THE MAXIMAL EXCESS CHARGE IN REDUCED HARTREE-FOCK MOLECULE

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Abstract. We consider a molecule described by the Hartree-Fock model without the exchange term. We prove that nucleuses of total charge $Z$ can bind at most $Z + C$ electrons, where $C$ is a constant independent of $Z$.

1. Introduction

We denote by $N > 0$ and $K > 0$ the total number of electrons and nucleuses, respectively. Our model is described by an energy functional defined on one-body density matrices. An one-body density matrix $\gamma$ is a self-adjoint operator on $L^2(\mathbb{R}^3)$ satisfying $0 \leq \gamma \leq 1$ and $\text{tr} \gamma < \infty$. The kernel can be written as $\gamma(x, y) = \sum_{i \geq 1} n_i \varphi_i(x) \varphi_i^*(y)$, with the eigenfunctions $\varphi_i$, such that $\gamma \varphi_i = n_i \varphi_i$. Then we define the one-particle electron density $\rho_\gamma$ by $\rho_\gamma(x) = \gamma(x, x)$. The reduced Hartree-Fock (RHF) functional is given by the functional

$$E_{\text{RHF}}(\gamma) = \text{tr} \left[ \left( -\frac{1}{2} \Delta - V_Z \right) \gamma \right] + D[\rho_\gamma],$$

where

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

Here $V_Z$ is the Coulomb potential

$$V_Z(x) = \sum_{i=1}^{K} \frac{z_i}{|x - R_i|}, \quad Z = \sum_{i=1}^{K} z_i,$$

where $z_1, \ldots, z_K > 0$ are the charges of fixed nuclei located at $R_1, \ldots, R_K \in \mathbb{R}^3$. For all $N > 0$ and $z_i > 0$, we define the energy by

$$E_{\text{RHF}}(N, Z) = \inf \{ E_{\text{RHF}}(\gamma) : \gamma \in \mathcal{P}, \text{tr} \gamma = N \}$$

where $\mathcal{P} = \{ \gamma : \gamma = \gamma^\dagger, 0 \leq \gamma \leq 1, (-\Delta + 1)^{1/2} \gamma (-\Delta + 1)^{1/2} \in \mathcal{S}^1 \}$, and $\mathcal{S}^1$ is the set of trace-class operators.

Our interest is to investigate the maximum ionization $N - Z$. It is believed (see [7 Chapter 12]) that real atoms in nature can only bind one, or possibly two extra electrons. This ionization conjecture has only been showed for the atomic case ($K = 1$) in the reduced Hartree-Fock model [11] and full Hartree-Fock model [12]. Recently, Frank et.al proved this conjecture also in the Thomas-Fermi-Dirac-von Weizsäcker model [1] and the Müller model [2]. However, they only dealt with the atomic case.
In this article, we will prove

**Theorem 1.1** (Maximal ionization). *We assume \( z_{\min} := \min_{1 \leq j \leq K} z_j \geq \delta z_{\max} := \max_{1 \leq j \leq K} z_j \), and \( R_{\min} = \min_{i \neq j} |R_i - R_j| \geq c_0 \) with some \( c_0, \delta > 0 \) independent of \( Z \). There is a constant \( C_K > 0 \) depending on \( K \) such that for all \( Z > 0 \), if reduced Hartree-Fock functional has a minimizer, then \( N \leq Z + C_K \) holds true.

**Remark 1.2.** Presumably, the true \( C_K \) behaves linearly on \( K \) but this is still open.

This article is organized as follows. In Section 2 we derive the exterior estimate for the number of electrons in \( A_r \). For the proof, we combine the Lieb’s argument in [5] and the moving plane method [1, 2]. In section 3 we compare our minimizer with the minimizer of an effective exterior functional. In Section 4 we study TF theory for molecules, in particular we prove Sommerfeld bounds. The proof of Theorem 1.1 is given in Section 7 by using Solovej’s argument relying on an initial step given in Section 5 and an iteration step in Section 6.

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## 2. \( L^1 \) exterior estimate

First, we choose smooth localizing functions \( \theta_j \in C^\infty(\mathbb{R}^3), \ j = 0, 1, \ldots, K \) with the following properties:

**Definition 2.1.** Let \( \lambda \in (0, 1/2] \).

(i) For \( j \geq 1 \) we have \( \theta_j(x) = \theta(|x - R_j|/R_0) \), with smooth \( \theta \) satisfying \( 0 \leq \theta \leq 1 \) and \( \theta(t) = 1 \) if \( t < 1 \) and \( \theta(t) = 0 \) if \( t > 1 + \lambda \).

(ii) \( \sum_{j=0}^{K} \theta_j(x)^2 = 1 \) (which defines \( \theta_0 \)).

These properties imply

(iii) \( |\nabla \theta_j(x)| \leq CR_0^{-1} \) for all \( j \).

In the reminder of this article we will use \( \gamma^{RHF} \) to mean a minimizer for reduced Hartree-Fock functional. We put \( \rho^{RHF} := \rho_{\gamma^{RHF}}, \ \gamma_j := \theta_j \gamma^{RHF} \theta_j \), and \( \rho_j := \rho_{\gamma_j}, \ j = 0, 1 \ldots, K \). For any \( r > 0 \), we denote \( A_r := \{ x \in \mathbb{R}^3 : |x - R_j| > r, \ \forall j = 1, \ldots, K \} \).

We introduce here the screened potential defined by

\[
\Phi_r^{RHF}(x) := V_Z(x) - \int_{A_r^c} \frac{\rho^{RHF}(y)}{|x - y|} \, dy,
\]

where \( A_r^c \) stands for the complement of \( A_r \). Our first goal is to control the integral \( \int_{A_{R_0}} \rho^{RHF} \), where \( R_0 := \min(1, R_{\min}/4) \). Namely, we will show
Theorem 2.2. Let
\[
\varphi(x) := \sum_{j=1}^{K} \mu_j |x - R_j|^{-1}, \quad \mu_j = \frac{z_j}{Z}.
\]

Then it holds that
\[
\left( \int_{A_{R_0}} \rho_{\text{RHF}}(x) dx \right)^2 \leq C \left( \frac{1}{R_0^2} + \sup_{x \in A_{R_0/3}} \varphi(x)^{-1} \Phi_{R_0/3}(x) \right) \int_{A_{R_0/3}} \rho_{\text{RHF}}.
\]

Proof. The reduced Hartree-Fock minimizer \( \gamma_{\text{RHF}} = \sum_{i=1}^{\infty} \lambda_i \langle u_i \rangle \) satisfies the RHF equation \( H_{\gamma_{\text{RHF}}} u_i = \varepsilon_i u_i \) with \( \varepsilon_i \leq 0 \) (see [11, Theorem 1]). Here \( H_{\gamma} \) is defined by
\[
H_{\gamma} = -\frac{1}{2} \Delta - V(x) + \rho_{\gamma_{\text{RHF}}} \ast |x|^{-1}.
\]

Now we use the Lieb’s method in [5]. By the RHF equation, we have
\[
0 \geq \sum_{i=1}^{\infty} \varepsilon_i \int |u_i(x)|^2 \varphi(x)^{-1} \theta_0(x)^2 \, dx
\]
\[
= \sum_{i=1}^{\infty} \frac{1}{2} \int \nabla (u_i(x)^* \varphi(x)^{-1} \theta_0(x)^2) \cdot \nabla u_i(x) \, dx - \int \rho_0 V \varphi^{-1}
\]
\[
+ \iint \rho_{\text{RHF}}(x) \rho_{\text{RHF}}(y) \frac{\varphi(x)^{-1} \theta_0(x)^2}{|x - y|} \, dx \, dy.
\]

Next, we use the

Proposition 2.3 (IMS formula). For \( u \in H^1(\mathbb{R}^3) \) and \( \eta \in C^1(\mathbb{R}^3) \) satisfying \( \|\nabla \eta\|_{\infty} \leq C \) we have
\[
\text{Re} \int \nabla (\eta^2 u^*) \cdot \nabla u = \int |\nabla u|^2 - \int |\nabla \eta|^2 |u|^2.
\]

Then we deduce that
\[
\text{Re} \int \nabla (u_i(x)^* \varphi(x)^{-1} \theta_0(x)^2) \cdot \nabla u_i(x) \, dx = \int |\nabla (u_i(x) \varphi(x)^{-1/2} \theta_0(x)^2)|^2 \, dx - \int |\nabla (\theta_0 \varphi^{-1/2})|^2 |u_i|^2.
\]

By definition, \( |\nabla \theta_0 \varphi^{-1/2}|^2 \leq C R_0^{-2} \) holds. Hence
\[
\int \nabla (u_i(x)^* \varphi(x)^{-1} \theta_0(x)^2) \cdot \nabla u_i(x) \, dx \geq - \frac{C}{R_0^2} \int |u_i(x)|^2 \, dx.
\]

We note from the triangle inequality that
\[
\varphi(x)^{-1} + \varphi(y)^{-1} = \sum_{j=1}^{K} \mu_j \frac{|x - R_j| + |y - R_j|}{\varphi(x) \varphi(y) |x - R_j||y - R_j|} \geq \sum_{j=1}^{K} \frac{\mu_j |x - y|}{\varphi(x) \varphi(y) |x - R_j||y - R_j|}.
\]
Then it holds that
\[
\int \int \frac{\rho_{\text{RHF}}(x)\rho_{\text{RHF}}(y)}{|x-y|} \varphi(x)^{-1}\theta_0(x)^2 \, dx \, dy
= \int \int \frac{\rho_{\text{RHF}}(x)\rho_{\text{RHF}}(y)}{|x-y|} \varphi(x)^{-1}(1 - \theta_0(y)^2)\theta_0(x)^2 \, dx \, dy
+ \frac{1}{2} \int \int \frac{\rho_{\text{RHF}}(x)\rho_{\text{RHF}}(y)}{|x-y|}(\varphi(x)^{-1} + \varphi(y)^{-1})\theta_0(y)^2\theta_0(x)^2 \, dx \, dy
\geq \int \int \frac{\rho_{\text{RHF}}(x)\rho_{\text{RHF}}(y)}{|x-y|} \varphi(x)^{-1}(1 - \theta_0(y)^2)\theta_0(x)^2 \, dx \, dy
+ \frac{1}{2} \sum_{j=1}^{K} \mu_j \left( \int \frac{\rho_0(x)dx}{\varphi(x)|x-R_j|} \right)^2.
\]

Furthermore, we may estimate
\[
\int \int \frac{\rho_{\text{RHF}}(x)\rho_{\text{RHF}}(y)}{|x-y|} \varphi(x)^{-1}(1 - \theta_0(y)^2)\theta_0(x)^2 \, dx \, dy
\geq \sum_{j=1}^{K} \int \int_{|y-R_j|<R_0/2} \frac{\rho_{\text{RHF}}(x)\rho_{\text{RHF}}(y)}{|x-y|} \varphi(x)^{-1}\theta_0(x)^2 \, dx \, dy.
\]

These estimates lead that
\[
0 \geq -\frac{C}{R_0^2} \int_{A_{R_0}} \rho_{\text{RHF}} \, dx - C \int \rho_{\text{RHF}}(x)\varphi^{-1}(x)\Phi_{R_0/2}(x) \, dx
+ \frac{1}{2} \sum_{j=1}^{K} \mu_j \left( \int \frac{\rho_0(x)dx}{\varphi(x)|x-R_j|} \right)^2.
\]

Furthermore, by the convexity, we deduce from \( \sum_{j=1}^{K} \mu_j (\varphi(x)|x-R_j|)^{-1} = 1 \) that
\[
\sum_{j=1}^{K} \mu_j \left( \int \frac{\rho_0(x)dx}{\varphi(x)|x-R_j|} \right)^2 \geq \left( \int \rho_0(x)dx \right)^2.
\]

Together with these estimates, we have
\[
\left( \int_{A_{R_0}} \rho_0^{\text{RHF}}(x) dx \right)^2 \leq \frac{C}{R_0^2} \int_{A_{R_0}} \rho_{\text{RHF}} \, dx
+ C \int_{A_{R_0}} \rho_{\text{RHF}}(x)\varphi^{-1}(x)\Phi_{R_0/2}(x) \, dx.
\]
Hence we arrive at
\[
\frac{1}{2} \left( \int_{A_{(1+\lambda)R_0}} \rho_{\text{RHF}}(x) \, dx \right)^2 \leq \frac{C}{R_0^2} \int_{A_{R_0}} \rho_{\text{RHF}} \, dx \\
+ C \sup_{x \in A_{R_0/2}} \varphi(x)^{-1} \left[ \Phi_{R_0/2}^{\text{RHF}}(x) \right]_+ + \int_{A_{R_0}} \rho_{\text{RHF}}.
\]
Replacing $R_0$ to $(1 + \lambda)^{-1} R_0$ and choosing $\lambda = 1/2$, we have the claim. \qed

Following, we will use the cut-off functions
\[
\chi^+_r = 1_{A_r}
\]
and a smooth function $\eta_r : \mathbb{R}^3 \to [0, 1]$ satisfying
\[
\chi^+_r \geq \eta_r \geq \chi^+_r(1+\lambda)r, \quad |\nabla \eta_r| \leq C(\lambda r)^{-1}.
\]
The next lemma is a modification of \cite[Lemma 7]{2} and \cite[Lemma 5]{3}.

**Lemma 2.4.** For all $r \in (0, R_0]$, $s > 0$, and for all $\lambda \in (0, 1/2]$ we have
\[
\int_{A_r} \rho_{\text{RHF}}(x) \, dx \leq C \sum_{j=1}^{K} \int_{r \leq |x-R_j| < (1+\lambda)r} \rho_{\text{RHF}}(x) \, dx \\
+ C \left( \sup_{x \in A_r} \varphi(x)^{-1} \left[ \Phi_r^{\text{RHF}}(x) \right]_+ + s + (\lambda^2 s)^{-1} + \lambda^{-1} + \frac{1}{R_0^3} \right) \\
+ C \left( s^2 \text{tr}(-\Delta \eta_r \gamma_{\text{RHF}} \eta_r) \right)^{3/5}.
\]

**Proof.** As \cite[Corollary 1]{3}, we can obtain the binding inequality
\[
E_{\text{RHF}}(N, Z) \leq E_{\text{RHF}}(N - M, Z) + E_{\text{RHF}}(M, 0) \quad \forall M > 0.
\]
For fixed $\lambda \in (0, 1/2]$, and any $s, l > 0, \nu \in S^2$ we choose
\[
\chi_{j}^{(i)}(x) = g_i \left( \frac{\nu \cdot h_j(x) - l}{s} \right), \quad i = 1, 2,
\]
where $g_i : \mathbb{R} \to \mathbb{R}$ and $\theta : \mathbb{R}^3 \to \mathbb{R}^3$ satisfy
\[
g_1^2 + g_2^2 = 1, \quad g_1(t) = 1 \text{ if } t \leq 0, \quad \text{supp } g_1 \subset \{ t \leq 1 \}, \quad |\nabla g_1| + |\nabla g_2| \leq C.
\]
Here $h_j : \mathbb{R}^3 \to \mathbb{R}^3$ is the function satisfying $|h_j(x)| \leq |x-R_j|, h_j(x) = 0$ if $|x-R_j| \leq r$; $h_j(x) = x - R_j$ if $|x-R_j| \geq (1+\lambda)r$, and $|\nabla h_j(x)| \leq C\lambda^{-1}$. We denote $\gamma_j := \chi_j^i \gamma_j \chi_j^i$ for $j = 1, \ldots, K$ and $i = 1, 2$, where $\gamma_j$ is as in Definition 2.1. We note that the supports of $\gamma_j$, $i = 1, \ldots, K$, are mutually disjoint by definitions. Then, by using the
IMS formula, we have

\[
\mathcal{E}^{\text{RHF}}(\gamma) \leq \mathcal{E}^{\text{RHF}}\left(\sum_{j=1}^{K} \gamma_{j}^{(1)}\right) + \mathcal{E}^{\text{RHF}}_{V_{\gamma_{0}}=0}(\gamma_{0}) + \sum_{j=1}^{K} \mathcal{E}^{\text{RHF}}_{V_{\gamma_{0}}=0}(\gamma_{j}^{(2)})
\]

\[
= \sum_{j=1}^{K} \sum_{i=1,2} \mathcal{E}^{\text{RHF}}(\gamma_{j}^{(i)}) + \mathcal{E}^{\text{RHF}}_{\gamma_{0}} + \sum_{1 \leq i < j \leq K} 2D(\rho_{\gamma_{i}^{(1)}}, \rho_{\gamma_{j}^{(1)}})
\]

\[
+ \sum_{j=1}^{K} \text{tr}(V \gamma_{j}^{(2)}) + \text{tr}(V \gamma_{0})
\]

\[
= \sum_{j=0}^{K} \mathcal{E}^{\text{RHF}}(\gamma_{j}) + \sum_{1 \leq i < j \leq K} 2D(\rho_{\gamma_{i}^{(1)}}, \rho_{\gamma_{j}^{(1)}}) + \sum_{j=1}^{K} \text{tr}(V \gamma_{j}^{(2)}) + \text{tr}(V \gamma_{0})
\]

\[
+ \sum_{j=1}^{K} \left( \sum_{i=1,2} \int |\nabla \chi_{j}^{(i)}|^2 \rho_{j} - \int \int \frac{\chi_{j}^{(2)}(x)^2 \rho_{j}(x) \rho_{j}(y) \chi_{j}^{(1)}(y)^2}{|x-y|} dxdy \right)
\]

Again by the IMS formula, we arrive at

\[
0 \leq \sum_{1 \leq i < j \leq K} 2D(\rho_{\gamma_{i}^{(1)}}, \rho_{\gamma_{j}^{(1)}}) + \sum_{j=1}^{K} \text{tr}(V \gamma_{j}^{(2)}) + \text{tr}(V \gamma_{0})
\]

\[
+ \sum_{j=1}^{K} \left( \sum_{i=1,2} \int |\nabla \chi_{j}^{(i)}|^2 \rho_{j} - \int \int \frac{\chi_{j}^{(2)}(x)^2 \rho_{j}(x) \rho_{j}(y) \chi_{j}^{(1)}(y)^2}{|x-y|} dxdy \right)
\]

\[
+ \sum_{j=0}^{K} \text{tr}(V \gamma_{0}) - \sum_{j=1}^{K} 2D(\rho_{0}, \rho_{j}) - \sum_{1 \leq i < j \leq K} 2D(\rho_{i}, \rho_{j}).
\]

By constructions, we obtain

\[
2D(\rho_{\gamma_{i}^{(1)}}, \rho_{\gamma_{j}^{(1)}}) - 2D(\rho_{i}, \rho_{j}) \leq -4D(\rho_{\gamma_{i}^{(1)}}, \rho_{\gamma_{j}^{(2)}}),
\]

and

\[
\sum_{i=1,2} \int |\nabla \chi_{j}^{(i)}|^2 \rho_{j} \leq C(1 + (\lambda s)^{-2}) \int_{\nu \cdot h_{j}(x) - \lambda s \leq t \leq \nu \cdot h_{j}(x)} \rho_{j}(x) dx.
\]

We note that

\[
\text{tr}(V \gamma_{0}) - \sum_{j=1}^{K} 2D(\rho_{0}, \rho_{j}) \leq \int_{\mathbb{R}^3} \rho_{0}(x) \Phi^{\text{RHF}}_{\mu_{0}}(x) dx.
\]
Then it follows that for all $j$

$$
\int V(x) \chi_j^{(2)}(x)^2 \rho_j(x) \, dx - \sum_{i=1}^{K} \int \int \frac{\chi_j^{(2)}(x)^2 \rho_j(x) \rho_i(y) \chi_i^{(1)}(y)^2}{|x - y|} \, dxdy \\
\leq \int \chi_j^{(2)}(x)^2 \rho_j(x) \Phi_{RHF}^{RHF}(x) \, dx - \int \int_{|y - R_j| \geq r} \frac{\chi_j^{(2)}(x)^2 \rho_j(x) \rho_j(y) \chi_j^{(1)}(y)^2}{|x - y|} \, dxdy \\
\leq \int_{l \leq \nu \cdot h_j(x)} \rho_j(x) |\Phi_{RHF}^{RHF}(x)|_+ \, dx - \int \int_{\nu \cdot h_j(y) \leq l \leq \nu \cdot h_j(x) - s} \chi_j^+(y) \rho_j(x) \rho_j(y) \frac{\rho_j(x) \rho_j(y)}{|x - y|} \, dxdy.
$$

Since $h_j(x) = x - R_j$ when $|x - R_j| > (1 + \lambda)r$, we get

$$
\int \int_{\nu \cdot h_j(y) \leq l \leq \nu \cdot h_j(x) - s} \chi_j^+(y) \rho_j(x) \rho_j(y) \frac{\rho_j(x) \rho_j(y)}{|x - y|} \, dxdy
\geq \int \int_{\nu \cdot h_j(y) \leq l \leq \nu \cdot h_j(x) - s} \chi_j^+(1+\lambda)r(y) \chi_j^+(1+\lambda)r(x) \frac{\rho_j(x) \rho_j(y)}{|x - y|} \, dxdy.
$$

With these inequality, we have that

$$
\sum_{j=1}^{K} \int \int_{\nu \cdot h_j(y) \leq l \leq \nu \cdot h_j(x) - s} \chi_j^+(1+\lambda)r(y) \chi_j^+(1+\lambda)r(x) \frac{\rho_j(x) \rho_j(y)}{|x - y|} \, dxdy
\leq C \sum_{j=1}^{K} \left[ (1 + (\lambda s)^{-2}) \int_{\nu \cdot h_j(x) - s \leq l \leq \nu \cdot h_j(x)} \rho_j(x) \, dx + \int_{l \leq \nu \cdot h_j(x)} \rho_j(x) |\Phi_{RHF}^{RHF}(x)|_+ \, dx \\
+ \frac{1}{R_0^2} \int_{R_0 \leq |x - R_j| \leq (1 + \lambda)R_0} \rho_j \right] + \int_{\mathbb{R}^3} \rho_0(x) |\Phi_{RHF}^{RHF}(x)|_+ \, dx. \tag{2.1}
$$

for all $s, l > 0$ and $\nu \in S^2$. Now we integrate (2.1) over $R_0 > l > 0$, then average over $\nu \in S^2$ and use

$$
\int_{S^2} \nu \cdot x \, d\nu = \frac{|x|}{4}, \text{ for all } x \in \mathbb{R}^3.
$$

For the left side, we also use Fubini’s theorem and

$$
\int_{0}^{\infty} \left( 1(b \leq l \leq a - s) + 1(-a \leq l \leq -b - s) \right) \, dl \geq [(a - b)_+ - 2s]_+ \quad
$$

with $a = \nu \cdot (x - R_j), b = \nu \cdot (y - R_j)$. For the right side, we use the fact that \{x : \nu \cdot h_j(x) \geq l\} \subset \{x : |x - R_j| \geq r\} by construction. We note that $|x - R_j| \leq \varphi(x)^{-1}$ on $r \leq |x - R_j| \leq (1 + \lambda)R_0$ and $R_0 \leq \varphi(x)^{-1}$ in $A_{R_0}$. Together with these facts, we
find that
\[
\frac{1}{8} \sum_{j=1}^{K} \left( \int_{(1+\lambda)\rho \leq |x-R_j| \leq R_0} \rho_{\text{RHF}} \right)^2 \\
\leq C \left( \sup_{x \in A_r} \phi(x)^{-1} \Phi_{\text{RHF}}(x) \right) + s + (\lambda^2 s)^{-1} + \frac{1}{R_0} \int_{A_r} \rho_{\text{RHF}}(x) dx \\
+ C s D \left( \chi_r^+ \rho_{\text{RHF}} \right).
\]

For the left side, we use
\[
\left( \int_{(1+\lambda)\rho \leq |x-R_j| \leq R_0} \rho_{\text{RHF}} \right)^2 \geq \frac{1}{2} \left( \int_{r \leq |x-R_j| \leq R_0} \rho_{\text{RHF}} \right)^2 - \left( \int_{r \leq |x-R_j| \leq (1+\lambda)\rho} \rho_{\text{RHF}} \right)^2.
\]

For the right side, by the Lieb-Thirring inequality,
\[
D(\chi_r^+ \rho_{\text{RHF}}) \leq C \|\chi_r^+ \rho_{\text{RHF}}\|_{L^{6/5}}^2 \\
\leq C \|\chi_r^+ \rho_{\text{RHF}}\|_{L^1} \|\chi_r^+ \rho_{\text{RHF}}\|_{L^{5/3}}^2 \\
\leq C \|\chi_r^+ \rho_{\text{RHF}}\|_{L^1} \left( \text{tr}(-\Delta \eta \gamma_{\text{RHF}} \eta_{\text{RHF}}) \right)^{1/2}.
\]

Hence, by Lemma 2.2, we have
\[
\left( \sum_{j=1}^{K} \int_{r \leq |x-R_j| \leq R_0} \rho_{\text{RHF}} \right)^2 + \left( \int_{A_r} \rho_{\text{RHF}}(x) dx \right)^2 \\
\leq C \sum_{j=1}^{K} \left( \int_{r \leq |x-R_j| \leq (1+\lambda)\rho} \rho_{\text{RHF}} \right)^2 \\
+ C \left( \sup_{x \in A_r} \phi(x)^{-1} \Phi_{\text{RHF}}(x) \right) + s + (\lambda^2 s)^{-1} + \lambda^{-1} + R_0^{-2} \int_{A_r} \rho_{\text{RHF}} \\
+ C s \|\chi_r^+ \rho_{\text{RHF}}\|_{L^1} \left( \text{tr}(-\Delta \eta \gamma_{\text{RHF}} \eta_{\text{RHF}}) \right)^{1/2}.
\]

Consequently, we arrive at
\[
\left( \int_{A_r} \rho_{\text{RHF}}(x) dx \right)^2 \\
\leq C \sum_{j=1}^{K} \left( \int_{r \leq |x-R_j| \leq (1+\lambda)\rho} \rho_{\text{RHF}} \right)^2 \\
+ C \left( \sup_{x \in A_r} \phi(x)^{-1} \Phi_{\text{RHF}}(x) \right) + s + (\lambda^2 s)^{-1} + \lambda^{-1} + \frac{1}{R_0^2} \int_{A_r} \rho_{\text{RHF}} \\
+ C s \|\chi_r^+ \rho_{\text{RHF}}\|_{L^1} \left( \text{tr}(-\Delta \eta \gamma_{\text{RHF}} \eta_{\text{RHF}}) \right)^{1/2}.
\]

We now use the fact that for any \(a, c_i, p_i > 0\) if \(na^2 \leq \sum_{i=1}^{n} c_i a^{2-p_i}\) then it follows that \(a \leq \sum_{i=1}^{n} c_i\) (see the last line in the proof of [2, Lemma 7]). Then the proof of Lemma 2.4 is complete. \(\square\)
3. Splitting Outside from Inside

Our next task is to extend the conclusion of [2, Section 4]. We may choose
\[ \eta_-^2 + \eta_+^2 + \eta_r^2 = 1 \]
with
\[ \text{supp } \eta_- \subset A_r^c, \quad \text{supp } \eta_+ \subset A_{(1-\lambda)r} \cap A_{(1+\lambda)r}^c, \]
\[ \eta_-(x) = 1 \text{ if } x \in A_{(1-\lambda)r}, \]
\[ \sum_{\# = +, -, r} |\nabla \eta_{\#}|^2 \leq C(\lambda r)^{-2}. \]

Next, we introduce the screened RHF functional by
\[ E_{\text{RHF}}^r(\gamma) := \text{tr} \left( -\frac{\Delta}{2} - \Phi_{\text{RHF}}^r \right) \gamma + D(\rho). \]

In this section, we will prove

**Lemma 3.1.** For all \( r \in (0, R_0], \lambda \in (0, 1/2] \), and for any \( 0 \leq \gamma \leq 1 \) satisfying
\[ \text{supp } \rho_\gamma \subset A_r, \quad \text{tr } \gamma \leq \int_{A_r} \rho_{\text{RHF}}^r, \]

it holds that
\[ E_{\text{RHF}}^r(\eta_\gamma^r \eta_\gamma) \leq E_{\text{RHF}}^r(\gamma) + R, \]
where
\[ R \leq C \left( 1 + (\lambda r)^{-2} \right) \int_{A_{(1-\lambda)r} \cap A_{(1+\lambda)r}^c} \rho_{\text{RHF}}^r + C\lambda r^3 \sup_{x \in A_{(1-\lambda)r}} [\Phi_{\text{RHF}}^r(1-\lambda)(x)]_{5/2}^+. \] (3.1)

**Proof.** It suffices to show that
\[ E_{\text{RHF}}^r(\eta_-^r \eta_-^\gamma) + E_{\text{RHF}}^r(\eta_+^r \eta_\gamma) - R \leq E_{\text{RHF}}^r(\gamma) \]
\[ \leq E_{\text{RHF}}^r(\eta_-^r \eta_-^\gamma) + E_{\text{RHF}}^r(\gamma). \]

**Upper bound.** From the minimizing property and the fact that \( N \mapsto E_{\text{RHF}}^r(N, Z) \) is non-increasing, we have
\[ E_{\text{RHF}}^r(\gamma^r) \leq E_{\text{RHF}}^r(\gamma + \eta_-^r \eta_-^\gamma). \]

By direct computation, we have
\[ E_{\text{RHF}}^r(\gamma + \eta_-^r \eta_-^\gamma) = E_{\text{RHF}}^r(\eta_-^r \eta_-^\gamma) + E_{\text{RHF}}^r(\gamma) + \int \int \frac{\eta_-^r(x)^2 \rho_{\text{RHF}}^r(x) \rho_\gamma(y)}{|x - y|} dxdy \]
\[ \leq E_{\text{RHF}}^r(\eta_-^r \eta_-^\gamma) + E_{\text{RHF}}^r(\gamma) + \int \int \frac{\rho_{\text{RHF}}^r(x) \rho_\gamma(y)}{|x - y|} dxdy \]
\[ = E_{\text{RHF}}^r(\eta_-^r \eta_-^\gamma) + E_{\text{RHF}}^r(\gamma). \]
Lower bound. By the IMS formula, we have

\[
\mathcal{E}_{\text{RHF}}(\gamma_{\text{RHF}}) \geq \mathcal{E}_{\text{RHF}}(\eta_-\gamma_{\text{RHF}}\eta_-) + \mathcal{E}_{\text{RHF}}(\eta_+\gamma_{\text{RHF}}\eta_+)
\]

\[
+ \mathcal{E}_{\text{RHF}}(\eta_r\gamma_{\text{RHF}}\eta_r) - \sum_{\#=-,+,r} \int |\nabla \eta_\#|^2 \rho_{\text{RHF}}
\]

\[
+ \int \int \frac{\eta_r(x)^2 \rho_{\text{RHF}}(x) \rho_{\text{RHF}}(y)(\eta_-(y)^2 + \eta_+(y)^2)}{|x-y|} \, dx \, dy
\]

\[
+ \int \int \frac{\eta_+(x)^2 \rho_{\text{RHF}}(x) \rho_{\text{RHF}}(y)(\eta_-(y)^2)}{|x-y|} \, dx \, dy.
\]

By construction, we see that

\[
- \sum_{\#=-,+,r} \int |\nabla \eta_\#|^2 \rho_{\text{RHF}} \geq -C(\lambda r)^{-2} \int_{A_{(1-\lambda)r}^c \cap A_{(1+\lambda)r}^c} \rho_{\text{RHF}}.
\]

Moreover, we get

\[
\mathcal{E}_{\text{RHF}}(\eta_r\gamma_{\text{RHF}}\eta_r) + \int \int \frac{\eta_r(x)^2 \rho_{\text{RHF}}(x) \rho_{\text{RHF}}(y)(\eta_-(y)^2 + \eta_+(y)^2)}{|x-y|} \, dx \, dy
\]

\[
\geq \mathcal{E}_{\text{RHF}}(\eta_r\gamma_{\text{RHF}}\eta_r) + \int \int \frac{\eta_r(x)^2 \rho_{\text{RHF}}(x) \rho_{\text{RHF}}(y)(1+\chi_+^c)}{|x-y|} \, dx \, dy
\]

\[
\geq \mathcal{E}_{\text{RHF}}(\eta_r\gamma_{\text{RHF}}\eta_r).
\]

Similarly, it follows that

\[
\mathcal{E}_{\text{RHF}}(\eta_+\gamma_{\text{RHF}}\eta_+) + \int \int \frac{\eta_+(x)^2 \rho_{\text{RHF}}(x) \rho_{\text{RHF}}(y)(\eta_-(y)^2)}{|x-y|} \, dx \, dy
\]

\[
\geq \mathcal{E}_{\text{RHF}}(\eta_+\gamma_{\text{RHF}}\eta_+) + \int \int \frac{\eta_+(x)^2 \rho_{\text{RHF}}(x) \rho_{\text{RHF}}(y)1_{A_{(1-\lambda)r}^c}(y)}{|x-y|} \, dx \, dy
\]

\[
\geq \mathcal{E}_{\text{RHF}}(\eta_+\gamma_{\text{RHF}}\eta_+)
\]

\[
\geq \text{tr} \left(-\Delta - \Phi_{(1-\lambda)r}\right) \eta_+\gamma_{\text{RHF}}\eta_+.
\]

Applying Lieb-Thirring inequality with \( V = \Phi_{(1-\lambda)r} \mathbb{1}_{\text{supp} \eta_+} \), we see that

\[
\text{tr} \left(-\Delta - \Phi_{(1-\lambda)r}\right) \eta_+\gamma_{\text{RHF}}\eta_+ \geq \text{tr} \left(-\Delta - V\right)_-
\]

\[
\geq -C \sum_{j=1}^{K} \int_{(1-\lambda)r \leq |x-R_j| \leq (1+\lambda)r} \left[\Phi_{(1-\lambda)r}\right]^{5/2}_+
\]

\[
\geq -C\lambda r^3 \sup_{x \in A_{(1-\lambda)r}} \left[\Phi_{(1-\lambda)r}(x)\right]^{5/2}_+.
\]
Hence
\[ E_{\text{RHF}}(\gamma_{\text{RHF}}) \geq E_{\text{RHF}}(\eta^{-\gamma_{\text{RHF}}}\eta^{-}) + E_{\text{RHF}}(\eta^{-\gamma_{\text{RHF}}}) \]
\[ - C(1 + \lambda r)^{-2} \int_{A^{(1-\lambda)r}\cap A^{(1+\lambda)r}} \rho_{\text{RHF}} \]
\[ - C\lambda r^3 \sup_{x \in A^{(1-\lambda)r}} [\Phi_{\text{RHF}}(x)]^{5/2}_+. \]

This completes the proof.

By pursuing the above reasoning, one can show Lemma 3.2. For any \( r \in (0, R_0] \) and any \( \lambda \in (0, 1/2] \) we have
\[ \text{tr} \left( -\frac{\Delta}{2} \eta^{-\gamma_{\text{RHF}}} \eta^{-} \right) \leq C(1 + (\lambda r)^{-2}) \int_{A^{(1-\lambda)r}} \rho_{\text{RHF}} + C\lambda r^3 \sup_{x \in A^{(1-\lambda)r}} [\Phi_{\text{RHF}}(x)]^{5/2}_+ \]
\[ + C \sup_{x \in A_r} [\varphi(x)^{-1}\Phi_{\text{RHF}}(x)]^{7/3}_+. \] (3.2)

Proof. We apply Lemma 3.1 with \( \gamma = 0 \) and obtain \( E_{\text{RHF}}(\eta^{-\gamma_{\text{RHF}}}\eta^{-}) \leq R \). On the other hand, by the kinetic Lieb-Thirring inequality and the fact that the ground state energy in Thomas-Fermi theory is \(-\text{const.} \sum_{j=1}^K z_j^{7/3} \) [4, 6], we have
\[ E_{\text{RHF}}(\eta^{-\gamma_{\text{RHF}}}) \geq \text{tr} \left( -\frac{\Delta}{4} \eta^{-\gamma_{\text{RHF}}} \right) - C \sup_{x \in A_r} [\varphi(x)^{-1}\Phi_{\text{RHF}}(x)]^{7/3}_+. \]

Therefore,
\[ \text{tr} \left( -\frac{\Delta}{2} \eta^{-\gamma_{\text{RHF}}} \right) \leq C R + C \sup_{x \in A_r} [\varphi(x)^{-1}\Phi_{\text{RHF}}(x)]^{7/3}_+ \]

which implies the conclusion.

4. Sommerfeld estimates

In this section, we will show the Sommerfeld asymptotics for molecules. Let \( \Gamma_j \) be the Voronoi cell \( \Gamma_j := \{ x \in \mathbb{R}^3 : |x - R_j| < |x - R_i| \text{ for all } i \neq j \} \). The following theorem has been essentially proven in [12, Theorem 4.6] and [9, Lemma 3.11]

Theorem 4.1 (Sommerfeld asymptotics). Let \( r \in (0, R_0] \) and \( \varphi \) be the TF potential satisfying \( \Delta \varphi = 4\pi c_{\text{TF}}^{-3/2} [\varphi - \mu]^{3/2}_+ \) in \( A_r \), where \( c_{\text{TF}} = 2^{-1}(3\pi^2)^{2/3} \). We assume
$\lim_{s \to +r} \inf_{\partial A_s} \varphi > \mu$. Then for any $x \in A_r$ it follows that

$$\max \left\{ \max_{1 \leq j \leq K} \omega_a^-(x - R_j), \max_{1 \leq j \leq K} \frac{\nu_j(\mu, r)}{|x - R_j|} \right\} \leq \varphi(x) \leq \sum_{j=1}^{K} \omega_a^+(x - R_j) + \mu,$$

where $\nu_j(\mu, r) := \inf_{|x - R_j| = r} \max\{\mu|x - R_j|, \omega_a^-(x - R_j)|x - R_j|\}$ and

$$a(r) := \liminf_{s \to +r} \inf_{\partial A_s} \left( c_s r^{-4} \varphi^{-1} - 1 \right)^{1/2}, \quad \omega_a^-(x) := c_s |x|^{-4} \left( 1 + a(r) \frac{|x|^{-1}}{\xi} \right)^{-2},$$

$$A(r) := \liminf_{s \to +r} \inf_{\partial A_s} \left( c_s^{-1} s^4 (\varphi - \mu) - 1 \right), \quad \omega_a^+(x) := c_s |x|^{-4} \left( 1 + A(r) \frac{|x|^{-1}}{\xi} \right).$$

Here $\xi = (-7 + \sqrt{73})/2 \sim 0.77$ and $c_s = 3^4 2^{-3} \pi^2$.

**Proof.** **Step 1** By assumption, there is a $r_0 \in (r, R_0)$ such that $\inf_{\partial A_r} \varphi > \mu \geq 0$ for any $s \in (r, r_0)$. Hence $a(r)$ is well-defined for any $s \in (r, r_0)$. We prove the claim with $r$ replaced by arbitrary $s \in (r, r_0)$ and take the limit $s \to r$.

**Step 2** (Lower bound) We consider $f(x) := \max\{\max_{1 \leq j \leq K} \omega_a^-(x - R_j), \max_{1 \leq j \leq K} \nu_j|x - R_j| \}$ on $A_r$. Since $\inf_{\partial A_s} \varphi > \mu$, we have $a(s) > -1$. By definition, we have

(a) $\omega_a^-(x - R_j)|x - R_j|$ is positive and radial for $|x - R_j| \geq s$.

(b) $\omega_a^-(x - R_j) = \inf_{\partial A_s} \varphi > \mu$ for any $|x - R_j| = s$.

(c) $\Delta \omega_a^-(x - R_j) \geq 4 \pi c_{TF}^{-3/2} (\omega_a^-(x - R_j))^{3/2}$ for any $|x - R_j| > s$.

Indeed, (a) and (b) are followed from the definition. (c) is obtained in [12], Eq. (38)]. From (a) and (b), and $\mu|x - R_j|$ is increasing, there is a $R \in (s, \infty)$ so that $\omega_a^-(|x - R_j| = R) = \mu$ and

$$\nu_j = \inf_{|x - R_j| = R} \max\{\mu|x - R_j|, \omega_a^-(x - R_j)|x - R_j| \} = \mu R.$$ \hfill (4.1)

Moreover, for any $x \in A_s$

$$f(x) = \begin{cases} \max_{1 \leq j \leq K} \omega_a^-(x - R_j) & \text{if } f(x) > \mu \\ \max_{1 \leq j \leq K} \nu_j|x - R_j| & \text{if } f(x) \leq \mu. \end{cases}$$

Thus, by (b) we have $f|_{\partial A_s} = \omega_a^-(x - R_j)|_{|x - R_j| = s} = \inf_{\partial A_s} \varphi$. Let $u := f - \varphi$. It suffices to show that $\Delta u \geq 0$ in $A_s \cap \{u > 0\}$. From $\Delta u = \Delta f - 4 \pi c_{TF}^{-3/2} (\varphi - \mu)^{3/2}$ we will show that

$$\Delta f \geq 4 \pi c_{TF}^{-3/2} (f - \mu)^{3/2}$$

in $A_r$.

For any nonnegative function $\psi \in C^\infty_c (A_r \cap \{f > \mu\})$ we may compute

$$\int_{\mathbb{R}^3} f \Delta \psi = \sum_{j=1}^{K} \int_{\Gamma_j} \text{div}(\omega_a^-(x - R_j) \nabla \psi(x)) \, dx - \sum_{j=1}^{K} \int_{\Gamma_j} \nabla \omega_a^-(x - R_j) \cdot \nabla \psi(x) \, dx$$

$$= \sum_{j=1}^{K} \int_{\partial \Gamma_j} \omega_a^-(x - R_j) \nu_j \cdot \nabla \psi(x) \, dS - \sum_{j=1}^{K} \int_{\Gamma_j} \nabla \omega_a^-(x - R_j) \cdot \nabla \psi(x) \, dx$$
by Gauss’s theorem. Here $n_j$ is the outward normal of $\partial \Gamma_j$. We note that the first integral is zero by the fact that $n_j = -n_k$ on $\partial \Gamma_j \cap \partial \Gamma_k$. Similarly,

$$- \sum_{j=1}^{K} \int_{\Gamma_j} \nabla \omega_a^-(x - R_j) \cdot \nabla \psi(x) \, dx$$

$$= - \sum_{j=1}^{K} \int_{\Gamma_j} \text{div}(\psi(x) \nabla \omega_a^-(x - R_j)) \, dx + \sum_{j=1}^{K} \int_{\Gamma_j} \psi(x) \Delta \omega_a^-(x - R_j) \, dx$$

$$\geq - \sum_{j=1}^{K} \int_{\partial \Gamma_j} (\psi(x) n_j \cdot \nabla \omega_a^-(x - R_j)) \, dS + 4\pi c_{\text{TF}}^{-3/2} \int \psi f(x)^{3/2} \, dx.$$ 

From the fact that $n_j \cdot \nabla \omega_a^-(x - R_j) \leq 0$ on $\partial \Gamma_j$ (because $\Gamma_j$ is convex), we have

$$\int_{\mathbb{R}^3} f \Delta \psi \geq 4\pi c_{\text{TF}}^{-3/2} \int \psi [f - \mu]_+^{3/2},$$

and thus $\Delta f \geq 4\pi c_{\text{TF}}^{-3/2} [f - \mu]_+^{3/2}$ in $A_r \cap \{f > \mu\}$. We note $\omega_a^-$ is subharmonic and $|x - R_j|^{-1}$ is harmonic on $A_r$. Thus $\Delta u \geq 0$ in $A_r$. We pick any nonnegative function $\psi \in C^\infty_c(A_r)$ and a $0 \leq \xi_n \in C_c^\infty(\{f > \mu\})$ so that $\xi_n \rightarrow -\mathds{1}_{\{f > \mu\}}$ pointwise in $\text{supp} \psi$. Then, with the above results, we find

$$\int f \Delta \psi = \int f \Delta (\xi_n \psi) + \int f \Delta (1 - \xi_n) \psi \geq 4\pi c_{\text{TF}}^{-3/2} \int [f - \mu]_+^{3/2} \xi_n \psi \rightarrow 4\pi c_{\text{TF}}^{-3/2} \int [f - \mu]_+^{3/2} \psi$$

by monotone convergence theorem. Hence $\Delta u \geq 0$ in $A_r \cap \{u > 0\}$ holds. From the maximum principle, $A_r \cap \{u > 0\}$ is empty. Hence $f \leq \varphi$ follows.

**Step 3** (upper bound) We consider $g(x) := \sum_{j=1}^{K} \omega_A^+(x - R_j) + \mu$. Since $\Delta \omega_A^+ \leq 4\pi c_{\text{TF}}^{-3/2} (\omega_A^+)_{3/2}$ in $A_r$ it satisfies, by $\omega_A^+|_{\partial A_r} = \sup_{\partial A_r} \varphi - \mu$, that $\Delta g \leq 4\pi c_{\text{TF}}^{-3/2} [g - \mu]_+^{3/2}$ in $A_r$. Thus for any $x \in \partial A_r$ we have $g(x) \geq \omega_A^+(x) + \mu = \sup_{\partial A_r} \varphi(x)$. Let $u := \varphi - g$. Then we have, on $g < \varphi$,

$$\Delta u \geq 4\pi c_{\text{TF}}^{-3/2} ([g - \mu]_+^{3/2} - [\varphi - \mu]_+^{3/2}) \leq 0.$$ 

Hence we learn $\varphi \leq g$ on $A_r$ by the maximum principle. \square

Next, we improve the upper bound. Namely, we will show

**Theorem 4.2** (Refined upper bound). Let $r \in (0, R_0]$, $\mu \geq 0$, and $\varphi$ is continuous on $A_r$ and vanish at infinity. We assume $\Delta \varphi = 4\pi c_{\text{TF}}^{-3/2} [\varphi - \mu]_+^{3/2}$ in $A_r$. Then it holds that

$$\varphi(x) \leq \omega_{A_1, A_2}^j (x - R_j) + \mu \quad \text{for } x \in A_r \cap \Gamma_j,$$
Proof. We prove the upper bound with $r$ replaced by any $s \in (r, R_0)$. Then $A_i^j(s) = B_i^j(s)$ for $i = 1, 2$. Our strategy is to apply the maximum principle to the function

$$u(x) := \varphi(x) - \left( \sum_{j=1}^K \omega_{B_1,B_2}^j(x - R_j) \mathbb{1}_{\Gamma_j}(x) + \mu \right).$$

By definition, we have $u(x) \leq 0$ on $\partial A_r$. Hence it suffices to show that $-\Delta u \leq 0$ in $A_r \cap \{u > 0\}$.

For any nonnegative function $\psi \in C^\infty_c(A_r \cap \{u > 0\})$ we may compute

$$\int_{\mathbb{R}^3} u(x)\Delta \psi(x) \, dx = \int_{\mathbb{R}^3} \varphi(x)\Delta \psi(x) \, dx - \sum_{j=1}^K \int_{\Gamma_j} \omega_{B_1,B_2}^j(x - R_j) \Delta \psi(x) \, dx.$$

The second integral is

$$\sum_{j=1}^K \int_{\Gamma_j} \omega_{B_1,B_2}^j(x - R_j) \Delta \psi(x) \, dx = \sum_{j=1}^K \int_{\partial \Gamma_j} \omega_{B_1,B_2}^j(x - R_j) n_j \cdot \nabla \psi(x) \, dx - \sum_{j=1}^K \int_{\Gamma_j} \nabla \omega_{B_1,B_2}^j(x - R_j) \cdot \nabla \psi(x) \, dx,$$

by Gauss's theorem. The first integral is vanish from the continuity. We note that $\Delta \omega_{B_1,B_2}^j \leq 4\pi c_T^{-3/2} (\omega_{B_1,B_2}^j)^{3/2}$ for $|x| \neq 0$. Then we have

$$\int_{\mathbb{R}^3} u(x)\Delta \psi(x) \, dx \geq \sum_{j=1}^K \int_{\partial \Gamma_j} \psi(x) n_j \cdot \nabla \omega_{B_1,B_2}^j(x - R_j) \, dx.$$

By direct computation, we see

$$\nabla \omega_{B_1,B_2}^j(x) = c_s \frac{x}{|x|^6} \left( B_1^j(\eta - 4) \left( \frac{|x|}{R_j} \right)^\eta - B_2^j(4 + \xi) \left( \frac{r}{|x|} \right)^\xi - 4 \right).$$
From the convexity of $\Gamma_j$, we learn $n_j \cdot (x - R_j) \geq 0$ on $\partial \Gamma_j$. Hence $n_j \cdot \nabla \omega^j_{B_1, B_2}(x - R_j) \geq 0$. This shows $\Delta u \geq 0$. \hfill \Box

5. INITIAL STEP

From now on, we assume $N \geq Z \geq 1$. In this section our goal is

**Lemma 5.1** (initial step). There is a universal constant $C_1 > 0$ so that

$$\sup_{x \in \partial A_r} \left| \int_{A_r^c} \frac{\rho^{RHF}(y) - \rho^{TF}(y)}{|x - y|} \, dy \right| \leq C_1 Z^{49/36 - a} r^{1/12}, \quad (5.1)$$

for all $r \in (0, R_0]$ with $a = 1/198$.

**Proof.** The strategy is to bound $\mathcal{E}^{RHF}(\gamma^{RHF})$ from above and below using the semi-classical estimates.

**Upper bound.** We will show that

$$\mathcal{E}^{RHF}(\gamma^{RHF}) \leq \mathcal{E}^{TF}(\rho^{TF}) + C Z^{25/11}. \quad (5.2)$$

Since $E^{RHF}(N, Z)$ is non-increasing in $N$ we have

$$\mathcal{E}^{RHF}(\gamma^{RHF}) \leq \inf \{ \mathcal{E}^{RHF}(\gamma) : 0 \leq \gamma \leq 1, \, \text{tr} \, \gamma \leq N \}.$$

We now use the following lemma as in [2, Lemma 11] and [12, Lemma 8.2].

**Lemma 5.2.** For fixed $s > 0$ and smooth $g : \mathbb{R}^3 \to [0, 1]$ satisfying $\text{supp} \, g \subset \{|x| < s\}$, $\int g^2 = 1$, $\int |\nabla g|^2 \leq C s^{-2}$ it follows that

(i) For any $V : \mathbb{R}^3 \to \mathbb{R}$ with $[V]_+, [V - V * g^2]_+ \in L^{5/2}$ and for any $0 \leq \gamma \leq 1$

$$\text{tr} \left( -\frac{\Delta}{2} - V \right) \gamma \geq -2^{5/2}(15\pi^2)^{-1} \int [V]_+^{5/2} - C s^{-2} \text{tr} \, \gamma$$

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

(ii) If $[V]_+ \in L^{5/2} \cap L^{3/2}$, then there is a density-matrix $\gamma$ so that $\rho_\gamma = 2^{5/2}(6\pi^2)^{-1}[V]_+^{3/2} * g^2$.

$$\text{tr} \left( -\frac{\Delta}{2} \right) \leq 2^{3/2}(5\pi^2)^{-1} \int [V]_+^{5/2} + C s^{-2} \int [V]_+^{3/2}.$$

We introduce the Thomas-Fermi potential ($\rho^{TF}$ is the minimizer for the neutral TF molecule)

$$\varphi^{TF}(x) = V_Z(x) - \rho^{TF} * |x|^{-1}$$

and apply Lemma 5.2 (2) with $V = \varphi^{TF}$ and a spherically symmetric $g$ to obtain a density matrix $\gamma'$. Because of the Thomas-Fermi equation we have

$$\rho_{\gamma'} = 2^{5/2}(6\pi^2)^{-1}(\varphi^{TF})^{3/2} * g^2 = \rho^{TF} * g^2.$$

Since

$$\text{tr} \, \gamma' = \int \rho_{\gamma'} = \int \rho^{TF} = Z \leq N,$$
we obtain
\[
\inf \{ \mathcal{E}^{\text{RHF}}(\gamma) : 0 \leq \gamma \leq 1, \ \text{tr} \gamma \leq N \} \leq \mathcal{E}^{\text{RHF}}(\gamma').
\]
Again, by Lemma 5.2 (2),
\[
\mathcal{E}^{\text{RHF}}(\gamma') \leq 2^{3/2}(5\pi^2)^{-1} \int [V]^{5/2}_+ + C_0^{-2} \int [V]^{3/2}_+ \int V_Z(\rho^{\text{TF}} \ast g^2) + D(\rho^{\text{TF}} \ast g^2)
\]
\[
\leq \frac{3}{10} C_0 \int_{\mathbb{R}^3} \rho^{\text{TF}}(x)^{5/3} dx - \int V_Z \rho^{\text{TF}} + D(\rho^{\text{TF}})
\]
\[
+ C s^{-2} \int \rho^{\text{TF}} + \int (V_Z - V_Z \ast g^2) \rho^{\text{TF}}
\]
\[
= \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + C s^{-2} \int \rho^{\text{TF}} + \int (V_Z - V_Z \ast g^2) \rho^{\text{TF}}.
\]
In the second inequality, we have used \([g^2 \ast |x|^{-1} \ast g^2](x - y) \leq |x - y|^{-1}\). This fact follows from Fourier transform. By Newton’s theorem,
\[
V_Z - V_Z \ast g^2 = \sum_{j=1}^K z_j (|x - R_j|^{-1} \mathbf{1}(|x - R_j| \leq s)). \tag{5.3}
\]
Then, by the H"older inequality,
\[
\int (V_Z - V_Z \ast g^2) \rho^{\text{TF}} \leq \left( \int_{\mathbb{R}^3} \rho^{\text{TF}}(x)^{5/3} dx \right)^{3/5} \left( \int (V_Z - V_Z \ast g^2)^{5/2} dx \right)^{2/5}
\]
\[
\leq C Z^{12/5} \left( \sum_{i=1}^K z_i / Z \int_{|x - R_i| \leq s} |x - R_i|^{-5/2} dx \right)^{2/5}
\]
\[
\leq C Z^{12/5} s^{1/5},
\]
where we have used (5.3) and the convexity of \(x^{5/2}\). Thus, after optimization in \(s\), we get
\[
\mathcal{E}^{\text{RHF}}(\gamma') \leq \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + C Z^{25/11}.
\]
This shows the desired upper bound.

**Lower bound.** We will show that
\[
\mathcal{E}^{\text{RHF}}(\gamma^{\text{RHF}}) \geq \mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) + D(\rho^{\text{RHF}} - \rho^{\text{TF}}) - C Z^{25/11}. \tag{5.4}
\]
We can write
\[
\mathcal{E}^{\text{RHF}}(\gamma^{\text{RHF}}) = \text{tr} \left( -\frac{\Delta}{2} - \varphi^{\text{TF}} \right) \gamma^{\text{RHF}} + D(\rho^{\text{RHF}} - \rho^{\text{TF}}) D(\rho^{\text{TF}}).
\]
Then, from Lemma 5.2 (1) we have
\[
\text{tr} \left( -\frac{\Delta}{2} - \varphi^{\text{TF}} \right) \gamma^{\text{RHF}} \geq -2^{5/2}(15\pi^2)^{-1} \int \varphi^{\text{TF}}(x)^{5/2} dx - C s^{-2} \text{tr} \gamma^{\text{RHF}}
\]
\[
- C \left( \int \varphi^{\text{TF}}(x)^{5/2} dx \right) \left( \int [\varphi^{\text{TF}} - \varphi^{\text{TF}} \ast g^2]_+^{5/2} \right)^{2/5}.
\]
By the TF equation, we see that
\[ \int_{\mathbb{R}^3} \varphi_{TF}^{5/2} dx = C \int_{\mathbb{R}^3} \rho_{TF}^{5/3} \leq C Z^{7/3}. \]
Since \( V - V \ast g^2 \geq 0 \), because \( V \) is superharmonic, we obtain
\[ \int [\varphi_{TF} - \varphi_{TF} \ast g]^2 dx \leq \int [V - V \ast g]^2 dx \leq C Z^{5/2} s^{1/2}. \]
Hence we see that
\[ \text{tr} \left( - \frac{\Delta}{2} - \varphi_{TF} \right) \gamma_{RHF} \geq -2^{5/2} (15 \pi^2)^{-1} \int \varphi_{TF}^{5/2} dx - Cs^{-2} Z - C Z^{12/5} s^{1/5}. \]
Optimizing over \( s > 0 \), we get
\[ \text{tr} \left( - \frac{\Delta}{2} - \varphi_{TF} \right) \gamma_{RHF} \geq -2^{5/2} (15 \pi^2)^{-1} \int \varphi_{TF}^{5/2} dx - C Z^{25/11}. \]
Using the relation from the TF equation
\[ -2^{5/2} (15 \pi^2)^{-1} \int \varphi_{TF}^{5/2} dx - D(\rho_{TF}) = E(\rho_{TF}), \]
we arrive at the lower bound (5.4).

**Conclusion.** Combining (5.2) and 5.4 we infer that
\[ D(\rho_{RHF} - \rho_{TF}) \leq C Z^{25/11}. \] (5.5)

The following lemma is taken from [12, Cor. 9.3] and [2, Lemma 12].

**Lemma 5.3 (Coulomb estimate).** For every \( f \in L^{5/3}(\mathbb{R}^3) \cap L^{6/5}(\mathbb{R}^3) \) and \( x \in \mathbb{R}^3 \), we have
\[ \left| \int_{|y| < |x|} \frac{f(y)}{|x-y|^3} dy \right| \leq C \| f \|_{L^{5/3}}^{5/6} (|x| D(f))^{1/12}. \]

Using this Coulomb estimate with \( f(y) = (\rho_{RHF} - \rho_{TF})(y + R_j) \), we find that, for \( r \in (0, R_0) \),
\[ |\Phi_{r}^{RHF}(x) - \Phi_{r}^{TF}(x)| \leq \sum_{j=1}^{K} \left| \int_{|y| < r} \frac{\rho_{RHF}^{5/3} - \rho_{TF}^{5/3}}{|x - R_j - y|^{1/2}} dy \right| \leq C \| \rho_{RHF}^{5/3} - \rho_{TF}^{5/3} \|_{L^{5/3}}^{5/6} (r D(\rho_{RHF} - \rho_{TF}))^{1/12} \leq C \| \rho_{RHF}^{5/3} - \rho_{TF}^{5/3} \|_{L^{5/3}}^{5/6} r^{1/12} Z^{25/132}, \] (5.6)
where we have used the harmonicity. Combining this with the kinetic energy estimates
\[ \int (\rho_{RHF}^{5/3})^{7/3} \leq C Z^{7/3}, \quad \int (\rho_{TF}^{5/3})^{7/3} \leq C Z^{7/3}, \]
we find that
\[ \sup_{x \in \partial A_r} |\Phi_{r}^{RHF}(x) - \Phi_{r}^{TF}(x)| \leq C Z^{179/132} r^{1/12}, \]
for all \( r \in (0, R_0) \). Since \( 179/132 = 49/36 - 1/198 \), this implies the desired bound (5.1). \( \square \)
6. **Iterative Step**

In this section, we will prove

**Theorem 6.1 (iterative step).** There are universal constants $C_2, \beta, \delta, \varepsilon > 0$ such that, if

$$
\sup_{x \in \partial A_s} \left| \int_{A_s} \frac{\rho \text{RHF}(y) - \rho \text{TF}(y)}{|x - y|} \, dy \right| \leq \beta s^{-4}, \quad \forall s \leq D,
$$

(6.1)

for some $D \in [Z^{-1/3}, R_0]$, then, for $r := D^{1+\delta}$, it follows that

$$
\sup_{x \in \partial A_s} \left| \int_{A_s} \frac{\rho \text{RHF}(y) - \rho \text{TF}(y)}{|x - y|} \, dy \right| \leq C_2 s^{-4+\varepsilon}, \quad \forall s \in \left[ r^{1+\delta}, \min\{r^{1+\delta}, \tilde{r}\} \right],
$$

(6.2)

where $\tilde{r} := (2R_0)^{-1} r^{1+\delta} R_{\min}^{\varepsilon}$.  

**Step 1** We collect some consequences of (6.1).

**Lemma 6.2.** We assume that (6.1) holds true for some $\beta, D \in (0, R_0]$. Then, if $r \in (0, D]$, we have

$$
\sup_{x \in A_r} \varphi(x)^{-1} [\Phi_{\text{RHF}}^r(x)]_+ \leq \frac{C}{r^3},
$$

(6.3)

$$
\left| \sum_{j=1}^K \int_{|x - R_j| < r} (\rho \text{RHF} - \rho \text{TF}) \right| \leq \frac{\delta^{-1} \beta}{r^3},
$$

(6.4)

$$
\int_{A_r} \rho \text{RHF} \leq \frac{C}{r^3},
$$

(6.5)

$$
\int_{A_r} (\rho \text{RHF})^{5/3} \leq \frac{C}{r^7},
$$

(6.6)

$$
\text{tr}(-\Delta \eta_r^{\alpha \text{RHF}} \eta_r) \leq C \left( \frac{1}{r^7} + \frac{1}{\lambda^2 r^5} \right), \quad \forall \lambda \in (0, 1/2].
$$

(6.7)

**Proof.** First, we split

$$
\Phi_{\text{RHF}}^r(x) = \Phi_{\text{RHF}}^r(x) - \Phi_{\text{TF}}^r(x) + \Phi_{\text{TF}}^r(x).
$$

Moreover, we may write

$$
\Phi_{\text{TF}}^r(x) = \varphi_{\text{TF}}(x) + \int \frac{\rho_{\text{TF}}(y)}{|x - y|} \, dy - \sum_{j=1}^K \int_{|y - R_j| < r} \frac{\rho_{\text{TF}}(y)}{|x - y|} \, dy
$$

$$
= \varphi_{\text{TF}}(x) + \int_{A_r} \frac{\rho_{\text{TF}}(y)}{|x - y|} \, dy.
$$
Using the Sommerfeld bound $\varphi^{\text{TF}}(x) \leq c|x - R_j|^{-4}$ on $A_r \cap \Gamma_j$ and the TF equation $c_{\text{TF}}\rho^{\text{TF}}(x)^{2/3} = \varphi^{\text{TF}}(x)$, we have

$$\varphi^{\text{TF}}(x) + \int_{A_r} \frac{\rho^{\text{TF}}(y)}{|x-y|} \, dy \leq C \sum_{j=1}^{K} \left( |x-R_j|^{-4} + \int_{|y|>s} \frac{dy}{|x-R_j-y| |y|^6} \right) \leq Cr^{-4},$$

for $x \in A_r$, where we have used Newton’s theorem. Hence, by assumption (6.1), it holds that $|\Phi^{\text{RHF}}_r(x)| \leq Cr^{-4}$ for any $x \in \partial A_r$. We note that $-\Delta \Phi^{\text{RHF}}_s(x) = 4\pi \mathbb{1}_{A_r}(x)\rho^{\text{HF}}(x)$ in the distributional sense, and hence $\Phi^{\text{RHF}}_s$ is harmonic in $A_r$. As in [1, Lemma 6.5], we need the following lemma.

**Lemma 6.3.** Let $f : A_r \to \mathbb{R}$ and $g : A_r \to \mathbb{R}_+$. We assume that $f, g$ are harmonic and continuous in $A_r$ and vanishing at infinity. If $g(x) \geq C_0^{-1} r^{-1}$ on $\partial A_r$, then it holds that

$$\sup_{x \in A_r} g(x)^{-1} f(x) \leq C_0 r \sup_{x \in \partial A_r} f(x).$$

**Proof of Lemma.** Let $h(x) := f(x) - F_r g(x)$ with $F_r = C_0 r \sup_{x \in \partial A_r} f(z)$. Since $f, g$ are harmonic in $A_r$, by the maximum principle, we have

$$\sup_{x \in A_r} h(x) = \max \left\{ \sup_{x \in \partial A_r} (f(x) - F_r g(x)), 0 \right\} = 0$$

Therefore, for any $x \in A_r$ we learn

$$f(x)g(x)^{-1} = h(x)g(x)^{-1} + F_r \leq F_r,$$

and thus the lemma follows. \qed

Now we apply this lemma with $f = [\Phi^{\text{RHF}}_r]_+$ and $g(x) = \varphi(x)$. We note that $\varphi(x) \geq \delta r^{-1}$ on $\partial A_r$, where $\delta$ is independent of $Z$ (recall our assumption of Theorem 1.1). Then we have

$$\sup_{x \in A_r} \varphi(x)^{-1} [\Phi^{\text{RHF}}_r(x)]_+ \leq \delta^{-1} r \sup_{x \in \partial A_r} [\Phi^{\text{RHF}}_r(x)]_+ \leq Cr^{-3},$$

which proves (6.3).

Next, we note that

$$\sum_{j=1}^{K} \int_{|y-R_j|<r} \left( \rho^{\text{TF}}(y) - \rho^{\text{RHF}}(y) \right) \, dy = \lim_{|x| \to \infty} \varphi(x)^{-1} \left( \int_{A_r^c} \rho^{\text{RHF}}(y) - \rho^{\text{TF}}(y) \, dy \right).$$

Then (6.4) follows from Lemma 6.3 and (6.1).

Now we prove (6.5) and (6.7). By (6.4), we have

$$\int_{A_r \cap \partial A_r^c} \rho^{\text{RHF}}(x) \, dx = \int_{A_r^c} (\rho^{\text{RHF}}(x) - \rho^{\text{TF}}(x)) \, dx - \int_{A_r^c} (\rho^{\text{RHF}}(x) - \rho^{\text{TF}}(x)) \, dx$$

$$+ \sum_{j=1}^{K} \int_{3/5 \leq |x-R_j| \leq r} \rho^{\text{TF}}(x) \, dx$$

$$\leq Cr^{-3},$$
where we have used the Sommerfeld asymptotics $\rho^{\text{TF}}(x) \leq C|x - R_j|^{-6}$ on $A_r \cap \Gamma_j$. Inserting this and the bound (6.3) into the bound from Lemma 3.2, we obtain

$$\text{tr} \left( -\frac{\Delta}{2} \eta_r \gamma^{\text{RHF}} \eta_r \right) \leq C \left( (\lambda r)^{-2} \int_{A_r} \rho^{\text{RHF}} + \lambda^{-2} r^{-5} + r^{-7} \right). \quad (6.8)$$

Replacing $r$ by $r/3$ in the above estimate, we get

$$\text{tr} \left( -\frac{\Delta}{2} \eta_{r/3} \gamma^{\text{RHF}} \eta_{r/3} \right) \leq C \left( (\lambda r)^{-2} \int_{A_r} \rho^{\text{RHF}} + \lambda^{-2} r^{-5} + r^{-7} \right). \quad (6.9)$$

From Lemma 2.4, replacing $r$ by $r/3$ and choosing $r = s$, we find that

$$\int_{A_r/3} \rho^{\text{RHF}}(x) dx \leq C \sum_{j=1}^{K} \int_{r/3 \leq |x - R_j| < r} \rho^{\text{RHF}}(x) dx + C \sum_{j=1}^{K} \left[ (r^2 \text{tr}(-\Delta \eta_{r/3} \gamma^{\text{RHF}} \eta_{r/3}))^{3/5} \right]$$

$$+ C \left( \sup_{x \in A_r/3} [\varphi(x)^{-1} \Phi^{\text{RHF}}(x)] + r + (\lambda^2 r)^{-1} + \frac{1}{R_0^2} + \frac{1}{\lambda} \right).$$

Inserting (6.3) and (6.8) into the latter estimate leads to

$$\int_{A_r} \rho^{\text{RHF}}(x) dx \leq \int_{A_r/3} \rho^{\text{RHF}}(x) dx \leq C \left( \frac{1}{r^3} + \frac{1}{\lambda^2 r} \right)$$

$$+ C \left( \frac{1}{\lambda^2} \int_{A_r} \rho^{\text{RHF}}(x) dx + \frac{1}{\lambda^2 r^3} + \frac{1}{r^5} \right)^{3/5},$$

which implies (6.5) immediately. Here we have chosen $\lambda = 1/2$. Inserting (6.3) into (6.8), we obtain (6.4).

Finally, from (6.7) and the kinetic Lieb-Thirring inequality, we have

$$\int_{A_r} (\rho^{\text{RHF}})^{5/3} \leq \int (\eta_{r/3}^{2} \rho^{\text{RHF}})^{5/3} \leq C \text{tr} \left( -\frac{\Delta}{2} \eta_{r/3} \gamma^{\text{RHF}} \eta_{r/3} \right) \leq C \left( \frac{1}{r^7} + \frac{1}{r^5} \right),$$

which implies (6.6).

**Step 2** We introduce the exterior Thomas-Fermi energy functional

$$\mathcal{E}_r^{\text{TF}}(\rho) = \frac{3}{10} c_{\text{TF}} \int \rho^{5/3} - \int V_r \rho + D(\rho), \quad V_r(x) = \chi^+_r \Phi^{\text{RHF}}(x)$$

**Lemma 6.4.** The TF functional $\mathcal{E}_r^{\text{TF}}(\rho)$ has a unique minimizer $\rho_r^{\text{TF}}$ over

$$0 \leq \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3), \quad \int \rho \leq Z - \int_{A_r^c} \rho^{\text{RHF}}(y) dy.$$ 

This minimizer is supported on $A_r$ and satisfies the TF equation

$$c_{\text{TF}} \rho_r^{\text{TF}}(x)^{2/3} = [\varphi_r^{\text{TF}}(x) - \mu_r^{\text{TF}}]_+$$

with $\varphi_r^{\text{TF}}(x) = V_r(x) - \rho_r^{\text{TF}} \star |x|^{-1}$ and a constant $\mu_r^{\text{TF}} \geq 0$. Moreover,
(i) If $\mu_{TF}^r > 0$, then

$$\int \rho_{TF}^r = Z - \int_{A_{\varepsilon}} \rho_{RHF}^r(y) dy.$$ 

(ii) If (6.1) holds true for some $\beta, D \in (0, 1]$, then

$$\int (\rho_{TF}^r)^{5/3} \leq C r^{-7}, \forall r \in (0, D].$$

**Proof.** The existence of $\rho_{TF}^r$, the TF equation, and (i) follow from [1][Theorem 4.1 (i)]. From the TF equation and the fact that $\varphi_{TF}^r \leq V_r = 0$ on $A_r$, we learn $\text{supp} \rho_{TF}^r \subset A_r$.

Moreover, by the minimizing property of $\rho_{TF}^r$ and (6.3) we obtain

$$0 \geq \mathcal{E}^r_{TF}(\rho_{TF}^r) \geq \frac{3}{10} c_{TF} \int (\rho_{TF}^r)^{5/3} - C r^{-3} \sum_{j=1}^{K} \frac{z_j}{Z} \int \left[ \frac{\rho_{TF}^r(x)}{|x - R_j|} \right] dx + D(\rho_{TF}^r)$$

$$\geq \frac{3c_{TF}}{20} \int (\rho_{TF}^r)^{5/3} - C (r^{-3})^{7/3},$$

where we have used $\inf_{\rho \geq 0} \mathcal{E}^r(\rho) \geq C \sum_{j=1}^{K} \frac{z_j^{7/3}}{z_j}$. Thus the conclusion holds true. $\Box$

We will use the next lemma.

**Lemma 6.5** (Chemical potential estimate). If $\mu_{TF}^r < \inf_{x \in A_r} \varphi_{TF}^r$, then we have $\mu_{TF}^r = 0$.

**Proof.** We suppose contrary $\mu_{TF}^r > 0$. Then it holds that

$$\int_{\mathbb{R}^3} \rho_{TF}^r(y) dy = Z - \int_{A_{\varepsilon}} \rho_{RHF}^r(y) dy. \quad (6.10)$$

By Theorem 4.2 on some $|x - R_j| \geq r$, we have

$$\nu_j(\mu_{TF}^r, r) \leq |x - R_j| \varphi_{TF}^r(x).$$

By definition, for large $|x - R_j|$ we have

$$\nu_j(\mu_{TF}^r, r) \geq \mu_{TF}^r \inf_{|x - R_j| = r} \max \left\{ \frac{c_S |x - R_j|^{-3}}{\mu_{TF}^r(1 + a(r))} \right\}$$

$$\geq (\mu_{TF}^r)^{3/4} c_S^{1/4} (1 + a(r))^{-1/2}.$$ 

Moreover, we can estimate that, on some $x \in \Gamma_j$,

$$\lim_{x \in \Gamma_j, |x - R_j| \to \infty} |x - R_j| \varphi_{TF}^r(x) \leq Z - \int_{A_{\varepsilon}} \rho_{RHF}^r(y) dy - \int_{\mathbb{R}^3} \rho_{TF}^r(y) dy.$$ 

Hence, we have

$$0 < (\mu_{TF}^r)^{3/4} \leq C \left( Z - \int_{A_{\varepsilon}} \rho_{RHF}^r(y) dy - \int_{\mathbb{R}^3} \rho_{TF}^r(y) dy \right).$$
Thus, it follows that
\[
\int_{\mathbb{R}^3} \rho_r^{\text{TF}}(y) \, dy < Z - \int_{A_r^c} \rho^{\text{RHF}}(y) \, dy.
\]
This contradicts to (6.10).

**Step 3** Now we compare \( \rho_r^{\text{TF}} \) with \( 1_{A_r} \rho_r^{\text{TF}} \).

**Lemma 6.6.** Let \( \bar{r} = (2R_0)^{-1} \frac{\xi}{\epsilon_0} R_{\text{min}}^{\frac{3}{2}} \). We can choose a universal constant \( \beta > 0 \) small enough such that, if (6.1) holds true for some \( D \in [Z^{-1/3}, R_0] \), and if \( r \in [Z^{-1/3}, D] \) then \( \mu_r^{\text{TF}} = 0 \) and for any \( s \in [r, \bar{r}] \)

\[
\begin{align*}
\sup_{x \in \partial A_s} |\varphi_r^{\text{TF}}(x) - \varphi^{\text{TF}}(x)| & \leq C(r/s)^{\xi}s^{-4}, \\
\sup_{x \in \partial A_s} |\rho_r^{\text{TF}}(x) - \rho^{\text{TF}}(x)| & \leq C(r/s)^{\xi}s^{-6}.
\end{align*}
\]

Here \( \xi = (\sqrt{73} - 7)/2 \sim 0.77 \).

**Proof.** We recall Theorem 4.1, that is, in \( A_r \cap \Gamma_j \)

\[
K \left( 1 + A(r) \left( \frac{r}{|x - R_j|} \right) \xi \right) \geq \frac{\varphi^{\text{TF}}(x)}{c_s|x - R_j|^{-4}} \geq \left( 1 + a(r) \left( \frac{r}{|x - R_j|} \right) \xi \right)^{-2},
\]  

\[
K^{3/2} \left( 1 + A(r) \left( \frac{r}{|x - R_j|} \right) \xi \right)^{3/2} \geq \frac{\rho^{\text{TF}}(x)}{(c_s/\epsilon_0)^{3/2} |x - R_j|^{-6}} \geq \left( 1 + a(r) \left( \frac{r}{|x - R_j|} \right) \xi \right)^{-3}.
\]

From this, we have \( C|x - R_j|^{-6} \geq \rho^{\text{TF}}(x) \geq C^{-1}|x - R_j|^{-6} \) for \( x \in A_r \cap \Gamma_j \), and hence

\[
Cr^{-3} \geq \int_{A_r} \rho^{\text{TF}}(x) \geq C^{-1}r^{-3}
\]

for any \( r \in [Z^{-1/3}, R_0] \).

**Lemma 6.7.** For every \( r \in (0, R_0] \), we have

\[
\tilde{\mathcal{E}}_r(\chi_r^{+} \rho^{\text{TF}}) \leq \tilde{\mathcal{E}}_r(\rho)
\]

for all \( 0 \leq \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3) \) with \( \text{supp} \rho \subset A_r \), where

\[
\tilde{\mathcal{E}}_r(\rho) = \frac{3}{10} \epsilon_0 \int \rho^{5/3} - \int \Phi_r^{\text{TF}} \rho + D(\rho).
\]

**Proof.** For all \( 0 \leq \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3) \) with \( \text{supp} \rho \subset A_r \), by the minimality of \( \rho^{\text{TF}} \) we have

\[
\mathcal{E}^{\text{TF}}(\rho^{\text{TF}}) \leq \mathcal{E}^{\text{TF}}(1_{A_r} \rho^{\text{TF}} + \rho).
\]
Since $\mathbf{1}_{A_r} \rho_{\text{TF}}$ and $\rho$ have disjoint supports, we can write
\[ E_{\text{TF}}(\mathbf{1}_{A_r} \rho_{\text{TF}} + \rho) = E_{\text{TF}}(\mathbf{1}_{A_r} \rho_{\text{TF}}) + E_{\text{TF}}(\rho) + \iint_{A_r} \rho(x) \rho_{\text{TF}}(y) \frac{dxdy}{|x-y|} \]
\[ = E_{\text{TF}}(\mathbf{1}_{A_r} \rho_{\text{TF}}) + \widetilde{E}_r(\rho). \]

In particular, we can apply the latter equality with $\rho = \chi_r^+ \rho_{\text{TF}}$ and obtain
\[ E_{\text{TF}}(\rho_{\text{TF}}) = E_{\text{TF}}(\mathbf{1}_{A_r} \rho_{\text{TF}} + \chi_r^+ \rho_{\text{TF}}) \]
\[ = E_{\text{TF}}(\mathbf{1}_{A_r} \rho_{\text{TF}}) + \widetilde{E}_r(\chi_r^+ \rho_{\text{TF}}). \]

Thus
\[ 0 \leq E_{\text{TF}}(\mathbf{1}_{A_r} \rho_{\text{TF}} + \rho) - E_{\text{TF}}(\rho_{\text{TF}}) = \widetilde{E}_r(\rho) - \widetilde{E}_r(\chi_r^+ \rho_{\text{TF}}). \]
This completes the proof. \qed

Now using this Lemma with $\rho = \rho_{r_{\text{TF}}}$ and the identity
\[ \widetilde{E}_r(\rho) = E_r(\rho_{\text{TF}}) + \int (\Phi_{\text{RHF}}^r - \Phi_{\text{TF}}^r) \rho, \]
we find that
\[ E^r_r(\chi_r^+ \rho_{\text{TF}}) \leq E_r(\rho_{\text{TF}}) - \int (\Phi_{\text{RHF}}^r - \Phi_{\text{TF}}^r)(\chi_r^+ \rho_{\text{TF}} - \rho_{r_{\text{TF}}}). \tag{6.15} \]

Since $\Phi_{r_{\text{RHF}}}(x) - \Phi_{r_{\text{TF}}}(x)$ is harmonic in $A_r$, we deduce from (6.1) that
\[ \sup_{x \in A_r} |\Phi_{r_{\text{RHF}}}(x) - \Phi_{r_{\text{TF}}}(x)| = \sup_{x \in \partial A_r} |\Phi_{r_{\text{RHF}}}(x) - \Phi_{r_{\text{TF}}}(x)| \leq \beta r^{-4}. \]

Therefore, we get
\[ \int (\Phi_{r_{\text{RHF}}}(x) - \Phi_{r_{\text{TF}}}(x))(\chi_r^+ \rho_{\text{TF}} - \rho_{r_{\text{TF}}}) \leq \beta r^{-4} \int (\chi_r^+ \rho_{\text{TF}} + \rho_{r_{\text{TF}}}) \]
\[ \leq C \beta r^{-7}, \]
where we have used the upper bound in (6.14), and by (6.3),
\[ \int \rho_{r_{\text{TF}}} \leq Z - \int A_{r_{\text{TF}}} \rho_{r_{\text{TF}}} \leq \int A_r \rho_{\text{RHF}} \leq C r^{-3}. \]

Here we have used the assumption $N \geq Z$. Hence (6.15) reduces to
\[ E^r_r(\chi_r^+ \rho_{\text{TF}}) \leq E_r(\rho_{\text{TF}}) + C \beta r^{-7}. \tag{6.16} \]

We want to compare $\chi_r^+ \rho_{\text{TF}}$ with $\rho_{r_{\text{TF}}}$ using the minimality property of the latter as [1] Proof of Lemma 6.8]. Using (6.4), (6.14), we have
\[ \int A_r \rho_{\text{TF}}(x) dx - \left( Z - \int A_{r_{\text{TF}}} \rho_{r_{\text{TF}}}(y) dy \right) \leq \int A_r (\rho_{\text{RHF}} - \rho_{\text{TF}}) \leq C \beta \int A_r \rho_{\text{TF}}. \]
This can be rewritten as
\[ \int A_r (1 - C \beta) \rho_{\text{TF}} \leq \left( Z - \int A_{r_{\text{TF}}} \rho_{r_{\text{TF}}}(y) dy \right). \tag{6.17} \]
In the following, we choose \( \beta > 0 \) small enough such that \( C\beta \leq 1/2 \). Since \( \int (C\rho)^{5/3} + D(C\rho) \leq \int \rho^{5/3} + D[\rho] \) for \( C \leq 1 \), using (6.3) and (6.4) we may estimate

\[
\mathcal{E}_r^{\text{TF}}((1 - C\beta)\chi_r^+ \rho^{\text{TF}}) - \mathcal{E}_r^{\text{TF}}(\chi_r^+ \rho^{\text{TF}}) \leq C\beta \int_{A_r} \Phi_r^{\text{RHF}} \rho^{\text{TF}} \leq C\beta r^{-7}.
\]

Therefore, from (6.16) we derive that

\[
\mathcal{E}_r^{\text{TF}}((1 - C\beta)\chi_r^+ \rho^{\text{TF}}) \leq \mathcal{E}_r^{\text{TF}}(\rho^{\text{TF}}) + C\beta r^{-7}.
\]

Combining with (6.17) and the minimality of \( \rho_r^{\text{TF}} \), we obtain

\[
\mathcal{E}_r^{\text{TF}}((1 - C\beta)\chi_r^+ \rho^{\text{TF}}) + \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) - 2\mathcal{E}_r^{\text{TF}}(\frac{(1 - C\beta)\chi_r^+ \rho^{\text{TF}} + \rho_r^{\text{TF}}}{2}) \leq C\beta r^{-7}.
\]

By the convexity of \( \rho^{5/3} \) and \( D[\rho] \), we have

\[
D[(1 - C\beta)\chi_r^+ \rho^{\text{TF}} - \rho_r^{\text{TF}}] \leq C\beta r^{-7}. 
\]

(6.18)

We also derive that

\[
\int \left[ \left((1 - C\beta)\chi_r^+ \rho^{\text{TF}}(x)\right)^{5/3} + \rho_r^{\text{TF}}(x)^{5/3} 
- 2 \left(\frac{(1 - C\beta)\chi_r^+ \rho^{\text{TF}}(x) + \rho_r^{\text{TF}}(x)}{2}\right)^{5/3}\right] dx \leq C\beta r^{-7}. 
\]

(6.19)

From (6.18) and the convexity of Coulomb term \( D[\cdot] \), we learn that

\[
D(\chi_r^+ \rho^{\text{TF}} - \rho_r^{\text{TF}}) \leq 2D[\chi_r^+ \rho^{\text{TF}} - (1 - C\beta)\chi_r^+ \rho^{\text{TF}}] + 2D[(1 - C\beta)\chi_r^+ \rho^{\text{TF}} - \rho_r^{\text{TF}}] 
\leq (C\beta)^2 D(\chi_r^+ \rho^{\text{TF}}) + C\beta r^{-7} 
\leq C\beta r^{-7}, 
\]

(6.20)

where the last inequality follows from choosing \( C\beta \leq 1 \).

Now we apply the fact that \( f \star |x|^{-1} \leq C\|f\|_{L^5}D[f]^{1/7} \) (see (6.3)) with \( f = \pm(\chi_r^+ \rho^{\text{TF}} - \rho_r^{\text{TF}}) \). Then using (6.4) and \( \int_{A_r}(\rho^{\text{TF}})^{5/3} \leq Cr^{-7} \), we have

\[
|(\chi_r^+ \rho^{\text{TF}} - \rho_r^{\text{TF}}) \star |x|^{-1}| \leq C\beta^{1/7} r^{-4}.
\]

Combining this with assumption (6.11), we get

\[
|\varphi_r^{\text{TF}}(x) - \varphi_r^{\text{TF}}(x)| = |\Phi_r^{\text{RHF}}(x) - \Phi_r^{\text{TF}}(x) + (\chi_r^+ \rho^{\text{TF}} - \rho_r^{\text{TF}}) \star |x|^{-1}| 
\leq C(\beta + \beta^{1/7})r^{-4}, \quad \forall x \in A_r.
\]

We note that \( Cr^{-4} \geq \varphi_r^{\text{TF}}(x) \geq C^{-1}r^{-4} \) for \( x \in A_r \) by the Sommerfeld bound. Therefore, if \( \beta > 0 \) is sufficiently small, we deduce that

\[
Cr^{-4} \geq \varphi_r^{\text{TF}}(x) \geq C^{-1}r^{-4} \quad \forall x \in A_r.
\]

(6.21)
In order to obtain a refined version of this, we need to show that $\mu_r^{\text{TF}} = 0$. Thus we apply Lemma 6.8 and thus conclude $\mu_r^{\text{TF}} = 0$ if

$$\mu_r^{\text{TF}} < \inf_{x \in \partial A_r} \varphi_r^{\text{TF}}(x).$$

We now suppose that (6.22) fails. Then from (6.21) we find that

$$\mu_r^{\text{TF}} \geq \inf_{x \in A_r} \varphi_r^{\text{TF}}(x) \geq C^{-1}r^{-4}.$$

On the other hand, $\varphi_r^{\text{TF}}(x) \leq \Phi_r^{\text{RHF}}(x) \leq Cr^{-3}\varphi(x)$ by (6.3). Therefore, from the TF equation

$$c_r^\text{TF} \rho_r^{\text{TF}}(x)^{2/3} = [\varphi_r^{\text{TF}}(x) - \mu_r^{\text{TF}}]_+ \leq [Cr^{-3}\varphi(x) - C^{-1}r^{-4}]_+,$$

we find that $\rho_r^{\text{TF}}(x) = 0$ on $A_{C^{-2}}$. Since the integrand in (6.19) is pointwise nonnegative, we can restrict the integral on $A_{C^{-2}}$. Then using $\rho_r^{\text{TF}}(x) = 0$ on $A_{C^{-2}}$, we derive from (6.19) that

$$C\beta r^{-7} \geq \int_{A_{C^{-2}}} ((1 - C\beta) \rho_r^{\text{TF}}(x))^{5/3} \, dx \geq C^{-1}(1 - C\beta)^{5/3} r^{-7}.$$

Thus we get $C^{-1}(1 - C\beta)^{5/3} r^{-7} \leq C\beta r^{-7}$ and a contradiction if $\beta > 0$ is sufficiently small. Then we can choose $\beta > 0$ small enough such that $\mu_r^{\text{TF}} = 0$. Hence we can use Theorem 4.1 and Theorem 4.2 for $\varphi_r^{\text{TF}}$ and $\varphi_r^{\text{TF}}$, and therefore we arrive at, for $x \in A_r \cap \Gamma_j$,

$$|\varphi_r^{\text{TF}}(x) - \varphi_r^{\text{TF}}(x)| \leq c_4|\phi(x) - r_j|^{-4} \left(A_1^2(r) \left(\frac{|x - R_j|}{r_j}\right)^{\eta} + (A_2^3(r) + 2a(r) \left(\frac{r}{|x - R_j|}\right)^{\xi})\right),$$

where we have used the fact that $(1 + t)^{-2} \geq 1 - 2t$ for $t \in (-1, \infty)$. Since $r \leq s \leq \bar{r}$, it holds that $(s/R_j)^{\eta} \leq (R_0)^{-(\xi + \eta)}(r/s)^{\xi}$. If we note that $A_1^2(r) \leq C$ and $a(r) \leq C$ by (6.21), then (6.11) follows. Proceeding this way one can arrive at (6.12) from the fact that, for any $t \in (0, T]$, $(1 + t)^{3/2} \leq 1 + t((1 + T)^{3/2} - 1)T^{-1}$. Then the proof is complete.

**Step 4** In this step, we compare $\rho_r^{\text{TF}}$ with $1_{A_r}\rho_r^{\text{RHF}}$.

**Lemma 6.8.** Let $\beta > 0$ be as in Lemma 6.6. We assume that (6.1) holds for some $D \in [Z^{-1/3}, R_0]$. Then, if $r \leq [Z^{-1/3}, D]$, we have

$$D(\rho_r^{\text{TF}} - 1_{A_r}\rho_r^{\text{RHF}}) \leq C^{-7+1/3}.$$

**Proof.** **Upper Bound.** We will prove that

$$\mathcal{E}_r^{\text{RHF}}(\rho_r^{\text{RHF}})^{\eta_r} \leq \mathcal{E}_r^{\text{TF}}(\rho_r^{\text{TF}}) + C^{-7}(r^{2/3} + \lambda^2r^2 + \lambda).$$

(6.23)

We use Lemma 5.2 (2) with $V_r := 1_{A_r}\varphi_r^{\text{RHF}}$, $s \leq r$ to be chosen later and $g$ spherically symmetric to obtain a density matrix $\tilde{\gamma}$ as in the statement. Since $\mu_r^{\text{TF}} = 0$ by Lemma 6.6 we deduce from the TF equation in Lemma 6.4 that

$$\rho_{\tilde{\gamma}} = 2^{5/2}(6\pi^2)^{-1} (1_{A_r}(\varphi_r^{\text{TF}})^{3/2}) \ast g^2 = (1_{A_r}\rho_r^{\text{TF}}) \ast g^2.$$
Since $\rho_{\tilde{\gamma}}$ is supported in $A_r$ and
\[
\text{tr} \tilde{\gamma} = \int \rho_{\tilde{\gamma}} = \int_{A_r} \rho_{r}^{\text{TF}} \leq \int_{A_r} \rho_{r}^{\text{RHF}},
\]
we may apply Lemma 3.1 and obtain $\mathcal{E}_{r}^{\text{RHF}}(\eta_{r}^{\text{RHF}} \gamma_r \eta_r) \leq \mathcal{E}_{r}^{\text{RHF}}(\tilde{\gamma}) + \mathcal{R}$. Next, we bound $\mathcal{E}_{r}^{\text{RHF}}(\tilde{\gamma})$. By the semiclassical estimate from Lemma 5.2 (2), we have
\[
\mathcal{E}_{r}^{\text{RHF}}(\tilde{\gamma}) \leq \frac{2^{3/2}(5\pi^2)^{-1}}{} \int [V_{r}]_{+}^{5/2} + C \cdot S^{-2} \int [V_{r}]_{+}^{3/2} + D(\rho_{r}^{\text{TF}} \ast g^2) - \int \Phi_{r}^{\text{RHF}}(1_{A_r} \rho_{r}^{\text{TF}} \ast g^2) \\
\leq \frac{2^{3/2}(5\pi^2)^{-1}}{} \int [\varphi_{r}^{\text{TF}}]_{+}^{5/2} + C \cdot S^{-2} \int \rho_{r}^{\text{TF}} - \int A_r \Phi_{r}^{\text{RHF}} \rho_{r}^{\text{TF}} \\
+ D(\rho_{r}^{\text{TF}}) + \int_{A_r} (\Phi_{r}^{\text{RHF}} - \Phi_{r}^{\text{RHF}} \ast g^2) \rho_{r}^{\text{TF}} + \int_{A_r \cap A_r^{c} \ast s} \Phi_{r}^{\text{RHF}} \rho_{r}^{\text{TF}} \\
\leq \mathcal{E}_{r}^{\text{TF}}(\rho_{r}^{\text{TF}}) + C \cdot S^{-2} \int \rho_{r}^{\text{TF}} + \int_{A_r \cap A_r^{c} \ast s} \Phi_{r}^{\text{RHF}} \rho_{r}^{\text{TF}},
\]
(6.24)
where we have used $\Phi_{r}^{\text{RHF}} \ast g^2 \geq \Phi_{r}^{\text{RHF}}$ on $A_r$ in the second inequality. This fact follows from Newton’s theorem and the assumption $s \leq r$. According to (6.5), we get
\[
\int \rho_{r}^{\text{TF}} \leq \int A_r \rho_{r}^{\text{RHF}} \leq Cr^{-3}.
\]
We note that $\rho_{r}^{\text{TF}}(x) \leq C|x - R_j|^{-6}$ on $A_r \cap \Gamma_j$, and if $r \leq |x - R_j| < r + s$ then $x \in \Gamma_j$,
\[
\int_{A_r \cap A_r^{c} \ast s} \Phi_{r}^{\text{RHF}} \rho_{r}^{\text{TF}} \leq Cr^{-3} \sum_{j=1}^{K} \int_{r \leq |x - R_j| \leq r + s} |x - R_j|^{-7} dx \leq Csr^{-8}.
\]
We choose $s = r^{5/3}$ and get
\[
\mathcal{E}_{r}^{\text{RHF}}(\tilde{\gamma}) \leq \mathcal{E}_{r}^{\text{TF}}(\rho_{r}^{\text{TF}}) + Cr^{-7+2/3}.
\]
Finally, since $\lambda \leq 1/2$, we have
\[
\mathcal{R} \leq C(\lambda^{-2}r^{-5} + \lambda r^{-7}).
\]
Hence we obtain the desired upper bound.

**Lower bound.** We will prove
\[
\mathcal{E}_{r}^{\text{RHF}}(\eta_{r}^{\text{RHF}} \gamma_r \eta_r) \geq \mathcal{E}_{r}^{\text{TF}}(\rho_{r}^{\text{TF}}) + D(\eta_{r}^{2} \rho_{r}^{\text{RHF}} - \rho_{r}^{\text{TF}}) - Cr^{-7+1/3}.
\]
We can estimate
\[ E_r^{\text{RHF}}(\eta r^{\text{RHF}}) = \text{tr} \left( -\frac{\Delta}{2} - \varphi_r^{\text{TF}} \eta r^{\text{RHF}} \right) + D(\eta r^2 \rho^{\text{RHF}} - \rho_r^{\text{TF}}) + D(\rho_r^{\text{TF}}) \]
\[ \geq -2^{5/2}(15\pi^2)^{-1} \int |\varphi_r^{\text{TF}}|^{5/2} - C_{s^{-2}} \int \eta r^2 \rho^{\text{RHF}} \]
\[ C \left( \int |\varphi_r^{\text{TF}}|^{5/2} \right)^{3/5} \left( \int |\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} \ast g|^2 \right)^{2/5} \]
\[ + D(\eta r^2 \rho^{\text{RHF}} - \rho_r^{\text{TF}}) - D(\rho_r^{\text{TF}}) \]
\[ = E_r^{\text{TF}}(\rho_r^{\text{TF}}) + D(\eta r^2 \rho^{\text{RHF}} - \rho_r^{\text{TF}}) - C_{s^{-2}} \int \eta r^2 \rho^{\text{RHF}} \]
\[ - C \left( \int |\varphi_r^{\text{TF}}|^{5/2} \right)^{3/5} \left( \int |\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} \ast g|^2 \right)^{2/5} . \]

We note
\[ \int \eta r^2 \rho^{\text{RHF}} \leq Cr^{-3}, \]
\[ \int |\varphi_r^{\text{TF}}|^{5/2} = C \int (\rho_r^{\text{TF}})^{5/3} \leq Cr^{-7}. \]

We know \(|x|^{-1} - |x|^{-1} \ast g^2 \geq 0\) and thus \(\rho_r^{\text{TF}} \ast (|x|^{-1} - |x|^{-1} \ast g^2) \geq 0\). Since the TF equation \(\varphi_r^{\text{TF}} = \chi_r^{+} \phi_r^{\text{RHF}} - \rho_r^{\text{TF}} \ast |x|^{-1}\), we have
\[ \varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} \ast g^2 \leq \chi_r^{+} \phi_r^{\text{RHF}} - (\chi_r^{+} \phi_r^{\text{RHF}}) \ast g^2 =: f. \]

By Newton’s theorem, we infer that \(\text{supp} f \subset \bigcup_{j=1}^{K} \{x: r - s \leq |x - R_j| \leq r + s\}\).

Hence, by \(|f(x)| \leq Cr^{-4}\), we have
\[ |\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} \ast g^2|_+ \leq Cr^{-4} \sum_{j=1}^{K} 1(r - s \leq |x - R_j| \leq r + s). \]

Together with these facts, we learn
\[ \int |\varphi_r^{\text{TF}} - \varphi_r^{\text{TF}} \ast g^2|^{5/2} \leq Cr^{-8}s. \]

We conclude that
\[ E_r^{\text{RHF}}(\eta r^{\text{RHF}}) \geq E_r^{\text{TF}}(\rho_r^{\text{TF}}) + D(\eta r^2 \rho^{\text{RHF}} - \rho_r^{\text{TF}}) - C(s^{-2}r^{-3} + r^{-37/5}s^{2/5}). \]

Then we choose \(s = r^{11/6}\) and arrive at the desired lower bound.

**Conclusion** Combining the upper and lower bound, we learn
\[ D[\eta r^2 \rho^{\text{RHF}} - \rho_r^{\text{TF}}] \leq Cr^{-7}(r^{1/3} + \lambda^{-2}r^2 + \lambda). \]
Using the Hardy-Littlewood-Sobolev inequality, we have
\[
D[\chi_r^+ \rho^{\text{RHF}} - \eta_r^2 \rho^{\text{RHF}}] \leq C \| \mathbf{1}_{A_r \cap \Lambda^* (1 + \lambda r)} \rho^{\text{RHF}} \|_{L^{6/5}}^2
\]
\[
\leq C \left( \int_{A_r} \rho^{\text{RHF}}(x)^{5/3} \, dx \right)^{6/5} \left( \sum_{j=1}^{K} \int_{r \leq |x-R_j| \leq (1+\lambda)r} \rho^{\text{RHF}}(x) \, dx \right)^{7/15}
\]
\[
= C \lambda^{7/15} r^{-7}.
\]

By convexity of the Coulomb energy,
\[
D[\chi_r^+ \rho^{\text{RHF}} - \rho_r^{\text{TF}}] \leq 2D[\chi_r^+ \rho^{\text{RHF}} - \eta_r^2 \rho^{\text{RHF}}] + 2D[\eta_r^2 \rho^{\text{RHF}} - \rho_r^{\text{TF}}]
\]
\[
\leq Cr^{-7}(\lambda^{7/15} + r^{1/3} + \lambda^{-2} r^2),
\]
for any \( \lambda \in (0, 1/2) \). We choose \( \lambda = r^{30/37} \) and get
\[
D[\chi_r^+ \rho^{\text{RHF}} - \rho_r^{\text{TF}}] \leq Cr^{-7+1/3}.
\]

This completes the proof.

Step 5

We now prove Theorem 6.1. Let \( r \in [Z^{-1/3}, D] \), \( s \in [r, \bar{r}] \) and \( x \in \partial A_s \). We may split
\[
\Phi^{\text{RHF}}_s(x) - \Phi^{\text{TF}}_s(x) = \varphi^{\text{TF}}_s(x) - \varphi^{\text{TF}}_s(x) + \int_{A_s} \frac{\rho^{\text{TF}}_r(y) - \rho^{\text{TF}}_r(y)}{|x-y|} \, dy
\]
\[
+ \sum_{i=1}^{K} \int_{|y-R_i| < s} \frac{\rho^{\text{TF}}_r(y) - \chi_r^+ \rho^{\text{RHF}}(y)}{|x-y|} \, dy.
\]

We know
\[
|\varphi^{\text{TF}}_r(x) - \varphi^{\text{TF}}_r(x)| \leq C \left( \frac{r}{s} \right)^{\xi} s^{-4}
\]
and
\[
\int_{A_r} \frac{\rho^{\text{TF}}_r(y) - \rho^{\text{TF}}_r(y)}{|x-y|} \, dy \leq C \left( \frac{r}{s} \right)^{\xi} s^{-4}.
\]

We note that \( \mathbf{1}_{|y-R_i| < s}(\rho^{\text{TF}}_r - \chi_r^+ \rho^{\text{RHF}}) \ast |x|^{-1} \) is harmonic in \( |x-R_i| \geq s \) for any \( i = 1, \ldots, K \). Hence we get from the Coulomb estimate that
\[
\left| \int_{|y-R_i| < s} \frac{\rho^{\text{TF}}_r(y) - \chi_r^+ \rho^{\text{RHF}}(y)}{|x-y|} \, dy \right| \leq \sup_{|x-R_i| = s} \left| \int_{|y-R_i| < s} \frac{\rho^{\text{TF}}_r(y) - \chi_r^+ \rho^{\text{RHF}}(y)}{|x-y|} \, dy \right|
\]
\[
\leq C \| \rho^{\text{TF}}_r - \chi_r^+ \rho^{\text{RHF}} \|_{L^{5/3}} (sD(\rho^{\text{TF}}_r - \chi_r^+ \rho^{\text{RHF}}))^{1/12}
\]
\[
\leq C s^{-7/2} (r^{-7+1/3} s)^{1/12}
\]
\[
= C s^{-4+1/36} \left( \frac{s}{r} \right)^{4+1/12 - 1/36}.
\]

In conclusion,
\[
\sup_{x \in \partial A_s} |\Phi^{\text{RHF}}_s(x) - \Phi^{\text{TF}}_s(x)| \leq C \left( \frac{r}{s} \right)^{\xi} s^{-4} + C \left( \frac{s}{r} \right)^{5} s^{-4+1/36}.
\] 
(6.25)
Now we choose a constant \( \delta \in (0,1) \) such that
\[
\frac{1 + \delta}{1 - \delta} \left( \frac{49}{36} - a \right) < \frac{49}{36}, \quad \frac{1}{36} - \frac{10\delta}{1 - \delta} > 0.
\]

**Case 1** \( D^{1+\delta} \leq Z^{-1/3} \).

Let \( r = D^{1+\delta} \). By the initial step, for any \( s \leq r^{1+\delta} \leq (Z^{-1/3})(1-\delta)/(1+\delta) \), we have
\[
|\Phi_{s}^{\text{RHF}}(x) - \Phi_{s}^{\text{TF}}(x)| \leq CZ^{49/36-a} s^{1/12} \leq Cs^{1/12-3(1-\delta)/(1+\delta)(49/36-a)} = Cs^{-4+\epsilon_1}.
\]

**Case 2** \( D^{1+\delta} \geq Z^{-1/3} \).

In this case, we use (6.25) with \( r = D^{1+\delta} \). For any \( D \leq s \leq D^{1-\delta} \) we learn
\[
s^{2\delta/(1-\delta)} \leq r/s \leq s^{\delta}.
\]

Thus we deduce from (6.25) that
\[
|\Phi_{s}^{\text{RHF}}(x) - \Phi_{s}^{\text{TF}}(x)| \leq Cs^{-4+\epsilon_2} + Cs^{-4+1/36-10\delta/(1-\delta)} \leq Cs^{-4+\epsilon_2}.
\]

Hence we conclude that in both cases
\[
|\Phi_{s}^{\text{RHF}}(x) - \Phi_{s}^{\text{TF}}(x)| \leq Cs^{-4+\epsilon}, \quad \forall s \in \left[ r^{1+\delta}, \min\{r^{1+\delta}, r^*\} \right].
\]

This completes the proof. \( \square \)

### 7. Screened Potential Estimate

Now we can prove the following theorem.

**Theorem 7.1** (screened potential estimate). There are universal constants \( C, \epsilon, D > 0 \) such that
\[
\sup_{x \in \partial A_r} \left| \int_{A_r^c} \frac{\rho_{\text{RHF}}(y) - \rho_{\text{TF}}(y)}{|x - y|} dy \right| \leq Cr^{-4+\epsilon} \quad \forall r \leq D.
\]

**Proof.** The proof is essentially same as [9, Theorem 5.1]. Let \( \sigma = \max\{C_1, C_2\} \). We may assume \( \beta < \sigma \). We put \( D_0 = Z^{-1/3} \). From Lemma 5.1 we learn
\[
\sup_{x \in \partial A_r} \left| \int_{A_r^c} \frac{\rho_{\text{RHF}}(y) - \rho_{\text{TF}}(y)}{|x - y|} dy \right| \leq \sigma r^{-4+\epsilon} \quad \forall r \leq D_0 = Z^{-1/3}.
\]

Now we define
\[
M := \sup \left\{ r \in \mathbb{R} : \sup_{x \in \partial A_s} \left| \int_{A_r^c} \frac{\rho_{\text{RHF}}(y) - \rho_{\text{TF}}(y)}{|x - y|} dy \right| \leq \sigma s^{-4+\epsilon}, \forall s \leq r^{1+\delta} \right\}.
\]

Next, we suppose that

1. \( M < R_0 \)

and
(2) \( M_1 \), \( \min \{ M_1 , \tilde{M} \} \neq \emptyset \).

If \( D_0 < M \), then there is a sequence such that \( D_n \to M \) and \( D_0 \leq D_n \leq M \) for large \( n \). From this and Lemma 6.1, we see

\[
\sup_{x \in \partial A_r} \left| \int_{A_r^c} \frac{\rho^{RHF}(y) - \rho^{TF}(y)}{|x - y|} \, dy \right| \leq \sigma r^{-4+\varepsilon}, \quad \forall r \in \left[ D_n \frac{1}{1+\delta}, \min \left\{ D_n \frac{1}{1+\delta}, \tilde{D}_n \right\} \right].
\]

From (2), we have

\[
M_1 \frac{1}{1+\delta} \in \left( D_n \frac{1}{1+\delta}, \min \left\{ D_n \frac{1}{1+\delta}, \tilde{D}_n \right\} \right) \neq \emptyset
\]

for large \( n \). This contradicts to the definition of \( M \). If \( D_0 = M \), then \( D_0 \leq R_0 \) and

\[
\sup_{x \in \partial A_r} \left| \int_{A_r^c} \frac{\rho^{RHF}(y) - \rho^{TF}(y)}{|x - y|} \, dy \right| \leq \sigma r^{-4+\varepsilon}, \quad \forall r \leq \min \{ M, \tilde{M} \}
\]

This together with (2) again contradicts to the definition of \( M \). Finally, if \( D_0 > M \) then we choose \( M' \in (M, \min \{ 1, D_0 \}) \). This contradicts to (7.1). Hence at least one of (1) and (2) cannot hold. If (1) is true, then \( M \geq c R_0 \eta (1+\delta) \). Therefore we arrive at

\[
M \geq \min \left\{ R_0, c R_0 \eta (1+\delta) \right\} \geq D^{1+\delta},
\]

where \( D \) is the universal constant. Then the theorem follows.

Proof of Theorem 1.1 Since \( N \leq 2Z + K \) \( \left[ 5 \right] \), it remain to consider the case \( N \geq Z \geq 1 \). By Theorem 7.1, we can find universal constants \( C, \varepsilon, D > 0 \) such that,

\[
\sup_{x \in \partial A_r} \left| \int_{A_r^c} \frac{\rho^{RHF}(y) - \rho^{TF}(y)}{|x - y|} \, dy \right| \leq C r^{-4+\varepsilon}, \quad \forall r \leq D.
\]

In particular, (6.1) holds true with a universal constant \( \beta = CD^\varepsilon \). We can choose \( D \) sufficiently small so that \( D \leq 1 \) and \( \beta \leq 1 \), which allow us to apply Lemma 6.2. Then using (6.4) and (6.5) with \( r = D \), we find that

\[
\int_{A_D} \rho^{RHF} + \sum_{j=1}^{K} \int_{|x-R_j| < D} (\rho^{RHF} - \rho^{TF}) \leq C.
\]

Combining with \( \int \rho^{TF} = Z \), we obtain the ionization bound

\[
N = \int \rho^{RHF} = \int_{A_D} \rho^{RHF} + \sum_{j=1}^{K} \int_{|x-R_j| < D} (\rho^{RHF} - \rho^{TF}) + \sum_{j=1}^{K} \int_{|x-R_j| < D} \rho^{TF} \leq C + Z.
\]

This completes the proof.
THE MAXIMAL EXCESS CHARGE IN REDUCED HARTREE-FOCK MOLECULE

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