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 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 strictly convex with respect to the electronic density, and allows for a comprehensive analysis (Part I). 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 in Part II 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 both the spectral and the pseudospectral discretization methods.

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 category. It is not very much used in practice, but is interesting from a mathematical viewpoint. 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 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 pseudospectral Fourier, more commonly called planewave,
discretization of the periodic version 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 plane wave discretization of orbital-free and Kohn-Sham models. In Section 3, we provide a priori error estimates for the plane wave discretization of the TFW model. Our estimates refine and complement some of the results given in [10]. In Part II, we deal with the Kohn-Sham LDA model.

2 Basic Fourier analysis for plane wave discretization methods

Throughout this article, we denote by $\Gamma$ the simulation cell, by $R$ the periodic lattice, and by $R^*$ the dual lattice. For simplicity, we assume that $\Gamma = [0, L)^3$ ($L > 0$), but our arguments can be straightforwardly extended to rectangular simulation cells ($\Gamma = [0, L_x) \times [0, L_y) \times [0, L_z)$). For $\Gamma = [0, L)^3$, $R$ is the cubic lattice $LZ^3$, and $R^* = 2\pi Z^3$. For $k \in R^*$, we denote by $e_k(x) = |\Gamma|^{-1/2} e^{i k \cdot x}$ the plane wave with wavevector $k$. The family $(e_k)_{k \in R^*}$ forms an orthonormal basis of $L^2_\#(\Gamma, \mathbb{C}) := \{ u \in L^2_{\text{loc}}(\mathbb{R}^3, \mathbb{C}) | u \ R\text{-periodic} \}$, and for all $u \in L^2_\#(\Gamma, \mathbb{C})$,

$$u(x) = \sum_{k \in R^*} \hat{u}_k e_k(x)$$

with

$$\hat{u}_k = (e_k, u)_{L^2_\#} = |\Gamma|^{-1/2} \int_{\Gamma} u(x) e^{-i k \cdot x} dx.$$

In our analysis, we will only consider real valued functions. We therefore introduce the Sobolev spaces of real valued functions

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

$s \in \mathbb{R}$, endowed with the inner products

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

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

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

(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, $r \leq s$, is

$$\Pi_{N_c} v = \sum_{k \in R^* \ | \ |k| \leq \frac{2\pi}{L} N_c} \tilde{v}_k e_k.$$
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 \( r \leq s \), we have for each \( v \in H^s_\#(\Gamma) \),

\[
\|v - \Pi_{N_c} v\|_{H^s_\#} = \min_{v_{N_c} \in V_{N_c}} \|v - v_{N_c}\|_{H^s_\#} \leq \left( \frac{L}{2\pi} \right)^{s-r} N_c^{-(s-r)} \|v - \Pi_{N_c} v\|_{H^s_\#} \\
\leq \left( \frac{L}{2\pi} \right)^{s-r} N_c^{-(s-r)} \|v\|_{H^s_\#}. \tag{2}
\]

For \( N_g \in \mathbb{N} \setminus \{0\} \), we denote by \( \hat{\phi}^{\text{FFT},N_g} \) the discrete Fourier transform on the cartesian grid \( \mathcal{G}_{N_g} := \frac{1}{L} \mathbb{Z}^3 \) of the function \( \phi \in C^0_\#(\Gamma) \). Recall that if \( \phi = \sum_{k \in \mathbb{R}^*} \hat{\phi}_k e^i \) \( \epsilon \in G^0_\#(\Gamma) \), the discrete Fourier transform of \( \phi \) is the \( N_g \mathbb{R}^* \)-periodic sequence \( \hat{\phi}^{\text{FFT},N_g} = (\hat{\phi}^{\text{FFT},N_g}_k)_{k \in \mathbb{R}^*} \) where

\[
\hat{\phi}^{\text{FFT},N_g}_k = \frac{1}{N_g^3} \sum_{x \in \mathcal{N}_g \cap \Gamma} \phi(x) e^{-i k \cdot x} = |\Gamma|^{-1/2} \sum_{k \in \mathbb{R}^*} \hat{\phi}_k e^{i \pi N_g / L} + e^{-i \pi N_g y / L} \quad (N_g \text{ odd}),
\]

\[
\hat{\phi}^{\text{FFT},N_g}_k = \frac{1}{N_g^3} \sum_{x \in \mathcal{N}_g \cap \Gamma} \phi(x) e^{-i k \cdot x} = |\Gamma|^{-1/2} \sum_{k \in \mathbb{R}^*} \hat{\phi}_k e^{i \pi N_g / L} \quad (N_g \text{ even}),
\]

\((W^{1D}_{N_g} \in C^\infty([0, L]) \text{ and dim}(W^{1D}_{N_g}) = N_g)\), and \( W^{3D}_{N_g} = W^{1D}_{N_g} \otimes W^{1D}_{N_g} \otimes W^{1D}_{N_g} \). Note that \( W^{3D}_{N_g} \) is a subspace of \( H^s_\#(\Gamma) \) of dimension \( N_g^3 \), for all \( s \in \mathbb{R} \), and that if \( N_g \) is odd,

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

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

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

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

\[
\mathcal{I}_{N_g}(\phi) = |\Gamma|^{1/2} \sum_{k \in \mathbb{R}^*} |k|\infty \leq \frac{2\pi}{L} (\frac{N_g - 1}{2}) \hat{\phi}^{\text{FFT},N_g}_k e_k \quad (N_g \text{ odd}).
\]

It is easy to check that if \( \phi \) 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 real-valued function of \( C_0^0(\Gamma) \) and \( v_{N_c} \) and \( w_{N_c} \) be two functions of \( V_{N_c} \). Then
   \[
   \int_\Gamma I_{N_g}(Vv_{N_c}, w_{N_c}) = \int_\Gamma I_{N_g}(V)v_{N_c}, w_{N_c}
   \]  
   \[ (5) \]
   \[
   \left| \int_\Gamma I_{N_g}(V|v_{N_c}|^2) \right| \leq \|V\|_{L^\infty} \|v_{N_c}\|_{L^2_{\#}}^2
   \]  
   \[ (6) \]

2. Let \( s > 3/2, 0 \leq r \leq s \), and \( V \) a function of \( H_{\#}^s(\Gamma) \). Then,
   \[
   \| (1 - I_{N_g})(V) \|_{H^r_{\#}} \leq C_{r,s}N_g^{-s} \| V \|_{H^r_{\#}}
   \]  
   \[ (7) \]
   \[
   \left\| \Pi_{2N_c}(I_{N_g}(V)) \right\|_{L^2_{\#}}^2 \leq \left( \int_\Gamma I_{N_g}(|V|^2) \right)^{1/2}
   \]  
   \[ (8) \]
   \[
   \left\| \Pi_{2N_c}(I_{N_g}(V)) \right\|_{H^r_{\#}} \leq (1 + C_{s,s}) \| V \|_{H^r_{\#}}
   \]  
   \[ (9) \]
   for constants \( C_{r,s} \) independent of \( V \). Besides if there exists \( m > 3 \) and \( C \in \mathbb{R}_+ \) such that \( |\hat{V}_k| \leq C|k|^{-m} \), then there exists a constant \( C_V \) independent of \( N_c \) and \( N_g \) such that
   \[
   \|\Pi_{2N_c}(1 - I_{N_g})(V)\|_{H^r} \leq C_V N_c^{r+3/2} N_g^{-m}
   \]  
   \[ (10) \]

3. Let \( \phi \) is 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 \( v_{N_c} \in V_{N_c} \),
   \[
   \left| \int_\Gamma I_{N_g}(\phi(|v_{N_c}|^2)) \right| \leq C_\phi \left( |\Gamma| + \|v_{N_c}\|_{L^4_{\#}}^4 \right).
   \]  
   \[ (11) \]

Proof For \( z_{2N_c} \in V_{2N_c} \), it holds
   \[
   \int_\Gamma I_{N_g}(Vz_{2N_c}) = \sum_{x \in G_{N_g} \cap \Gamma} V(x)z_{2N_c}(x)
   \]
   \[
   = \sum_{x \in G_{N_g} \cap \Gamma} (I_{N_g}(V))(x)z_{2N_c}(x)
   \]
   \[
   = \int_\Gamma I_{N_g}(V)z_{2N_c}
   \]  
   \[ (12) \]
   since \( I_{N_g}(V)z_{2N_c} \in V_{4N_c} \). 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
   \[
   \left| \int_\Gamma I_{N_g}(V|v_{N_c}|^2) \right| = \left| \sum_{x \in G_{N_g} \cap \Gamma} \left( \frac{L}{N_g} \right)^3 V(x)|v_{N_c}(x)|^2 \right|
   \]
   \[
   \leq \|V\|_{L^\infty} \left| \sum_{x \in G_{N_g} \cap \Gamma} \left( \frac{L}{N_g} \right)^3 |v_{N_c}(x)|^2 \right|
   \]
   \[
   = \|V\|_{L^\infty} \int_\Gamma |v_{N_c}|^2.
   \]
Hence (6). The estimate (7) is proved in [4]. To prove (8), we notice that
\[ \| \Pi_{2N_c}(I_{N_g}(V)) \|_{L^2}^2 \leq \| I_{N_g}(V) \|_{L^2}^2 \]
\[ = \int_{\Gamma} (I_{N_g}(V))^*(I_{N_g}(V)) \]
\[ = \sum_{x \in \mathcal{G} \cap \Gamma} (I_{N_g}(V))(x)^*(I_{N_g}(V))(x) \]
\[ = \sum_{x \in \mathcal{G} \cap \Gamma} |V(x)|^2 \]
\[ = \int_{\Gamma} I_{N_g}(|V|^2). \]

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
\[ \Pi_{2N_c}(I_{N_g}(V)) = |\mathcal{G}|^{1/2} \sum_{k \in \mathcal{R}^+ \mid |k| \leq \frac{2\pi}{N_c}} \hat{\tilde{V}}_{k}^{\text{FFT}, N_c} e^{i k} \]
\[ = \sum_{k \in \mathcal{R}^+ \mid |k| \leq \frac{4\pi}{N_c}} \left( \sum_{K \in \mathcal{R}^+ \{0\}} \hat{\tilde{V}}_{k+N_g K} \right) e^{i k}. \]

From (13), we obtain
\[ \| \Pi_{2N_c}(1 - I_{N_g})(V) \|_{H^s}^2 = \sum_{k \in \mathcal{R}^+ \mid |k| \leq \frac{4\pi}{N_c}} (1 + |k|^2)^s \left( \sum_{K \in \mathcal{R}^+ \{0\}} \hat{\tilde{V}}_{k+N_g K} \right)^2 \]
\[ = \left( \sum_{k \in \mathcal{R}^+ \mid |k| \leq \frac{4\pi}{N_c}} (1 + |k|^2)^s \right) \max_{k \in \mathcal{R}^+ \mid |k| \leq \frac{4\pi}{N_c}} \left( \sum_{K \in \mathcal{R}^+ \{0\}} \hat{\tilde{V}}_{k+N_g K} \right)^2. \]

On the one hand,
\[ \sum_{k \in \mathcal{R}^+ \mid |k| \leq \frac{4\pi}{N_c}} (1 + |k|^2)^s \sim \frac{32\pi}{N_c} \frac{32\pi}{2s+3} \left( \frac{4\pi}{L} \right)^{2s+3} L^{2s+3}, \]
and on the other hand, we have for each \( k \in \mathcal{R}^+ \) such that \( |k| \leq \frac{4\pi}{N_c} \),
\[ \left| \sum_{K \in \mathcal{R}^+ \{0\}} \hat{\tilde{V}}_{k+N_g K} \right| \leq C \sum_{K \in \mathcal{R}^+ \{0\}} \frac{1}{|k + N_g K|^m} \]
\[ \leq C_0 \left( \frac{L}{2\pi} \right)^m N_{g}^{-m}, \]
where
\[ C_0 = \max_{y \in \mathcal{R}^+ \mid |y| \leq 1/2} \sum_{K \in \mathbb{Z}^2 \{0\}} \frac{1}{|y - K|^m}. \]
The estimate (10) then easily follows. Let us finally prove (11). Using (3) and (4), we have

\[ \left| \int_{\Gamma} I_{N_g}(\phi(|v_N|^2)) \right| = \left| \sum_{x \in \mathbb{Z}^3 \cap \Gamma} \left( \frac{L}{N_g} \right)^3 \phi(|v_N(x)|^2) \right| \leq C_{\phi} \left| \sum_{x \in \mathbb{Z}^3 \cap \Gamma} \left( \frac{L}{N_g} \right)^3 (1 + |v_N(x)|^4) \right| = C_{\phi} \int_{\Gamma} (1 + |v_N|^4) = C_{\phi} \left( |\Gamma| + \|v_N\|_{L^4}^4 \right). \]

This completes the proof of Lemma 2.1. □

3 Thomas-Fermi-von-Weizsäcker 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 \( N \) the number of electrons in the simulation cell and by

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

the set of admissible densities, the TFW problem reads

\[ I_{\text{TFW}} = \inf \left\{ E_{\text{TFW}}(\rho), \rho \in \mathcal{R}_N \right\}, \]

where

\[ E_{\text{TFW}}(\rho) = \frac{C_W}{2} \int_{\Gamma} |\nabla \sqrt{\rho}|^2 + C_{\text{TF}} \int_{\Gamma} \rho^{5/3} + \int_{\Gamma} \rho V_{\text{ion}} + \frac{1}{2} D_{\Gamma}(\rho, \rho). \]

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

\[ D_{\Gamma}(\rho, \rho') := 4\pi \sum_{k \in \mathbb{R}^* \setminus \{0\}} |k|^{-2} \rho_k^* \rho_k. \]

We finally make the assumption that \( V_{\text{ion}} \) is a periodic potential such that

\[ \exists m > 3, \ C \geq 0 \text{ s.t. } \forall k \in \mathbb{R}^*, \ |\tilde{V}_{\text{ion}}^k| \leq C |k|^{-m}. \]

Note that this implies that \( V_{\text{ion}} \) is in \( H^{m-3/2-\epsilon}_{\#}(\Gamma) \) for all \( \epsilon > 0 \). It is convenient to reformulate the TFW model in terms of \( v = \sqrt{\rho} \). It can be seen that

\[ I_{\text{TFW}} = \inf \left\{ E_{\text{TFW}}(v), v \in H^1_{\#}(\Gamma), \int_{\Gamma} |v|^2 = N \right\}, \]

where

\[ E_{\text{TFW}}(v) = \frac{C_W}{2} \int_{\Gamma} |\nabla v|^2 + C_{\text{TF}} \int_{\Gamma} |v|^{10/3} + \int_{\Gamma} V_{\text{ion}} |v|^2 + \frac{1}{2} D_{\Gamma}(|v|^2, |v|^2). \]
It is well known [6] that (14) has a unique minimizer $\rho^0$, and that the minimizers of (16) are $u$ and $-u$, where $u = \sqrt{\rho^0}$. Besides, the function $u$ is in $H^{m+1/2-\epsilon}_\#(\Gamma)$ for any $\epsilon > 0$ (and therefore in $C^2_\#(\Gamma)$ since $m + 1/2 - \epsilon > 7/2$ for $\epsilon$ small enough), is positive everywhere in $\Gamma$ and satisfies the Euler equation
\[
-CW^2 \Delta u + \left(\frac{5}{3} C_{TF} u^{4/3} + V_{\text{ion}} + V_{\text{Coulomb}}^{\rho} \right) u = \lambda u
\]
for some $\lambda \in \mathbb{R}$, where
\[
V_{\rho}^{\text{Coulomb}}(x) = 4\pi \sum_{k \in \mathbb{R}^* \setminus \{0\}} |k|^{-2} \rho_k \epsilon_k(x)
\]
is the periodic Coulomb potential generated by the periodic charge distribution $\rho$. Recall that $V_{\rho}^{\text{Coulomb}}$ can also be defined as the unique solution in $H^1_\#(\Gamma)$ to
\[
\begin{align*}
-\Delta V_{\rho}^{\text{Coulomb}} &= 4\pi \left( \rho - |\Gamma|^{-1} \int_\Gamma \rho \right) \\
\int_\Gamma \rho V_{\rho}^{\text{Coulomb}} &= 0.
\end{align*}
\]
The planewave discretization of the TFW model is obtained by choosing
\begin{enumerate}
\item an energy cut-off $E_c > 0$ or, equivalently, a finite dimensional Fourier space $V_{N_c}$, the integer $N_c$ being related to $E_c$ through the relation $N_c := \lfloor \sqrt{2E_c} L/2\pi \rfloor$;
\item a cartesian grid $G_{N_g}$ with step size $L/N_g$ where $N_g \in \mathbb{N}^*$ is such that $N_g \geq 4N_c + 1$,
\end{enumerate}
and by considering the finite dimensional minimization problem
\[
I_{N_c,N_g}^{\text{TFW}} = \inf \left\{ E_{N_g}^{\text{TFW}}(v_{N_c}), \; v_{N_c} \in V_{N_c}, \; \int_\Gamma |v_{N_c}|^2 = \mathcal{N} \right\},
\]
where
\[
E_{N_g}^{\text{TFW}}(v_{N_c}) = \frac{C_W}{2} \int_\Gamma |\nabla v_{N_c}|^2 + C_{TF} \int_\Gamma \mathcal{I}_{N_g}(|v_{N_c}|^{10/3}) + \int_\Gamma \mathcal{I}_{N_g}(V_{\text{ion}})|v_{N_c}|^2 + \frac{1}{2} D_{\Gamma}(|v_{N_c}|^2,|v_{N_c}|^2),
\]
and $\mathcal{I}_{N_g}$ denoting the interpolation operator introduced in the previous section. The Euler equation associated with (17) can be written as a nonlinear eigenvalue problem
\[
\forall v_{N_c} \in V_{N_c}, \quad \langle \left( \overline{H}_{\rho}^{N_g} \right) u_{N_c,N_g}, v_{N_c} \rangle_{H^{-1}_\# \mathcal{H}_\#^2} = 0
\]
where we have denoted by
\[
\overline{H}_{\rho}^{N_g} = -\frac{C_W}{2} \Delta + \mathcal{I}_{N_g} \left( \frac{5}{3} C_{TF} \rho^{2/3} + V_{\text{ion}} \right) + V_{\rho}^{\text{Coulomb}}
\]
the pseudo-spectral TFW Hamiltonian associated with the density $\rho$, and by $\lambda_{N_c,N_g}$ the Lagrange multiplier of the constraint $\int_\Gamma |v_{N_c}|^2 = \mathcal{N}$. We therefore have
\[
-CW^2 \Delta u_{N_c,N_g} + \Pi_{N_c} \left( \mathcal{I}_{N_g} \left( \frac{5}{3} C_{TF} |u_{N_c,N_g}|^{4/3} + V_{\text{ion}} \right) + V_{u_{N_c,N_g}}^{\text{Coulomb}} \right) u_{N_c,N_g} = \lambda_{N_c,N_g} u_{N_c,N_g},
\]
Under the condition that $N_g \geq 4N_c + 1$, we have for all $\phi \in C^0_\#(\Gamma)$,

$$\forall (k, l) \in \mathbb{R}^* \times \mathbb{R}^* \text{ s.t. } |k|, |l| \leq \frac{2\pi}{L}N_c, \quad T_{N_g}(\phi) e_k e_l = \tilde{\phi}_{N_g}^{\text{FFT}}(k, l),$$

so that, $H_{u_{N_c, N_g}}$ is defined on $V_{N_c}$ by the Fourier matrix

$$[\tilde{H}_{u_{N_c, N_g}}]_{kl}^{N_g} = \frac{C_W}{2}|k|^2\delta_{kl} + \frac{5}{3}C_{\text{TP}}^{\text{FFT}}[u_{N_c, N_g}]^{4/3}_{kl} + (V^{\text{ion}})^{\text{FFT}, N_g}_{kl} + 4\pi\left(\frac{|u_{N_c, N_g}|^2}{|k - l|^2}\right)(1 - \delta_{kl}),$$

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)

$$T_{N_c}^{\text{FW}} = \inf \left\{ E^{\text{FW}}(u_{N_c}), \; u_{N_c} \in V_{N_c}, \; \int_{\Gamma} |u_{N_c}|^2 = N \right\}. \quad (18)$$

Any minimizer $u_{N_c}$ to (18) satisfies the elliptic equation

$$-\frac{C_W}{2}\Delta u_{N_c} + \Pi_{N_c} \left[ \frac{5}{3}C_{\text{TP}} |u_{N_c}|^{4/3}u_{N_c} + V^{\text{ion}}u_{N_c} + V^{\text{Coulomb}}_{u_{N_c}} \right] = \lambda_{N_c} u_{N_c}, \quad (19)$$

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

**Theorem 3.1** For each $N_c \in \mathbb{N}$, we denote by $u_{N_c}$ a minimizer to (18) 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 (17) 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

$$\|u_{N_c} - u\|^{s}_{H^{s}_{\#}} \leq C_sN_c^{-(m-s+1/2-\epsilon)}; \quad (20)$$

$$|\lambda_{N_c} - \lambda| \leq C\epsilon N_c^{(2m-1-\epsilon)}; \quad (21)$$

$$\gamma\|u_{N_c} - u\|^2_{H^{s}_{\#}} \leq T^{\text{FW}, N_c}_{\text{FW}, N_g} - T^{\text{FW}, N_c}_{\text{FW}} \leq C\|u_{N_c} - u\|^2_{H^{s}_{\#}}; \quad (22)$$

$$\|u_{N_c, N_g} - u_{N_c}\|^{s}_{H^{s}_{\#}} \leq C_sN_c^{3/2+(s-1)\epsilon}N_g^{-m}; \quad (23)$$

$$|\lambda_{N_c, N_g} - \lambda_{N_c}| \leq C\epsilon^{3/2}N_g^{-m}; \quad (24)$$

$$\|T^{\text{FW}, N_c}_{\text{FW}, N_g} - T^{\text{FW}, N_c}_{\text{FW}}\| \leq C\epsilon^{3/2}N_g^{-m}; \quad (25)$$

for all $-m + 3/2 < s < m + 1/2$ and for some constants $\gamma > 0$, $C \geq 0$ 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 [9], which are used to perform multimillion atom DFT calculations. Some of these models however are not well posed (the energy functional is not bounded below [1]), 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.

**Proof** of Theorem 3.1 The estimates (20), (21) and (22) originate from arguments already introduced in [2]. 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 [2] is the presence of the Coulomb term $D_T(|v|^2, |u|^2)$, for which the following estimates are available:

$$0 \leq D_T(\rho, \rho) \leq C\|\rho\|_{L^2_\#}^2, \quad \text{for all } \rho \in L^2_\#(\Gamma),$$

$$|D_T(\rho, \rho)| \leq C\|\rho\|_{L^2_\#}^2, \quad \text{for all } \rho \in L^2_\#(\Gamma),$$

$$|D_T(\rho, \rho)| \leq C\|\rho\|_{L^2_\#}^2, \quad \text{for all } \rho \in L^2_\#(\Gamma),$$

$$\|V_{\rho}^{\text{Coulomb}}\|_{L^\infty} \leq C\|\rho\|_{L^2_\#}, \quad \text{for all } \rho \in L^2_\#(\Gamma),$$

$$\|V_{\rho}^{\text{Coulomb}}\|_{H^{\infty+2}_\#} \leq C\|\rho\|_{H^{6}_\#}, \quad \text{for all } \rho \in H^{6}_\#(\Gamma).$$

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

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

$$|f(t_2) - f(t_1)| \leq \frac{70}{27} C_{TF} \max(t_1^{1/3}, t_2^{1/3}) |t_2 - t_1|^2. \quad (31)$$

The first and second derivatives of $E^{\text{TFW}}$ at the unique positive minimizer $u = \sqrt{\rho^3}$ of (16) are respectively given by

$$\langle E^{\text{TFW}}(u), v \rangle_{H^{-1}_\#, H^1_\#} = 2 \langle H_{\rho} u, v \rangle$$

$$\langle E^{\text{TFW}}(u), v \rangle_{H^{-2}_\#, H^0_\#} = 2 \langle H_{\rho} v, w \rangle + 4D_T(\rho, \rho) + 4 \int_{\Gamma} F(|u|^2) |u|^2 vw,$$

where we have denoted by

$$H_{\rho} = -\frac{C_W}{2} \Delta + f(\rho) + V^{\text{ion}} + V_{\rho}^{\text{Coulomb}}$$

the TFW Hamiltonian associated with the density $\rho$. We recall (see [6] and the proof of Lemma 2 in [2]) that (i) $u \in H^{m+1/2}_\#(\Gamma) \cap C^2(\Gamma)$ for each $\epsilon > 0$, (ii) $u > 0$ on $\mathbb{R}^3$, (iii) $\lambda$ is the ground state eigenvalue of $H_{\rho}$ and is non-degenerate. Using (26), (27) and the fact that $f' > 0$ on $(0, +\infty)$, we can then show (see the proof of Lemma 1 in [2]) that there exist $\beta > 0$, $\gamma > 0$ and $M \geq 0$ such that for all $v \in H^1_\#(\Gamma)$,

$$0 \leq \langle (H_{\rho} - \lambda)v, v \rangle_{H^{-1}_\#, H^1_\#} \leq M \|v\|_{H^1_\#}^2 \quad (32)$$

$$\beta \|v\|_{H^1_\#}^2 \leq \langle (E^{\text{TFW}}(u) - 2\lambda)v, v \rangle_{H^{-1}_\#, H^1_\#} \leq M \|v\|_{H^1_\#}^2 \quad (33)$$

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

$$\gamma \|v - u\|_{H^1_\#}^2 \leq \langle (H_{\rho} - \lambda)(v - u), (v - u) \rangle_{H^{-1}_\#, H^1_\#.} \quad (34)$$

Remark that

$$E^{\text{TFW}}(u_{N_c}) - E^{\text{TFW}}(u) = \langle (H_{\rho} - \lambda)(u_{N_c} - u), (u_{N_c} - u) \rangle_{H^{-1}_\#, H^1_\#}$$

$$+ \frac{1}{2} D_T(|u_{N_c}|^2 - |u|^2, |u_{N_c}|^2 - |u|^2)$$

$$+ \int_{\Gamma} F(|u_{N_c}|^2) - F(|u|^2) - f(|u|^2)(|u_{N_c}|^2 - |u|^2) \quad (35)$$
and using (34), the positivity of the bilinear form $D_{\Gamma}$, and the convexity of the function $F$, we obtain that

$$I_{N_{c}}^{TFW} - I_{N_{c}}^{TFW} = E^{TFW}(u_{N_{c}}) - E^{TFW}(u) \geq \gamma \|u_{N_{c}} - u\|_{H_{\#}^{1}}^{2}.$$  

For each $N_{c} \in \mathbb{N}$, $\vec{u}_{N_{c}} = N^{1/2} \Pi_{N_{c}} u/\|\Pi_{N_{c}} u\|_{L_{\#}^{2}}$ satisfies $\vec{u}_{N_{c}}$ and $\|\vec{u}_{N_{c}}\|_{L_{\#}^{2}} = N^{1/2}$, and the sequence $(\vec{u}_{N_{c}})_{N_{c} \in \mathbb{N}}$ converges to $u$ in $H_{\#}^{m+1/2-\epsilon}(\Gamma)$ for each $\epsilon > 0$. As the functional $E^{TFW}$ is continuous on $H_{\#}^{1}(\Gamma)$, we have

$$\|u_{N_{c}} - u\|_{H_{\#}^{1}}^{2} \leq \gamma^{-1} (I_{N_{c}}^{TFW} - I_{N_{c}}^{TFW}) \leq \gamma^{-1} (E^{TFW}(\vec{u}_{N_{c}}) - E^{TFW}(u)) \xrightarrow{N_{c} \to \infty} 0.$$  

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

$$\lambda_{N_{c}} = N^{-1} \left[ \frac{1}{2} \int_{\Gamma} |\nabla u_{N_{c}}|^{2} + \int_{\Gamma} f(|u_{N_{c}}|^{2})|u_{N_{c}}|^{2} + \int_{\Gamma} V^{\text{ion}}|u_{N_{c}}|^{2} + D_{\Gamma}(|u_{N_{c}}|^{2}, |u_{N_{c}}|^{2}) \right] \xrightarrow{N_{c} \to \infty} \lambda.$$  

As $f(|u_{N_{c}}|^{2})u_{N_{c}} + V^{\text{ion}}u_{N_{c}} + V^{\text{Coulomb}}u_{N_{c}}$ is bounded in $L_{\#}^{2}(\Gamma)$, uniformly in $N_{c}$, we deduce from (19) that the sequence $(u_{N_{c}})_{N_{c} \in \mathbb{N}}$ is bounded in $H_{\#}^{2}(\Gamma)$, hence in $L^{\infty}(\Gamma)$. Now

$$\Delta (u_{N_{c}} - u) = 2C_{W}^{-1} \left[ \Pi_{N_{c}} \left( f(|u_{N_{c}}|^{2})u_{N_{c}} - f(|u|^{2})u + V^{\text{ion}}(u_{N_{c}} - u) + \lambda_{N_{c}} (u_{N_{c}} - u) - (\lambda_{N_{c}} - \lambda)u \right) \right].$$  

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 $C_{\#}^{0,1/2}(\Gamma)$. By a simple bootstrap argument, one can see that the convergence also holds in $H_{\#}^{m+1/2-\epsilon}(\Gamma)$ for each $\epsilon > 0$. The upper bound in (22) is obtained from (35), remarking that

$$0 \leq \int_{\Gamma} F(|u_{N_{c}}|^{2}) - F(|u|^{2}) - f(|u|^{2})(|u_{N_{c}}|^{2} - |u|^{2})$$

$$\leq \frac{35}{9} C_{TF} \int_{\Gamma} \max(|u_{N_{c}}|^{4/3}, |u|^{4/3})|u_{N_{c}} - u|^{2}$$

$$\leq \frac{35}{9} C_{TF} \left( \max_{N_{c} \in \mathbb{N}} \|u_{N_{c}}\|_{L^{\infty}} \right)^{4/3} \|u_{N_{c}} - u\|_{L_{\#}^{2}}^{2}$$

and that

$$0 \leq D_{\Gamma}(|u_{N_{c}}|^{2} - |u|^{2}, |u_{N_{c}}|^{2} - |u|^{2}) \leq C \|u_{N_{c}}|^{2} - |u|^{2}\|_{L_{\#}^{2}}$$

$$\leq 4C \left( \max_{N_{c} \in \mathbb{N}} \|u_{N_{c}}\|_{L^{\infty}} \right)^{2} \|u_{N_{c}} - u\|_{L_{\#}^{2}}^{2}.$$
The uniqueness of \( u_N \) for \( N \), large enough can then be checked as follows. First, \( (u_N, \lambda_N) \) satisfies the variational equation
\[
\forall u_N \in V_N, \quad \langle (H_{|u_N|^2} - \lambda_N)u_N, v_N \rangle_{H^{-1}_\#H^1_\#} = 0.
\]

Therefore \( \lambda_N \) is the variational approximation in \( V_N \) of some eigenvalue of \( H_{|u_N|^2} \). As \( (u_N)_{N \in \mathbb{N}} \) converges to \( u \) in \( L^\infty(\Gamma) \), \( H_{|u_N|^2} - H_{\rho}^0 \) converges to 0 in operator norm. Consequently, the \( n^{th} \) eigenvalue of \( H_{|u_N|^2} \) converges to the \( n^{th} \) eigenvalue of \( H_{\rho}^0 \) when \( N \) goes to infinity, the convergence being uniform in \( n \). Together with the fact that the sequence \( (\lambda_N)_{N \in \mathbb{N}} \) converges to \( \lambda \), the non-degenerate ground state eigenvalue of \( H_{\rho}^0 \), this implies that for \( N \) large enough, \( \lambda_N \) is the ground state eigenvalue of \( H_{|u_N|^2} \) in \( V_N \) and for all \( v_N \in V_N \) such that \( \|v_N\|_{L^2_\#} = N^{1/2} \) and \( (v_N, u_N)_{L^2_\#} \geq 0 \),
\[
E^{TFW}(v_N) - E^{TFW}(u_N) = \langle (H_{|u_N|^2} - \lambda_N)(v_N - u_N), (v_N - u_N) \rangle_{H^{-1}_\#H^1_\#} + \frac{1}{2} D_1(|v_N|^2 - |u_N|^2, |v_N|^2 - |u_N|^2)
+ \int_\Gamma F(|v_N|^2) - F(|u_N|^2) - f(|u_N|^2)(|v_N|^2 - |u_N|^2)
\geq \langle (H_{|u_N|^2} - \lambda_N)(v_N - u_N), (v_N - u_N) \rangle_{H^{-1}_\#H^1_\#}
\geq \frac{\gamma}{2} \|v_N - u_N\|_{H^1_\#}^2.
\] (36)

It easily follows that for \( N \) large enough, (18) has a unique minimizer \( u_N \) such that \( (u_N, u)_{L^2_\#} \geq 0 \).

Let us now establish the rates of convergence of \( |\lambda_N - \lambda| \) and \( \|u_N - u\|_{H^\#_\#} \). First,
\[
\lambda_N - \lambda = N^{-1} \left[ \langle (H_{|u|^2} - \lambda)(u_N - u), (u_N - u) \rangle_{H^{-1}_\#H^1_\#} + \int_\Gamma w_N(u_N - u) \right]
\]
with
\[
w_N = \frac{f(|u_N|^2) - f(|u|^2)}{u_N - u} |u_N|^2 + V_{Coulomb}(u_N + u).
\]

We know that the sequence \( (u_N)_{N \in \mathbb{N}} \) converges to \( u \) in \( H^{m+1/2-\epsilon}_\#(\Gamma) \) and that \( u > 0 \) in \( \mathbb{R}^3 \). Consequently, for \( N \) large enough, the function \( u_N \) (which is continuous and \( R \)-periodic) is bounded away from 0, uniformly in \( N \). As \( f \in C^\infty((0, +\infty)) \), the function \( w_N \) is uniformly bounded in \( H^{m-3/2-\epsilon}_\#(\Gamma) \) (at least for \( N \) 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 \( N \) large enough,
\[
|\lambda_N - \lambda| \leq C_r \left( \|u_N - u\|_{H^1_\#} + \|u_N - u\|_{H^{r-\epsilon}_\#} \right).
\] (37)

In order to evaluate the \( H^{1/2}_\# \)-norm of the error \( (u_N - u) \), we first notice that
\[
\forall u_N \in V_N, \quad \|u_N - u\|_{H^{1/2}_\#} \leq \|u_N - v_N\|_{H^1_\#} + \|v_N - u\|_{H^{1/2}_\#},
\] (38)
and that
\[
\|u_N - v_N\|_{H^{1/2}_\#} \leq \beta^{-1} \langle (E^{TFW''}(u) - 2\lambda)(u_N - v_N), (u_N - v_N) \rangle_{H^{-1}_\#H^1_\#}
\geq \beta^{-1} \langle (E^{TFW''}(u) - 2\lambda)(u_N - u), (u_N - v_N) \rangle_{H^{-1}_\#H^1_\#}
+ \langle (E^{TFW''}(u) - 2\lambda)(u - v_N), (u_N - v_N) \rangle_{H^{-1}_\#H^1_\#}.
\] (39)
For all $z_{N_c} \in V_{N_c}$,
$$
\langle (E_{TFW}''(u) - 2\lambda)(u_{N_c} - u), z_{N_c} \rangle_{H_{\#}^{-1}, H_{\#}^1}
$$
$$
= -2 \int_{\Gamma} f(|u_{N_c}|^2)u_{N_c} - f(|u|^2)u - 2f'(|u|^2)|u|^2(u_{N_c} - u)z_{N_c}
- 2D_T((u_{N_c} - u)(u_{N_c} + u), (u_{N_c} - u)z_{N_c}) - 2D_T((u_{N_c} - u)^2, uz_{N_c})
+ 2(\lambda N_{c} - \lambda) \int_{\Gamma} u_{N_c}z_{N_c}.
$$
(40)

On the other hand, we have for all $v_{N_c} \in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_{\#}} = N^{1/2}$,
$$
\int_{\Gamma} u_{N_c}(u_{N_c} - v_{N_c}) = N - \int_{\Gamma} u_{N_c}v_{N_c} = \frac{1}{2}\|u_{N_c} - v_{N_c}\|_{L^2_{\#}}^2.
$$
Using (28), (31), (37) with $r = 0$ and the above equality, we therefore obtain for all $v_{N_c} \in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_{\#}} = N^{1/2}$,
$$
\left| \langle (E_{TFW}''(u) - 2\lambda)(u_{N_c} - u), (u_{N_c} - v_{N_c}) \rangle_{H_{\#}^{-1}, H_{\#}^1} \right|
\leq C \left( \|u_{N_c} - u\|_{H_{\#}^1}^2 \|u_{N_c} - v_{N_c}\|_{H_{\#}^1}^2
+ \|u_{N_c} - u\|_{H_{\#}^1}^2 + \|v_{N_c} - u\|_{H_{\#}^1}^2 \right) \|u_{N_c} - v_{N_c}\|_{L^2_{\#}}^2.
$$
(41)

Therefore, for $N_c$ large enough, we have for all $v_{N_c} \in V_{N_c}$ such that $\|v_{N_c}\|_{L^2_{\#}} = N^{1/2}$,
$$
\|u_{N_c} - v_{N_c}\|_{H_{\#}^1} \leq C \left( \|u_{N_c} - u\|_{H_{\#}^1}^2 + \|v_{N_c} - u\|_{H_{\#}^1}^2 \right).
$$
Together with (38), this shows that there exists $N \in \mathbb{N}$ and $C \in \mathbb{R}^+$ such that for all $N_c \geq N$,
$$
\forall v_{N_c} \in V_{N_c} \text{ s.t. } \|v_{N_c}\|_{L^2_{\#}} = N^{1/2}, \quad \|u_{N_c} - u\|_{H_{\#}^1} \leq C\|v_{N_c} - u\|_{L^2_{\#}}.
$$
By a classical argument (see e.g. the proof of Theorem 1 in [2]), we deduce from (2) and the above inequality that
$$
\|u_{N_c} - u\|_{H_{\#}^1} \leq C \min_{v_{N_c} \in V_{N_c}} \|v_{N_c} - u\|_{H_{\#}^1} \leq CN^{-(m-1/2-\epsilon)},
$$
(42)
for some constants $C$ independent of $N_c$.

For $w \in L^2_{\#}(\Gamma)$, we denote by $\psi_w$ the unique solution to the adjoint problem
$$
\left\{ \begin{array}{l}
\text{find } \psi_w \in u^+ \text{ such that } \\
\forall v \in u^+, \quad \langle (E_{TFW}''(u) - 2\lambda)\psi_w, v \rangle_{H_{\#}^{-1}, H_{\#}^1} = \langle w, v \rangle_{H_{\#}^{-1}, H_{\#}^1},
\end{array} \right.
$$
(43)
where
$$
u^+ = \left\{ v \in H_{\#}^1(\Gamma) \mid \int_{\Gamma} \psi v = 0 \right\}.
$$
The function $\psi_w$ is solution to the elliptic equation
$$
-\frac{C_w}{2} \Delta \psi_w + (V_{\text{ion}} + V_{\text{u}u_{\psi_w}} + V_{\text{u}u_{\psi_w}} + f(u^2) + 2f'(u^2)u^2 - \lambda) \psi_w + 2V_{u^3_{\psi_w}}u
= 2 \left( \int_{\Gamma} f'(u^2)u^3 \psi_w + D_{\Gamma}(u^2, w_1) \right) u + w - (w, u)_{L^2_{\#}} u,
$$
from which we deduce that if \( w \in H^r_{\#}(\Gamma) \) for some \( 0 \leq r < m - 3/2 \), then \( \psi_w \in H^{r+2}_{\#}(\Gamma) \) and
\[
\|\psi_w\|_{H^{r+2}_{\#}} \leq C_r \|w\|_{H^r_{\#}} ,
\]
for some constant \( C_r \) independent of \( w \). Let \( u^*_{\psi_N} \) be the orthogonal projection, for the \( L^2_{\#} \) inner product, of \( u_{\psi_N} \) on the affine space \( \{ v \in L^2_{\#}(\Gamma) : \int_{\Gamma} uv = N \} \). One has
\[
u^*_{\psi_N} \in H^1_{\#}(\Gamma), \quad u^*_{\psi_N} - u \in u^+, \quad u^*_{\psi_N} - u_{\psi_N} = \frac{1}{2N} \|u_{\psi_N} - u\|^2_{L^2_{\#}},
\]
from which we infer that
\[
\begin{align*}
\|u_{\psi_N} - u\|^2_{L^2_{\#}} &= \int_{\Gamma} (u_{\psi_N} - u)(u_{\psi_N} - u) + \int_{\Gamma} (u_{\psi_N} - u)(u_{\psi_N} - u^*) \\
&= \int_{\Gamma} (u_{\psi_N} - u)(u_{\psi_N} - u) - \frac{1}{2N} \|u_{\psi_N} - u\|^2_{L^2_{\#}} \int_{\Gamma} (u_{\psi_N} - u)u \\
&= \int_{\Gamma} (u_{\psi_N} - u)(u_{\psi_N} - u) + \frac{1}{2N} \|u_{\psi_N} - u\|^2_{L^2_{\#}}(N - \int_{\Gamma} u_{\psi_N}u) \\
&= \int_{\Gamma} (u_{\psi_N} - u)(u_{\psi_N} - u) + \frac{1}{4N} \|u_{\psi_N} - u\|^2_{L^2_{\#}} \\
&= (u_{\psi_N} - u, u_{\psi_N} - u)_{H^{-1}_{\#},H^1_{\#}} + \frac{1}{4N} \|u_{\psi_N} - u\|^2_{L^2_{\#}} \\
&= ((E^{TFW}'(u) - 2\lambda)\psi_{u_{\psi_N} - u}, u^*_{\psi_N} - u)_{H^{-1}_{\#},H^1_{\#}} + \frac{1}{4N} \|u_{\psi_N} - u\|^2_{L^2_{\#}} \\
&= \frac{1}{2N} \|u_{\psi_N} - u\|^2_{L^2_{\#}}((E^{TFW}'(u) - 2\lambda)u, \psi_{u_{\psi_N} - u})_{H^{-1}_{\#},H^1_{\#}} \\
&= \frac{2}{N} \|u_{\psi_N} - u\|^2_{L^2_{\#}} \int_{\Gamma} f'(u^2)u^3\psi_{u_{\psi_N} - u} + D_G(u^2, u\psi_{u_{\psi_N} - u}).
\end{align*}
\]
For all \( \psi_{\psi_N} \in V_{\psi_N} \), it therefore holds
\[
\|u_{\psi_N} - u\|^2_{L^2_{\#}} = ((E^{TFW}'(u) - 2\lambda)(u_{\psi_N} - u), \psi_{u_{\psi_N} - u} - \psi_{\psi_N})_{H^{-1}_{\#},H^1_{\#}} \\
+((E^{TFW}'(u) - 2\lambda)(u_{\psi_N} - u), \psi_{\psi_N})_{H^{-1}_{\#},H^1_{\#}} + \frac{1}{4N} \|u_{\psi_N} - u\|^2_{L^2_{\#}} \\
+ \frac{2}{N} \|u_{\psi_N} - u\|^2_{L^2_{\#}} \int_{\Gamma} f'(u^2)u^3\psi_{u_{\psi_N} - u} + D_G(u^2, u\psi_{u_{\psi_N} - u}).
\]
Using (28), (31), (37) with \( r = 0 \) and (40), we obtain that for all \( \psi_{\psi_N} \in V_{\psi_N} \cap u^+ \),
\[
\begin{align*}
\left|((E^{TFW}(u) - 2\lambda)(u_{\psi_N} - u), \psi_{\psi_N})_{H^{-1}_{\#},H^1_{\#}}\right| &\leq C\left(\|u_{\psi_N} - u\|^2_{H^1_{\#}} + \|u_{\psi_N} - u\|^2_{L^2_{\#}}\right)\|\psi_{\psi_N}\|_{H^1_{\#}} \\
\|u_{\psi_N} - u\|^2_{L^2_{\#}} &= \left(\|u_{\psi_N} - u\|^2_{H^1_{\#}} + \|u_{\psi_N} - u\|^2_{L^2_{\#}}\right)\|\psi_{\psi_N}\|_{H^1_{\#}}.
\end{align*}
\]
Let us denote by \( \Pi^1_{V_{\psi_N} \cap u^+} \) the orthogonal projector on \( V_{\psi_N} \cap u^+ \) for the \( H^1_{\#} \) inner product and by \( \psi_{\psi_N}^0 = \Pi^1_{V_{\psi_N} \cap u^+}\psi_{u_{\psi_N} - u} \). Noticing that
\[
\|\psi_{\psi_N}^0\|_{H^1_{\#}} \leq \|\psi_{u_{\psi_N} - u}\|_{H^1_{\#}} \leq \beta^{-1} M\|u_{\psi_N} - u\|_{L^2_{\#}},
\]

we obtain from (33), (45) and (46) that there exists $N \in \mathbb{N}$ and $C \in \mathbb{R}_+$ such that for all $N_c \geq N$,
\[ \|u_{N_c} - u\|_{L^2_{\#}}^2 \leq C \left( \|u_{N_c} - u\|_{L^2_{\#}} + \|u_{N_c} - u\|_{H^1_{\#}}^2 + \|u_{N_c} - u\|_{H^1_{\#}} \|\psi_{u_{N_c} - u} - \psi_{N_c}\|_{H^1_{\#}} \right). \]

Lastly, for all $v \in u^\perp$ and all $N_c \in \mathbb{N}^*$
\[ \|v - \Pi_{V_{N_c} \cap u^\perp} v\|_{H^1_{\#}} \leq \left( 1 + \frac{N^{1/2}}{2\pi L^{1/2} N_c \int u} \right) \|v - \Pi_{N_c} v\|_{H^1_{\#}}, \tag{47} \]
so that, in view of (2) and (44)
\[ \|\psi_{u_{N_c} - u} - \psi_{N_c}\|_{H^1_{\#}} \leq C \|\psi_{u_{N_c} - u} - \Pi_{N_c} \psi_{u_{N_c} - u}\|_{H^1_{\#}} \leq C N_c^{-1} \|\psi_{u_{N_c} - u}\|_{H^2_{\#}} \leq C N_c^{-1} \|u_{N_c} - u\|_{L^2_{\#}}. \]

Therefore,
\[ \|u_{N_c} - u\|_{L^2_{\#}} \leq C \left( \|u_{N_c} - u\|_{H^1_{\#}}^2 + N_c^{-1} \|u_{N_c} - u\|_{H^1_{\#}} \right) \leq C N_c^{-(m+1/2-\epsilon)}. \]

By means of the inverse inequality
\[ \forall v_{N_c} \in V_{N_c}, \quad \|v_{N_c}\|_{H^r_{\#}} \leq \left( \frac{2\pi}{L} \right)^{(r-s)} N_c^{r-s} \|v_{N_c}\|_{H^s_{\#}}, \tag{48} \]
which holds true for all $s \leq r$ and all $N_c \geq 1$, we obtain that
\[ \|u_{N_c} - u\|_{H^r_{\#}} \leq C_s N_c^{-(m-s+1/2-\epsilon)} \quad \text{for all } 0 \leq s < m + 1/2. \tag{49} \]
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
\[
\int_{\Gamma} w(u_{N_c} - u) = \langle (E^{TFW''}(u) - 2\lambda)(u_{N_c} - u), \Pi^1_{V_{N_c} \cap u^\perp} \psi_w \rangle_{H^{-1}_{\#}, H^1_{\#}} \\
+ \langle (E^{TFW''}(u) - 2\lambda)(u_{N_c} - u), \psi_w - \Pi^1_{V_{N_c} \cap u^\perp} \psi_w \rangle_{H^{-1}_{\#}, H^1_{\#}} \\
+ \frac{2}{N} \|u_{N_c} - u\|_{L^2_{\#}}^2 \left[ \int_{\Gamma} f'(u)^2 u^3 \psi_w + D_{\Gamma}(u^2, u\psi_w) \right] \\
- \frac{1}{2N} \|u_{N_c} - u\|_{L^2_{\#}} \int_{\Gamma} uw. \tag{50} \]
Combining (33), (44), (46), (47), (49) and (50), we obtain that there exists a constant $C \in \mathbb{R}_+$ such that for all $N_c$ large enough and all $w \in H^r_{\#}(\Gamma)$,
\[
\int_{\Gamma} w(u_{N_c} - u) \leq C' \left( \|u_{N_c} - u\|_{H^1_{\#}}^2 + N_c^{-(r+1)} \|u_{N_c} - u\|_{H^1_{\#}} \right) \|w\|_{H^r_{\#}} \\
\leq C N_c^{-(m+r+1/2-\epsilon)} \|w\|_{H^r_{\#}}.
\]
Therefore
\[ \|u_{N_c} - u\|_{H^r_{\#}} = \sup_{w \in H^r_{\#}(\Gamma) \setminus \{0\}} \frac{\int_{\Gamma} w(u_{N_c} - u)}{\|w\|_{H^r_{\#}}} \leq C N_c^{-(m+r+1/2-\epsilon)}, \tag{51} \]
for some constant $C \in \mathbb{R}_+$ independent of $N_c$. Using (37), (42) and (51), we end up with
\[ |\lambda_N - \lambda| \leq CN_c^{-(2m-1-\epsilon)}. \]

Let us now turn to the pseudospectral approximation (17) of (16). First, we notice that
\[ C \leq \Pi_{N_c,N_g} \leq C \frac{N_c^{5/3}}{\Gamma} + \|V\|_{L^\infty N_c} \]
from which we infer that $u_{N_c,N_g}$ is uniformly bounded in $H^1_\#(\Gamma)$. We then see that
\[ \lambda_{N_c,N_g} = \mathcal{N}^{-1} \left[ \frac{C_w}{2} \int_\Gamma \nabla \left| u_{N_c,N_g} \right|^2 + \int_\Gamma \Pi_{N_c,N_g} \left( V^{\text{ion}} |u_{N_c,N_g}|^2 + f(|u_{N_c,N_g}|^2) |u_{N_c,N_g}|^2 \right) \right. \]
\[ \left. + \mathcal{D}_\Gamma \left( |u_{N_c,N_g}|^2, |u_{N_c,N_g}|^2 \right) \right] . \]

Using (6), (11) and (26), we obtain that $\lambda_{N_c,N_c}$ also is uniformly bounded. Now,
\[ \Delta u_{N_c,N_g} = 2C_w^{-1} \Pi_{N_c} \left( \mathcal{I}_{N_g} \left( f(|u_{N_c,N_g}|^2) |u_{N_c,N_g}| \right) \right) + 2C_w^{-1} \Pi_{N_c} \left( \mathcal{I}_{N_g} \left( V^{\text{ion}} u_{N_c,N_g} \right) \right) \]
\[ + 2C_w^{-1} \Pi_{N_c} \left( V^{\text{Coulomb}} |u_{N_c,N_g}|^2 u_{N_c,N_g} \right) - 2C_w^{-1} \lambda_{N_c,N_c} u_{N_c,N_g}, \]
and we deduce from (4), (6) and (8) that
\[ \left\| \Pi_{N_c} \left( \mathcal{I}_{N_g} \left( f(|u_{N_c,N_g}|^2) |u_{N_c,N_g}| \right) \right) \right\|_{L^\infty \#} \leq \left( \int_\Gamma \left( \mathcal{I}_{N_g} \left( f(|u_{N_c,N_g}|^2) \right) \right)^2 \right)^{1/2} \left( \sum_{x \in \mathcal{D}_{N_g} \cap \Gamma} \left( \frac{L}{N_g} \right)^3 \left| f(|u_{N_c,N_g}(x)|^2) \right|^2 \right)^{1/2} \leq \frac{5}{3} C_T F \left\| u_{N_c,N_g} \right\|_{L^\infty \#}^{1/3} \left\| u_{N_c,N_g} \right\|_{L^\infty \#}^{2/3}, \]
and that
\[ \left\| \Pi_{N_c} \left( \mathcal{I}_{N_g} \left( V^{\text{ion}} u_{N_c,N_g} \right) \right) \right\|_{L^\infty \#} \leq \left\| \Pi_{2N_c} \left( \mathcal{I}_{N_g} \left( V^{\text{ion}} u_{N_c,N_g} \right) \right) \right\|_{L^\infty \#} \leq \left( \int_\Gamma \mathcal{I}_{N_g} \left( |V^{\text{ion}}|^2 |u_{N_c,N_g}|^2 \right) \right)^{1/2} \leq \left\| V^{\text{ion}} \right\|_{L^\infty \#} \mathcal{N}^{1/2}. \]

Besides, using (29),
\[ \left\| \Pi_{N_c} \left( V^{\text{Coulomb}} |u_{N_c,N_g}|^2 u_{N_c,N_g} \right) \right\|_{L^\infty \#} \leq \left\| V^{\text{Coulomb}} |u_{N_c,N_g}|^2 u_{N_c,N_g} \right\|_{L^\infty \#} \leq \mathcal{N}^{1/2} \left\| V^{\text{Coulomb}} |u_{N_c,N_g}|^2 \right\|_{L^\infty} \leq \mathcal{N}^{1/2} \left\| u_{N_c,N_g} \right\|_{L^\infty \#}^{2}.
As \( u_{N_c,N_g} \) is uniformly bounded in \( H^1_\#(\Gamma) \), and therefore in \( L^4_\#(\Gamma) \), we get
\[
\|u_{N_c,N_g}\|_{H^2_\#}^2 = \left(\|u_{N_c,N_g}\|_{L^2_\#}^2 + \|\Delta u_{N_c,N_g}\|_{L^2_\#}^2\right)^{1/2} \leq C \left(1 + \|u_{N_c,N_g}\|_{L^\infty}^{1/2}\right) \leq C \left(1 + \|u_{N_c,N_g}\|_{H^2_\#}\right).
\]
Therefore \( u_{N_c,N_g} \) is uniformly bounded in \( H^2_\#(\Gamma) \), hence in \( L^\infty(\mathbb{R}^3) \).

Returning to (52) and using (9) 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),
\[
\frac{\gamma}{2} \|u_{N_c,N_g} - u_{N_c}\|_{H^1}^2 \leq E^{TFW}(u_{N_c,N_g}) - E^{TFW}(u_{N_c}) = E^{TFW}_{N_g}(u_{N_c,N_g}) - E^{TFW}_{N_g}(u_{N_c}) + \int_{\Gamma} ((1 - \mathcal{I}_{N_g})(V)) |u_{N_c,N_g}|^2 - |u_{N_c}|^2 \leq \int_{\Gamma} ((1 - \mathcal{I}_{N_g})(V)) |u_{N_c,N_g}|^2 - |u_{N_c}|^2 + \int_{\Gamma} ((1 - \mathcal{I}_{N_g})(V)) |u_{N_c,N_g}|^2 - |u_{N_c}|^2,
\]
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 implies, using (5) and (10), that
\[
\left|\int_{\Gamma} (1 - \mathcal{I}_{N_g})(V)(|u_{N_c,N_g}|^2 - |u_{N_c}|^2)\right| \leq \|\Pi_{N_c} (1 - \mathcal{I}_{N_g}) (g(u_{N_c},u_{N_c,N_g}))(u_{N_c,N_g} - u_{N_c})\|_{L^2_\#} \leq C N_{c/2}^{-2} N_{g/2}^{-7/2} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#}^2.
\]
On the other hand,
\[
\left|\int_{\Gamma} (1 - \mathcal{I}_{N_g})(V)(|u_{N_c,N_g}|^2 - |u_{N_c}|^2)\right| \leq \|\Pi_{2N_c} (1 - \mathcal{I}_{N_g})(V)\|_{L^2_\#} \|u_{N_c,N_g} + u_{N_c}\|_{L^\infty} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#} \leq C N_{c/2}^{-2} N_{g}^{-m} \|u_{N_c,N_g} - u_{N_c}\|_{L^2_\#}.
\]
Therefore,
\[
\|u_{N_c,N_g} - u_{N_c}\|_{H^1_\#} \leq C N_{c/2}^{-2} N_{g}^{-7/2}.
\]
We then deduce from (54) and the inverse inequality (48) 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 (52), 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 (53) and (54) can therefore be improved, yielding

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

and

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

We deduce (23) from the inverse inequality (48). 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 \( k^{th} \) Fourier coefficient of \( (V^\text{ion} + f([u_{N_c,N_g}]^2)) \) is bounded by \( C|k|^{-m} \) where the constant \( C \) does not depend on \( N_c \) and \( N_g \). Using the equality

\[
\lambda_{N_c,N_g} - \lambda_{N_c} = N^{-1}\left[(H|u_{N_c,N_g}|^2 - \lambda_{N_c})(u_{N_c,N_g} - u_{N_c}),(u_{N_c,N_g} - u_{N_c})\right]_{H^{-1}_\#,H^1_\#} \\
- \int_\Gamma (1 - \mathcal{I}_{N_g})(V^\text{ion} + f([u_{N_c,N_g}]^2))|u_{N_c,N_g}|^2 \\
+ D_{\Gamma}([u_{N_c,N_g}]^2,|u_{N_c,N_g}|^2 - |u_{N_c}|^2) + \int_\Gamma f([u_{N_c,N_g}]^2) - f([u_{N_c}]^2)|u_{N_c,N_g}|^2,
\]

(23) and (28), we obtain (24). A similar calculation leads to (25).

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

\[
E_{TFW}^{TPW}(v_{N_c}) - E_{TFW}^{TPW}(u_{N_c,N_g}) = \text{ (55) }
\]

\[
\left( \langle \mathcal{H}u_{N_c,N_g} - \lambda_{N_c,N_g} \rangle (v_{N_c} - u_{N_c,N_g}), (v_{N_c} - u_{N_c,N_g}) \right)_{H^{-1}_\#,H^1_\#} \\
+ \frac{1}{2}D_{\Gamma}(|v_{N_c}|^2 - |u_{N_c,N_g}|^2,|v_{N_c}|^2 - |u_{N_c,N_g}|^2) \\
+ \sum_{x \in \mathcal{D}N_g \cap \Gamma} \left( \frac{L}{N_g} \right)^3 \left( F([v_{N_c}(x)]^2) - F([u_{N_c}(x)]^2) - f([u_{N_c}(x)]^2)(|[v_{N_c}(x)]^2 - |u_{N_c}(x)|^2) \right)
\]

\[
\geq \left( \langle \mathcal{H}u_{N_c,N_g} - \lambda_{N_c,N_g} \rangle (v_{N_c} - u_{N_c,N_g}), (v_{N_c} - u_{N_c,N_g}) \right)_{H^{-1}_\#,H^1_\#}. \text{ (56) }
\]

As \( u_{N_c,N_g} \) converges to \( u \) in \( H^{2}_\#(\Gamma) \), the operator \( \tilde{\mathcal{H}}_{N_g}^{N_c} |_{|_{N_c,N_g}|^2} = H^\rho \) 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 \( \|v_{N_c}\|_{L^2_\#} = N^{1/2} \) and \( (v_{N_c},u_{N_c})_{L^2_\#} \geq 0 \),

\[
\left( \langle \mathcal{H}u_{N_c,N_g} - \lambda_{N_c,N_g} \rangle (v_{N_c} - u_{N_c,N_g}), (v_{N_c} - u_{N_c,N_g}) \right)_{H^{-1}_\#,H^1_\#} \geq \frac{\gamma}{2} \|v_{N_c} - u_{N_c,N_g}\|_{H^1_\#}^2.
\]

Thus the uniqueness of \( u_{N_c,N_g} \) for \( N_c \) large enough. \( \square \)

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