A short proof of the ionization conjecture in Müller theory

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Abstract. We prove that in Müller theory, a nucleus of charge \( Z \) can bind at most \( Z + C \) electrons for a constant \( C \) independent of \( Z \).

1. Introduction

In Müller theory \([12]\), the energy of an atom is given by the functional

\[
E^M(\gamma) = \text{Tr}(-\Delta \gamma) - \int_{\mathbb{R}^3} \frac{Z \rho_\gamma(x)}{|x|} \, dx + D(\rho_\gamma) - X(\gamma^{1/2}).
\]

Here \( \gamma \) is the density matrix of the electrons and \( \rho_\gamma(x) = \gamma(x, x) \) is its density. The Coulomb repulsion between the electrons is modeled by

\[
D(\rho_\gamma) = \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho_\gamma(x) \rho_\gamma(y)}{|x - y|} \, dx \, dy
\]

and the exchange energy is described by

\[
X(\gamma^{1/2}) = \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\gamma^{1/2}(x, y)|^2}{|x - y|} \, dx \, dy.
\]

The ground state energy is then given by

\[
E^M(N) = \inf \left\{ E^M(\gamma) \mid 0 \leq \gamma \leq 1 \text{ on } L^2(\mathbb{R}^3), \text{Tr} \gamma = N \right\}.
\]

Here we ignore the electron spin for the sake of simplicity. Moreover, for our mathematical treatment we do not need to assume that the parameters \( Z > 0 \) (the nuclear charge) and \( N > 0 \) (the number of electrons) are integers.

Müller theory is a modification of Hartree–Fock theory, where the usual exchange energy \( X(\gamma) \) is replaced by \( X(\gamma^{1/2}) \). On one hand, like Hartree–Fock theory \([2]\), Müller theory correctly reproduces the Scott and Dirac–Schwinger corrections to Thomas–Fermi theory; see \([14]\). On the other hand, unlike the Hartree–Fock functional, the Müller functional is convex \([3]\) and this leads to various mathematical simplifications. In particular, it follows from the discussion in \([3\), Subsection I.C\] that the density of any minimizer (if it exists) is radially symmetric.

1991 Mathematics Subject Classification. 81V45.
Key words and phrases. Maximal ionization, Müller density-matrix-functional theory.
The first author was supported in part by U.S. NSF Grant DMS-1363432.
The third author was supported in part by Conicyt (Chile) through CONICYT–FCHA/Doctorado Nacional/2014 Project # 116–0856 and Iniciativa Científica Milenio (Chile) through Millenium Nucleus RC–120002 “Física Matemática”.

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In [3], it was shown that the Müller functional has a minimizer if \( N \leq Z \), and it was conjectured that there is no minimizer if \( N > N_c(Z) \) for a critical electron number \( N_c(Z) < \infty \). As pointed out in [3], in Müller theory some electrons may form a nontrivial bound state at infinity, and therefore it is unclear how to apply the standard method of “multiplying the Euler-Lagrange equation by \(|x|\)” by Benguria and Lieb [1, 8, 9].

In [6], we used a different method to justify this conjecture and proved

**Theorem 1.1.** There is a constant \( C > 0 \) such that for all \( Z > 0 \), the Müller variational problem (1.1) has no minimizer if \( N > Z + C \).

The proof of Theorem 1.1 in [6] is adapted from our previous work on Thomas–Fermi–Dirac–von Weizsäcker theory [5]. It consists of two main ingredients. The first one is a new strategy to control the number of electrons far away from the nucleus, which is inspired by [13] and [4]. The second one is a comparison with Thomas–Fermi theory, following Solovej’s fundamental work on Hartree–Fock theory [16]. In [6], we did not use the convexity of Muller functional in order to illustrate the generality of our strategy. In fact, our proof has been generalized in [7] to cover a class of non-convex models between Müller and Hartree–Fock.

In this short note, we will provide a shorter proof of Theorem 1.1 by using the convexity of Müller functional and following Solovej’s proof in reduced Hartree–Fock theory [15].

**Acknowledgement.** The first and second author are grateful to the organizers of the QMath 13 conference and for the invitation to speak there.

### 2. Exterior \( L^1 \)-estimate

Throughout the paper we will assume that \( N \geq Z \) and that the variational problem \( E^M(N) \) has a minimizer \( \gamma_0 \). As mentioned before we know that the density \( \rho_0 = \rho_{\gamma_0} \) is radially symmetric. In many places we will use Newton’s theorem

\[
\int_{|y| < |x|} \frac{\rho_0(y)}{|x - y|} \, dy = \frac{1}{|x|} \int_{|y| < |x|} \rho_0(y) \, dy.
\]

We start by proving a simple bound, which in particular verifies the conjecture in [3] that there is a critical electron number \( N_c(Z) < \infty \).

**Lemma 2.1.** \( N \leq 2Z + C(Z^{2/3} + 1) \).

**Proof.** For any partition of unity \( \chi_1^2 + \chi_2^2 = 1 \), we have the binding inequality

\[
E^M(\gamma_0) \leq E^M(\chi_1 \gamma_0 \chi_1) + E^M_{Z=0}(\chi_2 \gamma_0 \chi_2).
\]

We choose

\[
\chi_j(x) = g_j \left( \frac{\nu \cdot x - \ell}{s} \right)
\]

with \( s > 0, \ell > 0, \nu \in S^2 \), and \( g_j : \mathbb{R} \to \mathbb{R}^+ \) satisfying

\[
g_1^2 + g_2^2 = 1, \quad g_1(t) = 1 \text{ if } t \leq 0, \quad g_1(t) = 0 \text{ if } t \geq 1, \quad |\nabla g_1| + |\nabla g_2| \leq C.
\]

By the IMS formula and the fact that

\[
X(\chi_j \gamma_0^{1/2} \chi_j) \leq X((\chi_j \gamma_0 \chi_j)^{1/2})
\]
Next, we integrate over $\ell$ theorem and

$$s > (which follows by an easy energy comparison; see \([6] for the right side) and

$$N \leq 2Z + C(Z^{2/3} + 1).$$

In order to improve the bound in Lemma \([2.1] we use the following observation. Heuristically, the electrons in the exterior region $|x| \geq r$ feel the rest of the system as an “effective nucleus” with the screened nuclear charge

$$Z_r = Z - \int_{|x| < r} \rho_0(x) \, dx.$$

Therefore, by modifying the proof of Lemma \([2.1] we can control the number of exterior electrons in terms of $Z_r$. We still lose a factor 2, but this is not a big problem because $Z_r$ is much smaller than $Z$ (if $r$ is not too small).
Throughout the paper, we will use the cut-off functions 
\begin{equation}
\chi^+_r(x) = 1(|x| \geq r), \quad \chi^+_r \geq \eta_r \geq \chi^+_1, \quad |\nabla \eta_r| \leq C(\lambda r)^{-1}.
\end{equation}
We have the following upgraded version of Lemma 2.1.

**Lemma 2.2 (Exterior $L^1$-estimate).** For all $r > 0$, $s > 0$ and $\lambda \in (0, 1/2]$, 
\begin{equation}
\int \chi^+_r \rho_0 \leq C \int_{r < |x| < (1 + \lambda)^2 r} \rho_0 + C \left( |Zr| + s + \lambda^{-2} s^{-1} + \lambda^{-1} \right) + C \left( s^2 \text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{3/5} + C \left( s^2 \text{Tr}(-\Delta \eta_r \gamma_0 \eta_r) \right)^{1/3}.
\end{equation}

**Proof.** We use the binding inequality (2.1) with 
\begin{equation}
\chi_j(x) = g_j \left( \frac{\nu \cdot \theta(x) - \ell}{s} \right)
\end{equation}
where $\theta : \mathbb{R}^3 \to \mathbb{R}^3$ satisfies 
\begin{equation}
|\theta(x)| \leq |x|, \quad \theta(x) = 0 \text{ if } |x| \leq r, \quad \theta(x) = x \text{ if } |x| \geq (1 + \lambda)r, \quad |\nabla \theta| \leq C \lambda^{-1}
\end{equation}
and proceed similarly as in Lemma 2.1. See [6] Lemma 7 for details.

\hfill $\Box$

3. Comparison with Thomas–Fermi theory

In this section, we control the electron density in the exterior region $\{|x| \geq r\}$ in Müller theory by comparison with Thomas–Fermi (TF) theory. Recall that in usual TF theory, the ground state energy is obtained by minimizing the density functional
\begin{equation}
\mathcal{E}^\text{TF}(\rho) = c^\text{TF} \int_{\mathbb{R}^3} \rho^{5/3}(x) \, dx - \int_{\mathbb{R}^3} \frac{Z \rho(x)}{|x|} \, dx + D(\rho), \quad c^\text{TF} = \frac{3}{5}(6\pi^2)^{2/3},
\end{equation}
over all $0 \leq \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3)$. The TF minimizer $\rho^\text{TF}$ is unique and has total mass $\int \rho^\text{TF} = Z$. Here, as in [15], we will consider TF theory restricted to the exterior region $\{|x| \geq r\}$.

**Lemma 3.1 (Exterior TF theory).** Let $r > 0$ and $z \in \mathbb{R}$. Then the TF functional 
\begin{equation}
\mathcal{E}_r^\text{TF}(\rho) = c^\text{TF} \int_{\mathbb{R}^3} \rho(x)^{5/3} \, dx - \int_{\mathbb{R}^3} \frac{z \rho(x)}{|x|} \, dx + D(\rho)
\end{equation}
has a unique minimizer $\rho_r^\text{TF}$ among all densities satisfying
\begin{equation}
0 \leq \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3), \quad \text{supp}\rho \subset \{|x| \geq r\}.
\end{equation}
The minimizer $\rho_r^\text{TF}$ is radially symmetric, has total mass $\int \rho_r^\text{TF} = [z]_+$, has bounded kinetic energy 
\begin{equation}
\int (\rho_r^\text{TF})^{5/3} \leq C|z|^7
\end{equation}
and satisfies the TF equation
\begin{equation}
\frac{5c^\text{TF}}{3}(\rho_r^\text{TF})^{2/3} = [\varphi_r^\text{TF}]_+ \quad \text{in } \{|x| > r\}
\end{equation}
with 
\begin{equation}
\varphi_r^\text{TF}(x) = \frac{z \chi^2_r(x)}{|x|} - \rho_r^\text{TF}*|x|^{-1}.
\end{equation}
Moreover, for every fixed $\kappa > 0$, there is an $\alpha(\kappa) > 0$ such that if $z r^3 \geq \kappa$ and $|x| r^{-1} \geq \alpha(\kappa)$, then we have the Sommerfeld estimate

$$
(3.3) \quad \left| \rho^\text{TF}_r(x) - (5\pi^{-1} G^\text{TF})^3 |x|^{-6} \right| \leq C |x|^{-\epsilon} (|x| r^{-1})^{-\zeta}
$$

with $\zeta = (\sqrt{15} - 1)/2 \approx 0.77$. For the full $\rho^\text{TF}$, for all $x \neq 0$ we have

$$
(3.4) \quad 0 \geq \rho^\text{TF}_r(x) - (5\pi^{-1} G^\text{TF})^3 |x|^{-6} \geq -C |x|^{-\epsilon} (|x| z^{1/3})^{-\zeta}.
$$

**Proof.** See [15, Appendix B]. In fact, (3.3) is slightly stronger than [15, Theorem B3] and it is taken from [16, Lemma 4.4]. The bound (3.4) is taken from [16, Theorems 5.2, 5.4]. \hfill \Box

**Convention.** In what follows, $\rho^\text{TF}_r$ denotes the minimizer from Lemma 3.1 with the choice $z = Z_r$ from (2.2).

The main result in this section is the following

**Lemma 3.2 (Comparison with TF).** For all $r \geq s > 0$ and $\lambda \in (0, 1/2]$,

$$
(3.5) \quad D(\eta^2_2 \rho_0 - \rho^\text{TF}_r) \leq C s^{-2} \int_{\mathbb{R}^3} \chi_r^+ \rho_0 + C \left[ Z_r \right]^{12/5} s^{-1/2} s^{2/5} + \mathcal{R}
$$

where

$$
\mathcal{R} = C \left( 1 + (\lambda r)^{-2} \right) \int_{(1-\lambda)r \leq |x| \leq (1+\lambda)r} \rho_0 + C \lambda r^{1/2} \left[ Z_r \right]^{5/2}
$$

$$
+ C \left( \text{Tr}(-\Delta \eta_2 \rho_0) \right)^{1/2} \left( \int \chi_r^+ \rho_0 \right)^{1/2}.
$$

To prove this lemma we will use the following semi-classical estimates from [16, Lemma 8.2].

**Lemma 3.3 (Semi-classical analysis).** Let $L_{sc} = (15\pi^2)^{-1}$. For every $s > 0$, fix a smooth function $g_s : \mathbb{R}^3 \rightarrow [0, \infty)$ such that

$$
\text{supp } g_s \subset \{ |x| \leq s \}, \quad \int g_s^2 = 1, \quad \int |\nabla g_s|^2 \leq C s^{-2}.
$$

(i) For all $V : \mathbb{R}^3 \rightarrow \mathbb{R}$ such that $[V]_{+}, [V - V * g_s^2]_{+} \in L^{5/2}$ and for all density matrices $0 \leq \gamma \leq 1$, we have

$$
\text{Tr}((-\Delta - V) \gamma) \geq -L_{sc} \int [V]^{5/2} + C s^{-2} \text{Tr} \gamma
$$

$$
- C \left( \int [V]^{5/2} \right)^{3/5} \left( \int [V - V * g_s^{5/2}]^{2/5} \right)^{2/5}.
$$

(ii) If $V_+ \in L^{5/2}(\mathbb{R}^3) \cap L^{3/2}(\mathbb{R}^3)$, then there is a density matrix $\gamma$ such that

$$
\rho_\gamma = \frac{5}{2} L_{sc} [V]^{3/2} * g_s^2
$$

and

$$
(3.7) \quad \text{Tr}(-\Delta \gamma) \leq \frac{3}{2} L_{sc} \int [V]^{5/2} + C s^{-2} \int [V]^{3/2}.
$$
Proof of Lemma 3.2

Step 1. First, we show that the exterior density matrix \( \eta_\gamma \eta_\gamma \) essentially minimizes the exterior reduced Hartree-Fock functional

\[
\mathcal{E}_r^{\text{RHF}}(\gamma) = \text{Tr}(-\Delta \gamma) - \int_{\mathbb{R}^3} \frac{Z_r \rho_\gamma(x)}{|x|} \, dx + D(\rho_\gamma),
\]

where \( Z_r \) is given by (2.2). Indeed, for all \( r > 0, \lambda \in (0,1/2] \) and for all density matrices

\[
0 \leq \gamma \leq 1, \quad \text{supp}(\rho_\gamma) \subset \{|x| \geq r\}, \quad \text{Tr} \gamma \leq \int \chi_r^+ \rho_0,
\]

we have

\[
(3.8) \quad \mathcal{E}_r^{\text{RHF}}(\eta_\gamma \eta_\gamma) \leq \mathcal{E}_r^{\text{RHF}}(\gamma) + \mathcal{R}
\]

The proof of (3.8) is straightforward, using a trial state argument. We refer to [6, Lemma 9] for details.

Step 2. Now we bound the right side of (3.8) by choosing \( \gamma \) as in Lemma 3.3 (ii) with \( V = \chi_{r+s} \varphi_{r}^{\text{TF}} \geq 0 \). Note that \( \rho_\gamma = (\chi_{r+s} \rho_\gamma^{\text{TF}}) * g_s^2 \) by the TF equation, and hence

\[
\text{supp} \rho_\gamma \subset \{|x| \geq r\}, \quad \text{Tr} \gamma = \int \rho_\gamma = \int \chi_{r+s} \rho_\gamma^{\text{TF}} \leq \int \rho_\gamma^{\text{TF}} = Z_r \leq \int \chi_r^+ \rho_0.
\]

The last inequality here comes from our assumption \( N = \int \rho_0 \geq Z \). On the other hand, by the semi-classical estimate (3.7),

\[
(3.9) \quad \mathcal{E}_r^{\text{RHF}}(\gamma) \leq \frac{3}{2} L_{\text{sc}} \int |\varphi_r^{\text{TF}}|^{5/2} - \int \frac{Z_r}{|x|} \rho_\gamma + D(\rho_\gamma) + C s^{-2} \int |\varphi_r^{\text{TF}}|^{3/2} \rho_r^{\text{TF}}
\]

and Newton’s theorem

\[
\int |x|^{-1} \rho_\gamma = \int (|x|^{-1} * g_s^2)(\chi_{r+s} \rho_\gamma^{\text{TF}}) = \int |x|^{-1}(\chi_{r+s} \rho_\gamma^{\text{TF}}).
\]

Finally, we bound the error term by using (3.1) and H"older’s inequality:

\[
\int_{r \leq |x| \leq r+s} \frac{Z_r}{|x|} \rho_r^{\text{TF}} \leq C \frac{|Z_r^\gamma|}{r} \int \left( \int_{r \leq |x| \leq r+s} (\rho_r^{\text{TF}}(x))^5 \, dx \right)^{3/5} \left( \int_{r \leq |x| \leq r+s} (\rho_r^{\text{TF}}(x))^2 \, dx \right)^{2/5}
\]

\[
\leq C \frac{|Z_r^\gamma|}{r} \left( \frac{|Z_r^\gamma|^3}{r} \right)^{3/5} \left( \frac{r^2 s}{2} \right)^{2/5} = C \frac{|Z_r^\gamma|^{12/5}}{r^{1/5} s^{2/5}}.
\]

Step 3. To bound the left side of (3.8), we write

\[
\mathcal{E}_r^{\text{RHF}}(\eta_\gamma \eta_\gamma) = \text{Tr}((-\Delta - \varphi_r^{\text{TF}}) \eta_\gamma \eta_\gamma) - D(\rho_r^{\text{TF}}) + D(\eta_\gamma \rho_0 - \rho_r^{\text{TF}})
\]

and use the semi-classical estimate (3.6) with \( V = \varphi_r^{\text{TF}} \). Note that by Newton’s theorem,

\[
-\rho_r^{\text{TF}} * (|x|^{-1} - |x|^{-1} * g_s^2) \leq 0
\]

and

\[
[\chi_r^+ | \cdot |^{-1} - (\chi_r^+ | \cdot |^{-1} * g_s^2)]^+(x) \leq [\chi_r^+ | \cdot |^{-1} - \chi_{r+s}^+ (| \cdot |^{-1} * g_s^2)]^+(x) = (\chi_r^+ (x) - \chi_{r+s}^+ (x)) |x|^{-1}.
\]
Therefore, when $Z_r \geq 0$ and $r \geq s$ we can bound
\begin{equation}
(3.11) \quad [\varphi^T_r - \varphi^T_r + g_s^2]_+ \leq [Z_r]_+ (\chi^+_r(x) - \chi^+_{r+s}(x))|x|^{-1}.
\end{equation}

Using the TF equation (3.2) and the TF kinetic energy bound (3.1), we get, similarly to (3.10),
\begin{equation}
(3.12) \quad \left( \int (|\varphi^T_r|^{5/2}) \right)^{3/5} \left( \int (|\varphi^T_r - \varphi^T_r + g_s^2|^{5/2}) \right)^{2/5} \leq C \|\rho^T_r\|_{L^{5/3}} [Z_r]_+ r^{4/5 - 1/2} s^{2/5}
\end{equation}

Note that (3.12) holds independently of the sign of $Z_r$ since $[\varphi^T_r]_+ = 0$ if $Z_r \leq 0$. Thus,
\begin{equation}
(3.13) \quad \mathcal{E}_r^{RHF}(\eta \gamma \eta_r) = \text{Tr}((-\Delta - \varphi^T_r) \eta_r \gamma \eta_r) - D(\rho^T_r) + D(\eta^2_r \rho_0 - \rho^T_r)
\end{equation}

Putting together (3.8), (3.9), (3.10) and (3.13), we obtain (3.5). \qed

In order to translate (3.5) into an $L^1$-estimate, we will need

**Lemma 3.4.** For every $f \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$ and $x \in \mathbb{R}^3$, we have
\begin{equation}
\left| \int_{|y| < r} f(y) \, dy \right| \leq C \|f\|_{L^{5/3}}^{6/3} D(f)_{1/2}^{1/3}. \quad \forall x \in \mathbb{R}^3.
\end{equation}

**Proof.** From [16 Cor. 9.3] (see also [5 Lem. 18]) we have
\begin{equation}
\left| \int_{|y| < \lambda x} \frac{f(y)}{|x-y|} \, dy \right| \leq C \|f\|_{L^{5/3}}^{6/3} (|x| D(f))_{1/2}^{1/3}, \quad \forall x \in \mathbb{R}^3.
\end{equation}
Choosing $x = rv$ and averaging over $v \in S^2$, we get the conclusion. \qed

We finish this section by proving some a-priori estimates for $\chi^+_r \rho_0$.

**Lemma 3.5 (A-priori estimates).** Assume that
\begin{equation}
(3.14) \quad |Z_r| \leq Cr^{-3}, \quad \forall r \in (0, D]
\end{equation}

for some $D \leq 1$. Then
\begin{equation}
(3.15) \quad \int \chi^+_r \rho_0 \leq Cr^{-3}, \quad \forall r \in (0, D],
\end{equation}

\begin{equation}
(3.16) \quad \int \chi^+_r \rho_0^{5/3} \leq Cr^{-7}, \quad \forall r \in (0, D],
\end{equation}

\begin{equation}
(3.17) \quad \text{Tr}(-\Delta \eta_r \gamma \eta_r) \leq Cr^{-7}, \quad \forall r \in (0, D].
\end{equation}

Here the constants are independent of $D$ and the cut-off function $\eta_r$ satisfies (2.3) with $\lambda \in [r/2, 1/2]$.
PROOF. We can choose \( \gamma = 0 \) in (3.18) to get \( E_{\text{RHF}}^\gamma(\rho_0, \gamma) \leq R \). Using the kinetic Lieb–Thirring inequality and TF lower bound, we find that

\[
\text{Tr}(-\Delta \eta \gamma \rho_0) \leq C(\lambda r)^{-2} \left( Z_{(1-\lambda)r} - Z_r + \int \chi_r^+ \rho_0 \right) + C\lambda r^{1/2} [Z_{(1-\lambda)r}]^{5/2} + C \left( \text{Tr}(-\Delta \eta \gamma \rho_0) \right)^{1/2} \left( \int \chi_r^+ \rho_0 \right)^{1/2} + C[Z_r]^{7/3}.
\]

This bound, (3.14) and the choice \( \lambda \geq r/2 \) imply that

\[
(3.18) \quad \text{Tr}(-\Delta \eta \gamma \rho_0) \leq C \left( r^{-4} \int \chi_r^+ \rho_0 + r^{-7} \right), \quad \forall r \in (0, D].
\]

We recall that the estimate in Lemma 2.2 with \( \lambda \geq r/2 = s/2 \) gives

\[
\int \chi_r^+ \rho_0 \leq C \int_{r < |x| < (1 + \lambda)r} \rho_0 + C \left( |Z_r| + r^{-3} \right)
+ C \left( r^2 \text{Tr}(-\Delta \eta \gamma \rho_0) \right)^{3/5} + C \left( r^2 \text{Tr}(-\Delta \eta \gamma \rho_0) \right)^{1/3}.
\]

By inserting (3.14) and (3.18) into this bound we deduce that

\[
\int \chi_r^+ \rho_0 \leq C(\rho_0 - Z_{(1+\lambda)r}) + C r^{-3}, \quad \forall r \in (0, D].
\]

We can replace \( r \) by \((1 + \lambda)^{-2} r \) and use (3.14) to get (3.18). Inserting (3.14) into (3.18) yields (3.17). Moreover, by (3.17) and the kinetic Lieb–Thirring inequality, we have

\[
\int \chi_r^+ \rho_0^{5/3} \leq \int (\rho_0 \rho_0)^{5/3} \leq C \text{Tr}(-\Delta \eta \gamma \rho_0) \leq C r^{-7}, \quad \forall r \in (0, D].
\]

Replacing \( r \) by \( r/2 \) we obtain (3.16).

4. Proof of the main result

Now we prove Theorem 1.1. Since the (usual) TF minimizer \( \rho^{\text{TF}} \) has total mass \( Z \), Theorem 1.1 is a direct consequence of the following

Theorem 4.1 (Comparison with TF density). There are universal constants \( C > 0, \epsilon > 0 \) such that for all \( N \geq Z \geq 1 \) and \( r > 0 \),

\[
(4.1) \quad \left| \int_{|x| < r} \left( \rho_0(x) - \rho^{\text{TF}}(x) \right) dx \right| \leq C(1 + r^{-3+\epsilon}).
\]

Note that the left side of (4.1) is \( |Z_r - Z_r^{\text{TF}}| \) where

\[
Z_r^{\text{TF}} := Z - \int_{|x| < r} \rho^{\text{TF}}(x) dx = \int_{|x| \geq r} \rho^{\text{TF}}(x) dx.
\]

Recall that by the Sommerfeld estimate (3.3), for all \( r > 0 \) we have

\[
(4.2) \quad Z_r^{\text{TF}} = a^{\text{TF}} r^{-3} \left( 1 + O((rZ^{1/3})^{3/5}) \right), \quad a^{\text{TF}} := \frac{4(5C_{\text{TF}})^3}{3\pi^2}.
\]

Thus, (4.1) tells us that the screened nuclear charge \( Z_r \) can be approximated well by TF theory up to the distance \( o(1) \), which is remarkably larger than the semi-classical distance \( O(Z^{-1/3}) \).

We will prove Theorem 4.1 using a bootstrap argument as in [15].
Lemma 4.2 (Initial step). There is a universal constant $C_1 > 0$ such that

$$
(4.3) \left| \int_{|x|<r} \left( \rho_0(x) - \rho_{\text{TF}}(x) \right) \, dx \right| \leq C_1 (Z^{1/3}r)^{179/44} r^{-3/2} \epsilon^{1/11}, \quad \forall r > 0.
$$

**Proof.** By writing $E^M(\gamma) = E^{\text{RHF}}(\gamma) - X(\gamma^{1/2})$, we obtain

$$
E^{\text{RHF}}(\gamma_0) \leq \inf \{ E^{\text{RHF}}(\gamma) : 0 \leq \gamma \leq 1, \, \text{Tr} \, \gamma \leq N \} + X(\gamma_0^{1/2}).
$$

Then we can use the semi-classical analysis as in the proof of Lemma 3.2 (now with $\epsilon$) to obtain

$$
(4.4) \int |\varphi - \varphi_{\text{TF}}| \leq CZ^{5/2} s^{1/2}.
$$

We thus obtain

$$
D(\rho_0 - \rho_{\text{TF}}) \leq \int \frac{Z}{|x|} \rho_{\text{TF}} + C s^{-2} + C \| \rho_{\text{TF}} \|_{L^2} Z s^{1/5} + X(\gamma_0^{1/2}).
$$

Using the a-priori estimates

$$
N \leq CZ, \quad \int (\rho_{\text{TF}})^{5/3} \leq CZ^{7/3}, \quad X(\gamma_0^{1/2}) \leq CZ^{5/3}
$$

and optimizing over $s > 0$, we get $D(\rho_0 - \rho_{\text{TF}}) \leq CZ^{25/11}$. The desired estimate (4.3) then follows from Lemma 3.4.

Lemma 4.3 (Iterative step). There are universal constants $C_2, \delta, \epsilon > 0$ such that, if for some $D \leq 1$

$$
(4.4) \left| \int_{|x|<r} \left( \rho_0(x) - \rho_{\text{TF}}(x) \right) \, dx \right| \leq \left( a^{\text{TF}} / 2 \right) r^{-3}, \quad \forall r \in (0, D),
$$

then

$$
(4.5) \left| \int_{|x|<r} \left( \rho_0(x) - \rho_{\text{TF}}(x) \right) \, dx \right| \leq C_2 r^{-3+\epsilon}, \quad \forall r \in [D, D^{1-\delta}].
$$

**Proof.** Let $R \geq D \geq r$. Since $\int \rho_{\text{TF}} = Z_r$ (see Lemma 3.1), we have the key identity

$$
(4.6) \int_{|x|<R} \left( \rho_{\text{TF}} - \rho_0 \right) = Z_r - \int_{|x|<R} \chi_r^+ \rho_0 - \int_{|x|\geq R} \rho_{\text{TF}}
$$

In order to estimate the first term on the right hand side, we start by establishing (3.14). If $r \geq Z^{-1/3}$ we estimate $|Z_r| \leq |Z_{\text{TF}}^r| + |Z_r - Z_{\text{TF}}^r|$ and bound $|Z_{\text{TF}}^r|$ by (4.2) (this requires $r \geq Z^{-1/3}$) and use the assumption (4.4). On the other hand, if $r \leq Z^{-1/3}$, the bound $|Z_r| \leq CZ \leq Cr^{-3}$ follows by our a-priori bound in Lemma 3.3. This proves (4.4).

Therefore, we can apply Lemma 5.3 and Lemma 4.3 and obtain the bounds (4.15), (4.16) and (4.17). We want to use these in Lemma 5.2 to bound $D(\rho_{\text{TF}}^2 - \rho_0 - \rho_{\text{TF}}^2)$. First, we use Lemma 5.5 to obtain

$$
R \leq C(r^{-3} + \lambda^{-2} r^{-5} + \lambda r^{-7} + r^{-5}) \leq C(\lambda^{-2} r^{-5} + \lambda r^{-7}).
$$
For the other error terms in Lemma 3.2 we choose \( s = r^{11/6} \), so that
\[
C |Z_r|^{12/5} r^{-1/5} s^{2/5} + Cs^{-2} \int \chi_r^+ \rho_0 \leq Cr^{-7+1/3}
\]
and finally obtain
\[
D(\eta_r^2 \rho_0 - \rho_r^{\text{TF}}) \leq Cr^{-7} \left( r^{1/3} + \lambda^{-2} r^2 + \lambda \right).
\]

Inserting this bound, as well as (5.11), (5.11a) and (5.11b), into Lemma 5.1 we obtain
\[
\int_{|x| \leq R} \left( \eta_r^2 \rho_0 - \rho_r^{\text{TF}} \right) \leq Cr^{-3} \left( r^{1/3} + \lambda^{-2} r^2 + \lambda \right)^{1/12} \left( R/r \right)^{13/12}.
\]

Moreover, from (5.10) and \( 0 \leq \chi_r^+ - \eta_r^2 \leq 1 (r \leq |x| \leq (1 + \lambda) r) \) it follows that
\[
\int |\chi_r^+ \rho_0 - \eta_r^2 \rho_0| \leq \|\chi_r^+ \rho_0\|_{L^5/3} ||\chi_r^+ - \eta_r^2\|_{L^5/3} \leq Cr^{-3} \lambda^{2/5}.
\]

Combining these estimates and choosing \( \lambda = r^{1/3} \), we conclude that
\[
(4.7) \quad \int_{|x| \leq R} \left( \chi_r^+ \rho_0 - \rho_r^{\text{TF}} \right) \leq Cr^{-3+1/36} (R/r)^{13/12}.
\]

Next, we use the Sommerfeld asymptotics to bound \( (\rho_r^{\text{TF}} - \rho_r^{\text{TF}}) \) on \( \{|x| \geq R\} \). We will assume that \( R \geq Lr \geq L^2 Z^{-1/3} \) for a universal constant \( L > 0 \) to be determined. From (4.2), by choosing \( L > 0 \) large enough, we have
\[
Z_r^{\text{TF}} \geq (3a^{\text{TF}} / 4)r^{-3}, \quad \forall r \geq LZ^{-1/3}.
\]

Combining this bound with (4.2) we infer that
\[
Z_r \geq (a^{\text{TF}} / 4)r^{-3}, \quad \forall r \geq LZ^{-1/3}.
\]

Because of this we can, after increasing \( L \) if necessary, apply the Sommerfeld estimate (5.3) and deduce that
\[
\left| \int_{|x| \geq R} \rho_r^{\text{TF}}(x) dx - a_r^{\text{TF}} R^{-3} \right| \leq CR^{-3} (R/r)^{-\zeta}, \quad \forall R \geq Lr.
\]

Combining the latter estimate and (4.2) (with \( r \) replaced by \( R \)), we finally obtain
\[
(4.8) \quad \left| \int_{|x| \geq R} \left( \rho_r^{\text{TF}} - a_r^{\text{TF}} \right) \right| \leq CR^{-3} (R/r)^{-\zeta}, \quad \forall R \geq Lr.
\]

Now let us conclude. From the bound (4.3) in the initial step, by choosing universal constants \( \delta > 0 \) and \( \varepsilon > 0 \) small enough we have
\[
\left| \int_{|x| < r} \left( \rho_0 - \rho_r^{\text{TF}} \right) \right| \leq Cr^{-3+\varepsilon}, \quad \forall r \leq (L^2 Z^{-1/3})^{(1-\delta)^2}.
\]

Therefore, (4.5) holds true if \( D \leq (L^2 Z^{-1/3})^{1-\delta} \). It remains to consider the case \((L^2 Z^{-1/3})^{1-\delta} \leq D \leq 1 \). We choose \( r = L^{-1} D^{(1-\delta)^{-1}} \). Then we have \( D \geq Lr \geq L^2 Z^{-1/3} \). Therefore, for all \( R \in [D, D^{1-\delta}] \), by inserting (4.7) and (4.8) into (4.6), we get
\[
\left| \int_{|x| < R} \left( \rho_0 - \rho_r^{\text{TF}} \right) \right| \leq CR^{-3+1/36} (R/r)^{13/12} + CR^{-3} (R/r)^{-\zeta}.
\]
Using $r \geq L^{-1} R^{(1-\delta)^{-2}}$ we deduce that
\[
\left| \int_{|x|<R} \left( \rho_0 - \rho_{\text{TF}} \right) \right| \leq C R^{-3+\varepsilon}, \quad \forall R \in [D, D^{1-\delta}]
\]
if the universal constants $\delta > 0$ and $\varepsilon > 0$ are chosen small enough.

Now we are ready to provide the

**Proof of Theorem 4.1.** We use the notations in Lemma 4.2 and Lemma 4.3. Let $\beta = a^{\text{TF}}/2$ and $C_0 = \max\{C_1, C_2, a^{\text{TF}}\}$. The constant $\varepsilon > 0$ in Lemma 4.3 can be chosen to satisfy $\varepsilon \leq 1/66$. Let $D_n := Z^{-\frac{1}{3}(1-\delta)^{-1}}$ for $n = 0, 1, 2, \ldots$

From Lemma 4.2 we have

\[
(4.9) \quad \left| \int_{|x|<r} \left( \rho_0(x) - \rho_{\text{TF}}(x) \right) \, dx \right| \leq C_0 r^{-3+\varepsilon}, \quad \forall r \in (0, D_0].
\]

On the other hand, from Lemma 4.3 we deduce by induction that if

$C_0 (D_n)^{\varepsilon} \leq \beta$,

then

\[
(4.10) \quad \left| \int_{|x|<r} \left( \rho_0(x) - \rho_{\text{TF}}(x) \right) \, dx \right| \leq C_0 r^{-3+\varepsilon}, \quad \forall r \in (0, D_{n+1}].
\]

Note that $D_n \to 1$ as $n \to \infty$ and that $C_0 > \beta$. Thus, there is a minimal $n_0 \in \{0, 1, 2, \ldots\}$ such that $C_0 (D_{n_0})^{\varepsilon} > \beta$. If $n_0 \geq 1$, then $C_0 (D_{n_0-1})^{\varepsilon} \leq \beta$ and therefore by the preceding argument

\[
(4.11) \quad \left| \int_{|x|<r} \left( \rho_0(x) - \rho_{\text{TF}}(x) \right) \, dx \right| \leq C_0 r^{-3+\varepsilon}, \quad \forall r \in (0, D_{n_0}].
\]

If $n_0 = 0$, then (4.10) reduces to (4.9). Since $D_{n_0} \geq D := (C_0^{-1} \beta)^{1/\varepsilon}$, we have

\[
(4.11) \quad \left| \int_{|x|<r} \left( \rho_0(x) - \rho_{\text{TF}}(x) \right) \, dx \right| \leq C_0 r^{-3+\varepsilon}, \quad \forall r \in (0, D].
\]

Note that $D \in (0, 1]$ is a universal constant. Using the exterior estimates (3.15) and (4.2) with $r = D$, we get

\[
(4.12) \quad \int_{|x| \geq D} (\rho_0(x) + \rho_{\text{TF}}(x)) \, dx \leq C.
\]

From (4.11) and (4.12), we obtain (4.1). \hfill \Box

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