thomas-Fermi-von Weizsäcker (TFW) model and for the spectral discretization of the Kohn-Sham model, within the local density approximation (LDA). These models allow to compute approximations of the ground state energy and density of molecular systems in the condensed phase. The TFW model is stricly convex with respect to the electronic density, and allows for a comprehensive analysis. This is not the case for the Kohn-Sham LDA model, for which the uniqueness of the ground state electronic density is not guaranteed. Under a coercivity assumption on the second order optimality condition, we prove that for large enough energy cut-offs, the discretized Kohn-Sham LDA problem has a minimizer in the vicinity of any Kohn-Sham ground state, and that this minimizer is unique up to unitary transform. We then derive optimal *a priori* error estimates for the spectral discretization method.

1 Introduction

Density Functional Theory (DFT) is a powerful method for computing ground state electronic energies and densities in quantum chemistry, materials science, molecular biology and nanosciences. The models originating from DFT can be classified into two categories: the orbital-free models and the Kohn-Sham models. The Thomas-Fermi-von Weizsäcker (TFW) model falls into the first

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category. It is not very much used in practice, but is interesting from a mathematical viewpoint [1, 7, 12]. It indeed serves as a toy model for the analysis of the more complex electronic structure models routinely used by Physicists and Chemists. At the other extremity of the spectrum, the Kohn-Sham models [8, 11] are among the most widely used models in Physics and Chemistry, but are much more difficult to deal with. We focus here on the numerical analysis of the TFW model on the one hand, and of the Kohn-Sham model, within the local density approximation (LDA), on the other hand. More precisely, we are interested in the spectral and pseudospectral Fourier, more commonly called planewave, discretizations of the periodic versions of these two models. In this context, the simulation domain, sometimes referred to as the supercell, is the unit cell of some periodic lattice of $\mathbb{R}^3$. In the TFW model, periodic boundary conditions (PBC) are imposed to the density; in the Kohn-Sham framework, they are imposed to the Kohn-Sham orbitals (Born-von Karman PBC). Imposing PBC at the boundary of the simulation cell is a standard method to compute condensed phase properties with a limited number of atoms in the simulation cell, hence at a moderate computational cost.

This article is organized as follows. In Section 2, we briefly introduce the functional setting used in the formulation and the analysis of the planewave discretization of orbital-free and Kohn-Sham models. In Section 3, we provide *a priori* error estimates for the planewave discretization of the TFW model, including numerical integration. In Section 4, we deal with the Kohn-Sham LDA model.

2 Basic Fourier analysis for planewave discretization methods

Throughout this article, we denote by Γ the simulation cell, by $\mathcal{R}$ the periodic lattice, and by $\mathcal{R}^*$ the dual lattice. For simplicity, we assume that $\Gamma = [0, L)^3$ ($L > 0$), in which case $\mathcal{R}$ is the cubic lattice $L\mathbb{Z}^3$, and $\mathcal{R}^* = \frac{2\pi}{L}\mathbb{Z}^3$. Our arguments can be easily extended to the general case. For $k \in \mathcal{R}^*$, we denote by $e_k(x) = |\Gamma|^{-1/2} e^{ik\cdot x}$ the planewave with wavevector k. The family $(e_k)_{k\in\mathcal{R}^*}$ forms an orthonormal basis of

$$L^2_\#(\Gamma, \mathbb{C}) := \left\{ u \in L^2_{\rm loc}(\mathbb{R}^3, \mathbb{C}) \mid u \ \mathcal{R}\text{-periodic} \right\},$$

and for all $u \in L^2_\#(\Gamma, \mathbb{C})$,

$$u(x) = \sum_{k\in\mathcal{R}^*} \widehat{u}_k \, e_k(x) \qquad \text{with} \qquad \widehat{u}_k = (e_k, u)_{L^2_\#} = |\Gamma|^{-1/2} \int_\Gamma u(x) e^{-ik\cdot x} \, dx.$$

In our analysis, we will mainly consider real valued functions. We therefore introduce the Sobolev spaces of real valued $\mathcal{R}$-periodic functions

$$H^s_\#(\Gamma) := \left\{ u(x) = \sum_{k\in\mathcal{R}^*} \widehat{u}_k\, e_k(x) \mid \sum_{k\in\mathcal{R}^*} (1+|k|^2)^s |\widehat{u}_k|^2 < \infty \text{ and } \forall k,\ \widehat{u}_{-k} = \widehat{u}_k^* \right\},$$

$s \in \mathbb{R}$ (here and in the sequel a^* denotes the complex conjugate of the complex number a), endowed with the inner products

$$(u,v)_{H^s_\#} = \sum_{k\in\mathcal{R}^*} (1+|k|^2)^s\, \widehat{u}_k^*\, \widehat{v}_k.$$

For $N_c \in \mathbb{N}$, we denote by

$$V_{N_c} = \left\{ \sum_{k\in\mathcal{R}^* \mid |k| \le \frac{2\pi}{L} N_c} c_k e_k \mid \forall k,\ c_{-k} = c_k^* \right\} \tag{1}$$

(the constraints $c_{-k} = c_k^*$ imply that the functions of V_{N_c} are real valued). For all $s \in \mathbb{R}$, and each $v \in H^s_\#(\Gamma)$, the best approximation of v in V_{N_c} for *any* $H^r_\#$-norm, $r \le s$, is

$$\Pi_{N_c} v = \sum_{\boldsymbol{k}\in\mathcal{R}^* \mid |\boldsymbol{k}| \le \frac{2\pi}{L} N_c} \widehat{v}_k e_k.$$

The more regular v (the regularity being measured in terms of the Sobolev norms H^r), the faster the convergence of this truncated series to v: for all real numbers r and s with $r \le s$, we have for each $v \in H^s_\#(\Gamma)$,

$$\begin{aligned} \|v - \Pi_{N_c} v\|_{H^r_\#} = \min_{v_{N_c}\in V_{N_c}} \|v - v_{N_c}\|_{H^r_\#} &\le \left(\frac{L}{2\pi}\right)^{s-r} N_c^{-(s-r)} \|v - \Pi_{N_c} v\|_{H^s_\#} \\ &\le \left(\frac{L}{2\pi}\right)^{s-r} N_c^{-(s-r)} \|v\|_{H^s_\#}. \end{aligned} \tag{2}$$

For $N_g \in \mathbb{N}\setminus\{0\}$, we denote by $\widehat{\phi}^{\mathrm{FFT},N_g}$ the discrete Fourier transform on the carterisan grid $\mathcal{G}_{N_g} := \frac{L}{N_g}\mathbb{Z}^3$ of the function $\phi \in C^0_\#(\Gamma,\mathbb{C})$, where

$$C^0_\#(\Gamma,\mathbb{C}) := \left\{ u \in C^0(\mathbb{R}^3,\mathbb{C}) \mid u\ \mathcal{R}\text{-periodic} \right\}.$$

Recall that if $\phi = \sum_{k\in\mathcal{R}^*} \widehat{\phi}_k\, e_k \in C^0_\#(\Gamma,\mathbb{C})$, the discrete Fourier transform of ϕ is the $N_g\mathcal{R}^*$-periodic sequence $\widehat{\phi}^{\mathrm{FFT},N_g} = (\widehat{\phi}_k^{\mathrm{FFT},N_g})_{k\in\mathcal{R}^*}$ where

$$\widehat{\phi}_k^{\mathrm{FFT},N_g} = \frac{1}{N_g^3} \sum_{x\in\mathcal{G}_{N_g}\cap\Gamma} \phi(x) e^{-ik\cdot x} = |\Gamma|^{-1/2} \sum_{K\in\mathcal{R}^*} \widehat{\phi}_{k+N_g K}.$$

We now introduce the subspaces

$$W^{1\mathrm{D}}_{N_g} = \left| \begin{array}{ll} \mathrm{Span}\left\{ e^{ily} \mid l \in \frac{2\pi}{L}\mathbb{Z},\ |l| \le \frac{2\pi}{L}\left(\frac{N_g-1}{2}\right) \right\} & (N_g \text{ odd}), \\ \mathrm{Span}\left\{ e^{ily} \mid l \in \frac{2\pi}{L}\mathbb{Z},\ |l| \le \frac{2\pi}{L}\left(\frac{N_g}{2}\right) \right\} \oplus \mathbb{C}(e^{i\pi N_g y/L} + e^{-i\pi N_g y/L}) & (N_g \text{ even}), \end{array} \right.$$

($W_{N_g}^{1D} \in C_\#^\infty([0,L),\mathbb{C})$ and $\dim(W_{N_g}^{1D}) = N_g$), and $W_{N_g}^{3D} = W_{N_g}^{1D} \otimes W_{N_g}^{1D} \otimes W_{N_g}^{1D}$. Note that $W_{N_g}^{3D}$ is a subspace of $H_\#^s(\Gamma,\mathbb{C})$ of dimension N_g^3, for all $s \in \mathbb{R}$, and that if N_g is odd,

$$W_{N_g}^{3D} = \text{Span}\left\{ e_k \mid k \in \mathcal{R}^* = \frac{2\pi}{L}\mathbb{Z}^3, \ |k|_\infty \leq \frac{2\pi}{L}\left(\frac{N_g-1}{2}\right)\right\} \qquad (N_g \text{ odd}).$$

It is then possible to define the interpolation projector $\mathcal{I}_{N_g}$ from $C_\#^0(\Gamma,\mathbb{C})$ onto $W_{N_g}^{3D}$ by $[\mathcal{I}_{N_g}(\phi)](x) = \phi(x)$ for all $x \in \mathcal{G}_{N_g}$. It holds

$$\forall \phi \in C_\#^0(\Gamma,\mathbb{C}), \qquad \int_\Gamma \mathcal{I}_{N_g}(\phi) = \sum_{x \in \mathcal{G}_{N_g} \cap \Gamma} \left(\frac{L}{N_g}\right)^3 \phi(x). \tag{3}$$

The coefficients of the expansion of $\mathcal{I}_{N_g}(\phi)$ in the canonical basis of $W_{N_g}^{3D}$ is given by the discrete Fourier transform of ϕ. In particular, when N_g is odd, we have the simple relation

$$\mathcal{I}_{N_g}(\phi) = |\Gamma|^{1/2} \sum_{k \in \mathcal{R}^* \,|\, |k|_\infty \leq \frac{2\pi}{L}\left(\frac{N_g-1}{2}\right)} \widehat{\phi}_k^{\text{FFT},N_g} \, e_k \qquad (N_g \text{ odd}).$$

It is easy to check that if ϕ is real-valued, then so is $\mathcal{I}_{N_g}(\phi)$.

We will assume in the sequel that $N_g \geq 4N_c + 1$. We will then have for all $v_{4N_c} \in V_{4N_c}$,

$$\int_\Gamma v_{4N_c} = \sum_{x \in \mathcal{G}_{N_g} \cap \Gamma} \left(\frac{L}{N_g}\right)^3 v_{4N_c}(x) = \int_\Gamma \mathcal{I}_{N_g}(v_{4N_c}). \tag{4}$$

The following lemma gathers some technical results which will be useful for the numerical analysis of the planewave discretization of orbital-free and Kohn-Sham models.

Lemma 2.1 *Let $N_c \in \mathbb{N}^*$ and $N_g \in \mathbb{N}^*$ such that $N_g \geq 4N_c + 1$.*

1. *Let V be a function of $C_\#^0(\Gamma,\mathbb{C})$ and v_{N_c} and w_{N_c} be two functions of V_{N_c}. Then*

$$\int_\Gamma \mathcal{I}_{N_g}(V v_{N_c} w_{N_c}) = \int_\Gamma \mathcal{I}_{N_g}(V) v_{N_c} w_{N_c}; \tag{5}$$

$$\left| \int_\Gamma \mathcal{I}_{N_g}(V |v_{N_c}|^2) \right| \leq \|V\|_{L^\infty} \|v_{N_c}\|_{L_\#^2}^2. \tag{6}$$

2. *Let $s > 3/2$, $0 \leq r \leq s$, and V a function of $H_\#^s(\Gamma)$. Then,*

$$\left\|(1 - \mathcal{I}_{N_g})(V)\right\|_{H_\#^r} \leq C_{r,s} N_g^{-(s-r)} \|V\|_{H_\#^s}; \tag{7}$$

$$\left\|\Pi_{2N_c}(\mathcal{I}_{N_g}(V))\right\|_{L_\#^2} \leq \left(\int_\Gamma \mathcal{I}_{N_g}(|V|^2)\right)^{1/2}; \tag{8}$$

$$\left\|\Pi_{2N_c}(\mathcal{I}_{N_g}(V))\right\|_{H_\#^s} \leq (1 + C_{s,s}) \|V\|_{H_\#^s}, \tag{9}$$

for constants $C_{r,s}$ independent of V. Besides if there exists $m > 3$ and $C \in \mathbb{R}_+$ such that $|\widehat{V}_k| \leq C|k|^{-m}$, then there exists a constant C_V independent of N_c and N_g such that

$$\left\|\Pi_{2N_c}(1-\mathcal{I}_{N_g})(V)\right\|_{H^r_\#} \leq C_V N_c^{r+3/2} N_g^{-m}. \tag{10}$$

3. *Let ϕ be a Borel function from $\mathbb{R}_+$ to $\mathbb{R}$ such that there exists $C_\phi \in \mathbb{R}_+$ for which $|\phi(t)| \leq C_\phi(1+t^2)$ for all $t \in \mathbb{R}_+$. Then, for all $v_{N_c} \in V_{N_c}$,*

$$\left|\int_\Gamma \mathcal{I}_{N_g}(\phi(|v_{N_c}|^2))\right| \leq C_\phi\left(|\Gamma| + \|v_{N_c}\|^4_{L^4_\#}\right). \tag{11}$$

Proof For $z_{2N_c} \in V_{2N_c}$, it holds

$$\begin{aligned}\int_\Gamma \mathcal{I}_{N_g}(V z_{2N_c}) &= \sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 V(x) z_{2N_c}(x)\\ &= \sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 (\mathcal{I}_{N_g}(V))(x) z_{2N_c}(x)\\ &= \int_\Gamma \mathcal{I}_{N_g}(V)\, z_{2N_c}\end{aligned} \tag{12}$$

since $\mathcal{I}_{N_g}(V)z_{2N_c} \in V_{N_g+2N_c} \subset V_{2N_g}$ is exactly integrated. The function $v_{N_c}w_{N_c}$ being in V_{2N_c}, (5) is proved. Moreover, as $|v_{N_c}|^2 \in V_{4N_c}$, it follows from (4) that

$$\begin{aligned}\left|\int_\Gamma \mathcal{I}_{N_g}(V|v_{N_c}|^2)\right| &= \left|\sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 V(x)|v_{N_c}(x)|^2\right|\\ &\leq \|V\|_{L^\infty}\left|\sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 |v_{N_c}(x)|^2\right|\\ &= \|V\|_{L^\infty}\int_\Gamma |v_{N_c}|^2.\end{aligned}$$

Hence (6). The estimate (7) is proved in [6]. To prove (8), we notice that

$$\begin{aligned}\|\Pi_{2N_c}(I_{N_g}(V))\|^2_{L^2_\#} &\leq \|I_{N_g}(V)\|^2_{L^2_\#}\\ &= \int_\Gamma (I_{N_g}(V))^*(I_{N_g}(V))\\ &= \sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 (I_{N_g}(V))(x)^*(I_{N_g}(V))(x)\\ &= \sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 |V(x)|^2\\ &= \int_\Gamma I_{N_g}(|V|^2).\end{aligned}$$

The bound (9) is a straightforward consequence of (7):

$$\|\Pi_{2N_c}(I_{N_g}(V))\|_{H^s_\#} \leq \|I_{N_g}(V)\|_{H^s_\#} \leq \|V\|_{H^s_\#} + \|(1-I_{N_g})(V)\|_{H^s_\#} \leq (1+C_{s,s})\|V\|_{H^s_\#}.$$

Now, we notice that

$$\begin{aligned}\Pi_{2N_c}(\mathcal{I}_{N_g}(V)) &= |\Gamma|^{1/2} \sum_{k\in\mathcal{R}^* \,|\, |k|\leq \frac{4\pi}{L}N_c} \widehat{V}_k^{\mathrm{FFT},N_g} e_k \\ &= \sum_{k\in\mathcal{R}^* \,|\, |k|\leq \frac{4\pi}{L}N_c} \left(\sum_{K\in\mathcal{R}^*} \widehat{V}_{k+N_gK} \right) e_k. \qquad (13)\end{aligned}$$

From (13), we obtain

$$\begin{aligned}\left\|\Pi_{2N_c}(1-\mathcal{I}_{N_g})(V)\right\|^2_{H^s_\#} &= \sum_{k\in\mathcal{R}^* \,|\, |k|\leq \frac{4\pi}{L}N_c} (1+|k|^2)^s \left| \sum_{K\in\mathcal{R}^*\setminus\{0\}} \widehat{V}_{k+N_gK} \right|^2 \\ &\leq \left(\sum_{k\in\mathcal{R}^* \,|\, |k|\leq \frac{4\pi}{L}N_c} (1+|k|^2)^s \right) \max_{k\in\mathcal{R}^* \,|\, |k|\leq \frac{4\pi}{L}N_c} \left| \sum_{K\in\mathcal{R}^*\setminus\{0\}} \widehat{V}_{k+N_gK} \right|^2.\end{aligned}$$

On the one hand,

$$\sum_{k\in\mathcal{R}^* \,|\, |k|\leq \frac{4\pi}{L}N_c} (1+|k|^2)^s \underset{N_c\to\infty}{\sim} \frac{32\pi}{2s+3} \left(\frac{4\pi}{L}\right)^{2s} N_c^{2s+3},$$

and on the other hand, we have for each $k\in\mathcal{R}^*$ such that $|k|\leq \frac{4\pi}{L}N_c$,

$$\begin{aligned}\left| \sum_{K\in\mathcal{R}^*\setminus\{0\}} \widehat{V}_{k+N_gK} \right| &\leq C \sum_{K\in\mathcal{R}^*\setminus\{0\}} \frac{1}{|k+N_gK|^m} \\ &\leq C\, C_0 \left(\frac{L}{2\pi}\right)^m N_g^{-m}\end{aligned}$$

where

$$C_0 = \max_{y\in\mathbb{R}^3 \,|\, |y|\leq 1/2} \sum_{K\in\mathbb{Z}^3\setminus\{0\}} \frac{1}{|y-K|^m}.$$

The estimate (10) then easily follows. Let us finally prove (11). Using (3) and (4), we have

$$\begin{aligned}\left| \int_\Gamma \mathcal{I}_{N_g}(\phi(|v_{N_c}|^2)) \right| &= \left| \sum_{x\in\mathcal{G}_{N_g}\cap\Gamma} \left(\frac{L}{N_g}\right)^3 \phi(|v_{N_c}(x)|^2) \right| \\ &\leq C_\phi \left| \sum_{x\in\mathcal{G}_{N_g}\cap\Gamma} \left(\frac{L}{N_g}\right)^3 (1+|v_{N_c}(x)|^4) \right| \\ &= C_\phi \int_\Gamma (1+|v_{N_c}|^4) = C_\phi \left(|\Gamma| + \|v_{N_c}\|^4_{L^4_\#} \right).\end{aligned}$$

This completes the proof of Lemma 2.1. □

3 Planewave approximation of the TFW model

In the TFW model, as well as in any orbital-free model, the ground state electronic density of the system is obtained by minimizing an explicit functional of the density. Denoting by $\mathcal{N}$ the number of electrons in the simulation cell and by

$$\mathfrak{R}_{\mathcal{N}} = \left\{ \rho \geq 0 \mid \sqrt{\rho} \in H^1_\#(\Gamma),\ \int_\Gamma \rho = \mathcal{N} \right\}$$

the set of admissible densities, the TFW problem reads

$$I^{\rm TFW} = \inf \left\{ \mathcal{E}^{\rm TFW}(\rho),\ \rho \in \mathfrak{R}_{\mathcal{N}} \right\}, \tag{14}$$

where

$$\mathcal{E}^{\rm TFW}(\rho) = \frac{C_{\rm W}}{2} \int_\Gamma |\nabla \sqrt{\rho}|^2 + C_{\rm TF} \int_\Gamma \rho^{5/3} + \int_\Gamma \rho V^{\rm ion} + \frac{1}{2} D_\Gamma(\rho, \rho).$$

$C_{\rm W}$ is a positive real number ($C_{\rm W} = 1$, 1/5 or 1/9 depending on the context [8]), and $C_{\rm TF}$ is the Thomas-Fermi constant: $C_{\rm TF} = \frac{10}{3}(3\pi^2)^{2/3}$. The last term of the TFW energy models the periodic Coulomb energy: for ρ and ρ' in $H^{-1}_\#(\Gamma)$,

$$D_\Gamma(\rho, \rho') := 4\pi \sum_{k \in \mathcal{R}^* \setminus \{0\}} |k|^{-2} \widehat{\rho}_k^* \, \widehat{\rho}'_k.$$

We finally make the assumption that $V^{\rm ion}$ is a $\mathcal{R}$-periodic potential such that

$$\exists m > 3,\ C \geq 0 \text{ s.t. } \forall k \in \mathcal{R}^*,\ |\widehat{V}^{\rm ion}_k| \leq C |k|^{-m}. \tag{15}$$

Note that this implies that $V^{\rm ion}$ is in $H^{m-3/2-\epsilon}(\Gamma)$ for all $\epsilon > 0$, hence in $C^0_\#(\Gamma)$ since $m - 3/2 - \epsilon > 3/2$ for ϵ small enough. It is convenient to reformulate the TFW model in terms of $v = \sqrt{\rho}$. It can be easily seen that

$$I^{\rm TFW} = \inf \left\{ E^{\rm TFW}(v),\ v \in H^1_\#(\Gamma),\ \int_\Gamma |v|^2 = \mathcal{N} \right\}, \tag{16}$$

where

$$E^{\rm TFW}(v) = \frac{C_{\rm W}}{2} \int_\Gamma |\nabla v|^2 + C_{\rm TF} \int_\Gamma |v|^{10/3} + \int_\Gamma V^{\rm ion} |v|^2 + \frac{1}{2} D_\Gamma(|v|^2, |v|^2).$$

Let $F(t) = C_{\rm TF} t^{5/3}$ and $f(t) = F'(t) = \frac{5}{3} C_{\rm TF} t^{2/3}$. The function F is in $C^1([0, +\infty)) \cap C^\infty((0, +\infty))$, is strictly convex on $[0, +\infty)$, and for all $(t_1, t_2) \in \mathbb{R}_+ \times \mathbb{R}_+$,

$$|f(t_2^2) t_2 - f(t_1^2) t_2 - 2 f'(t_1^2) t_1^2 (t_2 - t_1)| \leq \frac{70}{27} C_{\rm TF} \max(t_1^{1/3}, t_2^{1/3})\, |t_2 - t_1|^2. \tag{17}$$

The first and second derivatives of $E^{\rm TFW}$ are respectively given by

$$\langle E^{\rm TFW\prime}(v), w\rangle_{H^{-1}_\#, H^1_\#} = 2\langle \mathcal{H}^{\rm TFW}_{|v|^2} v, w\rangle;$$
$$\langle E^{\rm TFW\prime\prime}(v)w_1, w_2\rangle_{H^{-1}_\#, H^1_\#} = 2\langle \mathcal{H}^{\rm TFW}_{|v|^2} w_1, w_2\rangle + 4D_\Gamma(vw_1, vw_2) + 4\int_\Gamma f'(|v|^2)|v|^2 w_1 w_2,$$

where we have denoted by $\mathcal{H}^{\rm TFW}_\rho$ the TFW Hamiltonian associated with the density ρ

$$\mathcal{H}^{\rm TFW}_\rho = -\frac{C_{\rm W}}{2}\Delta + f(\rho) + V^{\rm ion} + V^{\rm Coulomb}_\rho,$$

where

$$V^{\rm Coulomb}_\rho(x) = 4\pi \sum_{k\in\mathcal{R}^*\setminus\{0\}} |k|^{-2}\widehat{\rho}_k e_k(x)$$

is the $\mathcal{R}$-periodic Coulomb potential generated by the $\mathcal{R}$-periodic charge distribution ρ. Recall that $V^{\rm Coulomb}_\rho$ can also be defined as the unique solution in $H^1_\#(\Gamma)$ to

$$\left\{ \begin{array}{l} -\Delta V^{\rm Coulomb}_\rho = 4\pi \left(\rho - |\Gamma|^{-1}\int_\Gamma \rho\right) \\ \int_\Gamma V^{\rm Coulomb}_\rho = 0. \end{array}\right.$$

Let us recall (see [12] and the proof of Lemma 2 in [3]) that

- (14) has a unique minimizer ρ^0, and that the minimizers of (16) are u and $-u$, where $u = \sqrt{\rho^0}$;
- u is in $H^{m+1/2-\epsilon}_\#(\Gamma)$ for each $\epsilon > 0$ (hence in $C^2_\#(\Gamma)$ since $m+1/2-\epsilon > 7/2$ for ϵ small enough);
- $u > 0$ on $\mathbb{R}^3$;
- u satisfies the Euler equation

  $$\mathcal{H}^{\rm TFW}_{|u|^2}(u) = -\frac{C_{\rm W}}{2}\Delta u + \left(\frac{5}{3}C_{\rm TF}u^{4/3} + V^{\rm ion} + V^{\rm Coulomb}_{u^2}\right)u = \lambda u$$

  for some $\lambda \in \mathbb{R}$, (the ground state eigenvalue of $\mathcal{H}^{\rm TFW}_{\rho^0}$, that is non-degenerate).

The planewave discretization of the TFW model is obtained by choosing

1. an energy cut-off $E_{\rm c} > 0$ or, equivalently, a finite dimensional Fourier space V_{N_c}, the integer N_c being related to $E_{\rm c}$ through the relation $N_c := [\sqrt{2E_{\rm c}}\, L/2\pi]$;
2. a cartesian grid $\mathcal{G}_{N_g}$ with step size L/N_g where $N_g \in \mathbb{N}^*$ is such that $N_g \geq 4N_c + 1$,

and by considering the finite dimensional minimization problem

$$I_{N_c,N_g}^{\rm TFW} = \inf \left\{ E_{N_g}^{\rm TFW}(v_{N_c}),\ v_{N_c} \in V_{N_c},\ \int_\Gamma |v_{N_c}|^2 = \mathcal{N} \right\}, \qquad (18)$$

where

$$\begin{aligned} E_{N_g}^{\rm TFW}(v_{N_c}) &= \frac{C_{\rm W}}{2} \int_\Gamma |\nabla v_{N_c}|^2 + C_{\rm TF} \int_\Gamma \mathcal{I}_{N_g}(|v_{N_c}|^{10/3}) + \int_\Gamma \mathcal{I}_{N_g}(V^{\rm ion})|v_{N_c}|^2 \\ &\quad + \frac{1}{2} D_\Gamma(|v_{N_c}|^2, |v_{N_c}|^2), \end{aligned}$$

$\mathcal{I}_{N_g}$ denoting the interpolation operator introduced in the previous section. The Euler equation associated with (18) can be written as a nonlinear eigenvalue problem

$$\forall v_{N_c} \in V_{N_c}, \quad \langle (\widetilde{\mathcal{H}}^{{\rm TFW},N_g}_{|u_{N_c,N_g}|^2} - \lambda_{N_c,N_g}) u_{N_c,N_g}, v_{N_c} \rangle_{H^{-1}_\#, H^1_\#} = 0,$$

where we have denoted by

$$\widetilde{\mathcal{H}}^{{\rm TFW},N_g}_\rho = -\frac{C_{\rm W}}{2}\Delta + \mathcal{I}_{N_g}\left(\frac{5}{3} C_{\rm TF} \rho^{2/3} + V^{\rm ion} \right) + V^{\rm Coulomb}_\rho$$

the pseudospectral TFW Hamiltonian associated with the density ρ, and by λ_{N_c,N_g} the Lagrange multiplier of the constraint $\int_\Gamma |v_{N_c}|^2 = \mathcal{N}$. We therefore have

$$-\frac{C_{\rm W}}{2}\Delta u_{N_c,N_g} + \Pi_{N_c}\left[\left(\mathcal{I}_{N_g}\left(\frac{5}{3} C_{\rm TF} |u_{N_c,N_g}|^{4/3} + V^{\rm ion} \right) + V^{\rm Coulomb}_{|u_{N_c,N_g}|^2} \right) u_{N_c,N_g} \right] = \lambda_{N_c,N_g} u_{N_c,N_g}.$$

Under the condition that $N_g \geq 4N_c + 1$, we have for all $\phi \in C^0_\#(\Gamma)$,

$$\forall (k,l) \in \mathcal{R}^* \times \mathcal{R}^* \text{ s.t. } |k|,|l| \leq \frac{2\pi}{L} N_c, \quad \int_\Gamma \mathcal{I}_{N_g}(\phi)\, e_k^*\, e_l = \widehat{\phi}^{\rm FFT}_{k-l},$$

so that, $\widetilde{\mathcal{H}}^{\rm TFW}_{u_{N_c,N_g}}$ is defined on V_{N_c} by the Fourier matrix

$$\begin{aligned} [\widehat{\mathcal{H}}^{{\rm TFW},N_g}_{|u_{N_c,N_g}|^2}]_{kl} &= \frac{C_{\rm W}}{2}|k|^2 \delta_{kl} + \frac{5}{3} C_{\rm TF} \widehat{(|u_{N_c,N_g}|^{4/3})}^{{\rm FFT},N_g}_{k-l} + \widehat{(V^{\rm ion})}^{{\rm FFT},N_g}_{k-l} \\ &\quad + 4\pi \frac{\widehat{(|u_{N_c,N_g}|^2)}^{{\rm FFT},N_g}_{k-l}}{|k-l|^2} (1 - \delta_{kl}), \end{aligned}$$

where, by convention, the last term of the right hand side is equal to zero for $k = l$.

We also introduce the variational approximation of (16)

$$I_{N_c}^{\rm TFW} = \inf \left\{ E^{\rm TFW}(v_{N_c}),\ v_{N_c} \in V_{N_c},\ \int_\Gamma |v_{N_c}|^2 = \mathcal{N} \right\}. \qquad (19)$$

Any minimizer u_{N_c} to (19) satisfies the elliptic equation

$$-\frac{C_{\rm W}}{2}\Delta u_{N_c} + \Pi_{N_c}\left[\frac{5}{3}C_{\rm TF}|u_{N_c}|^{4/3}u_{N_c} + V^{\rm ion}u_{N_c} + V^{\rm Coulomb}_{|u_{N_c}|^2}u_{N_c}\right] = \lambda_{N_c}u_{N_c}, \tag{20}$$

for some $\lambda_{N_c} \in \mathbb{R}$.

The main result of this section is an extension of results previously obtained by A. Zhou [16].

Theorem 3.1 *For each $N_c \in \mathbb{N}$, we denote by u_{N_c} a minimizer to (19) such that $(u_{N_c}, u)_{L^2_\#} \geq 0$ and, for each $N_c \in \mathbb{N}$ and $N_g \geq 4N_c + 1$, we denote by u_{N_c,N_g} a minimizer to (18) such that $(u_{N_c,N_g}, u)_{L^2_\#} \geq 0$. Then for N_c large enough, u_{N_c} and u_{N_c,N_g} are unique, and the following estimates hold true*

$$\begin{aligned}
\|u_{N_c} - u\|_{H^s_\#} &\leq C_{s,\epsilon}N_c^{-(m-s+1/2-\epsilon)}; && (21)\\
|\lambda_{N_c} - \lambda| &\leq C_\epsilon N_c^{-(2m-1-\epsilon)}; && (22)\\
\gamma\|u_{N_c} - u\|^2_{H^1_\#} \leq I^{\rm TFW}_{N_c} - I^{\rm TFW} &\leq C\|u_{N_c} - u\|^2_{H^1_\#}; && (23)\\
\|u_{N_c,N_g} - u_{N_c}\|_{H^s_\#} &\leq C_s\, N_c^{3/2+(s-1)_+}N_g^{-m}; && (24)\\
|\lambda_{N_c,N_g} - \lambda_{N_c}| &\leq CN_c^{3/2}N_g^{-m}; && (25)\\
|I^{\rm TFW}_{N_c,N_g} - I^{\rm TFW}_{N_c}| &\leq CN_c^{3/2}N_g^{-m}, && (26)
\end{aligned}$$

for all $-m + 3/2 < s < m + 1/2$ and $\epsilon > 0$, and for some constants $\gamma > 0$, $C_{s,\epsilon} \geq 0$, $C_\epsilon \geq 0$, $C \geq 0$ and $C_s \geq 0$ independent of N_c and N_g.

Remark 1 *More complex orbital-free models have been proposed in the recent years [15], which are used to perform multimillion atom DFT calculations. Some of these models however are not well posed (the energy functional is not bounded from below [2]), and the others are not well understood from a mathematical point of view. For these reasons, we will not deal with those models in this article.*

3.1 A priori estimates for the variational approximation.

In this section, we prove the first part of Theorem 3.1, related to the variational approximation (19). The estimates (21), (22) and (23) originate from arguments already introduced in [3]. For brevity, we only recall the main steps of the proof and leave the details to the reader.

The difference between (16) and the problem dealt with in [3] is the presence of the Coulomb term $D_\Gamma(|v|^2,|v|^2)$, for which the following estimates are available:

$$\begin{aligned}
0 \le D_\Gamma(\rho,\rho) &\le C\|\rho\|_{L^2_\#}^2, \quad \text{for all } \rho \in L^2_\#(\Gamma), &(27)\\
|D_\Gamma(uv,uw)| &\le C\|v\|_{L^2_\#}\|w\|_{L^2_\#}, \quad \text{for all } (v,w)\in (L^2_\#(\Gamma))^2, &(28)\\
|D_\Gamma(\rho,vw)| &\le C\|\rho\|_{L^2_\#}\|v\|_{L^2_\#}\|w\|_{L^2_\#}, \quad \text{for all } (\rho,v,w)\in (L^2_\#(\Gamma))^3, &(29)\\
\|V_\rho^{\rm Coulomb}\|_{L^\infty} &\le C\|\rho\|_{L^2_\#}, \quad \text{for all } \rho \in L^2_\#(\Gamma), &(30)\\
\|V_\rho^{\rm Coulomb}\|_{H^{s+2}_\#} &\le C\|\rho\|_{H^s_\#}, \quad \text{for all } \rho \in H^s_\#(\Gamma). &(31)
\end{aligned}$$

Here and in the sequel, C denotes a non-negative constant which may depend on Γ, $V^{\rm ion}$ and $\mathcal{N}$, but not on the discretization parameters.

Using (27), (28) and the fact that $f'>0$ on $(0,+\infty)$, we can then show (see the proof of Lemma 1 in [3]) that there exist $\beta>0$, $\gamma>0$ and $M\ge 0$ such that for all $v\in H^1_\#(\Gamma)$,

$$0 \le \langle (\mathcal{H}^{\rm TFW}_{\rho^0}-\lambda)v,v\rangle_{H^{-1}_\#,H^1_\#} \le M\|v\|^2_{H^1_\#}, \qquad (32)$$

$$\beta\|v\|^2_{H^1_\#} \le \langle (E^{\rm TFW}{}''(u)-2\lambda)v,v\rangle_{H^{-1}_\#,H^1_\#} \le M\|v\|^2_{H^1_\#}, \qquad (33)$$

and for all $v\in H^1_\#(\Gamma)$ such that $\|v\|_{L^2_\#}=\mathcal{N}^{1/2}$ and $(v,u)_{L^2_\#}\ge 0$,

$$\gamma\|v-u\|^2_{H^1_\#} \le \langle (\mathcal{H}^{\rm TFW}_{\rho^0}-\lambda)(v-u),(v-u)\rangle_{H^{-1}_\#,H^1_\#}. \qquad (34)$$

Remarking that

$$\begin{aligned}
E^{\rm TFW}(u_{N_c}) - E^{\rm TFW}(u) &= \langle (\mathcal{H}^{\rm TFW}_{\rho^0}-\lambda)(u_{N_c}-u),(u_{N_c}-u)\rangle_{H^{-1}_\#,H^1_\#}\\
&\quad + \frac{1}{2}D_\Gamma(|u_{N_c}|^2-|u|^2,|u_{N_c}|^2-|u|^2)\\
&\quad + \int_\Gamma F(|u_{N_c}|^2)-F(|u|^2)-f(|u|^2)(|u_{N_c}|^2-|u|^2) \qquad (35)
\end{aligned}$$

and using (34), the positivity of the bilinear form D_Γ, and the convexity of the function F, we obtain that

$$I^{\rm TFW}_{N_c} - I^{\rm TFW} = E^{\rm TFW}(u_{N_c}) - E^{\rm TFW}(u) \ge \gamma\|u_{N_c}-u\|^2_{H^1_\#}.$$

For each $N_c\in\mathbb{N}$, $\widetilde{u}_{N_c}=\mathcal{N}^{1/2}\Pi_{N_c}u/\|\Pi_{N_c}u\|_{L^2_\#}$ satisfies $(\widetilde{u}_{N_c},u)_{L^2_\#}\ge 0$ and $\|\widetilde{u}_{N_c}\|_{L^2_\#}=\mathcal{N}^{1/2}$, and the sequence $(\widetilde{u}_{N_c})_{N_c\in\mathbb{N}}$ converges to u in $H^{m+1/2-\epsilon}_\#(\Gamma)$ for each $\epsilon>0$. As the functional $E^{\rm TFW}$ is continuous on $H^1_\#(\Gamma)$, we have

$$\|u_{N_c}-u\|^2_{H^1_\#} \le \gamma^{-1}\left(I^{\rm TFW}_{N_c}-I^{\rm TFW}\right) \le \gamma^{-1}\left(E^{\rm TFW}(\widetilde{u}_{N_c})-E^{\rm TFW}(u)\right) \underset{N_c\to\infty}{\longrightarrow} 0.$$

Hence, $(u_{N_c})_{N_c\in\mathbb{N}}$ converges to u in $H^1_\#(\Gamma)$, and we also have

$$\begin{aligned}\lambda_{N_c} &= \mathcal{N}^{-1}\left[\frac{C_{\rm W}}{2}\int_\Gamma |\nabla u_{N_c}|^2 + \int_\Gamma f(|u_{N_c}|^2)|u_{N_c}|^2 + \int_\Gamma V^{\rm ion}|u_{N_c}|^2 + D_\Gamma(|u_{N_c}|^2,|u_{N_c}|^2)\right] \\ &\underset{N_c\to\infty}{\longrightarrow} \mathcal{N}^{-1}\left[\frac{C_{\rm W}}{2}\int_\Gamma |\nabla u|^2 + \int_\Gamma f(|u|^2)|u|^2 + \int_\Gamma V^{\rm ion}|u|^2 + D_\Gamma(|u|^2,|u|^2)\right] \\ &= \lambda.\end{aligned}$$

As $f(|u_{N_c}|^2)u_{N_c} + V^{\rm ion}u_{N_c} + V^{\rm Coulomb}_{|u_{N_c}|^2}u_{N_c}$ is bounded in $L^2_\#(\Gamma)$, uniformly in N_c, we deduce from (20) that the sequence $(u_{N_c})_{N_c\in\mathbb{N}}$ is bounded in $H^2_\#(\Gamma)$, hence in $L^\infty(\Gamma)$. Now

$$\begin{aligned}\Delta(u_{N_c}-u) &= 2C_{\rm W}^{-1}\Big[\Pi_{N_c}\Big(f(|u_{N_c}|^2)u_{N_c} - f(|u|^2)u + V^{\rm ion}(u_{N_c}-u) + \\ &\qquad V^{\rm Coulomb}_{|u_{N_c}|^2}u_{N_c} - V^{\rm Coulomb}_{|u|^2}u\Big) \\ &\quad + (1-\Pi_{N_c})\left(f(|u|^2)u + V^{\rm ion}u + V^{\rm Coulomb}_{|u|^2}u\right) \\ &\quad -\lambda_{N_c}(u_{N_c}-u) - (\lambda_{N_c}-\lambda)u\Big].\end{aligned}$$

Observing that the right-hand side goes to zero in $L^2_\#(\Gamma)$ when N_c goes to infinity, we obtain that $(u_{N_c})_{N_c\in\mathbb{N}}$ converges to u in $H^2_\#(\Gamma)$, and therefore in $C^{0,1/2}_\#(\Gamma)$. In addition, we know from Harnack inequality [10] that $u>0$ in $\mathbb{R}^3$. Consequently, for N_c large enough, the function u_{N_c} (which is continuous and $\mathcal{R}$-periodic) is bounded away from 0, uniformly in N_c. As $f\in C^\infty(0,+\infty)$, one can see by a simple bootstrap argument that the convergence of $(u_{N_c})_{N_c\in\mathbb{N}}$ to u also holds in $H^{m+1/2-\epsilon}_\#(\Gamma)$ for each $\epsilon>0$. The upper bound in (23) is obtained from (35), remarking that

$$\begin{aligned}0 &\le \int_\Gamma F(|u_{N_c}|^2) - F(|u|^2) - f(|u|^2)(|u_{N_c}|^2-|u|^2) \\ &\le \frac{35}{9}C_{\rm TF}\int_\Gamma \max(|u_{N_c}|^{4/3},|u|^{4/3})|u_{N_c}-u|^2 \\ &\le \frac{35}{9}C_{\rm TF}\left(\max_{N_c\in\mathbb{N}}\|u_{N_c}\|_{L^\infty}\right)^{4/3}\|u_{N_c}-u\|^2_{L^2_\#},\end{aligned}$$

and that

$$\begin{aligned}0 &\le D_\Gamma(|u_{N_c}|^2-|u|^2,|u_{N_c}|^2-|u|^2) \le C\||u_{N_c}|^2-|u|^2\|^2_{L^2_\#} \\ &\le 4C\left(\max_{N_c\in\mathbb{N}}\|u_{N_c}\|_{L^\infty}\right)^2\|u_{N_c}-u\|^2_{L^2_\#}.\end{aligned}$$

The uniqueness of u_{N_c} for N_c large enough can then be checked as follows. First,

(u_{N_c}, λ_{N_c}) satisfies the variational equation

$$\forall v_{N_c} \in V_{N_c}, \quad \langle (\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2} - \lambda_{N_c}) u_{N_c}, v_{N_c} \rangle_{H^{-1}_\#, H^1_\#} = 0.$$

Therefore λ_{N_c} is the variational approximation in V_{N_c} of some eigenvalue of $\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2}$. As $(u_{N_c})_{N_c \in \mathbb{N}}$ converges to u in $L^\infty(\Gamma)$, $\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2} - \mathcal{H}^{\rm TFW}_{\rho^0}$ converges to 0 in operator norm. Consequently, the $n^{\rm th}$ eigenvalue of $\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2}$ converges to the $n^{\rm th}$ eigenvalue of $\mathcal{H}^{\rm TFW}_{\rho^0}$ when N_c goes to infinity, the convergence being uniform in n. Together with the fact that the sequence $(\lambda_{N_c})_{N_c \in \mathbb{N}}$ converges to λ, the non-degenerate ground state eigenvalue of $\mathcal{H}^{\rm TFW}_{\rho^0}$, this implies that for N_c large enough, λ_{N_c} is the ground state eigenvalue of $\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2}$ in V_{N_c} and for all $v_{N_c} \in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_\#} = \mathcal{N}^{1/2}$ and $(v_{N_c}, u_{N_c})_{L^2_\#} \geq 0$,

$$\begin{aligned} E^{\rm TFW}(v_{N_c}) - E^{\rm TFW}(u_{N_c}) &= \langle (\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2} - \lambda_{N_c})(v_{N_c} - u_{N_c}), (v_{N_c} - u_{N_c}) \rangle_{H^{-1}_\#, H^1_\#} \\ &\quad + \frac{1}{2} D_\Gamma(|v_{N_c}|^2 - |u_{N_c}|^2, |v_{N_c}|^2 - |u_{N_c}|^2) \\ &\quad + \int_\Gamma F(|v_{N_c}|^2) - F(|u_{N_c}|^2) - f(|u_{N_c}|^2)(|v_{N_c}|^2 - |u_{N_c}|^2) \\ &\geq \langle (\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2} - \lambda_{N_c})(v_{N_c} - u_{N_c}), (v_{N_c} - u_{N_c}) \rangle_{H^{-1}_\#, H^1_\#} \\ &\geq \frac{\gamma}{2} \|v_{N_c} - u_{N_c}\|^2_{H^1_\#}. \end{aligned} \qquad (36)$$

It easily follows that for N_c large enough, (19) has a unique minimizer u_{N_c} such that $(u_{N_c}, u)_{L^2_\#} \geq 0$.

Let us now establish the rates of convergence of $|\lambda_{N_c} - \lambda|$ and $\|u_{N_c} - u\|_{H^s_\#}$. First,

$$\begin{aligned} \lambda_{N_c} - \lambda &= \mathcal{N}^{-1} \bigg[\langle (\mathcal{H}^{\rm TFW}_{|u|^2} - \lambda)(u_{N_c} - u), (u_{N_c} - u) \rangle_{H^{-1}_\#, H^1_\#} \\ &\qquad + \int_\Gamma w_{N_c}(u_{N_c} - u) \bigg] \end{aligned} \qquad (37)$$

with

$$w_{N_c} = \frac{f(|u_{N_c}|^2) - f(|u|^2)}{u_{N_c} - u} |u_{N_c}|^2 + V^{\rm Coulomb}_{|u_{N_c}|^2}(u_{N_c} + u).$$

As u_{N_c} is bounded away from 0 and $f \in C^\infty((0, +\infty))$, the function w_{N_c} is uniformly bounded in $H^{m-3/2-\epsilon}_\#(\Gamma)$ (at least for N_c large enough). We therefore obtain that for all $0 \leq r < m - 3/2$, there exists a constant $C_r \in \mathbb{R}_+$ such that for all N_c large enough,

$$|\lambda_{N_c} - \lambda| \leq C_r \left(\|u_{N_c} - u\|^2_{H^1_\#} + \|u_{N_c} - u\|_{H^{-r}_\#} \right). \qquad (38)$$

In order to evaluate the $H^1_\#$-norm of the error $(u_{N_c} - u)$, we first notice that

$$\forall v_{N_c} \in V_{N_c}, \quad \|u_{N_c} - u\|_{H^1_\#} \leq \|u_{N_c} - v_{N_c}\|_{H^1_\#} + \|v_{N_c} - u\|_{H^1_\#}, \qquad (39)$$

and that

$$\begin{aligned}
\|u_{N_c}-v_{N_c}\|_{H^1_\#}^2 &\leq \beta^{-1}\,\langle (E^{\rm TFW}{}''(u)-2\lambda)(u_{N_c}-v_{N_c}),(u_{N_c}-v_{N_c})\rangle_{H^{-1}_\#,H^1_\#} \\
&= \beta^{-1}\bigg(\langle (E^{\rm TFW}{}''(u)-2\lambda)(u_{N_c}-u),(u_{N_c}-v_{N_c})\rangle_{H^{-1}_\#,H^1_\#} \\
&\qquad +\langle (E^{\rm TFW}{}''(u)-2\lambda)(u-v_{N_c}),(u_{N_c}-v_{N_c})\rangle_{H^{-1}_\#,H^1_\#}\bigg). \qquad (40)
\end{aligned}$$

For all $z_{N_c}\in V_{N_c}$,

$$\begin{aligned}
&\langle (E^{\rm TFW}{}''(u)-2\lambda)(u_{N_c}-u),z_{N_c}\rangle_{H^{-1}_\#,H^1_\#} \\
&\quad = -2\int_\Gamma [f(|u_{N_c}|^2)u_{N_c}-f(|u|^2)u_{N_c}-2f'(|u|^2)|u|^2(u_{N_c}-u)]z_{N_c} \\
&\qquad -2D_\Gamma((u_{N_c}-u)(u_{N_c}+u),(u_{N_c}-u)z_{N_c})-2D_\Gamma((u_{N_c}-u)^2,uz_{N_c}) \\
&\qquad +2(\lambda_{N_c}-\lambda)\int_\Gamma u_{N_c}z_{N_c}. \qquad (41)
\end{aligned}$$

On the other hand, we have for all $v_{N_c}\in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_\#}=\mathcal{N}^{1/2}$,

$$\int_\Gamma u_{N_c}(u_{N_c}-v_{N_c})=\mathcal{N}-\int_\Gamma u_{N_c}v_{N_c}=\frac{1}{2}\|u_{N_c}-v_{N_c}\|_{L^2_\#}^2.$$

Using (17), (29), (38) with $r=0$ and the above equality, we therefore obtain for all $v_{N_c}\in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_\#}=\mathcal{N}^{1/2}$,

$$\begin{aligned}
&\left|\langle (E^{\rm TFW}{}''(u)-2\lambda)(u_{N_c}-u),(u_{N_c}-v_{N_c})\rangle_{H^{-1}_\#,H^1_\#}\right| \\
&\quad \leq C\bigg(\|u_{N_c}-u\|_{H^1_\#}^2\,\|u_{N_c}-v_{N_c}\|_{H^1_\#} \\
&\qquad +\left(\|u_{N_c}-u\|_{H^1_\#}^2+\|u_{N_c}-u\|_{L^2_\#}\right)\|u_{N_c}-v_{N_c}\|_{L^2_\#}^2\bigg). \qquad (42)
\end{aligned}$$

Therefore, for N_c large enough, we have for all $v_{N_c}\in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_\#}=\mathcal{N}^{1/2}$,

$$\|u_{N_c}-v_{N_c}\|_{H^1_\#}\leq C\left(\|u_{N_c}-u\|_{H^1_\#}^2+\|v_{N_c}-u\|_{H^1_\#}\right).$$

Together with (39), this shows that there exists $N\in\mathbb{N}$ and $C\in\mathbb{R}_+$ such that for all $N_c\geq N$,

$$\forall v_{N_c}\in V_{N_c}\ \text{s.t.}\ \|v_{N_c}\|_{L^2_\#}=\mathcal{N}^{1/2},\quad \|u_{N_c}-u\|_{H^1_\#}\leq C\|v_{N_c}-u\|_{H^1_\#}.$$

By a classical argument (see e.g. the proof of Theorem 1 in [3]), we deduce from (2) and the above inequality that

$$\|u_{N_c}-u\|_{H^1_\#}\leq C\min_{v_{N_c}\in V_{N_c}}\|v_{N_c}-u\|_{H^1_\#}\leq C_{1,\epsilon}N_c^{-(m-1/2-\epsilon)}, \qquad (43)$$

for some constant $C_{1,\epsilon}$ independent of N_c. This completes the proof of the estimate in the $H^1_\#$–norm. We proceed with the analysis of the $L^2_\#$–norm.

For $w \in L^2_\#(\Gamma)$, we denote by ψ_w the unique solution to the adjoint problem

$$\left\{ \begin{array}{l} \text{find } \psi_w \in u^\perp \text{ such that} \\ \forall v \in u^\perp, \quad \langle (E^{\rm TFW''}(u) - 2\lambda)\psi_w, v\rangle_{H^{-1}_\#, H^1_\#} = \langle w, v\rangle_{H^{-1}_\#, H^1_\#}, \end{array} \right. \tag{44}$$

where

$$u^\perp = \left\{ v \in H^1_\#(\Gamma) \mid \int_\Gamma uv = 0 \right\}.$$

The function ψ_w is solution to the elliptic equation

$$\begin{aligned} -\frac{C_{\rm W}}{2}\Delta\psi_w + \left(V^{\rm ion} + V^{\rm Coulomb}_{u^2} + f(u^2) + 2f'(u^2)u^2 - \lambda\right)\psi_w + 2V^{\rm Coulomb}_{u\psi_w}u \\ = 2\left(\int_\Gamma f'(u^2)u^3\psi_w + D_\Gamma(u^2, u\psi_w)\right)u + \frac{1}{2}\left(w - (w,u)_{L^2_\#}u\right), \end{aligned}$$

from which we deduce that if $w \in H^r_\#(\Gamma)$ for some $0 \le r < m - 3/2$, then $\psi_w \in H^{r+2}_\#(\Gamma)$ and

$$\|\psi_w\|_{H^{r+2}_\#} \le C_r \|w\|_{H^r_\#}, \tag{45}$$

for some constant C_r independent of w. Let $u^*_{N_c}$ be the orthogonal projection, for the $L^2_\#$ inner product, of u_{N_c} on the affine space $\left\{ v \in L^2_\#(\Gamma) \mid \int_\Gamma uv = \mathcal{N} \right\}$. One has

$$u^*_{N_c} \in H^1_\#(\Gamma), \qquad u^*_{N_c} - u \in u^\perp, \qquad u^*_{N_c} - u_{N_c} = \frac{1}{2\mathcal{N}}\|u_{N_c} - u\|^2_{L^2_\#}u,$$

from which we infer that

$$
\begin{aligned}
\|u_{N_c}-u\|_{L^2_\#}^2 &= \int_\Gamma (u_{N_c}-u)(u_{N_c}^*-u) + \int_\Gamma (u_{N_c}-u)(u_{N_c}-u_{N_c}^*) \\
&= \int_\Gamma (u_{N_c}-u)(u_{N_c}^*-u) - \frac{1}{2\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^2 \int_\Gamma (u_{N_c}-u)u \\
&= \int_\Gamma (u_{N_c}-u)(u_{N_c}^*-u) + \frac{1}{2\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^2 \left(\mathcal{N} - \int_\Gamma u_{N_c}u\right) \\
&= \int_\Gamma (u_{N_c}-u)(u_{N_c}^*-u) + \frac{1}{4\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^4 \\
&= \langle u_{N_c}-u, u_{N_c}^*-u\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{4\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^4 \\
&= \langle (E^{\mathrm{TFW}''}(u)-2\lambda)\psi_{u_{N_c}-u}, u_{N_c}^*-u\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{4\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^4 \\
&= \langle (E^{\mathrm{TFW}''}(u)-2\lambda)(u_{N_c}-u), \psi_{u_{N_c}-u}\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{4\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^4 \\
&\quad + \frac{1}{2\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^2 \langle (E^{\mathrm{TFW}''}(u)-2\lambda)u, \psi_{u_{N_c}-u}\rangle_{H^{-1}_\#,H^1_\#} \\
&= \langle (E^{\mathrm{TFW}''}(u)-2\lambda)(u_{N_c}-u), \psi_{u_{N_c}-u}\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{4\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^4 \\
&\quad + \frac{2}{\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^2 \left[\int_\Gamma f'(u^2)u^3\psi_{u_{N_c}-u} + D_\Gamma(u^2, u\psi_{u_{N_c}-u})\right].
\end{aligned}
$$

For all $\psi_{N_c} \in V_{N_c}$, it therefore holds

$$
\begin{aligned}
\|u_{N_c}-u\|_{L^2}^2 &= \langle (E^{\mathrm{TFW}''}(u)-2\lambda)(u_{N_c}-u), \psi_{u_{N_c}-u}-\psi_{N_c}\rangle_{H^{-1}_\#,H^1_\#} \\
&\quad + \langle (E^{\mathrm{TFW}''}(u)-2\lambda)(u_{N_c}-u), \psi_{N_c}\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{4\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^4 \\
&\quad + \frac{2}{\mathcal{N}}\|u_{N_c}-u\|_{L^2_\#}^2 \left[\int_\Gamma f'(u^2)u^3\psi_{u_{N_c}-u} + D_\Gamma(u^2, u\psi_{u_{N_c}-u})\right]. \quad (46)
\end{aligned}
$$

Using (17), (29), (38) with $r=0$ and (41), we obtain that for all $\psi_{N_c} \in V_{N_c} \cap u^\perp$,

$$
\begin{aligned}
\left|\langle (E^{\mathrm{TFW}}(u)-2\lambda)(u_{N_c}-u), \psi_{N_c}\rangle_{H^{-1}_\#,H^1_\#}\right| &\le C\Big(\|u_{N_c}-u\|_{H^1_\#}^2 \\
&\quad + \|u_{N_c}-u\|_{L^2_\#}\left(\|u_{N_c}-u\|_{H^1_\#}^2 + \|u_{N_c}-u\|_{L^2_\#}\right)\Big)\|\psi_{N_c}\|_{H^1_\#}. \quad (47)
\end{aligned}
$$

Let us denote by $\Pi^1_{V_{N_c}\cap u^\perp}$ the orthogonal projector on $V_{N_c}\cap u^\perp$ for the $H^1_\#$ inner product and by $\psi^0_{N_c} = \Pi^1_{V_{N_c}\cap u^\perp}\psi_{u_{N_c}-u}$. Noticing that

$$
\|\psi^0_{N_c}\|_{H^1_\#} \le \|\psi_{u_{N_c}-u}\|_{H^1_\#} \le \beta^{-1}M\|u_{N_c}-u\|_{L^2_\#},
$$

we obtain from (33), (46) and (47) that there exists $N \in \mathbb{N}$ and $C \in \mathbb{R}_+$ such that for all $N_c \ge N$,

$$
\|u_{N_c}-u\|_{L^2_\#}^2 \le C\left(\|u_{N_c}-u\|_{L^2_\#}\|u_{N_c}-u\|_{H^1_\#}^2 + \|u_{N_c}-u\|_{H^1_\#}\|\psi_{u_{N_c}-u}-\psi^0_{N_c}\|_{H^1_\#}\right).
$$

Lastly, for all $v \in u^\perp$ and all $N_c \in \mathbb{N}^*$

$$\|v - \Pi^1_{V_{N_c}\cap u^\perp} v\|_{H^1_\#} \le \left(1 + \frac{\mathcal{N}^{1/2} L^{5/2}}{2\pi N_c \int_\Gamma u}\right) \|v - \Pi_{N_c} v\|_{H^1_\#}, \qquad (48)$$

so that, in view of (2) and (45)

$$\begin{aligned}
\|\psi_{u_{N_c}-u} - \psi^0_{N_c}\|_{H^1_\#} &\le C\|\psi_{u_{N_c}-u} - \Pi_{N_c}\psi_{u_{N_c}-u}\|_{H^1_\#} \\
&\le CN_c^{-1}\|\psi_{u_{N_c}-u}\|_{H^2_\#} \\
&\le CN_c^{-1}\|u_{N_c} - u\|_{L^2_\#}.
\end{aligned}$$

Therefore,

$$\begin{aligned}
\|u_{N_c} - u\|_{L^2_\#} &\le C\left(\|u_{N_c} - u\|^2_{H^1_\#} + N_c^{-1}\|u_{N_c} - u\|_{H^1_\#}\right) \\
&\le C_{0,\epsilon} N_c^{-(m+1/2-\epsilon)}.
\end{aligned}$$

By means of the inverse inequality

$$\forall v_{N_c} \in V_{N_c}, \quad \|v_{N_c}\|_{H^r_\#} \le \left(\frac{2\pi}{L}\right)^{(r-s)} {N_c}^{r-s} \|v_{N_c}\|_{H^s_\#}, \qquad (49)$$

which holds true for all $s \le r$ and all $N_c \ge 1$, we obtain that

$$\|u_{N_c} - u\|_{H^s_\#} \le C_{s,\epsilon} N_c^{-(m-s+1/2-\epsilon)} \qquad \text{for all } 0 \le s < m + 1/2. \qquad (50)$$

To complete the first part of the proof of Theorem 3.1, we still have to compute the $H^{-r}_\#$-norm of the error $(u_{N_c} - u)$ for $0 < r < m - 3/2$. Let $w \in H^r_\#(\Gamma)$. Proceeding as above we obtain

$$\begin{aligned}
\int_\Gamma w(u_{N_c} - u) &= \langle (E^{\mathrm{TFW}''}(u) - 2\lambda)(u_{N_c} - u), \Pi^1_{V_{N_c}\cap u^\perp}\psi_w\rangle_{H^{-1}_\#, H^1_\#} \\
&\quad + \langle (E^{\mathrm{TFW}''}(u) - 2\lambda)(u_{N_c} - u), \psi_w - \Pi^1_{V_{N_c}\cap u^\perp}\psi_w\rangle_{H^{-1}_\#, H^1_\#} \\
&\quad + \frac{2}{\mathcal{N}}\|u_{N_c} - u\|^2_{L^2_\#}\left[\int_\Gamma f'(u^2)u^3\psi_w + D_\Gamma(u^2, u\psi_w)\right] \\
&\qquad - \frac{1}{2\mathcal{N}}\|u_{N_c} - u\|^2_{L^2_\#}\int_\Gamma uw. \qquad (51)
\end{aligned}$$

Combining (33), (45), (47), (48), (50) and (51), we obtain that there exists a constant $C \in \mathbb{R}_+$ such that for all N_c large enough and all $w \in H^r_\#(\Gamma)$,

$$\begin{aligned}
\int_\Gamma w(u_{N_c} - u) &\le C'\left(\|u_{N_c} - u\|^2_{H^1_\#} + {N_c}^{-(r+1)}\|u_{N_c} - u\|_{H^1_\#}\right)\|w\|_{H^r_\#} \\
&\le C_{-r,\epsilon}\, N_c^{-(m+r+1/2-\epsilon)}\|w\|_{H^r_\#}.
\end{aligned}$$

Therefore

$$\|u_{N_c} - u\|_{H^{-r}_\#} = \sup_{w \in H^r_\#(\Gamma)\setminus\{0\}} \frac{\displaystyle\int_\Gamma w(u_{N_c} - u)}{\|w\|_{H^r_\#}} \le C_{-r,\epsilon}\, N_c^{-(m+r+1/2-\epsilon)}, \qquad (52)$$

for some constant $C_{-r,\epsilon} \in \mathbb{R}_+$ independent of N_c. Using (38), (43) and (52), we end up with

$$|\lambda_{N_c} - \lambda| \le C_\epsilon N_c^{-(2m-1-\epsilon)}.$$

3.2 A priori estimates for the full discretization.

Let us now turn to the pseudospectral approximation (18) of (16). First, we notice that

$$\begin{aligned}
\frac{C_{\rm W}}{2}\|\nabla u_{N_c,N_g}\|^2_{L^2_\#} - \|V^{\rm ion}\|_{L^\infty}\mathcal{N} &\le E^{\rm TFW}_{N_g}(u_{N_c,N_g}) \\
&\le E^{\rm TFW}_{N_g}(\mathcal{N}^{1/2}|\Gamma|^{-1/2}) \\
&\le C_{\rm TF}\mathcal{N}^{5/3}|\Gamma|^{-2/3} + \|V^{\rm ion}\|_{L^\infty}\mathcal{N},
\end{aligned}$$

from which we infer that u_{N,N_g} is uniformly bounded in $H^1_\#(\Gamma)$. We then see that

$$\begin{aligned}
\lambda_{N_c,N_g} &= \mathcal{N}^{-1}\left[\frac{C_{\rm W}}{2}\int_\Gamma |\nabla u_{N_c,N_g}|^2 + \int_\Gamma \mathcal{I}_{N_g}(V^{\rm ion}|u_{N_c,N_g}|^2 + f(|u_{N_c,N_g}|^2)|u_{N_c,N_g}|^2)\right. \\
&\qquad \left. + D_\Gamma(|u_{N_c,N_g}|^2, |u_{N_c,N_g}|^2)\right].
\end{aligned}$$

Using (6), (11) and (27), we obtain that λ_{N_c,N_g} also is uniformly bounded. Now,

$$\begin{aligned}
\Delta u_{N_c,N_g} &= 2C_{\rm W}^{-1}\Pi_{N_c}\left(\mathcal{I}_{N_g}\left(f(|u_{N_c,N_g}|^2)u_{N_c,N_g}\right)\right) + 2C_{\rm W}^{-1}\Pi_{N_c}\left(\mathcal{I}_{N_g}\left(V^{\rm ion}u_{N_c,N_g}\right)\right) \\
&\quad + 2C_{\rm W}^{-1}\Pi_{N_c}\left(V^{\rm Coulomb}_{|u_{N_c,N_g}|^2}u_{N_c,N_g}\right) - 2C_{\rm W}^{-1}\lambda_{N_c,N_g}u_{N_c,N_g}, \qquad (53)
\end{aligned}$$

and we deduce from (4), (6) and (8) that

$$\begin{aligned}
\left\|\Pi_{N_c}\left(\mathcal{I}_{N_g}\left(f(|u_{N_c,N_g}|^2)u_{N_c,N_g}\right)\right)\right\|_{L^2_\#} &\le \left(\int_\Gamma \left(\mathcal{I}_{N_g}(f(|u_{N_c,N_g}|^2))\right)^2 |u_{N_c,N_g}|^2\right)^{1/2} \\
&= \left(\sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 f(|u_{N_c,N_g}(x)|^2)^2|u_{N_c,N_g}(x)|^2\right)^{1/2} \\
&\le \frac{5}{3}C_{\rm TF}\|u_{N_c,N_g}\|^{1/3}_{L^\infty}\left(\sum_{x\in\mathcal{G}_{N_g}\cap\Gamma}\left(\frac{L}{N_g}\right)^3 |u_{N_c,N_g}(x)|^4\right)^{1/2} \\
&= \frac{5}{3}C_{\rm TF}\|u_{N_c,N_g}\|^{1/3}_{L^\infty}\|u_{N_c,N_g}\|^2_{L^4_\#},
\end{aligned}$$

and that

$$
\begin{aligned}
\|\Pi_{N_c}\left(\mathcal{I}_{N_g}\left(V^{\rm ion}u_{N_c,N_g}\right)\right)\|_{L^2_\#} &\leq \|\Pi_{2N_c}\left(\mathcal{I}_{N_g}\left(V^{\rm ion}u_{N_c,N_g}\right)\right)\|_{L^2_\#} \\
&\leq \left(\int_\Gamma \mathcal{I}_{N_g}(|V^{\rm ion}|^2|u_{N_c,N_g}|^2)\right)^{1/2} \\
&\leq \|V^{\rm ion}\|_{L^\infty}\mathcal{N}^{1/2}.
\end{aligned}
$$

Besides, using (30),

$$
\begin{aligned}
\|\Pi_{N_c}\left(V^{\rm Coulomb}_{|u_{N_c,N_g}|^2}u_{N_c,N_g}\right)\|_{L^2_\#} &\leq \|V^{\rm Coulomb}_{|u_{N_c,N_g}|^2}u_{N_c,N_g}\|_{L^2_\#} \\
&\leq \mathcal{N}^{1/2}\|V^{\rm Coulomb}_{|u_{N_c,N_g}|^2}\|_{L^\infty} \\
&\leq \mathcal{N}^{1/2}\|u_{N_c,N_g}\|^2_{L^4_\#}.
\end{aligned}
$$

As u_{N_c,N_g} is uniformly bounded in $H^1_\#(\Gamma)$, and therefore in $L^4_\#(\Gamma)$, we get

$$
\begin{aligned}
\|u_{N_c,N_g}\|_{H^2_\#} &= \left(\|u_{N_c,N_g}\|^2_{L^2_\#} + \|\Delta u_{N_c,N_g}\|^2_{L^2_\#}\right)^{1/2} \\
&\leq C\left(1+\|u_{N_c,N_g}\|^{1/3}_{L^\infty}\right) \\
&\leq C\left(1+\|u_{N_c,N_g}\|^{1/3}_{H^2_\#}\right).
\end{aligned}
$$

Therefore u_{N_c,N_g} is uniformly bounded in $H^2_\#(\Gamma)$, hence in $L^\infty(\mathbb{R}^3)$.

Returning to (53) and using (9), (15), and a bootstrap argument, we conclude that u_{N_c,N_g} is in fact uniformly bounded in $H^{7/2+\epsilon}_\#(\Gamma)$.

Next, using (36),

$$
\begin{aligned}
\frac{\gamma}{2}\|u_{N_c,N_g}-u_{N_c}\|^2_{H^1_\#} &\leq E^{\rm TFW}(u_{N_c,N_g}) - E^{\rm TFW}(u_{N_c}) \\
&= E^{\rm TFW}_{N_g}(u_{N_c,N_g}) - E^{\rm TFW}_{N_g}(u_{N_c}) \\
&\quad + \int_\Gamma ((1-\mathcal{I}_{N_g})(V))(|u_{N_c,N_g}|^2-|u_{N_c}|^2) \\
&\quad + \int_\Gamma (1-\mathcal{I}_{N_g})(F(|u_{N_c,N_g}|^2)-F(|u_{N_c}|^2)) \\
&\leq \int_\Gamma ((1-\mathcal{I}_{N_g})(V))(|u_{N_c,N_g}|^2-|u_{N_c}|^2) \\
&\quad + \int_\Gamma (1-\mathcal{I}_{N_g})(F(|u_{N_c,N_g}|^2)-F(|u_{N_c}|^2)).
\end{aligned}
$$

Let $g(t,t') = \frac{F(t'^2)-F(t^2)}{t'-t}$. For N_c large enough, u_{N_c} is uniformly bounded away from zero; besides, both u_{N_c} and u_{N_c,N_g} are uniformly bounded in $H^{7/2+\epsilon}_\#(\Gamma)$. Therefore, $g(u_{N_c},u_{N_c,N_g})$ is uniformly bounded in $H^{7/2+\epsilon}_\#(\Gamma)$. This implies that the Fourier coefficients of $g(u_{N_c}, u_{N_c,N_g})$ go to zero faster that $|k|^{-7/2}$, which in turn implies, using (5) and (10), that

$$\begin{aligned}
&\left|\int_\Gamma (1-\mathcal{I}_{N_g})(F(|u_{N_c,N_g}|^2) - F(|u_{N_c}|^2))\right| \\
&\quad = \left|\int_\Gamma (1-\mathcal{I}_{N_g})\left(g(u_{N_c}, u_{N_c,N_g})\right)\,(u_{N_c,N_g} - u_{N_c})\right| \\
&\quad \leq \left\|\Pi_{N_c}\left((1-\mathcal{I}_{N_g})\left(g(u_{N_c}, u_{N_c,N_g})\right)\right)\right\|_{L^2_\#} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#} \\
&\quad \leq C N_c^{3/2} N_g^{-7/2} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#}. \qquad (54)
\end{aligned}$$

On the other hand,

$$\begin{aligned}
&\left|\int_\Gamma ((1-\mathcal{I}_{N_g})(V))(|u_{N_c,N_g}|^2 - |u_{N_c}|^2)\right| \\
&\quad \leq \|\Pi_{2N_c}((1-\mathcal{I}_{N_g})(V))\|_{L^2_\#} \|u_{N_c,N_g} + u_{N_c}\|_{L^\infty} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#} \\
&\quad \leq C N_c^{3/2} N_g^{-m} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#}.
\end{aligned}$$

Therefore,

$$\|u_{N_c,N_g} - u_{N_c}\|_{H^1_\#} \quad \leq \quad C N_c^{3/2} N_g^{-7/2}. \qquad (55)$$

We then deduce from (55) and the inverse inequality (49) that $(u_{N_c,N_g})_{N_c,N_g \geq 4N_c+1}$ converges to u in $H^2_\#(\Gamma)$, and therefore in $L^\infty(\mathbb{R}^3)$. It follows that for N_c large enough, u_{N_c,N_g} is bounded away from zero, which, together with (53), implies that $(u_{N_c,N_g})_{N_c,N_g \geq 4N_c+1}$ is bounded in $H^{m+1/2-\epsilon}_\#(\Gamma)$. The estimates (54) and (55) can therefore be improved, yielding

$$\left|\int_\Gamma (1-\mathcal{I}_{N_g})(F(|u_{N_c,N_g}|^2) - F(|u_{N_c}|^2))\right| \leq C N_c^{3/2} N_g^{-(m+1/2-\epsilon)} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#}.$$

and

$$\|u_{N_c,N_g} - u_{N_c}\|_{H^1_\#} \leq C N_c^{3/2} N_g^{-m}.$$

We deduce (24) from the inverse inequality (49). For N_c large enough, u_{N_c,N_g} is bounded away from zero, so that $f(|u_{N_c,N_g}|^2)$ is uniformly bounded in $H^{m+1/2-\epsilon}_\#(\Gamma)$. Therefore, the $k^{\rm th}$ Fourier coefficient of $(V^{\rm ion} + f(|u_{N_c,N_g}|^2))$ is bounded by $C|k|^{-m}$ where the constant C does not depend on N_c and N_g. Using the equality

$$\begin{aligned}
\lambda_{N_c,N_g} - \lambda_{N_c} \quad = \quad \mathcal{N}^{-1}\Bigg[&\langle (\mathcal{H}^{\rm TFW}_{|u_{N_c}|^2} - \lambda_{N_c})(u_{N_c,N_g} - u_{N_c}), (u_{N_c,N_g} - u_{N_c})\rangle_{H^{-1}_\#, H^1_\#} \\
&- \int_\Gamma (1-\mathcal{I}_{N_g})(V^{\rm ion} + f(|u_{N_c,N_g}|^2))|u_{N_c,N_g}|^2 \\
&+ D_\Gamma(|u_{N_c,N_g}|^2, |u_{N_c,N_g}|^2 - |u_{N_c}|^2) \\
&+ \int_\Gamma (f(|u_{N_c,N_g}|^2) - f(|u_{N_c}|^2))|u_{N_c,N_g}|^2 \Bigg],
\end{aligned}$$

(24) and (29), we obtain (25). A similar calculation leads to (26).

Lastly, we have for all $v_{N_c} \in V_{N_c}$,

$$
\begin{aligned}
& E^{\rm TFW}_{N_g}(v_{N_c}) - E^{\rm TFW}_{N_g}(u_{N_c,N_g}) \qquad (56)\\
= \ & \langle (\widetilde{\mathcal{H}}^{\rm TFW}_{u_{N_c,N_g}} - \lambda_{N_c,N_g})(v_{N_c} - u_{N_c,N_g}), (v_{N_c} - u_{N_c,N_g})\rangle_{H^{-1}_\#, H^1_\#} \\
& + \frac{1}{2} D_\Gamma(|v_{N_c}|^2 - |u_{N_c,N_g}|^2, |v_{N_c}|^2 - |u_{N_c,N_g}|^2) \\
& + \sum_{x \in \mathcal{G}_{N_g} \cap \Gamma} \left(\frac{L}{N_g}\right)^3 \left(F(|v_{N_c}(x)|^2) - F(|u_{N_c}(x)|^2) - f(|u_{N_c}(x)|^2)(|v_{N_c}(x)|^2 - |u_{N_c}(x)|^2)\right) \\
\geq \ & \langle (\widetilde{\mathcal{H}}^{\rm TFW}_{u_{N_c,N_g}} - \lambda_{N_c,N_g})(v_{N_c} - u_{N_c,N_g}), (v_{N_c} - u_{N_c,N_g})\rangle_{H^{-1}_\#, H^1_\#}. \qquad (57)
\end{aligned}
$$

As u_{N_c,N_g} converges to u in $H^2_\#(\Gamma)$, the operator $\widetilde{\mathcal{H}}^{\mathrm{TFW},N_g}_{|u_{N_c,N_g}|^2} - \mathcal{H}^{\rm TFW}_{\rho^0}$ converges to zero in operator norm. Reasoning as in the proof of the uniqueness of u_{N_c}, we obtain that for N_c large enough and $N_g \geq 4N_c+1$, we have for all $v_{N_c} \in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_\#} = \mathcal{N}^{1/2}$ and $(v_{N_c}, u_{N_c})_{L^2_\#} \geq 0$,

$$
\langle (\widetilde{\mathcal{H}}^{\rm TFW}_{u_{N_c,N_g}} - \lambda_{N_c,N_g})(v_{N_c} - u_{N_c,N_g}), (v_{N_c} - u_{N_c,N_g})\rangle_{H^{-1}_\#, H^1_\#} \geq \frac{\gamma}{2} \|v_{N_c} - u_{N_c,N_g}\|^2_{H^1_\#}.
$$

Thus the uniqueness of u_{N_c,N_g} for N_c large enough.

4 Planewave approximation of the Kohn-Sham LDA model

The periodic Kohn-Sham LDA model with norm-conserving pseudopotentials [14] leads to the constrained optimization problem

$$
I^{\rm KS} = \inf \left\{ E^{\rm KS}(\Phi), \ \Phi \in \mathcal{M} \right\} \qquad (58)
$$

where

$$
\mathcal{M} = \left\{ \Phi = (\phi_1, \cdots, \phi_{\mathcal{N}})^T \in (H^1_\#(\Gamma))^{\mathcal{N}} \ | \ \int_\Gamma \phi_i \phi_j = \delta_{ij} \right\},
$$

$\mathcal{N}$ being the number of valence electron pairs in the simulation cell, and where

$$
E^{\rm KS}(\Phi) = \sum_{i=1}^{\mathcal{N}} \int_\Gamma |\nabla \phi_i|^2 + \int_\Gamma \rho_\Phi V_{\rm local} + 2 \sum_{i=1}^{\mathcal{N}} \langle \phi_i | V_{\rm nl} | \phi_i \rangle + J(\rho_\Phi) + E^{\rm LDA}_{\rm xc}(\rho_\Phi). \qquad (59)
$$

The density ρ_Φ associated with Φ, the Coulomb energy $J(\rho_\Phi)$ and the LDA exchange-correlation energy $E_{\rm xc}^{\rm LDA}(\rho_\Phi)$ are respectively defined as

$$\begin{aligned}\rho_\Phi(x) &= 2\sum_{i=1}^{\mathcal{N}} |\phi_i(x)|^2, \\ J(\rho_\Phi) &= \frac{1}{2} D_\Gamma(\rho_\Phi,\rho_\Phi) = 2\pi \sum_{k\in\mathcal{R}^*\setminus\{0\}} |k|^{-2} |\widehat{(\rho_\Phi)}_k|^2, \\ E_{\rm xc}^{\rm LDA}(\rho_\Phi) &= \int_\Gamma e_{\rm xc}^{\rm LDA}(\rho_{\rm c}(x)+\rho_\Phi(x))\,dx,\end{aligned}$$

where $\rho_{\rm c} \geq 0$ is the nonlinear core correction and where $e_{\rm xc}^{\rm LDA}(\rho)$ is an approximation of the exchange-correlation energy per unit volume in a uniform electron gas with charge density ρ [8].

The local and nonlocal contributions to the pseudopotential model the interactions between valence electrons on the one hand, and nuclei and core electrons on the other hand. The local contribution is represented by a function $V_{\rm local} \in C^0_\#(\Gamma)$ (and therefore defines a bounded self-adjoint operator on $L^2_\#(\Gamma)$); the nonlocal contribution is represented by the bounded self-adjoint operator $V_{\rm nl}$ defined on $L^2_\#(\Gamma)$ by

$$V_{\rm nl}\phi = \sum_{j=1}^{M} (\chi_j,\phi)_{L^2_\#}\,\chi_j,$$

where the functions χ_j are regular enough functions of $L^2_\#(\Gamma)$. In all what follows, we will assume that

$$\exists m > 3,\ C \geq 0 \text{ s.t. } \forall k \in \mathcal{R}^*,\ |\widehat{(V_{\rm local})}_k| \leq C|k|^{-m} \tag{60}$$

and that

$$\forall 1 \leq j \leq M, \quad \forall \epsilon > 0, \quad \chi_j \in H^{m-3/2-\epsilon}_\#(\Gamma). \tag{61}$$

Troullier-Martins pseudopotentials [14] constitute a popular class of pseudopotentials for which the Fourier coefficients $\widehat{(V_{\rm local})}_k$ decay as $|k|^{-m}$ with $m = 5$.

The function $\rho \mapsto e_{\rm xc}^{\rm LDA}(\rho)$ does not have a simple analytical expression. Although this function is of class C^∞ on the open set $(0,+\infty)$, DFT simulation softwares make use of approximate functions which are C^∞ on $(0,\rho_*)\cup(\rho_*,+\infty)$ but only $C^{1,1}$ in the neighborhood of the density $\rho_* := 3/(4\pi)$ (atomic units) [8]. In order not to deteriorate the convergence rate of the pseudospectral approximation, it is better to ressort to more regular approximations of the function $e^{\rm LDA}$ (see [5]). We will assume here that

$$\text{the function } \rho \mapsto e_{\rm xc}^{\rm LDA}(\rho) \text{ is in } C^1([0,+\infty)) \cap C^{[m]}((0,+\infty)), \tag{62}$$

$$e_{\rm xc}^{\rm LDA}(0) = 0, \quad \frac{de_{\rm xc}^{\rm LDA}}{d\rho}(0) = 0, \tag{63}$$

(where $[m]$ denotes the integer part of $[m]$) and that there exists $0 < \alpha \le 1$ and $C \in \mathbb{R}_+$ such that

$$\forall \rho \in \mathbb{R}_+ \setminus \{0\}\,, \qquad \left| \frac{d^2 e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho) \right| + \left| \rho \frac{d^3 e_{\rm xc}^{\rm LDA}}{d\rho^3}(\rho) \right| \le C(1+\rho^{\alpha-1}). \qquad (64)$$

Note that the Xα exchange-correlation functional ($e_{\rm xc}^{\rm X\alpha}(\rho) = -C_{\rm X}\rho^{4/3}$, where $C_{\rm X} > 0$ is a given constant) satisfies the assumptions (62)-(64) with $\alpha = 1/3$. Let us also remark that (62) and (64) imply that

$$e_{\rm xc}^{\rm LDA} \in C^{1,\alpha}([0,L]) \quad \text{for each } L > 0, \qquad (65)$$

a property we will make use of below. Lastly, we assume for simplicity that

$$\rho_{\rm c} \in C^\infty_\#(\Gamma). \qquad (66)$$

It is easy to prove that under assumptions (60)-(66), (58) has a minimizer $\Phi^0 = (\phi_1^0, \cdots, \phi_{\mathcal{N}}^0)^T$ with density $\rho^0 = \rho_{\Phi^0}$. The regularity assumptions on $V_{\rm local}$, on $e_{\rm xc}^{\rm LDA}$ and on the functions χ_j allow to state that the minimizer Φ^0 is in $[H^3_\#(\Gamma)]^{\mathcal{N}}$, and even in $[H_\#^{m+1/2-\epsilon}(\Gamma)]^{\mathcal{N}}$ for any $\epsilon > 0$, if at least one of the following conditions is satisfied: $e_{\rm xc}^{\rm LDA} \in C^{[m]}([0,+\infty))$ or $\rho_{\rm c} + \rho^0 > 0$ in $\mathbb{R}^3$. The former condition is not satisfied for usual LDA exchange-correlation functionals. On the other hand, it is satisfied for the Hartree (also called reduced Hartree-Fock) model, for which $e_{\rm xc}^{\rm LDA} = 0$. The latter condition seems to be satisfied in practice, but we were not able to establish it rigourously.

Let us introduce the Kohn-Sham Hamiltonian

$$\begin{aligned} \mathcal{H}_{\rho^0}^{\rm KS} &= -\frac{1}{2}\Delta + \left(V_{\rm local} + V_{\rho^0}^{\rm Coulomb} + \frac{de_{\rm xc}^{\rm LDA}}{d\rho}(\rho_{\rm c} + \rho^0) \right) + V_{\rm nl}. \\ &= h + \mathcal{V}_{\rho^0} \end{aligned}$$

where

$$h = -\frac{1}{2}\Delta + V_{\rm local} + V_{\rm nl}, \qquad (67)$$

and

$$\mathcal{V}_{\rho^0} = V_{\rho^0}^{\rm Coulomb} + \frac{de_{\rm xc}^{\rm LDA}}{d\rho}(\rho_{\rm c} + \rho^0). \qquad (68)$$

We notice that $E^{\rm KS\prime}(\Phi^0) = 4\mathcal{H}_{\rho^0}^{\rm KS}\Phi^0$ in $(H_\#^{-1}(\Gamma))^{\mathcal{N}}$ and thus the Euler equations associated with the minimization problem (58) read

$$\forall 1 \le i \le \mathcal{N}, \quad \mathcal{H}_{\rho^0}^{\rm KS}\phi_i^0 = \sum_{j=1}^{\mathcal{N}} \lambda_{ij}^0 \phi_j^0,$$

where the $\mathcal{N} \times \mathcal{N}$ matrix $\Lambda^0_{\mathcal{N}} = (\lambda^0_{ij})$, which is the Lagrange multiplier of the matrix constraint $\int_\Gamma \phi_i \phi_j = \delta_{ij}$, is symmetric.

In fact, (58) has an infinity of minimizers since any unitary transform of the Kohn-Sham orbitals Φ^0 is also a minimizer of the Kohn-Sham energy. This is a consequence of the following invariance property:

$$\forall \Phi \in \mathcal{M}, \quad \forall U \in \mathcal{U}(\mathcal{N}), \quad U\Phi \in \mathcal{M} \text{ and } E^{\mathrm{KS}}(U\Phi) = E^{\mathrm{KS}}(\Phi), \tag{69}$$

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

$$\mathcal{U}(\mathcal{N}) = \left\{ U \in \mathbb{R}^{\mathcal{N}\times\mathcal{N}} \mid U^T U = 1_{\mathcal{N}} \right\},$$

$1_{\mathcal{N}}$ denoting the identity matrix of rank $\mathcal{N}$. This invariance can be exploited to diagonalize the matrix of the Lagrange multipliers of the orthonormality constraints (see e.g. [8]), yielding the existence of a minimizer (still denoted by Φ^0) with same density ρ^0, such that

$$\mathcal{H}^{\mathrm{KS}}_{\rho^0} \phi^0_i = \epsilon^0_i \phi^0_i, \tag{70}$$

for some $\epsilon^0_1 \le \epsilon^0_2 \le \cdots \le \epsilon^0_{\mathcal{N}}$.

Remark 2 *The Kohn-Sham Hamiltonian $\mathcal{H}^{\mathrm{KS}}_{\rho^0}$ is an unbounded self-adjoint operator on $L^2_\#(\Gamma)$, bounded below, with compact resolvent. Its spectrum therefore is purely discrete. More precisely, it is composed of an increasing sequence of eigenvalues going to infinity, each of these eigenvalues being of finite multiplicity. It is not known whether ϵ^0_1, ..., $\epsilon^0_{\mathcal{N}}$ are the lowest eigenvalues (counted with their multiplicities) of $\mathcal{H}^{\mathrm{KS}}_{\rho^0}$ (Aufbau principle). However, it seems to be most often (though not always) the case in practice. On the other hand, the Aufbau principle is always satisfied for the* extended *Kohn-Sham model, for which the first order optimality conditions read*

$$\left\{ \begin{array}{l} \mathcal{H}^{\mathrm{KS}}_{\rho^0} \phi^0_i = \epsilon^0_i \phi^0_i \\ \\ \rho^0(x) = 2 \displaystyle\sum_{i=1}^{+\infty} n_i |\phi^0_i(x)|^2 \\ \displaystyle\int_\Gamma \phi^0_i \phi^0_j = \delta_{ij}, \quad 1 \le i, j < +\infty \\ n_i = 1 \textit{ if } \epsilon^0_i < \epsilon_{\mathrm{F}}, \quad n_i = 0 \textit{ if } \epsilon^0_i > \epsilon_{\mathrm{F}}, \quad 0 \le n_i \le 1 \textit{ if } \epsilon^0_i = \epsilon_{\mathrm{F}}, \quad \displaystyle\sum_{i=1}^{+\infty} n_i = \mathcal{N}, \end{array} \right.$$

where ϵ_{F} is the Fermi level (see [4] for details). In this article, we focus on the standard Kohn-Sham model with integer occupation numbers. We do not need to assume that the Aufbau principle is satisfied, but our analysis requires some coercivity assumption on the second order condition at Φ^0 (see (73)).

For each $\Phi = (\phi_1, \cdots, \phi_{\mathcal{N}})^T \in \mathcal{M}$, we denote by

$$T_\Phi \mathcal{M} = \left\{ (\psi_1, \cdots, \psi_{\mathcal{N}})^T \in (H^1_\#(\Gamma))^{\mathcal{N}} \mid \int_\Gamma \phi_i \psi_j + \psi_i \phi_j = 0 \right\}$$

the tangent space to $\mathcal{M}$ at Φ, and by

$$\Phi^{\perp\!\!\perp} = \left\{ \Psi = (\psi_1, \cdots, \psi_{\mathcal{N}})^T \in (H^1_\#(\Gamma))^{\mathcal{N}} \mid \int_\Gamma \phi_i \psi_j = 0 \right\}.$$

Let us recall (see e.g. Lemma 4 in [13]) that

$$T_\Phi \mathcal{M} = \mathcal{A}\Phi \oplus \Phi^{\perp\!\!\perp},$$

where $\mathcal{A} = \left\{ A \in \mathbb{R}^{\mathcal{N}\times\mathcal{N}} \mid A^T = -A \right\}$ is the space of the $\mathcal{N} \times \mathcal{N}$ antisymmetric real matrices.

Since the problem we are considering is a minimization problem, the second order condition further states

$$\forall W \in T_{\Phi^0}\mathcal{M}, \quad a_{\Phi^0}(W, W) \geq 0,$$

where

$$a_{\Phi^0}(\Psi, \Upsilon) = \frac{1}{4} E^{\mathrm{KS}\prime\prime}(\Phi^0)(\Psi, \Upsilon) - \sum_{i=1}^{\mathcal{N}} \epsilon_i^0 \int_\Gamma \psi_i \upsilon_i \tag{71}$$

$$= \sum_{i=1}^{\mathcal{N}} \langle (\mathcal{H}^{\mathrm{KS}}_{\rho^0} - \epsilon_i^0)\psi_i, \upsilon_i \rangle_{H^{-1}_\#, H^1_\#} + 4 \sum_{i,j=1}^{\mathcal{N}} D_\Gamma(\phi_i^0 \psi_i, \phi_j^0 \upsilon_j)$$
$$+ 4 \sum_{i,j=1}^{\mathcal{N}} \int_\Gamma \frac{d^2 e^{\mathrm{LDA}}_{\mathrm{xc}}}{d\rho^2} (\rho_{\mathrm{c}} + \rho^0) \phi_i^0 \psi_i \phi_j^0 \upsilon_j. \tag{72}$$

It follows from the invariance property (69) that

$$a_{\Phi^0}(\Psi, \Psi) = 0 \quad \text{for all } \Psi \in \mathcal{A}\Phi^0.$$

This leads us, as in [13], to make the assumption that a_{Φ^0} is positive definite on $\Phi^{0,\perp\!\!\perp}$, so that, as in Proposition 1 in [13], a_{Φ^0} is coercive on $\Phi^{0,\perp\!\!\perp}$ (for the $H^1_\#$ norm). Thus, in all what follows, we assume that there exists a positive constant c_{Φ^0} such that

$$\forall \Psi \in \Phi^{0,\perp\!\!\perp}, \quad a_{\Phi^0}(\Psi, \Psi) \geq c_{\Phi^0} \|\Psi\|^2_{H^1_\#}. \tag{73}$$

In the linear framework ($J = 0$ and $E^{\mathrm{LDA}}_{\mathrm{xc}} = 0$ in (59)), this condition amounts to assuming that there is a gap between the lowest $\mathcal{N}^{\mathrm{th}}$ and $(\mathcal{N}+1)^{\mathrm{st}}$ eigenvalues of the linear self-adjoint operator $h = -\frac{1}{2}\Delta + V_{\mathrm{local}} + V_{\mathrm{nl}}$.

The planewave approximation of (58) reads

$$I^{\rm KS}_{N_c,N_g} = \inf \left\{ E^{\rm KS}_{N_g}(\Phi_{N_c}),\ \Phi_{N_c} \in V_{N_c}^{\mathcal{N}} \cap \mathcal{M} \right\}, \tag{74}$$

where

$$\begin{aligned} E^{\rm KS}_{N_g}(\Phi) &= \sum_{i=1}^{\mathcal{N}} \int_\Gamma |\nabla \phi_i|^2 + \int_\Gamma \rho_\Phi V_{\rm local} + 2 \sum_{i=1}^{\mathcal{N}} \langle \phi_i | V_{\rm nl} | \phi_i \rangle \\ &\quad + J(\rho_\Phi) + \int_\Gamma \mathcal{I}_{N_g}(e_{\rm xc}^{\rm LDA}(\rho_{\rm c} + \Pi_{2N_c}\rho_\Phi)). \end{aligned} \tag{75}$$

Here N_c is a given positive integer, equal to $[\sqrt{2E_{\rm c}}\, L/2\pi]$, $E_{\rm c}$ denoting the so-called cut-off energy, and $N_g \geq 4N_c + 1$ is the number of integration points per direction used to evaluate the exchange-correlation contribution. The energy $E^{\rm KS}_{N_g}(\Phi)$ is defined for each $\Phi \in \mathcal{M}$. For $\Phi \in V_{N_c}^{\mathcal{N}} \cap \mathcal{M}$, $\Pi_{2N_c}\rho_\Phi = \rho_\Phi$, so that on this set, $E^{\rm KS}_{N_g}$ differs from $E^{\rm KS}$ only by the presence of the Fourier interpolation operator $\mathcal{I}_{N_g}$ in the exchange-correlation functional. Let us mention that in practice, the terms involving the local and nonlocal components of the pseudopotential are also computed by some interpolation procedure. However, these terms are calculated using spherical harmonics and a very fine one dimensional radial grid, so that the resulting integration error is usually much smaller than the interpolation error on the exchange-correlation term. Note that, in addition, the pseudopotential gives rise to linear contributions that can be computed very accurately once and for all (and not at each iteration of the self-consistent algorithm). We postpone the analysis of (74) to a forthcoming article [5], and focus here on the variational approximation

$$I^{\rm KS}_{N_c} = \inf \left\{ E^{\rm KS}(\Phi_{N_c}),\ \Phi_{N_c} \in V_{N_c}^{\mathcal{N}} \cap \mathcal{M} \right\} \tag{76}$$

of (58). The unitary invariance of the Kohn-Sham model must be taken into account in the derivation of optimal *a priori* error estimates. One way to take this invariance into account is to work with density matrices (see e.g. [4]). An alternative is to define for each $\Phi \in \mathcal{M}$ the set

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

and to use the fact that all the local minimizers of (76) are obtained by unitary transforms from the local minimizers of

$$I^{\rm KS}_{N_c} = \inf \left\{ E^{\rm KS}(\Phi_{N_c}),\ \Phi_{N_c} \in V_{N_c}^{\mathcal{N}} \cap \mathcal{M}^{\Phi^0} \right\}. \tag{77}$$

The main result of this section is the following.

Theorem 4.1 *Assume that (60)-(66) hold. Let Φ^0 be a local minimizer of (58) satisfying (73). Then there exists $r^0 > 0$ and N_c^0 such that for $N_c \geq N_c^0$, (77) has a unique local minimizer $\Phi_{N_c}^0$ in the set*

$$\left\{ \Phi_{N_c} \in V_{N_c}^{\mathcal{N}} \cap \mathcal{M}^{\Phi^0} \mid \|\Phi_{N_c} - \Phi^0\|_{H^1_\#} \leq r^0 \right\}.$$

If we assume either that $e_{\rm xc}^{\rm LDA} \in C^{[m]}([0, +\infty))$ or that $\rho_{\rm c} + \rho^0 > 0$ on Γ, then we have the following estimates:

$$\|\Phi_{N_c}^0 - \Phi^0\|_{H^s_\#} \leq C_{s,\epsilon} N_c^{-(m-s+1/2-\epsilon)}, \quad (78)$$

$$|\epsilon_{i,N_c}^0 - \epsilon_i^0| \leq C_\epsilon N_c^{-(2m-1-\epsilon)}, \quad (79)$$

$$\gamma \|\Phi_{N_c}^0 - \Phi^0\|_{H^1_\#}^2 \leq I_{N_c}^{\rm KS} - I^{\rm KS} \leq C \|\Phi_{N_c}^0 - \Phi^0\|_{H^1_\#}^2, \quad (80)$$

for all $-m+3/2 < s < m+1/2$ and $\epsilon > 0$, and for some constants $\gamma > 0$, $C_{s,\epsilon} \geq 0$, $C_\epsilon \geq 0$ and $C \geq 0$, where the ϵ_{i,N_c}^0's are the eigenvalues of the symmetric matrix $\Lambda_{N_c}^0$, the Lagrange multiplier of the matrix constraint $\int_\Gamma \phi_{i,N_c} \phi_{j,N_c} = \delta_{ij}$.

4.1 Some technical lemmas

For $\Phi = (\phi_1, \cdots, \phi_{\mathcal{N}})^T \in (H^1_\#(\Gamma))^{\mathcal{N}}$ and $\Psi = (\psi_1, \cdots, \psi_{\mathcal{N}})^T \in (H^1_\#(\Gamma))^{\mathcal{N}}$, we denote by $M_{\Phi,\Psi}$ the $\mathcal{N} \times \mathcal{N}$ matrix with entries

$$[M_{\Psi,\Phi}]_{ij} = \int_\Gamma \psi_i \phi_j.$$

The following lemma is useful for the analysis of (77). We recall that if A and B are symmetric $N \times N$ real matrices, the notation $A \leq B$ means that $x^T A x \leq x^T B x$ for all $x \in \mathbb{R}^N$.

Lemma 4.2

1. *Let $\Phi \in \mathcal{M}$ and $\Psi \in \mathcal{M}$. If $M_{\Psi,\Phi}$ is invertible, then $U_{\Psi,\Phi} = M_{\Psi,\Phi}^T (M_{\Psi,\Phi} M_{\Psi,\Phi}^T)^{-1/2}$ is the unique minimizer to the problem $\min_{U \in \mathcal{U}(\mathcal{N})} \|U\Psi - \Phi\|_{L^2_\#}$.*

2. *Let $\Phi \in \mathcal{M}$. Then*

$$\mathcal{M}^\Phi = \left\{ (1_{\mathcal{N}} - M_{W,W})^{1/2} \Phi + W \mid W \in \Phi^{\perp\!\!\perp}, \ 0 \leq M_{W,W} \leq 1_{\mathcal{N}} \right\}$$

where $1_{\mathcal{N}}$ denotes the identity matrix of rank $\mathcal{N}$.

3. *Let $\Phi = (\phi_1, \cdots, \phi_{\mathcal{N}})^T \in \mathcal{M}$. If $N_c \in \mathbb{N}$ is such that*

$$\dim(\text{span}(\Pi_{N_c}\phi_1, \cdots, \Pi_{N_c}\phi_{\mathcal{N}})) = \mathcal{N},$$

then the unique minimizer of the problem $\min_{\Phi_{N_c}\in V_{N_c}^{\mathcal{N}}\cap\mathcal{M}} \|\Phi_{N_c}-\Phi\|_{L^2_\#}$ *is*

$$\pi_{N_c}^{\mathcal{M}}\Phi = \left(M_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi}\right)^{-1/2}\Pi_{N_c}\Phi. \tag{81}$$

In addition, $\pi_{N_c}^{\mathcal{M}}\Phi\in V_{N_c}^{\mathcal{N}}\cap\mathcal{M}^{\Phi}$,

$$\|\pi_{N_c}^{\mathcal{M}}\Phi-\Phi\|_{L^2_\#}\le\sqrt{2}\|\Pi_{N_c}\Phi-\Phi\|_{L^2_\#}, \tag{82}$$

and for all N_c *large enough,*

$$\|\pi_{N_c}^{\mathcal{M}}\Phi-\Phi\|_{H^1_\#}\le\|\Phi\|_{H^1_\#}\|\Pi_{N_c}\Phi-\Phi\|_{L^2_\#}^2+\|\Pi_{N_c}\Phi-\Phi\|_{H^1_\#}. \tag{83}$$

4. *Let* N_c *such that dim*$(V_{N_c})\ge\mathcal{N}$ *and* $\Phi_{N_c}\in V_{N_c}^{\mathcal{N}}\cap\mathcal{M}$. *Then*

$$V_{N_c}^{\mathcal{N}}\cap\mathcal{M}^{\Phi_{N_c}}=\left\{(1_{\mathcal{N}}-M_{W_{N_c},W_{N_c}})^{1/2}\Phi_{N_c}+W_{N_c}\mid W_{N_c}\in V_{N_c}^{\mathcal{N}}\cap\Phi_{N_c}^{\perp\!\!\perp},\ 0\le M_{W_{N_c},W_{N_c}}\le 1_{\mathcal{N}}\right\}.$$

Proof In order to simplify the notation, we set $M=M_{\Psi,\Phi}$. For each $U\in\mathcal{U}(\mathcal{N})$,

$$\|U\Psi-\Phi\|_{L^2_\#}^2=2\mathcal{N}-2\mathrm{Tr}\,(MU).$$

Any critical point U of the problem

$$\max_{U\in\mathbb{R}^{\mathcal{N}\times\mathcal{N}}\mid U^TU=1_{\mathcal{N}}}\mathrm{Tr}\,(MU) \tag{84}$$

satisfies an Euler equation of the form $\Lambda U^T=M$ for some symmetric matrix Λ. Besides, $\mathrm{Tr}\,(MU)=\mathrm{Tr}\,(\Lambda)$ and $\Lambda^2=MM^T$. Any maximizer U of (84) therefore satisfies $M=(MM^T)^{1/2}U^T$. Consequently, if M is invertible, the maximizer of (84) is unique and reads $U_{\Psi,\Phi}=M^T(MM^T)^{-1/2}$. It also follows from the definition of the matrix M that $\Psi=M\Phi+W$ with $W\in\Phi^{\perp\!\!\perp}$. Thus,

$$U_{\Psi,\Phi}\Psi=M^T(MM^T)^{-1/2}M\Phi+\widetilde{W},$$

with $\widetilde{W}=U_{\Psi,\Phi}W\in\Phi^{\perp\!\!\perp}$.

Let us now prove the second statement. Each $\Psi\in(H^1_\#(\Gamma))^{\mathcal{N}}$ can be written as $\Psi=M\Phi+W$ for some matrix $M\in\mathbb{R}^{\mathcal{N}\times\mathcal{N}}$ and some $W\in\Phi^{\perp\!\!\perp}$. A simple calculation leads to

$$\int_\Gamma\psi_i\psi_j=[MM^T]_{ij}+[M_{W,W}]_{ij}.$$

Hence $\Psi=M\Phi+W\in\mathcal{M}$ if and only if $MM^T+M_{W,W}=1_{\mathcal{N}}$. In addition, $\Psi\in\mathcal{M}^\Phi$ if and only if $\Psi\in\mathcal{M}$ and $U_{\Psi,\Phi}=M^T(MM^T)^{-1/2}=1_{\mathcal{N}}$, that is to say if and only if M is symmetric, $0\le M_{W,W}\le 1_{\mathcal{N}}$ and $M=(1_{\mathcal{N}}-M_{W,W})^{1/2}$.

Let $(\chi_\mu)_{1\le\mu\le\dim(V_{N_c})}$ be an orthonormal basis of V_{N_c} (for the $L^2_\#$ inner product) and let $\widetilde{C}\in\mathbb{R}^{\dim(V_{N_c})\times\mathcal{N}}$ be the matrix with entries

$$\widetilde{C}_{\mu,i}=\int_\Gamma \phi_i\chi_\mu.$$

Note that

$$\Pi_{N_c}\phi_i=\sum_{\mu=1}^{\dim(V_{N_c})}\widetilde{C}_{\mu,i}\chi_\mu, \tag{85}$$

For all $\Phi_{N_c}=(\phi_{N_c,1},\cdots,\phi_{N_c,\mathcal{N}})^T\in V_{N_c}^{\mathcal{N}}\cap\mathcal{M}$, each $\phi_{N_c,i}$ can be expanded as

$$\phi_{N_c,i}=\sum_{\mu=1}^{\dim(V_{N_c})}C_{\mu i}\chi_\mu, \tag{86}$$

where the matrix $C=[C_{\mu i}]\in\mathbb{R}^{\dim(V_{N_c})\times\mathcal{N}}$ satisfies the constraint $C^TC=1_\mathcal{N}$. The expansions (85) and (86) can be recast into the more compact forms

$$\Pi_{N_c}\Phi=\widetilde{C}^T\mathcal{X}\qquad\text{and}\qquad\Phi_{N_c}=C^T\mathcal{X},$$

where we have denoted by $\mathcal{X}=(\chi_1,\cdots,\chi_{\dim(V_{N_c})})^T$. A simple calculation then leads to

$$\|\Phi_{N_c}-\Phi\|^2_{L^2_\#}=2\mathcal{N}-2\mathrm{Tr}\,(\widetilde{C}^TC). \tag{87}$$

Reasoning as above, we obtain that the unique solution to the problem

$$\max_{C\in\mathbb{R}^{\dim(V_{N_c})\times\mathcal{N}}\,|\,C^TC=1_\mathcal{N}}\mathrm{Tr}\,(\widetilde{C}^TC)$$

is $C=\widetilde{C}(\widetilde{C}^T\widetilde{C})^{-1/2}$. Note that the rank of the matrix $\widetilde{C}$ is $\mathcal{N}$ provided that $\dim(V_{N_c})$ is large enough so that the matrix $\widetilde{C}^T\widetilde{C}$ is invertible provided that $\dim(V_{N_c})$ is large enough. As a consequence, the unique solution to the problem $\min_{\Phi_{N_c}\in V_{N_c}^{\mathcal{N}}\cap\mathcal{M}}\|\Phi_{N_c}-\Phi\|_{L^2_\#}$ is $\pi_{N_c}^{\mathcal{M}}\Phi=(\widetilde{C}^T\widetilde{C})^{-1/2}\widetilde{C}^T\mathcal{X}=(\widetilde{C}^T\widetilde{C})^{-1/2}\Pi_{N_c}\Phi$. It is then easy to check that $\widetilde{C}^T\widetilde{C}=M_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi}$. Hence (81). Then, for all $U\in\mathbb{R}^{\mathcal{N}\times\mathcal{N}}$ such that $U^TU=1_\mathcal{N}$,

$$\|U\pi_{N_c}^{\mathcal{M}}\Phi-\Phi\|^2_{L^2_\#}=2(\mathcal{N}-\mathrm{Tr}\,(UM^{1/2}_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi})),$$

and the same argument as above leads to the result that this quantity is minimized for $U=M^{1/2}_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi}(M^{1/2}_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi}M^{1/2}_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi})^{-1/2}=1_\mathcal{N}$. Therefore, $\pi_{N_c}^{\mathcal{M}}\Phi\in\mathcal{M}^\Phi$.

We also infer from (87) that

$$\|\pi_{N_c}^{\mathcal{M}}\Phi-\Phi\|^2_{L^2_\#}=2\mathcal{N}-2\mathrm{Tr}\,\left((\widetilde{C}^T\widetilde{C})^{1/2}\right)=2\mathrm{Tr}\,\left(1_\mathcal{N}-(\widetilde{C}^T\widetilde{C})^{1/2}\right).$$

Besides, an easy calculation leads to

$$\|\Pi_{N_c}\Phi - \Phi\|^2_{L^2_\#} = \mathrm{Tr}\,\left(1_\mathcal{N} - \widetilde{C}^T\widetilde{C}\right).$$

Using the fact that

$$0 \leq \left(1_\mathcal{N} - (\widetilde{C}^T\widetilde{C})^{1/2}\right) \leq \left(1_\mathcal{N} - (\widetilde{C}^T\widetilde{C})^{1/2}\right)\left(1_\mathcal{N} + (\widetilde{C}^T\widetilde{C})^{1/2}\right) = 1_\mathcal{N} - \widetilde{C}^T\widetilde{C},$$

we obtain

$$\|\pi^\mathcal{M}_{N_c}\Phi - \Phi\|^2_{L^2_\#} = 2\mathrm{Tr}\,\left(1_\mathcal{N} - (\widetilde{C}^T\widetilde{C})^{1/2}\right) \leq 2\mathrm{Tr}\,\left(1_\mathcal{N} - \widetilde{C}^T\widetilde{C}\right) = 2\|\Pi_{N_c}\Phi - \Phi\|^2_{L^2_\#}.$$

Hence (82). We also have

$$\begin{aligned}
\|\pi^\mathcal{M}_{N_c}\Phi - \Phi\|_{H^1_\#} &\leq \|\pi^\mathcal{M}_{N_c}\Phi - \Pi_{N_c}\Phi\|_{H^1_\#} + \|\Pi_{N_c}\Phi - \Phi\|_{H^1_\#} \\
&= \|((M_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi})^{-1/2} - 1_\mathcal{N})\Pi_{N_c}\Phi\|_{H^1_\#} + \|\Pi_{N_c}\Phi - \Phi\|_{H^1_\#} \\
&\leq \|(M_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi})^{-1/2} - 1_\mathcal{N}\|_\mathrm{F}\|\Pi_{N_c}\Phi\|_{H^1_\#} + \|\Pi_{N_c}\Phi - \Phi\|_{H^1_\#} \\
&\leq \|(M_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi})^{-1/2} - 1_\mathcal{N}\|_\mathrm{F}\|\Phi\|_{H^1_\#} + \|\Pi_{N_c}\Phi - \Phi\|_{H^1_\#},
\end{aligned}$$

where $\|\cdot\|_\mathrm{F}$ denotes the Frobenius norm. We then notice that

$$M_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi} = 1_\mathcal{N} - M_{\Pi_{N_c}\Phi-\Phi,\Pi_{N_c}\Phi-\Phi}.$$

Consequently, for N_c large enough,

$$\|(M_{\Pi_{N_c}\Phi,\Pi_{N_c}\Phi})^{-1/2} - 1_\mathcal{N}\|_\mathrm{F} \leq \|M_{\Pi_{N_c}\Phi-\Phi,\Pi_{N_c}\Phi-\Phi}\|_\mathrm{F} \leq \|\Pi_{N_c}\Phi - \Phi\|^2_{L^2_\#}.$$

Therefore (83) is proved.

Lastly, the fourth assertion easily follows from the second one. □

Lemma 4.3 *Let*

$$K = \left\{W \in (L^2_\#(\Gamma))^\mathcal{N} \mid 0 \leq M_{W,W} \leq 1_\mathcal{N}\right\},$$

and $\mathcal{S} : K \to \mathbb{R}^{\mathcal{N}\times\mathcal{N}}_\mathrm{S}$ *(the space of the symmetric* $\mathcal{N}\times\mathcal{N}$ *real matrices) defined by*

$$\mathcal{S}(W) = (1_\mathcal{N} - M_{W,W})^{1/2} - 1_\mathcal{N}.$$

The function $\mathcal{S}$ *is continuous on* K *and differentiable on the interior* $\overset{\circ}{K}$ *of* K*. In addition,*

$$\forall W \in K, \quad \|\mathcal{S}(W)\|_F \leq \|W\|^2_{L^2_\#}, \tag{88}$$

and for all $(W_1, W_2, Z) \in K \times K \times (L^2_\#(\Gamma))^{\mathcal{N}}$ *such that* $\|W_1\|_{L^2_\#} \leq \frac{1}{2}$ *and* $\|W_2\|_{L^2_\#} \leq \frac{1}{2}$,

$$\begin{aligned} \|\mathcal{S}(W_1) - \mathcal{S}(W_2)\|_{\mathrm{F}} &\leq 2(\|W_1\|_{L^2_\#} + \|W_2\|_{L^2_\#})\|W_1 - W_2\|_{L^2_\#}, & (89)\\ \|(\mathcal{S}'(W_1) - \mathcal{S}'(W_2)) \cdot Z\|_{\mathrm{F}} &\leq 4\|W_1 - W_2\|_{L^2_\#}\|Z\|_{L^2_\#}, & (90)\\ \|(\mathcal{S}''(W_1)(Z, Z)\|_{\mathrm{F}} &\leq 4\|Z\|^2_{L^2_\#}. & (91) \end{aligned}$$

Proof Diagonalizing $M_{W,W}$ and using the properties of the function $t \mapsto (1-t)^{1/2} - 1$, we see that $\mathcal{S}$ is continuous on K and differentiable on $\overset{\circ}{K}$, and that

$$\|\mathcal{S}(W)\|_{\mathrm{F}} \leq \|M_{W,W}\|_{\mathrm{F}} \leq \|W\|^2_{L^2_\#}.$$

Hence (88). As

$$\mathcal{S}(W) + \frac{1}{2}\mathcal{S}(W)^2 = -\frac{1}{2}M_{W,W},$$

we have for all $W \in \overset{\circ}{K}$,

$$\begin{aligned} &\mathcal{S}'(W) \cdot Z + \frac{1}{2}\left[\mathcal{S}(W)(\mathcal{S}'(W) \cdot Z) + (\mathcal{S}'(W) \cdot Z)\mathcal{S}(W)\right] \\ &\qquad = -\frac{1}{2}\left[M_{W,Z} + M_{Z,W}\right]. \end{aligned}$$

Denoting by $A = \mathcal{S}'(W) \cdot Z$, we deduce from the above equality that

$$\|A\|^2_{\mathrm{F}} + \mathrm{Tr}\,(A^2\mathcal{S}(W)) \leq \|A\|_{\mathrm{F}}\|M_{W,Z}\|_{\mathrm{F}} \leq \|A\|_{\mathrm{F}}\|W\|_{L^2_\#}\|Z\|_{L^2_\#}.$$

As $|\mathrm{Tr}\,(A^2\mathcal{S}(W))| \leq \|A\|^2_{\mathrm{F}}\|\mathcal{S}(W)\|_2 \leq \|A\|^2_{\mathrm{F}}\|\mathcal{S}(W)\|_{\mathrm{F}} \leq \|A\|^2_{\mathrm{F}}\|W\|^2_{L^2_\#}$, we finally obtain the inequality

$$\|A\|_{\mathrm{F}}(1 - \|W\|^2_{L^2_\#}) \leq \|W\|_{L^2_\#}\|Z\|_{L^2_\#}, \tag{92}$$

which straightforwardly leads to (89) under the conditions $\|W_1\|_{L^2_\#} \leq \frac{1}{2}$ and $\|W_2\|_{L^2_\#} \leq \frac{1}{2}$. Lastly,

$$\begin{aligned} &(\mathcal{S}'(W_2) - \mathcal{S}'(W_1)) \cdot Z + \frac{1}{2}\left[\mathcal{S}(W_2)((\mathcal{S}'(W_2) - \mathcal{S}'(W_1)) \cdot Z) + ((\mathcal{S}'(W_2) - \mathcal{S}'(W_1)) \cdot Z)\mathcal{S}(W_2)\right] \\ &\quad + \frac{1}{2}\left[(\mathcal{S}'(W_1) \cdot Z)(\mathcal{S}(W_2) - \mathcal{S}(W_1)) + (\mathcal{S}(W_2) - \mathcal{S}(W_1))(\mathcal{S}'(W_1) \cdot Z)\right] = -\frac{1}{2}\left[M_{W_2 - W_1, Z} + M_{Z, W_2 - W_1}\right], \end{aligned}$$

so that still under the conditions $\|W_1\|_{L^2_\#} \leq \frac{1}{2}$ and $\|W_2\|_{L^2_\#} \leq \frac{1}{2}$,

$$\|(\mathcal{S}'(W_2) - \mathcal{S}'(W_1)) \cdot Z\|_{\mathrm{F}} \leq \frac{28}{9}\|W_2 - W_1\|_{L^2_\#}\|Z\|_{L^2_\#}.$$

Hence (90). Lastly, taking $W_2 = W_1 + tZ$ in (90) and letting t go to zero, we obtain (91). □

Lemma 4.4 *Let Φ^0 be a local minimizer of (58) satisfying (73). Then a_{Φ^0} defines a continuous bilinear form on $(H^1_\#(\Gamma))^{\mathcal{N}} \times (H^1_\#(\Gamma))^{\mathcal{N}}$, and there exists N_c^* such that for all $N_c \geq N_c^*$,*

$$\|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#} \leq 1, \tag{93}$$

$$a_{\Phi^0}(\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0, \pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) \geq \frac{c_{\Phi^0}}{2}\|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#}^2, \tag{94}$$

$$\forall W \in [\pi_{N_c}^{\mathcal{M}}\Phi^0]^{\perp\!\!\perp}, \quad a_{\Phi^0}(W,W) \geq \frac{c_{\Phi^0}}{2}\|W\|_{H^1_\#}^2. \tag{95}$$

In the sequel, we denote by C_{Φ^0} the continuity constant of a_{Φ^0}, i.e.

$$\forall (\Psi, \Psi') \in ((H^1_\#(\Gamma))^{\mathcal{N}})^2, \quad |a_{\Phi^0}(\Psi, \Psi')| \leq C_{\Phi^0}\|\Psi\|_{H^1_\#}\|\Psi'\|_{H^1_\#}. \tag{96}$$

Proof Estimate (93) immediately results from the closeness of $\pi_{N_c}^{\mathcal{M}}\Phi^0$ to Φ^0. Using the fact that $\pi_{N_c}^{\mathcal{M}}\Phi^0 \in \mathcal{M}^{\Phi^0}$ (see Lemma 4.2, point 3), we get

$$\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0 = \mathcal{S}(W)\Phi^0 + W \tag{97}$$

with $W \in [\Phi^0]^{\perp\!\!\perp}$, from which we derive, using (88), that

$$\begin{aligned} a_{\Phi^0}(\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0, \pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) &= a_{\Phi^0}(W,W) + 2a_{\Phi^0}(W, \mathcal{S}(W)\Phi^0) + a_{\Phi^0}(\mathcal{S}(W)\Phi^0, \mathcal{S}(W)\Phi^0) \\ &\geq c_{\Phi^0}\|W\|_{H^1_\#}^2 - 2C_{\Phi^0}\|W\|_{H^1_\#}\|\Phi^0\|_{H^1_\#}\|W\|_{L^2_\#}^2 - C_{\Phi^0}\|W\|_{L^2_\#}^4\|\Phi^0\|_{H^1_\#}^2 \\ &\geq \left(c_{\Phi^0} - 2C_{\Phi^0}\|W\|_{L^2_\#}\|\Phi^0\|_{H^1_\#} - C_{\Phi^0}\|W\|_{L^2_\#}^2\|\Phi^0\|_{H^1_\#}^2\right)\|W\|_{H^1_\#}^2. \end{aligned}$$

As by (82), $\|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{L^2_\#}$ goes to zero when N_c goes to infinity, so does $\|W\|_{L^2_\#}$. Using again (88), we deduce from (97) that $\|W\|_{H^1_\#} \underset{N_c\to\infty}{\sim} \|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#}$. Hence (94).

Finally, for each $W \in [\pi_{N_c}^{\mathcal{M}}\Phi^0]^{\perp\!\!\perp}$, $W^* = W - M_{W,\Phi^0}\Phi^0$ belongs to $[\Phi^0]^{\perp\!\!\perp}$. Remarking that $M_{W,\Phi^0} = M_{W,\Phi^0 - \pi_{N_c}^{\mathcal{M}}\Phi^0}$, we derive

$$\|M_{W,\Phi^0}\|_{\rm F} \leq \|M_{W,\Phi^0 - \pi_{N_c}^{\mathcal{M}}\Phi^0}\|_{\rm F} \leq \varepsilon(N_c)\|W\|_{L^2_\#}$$

where $\varepsilon(N_c) = \|\Phi^0 - \pi_{N_c}^{\mathcal{M}}\Phi^0\|_{L^2_\#} \to 0$ when N_c goes to infinity. Therefore,

$$\|W - W^*\|_{H^1_\#} \leq \varepsilon(N_c)\|\Phi^0\|_{H^1_\#}\|W\|_{H^1_\#}.$$

As

$$a_{\Phi^0}(W,W) = a_{\Phi^0}(W^*,W^*) + 2a_{\Phi^0}(W^*, W - W^*) + a_{\Phi^0}(W - W^*, W - W^*),$$

we obtain

$$
\begin{aligned}
a_{\Phi^0}(W,W) &\geq c_{\Phi^0}\|W^*\|_{H^1_\#}^2 - 2C_{\Phi^0}\|W^*\|_{H^1_\#}\|W-W^*\|_{H^1_\#} - C_{\Phi^0}\|W-W^*\|_{H^1_\#}^2 \\
&\geq \frac{c_{\Phi^0}}{2}\|W\|_{H^1_\#}^2
\end{aligned}
$$

for N_c large enough. □

Lemma 4.5 *There exists $C \geq 0$ such that*

1. *for all $(\Upsilon_1,\Upsilon_2,\Upsilon_3) \in \left((H^1_\#(\Gamma))^{\mathcal{N}}\right)^3$,*

$$
\left|\left(E^{\mathrm{KS}''}(\Phi^0+\Upsilon_1) - E^{\mathrm{KS}''}(\Phi^0)\right)(\Upsilon_2,\Upsilon_3)\right| \leq C\left(\|\Upsilon_1\|_{H^1_\#}^\alpha + \|\Upsilon_1\|_{H^1_\#}^2\right)\|\Upsilon_2\|_{H^1_\#}\|\Upsilon_3\|_{H^1_\#}.
$$

2. *for all $\Upsilon_1 \in (H^1_\#(\Gamma)\cap L^\infty_\#(\Gamma))^{\mathcal{N}}$ and $(\Upsilon_2,\Upsilon_3) \in \left((H^1_\#(\Gamma))^{\mathcal{N}}\right)^2$,*

$$
\left|\left(E^{\mathrm{KS}''}(\Phi^0+\Upsilon_1) - E^{\mathrm{KS}''}(\Phi^0)\right)(\Upsilon_2,\Upsilon_3)\right| \leq C\left(1+\|\Upsilon_1\|_{L^\infty}^{2-\alpha}\right)\|\Upsilon_1\|_{L^2_\#}^\alpha\|\Upsilon_2\|_{H^1_\#}\|\Upsilon_3\|_{H^1_\#}.
$$

Proof Let us denote by

$$
r_{\Phi^0}(\Upsilon_1,\Upsilon_2,\Upsilon_3) = \left(E^{\mathrm{KS}''}(\Phi^0+\Upsilon_1) - E^{\mathrm{KS}''}(\Phi^0)\right)(\Upsilon_2,\Upsilon_3)
$$

Splitting $r_{\Phi^0}(\Upsilon_1,\Upsilon_2,\Upsilon_3)$ in its Coulomb and exchange-correlation contributions, we obtain

$$
r_{\Phi^0}(\Upsilon_1,\Upsilon_2,\Upsilon_3) = r_{\Phi^0}^{\mathrm{Coulomb}}(\Upsilon_1,\Upsilon_2,\Upsilon_3) + r_{\Phi^0}^{\mathrm{xc}}(\Upsilon_1,\Upsilon_2,\Upsilon_3),
$$

with

$$
\begin{aligned}
r_{\Phi^0}^{\mathrm{Coulomb}}(\Upsilon_1,\Upsilon_2,\Upsilon_3) &= 16\sum_{i,j=1}^{\mathcal{N}}\left(D_\Gamma(\phi_i^0 \upsilon_{1,i},\upsilon_{2,j}\upsilon_{3,j}) + D_\Gamma(\phi_i^0\upsilon_{2,i},\upsilon_{1,j}\upsilon_{3,j}) + D_\Gamma(\phi_i^0\upsilon_{3,i},\upsilon_{1,j}\upsilon_{2,j})\right) \\
&\quad +16\sum_{i,j=1}^{\mathcal{N}} D_\Gamma(\upsilon_{1,i}\upsilon_{2,i},\upsilon_{1,j}\upsilon_{3,j}) + 8\sum_{i,j=1}^{\mathcal{N}} D_\Gamma(\upsilon_{1,i}^2,\upsilon_{2,j}\upsilon_{3,j}),
\end{aligned}
$$

and

$$
r_{\Phi^0}^{\mathrm{xc}}(\Upsilon_1,\Upsilon_2,\Upsilon_3) = r_{\Phi^0}^{\mathrm{xc},1}(\Upsilon_1,\Upsilon_2,\Upsilon_3) + r_{\Phi^0}^{\mathrm{xc},2}(\Upsilon_1,\Upsilon_2,\Upsilon_3),
$$

where

$$r_{\Phi^0}^{\rm xc,1}(\Upsilon_1,\Upsilon_2,\Upsilon_3) = 4\int_\Gamma \left(\frac{de_{\rm xc}^{\rm LDA}}{d\rho}(\rho_{\rm c}+\rho_{\Phi^0+\Upsilon_1}) - \frac{de_{\rm xc}^{\rm LDA}}{d\rho}(\rho_{\rm c}+\rho_{\Phi^0})\right)\left(\sum_{i=1}^{\mathcal N} \upsilon_{2,i}\upsilon_{3,i}\right),$$

$$\begin{aligned} r_{\Phi^0}^{\rm xc,2}(\Upsilon_1,\Upsilon_2,\Upsilon_3) &= 16\int_\Gamma \left[\frac{d^2e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho_{\rm c}+\rho_{\Phi^0+\Upsilon_1})\left(\sum_{i=1}^{\mathcal N}(\phi_i^0+\upsilon_{1,i})\upsilon_{2,i}\right)\left(\sum_{i=1}^{\mathcal N}(\phi_i^0+\upsilon_{1,i})\upsilon_{3,i}\right)\right. \\ &\qquad \left. -\frac{d^2e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho_{\rm c}+\rho_{\Phi^0})\left(\sum_{i=1}^{\mathcal N}\phi_i^0\upsilon_{2,i}\right)\left(\sum_{i=1}^{\mathcal N}\phi_i^0\upsilon_{3,i}\right)\right]. \end{aligned}$$

Using (29), we obtain that there exists a constant $C \geq 0$, such that for all $(\Upsilon_1,\Upsilon_2,\Upsilon_3) \in \left((H^1_\#(\Gamma))^{\mathcal N}\right)^3$,

$$|r_{\Phi^0}^{\rm Coulomb}(\Upsilon_1,\Upsilon_2,\Upsilon_3)| \leq C\left(\|\Upsilon_1\|_{L^2_\#}+\|\Upsilon_1\|_{L^2_\#}^2\right)\|\Upsilon_2\|_{H^1_\#}\|\Upsilon_3\|_{H^1_\#}. \qquad (98)$$

Using (64), we get

$$\begin{aligned} \left|\frac{de_{\rm xc}^{\rm LDA}}{d\rho}(\rho_{\rm c}+\rho_{\Phi^0+\Upsilon_1}) - \frac{de_{\rm xc}^{\rm LDA}}{d\rho}(\rho_{\rm c}+\rho_{\Phi^0})\right| &\leq C\left(|\rho_{\Phi^0+\Upsilon_1}-\rho_{\Phi^0}|+\alpha^{-1}|\rho_{\Phi^0+\Upsilon_1}-\rho_{\Phi^0}|^\alpha\right) \\ &\leq C\left[\rho_{\Upsilon_1}^{\alpha/2}+\rho_{\Upsilon_1}\right], \end{aligned}$$

from which we infer

$$|r_{\Phi^0}^{\rm xc,1}(\Upsilon_1,\Upsilon_2,\Upsilon_3)| \leq C\int_\Gamma \left(\rho_{\Upsilon_1}^{\alpha/2}+\rho_{\Upsilon_1}\right)\rho_{\Upsilon_2}^{1/2}\,\rho_{\Upsilon_3}^{1/2}. \qquad (99)$$

Introducing the function

$$\Phi(t) = \Phi^0 + t\Upsilon_1,$$

we can rewrite $r_{\Phi^0}^{\rm xc,2}(\Upsilon_1,\Upsilon_2,\Upsilon_3)$ as

$$\begin{aligned} r_{\Phi^0}^{\rm xc,2}(\Upsilon_1,\Upsilon_2,\Upsilon_3) &= 16\int_\Gamma \left[\frac{d^2e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho_{\rm c}+\rho_{\Phi(1)})\left(\sum_{i=1}^{\mathcal N}\phi_i(1)\upsilon_{2,i}\right)\left(\sum_{i=1}^{\mathcal N}\phi_i(1)\upsilon_{3,i}\right)\right. \\ &\qquad \left. -\frac{d^2e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho_{\rm c}+\rho_{\Phi(0)})\left(\sum_{i=1}^{\mathcal N}\phi_i(0)\upsilon_{2,i}\right)\left(\sum_{i=1}^{\mathcal N}\phi_i(0)\upsilon_{3,i}\right)\right] \\ &= 16\int_\Gamma\int_0^1 \left[\frac{d^2e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho_{\rm c}+\rho_{\Phi(t)})\left(\sum_{i=1}^{\mathcal N}\phi_i(t)\upsilon_{2,i}\right)\left(\sum_{i=1}^{\mathcal N}\upsilon_{1,i}\upsilon_{3,i}\right)\right. \\ &\qquad +\frac{d^2e_{\rm xc}^{\rm LDA}}{d\rho^2}(\rho_{\rm c}+\rho_{\Phi(t)})\left(\sum_{i=1}^{\mathcal N}\upsilon_{1,i}\upsilon_{2,i}\right)\left(\sum_{i=1}^{\mathcal N}\phi_i(t)\upsilon_{3,i}\right) \\ &\qquad \left. +2\frac{d^3e_{\rm xc}^{\rm LDA}}{d\rho^3}(\rho_{\rm c}+\rho_{\Phi(t)})\left(\sum_{i=1}^{\mathcal N}\phi_i(t)\upsilon_{1,i}\right)\left(\sum_{i=1}^{\mathcal N}\phi_i(t)\upsilon_{2,i}\right)\left(\sum_{i=1}^{\mathcal N}\phi_i(t)\upsilon_{3,i}\right)\right]dt. \end{aligned}$$

Thus, using again (64), we obtain

$$
\begin{aligned}
|r^{\mathrm{xc},2}_{\Phi^0}(\Upsilon_1,\Upsilon_2,\Upsilon_3)| &\leq C\int_\Gamma\int_0^1 (1+(\rho_{\mathrm{c}}+\rho_{\Phi(t)})^{\alpha-1})\rho_{\Phi(t)}^{1/2}\rho_{\Upsilon_1}^{1/2}\rho_{\Upsilon_2}^{1/2}\rho_{\Upsilon_3}^{1/2}\,dt \\
&\leq C\int_\Gamma\int_0^1 (1+\rho_{\Phi(t)}^{\alpha-1})\rho_{\Phi(t)}^{1/2}\rho_{\Upsilon_1}^{1/2}\rho_{\Upsilon_2}^{1/2}\rho_{\Upsilon_3}^{1/2}\,dt.
\end{aligned}
$$

Now,

$$
\begin{aligned}
&\int_0^1 \rho_{\Phi(t)}^{\alpha-1/2}dt = 2^{\alpha-1/2}\int_0^1 \left(\sum_{i=1}^{\mathcal{N}} {\phi_i^0}^2 + 2t\sum_{i=1}^{\mathcal{N}}\phi_i^0\upsilon_{1,i} + t^2\sum_{i=1}^{\mathcal{N}}\upsilon_{1,i}^2\right)^{\alpha-1/2} dt \\
&= 2^{\alpha-1/2}\int_0^1 \left(\sum_{i=1}^{\mathcal{N}} {\phi_i^0}^2 - \frac{\left(\sum_{i=1}^{\mathcal{N}}\phi_i^0\upsilon_{1,i}\right)^2}{\sum_{i=1}^{\mathcal{N}}\upsilon_{1,i}^2} + \left(t+\frac{\sum_{i=1}^{\mathcal{N}}\phi_i^0\upsilon_{1,i}}{\sum_{i=1}^{\mathcal{N}}\upsilon_{1,i}^2}\right)^2\left(\sum_{i=1}^{\mathcal{N}}\upsilon_{1,i}^2\right)\right)^{\alpha-1/2} dt \\
&\leq 2^{\alpha-1/2}\int_0^1 \left|t+\frac{\sum_{i=1}^{\mathcal{N}}\phi_i^0\upsilon_{1,i}}{\sum_{i=1}^{\mathcal{N}}\upsilon_{1,i}^2}\right|^{2\alpha-1}\left(\sum_{i=1}^{\mathcal{N}}\upsilon_{1,i}^2\right)^{\alpha-1/2} dt \leq \frac{1}{\alpha 2^{\alpha+1/2}}\rho_{\Upsilon_1}^{\alpha-1/2}.
\end{aligned}
$$

Therefore,

$$
|r^{\mathrm{xc},2}_{\Phi^0}(\Upsilon_1,\Upsilon_2,\Upsilon_3)| \leq C\int_\Gamma \left(\rho_{\Upsilon_1}^{\min(\alpha,1/2)}+\rho_{\Upsilon_1}\right)\rho_{\Upsilon_2}^{1/2}\rho_{\Upsilon_3}^{1/2}. \tag{100}
$$

Gathering (98), (99) and (100), we obtain the desired estimates. □

Lemma 4.6 *Let Φ^0 be a local minimizer of (58) satisfying (73). Then there exists $C \geq 0$ such that for all $\Psi \in \mathcal{M}$,*

$$
E^{\mathrm{KS}}(\Psi) = E^{\mathrm{KS}}(\Phi^0) + 2a_{\Phi^0}(\Psi-\Phi^0,\Psi-\Phi^0) + R(\Psi-\Phi^0), \tag{101}
$$

with

$$
|R(\Psi-\Phi^0)| \leq C\left(\|\Psi-\Phi^0\|_{H^1_\#}^{2+\alpha} + \|\Psi-\Phi^0\|_{H^1_\#}^4\right). \tag{102}
$$

Proof Using the fact that the first order optimality condition (70) also reads

$[E^{\rm KS}{}'(\Phi^0)]_i = 4\mathcal{H}^{\rm KS}_{\rho^0}\phi_i^0 = 4\epsilon_i^0\phi_i^0$ in $H^{-1}_\#(\Gamma)$, we have for all $\Psi \in \mathcal{M}$,

$$\begin{aligned} E^{\rm KS}(\Psi) &= E^{\rm KS}(\Phi^0) + \langle E^{\rm KS}{}'(\Phi^0), \Psi-\Phi^0\rangle_{H^{-1}_\#,H^1_\#} + \frac{1}{2}E^{\rm KS}{}''(\Phi^0)(\Psi-\Phi^0,\Psi-\Phi^0) \\ &+ \int_0^1 (E^{\rm KS}{}''(\Phi^0+s(\Psi-\Phi^0)) - E^{\rm KS}{}''(\Phi^0))(\Psi-\Phi^0,\Psi-\Phi^0)\,(1-s)\,ds \\ &= E^{\rm KS}(\Phi^0) + 4\sum_{i=1}^{\mathcal{N}}\epsilon_i^0\int_\Gamma \phi_i^0(\psi_i-\phi_i^0) + \frac{1}{2}E^{\rm KS}{}''(\Phi^0)(\Psi-\Phi^0,\Psi-\Phi^0) \\ &+ \int_0^1 (E^{\rm KS}{}''(\Phi^0+s(\Psi-\Phi^0)) - E^{\rm KS}{}''(\Phi^0))(\Psi-\Phi^0,\Psi-\Phi^0)\,(1-s)\,ds \\ &= E^{\rm KS}(\Phi^0) - 2\sum_{i=1}^{\mathcal{N}}\epsilon_i^0\int_\Gamma (\psi_i-\phi_i^0)^2 + \frac{1}{2}E^{\rm KS}{}''(\Phi^0)(\Psi-\Phi^0,\Psi-\Phi^0) \\ &+ \int_0^1 (E^{\rm KS}{}''(\Phi^0+s(\Psi-\Phi^0)) - E^{\rm KS}{}''(\Phi^0))(\Psi-\Phi^0,\Psi-\Phi^0)\,(1-s)\,ds \\ &= E^{\rm KS}(\Phi^0) + 2a_{\Phi^0}(\Psi-\Phi^0,\Psi-\Phi^0) + R(\Psi-\Phi^0), \end{aligned}$$

where

$$R(\Upsilon) = \int_0^1 (E^{\rm KS}{}''(\Phi^0+s\Upsilon) - E^{\rm KS}{}''(\Phi^0))(\Upsilon,\Upsilon)\,(1-s)\,ds.$$

The estimate (102) then straightforwardly follows from Lemma 4.5. □

4.2 Existence of a discrete solution

In this subsection, we derive, for N_c large enough, the existence of a unique local minimum of the discretized problem (77) in the neighborhood of $\pi^{\mathcal{M}}_{N_c}\Phi^0$.

Let

$$\mathcal{B}_{N_c} = \left\{ W^{N_c} \in V^{\mathcal{N}}_{N_c} \cap [\pi^{\mathcal{M}}_{N_c}\Phi^0]^{\perp\!\!\perp} \mid 0 \le M_{W^{N_c},W^{N_c}} \le 1 \right\},$$

and $\mathcal{E}_{N_c}$ be the energy functional defined on $\mathcal{B}_{N_c}$ by

$$\mathcal{E}_{N_c}(W^{N_c}) = E^{\rm KS}\left(\pi^{\mathcal{M}}_{N_c}\Phi^0 + \mathcal{S}(W^{N_c})\pi^{\mathcal{M}}_{N_c}\Phi^0 + W^{N_c}\right). \qquad (103)$$

According to the fourth assertion of Lemma 4.2, the application

$$\begin{array}{rccl} \mathcal{C}\ :& \mathcal{B}_{N_c} & \rightarrow & V^{\mathcal{N}}_{N_c} \cap \mathcal{M}^{\pi^{\mathcal{M}}_{N_c}\Phi^0} \\ & W^{N_c} & \mapsto & \pi^{\mathcal{M}}_{N_c}\Phi^0 + \mathcal{S}(W^{N_c})\pi^{\mathcal{M}}_{N_c}\Phi^0 + W^{N_c} \end{array}$$

defines a global map of $V^{\mathcal{N}}_{N_c} \cap \mathcal{M}^{\pi^{\mathcal{M}}_{N_c}\Phi^0}$ such that $\mathcal{C}(0) = \pi^{\mathcal{M}}_{N_c}\Phi^0$. Therefore the minimizers of

$$\inf\left\{ E^{\rm KS}(\Phi^{N_c}),\ \Phi^{N_c} \in V^{\mathcal{N}}_{N_c} \cap \mathcal{M}^{\pi^{\mathcal{M}}_{N_c}\Phi^0} \right\} \qquad (104)$$

are in one-to-one correspondence with those of the minimization problem

$$\inf \left\{ \mathcal{E}_{N_c}(W^{N_c}), \ W^{N_c} \in \mathcal{B}_{N_c} \right\}. \tag{105}$$

In a first stage, we prove that for N_c large enough, (105) has a unique solution in some neighborhood of 0. As a consequence (104) has a unique solution in the vicinity of $\pi_{N_c}^{\mathcal{M}}\Phi^0$ (for N_c large enough). In a second stage, we make use of the unitary invariance (69) to prove that for N_c large enough, (77) has a unique solution in the vicinity of Φ^0.

Lemma 4.7 *There exists $r > 0$ and N_c^0 such that for all $N_c \geq N_c^0$, the functional $\mathcal{E}_{N_c}$ has a unique critical point $W_0^{N_c}$ in the ball*

$$\left\{ W^{N_c} \in V_{N_c}^{\mathcal{N}} \cap [\pi_{N_c}^{\mathcal{M}}\Phi^0]^{\perp\!\!\perp} \mid \|W^{N_c}\|_{H^1_\#} \leq r \right\}.$$

Besides, $W_0^{N_c}$ is a local minimizer of (105) and we have the estimate

$$\|W_0^{N_c}\|_{H^1_\#} \leq \frac{32 C_{\Phi^0}^3}{c_{\Phi_0}^3} \|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#}. \tag{106}$$

Proof We infer from Lemma 4.6 that

$$\begin{aligned}
\mathcal{E}_{N_c}(W^{N_c}) &= E^{\rm KS}\left(\Phi^0 + (\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + \mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W^{N_c}\right) \\
&= E^{\rm KS}\left(\Phi^0\right) \\
&\quad + 2a_{\Phi^0}\left((\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + \mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W^{N_c}, (\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + \mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W^{N_c}\right) \\
&\quad + R\left((\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + \mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W^{N_c}\right) \\
&= E^{\rm KS}\left(\Phi^0\right) + 2a_{\Phi^0}(W^{N_c}, W^{N_c}) + 4a_{\Phi^0}\left(W^{N_c}, (\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0)\right) \\
&\quad + 2a_{\Phi^0}(\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0, \pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + \mathcal{R}_{N_c}(W^{N_c})
\end{aligned}$$

where

$$\begin{aligned}
\mathcal{R}_{N_c}(W_{N_c}) &= 2a_{\Phi^0}(\mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0, \mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0) \\
&\quad + 4a_{\Phi^0}(\mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0, (\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + W^{N_c}) \\
&\quad + R\left((\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + \mathcal{S}(W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W^{N_c}\right).
\end{aligned}$$

Thus,

$$\begin{aligned}
\forall W^{N_c} \in \mathcal{B}_{N_c}, \quad \mathcal{E}_{N_c}(W^{N_c}) &= \mathcal{E}_{N_c}(0) + 2a_{\Phi^0}(W^{N_c}, W^{N_c}) + 4a_{\Phi^0}\left(W^{N_c}, (\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0)\right) \\
&\quad + \mathcal{R}_{N_c}(W^{N_c}) - \mathcal{R}_{N_c}(0).
\end{aligned} \tag{107}$$

It follows from Lemma 4.6, (88) and the continuity of a_{Φ^0} on $(H^1_\#(\Gamma))^{\mathcal{N}}$ that

$$\begin{aligned}
\forall W^{N_c} \in \mathcal{B}_{N_c}, \quad |\mathcal{R}_{N_c}(W^{N_c})| \leq C_{\mathcal{R}} \Bigg(& \|W^{N_c}\|_{H^1_\#}^{2+\alpha} + \|W^{N_c}\|_{H^1_\#}^8 + \|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#}^{2+\alpha} \\
& + \|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#}^4 + \|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#}\|W^{N_c}\|_{H^1_\#}^2 \Bigg),
\end{aligned}$$

for a constant $C_{\mathcal{R}} \geq 0$ independent of N_c. Let us introduce for $N_c \geq 0$ and $r > 0$ the ball

$$B_{N_c}(r) = \left\{ W^{N_c} \in V_{N_c}^{\mathcal{N}} \cap [\pi_{N_c}^{\mathcal{M}} \Phi^0]^{\perp\!\!\perp} \mid a_{\Phi^0}(W^{N_c}, W^{N_c}) < r^2 a_{\Phi^0}(\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0, \pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0) \right\}.$$

We deduce from Lemma 4.4, that for all $r > 0$ and all $N_c \geq N_c^*$, we have

$$\forall W^{N_c} \in \partial B_{N_c}(r), \quad \sqrt{\frac{c_{\Phi^0}}{2C_{\Phi^0}}}\, r \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#} \leq \|W^{N_c}\|_{H^1_\#} \leq \sqrt{\frac{2C_{\Phi^0}}{c_{\Phi^0}}}\, r \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}.$$

Let $r_0 = 2(2C_{\Phi^0}/c_{\Phi_0})^{5/2}$. For all $r > r_0$, there exists $N_{c,r} \geq N_c^*$ such that

$$\forall N_c \geq N_{c,r}, \quad \partial B_{N_c}(r) \subset \mathcal{B}_{N_c} \quad \text{and} \quad \forall W^{N_c} \in \partial B_{N_c}(r), \quad \|W^{N_c}\|_{H^1_\#} \leq 1.$$

Therefore, for all $r > r_0$ and all $N_c \geq N_{c,r}$ we have $\partial B_{N_c}(r) \subset \mathcal{B}_{N_c}$ and

$\forall W^{N_c} \in \partial B_{N_c}(r)$,

$$\begin{aligned}
\mathcal{E}_{N_c}(W^{N_c}) \;\geq\;& \mathcal{E}_{N_c}(0) + c_{\Phi^0} \|W^{N_c}\|_{H^1_\#}^2 - 4C_{\Phi^0} \|W^{N_c}\|_{H^1_\#} \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#} \\
& - C_{\mathcal{R}} \bigg(\|W^{N_c}\|_{H^1_\#}^{2+\alpha} + \|W^{N_c}\|_{H^1_\#}^8 + 2\|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}^{2+\alpha} \\
& + 2\|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}^4 + \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#} \|W^{N_c}\|_{H^1_\#}^2 \bigg) \\
\geq\;& \mathcal{E}_{N_c}(0) + c_{\Phi^0} \|W^{N_c}\|_{H^1_\#}^2 - 4C_{\Phi^0} \|W^{N_c}\|_{H^1_\#} \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#} \\
& - 5C_{\mathcal{R}} \left(\|W^{N_c}\|_{H^1_\#}^{2+\alpha} + \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}^{2+\alpha} \right) \\
\geq\;& \mathcal{E}_{N_c}(0) + \frac{c_{\Phi^0}^2}{2C_{\Phi^0}} r(r - r_0) \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}^2 \\
& - 5C_{\mathcal{R}} \left(1 + \left(\frac{2C_{\Phi^0}}{c_{\Phi^0}} \right)^{1+\alpha/2} r^{2+\alpha} \right) \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}^{2+\alpha}.
\end{aligned}$$

As $\|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}$ goes to zero when N_c goes to infinity, we finally obtain that for all $r > r_0$, there exists some $N'_{c,r} \geq N_c^*$ such that for all $N_c \geq N'_{c,r}$,

$$\partial B_{N_c}(r) \subset \mathcal{B}_{N_c} \quad \text{and} \quad \forall W^{N_c} \in \partial B_{N_c}(r), \quad \mathcal{E}_{N_c}(W^{N_c}) > \mathcal{E}_{N_c}(0).$$

This proves that for each $N_c \geq N'_{c,2r_0}$, $\mathcal{E}_{N_c}$ has a minimizer $W_0^{N_c}$ in the ball $B_{N_c}(2r_0)$. In particular,

$$\|W_0^{N_c}\|_{H^1_\#} \leq \frac{32C_{\Phi^0}^3}{c_{\Phi_0}^3} \|\pi_{N_c}^{\mathcal{M}} \Phi^0 - \Phi^0\|_{H^1_\#}. \tag{108}$$

Let $W_1^{N_c}$ be a critical point of $\mathcal{E}_{N_c}$ such that $\|W_1^{N_c}\|_{L^2_\#} \leq \frac{1}{2}$. We denote by $\delta W^{N_c} = W_1^{N_c} - W_0^{N_c}$,

$$\begin{aligned}
\widetilde{\Phi}_{N_c}^0 &= \pi_{N_c}^{\mathcal{M}} \Phi^0 + \mathcal{S}(W_0^{N_c}) \pi_{N_c}^{\mathcal{M}} \Phi^0 + W_0^{N_c}, \\
\widetilde{\Phi}_{N_c}^1 &= \pi_{N_c}^{\mathcal{M}} \Phi^0 + \mathcal{S}(W_1^{N_c}) \pi_{N_c}^{\mathcal{M}} \Phi^0 + W_1^{N_c}.
\end{aligned}$$

As both $W_0^{N_c}$ and $W_1^{N_c}$ are critical points of $\mathcal{E}_{N_c}$, we have

$$\mathcal{E}'_{N_c}(W_0^{N_c}) \cdot (W_1^{N_c} - W_0^{N_c}) = 0,$$
$$\mathcal{E}'_{N_c}(W_1^{N_c}) \cdot (W_0^{N_c} - W_1^{N_c}) = 0,$$

so that

$$\left(\mathcal{E}'_{N_c}(W_1^{N_c}) - \mathcal{E}'_{N_c}(W_0^{N_c})\right) \cdot (W_1^{N_c} - W_0^{N_c}) = 0.$$

Using the expression (107) for $\mathcal{E}_{N_c}$, we can rewrite this equality as

$$a_{\Phi^0}(\delta W^{N_c}, \delta W^{N_c}) \quad = \quad b_{\Phi^0}^{N_c}(W_0^{N_c}, W_1^{N_c}, \delta W^{N_c}) + d_{\Phi^0}(\widetilde{\Phi}_{N_c}^0, \widetilde{\Phi}_{N_c}^1, W_0^{N_c}, W_1^{N_c}, \delta W^{N_c}),$$

where

$$\begin{aligned} b_{\Phi^0}^{N_c}(W_0^{N_c}, W_1^{N_c}, \delta W^{N_c}) \quad = \quad & -a_{\Phi^0}((\mathcal{S}(W_1^{N_c}) - \mathcal{S}(W_0^{N_c}))\pi_{N_c}^{\mathcal{M}}\Phi^0, (\mathcal{S}'(W_1^{N_c}) \cdot \delta W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + \delta W^{N_c}) \\ & -a_{\Phi^0}((((\mathcal{S}'(W_1^{N_c}) - \mathcal{S}'(W_0^{N_c})) \cdot \delta W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0, (\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0) + \mathcal{S}(W_0^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W_0^{N_c}) \\ & -a_{\Phi^0}((\mathcal{S}'(W_1^{N_c}) \cdot \delta W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0, \delta W^{N_c}) \end{aligned}$$

and

$$\begin{aligned} d_{\Phi^0}(\widetilde{\Phi}_{N_c}^0, \widetilde{\Phi}_{N_c}^1, W_0^{N_c}, W_1^{N_c}, \delta W^{N_c}) \quad = \quad & \frac{1}{4}\Big[R'(\widetilde{\Phi}_{N_c}^0 - \Phi^0) \cdot ((\mathcal{S}'(W_0^{N_c}) \cdot \delta W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + \delta W^{N_c}) \\ & -R'(\widetilde{\Phi}_{N_c}^1 - \Phi^0) \cdot ((\mathcal{S}'(W_1^{N_c}) \cdot \delta W^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + \delta W^{N_c})\Big]. \end{aligned}$$

Using Lemma 4.3 and (108), we obtain that there exists $\widetilde{C}_{\Phi^0}$ (depending only on Φ^0) and $\widetilde{N}_c$ such that for all $N_c \geq \widetilde{N}_c$,

$$|b_{\Phi^0}^{N_c}(W_0^{N_c}, W_1^{N_c}, \delta W^{N_c})| \quad \leq \quad \widetilde{C}_{\Phi^0}\left(\|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#} + \|W_1^{N_c}\|_{L^2_\#}\right)\|\delta W^{N_c}\|_{H^1_\#}^2.$$

On the other hand, remarking that for all $\Psi \in \mathcal{M}$ and all $\delta\Psi \in T_\Psi\mathcal{M}$,

$$R'(\Psi - \Phi^0) \cdot \delta\Psi = E^{\mathrm{KS}'}(\Psi) \cdot \delta\Psi - 4a_{\Phi^0}(\Psi - \Phi^0, \delta\Psi),$$

and introducing the path $(\Psi(t))_{t\in[0,1]}$, drawn on the manifold $\mathcal{M}$ and connecting $\widetilde{\Phi}_{N_c}^0$ and $\widetilde{\Phi}_{N_c}^1$, defined as

$$\Psi(t) = \Phi^0 + \mathcal{S}(tW_1^{N_c} + (1-t)W_0^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + tW_1^{N_c} + (1-t)W_0^{N_c},$$

we obtain

$$\begin{aligned} d_{\Phi^0}(\widetilde{\Phi}_{N_c}^0, \widetilde{\Phi}_{N_c}^1, W_0^{N_c}, W_1^{N_c}, \delta W^{N_c}) \quad = \quad & \frac{1}{4}\Big[E^{\mathrm{KS}'}(\Psi(0)) \cdot \Psi'(0) - E^{\mathrm{KS}'}(\Psi(1)) \cdot \Psi'(1)\Big] \\ & -a_{\Phi^0}(\Psi(0) - \Phi^0, \Psi'(0)) + a_{\Phi^0}(\Psi(1) - \Phi^0, \Psi'(1)) \\ = \quad & -\int_0^1 \Big[\frac{1}{4}E^{\mathrm{KS}''}(\Psi(t))(\Psi'(t), \Psi'(t)) + \frac{1}{4}E^{\mathrm{KS}'}(\Psi(t)) \cdot \Psi''(t) \\ & -a_{\Phi^0}(\Psi'(t), \Psi'(t)) - a_{\Phi^0}(\Psi(t) - \Phi^0, \Psi''(t))\Big]\,dt. \end{aligned}$$

As $\Psi(t) = (\psi_1(t), \cdots, \psi_{\mathcal{N}}(t)) \in \mathcal{M}$ for all $t \in [0,1]$, we have for all $1 \le i \le \mathcal{N}$ and all $t \in [0,1]$,

$$\int_\Gamma \psi_i'(t,x)^2\,dx = -\int_\Gamma \psi_i(t,x)\,\psi_i''(t,x)\,dx,$$

so that

$$\begin{aligned}
\frac{1}{4}E^{\rm KS'}(\Phi^0)\cdot\Psi''(t) - a_{\Phi^0}(\Psi'(t),\Psi'(t)) &= \sum_{i=1}^{\mathcal{N}} \epsilon_i^0 \int_\Gamma \phi_i^0 \psi_i''(t) \\
&\quad -\frac{1}{4}E^{\rm KS''}(\Phi^0)(\Psi'(t),\Psi'(t)) + \sum_{i=1}^{\mathcal{N}} \epsilon_i^0 \int_\Gamma \psi_i'(t)^2 \\
&= -\sum_{i=1}^{\mathcal{N}} \epsilon_i^0 \int_\Gamma (\psi_i(t)-\phi_i^0)\psi_i''(t) - \frac{1}{4}E^{\rm KS''}(\Phi^0)(\Psi'(t),\Psi'(t)).
\end{aligned}$$

Consequently,

$$\begin{aligned}
d_{\Phi^0}(\widetilde{\Phi}^0_{N_c}, \widetilde{\Phi}^1_{N_c}, W_0^{N_c}, W_1^{N_c}, \delta W^{N_c}) &= -\int_0^1 \left[\frac{1}{4}\left(E^{\rm KS''}(\Psi(t)) - E^{\rm KS''}(\Phi^0)\right)(\Psi'(t),\Psi'(t))\right. \\
+\frac{1}{4}\left(E^{\rm KS'}(\Psi(t)) - E^{\rm KS'}(\Phi^0)\right)\cdot\Psi''(t) &- \left.\sum_{i=1}^{\mathcal{N}} \epsilon_i^0 \int_\Gamma (\psi_i(t)-\phi_i^0)\psi_i''(t) - a_{\Phi^0}(\Psi(t)-\Phi^0, \Psi''(t))\right] dt.
\end{aligned}$$

Using Lemma 4.5, we obtain

$$\begin{aligned}
|d_{\Phi^0}(\widetilde{\Phi}^0_{N_c}, \widetilde{\Phi}^1_{N_c}, W_0^{N_c}, W_1^{N_c}, \delta W^{N_c})| &\le C\int_0^1 \left[\left(\|\Psi(t)-\Phi^0\|_{H^1_\#}^\alpha + \|\Psi(t)-\Phi^0\|_{H^1_\#}^2\right)\|\Psi'(t)\|_{H^1_\#}^2\right. \\
&\qquad \left.\|\Psi(t)-\Phi^0\|_{H^1_\#}\|\Psi''(t)\|_{H^1_\#}\right] dt.
\end{aligned}$$

As

$$\begin{aligned}
\Psi'(t) &= (\mathcal{S}'(tW_1^{N_c} + (1-t)W_0^{N_c})\cdot\delta W^{N_c})\pi^{\mathcal{M}}_{N_c}\Phi^0 + \delta W^{N_c}, \\
\Psi''(t) &= (\mathcal{S}''(tW_1^{N_c} + (1-t)W_0^{N_c})(\delta W^{N_c}, \delta W^{N_c}))\pi^{\mathcal{M}}_{N_c}\Phi^0,
\end{aligned}$$

we obtain that there exists some constant $C \in \mathbb{R}_+$ such that for N_c large enough,

$$|d_{\Phi^0}(\widetilde{\Phi}^0_{N_c}, \widetilde{\Phi}^1_{N_c}, W_0^{N_c}, W_1^{N_c}, \delta W^{N_c})| \le C\left(\|\pi^{\mathcal{M}}_{N_c}\Phi^0 - \Phi^0\|_{H^1_\#}^\alpha + \|W_1^{N_c}\|_{H^1_\#}^\alpha\right)\|\delta W^{N_c}\|_{H^1_\#}^2.$$

Thus,

$$\begin{aligned}
\frac{c_{\Phi^0}}{2}\|\delta W^{N_c}\|_{H^1_\#} &\le |a_{\Phi^0}(\delta W^{N_c}, \delta W^{N_c})| \\
&= |b^{N_c}_{\Phi^0}(W_0^{N_c}, W_1^{N_c}, \delta W^{N_c}) + d_{\Phi^0}(\widetilde{\Phi}^0_{N_c}, \widetilde{\Phi}^1_{N_c}, W_0^{N_c}, W_1^{N_c}, \delta W^{N_c})| \\
&\le C\left(\|\pi^{\mathcal{M}}_{N_c}\Phi^0 - \Phi^0\|_{H^1_\#}^\alpha + \|W_1^{N_c}\|_{H^1_\#}^\alpha\right)\|\delta W^{N_c}\|_{H^1_\#}^2.
\end{aligned}$$

This proves that there exists a constant $r > 0$ such that for all N_c large enough, $\|W_1^{N_c}\|_{H^1_\#} \le r$ implies $\delta W^{N_c} = 0$. Hence the result. □

As the mapping $B_{N_c}(2r_0) \ni W^{N_c} \mapsto \pi_{N_c}^{\mathcal{M}}\Phi^0 + \mathcal{S}(W_c^N)\pi_{N_c}^{\mathcal{M}}\Phi^0 + W^{N_c}$ defines a local map of $V_{N_c}^{\mathcal{N}} \cap \mathcal{M}^{\pi_{N_c}^{\mathcal{M}}\Phi^0}$ in the neighborhood of $\pi_{N_c}^{\mathcal{M}}\Phi^0$, we obtain that $\widetilde{\Phi}_{N_c}^0 = \pi_{N_c}^{\mathcal{M}}\Phi^0 + \mathcal{S}(W_0^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W_0^{N_c}$ is the unique local minimizer of

$$\inf\left\{E^{\mathrm{KS}}(\Phi_{N_c}),\ \Phi_{N_c} \in V_{N_c}^{\mathcal{N}} \cap \mathcal{M}^{\pi_{N_c}^{\mathcal{M}}\Phi^0}\right\},$$

in the vicinity of $\pi_{N_c}^{\mathcal{M}}\Phi^0$. Besides,

$$\begin{aligned}\|\widetilde{\Phi}_{N_c}^0 - \Phi^0\|_{H^1_\#} &\leq \|\widetilde{\Phi}_{N_c}^0 - \pi_{N_c}^{\mathcal{M}}\Phi^0\|_{H^1_\#} + \|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#} \\ &\leq \|S(W_0^{N_c})\pi_{N_c}^{\mathcal{M}}\Phi^0 + W_0^{N_c}\|_{H^1_\#} + \|\pi_{N_c}^{\mathcal{M}}\Phi^0 - \Phi^0\|_{H^1_\#} \\ &\leq C\|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^1_\#},\end{aligned}$$

for a constant C independent of N_c. We then have

$$\|M_{\widetilde{\Phi}_{N_c}^0,\Phi^0} - 1_{\mathcal{N}}\|_{\mathrm{F}} \leq \|\widetilde{\Phi}_{N_c}^0 - \Phi^0\|_{L^2_\#} \leq C\|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^1_\#}.$$

Let $\Phi_{N_c}^0 = U_{\widetilde{\Phi}_{N_c}^0,\Phi^0}\widetilde{\Phi}_{N_c}^0$, where $U_{\widetilde{\Phi}_{N_c}^0,\Phi^0} = M_{\widetilde{\Phi}_{N_c}^0,\Phi^0}^T(M_{\widetilde{\Phi}_{N_c}^0,\Phi^0}M_{\widetilde{\Phi}_{N_c}^0,\Phi^0}^T)^{-1/2}$. Then for each $N_c \geq N'_{c,2r_0}$, $\Phi_{N_c}^0$ is the unique local minimizer of (77) in the set

$$\left\{\Phi_{N_c} \in V_{N_c}^{\mathcal{N}} \cap \mathcal{M}^{\Phi^0} \mid \|\Phi_{N_c} - \Phi^0\|_{H^1_\#} \leq r^0\right\},$$

for some constant $r^0 > 0$ independent of N_c, and it satisfies

$$\|\Phi_{N_c}^0 - \Phi^0\|_{H^1_\#} \leq C\|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^1_\#}, \tag{109}$$

for some $C \in \mathbb{R}_+$ independent of N_c.

As $\Phi_{N_c}^0 \in \mathcal{M}^{\Phi^0}$, we can decompose $\Phi_{N_c}^0$ as

$$\Phi_{N_c}^0 = \Phi^0 + S_{N_c}^0\Phi^0 + W_{N_c}^0 \tag{110}$$

where $S_{N_c}^0 = \mathcal{S}(W_{N_c}^0)$ and $W_{N_c}^0 \in \Phi^{0,\perp\!\!\!\perp}$ (note that $W_{N_c}^0 \notin V_{N_c}^{\mathcal{N}}$ in general). As

$$\|S_{N_c}^0\|_{\mathrm{F}} \leq \|W_{N_c}^0\|_{L^2_\#}^2 \tag{111}$$

and $\|\Phi_{N_c}^0 - \Phi^0\|_{H^1_\#}$ goes to zero when N_c goes to infinity, we have, for N_c large enough,

$$\frac{1}{2}\|W_{N_c}^0\|_{L^2_\#} \leq \|\Phi_{N_c}^0 - \Phi^0\|_{L^2_\#} \leq 2\|W_{N_c}^0\|_{L^2_\#}, \tag{112}$$

$$\frac{1}{2}\|W_{N_c}^0\|_{H^1_\#} \leq \|\Phi_{N_c}^0 - \Phi^0\|_{H^1_\#} \leq 2\|W_{N_c}^0\|_{H^1_\#}. \tag{113}$$

The discrete solution $\Phi_{N_c}^0$ satisfies the Euler equations

$$\forall \Psi_{N_c} \in V_{N_c}^{\mathcal{N}}, \quad \langle \mathcal{H}_{\rho_{N_c}^0}^{\mathrm{KS}}\phi_{i,N_c}^0, \psi_i\rangle_{H^{-1}_\#,H^1_\#} = \sum_{j=1}^{\mathcal{N}}[\lambda_{N_c}^0]_{ij}(\phi_{j,N_c}^0, \psi_j)_{L^2_\#},$$

where $\rho^0_{N_c} = \rho_{\Phi^0_{N_c}}$ and where the $\mathcal{N}\times\mathcal{N}$ matrix $\Lambda^0_{N_c}$ is symmetric (but generally not diagonal). Of course, it follows from the invariance property (69) that (77) has a local minimizer of the form $U\Phi^0_{N_c}$ with $U \in \mathcal{U}(\mathcal{N})$ for which the Lagrange multiplier of the orthonormality constraints is a diagonal matrix.

4.3 A priori error estimates

We are now in position to derive *a priori* estimates for $\|\Phi^0_{N_c} - \Phi^0\|_{H^s_\#}$ and $(\Lambda^0_{N_c} - \Lambda^0)$, where we recall that $\Lambda_0 = \mathrm{diag}(\epsilon^0_1, \cdots, \epsilon^0_{\mathcal{N}})$.

Using (2), (109) and the inverse inequality (49), we obtain for each $s \geq 1$ such that $\Phi^0 \in \left(H^s_\#(\Gamma)\right)^{\mathcal{N}}$ and each $1 \leq r \leq s$,

$$
\begin{aligned}
\|\Phi^0_{N_c} - \Phi^0\|_{H^r_\#} &\leq \|\Phi^0_{N_c} - \Pi_{N_c}\Phi^0\|_{H^r_\#} + \|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^r_\#} \\
&\leq CN_c^{r-1}\|\Phi^0_{N_c} - \Pi_{N_c}\Phi^0\|_{H^1_\#} + \|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^r_\#} \\
&\leq CN_c^{r-1}\left(\|\Phi^0_{N_c} - \Phi^0\|_{H^1_\#} + \|\Phi^0 - \Pi_{N_c}\Phi^0\|_{H^1_\#}\right) + \|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^r_\#} \\
&\leq CN_c^{r-1}\|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^1_\#} + \|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^r_\#} \\
&\leq CN_c^{-(s-r)}\|\Pi_{N_c}\Phi^0 - \Phi^0\|_{H^s_\#}.
\end{aligned} \tag{114}
$$

In particular, for $s = 3$ and $r = 2$, we obtain that $\Phi^0_{N_c}$ converges to Φ^0 in $(H^2_\#(\Gamma))^{\mathcal{N}}$, hence in $(L^\infty_\#(\Gamma))^{\mathcal{N}}$.

We then proceed as in (37) and remark that

$$
\begin{aligned}
\lambda^0_{ij,N_c} - \lambda^0_{ij} &= \langle \mathcal{H}^{\rm KS}_{\rho^0_{N_c}} \phi^0_{i,N_c}, \phi^0_{j,N_c}\rangle_{H^{-1}_\#,H^1_\#} - \langle \mathcal{H}^{\rm KS}_{\rho^0} \phi^0_i, \phi^0_j\rangle_{H^{-1}_\#,H^1_\#} \\
&= \langle \mathcal{H}^{\rm KS}_{\rho^0}(\phi^0_{i,N_c} - \phi^0_i), (\phi^0_{j,N_c} - \phi^0_j)\rangle_{H^{-1}_\#,H^1_\#} \\
&\quad + \epsilon^0_i \int_\Gamma \phi^0_i(\phi^0_{j,N_c} - \phi^0_j) + \epsilon^0_j \int_\Gamma \phi^0_j(\phi^0_{i,N_c} - \phi^0_i) \\
&\quad + \int_\Gamma V^{\rm Coulomb}_{\phi^0_{i,N_c}\phi^0_{j,N_c}} (\rho^0_{N_c} - \rho^0) \\
&\quad + \int_\Gamma \left(\frac{de^{\rm LDA}_{\rm xc}}{d\rho}(\rho_{\rm c} + \rho^0_{N_c}) - \frac{de^{\rm LDA}_{\rm xc}}{d\rho}(\rho_{\rm c} + \rho^0)\right)\phi^0_{i,N_c}\phi^0_{j,N_c}.
\end{aligned} \tag{115}
$$

As, from (110),

$$
\epsilon^0_i \int_\Gamma \phi^0_i(\phi^0_{j,N_c} - \phi^0_j) + \epsilon^0_j \int_\Gamma \phi^0_j(\phi^0_{i,N_c} - \phi^0_i) = (\epsilon^0_i + \epsilon^0_j)[S^0_{N_c}]_{ij},
$$

we easily obtain, using the convergence of $\Phi^0_{N_c}$ to Φ^0 in $(H^1_\#(\Gamma) \cap L^\infty_\#(\Gamma))^{\mathcal{N}}$,

$$
\|\Lambda^0_{N_c} - \Lambda^0\|_{\rm F} \underset{N_c \to \infty}{\longrightarrow} 0. \tag{116}
$$

For $W \in (L^2_\#(\Gamma))^{\mathcal{N}}$, we introduce the adjoint problem

$$\left\{ \begin{array}{l} \text{find } \Psi_W \in \Phi^{0,\perp\!\!\perp} \text{ such that} \\ \forall Z \in \Phi^{0,\perp\!\!\perp},\ a_{\Phi^0}(\Psi_W, Z) = (W, Z)_{L^2_\#}, \end{array} \right. \tag{117}$$

the solution of whom exists and is unique by the coercivity assumption (73). Clearly,

$$\|\Psi_W\|_{H^1_\#} \leq C\|W\|_{L^2_\#}. \tag{118}$$

In addition, it follows from standard elliptic regularity arguments that

$$\|\Psi_W\|_{H^2_\#} \leq C\|W\|_{L^2_\#},$$

yielding

$$\|\Psi_W - \Pi_{N_c}\Psi_W\|_{L^2_\#} \leq C N_c^{-2}\|W\|_{L^2_\#} \tag{119}$$

$$\|\Psi_W - \Pi_{N_c}\Psi_W\|_{H^1_\#} \leq C N_c^{-1}\|W\|_{L^2_\#}. \tag{120}$$

Denoting by $\Psi = \Psi_{\Phi^0_{N_c} - \Phi^0}$ and using (110), we get

$$\begin{aligned} \|\Phi^0_{N_c} - \Phi^0\|^2_{L^2_\#} &= (\Phi^0_{N_c} - \Phi^0, \Phi^0_{N_c} - \Phi^0)_{L^2_\#} \\ &= (\Phi^0_{N_c} - \Phi^0, S^0_{N_c}\Phi^0)_{L^2_\#} + (\Phi^0_{N_c} - \Phi^0, W^0_{N_c})_{L^2_\#} \\ &= (\Phi^0_{N_c} - \Phi^0, S^0_{N_c}\Phi^0)_{L^2_\#} + a_{\Phi^0}(\Psi, W^0_{N_c}) \\ &= (\Phi^0_{N_c} - \Phi^0, S^0_{N_c}\Phi^0)_{L^2_\#} - a_{\Phi^0}(\Psi, S^0_{N_c}\Phi^0) + a_{\Phi^0}(\Psi, \Phi^0_{N_c} - \Phi^0) \\ &= (\Phi^0_{N_c} - \Phi^0, S^0_{N_c}\Phi^0)_{L^2_\#} - a_{\Phi^0}(\Psi, S^0_{N_c}\Phi^0) + a_{\Phi^0}(\Psi - \Pi_{N_c}\Psi, \Phi^0_{N_c} - \Phi^0) \\ &\quad + a_{\Phi^0}(\Pi_{N_c}\Psi, \Phi^0_{N_c} - \Phi^0). \end{aligned} \tag{121}$$

From the definition (71), the last term in the above expression reads

$$a_{\Phi^0}(\Pi_{N_c}\Psi, \Phi^0_{N_c} - \Phi^0) = \frac{1}{4}E^{\mathrm{KS}\prime\prime}(\Phi^0)(\Pi_{N_c}\Psi, \Phi^0_{N_c} - \Phi^0) - \sum_{i=1}^{N}\sum_{j=1}^{N}\lambda^0_{ij}\int_\Gamma(\phi^0_{j,N_c} - \phi^0_j)\Pi_{N_c}\psi_i,$$

so that from the definition of the continuous and discrete eigenvalue problems

$$\begin{aligned} 4a_{\Phi^0}(\Pi_{N_c}\Psi, \Phi^0_{N_c} - \Phi^0) &= E^{\mathrm{KS}\prime\prime}(\Phi^0)(\Pi_{N_c}\Psi, \Phi^0_{N_c} - \Phi^0) - E^{\mathrm{KS}\prime}(\Phi^0_{N_c})(\Pi_{N_c}\Psi) + E^{\mathrm{KS}\prime}(\Phi^0)(\Pi_{N_c}\Psi) \\ &\quad + 4\sum_{i=1}^{\mathcal{N}}\sum_{j=1}^{\mathcal{N}}(\lambda^0_{ij,N_c} - \lambda^0_{ij})\int_\Gamma \phi^0_{j,N_c}\Pi_{N_c}\psi_i. \end{aligned} \tag{122}$$

The definition of Π_{N_c} and the fact that $\Psi \in \Phi^{0,\perp\!\!\perp}$ yields

$$\int_\Gamma \phi^0_{j,N_c}\Pi_{N_c}\psi_i = \int_\Gamma(\phi^0_{j,N_c} - \phi^0_j)\psi_i,$$

which finally provides the estimate

$$\begin{aligned}\|\Phi^0_{N_c}-\Phi^0\|^2_{L^2_\#} &= (\Phi^0_{N_c}-\Phi^0, S^0_{N_c}\Phi^0)_{L^2_\#} - a_{\Phi^0}(\Psi, S^0_{N_c}\Phi^0) + a_{\Phi^0}(\Psi-\Pi_{N_c}\Psi, \Phi^0_{N_c}-\Phi^0) \\ &\quad -\frac{1}{4}\left(E^{\mathrm{KS}\prime}(\Phi^0_{N_c})(\Pi_{N_c}\Psi) - E^{\mathrm{KS}\prime}(\Phi^0)(\Pi_{N_c}\Psi) - E^{\mathrm{KS}\prime\prime}(\Phi^0)(\Phi^0_{N_c}-\Phi^0, \Pi_{N_c}\Psi)\right) \\ &\quad +\sum_{i=1}^{\mathcal{N}}\sum_{j=1}^{\mathcal{N}}(\lambda^0_{ij,N_c}-\lambda^0_{ij})\int_\Gamma(\phi^0_{j,N_c}-\phi^0_j)\psi_i. \end{aligned} \tag{123}$$

Using Lemma 4.5, (109), (111) and (120), we infer

$$\begin{aligned}\|\Phi^0_{N_c}-\Phi^0\|_{L^2_\#} &\le C\bigg(\|\Phi^0_{N_c}-\Phi^0\|^2_{L^2_\#} + N_c^{-1}\|\Phi^0_{N_c}-\Phi^0\|_{H^1_\#} + \|\Phi^0_{N_c}-\Phi^0\|^{1+\alpha}_{L^2_\#}\|\Phi^0_{N_c}-\Phi^0\|_{H^1_\#} \\ &\qquad + \|\Lambda^0_{N_c}-\Lambda^0\|_{\mathrm{F}}\|\Phi^0_{N_c}-\Phi^0\|_{L^2_\#}\bigg). \end{aligned} \tag{124}$$

We thus obtain, using (116) and the above estimate, that asymptotically, when N_c goes to infinity,

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

Reasoning as in (114), we obtain that for each $s \ge 1$ such that $\Phi^0 \in \left(H^s_\#(\Gamma)\right)^{\mathcal{N}}$ and each $0 \le r \le s$, there exists a constant C such that

$$\|\Phi^0_{N_c}-\Phi^0\|_{H^r_\#} \le C\, N_c^{-(s-r)}\|\Pi_{N_c}\Phi^0-\Phi^0\|_{H^s_\#}. \tag{125}$$

To proceed further, we need to make an assumption on the regularity of the exchange-correlation potential. In the sequel, we assume that

- either the function $\rho \mapsto e^{\mathrm{LDA}}_{\mathrm{xc}}(\rho)$ is in $C^{[m]}([0,+\infty))$;
- or the function $\rho_c+\rho^0$ is positive everywhere. As it is continuous on $\mathbb{R}^3$, this is equivalent to assuming that there exists a constant $\eta > 0$ such that for all $x \in \mathbb{R}^3$, $\rho_c(x)+\rho^0(x) \ge \eta$.

It follows by standard elliptic regularity arguments that Φ^0 then is in $(H^{m+1/2-\epsilon}_\#(\Gamma))^{\mathcal{N}}$ for any $\epsilon > 0$, and we deduce from (125) that (78) holds true for all $0 \le s < m+1/2$.

Then, following the same lines as in the proof of (38), we obtain the estimates

$$\left|\int_\Gamma V^{\mathrm{Coulomb}}_{\phi^0_{i,N_c}\phi^0_{j,N_c}}(\rho^0_{N_c}-\rho^0)\right| \le C\|\rho^0_{N_c}-\rho^0\|_{H^{-r}_\#},$$

and

$$\left|\int_\Gamma\left(\frac{de^{\mathrm{LDA}}_{\mathrm{xc}}}{d\rho}(\rho_{\mathrm{c}}+\rho^0) - \frac{de^{\mathrm{LDA}}_{\mathrm{xc}}}{d\rho}(\rho_{\mathrm{c}}+\rho^0_{N_c})\right)\phi^0_{i,N_c}\phi^0_{j,N_c}\right| \le c\|\rho^0_{N_c}-\rho^0\|_{H^{-r}_\#},$$

valid for all $0 \leq r < m - 3/2$. Using these estimates in (115), we are lead to

$$|\lambda^0_{ij,N_c} - \lambda^0_{ij}| \leq C \left(\|\Phi^0 - \Phi^0_{N_c}\|^2_{H^1_\#} + \|\rho^0_{N_c} - \rho^0\|_{H^{-r}_\#} \right).$$

Now,

$$\|\rho^0_{N_c} - \rho^0\|_{H^{-r}_\#} = \sup_{w \in H^r_\#(\Gamma)} \frac{\displaystyle\int_\Gamma (\rho^0_{N_c} - \rho^0) w}{\|w\|_{H^r_\#}}.$$

Noticing that

$$\rho^0_{N_c} - \rho^0 = \sum_{i=1}^{\mathcal{N}} |\phi^0_{i,N_c}|^2 - \sum_{i=1}^{\mathcal{N}} |\phi^0_i|^2 = \sum_{i=1}^{\mathcal{N}} (\phi^0_{i,N_c} - \phi^0_i)(\phi^0_{i,N_c} + \phi^0_i),$$

we deduce

$$\|\rho^0_{N_c} - \rho^0\|_{H^{-r}_\#} \leq C \|\Phi^0_{N_c} - \Phi^0\|_{H^{-r}_\#}, \tag{126}$$

since $\Phi^0_{N_c}$ converges, therefore is uniformly bounded in $H^r_\#(\Gamma)$. Thus

$$|\Lambda^0_{N_c} - \Lambda^0| \leq C \left(\|\Phi^0_{N_c} - \Phi^0\|^2_{H^1_\#} + C \|\Phi^0_{N_c} - \Phi^0\|_{H^{-r}_\#} \right). \tag{127}$$

The derivation of estimates for $\|\Phi^0_{N_c} - \Phi^0\|_{H^{-r}_\#}$ follows exactly the same lines as the derivation of the L^2 estimate: starting from the definition

$$\|\Phi^0_{N_c} - \Phi^0\|_{H^{-r}_\#} = \sup_{W \in (H^r_\#(\Gamma))^{\mathcal{N}}} \frac{(W, \Phi^0_{N_c} - \Phi^0)_{L^2_\#}}{\|W\|_{H^r_\#}},$$

and remarking that the solution Ψ_W to the adjoint problem (117) satisfies

$$\|\Psi_W\|_{H^{r+2}_\#} \leq C \|W\|_{H^r_\#},$$

we proceed as in (121) to get

$$\begin{aligned}
(W, \Phi^0_{N_c} - \Phi^0)_{L^2_\#} &= (W, S^0_{N_c}\Phi^0)_{L^2_\#} + (W, W^0_{N_c})_{L^2_\#} \\
&= (W, S^0_{N_c}\Phi^0)_{L^2_\#} + a_{\Phi^0}(\Psi_W, W^0_{N_c}) \\
&= (W, S^0_{N_c}\Phi^0)_{L^2_\#} - a_{\Phi^0}(\Psi_W, S^0_{N_c}\Phi^0) + a_{\Phi^0}(\Psi_W, \Phi^0_{N_c} - \Phi^0) \\
&= (W, S^0_{N_c}\Phi^0)_{L^2_\#} - a_{\Phi^0}(\Psi_W, S^0_{N_c}\Phi^0) + a_{\Phi^0}(\Psi_W - \Pi_{N_c}\Psi_W, \Phi^0_{N_c} - \Phi^0) \\
&\quad + a_{\Phi^0}(\Pi_{N_c}\Psi_W, \Phi^0_{N_c} - \Phi^0),
\end{aligned} \tag{128}$$

that yields

$$\begin{aligned}
\|\Phi^0_{N_c} - \Phi^0\|_{H^{-r}_\#} \leq C \Big(& \|\Phi^0_{N_c} - \Phi^0\|^2_{L^2_\#} + N_c^{-1-r} \|\Phi^0_{N_c} - \Phi^0\|_{H^1_\#} + \|\Phi^0_{N_c} - \Phi^0\|_{H^{-r}_\#} \|\Phi^0_{N_c} - \Phi^0\|_{H^1_\#} \\
& + \|\Lambda^0_{N_c} - \Lambda^0\|_{\mathrm{F}} \|\Phi^0_{N_c} - \Phi^0\|_{H^{-r}_\#} \Big).
\end{aligned} \tag{129}$$

The proof of (78) follows and then we get easily from (127) that

$$\|\Lambda^0_{N_c} - \Lambda^0\|_{\mathrm{F}} \leq C_\epsilon N_c^{-(2m-1-\epsilon)}. \tag{130}$$

Hence (79). Finally, (80) is a straightforward consequence of Lemma 4.6, (73), (96), and (109).

4.4 Numerical results

In order to evaluate the quality of the error bounds obtained in Theorem 4.1, we have performed numerical tests using the Abinit software [9] (freely available online, cf. http://www.abinit.org), whose main program allows one to find the total energy, charge density and electronic structure of systems (molecules and periodic solids) within Density Functional Theory (DFT), using pseudopotentials and a planewave basis.

We have run simulation tests with the Hartree functional (i.e. with $e_{\mathrm{xc}}^{\mathrm{LDA}} = 0$), for which there is no numerical integration error. In this particular case, the problems (74) (solved by Abinit) and (76) (analyzed in Theorem 4.1) are identical.

For Troullier-Martins pseudopotentials, the parameter m in Theorem 4.1 is equal to 5. Therefore, we expect the following error bounds (as functions of the cut-off energy $E_{\mathrm{c}} = \frac{1}{2}\left(\frac{2\pi N_c}{L}\right)^2$)

$$\begin{aligned}
\|\Phi^0_{N_c} - \Phi^0\|_{H^1_\#} &\leq C_{1,\epsilon} E_{\mathrm{c}}^{-2.25+\epsilon}, && (131)\\
\|\Phi^0_{N_c} - \Phi^0\|_{L^2_\#} &\leq C_{2,\epsilon} E_{\mathrm{c}}^{-2.75+\epsilon}, && (132)\\
|\epsilon^0_{i,N_c} - \epsilon^0_i| &\leq C_{3,\epsilon} E_{\mathrm{c}}^{-4.5+\epsilon}, && (133)\\
0 \leq I^{\mathrm{KS}}_{N_c} - I^{\mathrm{KS}} &\leq C_{4,\epsilon} E_{\mathrm{c}}^{-4.5+\epsilon}. && (134)
\end{aligned}$$

The first tests were performed with the Hydrogen molecule (H_2). The nuclei were clamped at the points with cartesian coordinates $r_1 = (-0.7; 0; 0)$ and $r_2 = (0.7; 0; 0)$ (in Bohrs). The simulation cell was a cube of side length $L = 10$ Bohrs. The so-obtained numerical errors are plotted in log-scales in Figures 1 and 2. The second series of tests were performed with the Nitrogen molecule (N_2). The nuclei were clamped at positions $r_1 = (-0.55; 0; 0)$ and $r_2 = (0.55; 0; 0)$ (in Angstroms), and the simulation cell was a cube of side length $L = 6$ Angstroms. The numerical errors for N_2 are plotted in Figures 3, 4 and 5. The reference values for Φ^0, ϵ_i^0 and I^{KS} for both H_2 and N_2 are those obtained for a cut-off energy equal to 500 Hartrees.

These results are in good agreement with the *a priori* error estimates (131)-(134) for both the H_2 and N_2 molecules

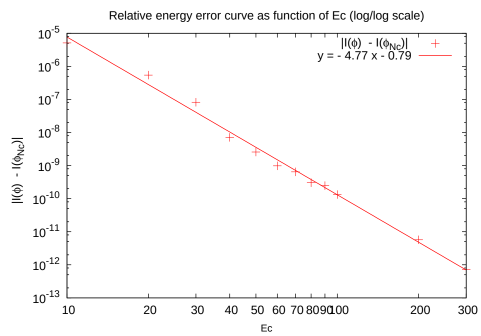

Figure 1: Error on the energy as a function of E_c for H_2

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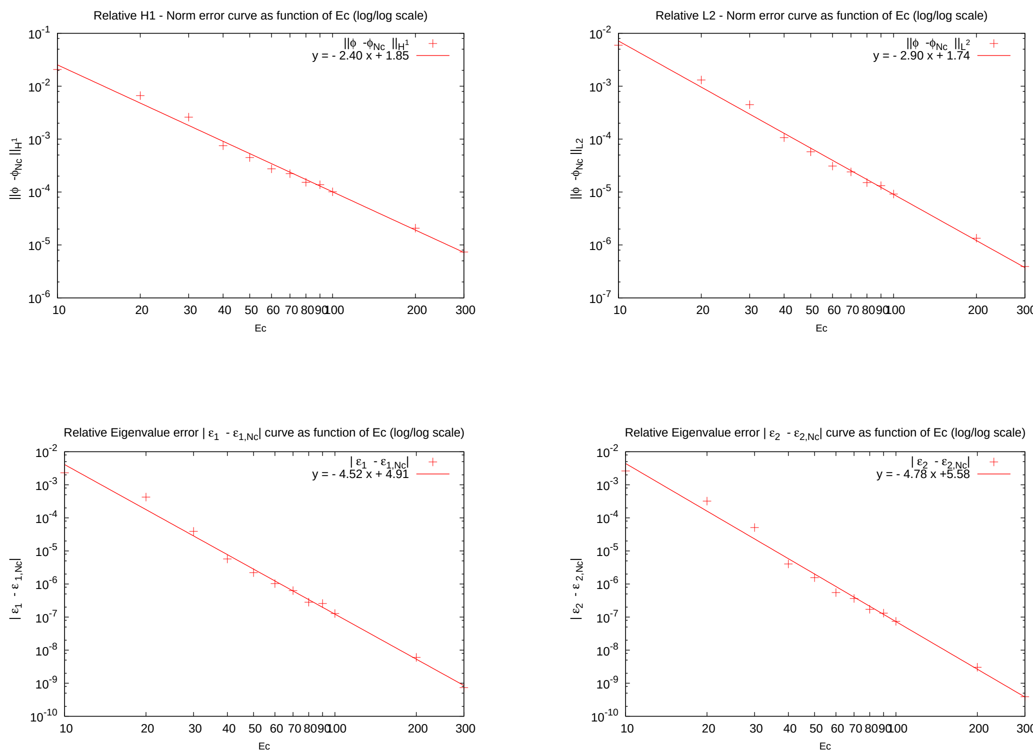

Figure 2: Errors on $\|\Phi^0_{N_c} - \Phi^0\|_{H^1_\#}$ (left) and $\|\Phi^0_{N_c} - \Phi^0\|_{L^2_\#}$ (right) and $|\epsilon^0_{i,N_c} - \epsilon^0_i|$ (bottom) as functions of $E_{\rm c}$ for H_2

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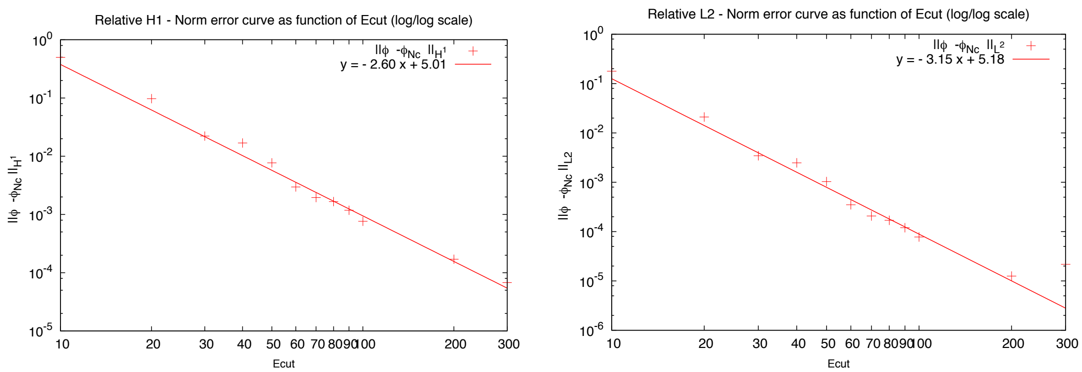

Figure 3: Errors on $\|\Phi^0_{N_c} - \Phi^0\|_{H^1_\#}$ (left) and $\|\Phi^0_{N_c} - \Phi^0\|_{L^2_\#}$ (right) as functions of E_c for N_2

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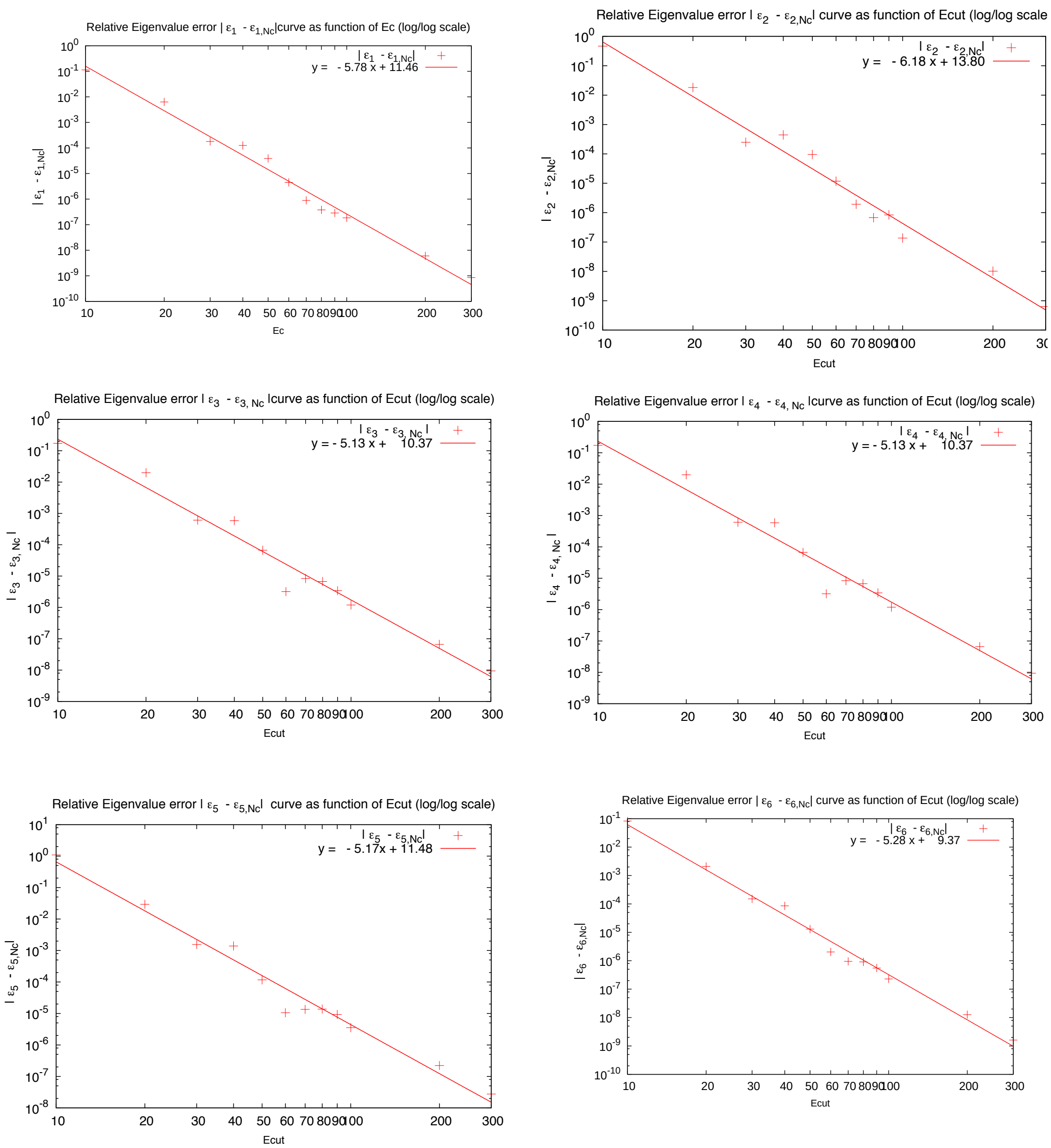

Figure 4: Errors on $|\epsilon^0_{i,N_c} - \epsilon^0_i|$ as functions of E_c for N_2

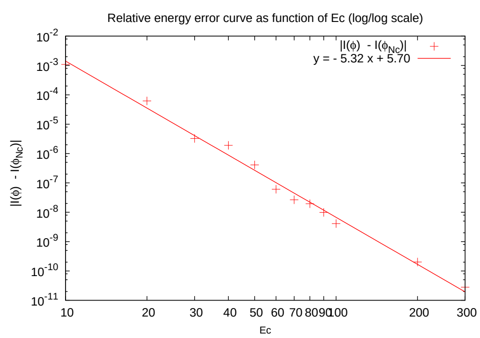

Figure 5: Error on the energy as a function of E_{c} for N_2