THE IONIZATION CONJECTURE IN HARTREE-FOCK THEORY

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Dec. 13, 2000

Abstract

We prove the ionization conjecture within the Hartree-Fock theory of atoms. More precisely, we prove that, if the nuclear charge is allowed to tend to infinity, the maximal negative ionization charge and the ionization energy of atoms nevertheless remain bounded. Moreover, we show that in Hartree-Fock theory the radius of an atom (properly defined) is bounded independently of its nuclear charge.

Contents

1 Introduction and main results

One of the great triumphs of quantum mechanics is that it explains the order in the periodic table qualitatively as well as quantitatively. In elementary chemistry it is discussed how quantum mechanics implies the shell structure of atoms which gives a qualitative understanding of the periodic table. In computational quantum chemistry it is found that quantum mechanics gives excellent agreement with the quantitative aspects of the periodic table. It is a very striking fact, however, that the periodic table is much more "periodic" than can be explained by the simple shell structure picture. As an examples it can be mentioned that e.g., the radii of different atoms belonging to the *same* group in the periodic table do not vary very much, although the number of electrons in the atoms can vary by a factor of 10. Another related example is the fact that the maximal negative ionization (the number of extra electrons that a neutral atom can bind) remains small (possibly no bigger than 2) even for atoms with large atomic number (nuclear charge). These experimental facts can to some extent be understood numerically, but there is no good qualitative explanation for them.

In the mathematical physics literature the problem has been formulated as follows (see e.g., problems 9 and 10 in [20]). Imagine that we consider 'the infinitely large periodic table', i.e., atoms with arbitrarily large nuclear charge Z, is it then still true that the radius and maximal negative ionization remain bounded? This question often referred to as the *ionization* conjecture is the subject of this paper.

To be completely honest neither the qualitative nor the quantitative explanations of the periodic table use the full quantum mechanical description. On one hand the simple qualitative shell structure picture ignores the interactions between the electrons in the atoms. On the other hand even in computational quantum chemistry one most often uses approximations to the full many body quantum mechanical description. There are in fact a hierarchy of models for the structure of atoms. The one which is usually consider most complete is the Schrödinger many-particle model. There are, however, even more complicated models, which take relativistic and/or quantum field theoretic corrections into account.

A description which is somewhat simpler than the Schrödinger model is the Hartree-Fock (HF) model. Because of its greater simplicity it has been more widely used in computational quantum chemistry than the full Schrödinger model. Although, chemists over the years have developed numerous generalizations of the Hartree-Fock model, it is still remarkable how tremendously successful the original (HF) model has been in describing the structure of atoms and molecules.

A model which is again much simpler than the Hartree-Fock model is the Thomas-Fermi (TF) model. In this model the problem of finding the structure of an atom is essentially reduced to solving an ODE. The TF model has some features, which are qualitatively wrong. Most notably it predicts that atoms do not bind to form molecules (Teller's no binding Theorem, see [14]).

In this work we shall show that the TF model is, indeed, a much better approximation to the more complicated HF model than generally believed. In fact, we shall show that it is only the outermost region of the atom which is not well described by the TF model.

As a simple corollary of this improved TF approximation we shall prove the *ionization conjecture* within HF theory. The corresponding results for the full Schrödinger theory are still open and only much simpler results are known (see e.g., [5, 12, 18, 19, 21]). In [3] the ionization conjecture was solved in the Thomas-Fermi-von Weizsäcker generalization of the Thomas-Fermi model. In [22] the ionization conjecture was solved in a simplified Hartree-Fock mean field model by a method very similar to the one presented here. In the simplified model the atoms are entirely spherically symmetric. In the full HF model, however, the atoms need not be spherically symmetric. This lack of spherical symmetry in the HF model is one of the main reasons for many of the difficulties that have to be overcome in the present paper, although this may not always be apparent from the presentation.

We shall now describe more precisely the results of this paper. In common for all the atomic models is that, given the number of electrons N and the nuclear charge Z, they describe how to find the electronic ground state density $\rho \in L^1(\mathbb{R}^3)$, with $\int \rho = N$. Or more precisely how to find *one* ground state density, since it may not be unique. In the TF model the ground state is described only by the density, whereas in the Schrödinger and HF models the density is derived from more detailed descriptions of the ground state. For all models we shall use the following definitions. We distinguish quantities in the different models by adding superscripts TF, HF. (In this work we shall not be concerned with the Schrödinger model at all.) Througout the paper we use units in which $\hbar = m = e = 1$, i.e., *atomic units.*

1.1. DEFINITION (Mean field potentials). Let ρ^{HF} and ρ^{TF} be the densities of atomic ground states in the HF and TF models respectively. We define the corresponding *mean field potentials*

$$\varphi^{\mathrm{HF}}(x) := Z|x|^{-1} - \rho^{\mathrm{HF}} * |x|^{-1} = Z|x|^{-1} - \int \rho^{\mathrm{HF}}(y)|x-y|^{-1}dy \tag{1}$$

$$\varphi^{\mathrm{TF}}(x) := Z|x|^{-1} - \rho^{\mathrm{TF}} * |x|^{-1} = Z|x|^{-1} - \int \rho^{\mathrm{TF}}(y)|x-y|^{-1}dy \tag{2}$$

and for all $R \geq 0$ the *screened nuclear potentials at radius R*

$$\Phi_R^{\mathrm{HF}}(x) := Z|x|^{-1} - \int_{|y|<R} \rho^{\mathrm{HF}}(y)|x-y|^{-1}dy. \tag{3}$$

$$\Phi_R^{\mathrm{TF}}(x) := Z|x|^{-1} - \int_{|y|<R} \rho^{\mathrm{TF}}(y)|x-y|^{-1}dy. \tag{4}$$

This is the potential from the nuclear charge Z screened by the electrons in the region $\{x : |x| < R\}$. The screened nuclear potential will be very important in the technical proofs in Sects. 10–13.

1.2. DEFINITION (Radius). Let again ρ^{HF} and ρ^{TF} be the densities of atomic ground states in the HF and TF models respectively. We define the radius $R_{Z,N}(\nu)$ to the ν last electrons by

$$\int_{|x|\geq R_{Z,N}^{\mathrm{TF}}(\nu)} \rho^{\mathrm{TF}}(x)\,dx = \nu, \quad \int_{|x|\geq R_{Z,N}^{\mathrm{HF}}(\nu)} \rho^{\mathrm{HF}}(x)\,dx = \nu.$$

We shall discuss Hartree-Fock theory in greater detail in Sect. 3 and Thomas-Fermi theory in greater detail in Sect. 4. For a complete discussion of TF theory we refer the reader to the original paper by Lieb and Simon [14] or the review by Lieb [8]. Here we shall just mention that the functions φ^{TF} and ρ^{TF} are the unique solutions to the set of equations

$$\Delta\varphi^{\mathrm{TF}}(x) = 4\pi\rho^{\mathrm{TF}}(x) - 4\pi Z\delta(x) \tag{5}$$

$$\rho^{\mathrm{TF}}(x) = 2^{3/2}(3\pi^2)^{-1}\left[\varphi^{\mathrm{TF}}(x) - \mu^{\mathrm{TF}}\right]_+^{3/2} \tag{6}$$

$$\int \rho^{\mathrm{TF}} = N. \tag{7}$$

Here $\mu^{\rm TF}$ is a non-negative parameter called the *chemical potential*, which is also uniquely determined from the equations. We have used the notation $[t]_+ = \max\{t, 0\}$ for all $t \in \mathbb{R}$. Instead of fixing N and determining $\mu^{\rm TF}$ (the 'canonical' picture) one could fix $\mu^{\rm TF}$ and determine N (the 'grand canonical' picture). The equation (5) is essentially equivalent to (2) and expresses the fact that $\varphi^{\rm TF}$ is the mean field potential generated by the positive charge Z and the negative charge distribution $-\rho^{\rm TF}$. The equations (6–7) state that $\rho^{\rm TF}$ is given by the semiclassical expression for the density of an electron gas of N electrons in the exterior potential $\varphi^{\rm TF}$. For a discussion of semiclassics we refer the reader to Sect. 8.

1.3. REMARK. The total energy of the atom in Thomas-Fermi theory is

$$\begin{aligned}\tfrac{3}{10}(3\pi^2)^{2/3}\int \rho^{\rm TF}(x)^{5/3}\,dx - Z\int \rho^{\rm TF}(x)|x|^{-1}dx\\ +\tfrac12\iint \rho^{\rm TF}(x)|x-y|^{-1}\rho^{\rm TF}(y)dx\,dy \quad\geq\quad -e_0 Z^{7/3}\end{aligned} \tag{8}$$

where e_0 is the total binding energy of a neutral TF atom of unit nuclear charge. Numerically [8],

$$e_0 = 2(3\pi^2)^{-2/3}\cdot 3.67874 = 0.7687. \tag{9}$$

For a neutral atom, where $N = Z$, the above inequality is an equality. The inequality states that in Thomas-Fermi theory the energy is smallest for a neutral atom.

We can now state two of the main results in this paper.

1.4. THEOREM (Potential Estimate). *For all $Z \geq 1$ and all integers N with $N \geq Z$ for which there exist Hartree-Fock ground states with $\int \rho^{\rm HF} = N$ we have*

$$|\varphi^{\rm HF}(x) - \varphi^{\rm TF}(x)| \leq A_\varphi |x|^{-4+\varepsilon_0} + A_1, \tag{10}$$

where $A_\varphi, A_1, \varepsilon_0 > 0$ are universal constants.

This theorem is proved in Section 13 on page 71. The significance of the power $|x|^{-4}$ is that for $N \geq Z$ we have $\lim_{Z\to\infty}\varphi^{\rm TF}(x) = 3^4 2^{-3}\pi^2|x|^{-4}$. The existence of this limit known as the Sommerfeld law [24] follows from Theorem 2.10 in [8], but we shall also prove it in Theorems 5.2 and 5.4 below.

Note that the bound in Theorem 1.4 is uniform in N and Z.

The second main theorem is the universal bound on the atomic radius mentioned in the beginning of the introduction. In fact, not only do we prove uniform bounds but we also establish a certain exact asymptotic formula for the radius of an "infinite atom".

1.5. THEOREM (The radius of an infinite neutral HF atom). *Both* $\liminf_{Z\to\infty} R^{\mathrm{HF}}_{Z,Z}(\nu)$ *and* $\limsup_{Z\to\infty} R^{\mathrm{HF}}_{Z,Z}(\nu)$ *are bounded and have the asymptotic behavior*

$$2^{-1/3}3^{4/3}\pi^{2/3}\nu^{-1/3} + o(\nu^{-1/3})$$

as $\nu \to \infty$.

The proof of this theorem can be found in Sect. 13 on page 71. The universal bound on the maximal ionization is given in Theorem 3.6. The proof is given in Sect. 13 on page 71. A universal bound on the ionization energy (the energy it takes to remove one electron) is formulated in Theorem 3.8. The proof is given in Sect. 13 on page 73.

The paper is organized as follows. In Sect. 2 we fix our notational conventions and give some basic prerequisites.

In Sect. 3 we discuss Hartree-Fock theory.

In Sects. 4 and 5 we discuss Thomas-Fermi theory. In particular we show that the TF model, indeed, has the universal behavior for large Z that we want to establish for the HF model. In the TF model the universality can be expressed very precisely through the Sommerfeld asymptotics.

In Sect. 6 we begin the more technical work. We show in this section that the HF atom in the region $\{x : |x| > R\}$ is determined to a good approximation, in terms of energy, from knowledge of the screened nuclear potential Φ^{HF}_R. It is this crucial step in the whole argument that I do not know how to generalize to the Schrödinger model or even to the case of molecules in HF theory.

For the outermost region of the atom one cannot use the energy to control the density. In fact, changing the density of the atom far from the nucleus will not affect the energy very much. Far away from the nucleus one must use the exact energy minimizing property of the ground state, i.e., that it satisfies a variational equation. This is done in Sect. 7 to estimate the L^1 norm of the density in a region of the form $\{x : |x| > R\}$.

In Sect. 8 we establish the semiclassical estimates that allow one to compare the HF model with the TF model. To be more precise, there is no semiclassical parameter in our setup, but we derive bounds that in a semiclassical limit would be asymptotically exact.

It turns out to be useful to use the electrostatic energy (or rather its square root) as a norm in which to control the difference between the densities in TF and HF theory. The properties of this norm, which we call the Coulomb norm, are discussed in Sect. 9.

Sects. 4-9 can be read almost independently.

In Sect. 10 we state and prove the main technical tool in the work. It is a comparison of the screened nuclear potentials in HF and TF theory. Using a comparison between the screened nuclear potentials at radius R one may use the result of the separation of the outside from the inside given in Sect. 6 to get good control on the outside region $\{x : |x| > R\}$. Using an iterative scheme one establishes the main estimate for all R. The two main technical lemmas are proved in Sect. 11 and Sect. 12 respectively.

Finally the main theorems are proved in Sect. 13.

The main results of this paper were announced in [23] and a sketch of the proof was given there.

2 Notational conventions and basic prerequisites

We shall throughout the paper use the definitions

$$\begin{aligned} B(r) &:= \left\{y \in \mathbb{R}^3 : |y| \le r\right\} && (11)\\ B(x,r) &:= \left\{y \in \mathbb{R}^3 : |y-x| \le r\right\} && (12)\\ A(r_1,r_2) &:= \left\{x \in \mathbb{R}^3 : r_1 \le |x| \le r_2\right\}. && (13) \end{aligned}$$

For any $r > 0$ we shall denote by χ_r the characteristic function of the ball $B(r)$ and by $\chi_r^+ = 1 - \chi_r$. We shall as in the introduction use the notation $[t]_\pm = (t)_\pm := \max\{\pm t, 0\}$.

Our convention for the Fourier transform is

$$\hat{f}(p) := (2\pi)^{-3/2} \int e^{ipx} f(x)\, dx. \tag{14}$$

Then

$$\widehat{f * g} = (2\pi)^{3/2} \hat{f}\hat{g}, \quad \|f\|_2 = \|\hat{f}\|_2, \quad |\hat{f}(p)| \le (2\pi)^{-3/2}\|f\|_1 \tag{15}$$

and

$$\iint f(x)|x-y|^{-1}\overline{g(y)}dx\, dy = 2(2\pi) \int \hat{f}(p)\overline{\hat{g}(p)}|p|^{-2}\, dp. \tag{16}$$

2.1. DEFINITION (Density Matrix). Here we shall use the definition that a *density matrix*, on a Hilbert space $\mathcal{H}$, is a positive trace class operator satisfying the operator inequality $0 \le \gamma \le I$. When $\mathcal{H}$ is either $L^2(\mathbb{R}^3)$ or $L^2(\mathbb{R}^3; \mathbb{C}^2)$ we write $\gamma(x, y)$ for the integral kernel for γ. It is 2×2 matrix valued in the case $L^2(\mathbb{R}^3; \mathbb{C}^2)$. We define the *density* $0 \le \rho_\gamma \in L^1(\mathbb{R}^3)$ corresponding to γ by

$$\rho_\gamma := \sum_j \nu_j |u_j(x)|^2, \tag{17}$$

where ν_j and u_j are the eigenvalues and corresponding eigenfunctions of γ. Then $\int \rho_\gamma = \mathrm{Tr}[\gamma]$.

2.2. REMARK. Whenever γ is a density matrix with eigenfunctions u_j and corresponding eigenvalues ν_j on either $L^2(\mathbb{R}^3)$ or $L^2(\mathbb{R}^3; \mathbb{C}^2)$ we shall write

$$\mathrm{Tr}\,[-\Delta\gamma] := \sum_j \nu_j \int |\nabla u_j(x)|^2\, dx. \tag{18}$$

If we allow the value $+\infty$ then the right side is defined for all density matrices. The expression $-\Delta\gamma$ may of course define a trace class operator for some γ, i.e., if the eigenfunctions u_j are in the Sobolev space H^2 and the right side above is finite. In this case the left side is well defined and is equal to the right side. On the other hand, the right side may be finite even though $-\Delta\gamma$ does not even define a bounded operator, i.e., if an eigenfunction is in H^1, but not in H^2. Then the sum on the right is really

$$\mathrm{Tr}\left[(-\Delta)^{1/2}\gamma(-\Delta)^{1/2}\right] = \mathrm{Tr}\,[\nabla \cdot \gamma\nabla]\,.$$

It is therefore easy to see that (18) holds not only for the spectral decomposition, but more generally, whenever γ can be written as $\gamma f = \sum_j \nu_j(u_j, f)u_j$, with

$0 \leq \nu_j$ (the u_j need not be orthonormal). The same is also true for the expression (17) for the density.

2.3. PROPOSITION. *The map $\gamma \mapsto \mathrm{Tr}[-\Delta\gamma]$ as defined above on all density matrices is affine and weakly lower semicontinuous*

Proof. Choose a basis $f_1, f_2, \ldots$ for L^2 consisting of functions from H^1. Then

$$\mathrm{Tr}[-\Delta\gamma] = \sum_m (\nabla f_m, \gamma \nabla f_m).$$

The affinity is trivial and the lower semicontinuity follows from Fatou's Lemma. $\square$

We are of course abusing notation when we define $\mathrm{Tr}[-\Delta\gamma]$ for all density matrices. This is, however, very convenient and should hopefuly not cause any confusion.

If V is a positive measurable function. We always identify V with a multiplication operator on L^2. If $V\rho_\gamma \in L^1(\mathbb{R}^3)$ we abuse notation and write

$$\mathrm{Tr}\,[V\gamma] := \int V\rho_\gamma.$$

As before if $V\gamma$ happens to be trace class then the left side is well defined and finite and is equal to the right side. Otherwise, we really have $\int V\rho_\gamma = \mathrm{Tr}\left[[V]_+^{1/2}\gamma[V]_+^{1/2}\right] - \mathrm{Tr}\left[[V]_-^{1/2}\gamma[V]_-^{1/2}\right]$.

2.4. LEMMA (The IMS formulas). *If u is in the Sobolev space $H^1(\mathbb{R}^3;\mathbb{C}^2)$ or $H^1(\mathbb{R}^3)$ and if $\Xi \in C^1(\mathbb{R}^3)$ is real, bounded, and has bounded derivative then*[1]

$$\mathrm{Re}\int \nabla\left(\Xi^2 u^*\right)\cdot\nabla u = \int |\nabla(\Xi u)|^2 - \int |\nabla\Xi|^2\,|u|^2. \tag{19}$$

If γ is a density matrix on $L^2(\mathbb{R}^3;\mathbb{C}^2)$ or $L^2(\mathbb{R}^3)$ and if $\Xi_1,\ldots,\Xi_m \in C^1(\mathbb{R}^3)$ are real, bounded, have bounded derivatives, and satisfy $\Xi_1^2+\ldots+\Xi_m^2 = 1$ then

$$\begin{aligned}\mathrm{Tr}\,[-\Delta\gamma] &= \mathrm{Tr}\,[-\Delta(\Xi_1\gamma\Xi_1)] - \mathrm{Tr}\left[(\nabla\Xi_1)^2\gamma\right] + \ldots \\ &\quad + \mathrm{Tr}\,[-\Delta(\Xi_m\gamma\Xi_m)] - \mathrm{Tr}\left[(\nabla\Xi_m)^2\gamma\right].\end{aligned} \tag{20}$$

Note that $\Xi_j\gamma\Xi_j$ again defines a density matrix (where we identified Ξ_j with a multiplication operator).

[1] We denote by u^* the complex conjugate of u. In the case when u takes values in $\mathbb{C}^2$ this refers to the complex conjugate matrix.

Proof. The identity (19) follows from a simple computation. If we sum this identity and use $\Xi_1^2 + \ldots + \Xi_m^2 = 1$ we obtain

$$\int |\nabla u|^2 = \int |\nabla(\Xi_1 u)|^2 - \int |\nabla \Xi_1|^2 |u|^2 + \ldots + \int |\nabla(\Xi_m u)|^2 - \int |\nabla \Xi_m|^2 |u|^2.$$

If we allow the value $+\infty$ this identity holds for all functions u in L^2. Thus (20) is a simple consequence of the definition (18). □

2.5. THEOREM (Lieb-Thirring inequality). *We have the Lieb-Thirring inequality*

$$\mathrm{Tr}\left[-\tfrac{1}{2}\Delta\gamma\right] \geq K_1 \int \rho_\gamma^{5/3}, \tag{21}$$

where $K_1 := 20.49$. *Equivalently, If* $V \in L^{5/2}(\mathbb{R}^3)$ *and if* γ *is any density matrix such that* $\mathrm{Tr}[-\Delta\gamma] < \infty$ *we have*

$$\mathrm{Tr}\left[-\tfrac{1}{2}\Delta\gamma\right] - \mathrm{Tr}\left[V\gamma\right] \geq -L_1 \int [V]_+^{5/2}, \tag{22}$$

where $L_1 := \frac{2}{5}\left(\frac{3}{5K_1}\right)^{2/3} = 0.038$.

The original proofs of these inequalities can be found in [15]. The constants here are taken from [6]. From the min-max principle it is clear that the right side of (22) is in fact a lower bound on the sum of the negative eigenvalues of the operator $-\frac{1}{2}\Delta - V$.

2.6. THEOREM (Cwikel-Lieb-Rozenblum inequality). *If* $V \in L^{3/2}(\mathbb{R}^3)$ *then the number of non-positive eigenvalues of* $-\frac{1}{2}\Delta - V$, *i.e.*, $\mathrm{Tr}\left[\chi_{(-\infty,0]}\left(-\frac{1}{2}\Delta - V\right)\right]$, *where* $\chi_{(-\infty,0]}$ *is the characteristic function of the interval* $(-\infty, 0]$, *satisfies the bound*

$$\mathrm{Tr}\left[\chi_{(-\infty,0]}\left(-\tfrac{1}{2}\Delta - V\right)\right] \leq L_0 \int [V]_+^{3/2}, \tag{23}$$

where $L_0 := 2^{3/2} 0.1156 = 0.3270$.

The original (independent) proofs can be found in Cwikel [4], Rozenblum [17], and Lieb [7]. The constant is from Lieb [7].

3 Hartree-Fock Theory

In Hartree-Fock theory, as opposed to Schrödinger theory, one does not consider the full N-body Hilbert space $\bigwedge^N L^2(\mathbb{R}^3;\mathbb{C}^2)$. One rather restricts attention to the pure wedge products (Slater determinants)

$$\Psi = (N!)^{-1/2} u_1 \wedge \ldots \wedge u_N, \tag{24}$$

where $u_1, \ldots, u_N \in L^2(\mathbb{R}^3;\mathbb{C}^2)$. Then one minimizes the energy expectation

$$\frac{(\Psi, H_{N,Z}\Psi)}{(\Psi,\Psi)}$$

of the Hamiltonian

$$H_{N,Z} := \sum_{i=1}^{N} \left(-\tfrac{1}{2}\Delta - \frac{Z}{|x|} \right) + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|} \tag{25}$$

over wave functions Ψ of the form (24) only.

If γ is the projection onto the N-dimensional space spanned by the functions $u_1, \ldots, u_N$, the energy depends only on γ. In fact,

$$\frac{(\Psi, H_{N,Z}\Psi)}{(\Psi,\Psi)} = \mathcal{E}^{\mathrm{HF}}(\gamma).$$

Here we have defined the *Hartree-Fock* energy functional

$$\begin{aligned} \mathcal{E}^{\mathrm{HF}}(\gamma) : &= \operatorname{Tr}\left[\left(-\tfrac{1}{2}\Delta - Z|x|^{-1}\right)\gamma\right] + \mathcal{D}(\gamma) - \mathcal{E}x(\gamma) \\ &= \operatorname{Tr}\left[-\tfrac{1}{2}\Delta\gamma\right] - \int Z|x|^{-1}\rho_\gamma(x)\,dx + \mathcal{D}(\gamma) - \mathcal{E}x(\gamma), \end{aligned} \tag{26}$$

where we have introduced the *direct Coulomb energy*, defined in terms of the Coulomb inner product D (see also (79) below), by

$$\mathcal{D}(\gamma) := D(\rho_\gamma, \rho_\gamma) = \tfrac{1}{2} \iint \rho_\gamma(x)|x-y|^{-1}\rho_\gamma(y)dx\,dy \tag{27}$$

and the *exchange Coulomb energy*

$$\mathcal{E}x(\gamma) := \tfrac{1}{2} \iint \operatorname{Tr}_{\mathbb{C}^2}\left[|\gamma(x,y)|^2\right]|x-y|^{-1}dx\,dy. \tag{28}$$

3.1. DEFINITION (The Hartree-Fock ground state). Let $Z > 0$ be a real number and $N \geq 0$ be an integer. The Hartree-Fock ground state energy is

$$E^{\mathrm{HF}}(N,Z) := \inf\left\{\mathcal{E}^{\mathrm{HF}}(\gamma) : \gamma^* = \gamma,\ \gamma = \gamma^2,\ \mathrm{Tr}[\gamma] = N\right\}.$$

If a minimizer γ^{HF} exists we say that the atom has an HF ground state described by γ^{HF}. In particular, its density is $\rho^{\mathrm{HF}}(x) = \rho_{\gamma^{\mathrm{HF}}}(x)$.

3.2. THEOREM (Bound on the Hartree-Fock energy). *For $Z > 0$ and any integer $N > 0$ we have*

$$E^{\mathrm{HF}}(N,Z) \geq -3(4\pi L_1)^{2/3} Z^2 N^{1/3},$$

where L_1 is the constant in the Lieb-Thirring inequality (22).

Proof. Let γ be an N dimensional projection. Since the last term in $H_{N,Z}$ is positive we see that $\mathcal{E}^{\mathrm{HF}}(\gamma) \geq \mathrm{Tr}\left[\left(-\frac{1}{2}\Delta - Z|x|^{-1}\right)\gamma\right]$. It the follows from the Lieb-Thirring inequality (22) that for all $R > 0$ we have

$$\mathcal{E}^{\mathrm{HF}}(\gamma) \geq -L_1 \int_{|x|<R} Z^{5/2}|x|^{-5/2}\,dx - ZNR^{-1}.$$

The estimate in the theorem follows by evaluating the integral and choosing the optimal value for R. □

3.3. REMARK. The function $N \mapsto E^{\mathrm{HF}}(N,Z)$ is non-increasing. This can be seen fairly easily by constructing a trial $N+1$-dimensional projection from any N-dimensional projection by adding an extra dimension corresponding to a function u concentrated far from the origin and with very small kinetic energy $\int|\nabla u|^2$. This trial projection can be constructed such that it has an energy arbitrarily close to the original N-dimensional projection. Therefore we also have that

$$E^{\mathrm{HF}}(N,Z) = \inf\left\{\mathcal{E}^{\mathrm{HF}}(\gamma) : \gamma^* = \gamma,\ \gamma^2 = \gamma,\ \mathrm{Tr}\gamma \leq N\right\}. \tag{29}$$

This Hartree-Fock minimization problem was studied by Lieb and Simon in [13]. They proved the following about the existence of minimizers.

3.4. THEOREM (Existence of HF minimizers). *If N is a positive integer such that $N < Z+1$ then there exists an N-dimensional projection γ^{HF} minimizing the functional $\mathcal{E}^{\mathrm{HF}}$ in (26), i.e., $E^{\mathrm{HF}}(N,Z) = \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})$ is a minimum.*

In the oppposite direction the following result was proved by Lieb [11].

3.5. THEOREM (Lieb's bound on the maximal ionization). *If N is a positive integer such that $N > 2Z+1$ there are no minimizers for the Hartree-Fock functional among N-dimensional projections, i.e., there does not exist an N-dimensional projection γ such that $\mathcal{E}^{\mathrm{HF}}(\gamma) = E^{\mathrm{HF}}(N, Z)$.*

This Theorem will, in fact, follow from the proof of Lemma 7.1 below (see page 35). Although this result is very good for $Z = 1$ it is far from optimal for large Z. In particular the factor 2 should rather be 1. This fact known as the ionization conjecture is one of the of the main results of the present work.

3.6. THEOREM (Optimal bound on maximal ionization charge). *There exists a universal constant $Q > 0$ such that for all positive integers satisfying $N \geq Z + Q$ there are no minimizers for the Hartree-Fock functional among N-dimensional projections.*

3.7. REMARK. Although, it is possible to calculate an exact value for the constant Q above it is quite tedious to do so. Moreover, the present work does not attempt to optimize this constant. The result of this work is mainly to establish that such a *finite* constant exists. This of course raises the very interesting question of finding a *good* estimate on the constant, but we shall not address this here.

The proof Theorem 3.6 is given in Sect. 13 on page 71.

3.8. THEOREM (Bound on the ionization energy). *The ionization energy of a neutral atom $E^{\mathrm{HF}}(Z-1, Z) - E^{\mathrm{HF}}(Z, Z)$ is bounded by a universal constant (in particular, independent of Z).*

This theorem is proved in Sect. 13 on page 73.

The variational equations (Euler-Lagrange equations) for the minimizer was also given in [13]. Since the Hartree-Fock variational equations shall be used later in this work, we shall derive them in Theorem 3.11 below.

We first note that the Hartree-Fock functional $\mathcal{E}^{\mathrm{HF}}$ may be extended from projections (i.e., density matrices with $\gamma^2 = \gamma$) to all density matrices. If $\mathrm{Tr}\,[-\Delta\gamma] < \infty$ all the terms of $\mathcal{E}^{\mathrm{HF}}$ are finite. In fact, $\mathrm{Tr}\,[Z|x|^{-1}\gamma]$ is finite by the Lieb-Thirring inequality (21) since $Z|x|^{-1} \in L^\infty(\mathbb{R}^3) + L^{5/2}(\mathbb{R}^3)$. The term $\mathcal{D}(\gamma)$ is finite by the Hardy-Littlewood-Sobolev inequality since $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3) \subset L^{6/5}(\mathbb{R}^3)$. Finally, $\mathcal{E}x(\gamma) \leq D(\gamma)$ since

$$D(\gamma) - \mathcal{E}x(\gamma) = \tfrac{1}{4}\sum_{i,j} \nu_i\nu_j \iint \frac{\|u_i(x)\otimes u_j(y) - u_j(x)\otimes u_i(y)\|^2_{\mathbb{C}^2\otimes\mathbb{C}^2}}{|x-y|} dx\, dy \geq 0,$$

when ν_i are the eigenvalues of γ with u_i being the corresponding eigenfunctions. If $\mathrm{Tr}\,[-\Delta\gamma] = \infty$ we set $\mathcal{E}^{\mathrm{HF}}(\gamma) := \infty$. It is clear that $\lim_n \mathcal{E}^{\mathrm{HF}}(\gamma_n) = \infty$ if $\lim_n \mathrm{Tr}\,[-\Delta\gamma_n] \to \infty$.

3.9. REMARK. It is important to realize that although $D(\gamma) - \mathcal{E}x(\gamma)$ is positive it is *not* a convex functional on the set of density matrices. In particular, the Hartree-Fock minimizer need not be unique. (A simple example of non-uniqueness occurs for the case $N = 1$. For a one-dimensional projection γ, it is clear that $D(\gamma) - \mathcal{E}x(\gamma) = 0$, hence the minimizer in this case is simply the projection onto a ground state of the operator $-\frac{1}{2}\Delta - Z|x|^{-1}$ on the space $L^2(\mathbb{R}^3;\mathbb{C}^2)$. There are many ground states since the spin can point in any direction.)

Another fact related to the non-convexity of the Hartree-Fock functional is the important observation first made by Lieb in [9] that the infimum of the Hartree-Fock functional is not lowered by extending the functional to all density matrices. For a simple proof of this see [1].

3.10. THEOREM (Lieb's variational principle). *For all non-negative integers N we have*

$$\inf\left\{\mathcal{E}^{\mathrm{HF}}(\gamma) : \gamma^* = \gamma,\ \gamma = \gamma^2,\ \mathrm{Tr}[\gamma] = N\right\} = \inf\left\{\mathcal{E}^{\mathrm{HF}}(\gamma) : 0 \leq \gamma \leq I,\ \mathrm{Tr}[\gamma] = N\right\}$$

and if the infimum over all density matrices (the inf on the right) is attained then so is the infimum over projections (the inf on the left).

We now come to the properties of the Hartree-Fock minimizers, especially that they satisfy the Hartree-Fock equations. These equations state that a minimizing N-dimensional projection γ^{HF} is the projection onto the N-dimensional space spanned by eigenfunctions with lowest possible eigenvalues for the *HF mean field operator*

$$H_{\gamma^{\mathrm{HF}}} := -\tfrac{1}{2}\Delta - Z|x|^{-1} + \rho^{\mathrm{HF}} * |x|^{-1} - \mathcal{K}_{\gamma^{\mathrm{HF}}}. \tag{30}$$

Here $\mathcal{K}_{\gamma^{\rm HF}}$ is the *exchange operator* defined by having the 2×2-matrix valued integral kernel

$$\mathcal{K}_{\gamma^{\rm HF}}(x,y) := |x-y|^{-1}\gamma^{\rm HF}(x,y).$$

Thus $\gamma^{\rm HF}(x,y)=\sum_{i=1}^N u_i(x)u_i(y)^*$, where $H_{\gamma^{\rm HF}}u_i=\varepsilon_i u_i$, and $\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_N\leq 0$ are the N lowest eigenvalues of $H_{\gamma^{\rm HF}}$ counted with multiplicities.

This self-consistent property of a minimizer $\gamma^{\rm HF}$ may equivalently be stated as in the theorem below.

3.11. THEOREM (Properties of HF minimizers). *If $\gamma^{\rm HF}$ with density $\rho^{\rm HF}$ is a projection minimizing the HF functional $\mathcal{E}^{\rm HF}$ under the constraint $\operatorname{Tr}[\gamma^{\rm HF}]=N$ then $\rho^{\rm HF}\in L^{5/3}(\mathbb{R}^3)\cap L^1(\mathbb{R}^3)$ and $H_{\gamma^{\rm HF}}$ defines a semibounded self-adjoint operator with form domain $H^1(\mathbb{R}^3;\mathbb{C}^2)$ having at least N non-positive eigenvalues. Moreover, $\gamma^{\rm HF}$ is the N-dimensional projection minimizing the map $\gamma\mapsto \operatorname{Tr}\left[H_{\gamma^{\rm HF}}\gamma\right]$.*

3.12. REMARK. The reader may worry that, because of degenerate eigenvalues of $H_{\gamma^{\rm HF}}$, the N-dimensional projection γ minimizing $\operatorname{Tr}\left[H_{\gamma^{\rm HF}}\gamma\right]$ may not be unique. That it is, indeed, unique was proved in [2].

Proof of Theorem 3.11. We note that $\operatorname{Tr}[\gamma^{\rm HF}]=N$, $\operatorname{Tr}[-\Delta\gamma^{\rm HF}]<\infty$, and the Lieb-Thirring inequality (21) implies that $\rho^{\rm HF}\in L^{5/3}(\mathbb{R}^3)\cap L^1(\mathbb{R}^3)$. From this it is easy to see that $\rho^{\rm HF}*|x|^{-1}$ is a bounded function (in fact, it is continuous and tends to 0 as $|x|\to\infty$). Moreover, in the operator sense $\mathcal{K}_{\gamma^{\rm HF}}\leq\rho^{\rm HF}*|x|^{-1}$. This follows, since for $f\in L^2(\mathbb{R}^3;\mathbb{C}^2)$ we have

$$\int\rho^{\rm HF}*|x|^{-1}|f(x)|^2dx-\iint f(x)^*\mathcal{K}_{\gamma^{\rm HF}}(x,y)f(y)dx\,dy \;=\; \sum_{i=1}^N\tfrac12\iint\frac{\|u_i(x)\otimes f(y)-f(x)\otimes u_i(y)\|^2_{\mathbb{C}^2\otimes\mathbb{C}^2}}{|x-y|}dx\,dy,$$

where $u_1,\ldots,u_N$ is a complete set of eigenfunctions of $\gamma^{\rm HF}$. It is therefore clear that $H_{\gamma^{\rm HF}}$ defines a semibounded operator with form domain $H^1(\mathbb{R}^3;\mathbb{C}^2)$. Thus it makes sense to compute $\operatorname{Tr}\left[H_{\gamma^{\rm HF}}\gamma\right]$ if and only if $\operatorname{Tr}[-\Delta\gamma]<\infty$.

Let γ' be an N-dimensional projection with $\operatorname{Tr}[-\Delta\gamma']<\infty$. We shall prove that

$$\operatorname{Tr}\left[H_{\gamma^{\rm HF}}\gamma'\right]\geq\operatorname{Tr}\left[H_{\gamma^{\rm HF}}\gamma^{\rm HF}\right].$$

For $0 \le t \le 1$, consider the density matrix $\gamma_t = (1-t)\gamma^{\mathrm{HF}} + t\gamma'$. It satisfies $\mathrm{Tr}[\gamma_t] = N$. By the Lieb variational principle, Theorem 3.10, we have that $\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) = \mathcal{E}^{\mathrm{HF}}(\gamma_0) \le \mathcal{E}^{\mathrm{HF}}(\gamma_t)$, for all $0 \le t \le 1$. Hence

$$0 \le \left.\frac{d\mathcal{E}^{\mathrm{HF}}(\gamma_t)}{dt}\right|_{t=0} = \mathrm{Tr}\left[H_{\gamma^{\mathrm{HF}}}\gamma'\right] - \mathrm{Tr}\left[H_{\gamma^{\mathrm{HF}}}\gamma^{\mathrm{HF}}\right].$$

The fact that $\mathrm{Tr}\left[H_{\gamma^{\mathrm{HF}}}\gamma\right]$ is minimized among N-dimensional projections implies in particular that $H_{\gamma^{\mathrm{HF}}}$ has at least N non-positive eigenvalues. $\square$

4 Thomas-Fermi Theory

In this section we discuss the facts needed from Thomas-Fermi theory. We focus only on the results that we shall use in our study of Hartree-Fock theory.

4.1. DEFINITION (Thomas-Fermi functional). Let $V \in L^{5/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ with

$$\inf\left\{\|W\|_{L^\infty(\mathbb{R}^3)} : V - W \in L^{5/2}(\mathbb{R}^3)\right\} = 0.$$

Corresponding to V we define the *Thomas-Fermi (TF) energy functional*

$$\mathcal{E}_V^{\mathrm{TF}}(\rho) = \tfrac{3}{10}(3\pi^2)^{2/3}\int \rho^{5/3} - \int V\rho + \tfrac{1}{2}\iint \rho(x)|x-y|^{-1}\rho(y)dx\,dy,$$

on functions ρ with $0 \le \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$.

Note that the Hardy-Littlewood-Sobolev inequality implies that $D(\rho,\rho) = \frac{1}{2}\iint \rho(x)|x-y|^{-1}\rho(y)dx\,dy$ is finite for functions $\rho \in L^{5/3} \cap L^1 \subset L^{6/5}$. Hence $\mathcal{E}_V^{\mathrm{TF}}$ is finite on these functions.

The proof of existence and uniqueness of minimizers to the TF functional and the characterization of their properties can be found in the work of Lieb and Simon [14] (see also [8]). We state the properties that we need in the following theorem.

4.2. THEOREM (The TF minimizer). *Let V be as in Definition 4.1. For all $N' \ge 0$ there exists a unique non-negative $\rho_V^{\mathrm{TF}} \in L^{5/3}(\mathbb{R}^3)$ such that $\int \rho_V^{\mathrm{TF}} \le N'$ and*

$$\mathcal{E}_V^{\mathrm{TF}}(\rho_V^{\mathrm{TF}}) = \inf\left\{\mathcal{E}_V^{\mathrm{TF}}(\rho) : \rho \in L^{5/3}(\mathbb{R}^3),\ \int \rho \le N'\right\}. \tag{31}$$

On the other hand there exists a (unique) **chemical potential** *(Lagrange multiplier)* $\mu_V^{\mathrm{TF}}(N')$, *with* $0 \leq \mu_V^{\mathrm{TF}}(N') \leq \sup V$, *such that* ρ_V^{TF} *is uniquely characterized by*

$$\begin{aligned} &\mathcal{E}_V^{\mathrm{TF}}(\rho_V^{\mathrm{TF}}) + \mu_V^{\mathrm{TF}}(N') \int \rho_V^{\mathrm{TF}} \\ &= \inf \left\{ \mathcal{E}_V^{\mathrm{TF}}(\rho) + \mu_V^{\mathrm{TF}}(N') \int \rho : 0 \leq \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3) \right\}. \end{aligned} \tag{32}$$

Moreover, ρ_V^{TF} *is the unique solution in* $L^{5/3} \cap L^1$ *to the* **Thomas-Fermi equation** *(the Euler-Lagrange equation for the variational problem (32))*

$$\tfrac{1}{2}(3\pi^2)^{2/3} \left(\rho_V^{\mathrm{TF}}(x)\right)^{2/3} = \left[V(x) - \rho_V^{\mathrm{TF}} * |x|^{-1} - \mu_V^{\mathrm{TF}}(N')\right]_+ . \tag{33}$$

If $\mu_V^{\mathrm{TF}}(N') > 0$ *then* $\int \rho_V^{\mathrm{TF}} = N'$. *Therefore* $\mu_V^{\mathrm{TF}}(N') \int \rho_V^{\mathrm{TF}} = \mu_V^{\mathrm{TF}}(N') N'$.

For all $0 < \mu$ *there is a unique minimizer* $0 \leq \rho \in L^{5/3} \cap L^1$ *to* $\mathcal{E}_V^{\mathrm{TF}}(\rho) + \mu \int \rho$. *(If* $\mu \geq \sup V$ *then* ρ *is simply zero).*

We shall be interested in properties of the *Thomas-Fermi potential*

$$\varphi_V^{\mathrm{TF}} := V(x) - \rho_V^{\mathrm{TF}} * |x|^{-1}. \tag{34}$$

The Thomas-Fermi equation (33) can be turned into the *Thomas-Fermi differential equation*

$$\Delta \varphi_V^{\mathrm{TF}} = 2^{7/2}(3\pi)^{-1} \left[\varphi_V^{\mathrm{TF}} - \mu_V^{\mathrm{TF}}(N')\right]_+^{3/2} + \Delta V, \tag{35}$$

which holds in distribution sense.

4.3. THEOREM (Maximal ionization). *There exists a non-negative real number* N_c, *possibly equal to* $+\infty$, *such that* $\mu_V^{\mathrm{TF}}(N') > 0$ *if and only if* $N' < N_c$. *Moreover,*

$$N_c \geq \liminf_{r \to \infty} (4\pi)^{-1} \int_{\mathcal{S}^2} r V(r\omega) d\omega, \tag{36}$$

where $d\omega$ *is the surface measure on the unit 2-sphere* $\mathcal{S}^2$.

Proof. Since $\mathcal{E}_V^{\mathrm{TF}}$ is a convex functional of ρ it is clear that $\mathcal{E}_V^{\mathrm{TF}}\left(\rho_V^{\mathrm{TF}}\right)$ is a convex and decreasing function of N'. Hence there is a value N_c such that $\mathcal{E}_V^{\mathrm{TF}}\left(\rho_V^{\mathrm{TF}}\right)$ is strictly decreasing for $N' < N_c$ and constant for $N' \geq N_c$. Thus if $N' \geq N_c$ then

$\int \rho_V^{\rm TF} = N_c$. Since $\int \rho_V^{\rm TF} = N'$ if $\mu_V^{\rm TF} > 0$ we must have $\mu_V^{\rm TF}(N') = \mu_V^{\rm TF}(N_c) = 0$ for $N' \geq N_c$. On the other hand since $\int \rho_V^{\rm TF} = N'$ if $N' < N_c$ we cannot have $\mu_V^{\rm TF}(N') = 0$ in this case. This proves the first assertion.

In order to prove the second assertion we may of course assume that $N_c < \infty$. Since $\mu_V^{\rm TF}(N_c) = 0$ we have for the corresponding Thomas-Fermi minimizer that

$$\begin{aligned}\int_{\mathcal{S}^2} \rho_V^{\rm TF}(r\omega)d\omega &= (\text{Const.}) \int_{\mathcal{S}^2} \left[V(r\omega) - \rho_V^{\rm TF} * |r\omega|^{-1}\right]_+^{3/2} d\omega \\ &\geq (\text{Const.}) \left[(4\pi)^{-1} \int_{\mathcal{S}^2} V(r\omega)d\omega - r^{-1} \int_{\mathbb{R}^3} \rho_V^{\rm TF}\right]_+^{3/2}\end{aligned}$$

where the last estimate follows from Jensen's inequality and Newton's Theorem. Since we are considering a TF minimizer $\rho_V^{\rm TF}$ such that $\int \rho_V^{\rm TF} = N_c$ it is clear that if (36) is violated then $\int_{\mathcal{S}^2} \rho_V^{\rm TF}(r\omega)d\omega > cr^{-3/2}$ for some positive constant c and all large enough r. Hence $N_c = \int \rho_V^{\rm TF} = \infty$ in contradiction with our assumption. $\square$

Proving a bound on N_c in the opposite direction is in general more difficult. We shall return to a partial converse to (36) in Corollary 4.8 below.

Usually the Thomas-Fermi model is studied for the potential V being the Coulomb potential, i.e., $Z|x|^{-1}$. In this case we denote $\rho_V^{\rm TF}$, $\varphi_V^{\rm TF}$, and $\mu_V^{\rm TF}$ simply by $\rho^{\rm TF}$, $\varphi^{\rm TF}$, and $\mu^{\rm TF}$. These are the functions discussed in the introduction. In fact, the equations (5) and (6) correspond to (33) and (35).

From Theorem 4.3 we see that in this case $N_c \geq Z$. We shall see below after Corollary 4.8 that indeed $N_c = Z$.

The first mathematical study of the atomic TF equation was done by Hille [16]; a much more complete analysis can be found in [14].

The function $\varphi^{\rm TF}$ satisfies the asymptotics $\varphi^{\rm TF}(x) \approx 3^4 2^{-3} \pi^2 |x|^{-4}$ for large x. The important thing to note about this asymptotics, first discovered by Sommerfeld [24], is that it is independent of Z. The Sommerfeld asymptotics is central to the present work and we shall prove a strong version of it in Theorems 5.2 and 5.4 below. Similar asymptotic estimates may be derived for the density using the TF equation (33). We shall more generally prove asymptotic bounds for $\varphi_V^{\rm TF}$, in the case when the potential V is harmonic in certain regions of space.

We now come to the main technical lemma in this section, which is a version of the Sommerfeld estimate.[2]

4.4. LEMMA (Sommerfeld estimate). *Assume that $\varphi \geq 0$ is a smooth function on $|x| > R$ and satisfies the differential equation*

$$\Delta\varphi(x) = 2^{7/2}(3\pi)^{-1}\varphi(x)^{3/2}, \quad \textit{for } |x| > R,$$

for some $R \geq 0$. Let $\zeta := (-7+\sqrt{73})/2 \approx 0.77$. Define

$$a(R) \;:=\; \liminf_{r\searrow R}\sup_{|x|=r}\left[\left(\frac{\varphi(x)}{3^4 2^{-3}\pi^2 r^{-4}}\right)^{-1/2} - 1\right] r^{\zeta}$$

and

$$A(R) \;:=\; \liminf_{r\searrow R}\sup_{|x|=r}\left[\frac{\varphi(x)}{3^4 2^{-3}\pi^2 r^{-4}} - 1\right] r^{\zeta}.$$

Then for $|x| > R$ we have

$$\left(1 + a(R)|x|^{-\zeta}\right)^{-2} \leq \frac{\varphi(x)}{3^4 2^{-3}\pi^2 |x|^{-4}} \leq \left(1 + A(R)|x|^{-\zeta}\right). \tag{37}$$

4.5. REMARK. It is important to realize that we are not assuming that φ is spherically symmetric. The lemma above can therefore not be proved by ODE techniques. By elliptic regularity the smoothness of φ would of course be a consequence of a much weaker assumption.

Proof of Lemma 4.4. We first prove that $\varphi(x) \to 0$ as $|x| \to \infty$. For this purpose consider $L > 4R$ and for $L/4 < |x| < L$ the function $f(x) = C[(|x| - L/4)^{-4} + (L - |x|)^{-4}]$. We compute

$$\begin{aligned}\Delta f &= C\Big[20\left((|x| - L/4)^{-6} + (L - |x|)^{-6}\right) \\ &\qquad + 8|x|^{-1}(L - |x|)^{-5} - 8|x|^{-1}(|x| - L/4)^{-5}\Big] \\ &\leq 44C(L - |x|)^{-6} + 20C(|x| - L/4)^{-6}.\end{aligned}$$

[2] A version of this Sommerfeld estimate was stated in the announcement [23]. The result stated was weaker than here in the sense that the exponents in the error terms were different for the upper and lower bounds. The result in the announcement also contained a minor error because the lower bound had been stated incorrectly. The better and correct version is the one stated and proved here.

On the other hand, $f(x)^{3/2} \geq C^{3/2}\left((|x|-L/4)^{-6}+(L-|x|)^{-6}\right)$. It is therefore clear that we can choose C independently of L such that $\Delta f \leq 2^{7/2}(3\pi)^{-1}f^{3/2}$. We claim that $\varphi(x) \leq f(x)$ for $L/4 < |x| < L$. This is trivial for $|x|$ close to $L/4$ or close to L since here $f(x)$ diverges whereas $\varphi(x)$ remains bounded. Consider the set $\{L/4 < |x| < L : \varphi(x) > f(x)\}$. This is an open set on which $\Delta(\varphi - f) \geq 2^{7/2}(3\pi)^{-1}(\varphi^{3/2} - f^{3/2}) > 0$, i.e., $\varphi - f$ is subharmonic on the set and is zero on its boundary. Hence $\varphi(x) \leq f(x)$ on the set which is a contradiction unless the set is empty. Thus for all $L > 4R$ we have $\varphi(L/2) \leq C\left((1/4)^{-4} + (1/2)^{-4}\right)L^{-4}$. Hence, $\varphi(x)|x|^4$ is bounded.

Next we turn to the proof of the main estimate. Let $R' > R$ and set $A' = A(R')$ and $a' = a(R')$. Then a' and A' are finite. We consider the two functions

$$\omega^+_{A'}(x) := 3^4 2^{-3}\pi^2|x|^{-4}(1+A'|x|^{-\zeta}) \quad \text{and} \quad \omega^-_{a'}(x) := 3^4 2^{-3}\pi^2|x|^{-4}(1+a'|x|^{-\zeta})^{-2}.$$

Note that by the definition of a' and A' both functions are well-defined and positive for $|x| > R'$. We claim that

$$\Delta\omega^+_{A'}(x) \leq 2^{7/2}(3\pi)^{-1}\omega^+_{A'}(x)^{3/2} \quad \text{and} \quad \Delta\omega^-_{a'}(x) \geq 2^{7/2}(3\pi)^{-1}\omega^-_{a'}(x)^{3/2}. \tag{38}$$

As we shall first show the lemma is a simple consequence of the estimates in (38). We give the proof for the upper bound. The lower bound is similar. Let

$$\Omega_+ := \left\{|x| > R' : \varphi(x) > \omega^+_{A'}(x)\right\}.$$

On Ω_+, $\varphi - \omega^+_{A'}$ is subharmonic. On the boundary of Ω_+, $\varphi - \omega^+_{A'}$ vanishes. For the subset $\partial\Omega_+ \cap \{x : |x| = R'\}$ this follows from the choice of A'. Since $\varphi(x)$ and $\omega^+_{A'}(x)$ both tend to zero as $|x|$ tends to infinity we conclude that $\Omega_+ = \emptyset$.

Therefore $\varphi(x) \leq \omega^+_{A(R')}(x)$ for $|x| > R'$. For $|x| > R$ we get $\varphi(x) \leq \liminf_{R' \searrow R} \omega^+_{A(R')}(x) = \omega^+_{A(R)}(x)$.

It remains to check (38). For $\omega^-_{a'}$ we get

$$\begin{aligned}\Delta\omega^-_{a'}(x) = 2^{7/2}(3\pi)^{-1}\omega^-_{a'}(x)^{3/2} \Big(& 1 + \left(1 - \tfrac{1}{6}\zeta(\zeta+7)\right)a'|x|^{-\zeta} \\ & + 6(1+a'|x|^{-\zeta})^{-1}(\zeta a'|x|^{-\zeta})^2\Big).\end{aligned}$$

Since $\zeta(\zeta+7) = 6$ and $1 + a'|x|^{-\zeta} > 0$ we see that $\Delta\omega^-_{a'}(x) \geq 2^{7/2}(3\pi)^{-1}\omega^-_{a'}(x)^{3/2}$.

For $\omega^+_{A'}$ we have

$$\begin{aligned}\Delta\omega^+_{A'}(x) &= 2^{7/2}(3\pi)^{-1}\omega^+_{A'}(x)^{3/2}(1+A'|x|^{-\zeta})^{-3/2}\left(1+\left(1+\frac{\zeta(\zeta+7)}{12}\right)A'|x|^{-\zeta}\right)\\ &\le 2^{7/2}(3\pi)^{-1}\omega^+_{A'}(x)^{3/2},\end{aligned}$$

where we have used that

$$(1+A'|x|^{-\zeta})^{3/2}\ge 1+\tfrac{3}{2}A'|x|^{-\zeta}=1+(1+\tfrac{1}{12}\zeta(\zeta+7))A'|x|^{-\zeta}.$$

□

We can immediately use this lemma to get estimates on φ_V^{TF} when $\mu_V^{\mathrm{TF}}=0$. For general μ_V^{TF} the result can be generalized as follows.

4.6. THEOREM (Sommerfeld estimate for general μ_V^{TF}). *Assume that V is continuous and harmonic for $|x|>R$ and satisfies $\lim_{|x|\to\infty}V(x)=0$. Consider the corresponding Thomas-Fermi potential φ_V^{TF}, which satisfies the TF differential equation (35). Assume that $\mu_V^{\mathrm{TF}}<\liminf_{r\searrow R}\inf_{|x|=r}\varphi_V^{\mathrm{TF}}(x)$. Define*

$$a(R) := \liminf_{r\searrow R}\sup_{|x|=r}\left[\left(\frac{\varphi_V^{\mathrm{TF}}(x)}{3^4 2^{-3}\pi^2 r^{-4}}\right)^{-1/2}-1\right]r^{\zeta} \tag{39}$$

and

$$A(R,\mu_V^{\mathrm{TF}}) := \liminf_{r\searrow R}\sup_{|x|=r}\left[\frac{\varphi_V^{\mathrm{TF}}(x)-\mu_V^{\mathrm{TF}}}{3^4 2^{-3}\pi^2 r^{-4}}-1\right]r^{\zeta}. \tag{40}$$

Then again, with $\zeta=(-7+\sqrt{73})/2\approx 0.77$, we find for all $|x|>R$

$$\varphi_V^{\mathrm{TF}}(x) \le 3^4 2^{-3}\pi^2|x|^{-4}\left(1+A(R,\mu_V^{\mathrm{TF}})|x|^{-\zeta}\right)+\mu_V^{\mathrm{TF}} \tag{41}$$

and

$$\varphi_V^{\mathrm{TF}}(x) \ge \max\left\{3^4 2^{-3}\pi^2|x|^{-4}\left(1+a(R)|x|^{-\zeta}\right)^{-2},\ \nu(\mu_V^{\mathrm{TF}})|x|^{-1}\right\}, \tag{42}$$

where

$$\nu(\mu_V^{\mathrm{TF}}) := \inf_{|x|\ge R}\max\left\{3^4 2^{-3}\pi^2|x|^{-3}\left(1+a(R)|x|^{-\zeta}\right)^{-2},\mu_V^{\mathrm{TF}}|x|\right\}. \tag{43}$$

Proof. Since $\rho_V^{\mathrm{TF}}\in L^{5/3}\cap L^1$ it is easy to see that $\rho_V^{\mathrm{TF}}*|x|^{-1}$ is continuous and tends to zero as x tends to infinity. Thus from the assumption on V it follows that φ_V^{TF} is continuous on $|x|>R$ and satisfies $\varphi_V^{\mathrm{TF}}(x)\to 0$ as $|x|\to\infty$.

Let $R' > R$ and set $A' = A(R', \mu_V^{\mathrm{TF}})$ and $a' = a(R')$. Then a' is well-defined if R' is close enough to R since then we may assume that $\varphi_V^{\mathrm{TF}}(x) > \mu_V^{\mathrm{TF}} \geq 0$ for all $|x| = R'$. Both a' and A' are finite. Using the notation from the proof of Lemma 4.4 we define

$$\omega^+_{\mu_V^{\mathrm{TF}},A'}(x) := \omega^+_{A'}(x) + \mu_V^{\mathrm{TF}} \quad \text{and} \quad \omega^-_{\mu_V^{\mathrm{TF}},a'}(x) := \max\left\{\omega^-_{a'}(x),\ \nu'|x|^{-1}\right\},$$

where

$$\nu' := \min_{|x|\geq R'} \max\left\{|x|\omega^-_{a'}(x),\ |x|\mu_V^{\mathrm{TF}}\right\}..$$

Note that, since we assume that $\varphi_V^{\mathrm{TF}}(x) > \mu_V^{\mathrm{TF}}$ for $|x| = R'$, we have that both $\omega^+_{A'}(x)$ and $\omega^-_{a'}(x)$ are positive for all $|x| > R'$. We also have that $\omega^-_{a'}(x) > \mu_V^{\mathrm{TF}}$ for $|x| = R$ and hence that $\omega^-_{a'}(x_0) = \mu_V^{\mathrm{TF}}$ at points x_0 where the minimum, defining ν', is attained. (Note that $|x|\omega^-_{a'}(x)$ is a radially decreasing function for $|x| > R'$.)

The proof of the present lemma is now similar to that of Lemma 4.4 if we can show that for $|x| > R'$

$$\Delta\omega^+_{\mu_V^{\mathrm{TF}},A'}(x) \leq 2^{7/2}(3\pi)^{-1}\left[\omega^+_{\mu_V^{\mathrm{TF}},A'}(x) - \mu_V^{\mathrm{TF}}\right]_+^{3/2} \tag{44}$$

and

$$\Delta\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) \geq 2^{7/2}(3\pi)^{-1}\left[\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) - \mu_V^{\mathrm{TF}}\right]_+^{3/2} \tag{45}$$

(in distribution sense). The inequality (44) follows immediately from the first inequality in (38). The inequality (45) is slightly more complicated. Note that the definitions of $\omega^-_{\mu_V^{\mathrm{TF}},a'}$ and of ν' imply that $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) = \nu'|x|^{-1}$ if $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) < \mu_V^{\mathrm{TF}}$ and $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) = \omega^-_{a'}(x)$ if $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) > \mu_V^{\mathrm{TF}}$. Thus if $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) < \mu_V^{\mathrm{TF}}$ we have that $\omega^-_{\mu_V^{\mathrm{TF}},a'}$ is harmonic. Hence (45) holds in this region. If $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) > \mu_V^{\mathrm{TF}}$ then $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) = \omega^-_{a'}(x)$ and (45) follows in this region from the second inequality in (38). Finally, since the maximum of two subharmonic functions is also subharmonic, it is clear that the distribution $\Delta\omega^-_{\mu_V^{\mathrm{TF}},a'}$ is a positive measure and in particular positive on the set (of Lebesgue measure) zero where $\omega^-_{\mu_V^{\mathrm{TF}},a'}(x) = \mu_V^{\mathrm{TF}}$. Hence, (45) holds in distribution sense for all $|x| > R$. □

As an application of the lower bound on φ_V^{TF} in (42) we can get an estimate on the chemical potential μ_V^{TF}.

4.7. COROLLARY (Chemical potential estimate). *With the assumptions and definitions in Theorem 4.6, in particular, if* $\mu_V^{\mathrm{TF}} < \liminf_{r\searrow R}\inf_{|x|=r}\varphi_V^{\mathrm{TF}}(x)$ *we have*

$$(\mu_V^{\mathrm{TF}})^{3/4} \leq \frac{2^{3/4}}{3\pi^{1/2}}(1+|a(R)|R^{-\zeta})^{1/2}\left(\lim_{r\to\infty}(4\pi)^{-1}\int_{\mathcal{S}^2} rV(r\omega)d\omega - \int_{\mathbb{R}^3}\rho_V^{\mathrm{TF}}(y)dy\right). \tag{46}$$

Proof. According to (42) we have $\nu(\mu_V^{\mathrm{TF}}) \leq \liminf_{|x|\to\infty}|x|\varphi_V^{\mathrm{TF}}(x)$. Using that V is harmonic and tends to zero at infinity we have that for all $r > R$

$$\liminf_{|x|\to\infty}|x|\varphi_V^{\mathrm{TF}}(x) \leq (4\pi)^{-1}\int_{\mathcal{S}^2} rV(r\omega)d\omega - \int_{\mathbb{R}^3}\rho_V^{\mathrm{TF}}(y)dy.$$

Moreover since, $\mu_V^{\mathrm{TF}} \geq 0$ the assumption $\mu_V^{\mathrm{TF}} < \liminf_{r\searrow R}\inf_{|x|=r}\varphi_V^{\mathrm{TF}}(x)$ implies that the spherical average of V is non-negative.

On the other hand, since $\left(1+|a(R)|R^{-\zeta}\right)^{-2} \leq \left(1+a(R)|x|^{-\zeta}\right)^{-2}$ for $|x| \geq R$, we have from (43) that $\nu(\mu_V^{\mathrm{TF}}) \geq \nu'$, where

$$\begin{aligned}\nu' &= \min_{|x|\geq R}\max\left\{3^4 2^{-3}\pi^2|x|^{-3}\left(1+|a(R)|R^{-\zeta}\right)^{-2}, \mu_V^{\mathrm{TF}}|x|\right\}\\ &= 3\cdot 2^{-3/4}\pi^{1/2}\left(1+|a(R)|R^{-\zeta}\right)^{-1/2}(\mu_V^{\mathrm{TF}})^{3/4}.\end{aligned}$$

□

This corollary immediately gives a partial converse to Theorem 4.3.

4.8. COROLLARY (Upper bound on maximal ionization). *If V is harmonic and continuous for $|x| > R$ and satisfies $V(x) \to 0$ as $|x| \to \infty$ and if moreover* $\mu_V^{\mathrm{TF}} < \liminf_{r\searrow R}\inf_{|x|=r}\varphi_V^{\mathrm{TF}}(x)$ *then*

$$\int \rho_V^{\mathrm{TF}} \leq \lim_{r\to\infty}(4\pi)^{-1}\int_{\mathcal{S}^2} rV(r\omega)d\omega.$$

In particular, if $\liminf_{r\searrow R}\inf_{|x|=r}\varphi_V^{\mathrm{TF}}(x) > 0$ *(which may not necessarily be true) we have*

$$N_c \leq \lim_{r\to\infty}(4\pi)^{-1}\int_{\mathcal{S}^2} rV(r\omega)d\omega.$$

4.9. REMARK. The limit above of course exists since by the harmonicity of V and since V tends to zero at infinity we have that $\int_{\mathcal{S}^2} rV(r\omega)d\omega$ is independent of r.

The difficulty in using Corollaries 4.7 and 4.8 in concrete examples lies in establishing the condition

$$\mu_V^{\mathrm{TF}} < \liminf_{r\searrow R} \inf_{|x|=r} \varphi_V^{\mathrm{TF}}(x). \tag{47}$$

5 Estimates on the standard atomic TF theory

In the usual atomic case the Coulomb potential $V(x) = Z|x|^{-1}$ is harmonic away from $x = 0$ and we can use Corollary 4.8 for all $R > 0$. Since $\rho^{\mathrm{TF}} * |x|^{-1}$ is a bounded function it follows that $\varphi^{\mathrm{TF}}(x) \to \infty$ as $x \to 0$. The condition (47) is therefore satisfied if R is chosen small enough. It therefore follows from Theorem 4.3 and Corollary 4.8 that $N_c = Z$. Thus the neutral atom corresponds to $\mu^{\mathrm{TF}} = 0$.

5.1. LEMMA. *Let φ_0^{TF} be the TF potential for the neutral atom then if φ^{TF} is the potential for a general $\mu^{\mathrm{TF}} \geq 0$ we have*

$$\varphi_0^{\mathrm{TF}}(x) \leq \varphi^{\mathrm{TF}}(x) \leq \varphi_0^{\mathrm{TF}}(x) + \mu^{\mathrm{TF}}.$$

Proof. See Corollary 3.8 (i) and (iii) in [8]. □

We now easily get an upper bound agreeing with the atomic Sommerfeld asymptotics.

5.2. THEOREM (Atomic Sommerfeld upper bound). *The atomic TF potential satisfies the bound*

$$\varphi^{\mathrm{TF}}(x) \leq \min\{3^4 2^{-3}\pi^2 |x|^{-4} + \mu^{\mathrm{TF}},\ Z|x|^{-1}\}$$

Proof. This follows immediately from and (34) and (41) together with the fact that ρ^{TF} is non-negative. Simply note that since $\varphi^{\mathrm{TF}}(x)|x| \to Z$ as $x \to 0$ we have that $A(0, \mu^{\mathrm{TF}}) = 0$ in (41). □

5.3. LEMMA (Lower bound on the TF potential). *In the atomic case we have for all $N > 0$ and $Z > 0$*

$$\varphi^{\mathrm{TF}}(x) \geq Z|x|^{-1} - \min\left\{N|x|^{-1}, \frac{22}{(9\pi)^{2/3}} Z^{4/3}\right\}.$$

Proof. We have by Newton's Theorem

$$\begin{aligned}\rho^{\mathrm{TF}} * |x|^{-1} &= |x|^{-1}\int_{|y|<|x|}\rho^{\mathrm{TF}}(y)dy + \int_{|y|>|x|}\rho^{\mathrm{TF}}(y)|y|^{-1}dy \\ &\leq \min\left\{N|x|^{-1},\ \int\rho^{\mathrm{TF}}(y)|y|^{-1}dy\right\}.\end{aligned}$$

From the Sommerfeld upper bound Theorem 5.2 and the TF equation (33) we have

$$\rho^{\mathrm{TF}}(x)^{2/3} \leq 2(3\pi^2)^{-2/3}\min\{3^4 2^{-3}\pi^2|x|^{-4},\ Z|x|^{-1}\}.$$

Hence

$$\rho^{\mathrm{TF}}(x) \leq \min\left\{c_1 Z^{3/2}|x|^{-3/2},\ c_2|x|^{-6}\right\},$$

where $c_1 := 2^{3/2}(3\pi^2)^{-1}$ and $c_2 := 3^5 2^{-3}\pi$. Let $r_0 := (c_2/c_1)^{2/9}Z^{-1/3}$. When $|x| = r_0$ the two functions, in the minimum above, are equal. Thus

$$\begin{aligned}\int\rho^{\mathrm{TF}}(y)|y|^{-1}dy &\leq 4\pi c_1 Z^{3/2}\int_0^{r_0} t^{-1/2}dt + 4\pi c_2\int_{r_0}^{\infty} t^{-5}dt = \frac{11\pi}{3}c_1^{8/9}c_2^{1/9}Z^{4/3} \\ &= \frac{22}{(9\pi)^{2/3}}Z^{4/3}.\end{aligned}$$

The lemma follows from the definition (34) of the TF potential. □

5.4. THEOREM (Atomic Sommerfeld Lower bound). *The TF potential satisfies*

$$\varphi^{\mathrm{TF}}(x) \geq \begin{cases} Z|x|^{-1} - 22(9\pi)^{-2/3}Z^{4/3}, & \text{if } |x| \leq \beta_0 Z^{-1/3} \\ \max\left\{\begin{array}{l} 3^4 2^{-3}\pi^2\left(1 + aZ^{-\zeta/3}|x|^{-\zeta}\right)^{-2}|x|^{-4}, \\ (Z-N)_+|x|^{-1}\end{array}\right\}, & \text{if } |x| \geq \beta_0 Z^{-1/3}\end{cases},$$

where $\beta_0 = \frac{(9\pi)^{2/3}}{44}$ *and* $\zeta = (-7+\sqrt{73})/2$ *as in Theorem 4.6 and* $a = 43.7$.

Proof. Let $R = (9\pi)^{2/3}Z^{-1/3}/44$. Note that for $|x| \leq R$ the bound we want to prove is identical to the bound in Lemma. 5.3.

If $N \geq Z$, i.e., $\mu^{\mathrm{TF}} = 0$ the lower bound follows from Theorem 4.6 since a is chosen so as to make the lower bound continuous at $|x| = R$ and at these points we clearly have $\varphi^{\mathrm{TF}}(x) > 0 = \mu^{\mathrm{TF}}$.

For general N the lower bound follows from the case $N = Z$ because of Lemma 5.1 and Lemma 5.3. □

We end this section by giving a bound on the *screened nuclear potential* $\Phi_R^{\rm TF}$ at radius R in the atomic TF theory.

5.5. LEMMA (Bound on $\Phi_R^{\rm TF}$). *We have*

$$\Phi_{|x|}^{\rm TF}(x) \le 3^4 2^{-1}\pi^2|x|^{-4} + \mu^{\rm TF}$$

Proof. We write $\Phi_{|x|}^{\rm TF}(x) = \varphi^{\rm TF}(x) + \int_{|y|>|x|}\rho^{\rm TF}(y)|x-y|^{-1}dy$. From Theorem 5.2 and the TF equation (33) we see that

$$\rho^{\rm TF}(y) \le 2^{3/2}(3\pi^2)^{-1}[\varphi^{\rm TF} - \mu^{\rm TF}]_+^{3/2} \le 2^{-3}3^5\pi|y|^{-6}$$

and hence

$$\begin{aligned}\int_{|y|>|x|}\rho^{\rm TF}(y)|x-y|^{-1}dy &\le \int_{|y|>|x|}2^{-3}3^5\pi|y|^{-6}|x-y|^{-1}dy\\ &= \int_{|y|>|x|}2^{-3}3^5\pi|y|^{-7}dy = 2^{-3}3^5\pi^2|x|^{-4}.\end{aligned}$$

The lemma follows from Theorem 5.2.

□

6 Separating the outside from the inside

We shall here control the energy coming from the regions far from the nucleus. Let $\gamma^{\rm HF}$ be an HF minimizer with $\mathrm{Tr}[\gamma^{\rm HF}] = N$. (We are thus assuming that N is such that a minimizer exists.)

6.1. DEFINITION (The localization function). Fix $0 < \lambda < 1$ and let $G : \mathbb{R}^3 \to \mathbb{R}$ be given by

$$G(x) = \begin{cases} 0 & \text{if } |x| \le 1\\ (\pi/2)(|x|-1)\left[(1-\lambda)^{-1}-1\right]^{-1} & \text{if } 1 \le |x| \le (1-\lambda)^{-1}\\ \pi/2 & \text{if } (1-\lambda)^{-1} \le |x|\end{cases}$$

We introduce the cutoff radius $r > 0$ and define the outside localization function $\theta_r(x) = \sin G(|x|/r)$. Then

$$0 \le \theta_r(x)\begin{cases} = 0 & \text{if } |x| \le r\\ \le 1 & \text{if } r \le |x| \le (1-\lambda)^{-1}r\\ = 1 & \text{if } (1-\lambda)^{-1}r \le |x|\end{cases}$$

and $|\nabla\theta_r(x)|^2 + |\nabla(1-\theta_r(x)^2)^{1/2}|^2 \le (\pi/(2\lambda r))^2$ (since $(1-\lambda)^{-1} - 1 \ge \lambda$).

We shall consider the HF minimizer restricted to the region $\{x : |x| > r\}$. We therefore define the exterior part of the minimizer

$$\gamma_r^{\mathrm{HF}} = \theta_r \gamma^{\mathrm{HF}} \theta_r \tag{48}$$

and its density $\rho_r^{\mathrm{HF}}(x) = \theta_r(x)^2 \rho^{\mathrm{HF}}(x)$. In order to control γ_r^{HF} we introduce an auxilliary functional defined on all density matrices with $\mathrm{Tr}\,[-\Delta\gamma] < \infty$ (See Remark 2.2) by

$$\mathcal{E}^{\mathrm{A}}(\gamma) = \mathrm{Tr}\left[(-\tfrac{1}{2}\Delta - \Phi_r^{\mathrm{HF}})\gamma\right] + \tfrac{1}{2}\iint\limits_{\substack{|x|\geq r\\ |y|\geq r}} \rho_\gamma(x)|x-y|^{-1}\rho_\gamma(y)dx\,dy, \tag{49}$$

where the screened nuclear potential Φ_r^{HF} is defined in (3) in Definition 1.1. Note that the functional $\mathcal{E}^{\mathrm{A}}$, in contrast to the HF functional $\mathcal{E}^{\mathrm{HF}}$ in (26), does not contain an exchange term.

The main result in this section is that γ_r^{HF} almost minimizes $\mathcal{E}^{\mathrm{A}}$. More precisely, we shall prove the following theorem.

6.2. THEOREM (The outside energy). *For all $0 < \lambda < 1$ and all $r > 0$ we have*

$$\mathcal{E}^{A}\left[\gamma_r^{\mathrm{HF}}\right] \leq \inf\left\{\mathcal{E}^{A}(\gamma) : \mathrm{supp}\ \rho_\gamma \subset \{y : |y| \geq r\},\ \int \rho_\gamma \leq \int \chi_r^{+}\rho^{\mathrm{HF}}\right\} + \mathcal{R}, \tag{50}$$

where the error is

$$\mathcal{R} = C_\lambda(r)\int\limits_{|x|\geq(1-\lambda)r} \rho^{\mathrm{HF}}(x)dx + 2L_1 \int\limits_{(1-\lambda)r\leq|x|\leq(1-\lambda)^{-1}r} \left[\Phi^{\mathrm{HF}}_{(1-\lambda)r}(x)\right]_+^{5/2} dx + \mathcal{E}x(\gamma_r^{\mathrm{HF}}) \tag{51}$$

with

$$C_\lambda(r) = \left(\frac{\pi^2}{8\left(\lambda(1-\lambda)r\right)^2} + \frac{\pi}{r\lambda}\right).$$

Here L_1 is the constant in the Lieb-Thirring inequality (22).

Proof. Besides θ_r we introduce two other localization functions

$$\theta_- = (1 - \theta^2_{r(1-\lambda)})^{1/2} \qquad \text{and} \qquad \theta_{(0)} = \left(\theta^2_{r(1-\lambda)} - \theta_r^2\right)^{1/2}.$$

Note that $\theta_-^2 + \theta_{(0)}^2 + \theta_r^2 = 1$ and that $(\nabla\theta_-)^2 + (\nabla\theta_{(0)})^2 + (\nabla\theta_r)^2 \leq (\pi/(2\lambda(1-\lambda)r))^2$. We introduce the inside part of the HF minimizer

$$\gamma_-^{\mathrm{HF}} = \theta_- \gamma^{\mathrm{HF}} \theta_-. \tag{52}$$

We shall prove (50) by showing that for all density matrices γ with supp $\rho_\gamma \subset \{x : |x| \geq r\}$ and $\int \rho_\gamma \leq \int \chi_r^+ \rho^{\text{HF}}$ we have

$$\mathcal{E}^{\text{A}}\left[\gamma_r^{\text{HF}}\right] + \mathcal{E}^{\text{HF}}\left[\gamma_-^{\text{HF}}\right] - \mathcal{R} \leq \mathcal{E}^{\text{HF}}\left[\gamma^{\text{HF}}\right] \leq \mathcal{E}^{\text{A}}[\gamma] + \mathcal{E}^{\text{HF}}\left[\gamma_-^{\text{HF}}\right], \tag{53}$$

with $\mathcal{R}$ given by (51). The estimate (50) follows immediately from (53).

Proof of the upper bound in (53): Since γ^{HF} is a minimizer for $\mathcal{E}^{\text{HF}}$ under the condition $\text{Tr}[\gamma^{\text{HF}}] \leq N$ (see (29)) we have for any density matrix $\widetilde{\gamma}$ with $\text{Tr}\left[\widetilde{\gamma}\right] \leq N$ that $\mathcal{E}^{\text{HF}}\left(\gamma^{\text{HF}}\right) \leq \mathcal{E}^{\text{HF}}\left(\widetilde{\gamma}\right)$. We take

$$\widetilde{\gamma} = \gamma_-^{\text{HF}} + \gamma.$$

Since the support of ρ_γ is disjoint from the support of θ_- we see that $\gamma_-^{\text{HF}}\gamma = 0$ and hence $\widetilde{\gamma}$ is a density matrix.

Note that

$$\text{Tr}\left[\widetilde{\gamma}\right] = \text{Tr}\left[\gamma_-^{\text{HF}}\right] + \int \rho_\gamma \leq \text{Tr}\left[\gamma_-^{\text{HF}}\right] + \int \chi_r^+ \rho^{\text{HF}} = \int (\theta_-^2 + \chi_r^+)\rho^{\text{HF}} \leq \int \rho^{\text{HF}} \leq N$$

We shall compute $\mathcal{E}^{\text{HF}}\left(\widetilde{\gamma}\right)$. The only terms in $\mathcal{E}^{\text{HF}}$ that are not linear in the density matrix (and thus do not simply split into a sum of terms for γ_-^{HF} and γ) are the exchange and direct Coulomb energies. Because of the support properties of γ_-^{HF} and γ we have that $\widetilde{\gamma}^2 = \left(\gamma_-^{\text{HF}}\right)^2 + \gamma^2$ and therefore even the exchange term satisfies

$$\mathcal{E}x\left(\widetilde{\gamma}\right) = \mathcal{E}x\left(\gamma_-^{\text{HF}}\right) + \mathcal{E}x\left(\gamma\right) \geq \mathcal{E}x\left(\gamma_-^{\text{HF}}\right).$$

We are thus left with the direct Coulomb energy. For this we find that

$$\mathcal{D}\left(\widetilde{\gamma}\right) = \mathcal{D}\left(\gamma_-^{\text{HF}}\right) + \mathcal{D}\left(\gamma\right) + \int \theta_-^2(y)\rho^{\text{HF}}(y)|x-y|^{-1}\rho_\gamma(y)dy.$$

By the choice of the support of θ_- we have that

$$\int \theta_-^2(y)\rho^{\text{HF}}(y)|x-y|^{-1}\rho_\gamma(x)dx\,dy \leq \int \left(\frac{Z}{|x|} - \Phi_r^{\text{HF}}(x)\right)\rho_\gamma(x)dx.$$

We have thus proved the upper bound in (53).

Proof of the lower bound in (53):

Let again the inside part of the HF minimizer be γ_-^{HF} defined by (52) and introduce also the middle part $\gamma_{(0)}^{\text{HF}} = \theta_{(0)}\gamma^{\text{HF}}\theta_{(0)}$. Since $\theta_-^2 + \theta_{(0)}^2 + \theta_r^2 = 1$ we have from the IMS formula (20) that

$$\begin{aligned}
\mathrm{Tr}\left[-\tfrac{1}{2}\Delta\gamma^{\mathrm{HF}}\right] &= \mathrm{Tr}\left[-\tfrac{1}{2}\Delta\left(\gamma_-^{\mathrm{HF}}+\gamma_{(0)}^{\mathrm{HF}}+\gamma_r^{\mathrm{HF}}\right)\right] \\
&\quad -\tfrac{1}{2}\mathrm{Tr}\left[\gamma^{\mathrm{HF}}\left((\nabla\theta_-)^2+(\nabla\theta_{(0)})^2+(\nabla\theta_r)^2\right)\right] \\
&\geq \mathrm{Tr}\left[-\tfrac{1}{2}\Delta\left(\gamma_-^{\mathrm{HF}}+\gamma_{(0)}^{\mathrm{HF}}+\gamma_r^{\mathrm{HF}}\right)\right] \\
&\quad -(\pi^2/8)\left(\lambda(1-\lambda)r\right)^{-2}\int\limits_{(1-\lambda)r<|x|<r(1-\lambda)^{-1}}\rho^{\mathrm{HF}}(x)dx. \qquad (54)
\end{aligned}$$

We now come to the lower bounds on the Coulomb terms. Note that

$$\begin{aligned}
1 &= \left(\theta_-^2(x)+\theta_{(0)}^2(x)+\theta_r^2(x)\right)\left(\theta_-^2(y)+\theta_{(0)}^2(y)+\theta_r^2(y)\right) \\
&\geq \theta_-^2(x)\theta_-^2(y)+\theta_r^2(x)\theta_r^2(y)+\theta_r^2(x)\left(\theta_-^2(y)+\theta_{(0)}^2(y)\right) \\
&\quad +\left(\theta_-^2(x)+\theta_{(0)}^2(x)\right)\theta_r^2(y)+\theta_{(0)}^2(x)^2\theta_-^2(y)+\theta_-^2(x)^2\theta_{(0)}^2(y).
\end{aligned}$$

Note that $\theta_-^2(x)+\theta_{(0)}^2(x)\geq\chi_r(x)$ and $\theta_-^2(x)\geq\chi_{(1-\lambda)r}$ We may therefore estimate the Coulomb kernel from below by

$$|x-y|^{-1}\geq\widetilde{V}(x,y),$$

where

$$\begin{aligned}
\widetilde{V}(x,y) &:= \theta_-^2(x)|x-y|^{-1}\theta_-^2(y)+\theta_r^2(x)|x-y|^{-1}\theta_r^2(y) \\
&\quad +\theta_r^2(x)|x-y|^{-1}\chi_r(y)+\chi_r(x)|x-y|^{-1}\theta_r^2(y) \qquad (55) \\
&\quad +\theta_{(0)}^2(x)|x-y|^{-1}\chi_{(1-\lambda)r}(y)+\chi_{(1-\lambda)r}(x)|x-y|^{-1}\theta_{(0)}^2(y).
\end{aligned}$$

The function $\widetilde{V}$ is pointwise positive and symmetric in x and y.

Recall that $\gamma^{\rm HF}$ is a projection onto the subspace spanned by the orthonormal vectors $u_1, u_2, \ldots, u_N$ and

$$\begin{aligned}
\mathcal{D}\left(\gamma^{\rm HF}\right) - \mathcal{E}x(\gamma^{\rm HF}) &= \tfrac14 \sum_{i,j} \iint \frac{\|u_i(x)\otimes u_j(y) - u_j(x)\otimes u_i(y)\|^2_{\mathbb{C}^2\otimes\mathbb{C}^2}}{|x-y|} dx\, dy \\
&\geq \tfrac14 \sum_{i,j} \iint \|u_i(x)\otimes u_j(y) - u_j(x)\otimes u_i(y)\|^2_{\mathbb{C}^2\otimes\mathbb{C}^2} \widetilde{V}(x,y) dx\, dy \\
&= \tfrac12 \iint \rho^{\rm HF}(x)\widetilde{V}(x,y)\rho^{\rm HF}(y) dx\, dy \\
&\quad - \tfrac12 \iint \mathrm{Tr}_{\mathbb{C}^2} \left|\gamma^{\rm HF}(x,y)\right|^2 \widetilde{V}(x,y) dx\, dy. \qquad (56)
\end{aligned}$$

We estimate these two terms independently. We obtain for the first term in (56)

$$\begin{aligned}
\tfrac12 \iint \rho^{\rm HF}(x)\widetilde{V}(x,y)\rho^{\rm HF}(y) dx\, dy &= \mathcal{D}\left(\gamma^{\rm HF}_-\right) + \mathcal{D}\left(\gamma^{\rm HF}_r\right) \\
&+ \int \left(\frac{Z}{|x|} - \Phi^{\rm HF}_r(x)\right) \rho^{\rm HF}_r(x) dx + \mathrm{Tr}\left[\left(\frac{Z}{|x|} - \Phi^{\rm HF}_{(1-\lambda)r}(x)\right)\gamma^{\rm HF}_{(0)}\right]. \qquad (57)
\end{aligned}$$

To estimate the last term in (56) we use that for all $|x| > r$

$$\theta_r(x)^2 \leq \theta_r(x) \leq (\pi/2)(|x|/r - 1)\left((1-\lambda)^{-1} - 1\right)^{-1}.$$

Thus if $|y| < r$ we have $|x-y|^{-1}\theta_r(x)^2 \leq (\pi/2)r^{-1}\left((1-\lambda)^{-1}-1\right)^{-1}$ and hence

$$\begin{aligned}
&\iint \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\rm HF}(x,y)\right|^2\right] |x-y|^{-1} \left(\chi_r(y)\theta_r^2(x) + \chi_{(1-\lambda)r}(y)\theta^2_{(0)}(x)\right) dx\, dy \\
&\leq \frac{\pi}{2r}\left((1-\lambda)^{-1}-1\right)^{-1}\left(1+(1-\lambda)^{-1}\right) \iint_{\substack{|y|\leq r\\ |x|\geq(1-\lambda)r}} \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\rm HF}(x,y)\right|^2\right] dx\, dy \\
&\leq \frac{\pi}{r\lambda} \iint_{\substack{|y|\leq r\\ |x|\geq(1-\lambda)r}} \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\rm HF}(x,y)\right|^2\right] dx\, dy.
\end{aligned}$$

Moreover, we only increase the last integral if we integrate over all $y \in \mathbb{R}^3$. Thus

$$\begin{aligned}
\iint_{\substack{|y|\leq r\\ |x|\geq(1-\lambda)r}} \mathrm{Tr}_{\mathbb{C}^2}\left|\gamma^{\rm HF}(x,y)\right|^2 dx\, dy &\leq \int_{|x|\geq(1-\lambda)r} \left(\mathrm{Tr}_{\mathbb{C}^2}\int \gamma^{\rm HF}(x,y)\gamma^{\rm HF}(y,x) dy\right) dx \\
&= \int_{|x|\geq(1-\lambda)r} \mathrm{Tr}_{\mathbb{C}^2}\left[\left(\gamma^{\rm HF}\right)^2(x,x)\right] dx.
\end{aligned}$$

If we now use that $(\gamma^{\rm HF})^2 = \gamma^{\rm HF}$ and that $\rho^{\rm HF}(x) = {\rm Tr}_{\mathbb{C}^2}\left[\gamma^{\rm HF}(x,x)\right]$ we obtain the estimate

$$\tfrac{1}{2}\iint {\rm Tr}_{\mathbb{C}^2}\left|\gamma^{\rm HF}(x,y)\right|^2 \widetilde{V}(x,y)dx\,dy \;\leq\; \mathcal{E}x\left[\gamma_-^{\rm HF}\right] + \mathcal{E}x[\gamma_r^{\rm HF}] + \frac{\pi}{r\lambda}\int\limits_{|x|\geq(1-\lambda)r} \rho^{\rm HF}(x)dx. \qquad (58)$$

If we combine (54), (57) and (58) we obtain

$$\mathcal{E}^{\rm HF}\left[\gamma^{\rm HF}\right] \;\geq\; \mathcal{E}^{\rm HF}\left[\gamma_-^{\rm HF}\right] + \mathcal{E}^{\rm A}\left[\gamma_r^{\rm HF}\right] - \mathcal{E}x[\gamma_r^{\rm HF}] + {\rm Tr}\left[\left(-\tfrac{1}{2}\Delta - \Phi^{\rm HF}_{(1-\lambda)r}\right)\gamma^{\rm HF}_{(0)}\right] - C_\lambda(r)\left(\frac{\pi^2}{8\left(\lambda(1-\lambda)r\right)^2} + \frac{\pi}{r\lambda}\right)\int\limits_{|x|\geq(1-\lambda)r}\rho^{\rm HF}(x)dx.$$

Since $0 \leq \gamma^{\rm HF}_{(0)} \leq I$ and the density of $\gamma^{\rm HF}_{(0)}$ is supported within the set

$$\left\{x : (1-\lambda)r \leq |x| \leq (1-\lambda)^{-1}r\right\}$$

we have from the Lieb-Thirring inequality (22) that

$${\rm Tr}\left[\left(-\tfrac{1}{2}\Delta - \Phi^{\rm HF}_{(1-\lambda)r}\right)\gamma^{\rm HF}_{(0)}\right] \geq -2L_1 \int\limits_{(1-\lambda)r\leq|x|\leq(1-\lambda)^{-1}r} \left[\Phi^{\rm HF}_{(1-\lambda)r}(x)\right]_+^{5/2} dx.$$

The factor of 2 above is due to the spin degrees of freedom. We have thus proved the lower bound in (53). □

As a consequence of this theorem and the Lieb-Thirring inequality (21) we get the following bound.

6.3. COROLLARY ($L^{5/3}$ bound on $\rho_r^{\rm HF}$). *Let K_1 denote the constant in the LT inequality (21) and e_0, as in (9), denote the TF energy of a neutral atom with unit nuclear charge and physical parameter values. Then*

$$\int \rho_r^{\rm HF}(y)^{5/3}dy \leq 2K_1^{-1}\mathcal{R} + \tfrac{6}{5}(3\pi^2)^{2/3}K_1^{-2}e_0\left[r\sup_{|x|=r}\Phi_r^{\rm HF}(x)\right]_+^{7/3}, \qquad (59)$$

where $\mathcal{R}$ was given in (51).

Proof. Since $\Phi_r^{\rm HF}$ is harmonic on the set $\{|x| > r\}$ and tends to zero at infinity we get for all $|y| > r$ that $\Phi_r^{\rm HF}(y) \le |y|^{-1} r \sup_{|x|=r} \Phi_r^{\rm HF}(x)$. Hence

$$\begin{aligned}\mathcal{E}^{\rm A}\left[\gamma_r^{\rm HF}\right] \ \ge\ & K_1 \int \rho_r^{\rm HF}(y)^{5/3} dy - \left[r \sup_{|x|=r} \Phi_r^{\rm HF}(x)\right] \int |y|^{-1} \rho_r^{\rm HF}(y) dy \\ & + \tfrac{1}{2} \iint \rho_r^{\rm HF}(y) |y-y'|^{-1} \rho_r^{\rm HF} \gamma'(y') dy\, dy'\end{aligned}$$

It follows from standard atomic Thomas-Fermi theory that the right hand side is bounded below by the energy of a neutral Thomas-Fermi atom with nuclear charge $\left[r \sup_{|x|=r} \Phi_r^{\rm HF}(x)\right]_+$ and with the constant K_1 in front of the first term. A simple scaling argument shows that this is $-\frac{3}{10}(3\pi^2)^{2/3} K_1^{-1} \left[r \sup_{|x|=r} \Phi_r^{\rm HF}(x)\right]_+^{7/3} e_0$.

By repeating this argument with only a fraction of the term $\int (\rho_r^{\rm HF})^{5/3}$ we conclude that for all $0 < t < 1$

$$(1-t) K_1 \int \rho_r^{\rm HF}(y)^{5/3} dy \le \mathcal{E}^{\rm A}\left[\gamma_r^{\rm HF}\right] + \tfrac{3}{10}(3\pi^2)^{2/3} (tK_1)^{-1} e_0 \left[r \sup_{|x|=r} \Phi_r^{\rm HF}(x)\right]_+^{7/3}.$$

Since $\mathcal{E}^{\rm A}\left[\gamma_r^{\rm HF}\right] \le \mathcal{R}$ (by choosing the trial $\gamma = 0$ in (50)) we get (59) if we choose $t = 1/2$. □

We still need to show how we can control the exchange term $\mathcal{E}x[\gamma_r^{\rm HF}]$. This is done using a standard inequality of Lieb [](or in an improved version by Lieb and Oxford []). They proved the inequality for general wave functions, but we need it here only for Hartree-Fock Slater determinants. For completeness we shall give a proof (with a worse constant) in the simple case we need here.

6.4. THEOREM (Exchange inequality). *For any trace class operator γ with $0 \le \gamma \le I$ we have the estimate*

$$\mathcal{E}x[\gamma] \le 1.68 \int \rho_\gamma^{4/3}$$

Proof. We shall here present a simple proof that the inequality holds with 1.68 replaced by 248.3. To get the much better constant one needs the more detailed analysis in []. We use the representation

$$|x|^{-1} = \pi^{-1} \int_0^\infty \chi_r * \chi_r(x) r^{-5} dr,$$

where χ_r again denotes the characteristic function of the ball of radius r centered at the origin. Thus we may write the exchange energy as

$$\mathcal{E}x[\gamma] = (2\pi)^{-1} \int_0^\infty \int_{\mathbb{R}^3} \mathrm{Tr}[\gamma X_{r,z} \gamma X_{r,z}] r^{-5} dz dr,$$

where $X_{r,z}$ is the multiplication operator $X_{r,z} f(x) = \chi_r(x-z) f(x)$.

We now use the two simple estimates $X_{r,z}\gamma X_{r,z} \leq X_{r,z}^2$ and $X_{r,z}\gamma X_{r,z} \leq \mathrm{Tr}[\gamma X_{r,z}^2] I$. We obtain

$$\mathrm{Tr}[\gamma X_{r,z}\gamma X_{r,z}] = \mathrm{Tr}[\gamma^{1/2} X_{r,z}(X_{r,z}\gamma X_{r,z}) X_{r,z}\gamma^{1/2}] \leq \mathrm{Tr}[\gamma X_{r,z}^2] = \rho_\gamma * \chi_r(z)$$

and

$$\mathrm{Tr}[\gamma X_{r,z}\gamma X_{r,z}] = \mathrm{Tr}[\gamma^{1/2} X_{r,z}(X_{r,z}\gamma X_{r,z}) X_{r,z}\gamma^{1/2}] \leq \mathrm{Tr}[\gamma X_{r,z}^2]^2 = (\rho_\gamma * \chi_r(z))^2.$$

If ρ_γ^* denotes the Hardy-Littlewood maximal function we have $\rho_\gamma * \chi_r(z) \leq (4\pi r^3/3)\rho_\gamma^*(z)$. Thus with $R(z) = \left((4\pi/3)\rho_\gamma^*(z)\right)^{-1/3}$ we can estimate

$$\begin{aligned} \mathcal{E}x[\gamma] &\leq (2\pi)^{-1} \int_{\mathbb{R}^3} \left(\int_0^{R(z)} \left(\frac{4\pi r^3}{3} \rho_\gamma^*(z) \right)^2 r^{-5} dr + \int_{R(z)}^\infty \frac{4\pi r^3}{3} \rho_\gamma^*(z) r^{-5} dr \right) dz \\ &= (4\pi/3)^{1/3} \int_{\mathbb{R}^3} \left(\rho_\gamma^*(z)\right)^{4/3} dz. \end{aligned}$$

If we finally apply the maximal inequality $\|f^*\|_p^p \leq (48p2^p/(\pi(p-1))\|f\|_p^p$, for all $p > 1$ ([25], p. 58) we obtain

$$\mathcal{E}x[\gamma] \leq \frac{384}{\pi} \left(\frac{8\pi}{3}\right)^{1/3} \int \rho_\gamma^{4/3} = 248.3 \int \rho_\gamma^{4/3}.$$

□

7 Exterior L^1 estimate

The aim of this section is to control $\int_{|x|>r} \rho^{\mathrm{HF}}(x) dx$, for all $r > 0$. As before ρ^{HF} is the density of a Hartree-Fock minimizer γ^{HF} with $\mathrm{Tr}[\gamma^{\mathrm{HF}}] = N$. Thus $\int \rho^{\mathrm{HF}} = N$.

The difficulty in estimating $\int_{|x|>r} \rho^{\mathrm{HF}}(x) dx$ is that this quantity cannot be controlled in terms of the energy $\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})$. More precisely, $\int_{|x|>r} \rho_\gamma(x) dx$ can be arbitrarily large even when $\mathcal{E}^{\mathrm{HF}}(\gamma)$ is arbitrarily close to the absolute minimum. The simple reason is that "adding electrons at infinity" will not raise the energy.

Therefore, in order to control $\int_{|x|>r}\rho^{\rm HF}(x)dx$, we must use the minimizing property of $\gamma^{\rm HF}$.

In contrast, it follows from the Lieb-Thirring inequality that $\int_{|x|>r}\rho^{\rm HF}(x)^{5/3}dx$ can be controlled in terms of the energy. By Hölder's inequality it then also follows that the integral of $\rho^{\rm HF}$ over any bounded set can be controlled by the energy.

The philosophy here will be, to use the minimizing property of $\gamma^{\rm HF}$, to control the integral of $\rho^{\rm HF}$ over an unbounded set, in terms of the integral over a bounded set.

Our main result in this section is stated in the next lemma. The proof of the lemma uses an idea of Lieb [11].

7.1. LEMMA (Exterior L^1 estimate). *For all $r>0$ and all $0<\lambda<1$ the density $\rho^{\rm HF}$ of an HF minimizer $\gamma^{\rm HF}$ satisfies the bound*

$$\int_{|x|>(1-\lambda)^{-1}r}\rho^{\rm HF}(x)dx \;\le\; 1+2\lambda^{-1}+2\left[\sup_{|x|=(1-\lambda)r}|x|\Phi^{\rm HF}_{(1-\lambda)r}(x)\right]_+ + \left(K_\lambda r^{-1}\int_{r<|x|<(1-\lambda)^{-1}r}\rho^{\rm HF}(x)dx\right)^{1/2},$$

where $K_\lambda := \left(\frac{2\lambda}{\pi}+(1-\lambda)^{-1}\right)\left(\frac{\pi}{2\lambda}\right)^2$. Here $\Phi^{\rm HF}_{(1-\lambda)r}$ is the screened nuclear potential introduced in Definition 1.1.

Proof. Since $\gamma^{\rm HF}$ is a minimizer we know that it satisfies the Hartree-Fock equations. I.e, according to Theorem 3.11, $\gamma^{\rm HF}$ is a projection onto a space spanned by functions $u_1,\ldots,u_N\in L^2(\mathbb{R}^3;\mathbb{C}^2)$ satisfying $H_{\gamma^{\rm HF}}u_i=\varepsilon_i u_i$, were $\varepsilon_i\le 0$.

Let $\Xi\in C^1(\mathbb{R}^3)$ have compact support away from $x=0$, be real and satisfy $\Xi(x)^2\le 1$. Then

$$0\ge\sum_{i=1}^N\varepsilon_i\int|u_i(x)|^2\,|x|\Xi(x)^2\,dx=\sum_{i=1}^N\int u_i(x)^*|x|\Xi(x)^2H_{\gamma^{\rm HF}}u_i(x)dx.$$

From the definition (30) of the mean field operator $H_{\gamma^{\rm HF}}$ we obtain

$$\begin{aligned}0 \;\ge\; & \sum_{i=1}^N\tfrac12\int\nabla\left(u_i(x)^*|x|\Xi(x)^2\right)\cdot\nabla u_i(x)dx-Z\int\rho^{\rm HF}\Xi^2\\ &+\iint\left[\rho^{\rm HF}(x)\rho^{\rm HF}(y)-\mathrm{Tr}_{\mathbb{C}^2}\left[|\gamma^{\rm HF}(x,y)|^2\right]\right]\frac{|y|\Xi(y)^2}{|x-y|}dx\,dy. \qquad (60)\end{aligned}$$

We consider separately the different terms above. By the IMS formula (19)

$$\begin{aligned}
&\mathrm{Re}\tfrac{1}{2}\int \nabla\left(u_i(x)^*|x|\Xi(x)^2\right)\cdot\nabla u_i(x)dx \\
&\quad= \tfrac{1}{2}\int \left|\nabla\left(\Xi(x)|x|^{1/2}u_i(x)\right)\right|^2 - \tfrac{1}{4}|x|^{-1}\Xi(x)^2\left|u_i(x)\right|^2 dx \\
&\qquad -\tfrac{1}{2}\int \left(\tfrac{1}{2}\nabla\left(\Xi(x)^2\right) + |x|\left(\nabla\Xi(x)\right)^2\right)\left|u_i(x)\right|^2 dx \\
&\quad\geq -\tfrac{1}{2}\int \left(\tfrac{1}{2}\nabla\left(\Xi(x)^2\right) + |x|\left(\nabla\Xi(x)\right)^2\right)\left|u_i(x)\right|^2 dx, \qquad (61)
\end{aligned}$$

where we have used Hardy's inequality $\int|\nabla f(x)|^2dx \geq \frac{1}{4}\int|x|^{-2}|f(x)|^2dx$.

For the Coulomb terms we estimate it using that

$$\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\mathrm{HF}}(x,y)\right|^2\right] = \tfrac{1}{2}\sum_{i,j=1}^{N}\|u_i(x)\otimes u_j(y) - u_j(x)\otimes u_i(y)\|^2_{\mathbb{C}^2\otimes\mathbb{C}^2}$$

is non-negative. Hence

$$\begin{aligned}
&\iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\mathrm{HF}}(x,y)\right|^2\right]\right]\frac{|y|\Xi(y)^2}{|x-y|}dx\,dy \\
&= \iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\mathrm{HF}}(x,y)\right|^2\right]\right]\frac{|y|\left(1-\Xi(x)^2\right)\Xi(y)^2}{|x-y|}dx\,dy \\
&\quad + \tfrac{1}{2}\iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\mathrm{HF}}(x,y)\right|^2\right]\right]\frac{|x|+|y|}{|x-y|}\Xi(x)^2\Xi(y)^2dx\,dy,
\end{aligned}$$

where we expressed the last term symmetrically in x and y. If we now use the triangle inequality and the fact $\int\mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\mathrm{HF}}(x,y)\right|^2\right]\Xi(y)^2dy \leq \rho^{\mathrm{HF}}(x)$, which follows from $\Xi(x)^2\leq 1$ and $(\gamma^{\mathrm{HF}})^2 = \gamma^{\mathrm{HF}}$, we arrive at

$$\begin{aligned}
&\iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\mathrm{HF}}(x,y)\right|^2\right]\right]\frac{|y|\Xi(y)^2}{|x-y|}dx\,dy \\
&\geq \iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[\left|\gamma^{\mathrm{HF}}(x,y)\right|^2\right]\right]\frac{|y|\left(1-\Xi(x)^2\right)\Xi(y)^2}{|x-y|}dx\,dy \\
&\quad + \tfrac{1}{2}\left(\int\rho^{\mathrm{HF}}\Xi^2\right)^2 - \tfrac{1}{2}\int\rho^{\mathrm{HF}}\Xi^2. \qquad (62)
\end{aligned}$$

Inserting the inequalities (61) and (62) into (60) gives

$$0 \geq -\tfrac{1}{2}\int\left(\tfrac{1}{2}\nabla\left(\Xi(x)^2\right) + |x|\left(\nabla\Xi(x)\right)^2\right)\rho^{\mathrm{HF}}(x)dx - Z\int\rho^{\mathrm{HF}}\Xi^2$$

$$+ \iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[|\gamma^{\mathrm{HF}}(x,y)|^2\right]\right] \frac{|y|\left(1-\Xi(x)^2\right)\Xi(y)^2}{|x-y|} dx\,dy$$

$$+ \tfrac{1}{2}\left(\int \rho^{\mathrm{HF}}\Xi^2\right)^2 - \tfrac{1}{2}\int \rho^{\mathrm{HF}}\Xi^2. \tag{63}$$

By an approximation argument it is clear that we can use (63) for any real function Ξ for which $\Xi^2 \leq 1$ and the function $\left(\nabla\left(\Xi(x)^2\right) + |x|\left(\nabla\Xi(x)\right)^2\right)$ is bounded. In particular we can choose Ξ identically equal to 1, which will recover Lieb's result from [11], i.e., $\int \rho^{\mathrm{HF}} \leq 2Z+1$.

We shall now choose $\Xi := \theta_r$, where θ_r is the localization function given in Definition 6.1. Then

$$\tfrac{1}{2}\nabla\left(\Xi(x)^2\right) + |x|\left(\nabla\Xi(x)\right)^2 \leq \frac{\pi}{2\lambda r} + (1-\lambda)^{-1} r \frac{\pi^2}{(2\lambda r)^2} = K_\lambda r^{-1} \tag{64}$$

and

$$\iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[|\gamma^{\mathrm{HF}}(x,y)|^2\right]\right] \frac{|y|\left(1-\Xi(x)^2\right)\Xi(y)^2}{|x-y|} dx\,dy$$

$$\geq \iint\limits_{|x|<(1-\lambda)r} \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[|\gamma^{\mathrm{HF}}(x,y)|^2\right]\right] \frac{|y|\theta_r(y)^2}{|x-y|} dx\,dy.$$

If we now use that $|x| < (1-\lambda)r$ and $y \in \operatorname{supp}\theta_r$ imply that $|y||x-y|^{-1} \leq \lambda^{-1}$ we obtain

$$\iint \left[\rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) - \mathrm{Tr}_{\mathbb{C}^2}\left[|\gamma^{\mathrm{HF}}(x,y)|^2\right]\right] \frac{|y|\left(1-\Xi(x)^2\right)\Xi(y)^2}{|x-y|} dx\,dy$$

$$\geq \iint\limits_{|x|<(1-\lambda)r} \rho^{\mathrm{HF}}(x)\rho^{\mathrm{HF}}(y) \frac{|y|\theta_r(y)^2}{|x-y|} dx\,dy - \lambda^{-1}\int \theta_r(y)^2 \rho^{\mathrm{HF}}(y)\,dy, \tag{65}$$

where we have also used that $\int \mathrm{Tr}_{\mathbb{C}^2}\left[|\gamma^{\mathrm{HF}}(x,y)|^2\right] dx = \rho^{\mathrm{HF}}(y)$.

If we insert (64) and (65) into (63) we arrive at

$$\begin{aligned} 0 \;\geq\; & -\frac{K_\lambda}{2r}\int_{r<|x|<(1-\lambda)^{-1}r} \rho^{\mathrm{HF}}(x)dx - \int \theta_r(y)^2|y|\Phi^{\mathrm{HF}}_{(1-\lambda)r}(y)\rho^{\mathrm{HF}}(y)dy \\ & + \tfrac{1}{2}\left(\int \rho^{\mathrm{HF}}\theta_r^2\right)^2 - \left(\tfrac{1}{2}+\lambda^{-1}\right)\int \rho^{\mathrm{HF}}\theta_r^2. \end{aligned}$$

Using now that $\Phi^{\rm HF}_{(1-\lambda)r}(y)$ tends to zero at infinity and is harmonic for $|y| > (1-\lambda)r$, which contains the support of θ_r, we see by a simple comparison argument that

$$\theta_r(y)^2|y|\Phi^{\rm HF}_{(1-\lambda)r}(y) \leq \theta_r(y)^2\left[\sup_{|x|=(1-\lambda)r}|x|\Phi^{\rm HF}_{(1-\lambda)r}(x)\right]_+ .$$

Thus

$$\begin{aligned} 0 \ \geq\ & \left(\int \rho^{\rm HF}\theta_r^2\right)^2 - \left(1+2\lambda^{-1}+2\left[\sup_{|x|=(1-\lambda)r}|x|\Phi^{\rm HF}_{(1-\lambda)r}(x)\right]_+\right)\int \rho^{\rm HF}\theta_r^2 \\ & -K_\lambda r^{-1}\int_{r<|x|<(1-\lambda)^{-1}r}\rho^{\rm HF}(x)dx. \end{aligned}$$

Finally, in order to arrive at the result of the lemma we simply use that $0 \geq X^2 - BX - C$ for $B, C > 0$ implies $X \leq B + \sqrt{C}$. $\square$

8 The semiclassical estimates

In this section we derive the relevant semiclassical estimates. We do not attempt to give optimal results. We shall be satisfied with what is needed for the application we have in mind. In a certain sense it is misleading to refer to the estimates in this section as *semiclassical*. Usually, semiclassics refers to the limit as Planck's constant $\hbar$ tends to zero. One then expands the relevant physical quantities like energy and density in powers of $\hbar$. In our setting there is, however, no semiclassical parameter which could play the role of Planck's constant. It is rather that we consider potentials for which the semiclassical expressions for the energy and density are approximately valid. We must then estimate the errors directly in terms of certain norms of the potential. The estimates are semiclassical in the sense that if one introduces a semiclassical parameter then the errors are of smaller order than the leading semiclassical expression.

We are interested in a semiclassical approximation to the sum of the negative eigenvalues of a Schrödinger operator

$$h := -\tfrac{1}{2}\Delta - V,$$

on $\mathbb{R}^3$. We shall in this section always assume that the potential $V : \mathbb{R}^3 \to \mathbb{R}$ is locally in L^1 and that its positive part satisfies that $[V]_+ \in L^{5/2}(\mathbb{R}^3)$. This ensures (by the Lieb-Thirring inequality or even by Sobolev's inequality) that h is bounded below and can be defined as a Friedrichs' extension from the domain $C_0^\infty(\mathbb{R}^3)$. [3]

The semiclassical approximation to the sum of the negative eigenvalues of h is given by

$$(2\pi)^{-3} \iint\limits_{\frac{1}{2}p^2 - V(x) \le 0} \tfrac{1}{2}p^2 - V(x)\ dp\, dx = -2^{3/2}(15\pi^2)^{-1} \int [V(x)]_+^{5/2}\, dx. \tag{66}$$

Moreover, the semiclassical approximation to the density, i.e., the sum of the absolute square of the eigenfunctions corresponding to the negative eigenvalues, is

$$(2\pi)^{-3} \int_{\frac{1}{2}p^2 - V(x) \le 0} 1 dp = 2^{3/2}(6\pi^2)^{-1}\, [V(x)]_+^{3/2}\,. \tag{67}$$

8.1. DEFINITION. For $s > 0$, let $g : \mathbb{R}^3 \to \mathbb{R}$ be the ground state of the Dirichlet Laplacian for a ball of radius s, i.e., the function with $g(x) = 0$ if $|x| > s$ and $g(x) = (2\pi s)^{-1/2}|x|^{-1}\sin(\pi|x|/s)$ if $|x| \le s$. Then

$$0 \le g \le 1, \quad \int g^2 = 1 \quad \int |\nabla g|^2 = (\pi/s)^2. \tag{68}$$

8.2. LEMMA (Semiclassical approximation). *We assume about the potential that* $[V]_+, [V - V * g^2]_+ \in L^{5/2}(\mathbb{R}^3)$ *with* g *as in Definition 8.1 above . Let* $e^{(1)} \le e^{(2)} \le \ldots < 0$, *denote the negative eigenvalues of* $h = -\frac{1}{2}\Delta - V$ *as an operator on* $L^2(\mathbb{R}^3)$. *Then for all* $0 < \delta < 1$, *all integers* $N > 0$, *and all* $s > 0$ *we have*

$$\begin{aligned}\sum_{j=1}^N e^{(j)} \ \ \ge \ \ & -2^{3/2}(15\pi^2)^{-1}(1-\delta)^{-3/2} \int [V]_+^{5/2} \\ & -\tfrac{1}{2}\pi^2 s^{-2} N - L_1 \delta^{-3/2} \left\| \left[V - V * g^2\right]_+ \right\|_{5/2}^{5/2}\end{aligned} \tag{69}$$

where L_1 *is the constant in the Lieb-Thirring estimate (22). If there are fewer than* N *negative eigenvalues the sum on the left refers simply to the sum over all the negative eigenvalues.*

[3] Note that we are not including spin. The operator h is acting in the space $L^2(\mathbb{R}^3)$ and *not* in the space $L^2(\mathbb{R}^3; \mathbb{C}^2)$.

On the other hand, if also $[V]_+ \in L^{3/2}(\mathbb{R}^3)$, *we can, for all* $s > 0$, *find a density matrix* γ *with* $\rho_\gamma(x) = 2^{3/2}(6\pi^2)^{-1}[V]_+^{3/2} * g^2(x)$ *such that*

$$\mathrm{Tr}[-\tfrac{1}{2}\Delta\gamma] = 2^{1/2}(5\pi^2)^{-1}\int [V]_+^{5/2} + \tfrac{1}{2}\pi^2 s^{-2}\int 2^{3/2}(6\pi^2)^{-1}[V]_+^{3/2}. \tag{70}$$

8.3. REMARK. We are not proving that the true density of the projection onto the negative eigenvalues of h is approximated by the semiclassical expression (67). We only claim that there is a 'good' trial density matrix. In the context where we shall use the semiclassics we shall infer the approximation of the true density by other means.

Proof of Lemma 8.2. We prove the result using the method of coherent states (see Thirring [26] and Lieb [8]).

For $u, p \in \mathbb{R}^3$ let $\Pi_{u,p}$ be the one-dimensional projection in $L^2(\mathbb{R}^3)$, projecting onto the space spanned by the function $f_{u,p}(x) := \exp(ipx)g(x-u)$. We then have the *coherent states identities*

$$\begin{aligned} \mathrm{Tr}[\Pi_{u,p}] &= 1, \text{ for all } p, u & (71)\\ (2\pi)^{-3}\iint \Pi_{u,p}\,dp\,du &= I, \text{ on } L^2(\mathbb{R}^3). & (72)\end{aligned}$$

We also have the identity

$$\mathrm{Tr}[-\tfrac{1}{2}\Delta\Pi_{u,p}] = \tfrac{1}{2}p^2 + \tfrac{1}{2}\int|\nabla g|^2 = \tfrac{1}{2}p^2 + \pi^2/(2s^2), \tag{73}$$

and for all density matrices γ

$$\begin{aligned} \mathrm{Tr}[-\tfrac{1}{2}\Delta\gamma] &= (2\pi)^{-3}\iint \tfrac{1}{2}p^2\,\mathrm{Tr}[\Pi_{u,p}\gamma]\,dp\,du - \pi^2/(2s^2)\mathrm{Tr}[\gamma] & (74)\\ \mathrm{Tr}[(V*g^2)\gamma] &= (2\pi)^{-3}\iint V(u)\mathrm{Tr}[\Pi_{u,p}\gamma]\,dp\,du\,. & (75)\end{aligned}$$

Proof of the lower bound (69): Let $f_1, f_2, \ldots \in L^2(\mathbb{R}^3)$ denote the normalized eigenfunctions of h corresponding to negative eigenvalues. It is clear that we may without loss of generality assume that there are N negative eigenvalues

We decompose the operator h as $h = -\frac{1}{2}(1-\delta)\Delta - V*g^2 + [-\frac{1}{2}\delta\Delta - (V - V*g^2)]$. We may then write $\sum_{j=1}^N e^{(j)} = \sum_{j=1}^N (f_j, hf_j) = \mathcal{A} + \mathcal{B}$, where

$$\mathcal{A} := \sum_{j=1}^N (f_j, [-\tfrac{1}{2}(1-\delta)\Delta - V*g^2]f_j), \quad \mathcal{B} := \sum_{j=1}^N (f_j, [-\tfrac{1}{2}\delta\Delta - (V - V*g^2)]f_j).$$

From (74) and (75) we hence obtain

$$\mathcal{A} = (2\pi)^{-3} \iint \left(\tfrac{1}{2}(1-\delta)p^2 - V(u)\right) \sum_{j=1}^{N} (f_j, \Pi_{u,p} f_j) dp\, du - N\pi^2(2s^2)^{-1}.$$

As a consequence of (71) we have that $0 \leq \sum_{j=1}^{N}(f_j, \Pi_{u,p} f_j) \leq 1$.

It is therefore clear that

$$\begin{aligned} \mathcal{A} &\geq (2\pi)^{-3} \iint_{(1-\delta)\frac{1}{2}p^2 - V(u) \leq 0} \left((1-\delta)\tfrac{1}{2}p^2 - V(u)\right) dp\, du - \pi^2(2s^2)^{-1}N \\ &= -2^{3/2}(15\pi^2)^{-1}(1-\delta)^{-3/2} \int [V]_+^{5/2} - \pi^2(2s^2)^{-1}N. \end{aligned}$$

The estimate (69) follows by applying the Lieb-Thirring estimate (22) to conclude that $\mathcal{B} \geq -L_1\delta^{-3/2} \| [V - V * g^2]_+ \|_{5/2}^{5/2}$.

Proof of the existence of γ. We shall prove that

$$\gamma := (2\pi)^{-3} \iint_{\frac{1}{2}p^2 - V(u) \leq 0} \Pi_{u,p} dp\, du$$

has the desired properties. From (72) we see that γ is a density matrix, i.e., $0 \leq \gamma \leq I$. The density corresponding to γ is easily computable

$$\rho_\gamma(x) = \gamma(x,x) = (2\pi)^{-3} \iint_{\frac{1}{2}p^2 - V(u) \leq 0} \Pi_{u,p}(x,x) dp\, du = 2^{3/2}(6\pi^2)^{-1} [V]_+^{3/2} * g^2(x).$$

From (73) we immediately obtain (70). □

Although we shall use the semiclassical approximation in the form given in the lemma we shall for completeness state a less technical semiclassical result which follows very easily from the lemma.

8.4. THEOREM (Semiclassical approximation). *Assume that* $0 \leq V \in L^{5/2}(\mathbb{R}^3) \cap L^{3/2}(\mathbb{R}^3)$ *and* $|\nabla V| \in L^{5/2}(R^3)$. *Let* $e^{(1)} \leq e^{(2)} \leq \ldots < 0$, *denote the negative eigenvalues of* $h = -\frac{1}{2}\Delta - V$ *as an operator on* $L^2(\mathbb{R}^3)$. *Then we have*

$$\sum_j e^{(j)} \geq -2^{3/2}(15\pi^2)^{-1} \int V(x)^{5/2} dx \left\{1 + A_{\mathrm{L}} \|V\|_{5/2}^{-3/2} \|\nabla V\|_{5/2}^{2/3} \|V\|_{3/2}^{1/2}\right\}^{5/3} \tag{76}$$

and

$$\sum_j e^{(j)} \leq -2^{3/2}(15\pi^2)^{-1}\int V(x)^{5/2}dx + \tfrac{3}{2}\pi^{2/3}\|V\|_{5/2}\|\nabla V\|_{5/2}^{2/3}\|V\|_{3/2}^{1/2} \tag{77}$$

where $A_{\mathrm{L}} := \frac{9}{4}2^{-9/10}(15\pi^2)^{3/5}\left(\frac{2\pi^2}{5}\right)^{1/3}L_0^{1/3}L_1^{4/15}$. *Here* L_0 *and* L_1 *are the constants in the CLR and Lieb-Thirring estimates (23) and (22) respectively.*

Proof. We may estimate

$$\begin{aligned}
\left|V(u) - V*g^2(u)\right| &\leq \int_{\mathbb{R}^3}\int_0^1 |\nabla V(u-ty)||y|g(y)^2 dt\,dy \\
&= \int_{\mathbb{R}^3}|\nabla V(u-y)||y|\int_0^1 t^{-4}g(y/t)^2 dtdy \\
&\leq (4\pi)^{-1}\int_{|y|\leq s}|\nabla V(u-y)||y|^{-2}dy,
\end{aligned}$$

where we have used that $\int_0^1 t^{-4}g(y/t)^2dt \leq |y|^{-3}\int_0^\infty t^2 g(t)^2 dt = (4\pi)^{-1}|y|^{-3}$ (identifying g with a function on $\mathbb{R}_+$). Hence

$$\|V - V*g^2\|_{5/2} \leq (4\pi)^{-1}\|\nabla V\|_{5/2}\int_{|y|\leq s}|y|^{-2}dy = s\|\nabla V\|_{5/2}. \tag{78}$$

For any density matrix γ, $\mathrm{Tr}[h\gamma]$ is an upper bound to the sum of the negative eigenvalues of h. From (70) we find for the density matrix constructed in Lemma 8.2 that

$$\begin{aligned}
\mathrm{Tr}[h\gamma] &= -2^{3/2}(15\pi^2)^{-1}\int [V]_+^{5/2} \\
&\quad + 2^{3/2}(6\pi^2)^{-1}\int [V(u)]_+^{3/2}\left[V(u) - V*g^2(u) + \tfrac{1}{2}\pi^2 s^{-2}\right]du.
\end{aligned}$$

The bound (77) follows from applying Hölder's inequality, (78), and optimizing in s.

By the CLR bound (23) we know that h has only finitely many negative eigenvalues and that their number N is bounded by $N \leq L_0\int [V]_+^{3/2}$. From (69) and (78) we therefore obtain

$$\begin{aligned}
\sum_j e^{(j)} &\geq -2^{3/2}(15\pi^2)^{-1}(1-\delta)^{-3/2}\int V^{5/2} \\
&\quad - L_0\pi^2(2s^2)^{-1}\int V^{3/2} - L_1\delta^{-3/2}s^{5/2}\int|\nabla V|^{5/2} \\
&= -2^{3/2}(15\pi^2)^{-1}(1-\delta)^{-3/2}\int V^{5/2} \\
&\quad - \tfrac{9}{4}\left(\tfrac{2}{5}\right)^{5/9}L_0^{5/9}L_1^{4/9}\pi^{10/9}\delta^{-2/3}\left(\int V^{3/2}\right)^{5/9}\left(\int|\nabla V|^{5/2}\right)^{4/9},
\end{aligned}$$

where we have optimized in the parameter s.

We now optimize in the parameter δ. Define δ' by $(1-\delta)^{-3/2} = (1-\delta')^{-2/3}$. (Note that $0<\delta<1$ if and only if $0<\delta'<1$.) Then $\delta^{-2/3} \le (4\delta'/9)^{-2/3}$. Thus

$$\sum_j e^{(j)} \ge -2^{3/2}(15\pi^2)^{-1}(1-\delta')^{-2/3}\int V^{5/2} - A_1\delta'^{-2/3}\left(\int V^{3/2}\right)^{5/9}\left(\int |\nabla V|^{5/2}\right)^{4/9},$$

where $A_1 := \left(\frac{9}{4}\right)^{5/3}\left(\frac{2\pi^2}{5}\right)^{5/9} L_0^{5/9}L_1^{4/9}$. Using that $\min_{\delta'}\left[(1-\delta')^{-2/3}a + \delta'^{-2/3}b\right] = a[1+(b/a)^{3/5}]^{5/3}$ we arrive at (76). □

We shall need the semiclassical estimates also for the operator h restricted to functions on the set $\{x : |x| \ge r\}$ satisfying Dirichlet boundary conditions.

8.5. LEMMA (Dirichlet Boundary conditions). *Let the assumptions be as in the beginning of Lemma 8.2. For $r>0$ let h_r denote the restriction of the operator $h = -\frac{1}{2}\Delta - V$ to functions on the set $\{x : |x| \ge r\}$ satisfying Dirichlet boundary conditions. Denote by $e^{(1)} \le e^{(2)} \le \ldots < 0$ the negative eigenvalues of h and by $e_r^{(1)} \le e_r^{(2)} \le \ldots < 0$ the negative eigenvalues of h_r. Then $\sum_j e^{(j)} \le \sum_j e_r^{(j)}$. Moreover, if γ is a density matrix on $L^2(\mathbb{R}^3)$ we may, for all $0<\lambda<1$, find a density matrix $\widetilde{\gamma}$ such that $\rho_{\widetilde{\gamma}}$ is supported in $\{x : |x| \ge r\}$ and $\rho_{\widetilde{\gamma}} \le \rho_\gamma$ and*

$$\mathrm{Tr}[h_r\widetilde{\gamma}] \le \mathrm{Tr}[h\gamma] + L_1\int_{|x|\le(1-\lambda)^{-1}r}[V]_+^{5/2} + \tfrac{1}{2}(\pi/(2\lambda r))^2\int_{|x|\le(1-\lambda)^{-1}r}\rho_\gamma.$$

Proof. That the Dirichlet eigenvalues are upper bounds to the eigenvalues on $\mathbb{R}^3$, is a well known simple consequence of the variational principle.

Let θ_r be the localization function from Definition 6.1. We shall choose $\widetilde{\gamma} = \theta_r\gamma\theta_r$. Then by the IMS formula (20) we have

$$\begin{aligned}\mathrm{Tr}[h\gamma] &= \mathrm{Tr}[h_r\theta_r\gamma\theta_r] + \mathrm{Tr}[h(1-\theta_r^2)^{1/2}\gamma(1-\theta_r^2)^{1/2}] \\ &\quad - \tfrac{1}{2}\mathrm{Tr}\left[\left((\nabla\theta_r)^2 + (\nabla(1-\theta_r^2)^{1/2})^2\right)\gamma\right].\end{aligned}$$

By the Lieb-Thirring inequality (22) we have $\mathrm{Tr}[h(1-\theta_r^2)^{1/2}\gamma(1-\theta_r^2)^{1/2}] \ge -L_1\int_{|x|\le(1-\lambda)^{-1}r}[V]_+^{5/2}$. Thus the lemma follows from the bound on the gradient of θ_r and $(1-\theta_r^2)^{1/2}$ given in Definition 6.1. □

9 The Coulomb norm estimates

In this section we introduce and study the Coulomb norm.

9.1. DEFINITION. For $f, g \in L^{6/5}(\mathbb{R}^3)$ we define the *Coulomb inner product*

$$D(f,g) := \tfrac{1}{2} \iint f(x)|x-y|^{-1}\overline{g(y)}dx\,dy \tag{79}$$

and the corresponding *Coulomb norm*,

$$\|g\|_{\mathrm{C}} := D(g,g)^{1/2}.$$

By the Hardy-Littlewood-Sobolev estimate we have

$$\|g\|_{\mathrm{C}} \leq \pi^{-1/6}2^{1/3}3^{-1/2}\|g\|_{6/5}. \tag{80}$$

In this sharp form the inequality was proved by Lieb [10]. Using the Fourier transform we may write

$$D(f,g) = (2\pi)\int \hat{f}(p)\overline{\hat{g}(p)}|p|^{-2}dp, \tag{81}$$

from which it follows that the Coulomb norm really is a norm on $L^{6/5}(\mathbb{R}^3)$.

The following estimate was first used in the context of atomic problems by Fefferman and Seco [5].

9.2. LEMMA (Coulomb norm estimate). *If $f \in L^6(\mathbb{R}^3)$ with $|\nabla f| \in L^2(\mathbb{R}^3)$ and $g \in L^{6/5}(\mathbb{R}^3)$ then*

$$\left|\int f\overline{g}\right| \leq (2\pi)^{-1/2}\|\nabla f\|_2\|g\|_{\mathrm{C}}.$$

Proof. Using Plancherel's identity and the representation (81) we have

$$\left|\int f\overline{g}\right| = \left|\int \hat{f}\overline{\hat{g}}\right| \leq \||p|\hat{f}(p)\|_2\||p|^{-1}\hat{g}(p)\|_2 = (2\pi)^{-1/2}\|\nabla f\|_2\|g\|_{\mathrm{C}}.$$

□

We shall next give some simple but very useful consequences of this estimate.

9.3. COROLLARY. *Consider $f \in L^{5/3}(\mathbb{R}^3) \cap L^{6/5}(\mathbb{R}^3)$. For all $x \in \mathbb{R}^3$ and $s > 0$ we have*

$$f * |x|^{-1} \leq (5/4)^{2/5}(\pi s)^{1/5}\|[f]_+\|_{L^{5/3}(B(x,s))} + (4\pi)^{1/2}s^{-1/2}\|f\|_{\mathrm{C}}. \tag{82}$$

For all $x \in \mathbb{R}^3$ and all $\kappa > 0$ denote by $A(|x|,\kappa)$ the annulus

$$A(|x|,\kappa) = \{y : (1-2\kappa)|x| \leq |y| \leq |x|\}$$

we then have

$$\begin{aligned}\int_{|y|<|x|} f(y)|x-y|^{-1}dy \quad &\leq \quad 2^{7/5}\pi^{2/5}(\kappa|x|)^{1/5}\,\|[f]_+\|_{L^{5/3}(A(|x|,\kappa))} \\ &\qquad + 4\pi^{1/2}\kappa^{-1}|x|^{-1/2}\|f\|_{\mathrm{C}}. \end{aligned}\tag{83}$$

9.4. REMARK. Note that we do not restrict to $\kappa \leq 1/2$. We do this to avoid having to check this condition in the applications of the corollary.

Proof of Corollary 9.3. Consider the function $\xi_s : \mathbb{R}^3 \to \mathbb{R}$ defined by

$$\xi_s(z) := \begin{cases} s^{-1}, & \text{if } |z| \leq s \\ |z|^{-1}, & \text{if } |z| \geq s \end{cases}.$$

It satisfies $\|\nabla\xi_s\|_2 \leq (4\pi/s)^{1/2}$. Hence from Lemma 9.2 we obtain

$$\begin{aligned} f * |x|^{-1} \quad &\leq \quad \int_{|y-x|\leq s} [f(y)]_+\left(|x-y|^{-1} - s^{-1}\right)dy + \int_{\mathbb{R}^3} f(y)\xi_s(x-y)dy \\ &\leq \quad (5/4)^{2/5}(\pi s)^{1/5}\|[f]_+\|_{L^{5/3}(B(x,s))} + (4\pi/s)^{1/2}\|f\|_{\mathrm{C}}, \end{aligned}$$

where we have used that $\int_{|y|<1}(|y|^{-1}-1)^{5/2}dy = \frac{5\pi^2}{4}$.

In order to prove the second half of the corollary we introduce the function $\Xi_{x,\kappa} : \mathbb{R}^3 \to \mathbb{R}^3$ given by

$$\Xi_{x,\kappa}(z) := \begin{cases} 1, & \text{if } |z| \leq (1-2\kappa)|x| \\ 1 - (|x|\kappa)^{-1}(|z| - |x|(1-2\kappa)), & \text{if } (1-2\kappa)|x| \leq |z| \leq (1-\kappa)|x| \\ 0, & \text{if } (1-\kappa)|x| \leq |z| \end{cases}.$$

Then $|\Xi_{x,\kappa}(z)| \leq 1$ and we can estimate

$$\int_{|y|<|x|} f(y)|x-y|^{-1}dy \quad \leq \quad \int_{A(|x|,\kappa)} [f(y)]_+|x-y|^{-1}dy$$

$$
\begin{aligned}
&\quad + \int_{\mathbb{R}^3} f(y)|x-y|^{-1}\Xi_{x,\kappa}(y)dy \\
&\le \|[f]_+\|_{L^{5/3}(A(|x|,\kappa))} \left(\int_{A(|x|,\kappa)} |x-y|^{-5/2}dy\right)^{2/5} \\
&\quad + \|f\|_{\mathrm{C}} \left(\int \left|\nabla_y \left(|x-y|^{-1}\Xi_{x,\kappa}(y)\right)\right|^2 dy\right)^{1/2}.
\end{aligned}
$$

It remains to estimate the two integrals above. For the first integral we find for $\kappa \le 1/2$

$$
\begin{aligned}
\int_{A(|x|,\kappa)} |x-y|^{-5/2}dy &= 2\pi|x|^{1/2}\int_{r=1-2\kappa}^{1}\int_{u=-1}^{1}(1-2ru+r^2)^{-5/4}r^2du\,dr \\
&= 2\pi|x|^{1/2}\alpha_1(\kappa),
\end{aligned}
$$

where

$$
\alpha_1(\kappa) := 4(2\kappa)^{1/2} - (4/3)(2\kappa)^{3/2} + (4/3)\sqrt{2}[1-(1-\kappa)^{1/2}(1+2\kappa)] \le 4(2\kappa)^{1/2}.
$$

The last inequality follows from a straightforward careful analysis of $\alpha_1(\kappa)$. For the second integral we get

$$
\begin{aligned}
\left(\int \left|\nabla_y \left(|x-y|^{-1}\Xi_{x,\kappa}(y)\right)\right|^2 dy\right)^{1/2} &\le \left(\int_{|x-y|>\kappa|x|} |x-y|^{-4}dy\right)^{1/2} \\
&\quad + (\kappa|x|)^{-1}\left(\int_{A(|x|,\kappa)} |x-y|^{-2}dy\right)^{1/2} \\
&= (4\pi)^{1/2}(\kappa|x|)^{-1/2}(1+\alpha_2(\kappa)^{1/2}),
\end{aligned}
$$

with

$$
\alpha_2(\kappa) := 1 + (1-\kappa)\ln\left(\frac{1-\kappa}{\kappa}\right) \le 1 - \ln\kappa \le \kappa^{-1},
$$

where we have used that

$$
\int_{A(|x|,\kappa)} |x-y|^{-2}dy = 2\pi|x|\int_{r=1-2\kappa}^{1}\int_{u=-1}^{1}(1-2ru+r^2)^{-1}r^2du\,dr = 4\pi\kappa|x|\alpha_2(\kappa).
$$

Using $(4\pi)^{1/2}\kappa^{-1/2}(1+\alpha_2(\kappa)^{1/2}) \le 4\pi^{1/2}\kappa^{-1}$ we get (83).

The estimate holds also for $\kappa > 1/2$ since the last term in (83) can be ignored in this case. $\square$

10 Main Estimate

We now restrict attention to the case $N \geq Z$. Throughout the remaining part of this paper $\rho^{\rm TF}, \varphi^{\rm TF}, \Phi_R^{\rm TF}, \rho^{\rm HF}, \varphi^{\rm HF}$ and $\Phi_R^{\rm HF}$ always refer to the problems with particle number N. In fact, since $N \geq Z$ the TF functions correspond to the neutral atom, i.e., $\mu^{\rm TF} = 0$. We shall suppress the dependence on N everywhere since it is held fixed throughout the discussion.

From now on we shall no longer explicitly compute the constants involved in the estimates. We shall use the notation (Const.) to refer to any universal (in principle explicitly computable) *positive* constant. Thus (Const.) does not mean the same constant in all equations or inequalities. Even within the same equation we shall use the notation (Const.) to refer to possibly different universal constants. Universal constants of particular importance will be given separate names. We begin by stating the main result of this section.

10.1. THEOREM (Main Estimate). *Assume $Z \geq 1$ and $N \geq Z$. There exist universal constants $0 < \varepsilon < 4$ and $C_M, C_\Phi > 0$ such that for all $x \in \mathbb{R}^3$ we have*

$$\left|\Phi_{|x|}^{\rm HF}(x) - \Phi_{|x|}^{\rm TF}(x)\right| \leq C_\Phi |x|^{-4+\varepsilon} + C_M. \tag{84}$$

We shall prove Theorem 10.1 by an iterative procedure. The first step is to control "small" x.

10.2. LEMMA (Control of region close to the nucleus).
Assume $Z \geq 1$ and $N \geq Z$. For all $\beta > 0$ and all $|x| \leq \beta Z^{-1/3}$ we have

$$\left|\Phi_{|x|}^{\rm HF}(x) - \Phi_{|x|}^{\rm TF}(x)\right| \leq A_\Phi \beta^{49/12-\varepsilon_1} |x|^{-4+\varepsilon_1},$$

where $\varepsilon_1 = 1/66$ and $A_\Phi > 0$ is a universal constant.

10.3. LEMMA (Iterative step). *Assume $N \geq Z$. For all $\delta > 0$ smaller than some universal constant there exist constants $\varepsilon_2, C'_\Phi > 0$ depending only on δ such that, given $\varepsilon', \sigma > 0$, there exists a constant $D = D(\varepsilon', \sigma) > 0$ depending only on ε', σ with the following property. For all $R_0 < D$ satisfying that $\beta_0 Z^{-1/3} \leq R_0^{1+\delta}$ (where $\beta_0 = \frac{(9\pi)^{2/3}}{44}$ as in Theorem 5.4) and that*

$$\left|\Phi_{|x|}^{\rm HF}(x) - \Phi_{|x|}^{\rm TF}(x)\right| \leq \sigma |x|^{-4+\varepsilon'} \tag{85}$$

holds for all $|x| \le R_0$, *there exists* $R_0' > R_0$ *such that*

$$\left|\Phi^{\mathrm{HF}}_{|x|}(x) - \Phi^{\mathrm{TF}}_{|x|}(x)\right| \le C'_\Phi |x|^{-4+\varepsilon_2} \tag{86}$$

for all x *with* $R_0 < |x| < R_0'$.

Lemmas 10.2 and 10.3 will allow us to control small and intermediate $|x|$ to control large $|x|$ we shall need the following two lemmas.

10.4. LEMMA (Bound on $\int(\rho^{\mathrm{HF}})^{5/3}$). *Assume* $N \ge Z$. *Given* $0 < \varepsilon', \sigma$, *there is a* $D > 0$ *such that if (85) holds for all* $|x| \le D$ *then we have*

$$\int_{|y|>|x|} \rho^{\mathrm{HF}}(y)^{5/3}\, dy \le (\mathrm{Const.})|x|^{-7}, \tag{87}$$

for all $|x| \le D$.

10.5. LEMMA (Bound on $\int \rho^{\mathrm{HF}}$). *Assume that (85) holds for all* $|x| \le R$ *for some* $R > 0$ *and some* $\varepsilon', \sigma > 0$. *Then for* $0 < r \le R$ *we have*

$$\left|\int_{|y|<r} (\rho^{\mathrm{HF}}(y) - \rho^{\mathrm{TF}}(y))\, dy\right| \le \sigma r^{-3+\varepsilon'}$$

and

$$\int_{|y|>r} \rho^{\mathrm{HF}}(y) dy \le (\mathrm{Const.})(1 + \sigma r^{\varepsilon'})\left(r^{-3} + 1\right).$$

We shall prove Lemma 10.2 in Sect. 11 and Lemmas 10.3 and 10.4 in Sect. 12. We end this section with the proofs of Lemma 10.5 and the main estimate Theorem 10.1.

Proof of Lemma 10.5. First note that for $0 < r \le R$ we have

$$\int_{|y|<r} (\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))\, dy = (4\pi)^{-1} r \int_{\omega\in\mathcal{S}^2} \int_{|y|<r} (\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))\, |r\omega - y|^{-1} dy\, d\omega.$$

Thus we have

$$\int_{|y|<r} (\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))\, dy = (4\pi)^{-1} r \int_{\omega\in\mathcal{S}^2} \Phi^{\mathrm{HF}}_r(r\omega) - \Phi^{\mathrm{TF}}_r(r\omega) d\omega.$$

Together with (85) this gives the first estimate above. Moreover, we also have that

$$\begin{aligned}\left|\int_{r/2<|y|<r} (\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))\, dy\right| &\leq \sup_{|y|=r} \left|\Phi_r^{\mathrm{HF}}(y) - \Phi_r^{\mathrm{TF}}(y)\right| \\ &\quad + \sup_{|y|=r/2} \left|\Phi_{r/2}^{\mathrm{HF}}(y) - \Phi_{r/2}^{\mathrm{TF}}(y)\right| \leq (\mathrm{Const.})\sigma r^{-3+\varepsilon'}.\end{aligned}$$

The TF equation (6), and the Sommerfeld estimate in Theorem 5.2 gives

$$\int_{|y|>r/2} \rho^{\mathrm{TF}}(y)\, dy \leq (\mathrm{Const.}) r^{-3}$$

and hence

$$\int_{r/2<|y|<r} \rho^{\mathrm{HF}}(y) dy \leq (\mathrm{Const.})(1 + \sigma r^{\varepsilon'}) r^{-3}.$$

From (85), the exterior L^1 estimate Lemma 7.1 (used with $\lambda = 1/2$ and r replaced by $r/2$), and Lemma 5.5 (recall that now $\mu^{\mathrm{TF}} = 0$) we immediately conclude the estimate on $\int_{|y|>r} \rho^{\mathrm{HF}}(y) dy$. □

We finally show how to use Lemmas 10.2–10.5 to prove the main estimate Theorem 10.1.

Proof of Theorem 10.1. We first show that we may choose $\delta > 0$ small enough such that if we choose $\widetilde{R}^{1+\delta} = \beta_0 Z^{-1/3}$ we have for all $|x| < \widetilde{R}$ that

$$\left|\Phi_{|x|}^{\mathrm{HF}}(x) - \Phi_{|x|}^{\mathrm{TF}}(x)\right| \leq C''_\Phi |x|^{-4+\frac{\varepsilon_1}{2}} \tag{88}$$

for a universal constant $C''_\Phi > 0$ and with ε_1 given in Lemma 10.2.

To see this let $\beta > 0$ be such that $\left(\beta Z^{-1/3}\right)^{1+\delta} = \beta_0 Z^{-1/3}$, i.e., $\beta^{1+\delta} = \beta_0 Z^{\delta/3}$. We then see from Lemma 10.2 that for all $|x| < \beta Z^{-1/3}$ we have

$$\begin{aligned}\left|\Phi_{|x|}^{\mathrm{HF}}(x) - \Phi_{|x|}^{\mathrm{TF}}(x)\right| &\leq A_\Phi \beta^{\frac{49}{12}-\frac{\varepsilon_1}{2}} Z^{-\frac{\varepsilon_1}{6}} |x|^{-4+\frac{\varepsilon_1}{2}} \\ &= A_\Phi (\beta_0 Z^{\delta/3})^{\left(\frac{49}{12(1+\delta)}-\frac{\varepsilon_1}{2(1+\delta)}\right)} Z^{-\frac{\varepsilon_1}{6}} |x|^{-4+\frac{\varepsilon_1}{2}}.\end{aligned}$$

Since $\widetilde{R}^{1+\delta} = \beta_0 Z^{-1/3}$, i.e., $\widetilde{R} = \beta Z^{-1/3}$ we see that if δ is small enough and C''_Φ is chosen appropriately then (88) holds for all $|x| < \widetilde{R}$.

We now assume that δ is also small enough that we may apply Lemma 10.3. This gives us constants $\varepsilon_2, C'_\Phi > 0$ and for all $\sigma, \varepsilon' > 0$ a $D > 0$ with the properties stated in Lemmas 10.3 and 10.4. We may without loss of generality assume that $D \leq 1$. Now choose $\sigma = \max\{C'_\Phi, C''_\Phi\}$ and $\varepsilon' = \min\{\varepsilon_1/2, \varepsilon_2\}$. Note that σ, ε, and D are now universal constants. We shall prove that for all $|x| \leq D$ we have

$$\left|\Phi^{\mathrm{HF}}_{|x|}(x) - \Phi^{\mathrm{TF}}_{|x|}(x)\right| \leq \sigma|x|^{-4+\varepsilon'}. \tag{89}$$

Since we are assuming that $D \leq 1$ it is sufficient to prove (89) with ε' replaced by $\varepsilon_1/2$ or ε_2. We have to prove that D belongs to the set

$$\mathcal{M} = \{0 < R \leq 1 : \text{Inequality (89) holds for all } |x| \leq R\}.$$

If this were not true we would have $D > R_0 := \sup \mathcal{M}$. In order to reach a contradiction we therefore assume this and hence in particular that $R_0 < 1$. From (88) it follows that either $\widetilde{R} > 1$ or $\widetilde{R} \in \mathcal{M}$. If $\widetilde{R} > 1$ then $R_0 = \sup \mathcal{M} = 1$ which contradicts our assumption. On the other hand if $\widetilde{R} \in \mathcal{M}$ then $R_0^{1+\delta} \geq \widetilde{R}^{1+\delta} = \beta_0 Z^{-1/3}$. It is then an immediate consequence of Lemma 10.3 that there exists $R'_0 \in \mathcal{M}$ with $R'_0 > R_0$ and this is of course also a contradiction. This establishes an inequality of the form (84) for all $|x| \leq D$.

We shall now prove (84) for $|x| > D$. We write

$$\left|\Phi^{\mathrm{HF}}_{|x|}(x) - \Phi^{\mathrm{TF}}_{|x|}(x)\right| \leq \left|\Phi^{\mathrm{HF}}_{D}(x) - \Phi^{\mathrm{TF}}_{D}(x)\right| + \left|\int_{D<|y|<|x|} \frac{(\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))}{|x-y|}\,dy\right|.$$

We shall estimate the last term using Lemma 10.4 and the similar bound

$$\int_{|y|>|x|} \rho^{\mathrm{TF}}(y)^{5/3}\,dy \leq (\mathrm{Const.})|x|^{-7},$$

which holds for all x by the Sommerfeld estimate Theorem 5.2 and the TF equation (6). Hence using Hölder's inequality we have

$$\begin{aligned}\left|\int\limits_{D<|y|<|x|} \frac{(\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))}{|x-y|}dy\right| \;\leq\;& (\mathrm{Const.})D^{-21/5}\left(\int_{|x-y|<D} |x-y|^{-5/2}dy\right)^{2/5} \\ & + D^{-1}\int_{|y|>D} (\rho^{\mathrm{TF}}(y) + \rho^{\mathrm{HF}}(y))\,dy.\end{aligned}$$

By Lemma 10.5 and the bound $\int_{|y|>D} \rho^{\mathrm{TF}}(y)\,dy \leq (\mathrm{Const.})D^{-3}$, which is again a consequence of the Sommerfeld estimate Theorem 5.2 and the TF equation (6), we see that this last expression is bounded by a universal constant.

Since $\Phi_D^{\mathrm{HF}}(x)-\Phi_D^{\mathrm{TF}}(x)$ is harmonic for $|x|>D$ and tends to zero at infinity we have for all $|x|>D$ that

$$\left|\Phi_D^{\mathrm{HF}}(x)-\Phi_D^{\mathrm{TF}}(x)\right| \leq \sup_{|z|=D}\left|\Phi_D^{\mathrm{HF}}(z)-\Phi_D^{\mathrm{TF}}(z)\right| \leq \sigma D^{-4+\varepsilon'},$$

which is also bounded by a universal constant. Thus (84) holds for all x. □

11 Control of region close to nucleus: proof of Lemma 10.2

In order to prove Lemma 10.2 we need some basic estimates.

11.1. LEMMA (Global $L^{5/3}$ and Coulomb norm estimates).
For all N and Z we have the bound

$$\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(y)^{5/3}dy \leq (\mathrm{Const.})Z^{7/3}. \tag{90}$$

Moreover, if $Z\geq 1$

$$\|\rho^{\mathrm{HF}}-\rho^{\mathrm{TF}}\|_{\mathrm{C}}^2 \leq (\mathrm{Const.})Z^{7(1-\varepsilon_3)/3}, \tag{91}$$

with $\varepsilon_3 := 2/77$.

Proof. Although we shall only use this result for $N\geq Z$ the proof is almost as easy without this restriction, so we treat the more general case here.

We first estimate the $L^{5/3}$ norm of ρ^{HF}. It is easy to see that $\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})\leq 0$. Thus since $\mathcal{D}(\gamma^{\mathrm{HF}})-\mathcal{E}x(\gamma^{\mathrm{HF}})\geq 0$ we have from the Lieb-Thirring inequality (21) that

$$0\geq \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) \geq \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - Z|y|^{-1}\right)\gamma^{\mathrm{HF}}\right] \geq \int \left(K_1\rho^{\mathrm{HF}}(y)^{5/3} - Z|y|^{-1}\rho^{\mathrm{HF}}(y)\right)dy.$$

If we use that $\int\rho^{\mathrm{HF}}=N$ and the inequality $ab\leq \frac{3}{5}a^{5/3}+\frac{2}{5}b^{5/2}$ we get for all $\delta>0$ and all $r>0$,

$$0\geq \int (K_1-\tfrac{3}{5}\delta^{5/3})\rho^{\mathrm{HF}}(y)^{5/3}dy - \tfrac{2}{5}\int_{|y|<r}(\delta^{-1}Z|y|^{-1})^{5/2}dy - NZr^{-1}.$$

Choosing $\delta^{5/3} = 5K_1/6$ and optimizing in r gives $\int (\rho^{\mathrm{HF}})^{5/3} \leq (\mathrm{Const.}) N^{1/3} Z^2$. If we use that, since there exists an HF minimizer with particle number N, we must have Lieb's bound $N \leq 2Z + 1$ (see Theorem 3.5) we arrive at (90).

We turn to the proof of (91). We rewrite the Hartree-Fock functional (26) as

$$\mathcal{E}^{\mathrm{HF}}(\gamma) = \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \varphi^{\mathrm{TF}}\right)\gamma\right] + \|\rho^{\mathrm{TF}} - \rho_\gamma\|_{\mathrm{C}}^2 - D(\rho^{\mathrm{TF}}, \rho^{\mathrm{TF}}) - \mathcal{E}x(\gamma), \qquad (92)$$

where we have used the definition $\varphi^{\mathrm{TF}}(y) = Z|y|^{-1} - \rho^{\mathrm{TF}} * |y|^{-1}$ and

$$\mathrm{Tr}\left[(\rho^{\mathrm{TF}} * |y|^{-1})\gamma\right] = 2D(\rho^{\mathrm{TF}}, \rho_\gamma) = \mathcal{D}(\gamma) + D(\rho^{\mathrm{TF}}, \rho^{\mathrm{TF}}) - \|\rho^{\mathrm{TF}} - \rho_\gamma\|_{\mathrm{C}}^2.$$

From the semiclassical estimate (69) and the fact that, when γ is a density matrix with $\mathrm{Tr}[\gamma] = N$ and h is a self-adjoint operator, then $\mathrm{Tr}[h\gamma]$ is an upper bound on the sum of the N lowest eigenvalues of h, we find

$$\begin{aligned}\mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \varphi^{\mathrm{TF}} + \mu^{\mathrm{TF}}\right)\gamma^{\mathrm{HF}}\right] \quad &\geq \quad -2^{5/2}(15\pi^2)^{-1}(1-\delta)^{-3/2}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} \\ &\qquad - \tfrac{1}{2}\pi^2 s^{-2} N - 2L_1\delta^{-3/2}\left\|\left[\varphi^{\mathrm{TF}} - \varphi^{\mathrm{TF}} * g^2\right]_+\right\|_{5/2}^{5/2},\end{aligned}$$

for all $0 < \delta < 1$ and all $s > 0$. Recall that the function g was given in Definition 8.1. Here we have used the semiclassical estimate for the space $L^2(\mathbb{R}^3; \mathbb{C}^2)$. The estimate above therefore has an extra factor of 2 in the first and the last term compared to (69). Thus

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) \geq{}& -2^{5/2}(15\pi^2)^{-1}(1-\delta)^{-3/2}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} - \mu^{\mathrm{TF}} N - D(\rho^{\mathrm{TF}}, \rho^{\mathrm{TF}}) \\ &+ \|\rho^{\mathrm{TF}} - \rho^{\mathrm{HF}}\|_{\mathrm{C}}^2 - \tfrac{1}{2}\pi^2 s^{-2} N - 2L_1\delta^{-3/2}\left\|\left[\varphi^{\mathrm{TF}} - \varphi^{\mathrm{TF}} * g^2\right]_+\right\|_{5/2}^{5/2} - \mathcal{E}x(\gamma^{\mathrm{HF}}).\end{aligned}$$

Since $|y|^{-1} - g^2 * |y|^{-1} \geq 0$ (because the function $|y|^{-1}$ is superharmonic) we have

$$\left\|\left[\varphi^{\mathrm{TF}} - \varphi^{\mathrm{TF}} * g^2\right]_+\right\|_{5/2}^{5/2} \leq Z\left\||y|^{-1} - g^2 * |y|^{-1}\right\|_{5/2}^{5/2} \leq 8\pi Z^{5/2} s^{1/2},$$

where we have used that $|y|^{-1} - g^2 * |y|^{-1}$ is non-negative, bounded by $|y|^{-1}$, and vanishes for $|y| > s$. If we insert this above and optimize in s we obtain

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) \quad \geq \quad & -2^{5/2}(15\pi^2)^{-1}(1-\delta)^{-3/2}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} - \mu^{\mathrm{TF}} N - D(\rho^{\mathrm{TF}}, \rho^{\mathrm{TF}}) \\ & + \|\rho^{\mathrm{TF}} - \rho^{\mathrm{HF}}\|_{\mathrm{C}}^2 - (\mathrm{Const.})\delta^{-6/5} N^{1/5} Z^2 - \mathcal{E}x(\gamma^{\mathrm{HF}}).\end{aligned} \qquad (93)$$

We choose $\delta := \frac{1}{2}Z^{-2/33}$ (this is not optimal). Then for $Z \geq 1$ we have $\delta \leq 1/2$ and thus $(1-\delta)^{-2/3} \leq 1 + (2^{5/2}-2)\delta$. Hence

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) \geq -2^{5/2}(15\pi^2)^{-1}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} - \mu^{\mathrm{TF}}N - D(\rho^{\mathrm{TF}},\rho^{\mathrm{TF}}) \\ +\|\rho^{\mathrm{TF}} - \rho^{\mathrm{HF}}\|_{\mathrm{C}}^2 - (\mathrm{Const.})Z^{7/3-2/33} - \mathcal{E}x(\gamma^{\mathrm{HF}}),\end{aligned} \tag{94}$$

where we have again used $N \leq 2Z+1$ and the fact that by (90) we have

$$2^{5/2}(15\pi^2)^{-1}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} = \tfrac{2}{3}\left[(3\pi^2)^{2/3}\tfrac{3}{10}\int (\rho^{\mathrm{TF}})^{5/3}\right] \leq (\mathrm{Const.})Z^{7/3}.$$

On the other hand, since γ^{HF} minimizes $\mathcal{E}^{\mathrm{HF}}$ among all density matrices γ with $\mathrm{Tr}[\gamma] \leq N$, we can find an upper bound to $\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})$ by choosing an appropriate trial density matrix. We choose as trial matrix γ an operator which acts identically on the two spin components. On each spin component we choose it to be the density matrix constructed in Lemma 8.2 satisfying (70) with $V = \varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}$. Note that the Thomas-Fermi equation (6) and the properties of γ stated in Lemma 8.2 imply that $\rho_\gamma = 2^{5/2}(6\pi^2)^{-1}[\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{3/2} * g^2 = \rho^{\mathrm{TF}} * g^2$ (the extra factor of 2 compared to Lemma 8.2 is of course due to the spin degeneracy). Thus $\mathrm{Tr}[\gamma] = \int \rho^{\mathrm{TF}} \leq N$.

From (26) and (70) we find, since $\mathcal{E}x(\gamma) \geq 0$, that

$$\mathcal{E}^{\mathrm{HF}}(\gamma) \leq 2^{3/2}(5\pi^2)^{-1}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} + \tfrac{1}{2}\pi^2 s^{-2}N - \int Z|y|^{-1}\rho_\gamma(y)dy + D(\rho_\gamma,\rho_\gamma)$$

Since $\iint g(x-z)^2|z-w|^{-1}g(y-w)^2 dw\,dz \leq |x-y|^{-1}$ we see that $D(\rho_\gamma,\rho_\gamma) \leq D(\rho^{\mathrm{TF}},\rho^{\mathrm{TF}})$. Thus from the definition (2) of φ^{TF} we can write

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma) \leq\ & 2^{3/2}(5\pi^2)^{-1}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} - \int [\varphi^{\mathrm{TF}}(y) - \mu^{\mathrm{TF}}]\,\rho^{\mathrm{TF}}(y)dy - \mu^{\mathrm{TF}}N \\ & - D(\rho^{\mathrm{TF}},\rho^{\mathrm{TF}}) + \tfrac{1}{2}\pi^2 s^{-2}N + \int Z\left(|y|^{-1} - g^2 * |y|^{-1}\right)\rho^{\mathrm{TF}}(y)dy\end{aligned}$$

If we use the TF equation (6), the estimate $\rho^{\mathrm{TF}}(y) \leq 2^{3/2}(3\pi^2)^{-1}Z^{3/2}|y|^{-3/2}$ which follows from the TF equation, and again the facts that $|y|^{-1} - g^2 * |y|^{-1}$ is non-negative, bounded by $|y|^{-1}$, and vanishes for $|y| > s$, we obtain after optimizing in s

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma) \leq\ & -2^{5/2}(15\pi^2)^{-1}\int [\varphi^{\mathrm{TF}} - \mu^{\mathrm{TF}}]_+^{5/2} - \mu^{\mathrm{TF}}N - D(\rho^{\mathrm{TF}},\rho^{\mathrm{TF}}) \\ & + (\mathrm{Const.})N^{1/5}Z^2.\end{aligned} \tag{95}$$

Comparing (94) and (95) and recalling that $\mathcal{E}^{\text{HF}}(\gamma) \geq \mathcal{E}^{\text{HF}}(\gamma^{\text{HF}})$ we get that

$$\|\rho^{\text{TF}} - \rho^{\text{HF}}\|_{\text{C}}^2 \leq (\text{Const.})Z^{7/3-2/15} + (\text{Const.})Z^{7/3-2/33} + \mathcal{E}x(\gamma^{\text{HF}}).$$

If we finally use the exchange inequality in Theorem 6.4 and the estimate (90) we see that

$$\mathcal{E}x(\gamma^{\text{HF}}) \leq 1.68\left(\int (\rho^{\text{HF}})^{5/3}\right)^{1/2}\left(\int (\rho^{\text{HF}})\right)^{1/2} \leq (\text{Const.})N^{1/2}Z^{7/6}.$$

Inserting this above and again using $N \leq 2Z+1$ we arrive at (91). □

End of proof of Lemma 10.2. We write

$$\Phi^{\text{HF}}_{|x|}(x) - \Phi^{\text{TF}}_{|x|}(x) = \int_{|y|<|x|} [\rho^{\text{TF}}(y) - \rho^{\text{HF}}(y)]\,|x-y|^{-1}dy.$$

Using the Coulomb norm estimate (83) we find

$$\begin{aligned}\left|\Phi^{\text{HF}}_{|x|}(x) - \Phi^{\text{TF}}_{|x|}(x)\right| \;\leq\;& 2^{7/5}\pi^{2/5}(\kappa|x|)^{1/5}\max\left\{\|\rho^{\text{TF}}\|_{L^{5/3}(\mathbb{R}^3)},\ \|\rho^{\text{HF}}\|_{L^{5/3}(\mathbb{R}^3)}\right\}\\ &+ 4\pi^{1/2}\kappa^{-1}|x|^{-1/2}\|\rho^{\text{HF}} - \rho^{\text{TF}}\|_{\text{C}}.\end{aligned}$$

Thus from Lemma 11.1 and the fact that $\int(\rho^{\text{TF}})^{5/3} \leq (\text{Const.})Z^{7/3}$ (which can be seen for instance from the Sommerfeld estimate Theorem 5.2 together with the TF equation (6)) we obtain

$$\begin{aligned}\left|\Phi^{\text{HF}}_{|x|}(x) - \Phi^{\text{TF}}_{|x|}(x)\right| \;\leq\;& (\text{Const.})(\kappa|x|)^{1/5}Z^{7/5}\\ &+ (\text{Const.})\kappa^{-1}|x|^{-1/2}Z^{7(1-\varepsilon_3)/36} = (\text{Const.})|x|^{1/12}Z^{7/6+7(1-\varepsilon_3)/36},\end{aligned}$$

where the last equality above follows from choosing the optimal value for κ.

Hence if $|x| \leq \beta Z^{-1/3}$ we have

$$\left|\Phi^{\text{HF}}_{|x|}(x) - \Phi^{\text{TF}}_{|x|}(x)\right| \leq A_\Phi \beta^{49/12-7\varepsilon_3/12}|x|^{-4+7\varepsilon_3/12}.$$

The lemma follows since $7\varepsilon_3/12 = 1/66$. □

12 Proof of the iterative step Lemma 10.3 and of Lemma 10.4

We begin by fixing some $0 < r$ such that (85) holds for all $|x| \leq r$.

We shall proceed as for the region close to the nucleus, but instead of directly comparing HF and TF. We shall introduce an intermediate TF theory. Namely, the TF theory defined as in Definition 4.1 from the functional $\mathcal{E}_r^{\mathrm{OTF}} := \mathcal{E}_{V_r}^{\mathrm{TF}}$ with the exterior potential $V = V_r$ given by

$$V_r(y) := \chi_r^+(y)\Phi_r^{\mathrm{HF}}(y) = \begin{cases} 0, & \text{if } |y| < r \\ \Phi_r^{\mathrm{HF}}(y), & \text{if } |y| \geq r \end{cases}$$

Here again $\chi_r^+ = 1 - \chi_r$ is the characteristic function of the set $\{x : |x| \geq r\}$. Note that this potential is harmonic and continuous on $|x| > r$. Let ρ_r^{OTF} denote the minimizer for the TF functional, $\mathcal{E}_r^{\mathrm{OTF}}(\rho)$, under the constraint $\int \rho \leq \int \rho^{\mathrm{HF}}\chi_r^+$. Denote the corresponding TF potential by

$$\varphi_r^{\mathrm{OTF}}(y) := V_r(y) - \rho_r^{\mathrm{OTF}} * |y|^{-1}$$

and the corresponding chemical potential by μ_r^{OTF}. We shall prove below (see Lemma 12.4) that if r is chosen appropriately then $\mu_r^{\mathrm{OTF}} = 0$.

Note that according to the Thomas-Fermi equation (33), ρ_r^{OTF} has support on the set $\{y : |y| \geq r\}$. Since V_r on the support of ρ_r^{OTF} is the potential coming from the true HF density for $|y| < r$ we may interpret ρ_r^{OTF} as the TF approximation for only the outside region, i.e., $|y| > r$, of the atom. The notation OTF refers to *Outside* TF.

12.1. LEMMA (Preliminary bounds on TF and OTF functions). *Assume that $N \geq Z$ then for all y*

$$\varphi^{\mathrm{TF}}(y) \leq 3^4 2^{-3}\pi^2|y|^{-4} \quad \textit{and} \quad \rho^{\mathrm{TF}}(y) \leq 3^5 2^{-3}\pi|y|^{-6}.$$

For all $|y| \geq \beta_0 Z^{-1/3}$ we have

$$\varphi^{\mathrm{TF}}(y) \geq (\mathrm{Const.})|y|^{-4} \quad \textit{and} \quad \rho^{\mathrm{TF}}(y) \geq (\mathrm{Const.})|y|^{-6}.$$

Given $\varepsilon', \sigma > 0$, and $r > 0$ such that (85) holds for all $|x| \leq r$ and $\sigma r^{\varepsilon'} \leq 1$ then for all $|y| \geq r$ we have

$$\rho_r^{\mathrm{OTF}}(y) \leq (\mathrm{Const.})r^{-6} \quad \textit{and} \quad \varphi_r^{\mathrm{OTF}}(y) \leq |V_r(y)| = |\Phi_r^{\mathrm{HF}}(y)| \leq (\mathrm{Const.})r^{-4}.$$

Proof. The upper bounds on the TF functions follow immediately from the Atomic Sommerfeld estimate Theorem 5.2) and the TF equation (6) if we recall that $\mu^{\mathrm{TF}} = 0$. The lower bounds follow from Theorem 5.4.

Since Φ_r^{HF} is harmonic on the set $\{|y| > r\}$ and tends to zero at infinity it follows from the assumptions on ε', σ, r that for all $|y| \geq r$ we have

$$|\Phi_r^{\mathrm{HF}}(y)| \leq \sup_{|z|=r} |\Phi_r^{\mathrm{HF}}(z)| \leq (\mathrm{Const.}) r^{-4},$$

where in the last inequality we have used the iterative assumption (85) and Lemma 5.5 for the case $\mu^{\mathrm{TF}} = 0$ and the fact that $\Phi_r^{\mathrm{TF}} \geq \varphi^{\mathrm{TF}} \geq 0$ (see e.g., Theorem 5.4). The inequality $\varphi_r^{\mathrm{OTF}}(y) \leq |V_r(y)|$ is trivial from the definition of φ_r^{OTF}.

Finally, from the TF equation (33) we conclude that for all $|y| \geq r$

$$\rho_r^{\mathrm{OTF}}(y) \leq (\mathrm{Const.}) V_r(y)^{3/2} \leq (\mathrm{Const.}) r^{-6}.$$

□

12.2. LEMMA (Preliminary comparison of HF and TF).
Assume that $N \geq Z$. Given $\varepsilon', \sigma > 0$, and $r > 0$ such that (85) holds for all $|x| \leq r$ then

$$\int \chi_r^+ \left(\rho^{\mathrm{TF}} - \rho^{\mathrm{HF}}\right) \leq \sigma r^{-3+\varepsilon'}. \tag{96}$$

Proof. We have

$$\int_{|y|<r} \left(\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y)\right) dy = (4\pi)^{-1} r \int_{\mathcal{S}^2} \left(\Phi_r^{\mathrm{HF}}(r\omega) - \Phi_r^{\mathrm{TF}}(r\omega)\right) d\omega$$

where $d\omega$ denotes the surface measure of the unit sphere $\mathcal{S}^2$. Thus according to (85) we have

$$\left| \int_{|y|<r} \left(\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y)\right) dy \right| \leq \sigma r^{-3+\varepsilon'}.$$

Since $\int \rho^{\mathrm{TF}} \leq N = \int \rho^{\mathrm{HF}}$ we have

$$\int \left(\chi_r^+ \rho^{\mathrm{TF}} - \chi_r^+ \rho^{\mathrm{HF}}\right) \leq \int_{|y|<r} \left(\rho^{\mathrm{HF}}(y) - \rho^{\mathrm{TF}}(y)\right) dy \leq \sigma r^{-3+\varepsilon'}.$$

□

For $|x| > r$ we may write

$$\Phi^{\mathrm{HF}}_{|x|}(x) - \Phi^{\mathrm{TF}}_{|x|}(x) = \mathcal{A}_1(r,x) + \mathcal{A}_2(r,x) + \mathcal{A}_3(r,x), \tag{97}$$

where

$$\begin{aligned}
\mathcal{A}_1(r,x) &= \varphi^{\mathrm{OTF}}_r(x) - \varphi^{\mathrm{TF}}(x) && (98)\\
\mathcal{A}_2(r,x) &= \int_{|y|>|x|} [\rho^{\mathrm{OTF}}_r(y) - \rho^{\mathrm{TF}}(y)]\, |x-y|^{-1} dy && (99)\\
\mathcal{A}_3(r,x) &= \int_{r<|y|<|x|} [\rho^{\mathrm{OTF}}_r(y) - \rho^{\mathrm{HF}}(y)]\, |x-y|^{-1} dy. && (100)
\end{aligned}$$

We turn first to estimating $\mathcal{A}_1$ and $\mathcal{A}_2$. Thus we need to control the difference between the full TF approximation and the TF approximation for the outside region. Our strategy is to first prove that $\varphi^{\mathrm{OTF}}_r(x)$ and $\varphi^{\mathrm{TF}}(x)$ are close on the set $\{|x| = r\}$. An application of the Sommerfeld estimates in Theorem 4.6 will then give excellent control on the difference $\varphi^{\mathrm{OTF}}_r(x) - \varphi^{\mathrm{TF}}(x)$ for all $|x| > r$. Controlling the behavior on the set $\{|x| = r\}$ is difficult and we begin with a weak estimate on the difference between ρ^{OTF}_r and ρ^{TF}. In fact, we first estimate the difference in Coulomb norm.

12.3. LEMMA (Coulomb norm comparison of TF and OTF). *Assume $N \geq Z$. Given constants $\varepsilon', \sigma > 0$ there exists a constant $D > 0$ depending only on ε', σ such that for all r with $\beta_0 Z^{-1/3} \leq r \leq D$ for which (85) holds for all $|x| \leq r$ we have*

$$\|\rho^{\mathrm{OTF}}_r - \chi^+_r \rho^{\mathrm{TF}}\|^2_{\mathrm{C}} \leq (\mathrm{Const.})\sigma r^{-7+\varepsilon'}. \tag{101}$$

Here again χ^+_r denotes the characteristic function of the set $\{y : |y| \geq r\}$. Moreover,

$$\mu^{\mathrm{OTF}}_r \leq (\mathrm{Const.})\sigma^{1/2} r^{-4+\frac{\varepsilon'}{2}}. \tag{102}$$

Proof. To prove this we make a perturbation analysis of the TF functional. We introduce the perturbation potential

$$W(x) = \Phi^{\mathrm{HF}}_r(x) - \Phi^{\mathrm{TF}}_r(x). \tag{103}$$

Then for all $|x| > r$

$$\Phi^{\mathrm{TF}}_r(x) = V_r(x) - W(x).$$

Note that W is harmonic for $|x| > r$ and tends to zero at infinity. Hence, since we assume that the iterative assumption (85) holds for $|x| = r$, we have

$$\sup_{|x|\geq r} |W(x)| = \sup_{|x|=r} |W(x)| \leq \sigma r^{-4+\varepsilon'}. \tag{104}$$

We claim that there exist two functions W_1, W_2 with supp $W_1 \subset \{x : |x| < 3r\}$ and supp $W_2 \subset \{x : |x| > 2r\}$ such that $W(x) = W_1(x) + W_2(x)$ and

$$\sup_{|x|\geq r} |W_1(x)| \leq \sup_{|x|=r} |W(x)| \leq \sigma r^{-4+\varepsilon'} \tag{105}$$

$$\int |\nabla W_2|^2 \leq \frac{76\pi}{3} r \sup_{|x|=r} |W(x)|^2 \leq \frac{76\pi}{3}\sigma^2 r^{-7+2\varepsilon'}. \tag{106}$$

In order to prove this we let

$$F(x) = \begin{cases} 0 & \text{if } |x| < 2r \\ (|x| - 2r)r^{-1}, & \text{if } 2r \leq |x| \leq 3r \\ 1 & \text{if } |x| > 3r \end{cases}.$$

Set $W_1(x) = (1 - F(x))W(x)$ and $W_2(x) = F(x)W(x)$. The first estimate (105) follows immediately from (104). By a simple integration by parts, similar to the one used to prove the IMS formula (19), we obtain (note that $W(x)$ behaves like $c|x|^{-1}$ and $|\nabla W(x)|$ behaves like $c|x|^{-2}$ at infinity so there are no contributions from infinity to the integration by parts)

$$\begin{aligned} \int |\nabla W_2|^2 &= \int |\nabla F|^2 |W|^2 - \int |F|^2 W \Delta W = \int |\nabla F|^2 |W|^2 \\ &\leq \sup_{|x|\geq r} |W(x)|^2 \int_{2r\leq|x|\leq 3r} r^{-2} dx = \frac{76\pi}{3} r \sup_{|x|\geq r} |W(x)|^2, \end{aligned}$$

where the second equality follows since W is harmonic on the support of F. The estimate (105) now also follows from (104).

We are now ready to estimate the TF densities. We shall use $\chi_r^+ \chi_R \rho^{\mathrm{TF}}$ for some $R \geq r$ (possibly R is infinity) as a trial density in $\mathcal{E}_r^{\mathrm{OTF}}$.

Since ρ_r^{OTF} minimizes $\mathcal{E}_r^{\mathrm{OTF}}(\rho) + \mu_r^{\mathrm{OTF}} \int \rho$ and $\mu_r^{\mathrm{OTF}} = 0$ unless $\int \rho_r^{\mathrm{OTF}} = \int \chi_r^+ \rho^{\mathrm{HF}}$ we have

$$\mu_r^{\mathrm{OTF}} \left(\int \chi_r^+ \rho^{\mathrm{HF}} - \int \chi_r^+ \chi_R \rho^{\mathrm{TF}} \right) \leq \mathcal{E}_r^{\mathrm{OTF}} \left(\chi_r^+ \chi_R \rho^{\mathrm{TF}} \right) - \mathcal{E}_r^{\mathrm{OTF}} (\rho_r^{\mathrm{OTF}}) \tag{107}$$

We write the left side as

$$\mathcal{E}_r^{\rm OTF}\left(\chi_r^+\chi_R\rho^{\rm TF}\right)-\mathcal{E}_r^{\rm OTF}\left(\rho_r^{\rm OTF}\right) = \mathcal{E}_r^{\rm OTF}\left(\chi_r^+\chi_R\rho^{\rm TF}\right)-\mathcal{E}_r^{\rm OTF}\left(\chi_r^+\rho^{\rm TF}\right) + \mathcal{E}_r^{\rm OTF}\left(\chi_r^+\rho^{\rm TF}\right)-\mathcal{E}_r^{\rm OTF}\left(\rho_r^{\rm OTF}\right). \quad (108)$$

We have for the first two terms

$$\begin{aligned}
&\mathcal{E}_r^{\rm OTF}\left(\chi_r^+\chi_R\rho^{\rm TF}\right)-\mathcal{E}_r^{\rm OTF}\left(\chi_r^+\rho^{\rm TF}\right)\\
&= \int \varphi^{\rm TF}\rho^{\rm TF}\chi_R^+ + \|\chi_R^+\rho^{\rm TF}\|_{\rm C}^2+\int\left(\Phi_r^{\rm HF}-\Phi_r^{\rm TF}\right)\chi_R^+\rho^{\rm TF}-\tfrac{3}{10}(3\pi^2)^{2/3}\int\chi_R^+(\rho^{\rm TF})^{5/3}\\
&\leq \int \varphi^{\rm TF}\rho^{\rm TF}\chi_R^+ + \|\chi_R^+\rho^{\rm TF}\|_{\rm C}^2+\sigma r^{-4+\varepsilon'}\int\chi_R^+\rho^{\rm TF}, \qquad (109)
\end{aligned}$$

and since $\mu^{\rm TF}=0$

$$\begin{aligned}
\mathcal{E}_r^{\rm OTF}(\chi_r^+\rho^{\rm TF})-\mathcal{E}_r^{\rm OTF}(\rho_r^{\rm OTF}) &= \int W(\rho_r^{\rm OTF}-\chi_r^+\rho^{\rm TF})-\|\rho_r^{\rm OTF}-\chi_r^+\rho^{\rm TF}\|_{\rm C}^2\\
&+\int_{|y|\geq r}\Big(\Big[\tfrac{3}{10}(3\pi^2)^{2/3}\rho^{\rm TF}(y)^{5/3}-\varphi^{\rm TF}(y)\rho^{\rm TF}(y)\Big]\\
&-\Big[\tfrac{3}{10}(3\pi^2)^{2/3}\rho_r^{\rm OTF}(y)^{5/3}-\varphi^{\rm TF}(y)\rho_r^{\rm OTF}(y)\Big]\Big)\,dy. \qquad (110)
\end{aligned}$$

Since $\rho^{\rm TF}$ satisfies the TF equation (6) we see that for fixed y the expression

$$\tfrac{3}{10}(3\pi^2)^{2/3}t^{5/3}-\varphi^{\rm TF}(y)t, \qquad t\geq 0$$

takes its minimal value for $t=\rho^{\rm TF}(y)$. Hence we conclude that the last integral above is negative. Thus combining (107)–(110) we have

$$\begin{aligned}
\mu_r^{\rm OTF}\left(\int\chi_r^+\rho^{\rm HF}-\int\chi_r^+\chi_R\rho^{\rm TF}\right) &\leq \int W(\rho_r^{\rm OTF}-\chi_r^+\rho^{\rm TF})-\|\rho_r^{\rm OTF}-\chi_r^+\rho^{\rm TF}\|_{\rm C}^2\\
&+\int\varphi^{\rm TF}\rho^{\rm TF}\chi_R^+ + \|\chi_R^+\rho^{\rm TF}\|_{\rm C}^2+\sigma r^{-4+\varepsilon'}\int\chi_R^+\rho^{\rm TF}.
\end{aligned}$$

Lemma 12.1 implies that $\|\chi_R^+\rho^{\rm TF}\|_{\rm C}^2\leq(\text{Const.})R^{-4}\int\chi_R^+\rho^{\rm TF}$. If we now also use Lemma 12.2 we arrive at

$$\begin{aligned}
\mu_r^{\rm OTF}\left(\int\chi_r^+\rho^{\rm HF}-\int\chi_r^+\chi_R\rho^{\rm TF}\right) &\leq \int W(\rho_r^{\rm OTF}-\chi_r^+\rho^{\rm TF})-\|\rho_r^{\rm OTF}-\chi_r^+\rho^{\rm TF}\|_{\rm C}^2\\
&+\Big((\text{Const.})R^{-4}+\sigma r^{-4+\varepsilon'}\Big)\int\rho^{\rm TF}\chi_R^+. \qquad (111)
\end{aligned}$$

This is the main estimate from which we shall derive the estimates of the lemma. We shall do this by choosing different values for R. One for the estimate (101) another for (102). We shall choose R such that

$$\int \chi_r^+ \chi_R \rho^{\mathrm{TF}} \le \int \chi_r^+ \rho^{\mathrm{HF}}. \tag{112}$$

Let $R_{\max}$ denote the largest possible R for which this holds. Then

$$\int \chi_{R_{\max}}^+ \rho^{\mathrm{TF}} = \left(\int \chi_r^+ \rho^{\mathrm{TF}} - \int \chi_r^+ \rho^{\mathrm{HF}} \right)_+ \le \sigma r^{-3+\varepsilon'}, \tag{113}$$

where the last inequality follows from Lemma 12.2. By Lemma 12.1 we have for all $R \ge r \ge \beta_0 Z^{-1/3}$ that

$$\int \chi_R^+ \rho^{\mathrm{TF}} \ge (\mathrm{Const.}) R^{-3}. \tag{114}$$

We shall now make the assumption that D is chosen so small that if $r \le D$ then $\sigma r^{\varepsilon'} \le 1$. Thus from (113) and (114) we conclude that

$$R_{\max}^{-4} \le (\mathrm{Const.}) \sigma^{4/3} r^{-4+\frac{4}{3}\varepsilon'} \le (\mathrm{Const.}) r^{-4}. \tag{115}$$

From (113) and (111) with $R = R_{\max}$ we get, again using the above assumption on D, that

$$\|\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}\|_{\mathrm{C}}^2 \le \int W(\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}) + (\mathrm{Const.}) \sigma r^{-7+\varepsilon'}. \tag{116}$$

We estimate the integral on the right by dividing it in two parts

$$\begin{aligned} \int W(\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}) &\le \int |W_1| (\rho_r^{\mathrm{OTF}} + \chi_r^+ \rho^{\mathrm{TF}}) + \int W_2 (\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}) \\ &\le \sigma r^{-4+\varepsilon'} \int_{r<|x|<3r} \rho_r^{\mathrm{OTF}}(x) + \chi_r^+(x) \rho^{\mathrm{TF}}(x) dx + \int W_2(\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}), \end{aligned}$$

where we have also used (105). From Lemma 12.1 we arrive at

$$\int W(\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}) \le (\mathrm{Const.}) \sigma r^{-7+\varepsilon'} + \int W_2 (\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}). \tag{117}$$

The last term in this estimate we now control using the Coulomb norm estimate Lemma 9.2. Note that ρ^{TF} and ρ_r^{OTF} both belong to $L^{6/5}$ since they are in $L^{5/3} \cap L^1$. We find from (106) that

$$\int W_2 (\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}) \le (\mathrm{Const.}) \sigma r^{-\frac{7}{2}+\varepsilon'} \|\rho_r^{\mathrm{OTF}} - \chi_r^+ \rho^{\mathrm{TF}}\|_{\mathrm{C}}. \tag{118}$$

Inserting the last two estimates into (116) gives (recall that $\sigma r^{\varepsilon'} \le 1$)

$$\|\rho_r^{\rm OTF} - \chi_r^+ \rho^{\rm TF}\|_{\rm C}^2 \le ({\rm Const.})\sigma r^{-7+\varepsilon'} + ({\rm Const.})\left(\sigma r^{-7+\varepsilon'}\right)^{1/2} \|\rho_r^{\rm OTF} - \chi_r^+ \rho^{\rm TF}\|_{\rm C}$$

and (101) follows immediately from this.

We now return to (111) and make a new choice for R. It follows from the first inequality in (115) that that we can find R with $R \le R_{\max}$ satisfying

$$R^{-4} = ({\rm Const.})\sigma^{1/2} r^{-4+\varepsilon'/2}.$$

Note that, since

$$R^{-4} \le ({\rm Const.})\sigma^{1/2} D^{\varepsilon'/2} r^{-4},$$

we can choose D small enough to ensure that $r \le R$. From (114) we have

$$\int \chi_R^+ \rho^{\rm TF} \ge ({\rm Const.})\sigma^{3/8} r^{-3+\frac{3}{8}\varepsilon'}. \tag{119}$$

It follows from (113) and (114) that we may assume that the constant in the definition of R is chosen such as to ensure that $\int \chi_R^+ \rho^{\rm TF} \ge 2\int \chi_{R_{\max}}^+ \rho^{\rm TF}$. Thus since (see (113))

$$\int \chi_r^+ \rho^{\rm HF} - \int \chi_r^+ \chi_R \rho^{\rm TF} \ge -\int \chi_{R_{\max}}^+ \rho^{\rm TF} + \int \chi_R^+ \rho^{\rm TF}$$

we have

$$\tfrac{1}{2}\int \chi_R^+ \rho^{\rm TF} \le \int \chi_r^+ \rho^{\rm HF} - \int \chi_r^+ \chi_R \rho^{\rm TF}.$$

Thus from (119), (117), (118), (101), and (111) we conclude (102). □

Using these fairly weak estimates we shall now show that the outside TF potential and density satisfy Sommerfeld type estimates.

12.4. LEMMA (Sommerfeld estimates for OTF). *Assume $N \ge Z$. Given constants $\varepsilon', \sigma > 0$ there exists a constant $D > 0$ depending only on ε', σ such that for all r with $\beta_0 Z^{-1/3} \le r \le D$ for which (85) holds for all $|x| \le r$ then $\mu_r^{\rm OTF} = 0$ and for all $|x| \ge r$ we have*

$$\varphi_r^{\rm OTF}(x) \le 3^4 2^{-3}\pi^2 |x|^{-4}\left(1 + Ar^\zeta |x|^{-\zeta}\right) \tag{120}$$

and

$$\varphi_r^{\rm OTF}(x) \ge 3^4 2^{-3}\pi^2 |x|^{-4}\left(1 + ar^\zeta |x|^{-\zeta}\right)^{-2}, \tag{121}$$

where a and A are universal constants (but not necessarily positive) and $a > -1$. Here as before $\zeta = (-7+\sqrt{73})/2 \approx 0.77$.

Proof. Note first that the potential V_r satisfies the assumptions in Theorem 4.6 with $R = r$. Hence the potential $\varphi_r^{\rm OTF}$ satisfies the Sommerfeld estimates described in the theorem. In order to get some useful estimates we however need to control the behavior of $\varphi_r^{\rm OTF}(x)$ for $|x| = r$. In particular, we need to establish that $\mu_r^{\rm OTF} < \inf_{|x|=r}\varphi_r^{\rm OTF}(x)$. In order to control $\varphi_r^{\rm OTF}(x)$ for $|x| = r$ we note that for all $|x| \geq r$ we have

$$\varphi_r^{\rm OTF}(x) = \varphi^{\rm TF}(x) + \left(\chi_r^+\rho^{\rm TF} - \rho_r^{\rm OTF}\right) * |x|^{-1} + W(x), \tag{122}$$

where as in (103), $W = \Phi_r^{\rm HF} - \Phi_r^{\rm TF}$. According to the Coulomb norm Corollary 9.3 we get for all $s > 0$ that

$$\begin{aligned} &\left|\left(\chi_r^+\rho^{\rm TF} - \rho_r^{\rm OTF}\right) * |x|^{-1}\right| \\ &\leq \ ({\rm Const.})s^{1/5}\max\{\|\chi_r^+\rho^{\rm TF}\|_{L^{5/3}(B(x,s))}, \|\rho_r^{\rm OTF}\|_{L^{5/3}(B(x,s))}\} \\ &\quad + ({\rm Const.})s^{-1/2}\|\chi_r^+\rho^{\rm TF} - \rho_r^{\rm OTF}\|_{\rm C}. \end{aligned}$$

From Lemma 12.1 we see that

$$\max\{\|\chi_r^+\rho^{\rm TF}\|_{L^{5/3}(B(x,s))}, \|\rho_r^{\rm OTF}\|_{L^{5/3}(B(x,s))}\} \leq ({\rm Const.})r^{-6}s^{9/5},$$

where we have assumed that D is such that $\sigma r^{\varepsilon'} \leq 1$. Inserting this and the estimate (101) from Lemma 12.3 above we obtain that for all $|x| \geq r$

$$\begin{aligned} \left|\left(\chi_r^+\rho^{\rm TF} - \rho_r^{\rm OTF}\right) * |x|^{-1}\right| &\leq ({\rm Const.})r^{-6}s^2 + ({\rm Const.})s^{-1/2}\left(\sigma r^{-7+\varepsilon}\right)^{1/2} \\ &= ({\rm Const.})\sigma^{2/5}r^{-4+2\varepsilon'/5} \end{aligned} \tag{123}$$

where we have optimized in s in order to get the last expression. Thus from (122), the iterative assumption (85), and Lemma 12.1 we obtain

$$\begin{aligned} \inf_{|x|=r}\varphi_r^{\rm OTF}(x) &\geq \inf_{|x|=r}\varphi^{\rm TF}(x) - ({\rm Const.})\sigma^{2/5}r^{-4+2\varepsilon'/5} \\ &\geq ({\rm Const.})r^{-4} - ({\rm Const.})\sigma^{2/5}r^{-4+2\varepsilon'/5}. \end{aligned}$$

We have used that since $\sigma r^{\varepsilon'} \leq 1$ the error from (123) is worse than the error from (85). Note that the constant in front of r^{-4} above is positive.

From Lemma 12.3 we know that $\mu_r^{\text{OTF}} \leq (\text{Const.})\sigma^{1/2}r^{-4+\varepsilon'/2}$ Hence we may choose D such that $\mu_r^{\text{OTF}} < \inf_{|x|=r} \varphi_r^{\text{OTF}}(x)$.

As above we of course also have

$$\sup_{|x|=r} \varphi_r^{\text{OTF}}(x) \leq (\text{Const.})r^{-4} + (\text{Const.})\sigma^{2/5}r^{-4+2\varepsilon'/5}.$$

Thus $(\text{Const.})r^{-4} \leq \inf_{|x|=r} \varphi_r^{\text{OTF}}(x) \leq \sup_{|x|=r} \varphi_r^{\text{OTF}}(x) \leq (\text{Const.})r^{-4}$.

That $\mu_r^{\text{OTF}} = 0$ follows from Corollary 4.7 as follows. By harmonicity of V_r we have

$$\lim_{r'\to\infty} (4\pi)^{-1} \int_{\mathcal{S}^2} r'V_r(r'\omega)d\omega = \int_{\mathcal{S}^2} r\Phi_r^{\text{HF}}(r\omega)d\omega = Z - \int \chi_r\rho^{\text{HF}}.$$

Thus from Corollary 4.7 we have if $\mu_r^{\text{OTF}} \neq 0$, i.e., if $\int \rho_r^{\text{OTF}} = \int \chi_r^+ \rho^{\text{HF}}$ that

$$0 < (\mu_r^{\text{OTF}})^{3/4} \leq (\text{Const.}) \left(Z - \int \chi_r\rho^{\text{HF}} - \int \rho_r^{\text{OTF}} \right) = (\text{Const.})(Z - \int \rho^{\text{HF}}),$$

which is a contradiction since $\int \rho^{\text{HF}} = N \geq Z$.

The estimates (120) and (121) now follow from Theorem 4.6. □

We are now ready to give the bounds on $\mathcal{A}_1$ and $\mathcal{A}_2$ defined in (98) and (99).

12.5. LEMMA (Control of $\mathcal{A}_1$ and $\mathcal{A}_2$).
Assume $N \geq Z$. Given constants $\varepsilon', \sigma > 0$ there exists a constant $D > 0$ depending only on ε', σ such that for all r with $\beta_0 Z^{-1/3} \leq r \leq D$ for which (85) holds for all $|x| \leq r$ we have for all $|x| \geq r$ that

$$|\mathcal{A}_1(r,x)| \leq (\text{Const.})r^\zeta|x|^{-4-\zeta} \tag{124}$$

and

$$|\mathcal{A}_2(r,x)| \leq (\text{Const.})r^\zeta|x|^{-4-\zeta}, \tag{125}$$

with $\zeta = (-7+\sqrt{73})/2 \approx 0.77$.

Proof. Combining Theorems 5.2, 5.4, with Lemma 12.4 and recalling that $\mu^{\text{TF}} = 0$ immediately gives the bound on $\mathcal{A}_1$.

If we use the TF equation (33) we obtain from Lemma 12.4 that for all $|y| \geq r$

$$\left|\rho_r^{\text{OTF}}(y) - 3^5 2^{-3}\pi|y|^{-6}\right| \leq (\text{Const.})r^\zeta|y|^{-6-\zeta}.$$

Of course we similarly have from Theorems 5.2, 5.4, and the TF equation (6) that

$$\rho^{\mathrm{TF}}(y) \quad \leq \quad 3^5 2^{-3}\pi|y|^{-6}$$

and

$$\rho^{\mathrm{TF}}(y) \quad \geq \quad 3^5 2^{-3}\pi|y|^{-6} - (\mathrm{Const.})Z^{-\zeta/3}|y|^{-6-\zeta}.$$

Since $r \geq \beta_0 Z^{-1/3}$ we conclude that for all $|y| > r$

$$|\rho^{\mathrm{TF}}(y) - \rho_r^{\mathrm{OTF}}(y)| \leq (\mathrm{Const.})r^{\zeta}|y|^{-6-\zeta}. \tag{126}$$

Thus

$$|\mathcal{A}_2| \leq (\mathrm{Const.})\int_{|y|>|x|} r^{\zeta}|y|^{-7-\zeta}\,dy$$

which gives the bound in (125). □

We turn now to estimating $\mathcal{A}_3$. This requires estimating the difference between ρ_r^{OTF} and ρ^{HF}. We again begin by estimating this difference in the Coulomb norm. More precisely, we estimate in Coulomb norm the difference between the "outside" TF density ρ_r^{OTF} and the "outside" HF density $\chi_r^+\rho_r^{\mathrm{HF}}$. This is done through a semiclassical analysis of the exterior region $\{|x| > r\}$.

12.6. LEMMA (Coulomb norm comparison of HF and OTF).
Assume $N \geq Z$. Given constants $\varepsilon', \sigma > 0$ there exists a constant $D > 0$ depending only on ε', σ such that for all r with $\beta_0 Z^{-1/3} \leq r \leq D$ for which (85) holds for all $|x| \leq r$ we have

$$\|\rho_r^{\mathrm{OTF}} - \chi_r^+\rho^{\mathrm{HF}}\|_{\mathrm{C}} \leq (\mathrm{Const.})r^{-\frac{7}{2}+\frac{1}{6}} \tag{127}$$

and

$$\int \left(\chi_r^+\rho^{\mathrm{HF}}\right)^{5/3} \leq (\mathrm{Const.})r^{-7}. \tag{128}$$

Proof. Let γ be the density matrix on $L^2(\mathbb{R}^3;\mathbb{C}^2)$, but diagonal in spin, constructed in the semiclassical approximation Lemma 8.2 for the potential $V = \varphi_r^{\mathrm{OTF}}$. Note that from Lemma 12.4 we have $\varphi_r^{\mathrm{OTF}}(y) \geq 0$ for $|y| \geq r$ and from its definition $\varphi_r^{\mathrm{OTF}}(y) \leq 0$ for $|y| < r$. From Lemma 8.2 we have that

$$\rho_\gamma = 2^{3/2}(3\pi^2)^{-1}\,[\varphi_r^{\mathrm{OTF}}]_+^{3/2} * g^2 = \rho_r^{\mathrm{OTF}} * g^2, \tag{129}$$

where we have used the TF equation (33) and the fact $\mu_r^{\mathrm{OTF}} = 0$ proved in Lemma 12.4. Here g was given in Definition 8.1. From Lemma 8.2 we also have

$$\begin{aligned}\operatorname{Tr}\left[-\tfrac{1}{2}\Delta\gamma\right] &\leq \frac{2^{3/2}}{5\pi^2}\int [\varphi_r^{\mathrm{OTF}}]_+^{5/2} + \tfrac{1}{2}\pi^2 s^{-2}\int \frac{2^{3/2}}{3\pi^2}[\varphi_r^{\mathrm{OTF}}]_+^{3/2} \\ &\leq \tfrac{3}{10}(3\pi^2)^{2/3}\int (\rho_r^{\mathrm{OTF}})^{5/3} + (\mathrm{Const.})s^{-2}r^{-3}. \qquad (130)\end{aligned}$$

(Note the factor of 2 in the formulas above compared to Lemma 8.2. This is due to the fact that there was no spin in Lemma 8.2.) The last inequality above follows from the Sommerfeld estimate for OTF given in Lemma 12.4.

According to Lemma 8.5 we may, for all $0 < \lambda' < 1$, choose a density matrix $\widetilde{\gamma}$ such that its density $\rho_{\widetilde{\gamma}}$ has support in $\{|x| \geq r\}$ and such that $\rho_{\widetilde{\gamma}} \leq \rho_\gamma$ and

$$\begin{aligned}\operatorname{Tr}\left[\left(-\tfrac{1}{2}\Delta - V_r\right)\widetilde{\gamma}\right] &\leq \operatorname{Tr}\left[\left(-\tfrac{1}{2}\Delta - V_r\right)\gamma\right] + (\mathrm{Const.})\int_{|x|\leq(1-\lambda')^{-1}r} [V_r]_+^{5/2} \\ &\quad + (\mathrm{Const.})(\lambda' r)^{-2}\int_{|x|\leq(1-\lambda')^{-1}r}\rho_\gamma.\end{aligned}$$

If we make the assumption that D is chosen to ensure that $\sigma r^{\varepsilon'} \leq 1$ we may use the estimate on V_r from Lemma 12.1 and use the same lemma to conclude that $\rho_\gamma(y) \leq (\mathrm{Const.})r^{-6}$ for all y. If we now make the choice that the parameter s which appears in the definition of the function g satisfies $s < r$ we get (recall that V_r and hence also $\varphi_r^{\mathrm{OTF}}-$ have support for $|x| \geq r$)

$$\begin{aligned}\operatorname{Tr}\left[\left(-\tfrac{1}{2}\Delta - V_r\right)\widetilde{\gamma}\right] &\leq \operatorname{Tr}\left[\left(-\tfrac{1}{2}\Delta - V_r\right)\gamma\right] + (\mathrm{Const.})\left(\lambda' r^{-7} + \lambda'^{-2}r^{-5}\right) \\ &= \operatorname{Tr}\left[\left(-\tfrac{1}{2}\Delta - V_r\right)\gamma\right] + (\mathrm{Const.})r^{-7+2/3},\end{aligned}$$

where we have made the choice $\lambda' = r^{2/3}$ and assumed that D is such that $\lambda' < 1/2$.

Since $\int\rho_{\widetilde{\gamma}} \leq \int\rho_\gamma = \int\rho_r^{\mathrm{OTF}} \leq \int\chi_r^+\rho^{\mathrm{HF}}$ we see from Theorem 6.2 that in terms of the auxiliary functional $\mathcal{E}^{\mathrm{A}}$ defined in (49)

$$\begin{aligned}\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] \leq \mathcal{E}^{\mathrm{A}}\left[\widetilde{\gamma}\right] + \mathcal{R} &\leq \operatorname{Tr}\left[\left(-\tfrac{1}{2}\Delta - V_r\right)\gamma\right] + (\mathrm{Const.})r^{-7+2/3} \\ &\quad + \tfrac{1}{2}\iint \rho_\gamma(x)|x-y|^{-1}\rho_\gamma(y)\,dx\,dy + \mathcal{R},\end{aligned}$$

where γ_r^{HF} and $\mathcal{R}$ were defined in (48) and (51) respectively in terms of a parameter $0 < \lambda < 1$ (different from the λ' used above). We have here used that

$\Phi_r^{\mathrm{HF}}\rho_{\widetilde{\gamma}} = V_r\rho_{\widetilde{\gamma}}$, since $\rho_{\widetilde{\gamma}}$ has support in $\{|x|\geq r\}$, and that

$$\tfrac{1}{2}\iint \rho_{\widetilde{\gamma}}(x)|x-y|^{-1}\rho_{\widetilde{\gamma}}(y)dx\,dy \leq \tfrac{1}{2}\iint \rho_{\gamma}(x)|x-y|^{-1}\rho_{\gamma}(y)dx\,dy$$

since $\rho_{\widetilde{\gamma}}\leq\rho_\gamma$.

Since $|x|^{-1}$ is superharmonic we have

$$\iint g(x-z)^2|z-w|^{-1}g(y-w)^2\,dz\,dw \leq |x-y|^{-1}$$

and we conclude that

$$\begin{aligned}\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] \;\leq\;& \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - V_r\right)\gamma\right] + (\mathrm{Const.})r^{-7+2/3}\\ &+\tfrac{1}{2}\iint \rho_r^{\mathrm{OTF}}(x)|x-y|^{-1}\rho_r^{\mathrm{OTF}}(y)dx\,dy + \mathcal{R}.\end{aligned}$$

From (129) and (130) we find that

$$\begin{aligned}\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] \;\leq\;& \mathcal{E}_r^{\mathrm{OTF}}(\rho_r^{\mathrm{OTF}}) + \int V_r\left(\rho_r^{\mathrm{OTF}} - \rho_r^{\mathrm{OTF}} * g^2\right) + (\mathrm{Const.})s^{-2}r^{-3}\\ &+(\mathrm{Const.})r^{-7+2/3} + \mathcal{R}.\end{aligned} \tag{131}$$

We have

$$\int V_r\left(\rho_r^{\mathrm{OTF}} - \rho_r^{\mathrm{OTF}} * g^2\right) = \int\left(V_r - V_r * g^2\right)\rho_r^{\mathrm{OTF}}.$$

Now since $V_r(y)$ is harmonic for $|y|>r$ we conclude that $V_r * g^2(y) = V_r(y)$ for $|y|>r+s$. Hence we get from Lemma 12.1 that

$$\int V_r\left(\rho_r^{\mathrm{OTF}} - \rho_r^{\mathrm{OTF}} * g^2\right) \leq (\mathrm{Const.})r^{-4}\int_{|y|<r+s}\rho_r^{\mathrm{OTF}} \leq (\mathrm{Const.})r^{-8}s. \tag{132}$$

We insert this into (131) and arrive at

$$\begin{aligned}\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] \;\leq\;& \mathcal{E}_r^{\mathrm{OTF}}(\rho_r^{\mathrm{OTF}}) + (\mathrm{Const.})(s^{-2}r^{-3} + r^{-8}s) + (\mathrm{Const.})r^{-7+2/3} + \mathcal{R}\\ =\;& \mathcal{E}_r^{\mathrm{OTF}}(\rho_r^{\mathrm{OTF}}) + (\mathrm{Const.})r^{-7+2/3} + \mathcal{R},\end{aligned} \tag{133}$$

with the choise $s = r^{5/3}$. Note that this agrees with our earlier condition $s<r$ if we choose $D\leq 1$.

We shall now estimate $\mathcal{R}$. We shall choose the λ used to define γ_r^{HF} and $\mathcal{R}$ in such a way that $\lambda\leq 1/2$. We then see that the constant $C_\lambda(r)$ in Theorem 6.2 satisfies $C_\lambda(r)\leq(\mathrm{Const.})(\lambda r)^{-2}$, since $\lambda\leq 1/2$ and $r\leq 1$. We see from Lemma 10.5 that

$$\int_{|y|>(1-\lambda)r}\rho^{\mathrm{HF}} \leq (\mathrm{Const.})r^{-3}, \tag{134}$$

where we have used that $r, \sigma r^{\varepsilon'} \le 1$.

Moreover, from Lemma 12.1 with r replaced by $(1-\lambda)r$ we have

$$\int_{(1-\lambda)r<|y|<(1-\lambda)^{-1}r} \left[\Phi^{\mathrm{HF}}_{(1-\lambda)r}(y)\right]_+^{5/2} dy \le (\mathrm{Const.})r^{-7}\lambda.$$

Hence we have

$$\mathcal{R} \le (\mathrm{Const.})\lambda^{-2}r^{-5} + (\mathrm{Const.})r^{-7}\lambda + \mathcal{E}x\left[\gamma_r^{\mathrm{HF}}\right].$$

If we now use the exchange inequality in Theorem 6.4 and (134) we get (recall that $\rho_r^{\mathrm{HF}} = \theta_r^2\rho^{\mathrm{HF}}$ is the density corresponding to γ_r^{HF})

$$\begin{aligned}\mathcal{E}x[\gamma_r^{\mathrm{HF}}] &\le (\mathrm{Const.})\int (\rho_r^{\mathrm{HF}})^{4/3} \le (\mathrm{Const.})\left(\int \rho_r^{\mathrm{HF}}\right)^{1/2}\left(\int (\rho_r^{\mathrm{HF}})^{5/3}\right)^{1/2}\\ &\le (\mathrm{Const.})r^{-3/2}\left(\mathcal{R}+r^{-7}\right)^{1/2},\end{aligned}$$

where we have also used that according to (59) and Lemma 12.1 we have

$$\int (\rho_r^{\mathrm{HF}})^{5/3} \le (\mathrm{Const.})\mathcal{R} + (\mathrm{Const.})r^{-7}. \tag{135}$$

We may therefore conclude that

$$\mathcal{R} \le (\mathrm{Const.})r^{-7}(r^2\lambda^{-2}+\lambda) + (\mathrm{Const.})r^{-5}. \tag{136}$$

We may use (135) and (136) to prove (128). Recall that $\rho_r^{\mathrm{HF}}(y) = \rho^{\mathrm{HF}}(y)$ if $|y| > (1-\lambda)^{-1}r$. Now (128) follows if we simply observe that (135) and (136) hold with r replaced by $r/2$ and $\lambda = 1/2$. We shall make a possible different choice of λ below.

We shall now prove a lower bound on $\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right]$. We write

$$\begin{aligned}\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] &= \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \Phi_r^{\mathrm{HF}}\right)\gamma_r^{\mathrm{HF}}\right] + \tfrac{1}{2}\iint \rho_r^{\mathrm{HF}}(x)|x-y|^{-1}\rho_r^{\mathrm{HF}}(y)dx\,dy\\ &= \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \Phi_r^{\mathrm{HF}} + \rho_r^{\mathrm{OTF}} * |x|^{-1}\right)\gamma_r^{\mathrm{HF}}\right] + \|\rho_r^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_{\mathrm{C}}^2\\ &\quad -\tfrac{1}{2}\iint \rho_r^{\mathrm{OTF}}(x)|x-y|^{-1}\rho_r^{\mathrm{OTF}}(y)dx\,dy.\end{aligned}$$

If we use that on the support of ρ_r^{HF} we have $\Phi_r^{\mathrm{HF}} = V_r$ we may write this as

$$\begin{aligned}\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] &= \mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta - \varphi_r^{\mathrm{OTF}}\right)\gamma_r^{\mathrm{HF}}\right] + \|\rho_r^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_{\mathrm{C}}^2\\ &\quad -\tfrac{1}{2}\iint \rho_r^{\mathrm{OTF}}(x)|x-y|^{-1}\rho_r^{\mathrm{OTF}}(y)\,dx\,dy.\end{aligned} \tag{137}$$

The trace may be bounded below by the sum of the first N' negative eigenvalues of the operator $-\frac{1}{2}\Delta-\varphi_r^{\mathrm{OTF}}$, where N' is the smallest integer larger than $\mathrm{Tr}[\gamma_r^{\mathrm{HF}}] = \int \rho_r^{\mathrm{HF}}$. From Lemma 8.2 (again with an extra factor of 2 due to spin) we therefore have that for all $s>0$ and all $0<\delta<1$

$$\begin{aligned}\mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta-\varphi_r^{\mathrm{OTF}}\right)\gamma_r^{\mathrm{HF}}\right] \;\geq\;& -\frac{2^{5/2}}{(15\pi^2)}(1-\delta)^{-3/2}\int(\varphi_r^{\mathrm{OTF}})_+^{5/2} \\ & -\pi^2 s^{-2}\left(\int \rho_r^{\mathrm{HF}}+1\right) \qquad (138)\\ & -2L_1\delta^{-3/2}\left\|\left[\varphi_r^{\mathrm{OTF}}-\varphi_r^{\mathrm{OTF}}*g^2\right]_+\right\|_{5/2}^{5/2}.\end{aligned}$$

We first estimate the last term. Since $\rho_r^{\mathrm{OTF}}*|x|^{-1}$ is superharmonic we have by the mean value property that $\rho_r^{\mathrm{OTF}}*|x|^{-1}\geq \rho_r^{\mathrm{OTF}}*|x|^{-1}*g^2$. Thus we have

$$\varphi_r^{\mathrm{OTF}}-\varphi_r^{\mathrm{OTF}}*g^2 = V_r - V_r*g^2+\rho_r^{\mathrm{OTF}}*|x|^{-1}*g^2-\rho_r^{\mathrm{OTF}}*|x|^{-1}\leq V_r-V_r*g^2.$$

The same argument which led to (132) gives that $V_r(y)-V_r*g^2(y)=0$ unless $r-s\leq|y|\leq r+s$. Since by Lemma 12.1 we have $|V_r(y)|\leq(\mathrm{Const.})r^{-4}$ (recall that V_r is supported on $\{|y|\geq r\}$) we obtain

$$\left\|\left[\varphi_r^{\mathrm{OTF}}-\varphi_r^{\mathrm{OTF}}*g^2\right]_+\right\|_{5/2}^{5/2}\leq(\mathrm{Const.})r^{-8}s,$$

if we assume that $s\leq r$. (Note that s here does not have to be chosen as in the upper bound).

From (134) we also get that $\int\rho_r^{\mathrm{HF}}\leq\int\rho^{\mathrm{HF}}\chi_r^+\leq(\mathrm{Const.})r^{-3}$.

Finally from the Sommerfeld estimate (120) and the fact that $\varphi_r^{\mathrm{OTF}}(x)$ is positive only if $V_r(x)>0$, i.e., only if $|x|\geq r$, we find that

$$\int(\varphi_r^{\mathrm{OTF}})_+^{5/2}\leq(\mathrm{Const.})r^{-7}.$$

We therefore see from (138) and the TF equation (33) (recall that $\mu_r^{\mathrm{OTF}}=0$, by Lemma 12.4) that if $0<\delta<1/2$ then

$$\begin{aligned}&\mathrm{Tr}\left[\left(-\tfrac{1}{2}\Delta-\varphi_r^{\mathrm{OTF}}\right)\gamma_r^{\mathrm{HF}}\right]\\ &\quad\geq\; \tfrac{3}{10}(3\pi^2)^{2/3}\int(\rho_r^{\mathrm{OTF}})^{5/3}-\int\varphi_r^{\mathrm{OTF}}\rho_r^{\mathrm{OTF}}\\ &\qquad-(\mathrm{Const.})\left(\delta r^{-7}+\delta^{-3/2}r^{-8}s\right)-(\mathrm{Const.})s^{-2}r^{-3}\\ &\quad=\; \tfrac{3}{10}(3\pi^2)^{2/3}\int(\rho_r^{\mathrm{OTF}})^{5/3}-\int\varphi_r^{\mathrm{OTF}}\rho_r^{\mathrm{OTF}}-(\mathrm{Const.})r^{-7+\frac{1}{3}},\end{aligned}$$

where we have chosen $\delta = r^{-2/5}s^{2/5}$ and $s = r^{11/6}$, which agrees with $s \le r$.

If we insert this last estimate into (137) awe obtain

$$\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] \ge \mathcal{E}_r^{\mathrm{OTF}}\left(\rho_r^{\mathrm{OTF}}\right) + \|\rho_r^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_{\mathrm{C}}^2 - (\mathrm{Const.})r^{-7+\frac{1}{3}}.$$

If we compare this with (133) we see that

$$\|\rho_r^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_{\mathrm{C}}^2 \le (\mathrm{Const.})r^{-7+\frac{1}{3}} + \mathcal{R}.$$

Finally, we use the Hardy-Littlewood-Sobolev inequality (80) and (128) to conclude that

$$\begin{aligned}
&\|\chi_r^{+}\rho^{\mathrm{HF}} - \rho_r^{\mathrm{HF}}\|_{\mathrm{C}} \\
&\le \ (\mathrm{Const.})\|\chi_r^{+}\rho^{\mathrm{HF}} - \rho_r^{\mathrm{HF}}\|_{6/5} \le (\mathrm{Const.})\left(\int_{r<|y|<(1-\lambda)^{-1}r}\rho^{\mathrm{HF}}(y)^{6/5}dy\right)^{5/6} \\
&\le \ (\mathrm{Const.})\left(\int_{r<|y|}\rho^{\mathrm{HF}}(y)^{5/3}dy\right)^{3/5}\left(\int_{r<|y|<(1-\lambda)^{-1}r}1dy\right)^{7/30} \le (\mathrm{Const.})\lambda^{7/30}r^{-7/2}.
\end{aligned}$$

We thus get from (136) that

$$\begin{aligned}
\|\chi_r^{+}\rho^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_{\mathrm{C}} &\le \|\chi_r^{+}\rho^{\mathrm{HF}} - \rho_r^{\mathrm{HF}}\|_{\mathrm{C}} + \|\rho_r^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_{\mathrm{C}} \\
&\le \ (\mathrm{Const.})r^{-\frac{7}{2}+\frac{1}{6}} + (\mathrm{Const.})r^{-7/2}(r\lambda^{-1} + \lambda + \lambda^{7/30})
\end{aligned}$$

which gives (127) if we choose $\lambda = \min\{1/2, r^{5/7}\}$. □

We may now estimate $\mathcal{A}_3$ defined in (100).

12.7. LEMMA (Controlling $\mathcal{A}_3$). *Assume $N \ge Z$. Given constants $\varepsilon', \sigma > 0$ there exists a constant $D > 0$ depending only on ε', σ such that for all r with $\beta_0 Z^{-1/3} \le r \le D$ for which (85) holds for all $|x| \le r$ we have for all $|x| \ge r$ that*

$$|\mathcal{A}_3(r,x)| \le \ (\mathrm{Const.})(|x|/r)^{1/12}r^{-4+\frac{1}{36}}. \tag{139}$$

Proof. We shall use the Coulomb norm estimate (83) with $f = \rho_r^{\mathrm{OTF}} - \chi_r^{+}\rho^{\mathrm{HF}}$. We then immediately see from (83), Lemma 12.6, and the fact, which follows from Lemma 12.4 and the TF equation (33), that $\rho_r^{\mathrm{OTF}}(y) \le (\mathrm{Const.})|y|^{-6}$, that

$$|\mathcal{A}_3(r,x)| \le (\mathrm{Const.})(\kappa|x|)^{1/5}r^{-21/5} + (\mathrm{Const.})\kappa^{-1}|x|^{-1/2}r^{-\frac{7}{2}+\frac{1}{6}}.$$

This gives (139) if we choose $\kappa = (\mathrm{Const.})(r/|x|)^{7/12}r^{\frac{5}{36}}$. □

Proof of Lemma 10.4. For $|x| \geq \beta_0 Z^{-1/3}$ the estimate in (87) follows from (128). For $|x| \leq \beta_0 Z^{-1/3}$ we get from (90) that

$$\int_{|y|>|x|} \rho^{\mathrm{HF}}(y)^{5/3}\, dy \leq \int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(y)^{5/3}\, dy \leq (\mathrm{Const.}) Z^{7/3} \leq (\mathrm{Const.}) |x|^{-7}.$$

$\square$

End of proof of the iterative Lemma 10.3. Let $D > 0$ depending on σ, ε' be the smaller of the values D occurring in Lemmas 12.5 and 12.7. We may without loss of generality assume that $D \leq 1$.

Given $\delta > 0$. We consider $R_0 < D$ satisfying $\beta_0 Z^{-1/3} \leq R_0^{1+\delta}$ and we assume that (85) holds for all $|x| \leq R_0$.

Set $R_0' = R_0^{1-\delta}$ and $r = R_0^{1+\delta}$. Then we have $\beta_0 Z^{-1/3} \leq r \leq R_0 < D$ and we can therefore apply Lemmas 12.5 and 12.7. Moreover $R_0' > R_0$. In order to prove (86) for $R_0 < |x| < R_0'$ we use (97) and Lemmas 12.5 and 12.7. We obtain that for all $|x| \geq r$

$$\left|\Phi_{|x|}^{\mathrm{HF}}(x) - \Phi_{|x|}^{\mathrm{TF}}(x)\right| \leq (\mathrm{Const.}) \left(r/|x|\right)^{\zeta} |x|^{-4} + (\mathrm{Const.}) \left(|x|/r\right)^{1/12} r^{-4+\frac{1}{36}}.$$

Moreover, for all $R_0 < |x| < R_0'$ we have

$$|x|^{\frac{2\delta}{1-\delta}} \leq \frac{r}{|x|} \leq |x|^{\delta}$$

and thus

$$\left|\Phi_{|x|}^{\mathrm{HF}}(x) - \Phi_{|x|}^{\mathrm{TF}}(x)\right| \leq (\mathrm{Const.}) \left(|x|^{-4+\zeta\delta} + |x|^{-4+\frac{1}{36}-\frac{73\delta}{9(1-\delta)}}\right).$$

It follows that if δ is small enough there exist $\varepsilon, C_\Phi' > 0$ such that (86) is satisfied.

$\square$

13 Proving the main results Theorems 1.4, 1.5, 3.6, and 3.8

The main result Theorem 3.6 on the maximal number of electrons N is a simple consequence of Lemma 10.5 and Theorem 10.1.

Proof of Theorem 3.6. We may of course assume that $N \geq Z$ and that $Z \geq 1$ (otherwise the result follows from Lieb's bound Theorem 3.5). Then $\int \rho^{\mathrm{TF}} = Z$. We can then use Lemma 10.5 with R chosen so small that $C_M \leq C_\Phi R^{-4+\varepsilon}$, because then (85) holds with $\sigma = 2C_\Phi$ and $\varepsilon' = \varepsilon$. We conclude from Lemma 10.5 that

$$\int \rho^{\mathrm{HF}} \leq \int_{|x|<R} \rho^{\mathrm{TF}}(x)\,dx + \sigma R^{-3+\varepsilon'} + (\mathrm{Const.})(1+\sigma R^{\varepsilon'})(1+R^{-3}) \leq Z + (\mathrm{Const.}),$$

since now R, σ, and ε' are universal constants. We have thus concluded the result of Theorem 3.6. $\square$

The asymptotics of the radius of an infinite atom given in Theorem 1.5 is a simple consequence of the main estimate Theorem 10.1 and the Sommerfeld asymptotics.

Proof of Theorem 1.5. Note that in the neutral case $N = Z$ we have from the main estimate Theorem 10.1 that

$$\begin{aligned}
\left|\int_{|x|>R} \rho^{\mathrm{TF}}(x) - \rho^{\mathrm{HF}}(x)\,dx\right| &= \left|\int_{|x|<R} \rho^{\mathrm{HF}}(x) - \rho^{\mathrm{TF}}(x)\,dx\right| \\
&= \left|(4\pi)^{-1} R \int_{\mathcal{S}^2} \Phi_R^{\mathrm{TF}}(R\omega) - \Phi_R^{\mathrm{HF}}(R\omega)\,d\omega\right| \\
&\leq C_\Phi R^{-3+\varepsilon} + C_M R.
\end{aligned}$$

Theorem 1.5 now easily follows from TF equation (6) and the Sommerfeld laws Theorem 5.2 and 5.4 for the case $N = Z$, i.e., $\mu^{\mathrm{TF}} = 0$. $\square$

The potential estimate in Theorem 1.4 is somewhat more difficult to prove.

Proof of Theorem 1.4. As in the proof of the main estimate Theorem 10.1 we separately treat small $|x|$, intermediate $|x|$, and large $|x|$.

We first consider small $|x|$. Note that

$$\varphi^{\mathrm{HF}}(x) - \varphi^{\mathrm{TF}}(x) = \int (\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))\,|x-y|^{-1} dy.$$

Thus using the Coulomb norm estimate (82) we obtain

$$\begin{aligned}
&\left|\int (\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y))\,|x-y|^{-1} dy\right| \\
&\leq (\mathrm{Const.}) s^{1/5} \max\left\{\|\rho^{\mathrm{TF}}\|_{L^{5/3}(B(x,s))}, \|\rho^{\mathrm{HF}}\|_{L^{5/3}(B(x,s))}\right\} \\
&\quad +(\mathrm{Const.}) s^{-1/2} \|\,(\rho^{\mathrm{TF}} - \rho^{\mathrm{HF}})\,\|_{\mathrm{C}}.
\end{aligned}$$

If we use Lemma 11.1 and optimize in s we arrive at

$$|\varphi^{\mathrm{HF}}(x) - \varphi^{\mathrm{TF}}(x)| \leq (\mathrm{Const.}) Z^{4/3-\varepsilon_3} \leq (\mathrm{Const.})|x|^{-4+3\varepsilon_3-4\delta+3\delta\varepsilon_3} \tag{140}$$

for some universal ε_3, if $|x|^{1+\delta} < \beta_0 Z^{-1/3}$.

We now turn to intermediate $|x|$. We shall choose a $D > 0$ such that, with the notation of Theorem 10.1, we have $C_M \leq C_\Phi D^{-4+\varepsilon}$. Then by Theorem 10.1 we have that (85) holds for all $|x| \leq D$ with $\sigma = 2C_\Phi$ and $\varepsilon' = \varepsilon$. We may now assume that $D \leq 1$ and that D is smaller than the values for D in Lemmas 12.5 and 12.6 corresponding to the above choices of σ and ε'.

Consider

$$(\beta_0 Z^{-1/3})^{\frac{1}{1+\delta}} \leq |x| < D^{\frac{1}{1+\delta}}.$$

Set $r = |x|^{1+\delta}$. Then $|x| \geq r$ and $\beta_0 Z^{-1/3} \leq r \leq D$. We shall use the notation from Section 12. We write

$$\varphi^{\mathrm{HF}}(x) - \varphi^{\mathrm{TF}}(x) = \varphi^{\mathrm{HF}}(x) - \varphi_r^{\mathrm{OTF}}(x) + \varphi_r^{\mathrm{OTF}}(x) - \varphi^{\mathrm{TF}}(x).$$

The difference between the last two terms was defined in (98) to be $\mathcal{A}_1(r, x)$ and this was estimated in Lemma 12.5.

We have

$$\varphi^{\mathrm{HF}}(x) - \varphi_r^{\mathrm{OTF}}(x) = \int \left(\rho_r^{\mathrm{OTF}}(y) - \chi_r^+(y)\rho^{\mathrm{HF}}(y)\right) |x-y|^{-1} dy.$$

Exactly as above, for small $|x|$, we now use Theorem 10.1, Lemma 12.6 and the Coulomb norm estimate (82) to conclude that

$$|\varphi^{\mathrm{HF}}(x) - \varphi_r^{\mathrm{OTF}}(x)| \leq (\mathrm{Const.}) r^{-4+\frac{1}{21}} \leq (\mathrm{Const.})|x|^{\left(-4+\frac{1}{21}\right)(1+\delta)},$$

If we combine this with (124) from Lemma 12.5 we obtain

$$|\varphi^{\mathrm{HF}}(x) - \varphi^{\mathrm{TF}}(x)| \leq (\mathrm{Const.}) \left(|x|^{-4+\zeta\delta} + |x|^{\left(-4+\frac{1}{21}\right)(1+\delta)}\right). \tag{141}$$

Combining (140) and (141) we see that by choosing δ small enough we have proved (10) for all $|x| \leq D^{\frac{1}{1+\delta}}$.

We turn to $|x| \geq D^{\frac{1}{1+\delta}}$, i.e., $|x|$ greater than some universal constant. Here we may write

$$|\varphi^{\mathrm{HF}}(x) - \varphi^{\mathrm{TF}}(x)| \leq \left|\Phi_{|x|}^{\mathrm{HF}}(x) - \Phi_{|x|}^{\mathrm{TF}}(x)\right| + \left|\int_{|y|>|x|} \left(\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y)\right) |x-y|^{-1} dy\right|.$$

The first term is controlled by the main estimate Theorem 10.1. If we use that according to Lemma 10.4 we have $\int_{|y|>|x|} \rho^{\mathrm{HF}}(y)^{5/3}dy \leq (\mathrm{Const.})$ and that the same estimate holds for the TF density (see Lemma 12.1) we may estimate the second term above as follows. Using Hölder's inequality we have

$$\begin{aligned}\left|\int\limits_{|x|<|y|}(\rho^{\mathrm{TF}}(y)-\rho^{\mathrm{HF}}(y))\,|x-y|^{-1}dy\right| &\leq (\mathrm{Const.})\left(\int_{|x-y|<1}|x-y|^{-5/2}dy\right)^{2/5}\\ &\quad+\int_{|x|<|y|}(\rho^{\mathrm{TF}}(y)+\rho^{\mathrm{HF}}(y))\,dy \leq (\mathrm{Const.}),\end{aligned}$$

where the last estimate follows from Lemma 10.5. □

We end the paper by giving the proof of the bound on the ionization energy in Theorem 3.8

Proof of Theorem 3.8. Since the HF energy is a non-increasing function of N we have that $0 \leq E^{\mathrm{HF}}(Z-1,Z) - E^{\mathrm{HF}}(Z,Z)$. In order to prove an upper bound we shall construct a trial density matrix γ for $\mathcal{E}^{\mathrm{HF}}$ with $\mathrm{Tr}[\gamma] \leq Z-1$. We then clearly have that $\mathcal{E}^{\mathrm{HF}}[\gamma] \geq E^{\mathrm{HF}}(Z-1,Z)$. Let θ_- be given in terms of appropriate $r, \lambda > 0$ as in the beginning of the proof of Theorem 6.2. We then choose as our trial matrix

$$\gamma_-^{\mathrm{HF}} = \theta_-\gamma^{\mathrm{HF}}\theta_-,$$

where γ^{HF} is the HF minimizer with $\mathrm{Tr}\left[\gamma^{\mathrm{HF}}\right] = Z$. According to the definition of θ_- we have

$$\mathrm{Tr}\left[\gamma_-^{\mathrm{HF}}\right] \leq Z - \int_{|y|>r} \rho^{\mathrm{HF}}(y)dy.$$

We choose $\lambda = 1/2$. Let $R > 0$ be such that $C_M = C_\Phi R^{-4+\varepsilon}$. We shall now choose r satisfying $r \leq R$. Then according to Theorem 10.1 we have that (85) holds for $|x| \leq r$ with $\sigma = 2C_\Phi$ and $\varepsilon' = \varepsilon$. From Lemma 10.5 we therefore conclude that

$$\begin{aligned}\int_{|y|>r}\rho^{\mathrm{HF}}(y)dy &= \int\rho^{\mathrm{HF}} - \int_{|y|<r}\rho^{\mathrm{HF}}(y)dy\\ &= \int_{|y|<r}\rho^{\mathrm{TF}}(y) - \rho^{\mathrm{HF}}(y)\,dy + \int_{|y|>r}\rho^{\mathrm{TF}}(y)\,dy\\ &\geq \int_{|y|>r}\rho^{\mathrm{TF}}(y)\,dy - (\mathrm{Const.})r^{-3+\varepsilon}\end{aligned}$$

where we have used that $\int \rho^{\mathrm{HF}} = \int \rho^{\mathrm{TF}} = Z$.

We may of course assume that Z is larger than some fixed universal constant. For Z less than a universal constant, the total energy $E^{\mathrm{HF}}(Z,Z)$ and hence the ionization energy $E^{\mathrm{HF}}(Z-1,Z) - E^{\mathrm{HF}}(Z,Z)$ are bounded by universal constants (see Theorem 3.2). We can therefore assume that $\beta_0 Z^{-1/3} < R$ and we shall choose $\beta_0 Z^{-1/3} < r$. It then follows from Theorem 5.4, the TF equation (6) (recall that we consider the case $\mu^{\mathrm{TF}} = 0$ and $N = Z$) that $\rho^{\mathrm{TF}}(y) \geq (\mathrm{Const.})|y|^{-6}$ for all $|y| \geq r$. Hence

$$\int_{|y|>r} \rho^{\mathrm{HF}}(y)dy \;\;\geq\;\; (\mathrm{Const.})r^{-3} - (\mathrm{Const.})r^{-3+\varepsilon}.$$

Thus we may choose r to be a small enough universal number (assuming that Z is large enough to allow $\beta_0 Z^{-1/3} < r$) to ensure that $\int_{|y|>r} \rho^{\mathrm{HF}}(y)dy \geq 1$ and hence that $\mathrm{Tr}\left[\gamma_-^{\mathrm{HF}}\right] \leq Z - 1$.

From the estimate (53) in the proof of Theorem 6.2 we have

$$\mathcal{E}^{\mathrm{HF}}\left[\gamma_-^{\mathrm{HF}}\right] \leq \mathcal{E}^{\mathrm{HF}}\left[\gamma^{\mathrm{HF}}\right] - \mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] + \mathcal{R} = E^{\mathrm{HF}}(Z,Z) - \mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] + \mathcal{R}$$

where as before $\gamma_r^{\mathrm{HF}} = \theta_r \gamma^{\mathrm{HF}} \theta_r$, $\mathcal{R}$ is given in (51), and the functional $\mathcal{E}^{\mathrm{A}}$ was defined in (49).

It remains to prove that

$$-\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] + \mathcal{R} \leq (\mathrm{Const.}). \tag{142}$$

As in (136) we conclude that $\mathcal{R} \leq (\mathrm{Const.})r^{-5} \leq (\mathrm{Const.})$, where we have used that r is a universal constant.

In order to estimate $\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right]$ we note that, since $\Phi_r^{\mathrm{HF}}(y)$ is harmonic for $|y| > r$ and tends to 0 at infinity, we have that for all $|y| \geq r$

$$\begin{aligned}
\Phi_r^{\mathrm{HF}}(y) \leq |y|^{-1} r \sup_{|x|=r} \Phi_r^{\mathrm{HF}}(x) \;\;&\leq\;\; |y|^{-1} r \sup_{|x|=r} |\Phi_r^{\mathrm{TF}}(x)| + |y|^{-1}\left(C_\Phi r^{-3+\varepsilon} + rC_M\right) \\
&\leq\;\; (\mathrm{Const.})r^{-3}|y|^{-1},
\end{aligned}$$

where we have used the main estimate Theorem 10.1 and the bound on Φ_r^{TF} in Lemma 5.5 with $\mu^{\mathrm{TF}} = 0$. If we use that r is some universal constant we get

$$\Phi_r^{\mathrm{HF}}(y) \leq (\mathrm{Const.})|y|^{-1}.$$

Using the Lieb-Thirring inequality (21) we see from the definition (49) of the auxiliary functional $\mathcal{E}^{\mathrm{A}}$ that

$$\begin{aligned}\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] \;\geq\; & K_1 \int \rho_r^{\mathrm{HF}}(y)^{5/3} dy - (\text{Const.}) \int \frac{\rho_r^{\mathrm{HF}}(y)}{|y|} dy \\ & + \tfrac{1}{2} \iint \rho_r^{\mathrm{HF}}(x)|x-y|^{-1}\rho_r^{\mathrm{HF}}(y) dx\, dy.\end{aligned}$$

Here again $\rho_r^{\mathrm{HF}} = \theta_r^2 \rho^{\mathrm{HF}}$ is the density corresponding to γ_r^{HF}. It follows from standard atomic TF theory that

$$\inf_{\rho \geq 0} \left\{ K_1 \int \rho(y)^{5/3} dy - (\text{Const.}) \int \frac{\rho(y)}{|y|} dy + \tfrac{1}{2} \iint \rho(x)|x-y|^{-1}\rho(y) dx\, dy \right\}$$

is some universal constant. Hence $\mathcal{E}^{\mathrm{A}}\left[\gamma_r^{\mathrm{HF}}\right] \geq -(\text{Const.})$ and we have proved (142). $\square$

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