Excess Charge for Pseudo-Relativistic Atoms in Hartree-Fock Theory

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Abstract. We prove within the Hartree-Fock theory of pseudo-relativistic atoms that the maximal negative ionization charge and the ionization energy of an atom remain bounded independently of the nuclear charge Z and the fine structure constant α as long as $Z\alpha$ is bounded.

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1 Introduction

A long standing open problem in the mathematical physics literature is the Ionization conjecture. It can be formulated as follows. Consider atoms with arbitrarily large nuclear charge Z, is it true that the radius (see Definition 1.8) and the maximal negative ionization remain bounded? A positive answer to this question in the non-relativistic Hartree-Fock model has been given by the second author in [23]. One of the aims of the present paper is to extend the result taking into account some relativistic effects. The ionization conjecture for the full Schrödinger theory is still open both in the non-relativistic and relativistic case. See [13], [16], [17], [6], [7] and [22] for some Z-dependent bounds on the maximal negative ionization. The best result is that $N(Z) = Z + O(Z^a)$ with $a = 47/56$ where $N(Z)$ denotes the maximal number of electrons a nucleus of charge Z binds (see [6], [7] and [22]) .

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As a model for an atom with nuclear charge Z and N electrons we consider (in units where $\hbar = m = e = 1$) the operator

$$H = \sum_{i=1}^{N} \alpha^{-1}\big(\sqrt{-\Delta_i + \alpha^{-2}} - \alpha^{-1} - \frac{Z\alpha}{|\mathbf{x}_i|}\big) + \sum_{1\le i<j\le N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}, \qquad (1)$$

where α is Sommerfeld's fine structure constant. The operator H acts on a dense subset of the N body Hilbert space $\mathcal{H}_F := \wedge_{i=1}^{N} L^2(\mathbb{R}^3;\mathbb{C}^q)$ of antisymmetric wave functions, where q is the number of spin states. The operator H is bounded from below on this subspace if $Z\alpha \le 2/\pi$ (see [9] for $N = 1$, [5] and [19] for $N \ge 1$). In this paper we will consider the sub-critical case $Z\alpha < 2/\pi$. Let us notice here that to define the operator H there is an issue. Indeed for $Z\alpha < 2/\pi$ the nuclear potential is only a small form perturbation of the kinetic energy and hence one needs to work with forms to define the operator H. This has been done in detail in [2].
The quantum ground state energy is the infimum of the spectrum of H considered as an operator acting on $\mathcal{H}_F$. In the Hartree-Fock approximation one restricts to wave-functions ψ which are pure wedge products, also called Slater determinants:

$$\psi(\mathbf{x}_1,\sigma_1,\mathbf{x}_2,\sigma_2,\ldots,\mathbf{x}_N,\sigma_N) = \tfrac{1}{\sqrt{N!}}\det(u_i(\mathbf{x}_j,\sigma_j))_{i,j=1}^{N}, \qquad (2)$$

with $\{u_i\}_{i=1}^{N}$ orthonormal in $L^2(\mathbb{R}^3;\mathbb{C}^q)$. The u_i's are also called orbitals. Notice that $\|\psi\|_{L^2(\mathbb{R}^{3N},\mathbb{C}^{qN})} = 1$. The Hartree-Fock ground state energy is

$$E^{\mathrm{HF}}(N,Z,\alpha) := \inf\{\mathrm{q}(\psi,\psi)|\psi \in \mathcal{Q}(H) \text{ and } \psi \text{ a Slater determinant}\},$$

with $\mathtt{q}$ the quadratic form defined by H and $\mathcal{Q}(H)$ the corresponding form domain.
One of the main result of the paper is the following.

THEOREM 1.1. *Let $Z \ge 1$ and $\alpha > 0$. Let $Z\alpha = \kappa$ and assume that $0 \le \kappa < 2/\pi$. There is a constant $Q > 0$ depending only on κ such that if N is such that a Hartree-Fock minimizer exists then $N \le Z + Q$.*[2]

The idea of the proof is the same as in [23]. One shows that the Thomas-Fermi model is a good approximation of the Hartree-Fock model except in the region far away from the nucleus. We first introduce some notation in order to introduce the Hartree-Fock and Thomas-Fermi models.

[2] In order to prove this result we need that $N < CZ$ for a positive constant C. We do not include a proof of this fact here for simplicity and since a much stronger result has been proved by Lieb in [13] for $\alpha Z < 1/2$. The needed extension of this result of Lieb to $\alpha Z < 2/\pi$ will appear in [3] (see Theorem 1.6 below).

1.1 NOTATION

Let e be the quadratic form with domain $H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^q)$ such that

$$\mathrm{e}(u, v) = (E(\mathbf{p})^{\frac{1}{2}}u, E(\mathbf{p})^{\frac{1}{2}}v) \text{ for all } u, v \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^q), \tag{3}$$

where $E(\mathbf{p})$ denotes the operator $E(i\nabla) = \sqrt{-\Delta + \alpha^{-2}}$. As usual (u, v) denotes the scalar product of u and v in $L^2(\mathbb{R}^3, \mathbb{C}^q)$. Let $V(\mathbf{x}) := Z\alpha/|\mathbf{x}|$ and v be the quadratic form with domain $H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^q)$ defined by

$$\mathrm{v}(u, v) = (V^{\frac{1}{2}}u, V^{\frac{1}{2}}v) \text{ for all } u, v \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^q). \tag{4}$$

From [10, 5.33 p.307] we have

$$\int_{\mathbb{R}^3} \frac{|f(\mathbf{x})|^2}{|\mathbf{x}|} \, d\mathbf{x} \leq \frac{2}{\pi} \int_{\mathbb{R}^3} |\mathbf{p}||\hat{f}(\mathbf{p})|^2 \, d\mathbf{p} \text{ for } f \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}) \tag{5}$$

with $\hat{f}$ the Fourier transform of f. Thus since $Z\alpha \leq 2/\pi$ and $E(\mathbf{p}) \geq |\mathbf{p}|$ it follows that $\mathrm{v}(u, u) \leq \mathrm{e}(u, u)$ for all $u \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^q)$.
In the following t denotes the quadratic form associated to the kinetic energy; i.e. for all $u, v \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^q)$

$$\mathrm{t}(u, v) := \alpha^{-1}\mathrm{e}(u, v) - \alpha^{-2}(u, v) = \alpha^{-1}(T(\mathbf{p})^{\frac{1}{2}}u, T(\mathbf{p})^{\frac{1}{2}}v), \tag{6}$$

with $T(\mathbf{p}) := E(\mathbf{p}) - \alpha^{-1}$.
A *density matrix* γ is a self-adjoint trace class operator that satisfies the operator inequality $0 \leq \gamma \leq Id$. A density matrix $\gamma : L^2(\mathbb{R}^3; \mathbb{C}^q) \to L^2(\mathbb{R}^3; \mathbb{C}^q)$ has an integral kernel

$$\gamma\,(\mathbf{x}, \sigma, \mathbf{y}, \tau) = \sum_j \lambda_j u_j(\mathbf{x}, \sigma) u_j(\mathbf{y}, \tau)^*, \tag{7}$$

where λ_j, u_j are the eigenvalues and corresponding eigenfunctions of γ. We choose the u_j's to be orthonormal in $L^2(\mathbb{R}^3, \mathbb{C}^q)$. Let $\rho_\gamma \in L^1(\mathbb{R}^3)$ denote the 1-particle density associated to γ given by

$$\rho_\gamma(\mathbf{x}) = \sum_{\sigma=1}^{q} \sum_j \lambda_j |u_j(\mathbf{x}, \sigma)|^2.$$

We define

$$\mathcal{A} := \{\gamma \text{ density matrix: } \operatorname{Tr}[T(\mathbf{p})\gamma] < +\infty\}, \tag{8}$$

where for $\gamma \in \mathcal{A}$ written as in (7) $\operatorname{Tr}[T(\mathbf{p})\gamma] := \operatorname{Tr}[E(\mathbf{p})\gamma] - \alpha^{-1} \operatorname{Tr}[\gamma]$ and

$$\operatorname{Tr}[E(\mathbf{p})\gamma] := \sum_j \lambda_j \mathrm{e}(u_j, u_j). \tag{9}$$

Similarly we use the following notation $\operatorname{Tr}[V\gamma] := \sum_j \lambda_j \mathrm{v}(u_j, u_j)$.

REMARK 1.2. *If $\gamma \in \mathcal{A}$ then $\rho_\gamma \in L^1(\mathbb{R}^3)$ since γ is trace class and $\rho_\gamma \in L^{4/3}(\mathbb{R}^3)$. The second inclusion follows from Daubechies' inequality, a generalization of the Lieb-Thirring inequality (see Theorem 2.3).*

1.2 Hartree-Fock theory

In Hartree-Fock theory one considers wave functions that are pure wedge products and that satisfy the right statistics: determinantal wave functions as in (2). To define the HF-energy functional it is convenient to use the one to one correspondence between Slater determinants and projections onto finite dimensional subspaces of $L^2(\mathbb{R}^3, \mathbb{C}^q)$. Indeed if ψ is given by (2) and γ is the projection onto the space spanned by $u_1, \ldots, u_N$ the energy expectation depends only on γ: $(\psi, H\psi) = \mathcal{E}^{\mathrm{HF}}(\gamma)$. Here $\mathcal{E}^{\mathrm{HF}}$ defines the HF-energy functional

$$\mathcal{E}^{\mathrm{HF}}(\gamma) = \alpha^{-1}\,\mathrm{Tr}[(T(\mathbf{p}) - V)\gamma] + \mathcal{D}(\gamma) - \mathcal{E}x\,(\gamma)\,, \tag{10}$$

where $\mathcal{D}(\gamma)$ is the direct Coulomb energy

$$\mathcal{D}(\gamma) = \tfrac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{x})\rho_\gamma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y},$$

and $\mathcal{E}x(\gamma)$ is the exchange Coulomb energy

$$\mathcal{E}x(\gamma) = \tfrac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\mathrm{Tr}_{\mathbb{C}^q}\left[|\gamma(\mathbf{x},\mathbf{y})|^2\right]}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y},$$

where we think of the integral kernel $\gamma(x, y)$ as a $q \times q$ matrix.
Using projections we can define as follows the HF-ground state.

Definition 1.3 (The HF-ground state). *Let $Z > 0$ be a real number and $N \geq 0$ be an integer. The HF-ground state energy is*

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

If a minimizer exists we say that the atom has a HF ground state described by γ^{HF}.

We may extend the definition of the HF-functional from projections to density matrices in $\mathcal{A}$. We first notice that if $\gamma \in \mathcal{A}$, then all the terms in $\mathcal{E}^{\mathrm{HF}}(\gamma)$ are finite. From (5) it follows that

$$\mathrm{Tr}[V\gamma] = \sum_j \lambda_j \mathrm{v}(u_j, u_j) \leq \sum_j \lambda_j \mathrm{e}(u_j, u_j) = \mathrm{Tr}[E(\mathbf{p})\gamma].$$

On the other hand if $\gamma \in \mathcal{A}$ then $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^{\frac{4}{3}}(\mathbb{R}^3)$ (see Remark 1.2). By Hölder's inequality $\rho_\gamma \in L^{\frac{6}{5}}(\mathbb{R}^3)$ and hence $\mathcal{D}(\gamma)$ is bounded by Hardy-Littlewood-Sobolev's inequality. The boundness of the exchange term follows from $0 \leq \mathcal{E}x(\gamma) \leq \mathcal{D}(\gamma)$. On the other hand if γ is a density matrix with $\gamma \notin \mathcal{A}$ then $\mathcal{E}^{\mathrm{HF}}(\gamma) = \infty$. Here we use also that $Z\alpha < 2/\pi$.
Extending the set where we minimize, we could have lowered the ground state energy and/or changed the minimizer. That this is not the case follows from Lieb's variational principle.

Theorem 1.4 (Lieb's variational principle, [12]). *For all N non-negative integers it holds that*

$$\inf\{\mathcal{E}^{\mathrm{HF}}(\gamma) : \gamma \in \mathcal{A},\ \gamma^2 = \gamma,\ \mathrm{Tr}[\gamma] = N\} = \inf\{\mathcal{E}^{\mathrm{HF}}(\gamma) : \gamma \in \mathcal{A},\ \mathrm{Tr}[\gamma] = N\},$$

and if the infimum over all density matrices is attained so is the infimum over projections.

The following existence theorem for the HF-minimizer in the pseudo-relativistic case has been recently proved in [2].

Theorem 1.5. *Let $Z\alpha < 2/\pi$ and let $N \geq 2$ be a positive integer such that $N < Z + 1$.*
Then there exists an N-dimensional projection $\gamma^{\mathrm{HF}} = \gamma^{\mathrm{HF}}(N, Z, \alpha)$ minimizing the HF-energy functional $\mathcal{E}^{\mathrm{HF}}$ given by (10), that is, $E^{\mathrm{HF}}(N, Z, \alpha)$ is attained. Moreover, one can write

$$\gamma^{\mathrm{HF}}(\mathbf{x}, \sigma, \mathbf{y}, \tau) = \sum_{i=1}^{N} u_i(\mathbf{x}, \sigma) u_i(\mathbf{y}, \tau)^*,$$

with $u_i \in L^2(\mathbb{R}^3, \mathbb{C}^q)$, $i = 1, \ldots, N$, orthonormal, such that the HF-orbitals $\{u_i\}_{i=1}^N$ satisfy:

1. $h_{\gamma^{\mathrm{HF}}} u_i = \varepsilon_i u_i$, *with* $0 > \varepsilon_N \geq \varepsilon_{N-1} \geq \cdots \geq \varepsilon_1 > -\alpha^{-1}$ *and*

$$h_{\gamma^{\mathrm{HF}}} := T(\mathbf{p}) - \frac{Z\alpha}{|\mathbf{x}|} + \rho^{\mathrm{HF}} * |\mathbf{x}|^{-1} - \mathcal{K}_{\gamma^{\mathrm{HF}}}, \tag{11}$$

where ρ^{HF} denotes the density of the HF-minimizer and for $f \in H^{\frac{1}{2}}(\mathbb{R}^3)$

$$(\mathcal{K}_{\gamma^{\mathrm{HF}}} f)(\mathbf{x}, \sigma) = \sum_{i=1}^{N} u_i(\mathbf{x}, \sigma) \sum_{\tau=1}^{q} \int_{\mathbb{R}^3} u_i(\mathbf{y}, \tau)^* f(\mathbf{y}, \tau) |\mathbf{x} - \mathbf{y}|^{-1} d\mathbf{y}.$$

2. $u_i \in C^\infty(\mathbb{R}^3 \setminus \{0\}, \mathbb{C}^q)$ *for* $i = 1, \ldots, N$;
3. $u_i \in H^1(\mathbb{R}^3 \setminus B_R(0))$ *for all* $R > 0$ *and* $i = 1, \ldots, N$.

In the opposite direction the following result gives an upper bound on the excess charge.

Theorem 1.6. *Let $\alpha Z < \frac{2}{\pi}$. If N is a positive integer such that $N > 2Z + 1$ there are no minimizers for the HF-energy functional.*

This theorem for $Z\alpha < 1/2$ was proved by Lieb in [13]. With an improved approximation argument the proof can be extended to $Z\alpha < 2/\pi$ (see [3]). Notice that both proofs work not only in the Hartree-Fock approximation but for the minimization problem on $\wedge^N L^2(\mathbb{R}^3)$.

Definition 1.7. *Let γ^{HF} be the HF-minimizer. The function*

$$\varphi^{\mathrm{HF}}(\mathbf{x}) := \frac{Z}{|\mathbf{x}|} - \int_{\mathbb{R}^3} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \textit{ for } \mathbf{x} \in \mathbb{R}^3,$$

is called the HF-mean field potential and

$$\Phi_R^{\mathrm{HF}}(\mathbf{x}) := \frac{Z}{|\mathbf{x}|} - \int_{|\mathbf{y}|<R} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \textit{ for } \mathbf{x} \in \mathbb{R}^3,$$

is the HF-screened nuclear potential.

Definition 1.8. *We define the HF-radius $R_{Z,N}^{\mathrm{HF}}(\nu)$ to the ν last electrons by*

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

1.3 A bit of Thomas-Fermi theory

In this subsection we present briefly the Thomas-Fermi theory and especially the result that will be used in the rest of the paper. We refer the interested reader to [11].

Let U be a potential in $L^{5/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ with

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

Then the TF-energy functional is defined by

$$\mathcal{E}_U^{\mathrm{TF}}(\rho) = \tfrac{3}{10}(\tfrac{6\pi^2}{q})^{\frac{2}{3}} \int_{\mathbb{R}^3} \rho(\mathbf{x})^{\frac{5}{3}} d\mathbf{x} - \int_{\mathbb{R}^3} U(\mathbf{x})\rho(\mathbf{x}) d\mathbf{x} + \tfrac{1}{2} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y},$$

on non-negative functions $\rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$. As before, q denotes the number of spin states.

We recall some properties of the TF-model, see [18].

Theorem 1.9. *Let U be as above. For all $N' \geq 0$ there exists a unique non-negative $\rho_U^{\mathrm{TF}} \in L^{5/3}(\mathbb{R}^3)$ such that $\int \rho_U^{\mathrm{TF}} \leq N'$ and*

$$\mathcal{E}_U^{\mathrm{TF}}(\rho_V^{\mathrm{TF}}) = \inf\{\mathcal{E}_U^{\mathrm{TF}}(\rho) : \rho \in L^{5/3}(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \rho(\mathbf{x})\, d\mathbf{x} \leq N'\}.$$

There exists a unique chemical potential $\mu_U^{\mathrm{TF}}(N')$, with $0 \leq \mu_U^{\mathrm{TF}}(N') \leq \sup U$, such that ρ_U^{TF} is uniquely characterized by

$$\begin{aligned} &\mathcal{E}_U^{\mathrm{TF}}(\rho_U^{\mathrm{TF}}) + \mu_U^{\mathrm{TF}}(N') \int_{\mathbb{R}^3} \rho_U^{\mathrm{TF}}(\mathbf{x})\, d\mathbf{x} \\ = \ &\inf\{\mathcal{E}_U^{\mathrm{TF}}(\rho) + \mu_U^{\mathrm{TF}}(N') \int_{\mathbb{R}^3} \rho(\mathbf{x})\, d\mathbf{x} : 0 \leq \rho \in L^{5/3}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)\}. \end{aligned}$$

Moreover $\rho_U^{\rm TF}$ *is the unique solution in* $L^{5/3}(\mathbb{R}^3)\cap L^1(\mathbb{R}^3)$ *to the TF-equation*

$$\tfrac{1}{2}(\tfrac{6\pi^2}{q})^{\frac{2}{3}}(\rho_U^{\rm TF}(\mathbf{x}))^{\frac{2}{3}} = \big[U(\mathbf{x}) - \rho_U^{\rm TF} * |\mathbf{x}|^{-1} - \mu_U^{\rm TF}(N')\big]_+ .$$

If $\mu_U^{\rm TF}(N')>0$ *then* $\int \rho_U^{\rm TF} = N'$. *For all* $\mu>0$ *there is a unique minimizer* $0\le\rho\in L^{5/3}(\mathbb{R}^3)\cap L^1(\mathbb{R}^3)$ *to* $\mathcal{E}_U^{\rm TF}(\rho)+\mu\int\rho$.

One defines the *TF-mean field potential* $\varphi_U^{\rm TF}$, the *TF-screened nuclear potential* $\Phi_{U,R}^{\rm TF}$ and the TF-radius $R_{N,Z}^{\rm TF}(\nu)$ to the ν last-electron similarly as in Definitions 1.7 and 1.8 replacing the HF-density with the TF-density.

Theorem 1.10. *If* $U(\mathbf{x})=Z/|\mathbf{x}|$ *(the Coulomb potential), then the minimizer of* $\mathcal{E}_U^{\rm TF}$, *under the condition* $\int\rho\le N$, *exists for every* N. *Moreover,* $\mu_U^{\rm TF}(N)=0$ *if and only if* $N\ge Z$.

When $U(\mathbf{x})=Z/|\mathbf{x}|$ we denote the minimizer of the TF-functional, under the condition $\int\rho\le Z$, simply by $\rho^{\rm TF}$ and $\int\rho^{\rm TF}=Z$. Correspondingly $\varphi^{\rm TF}$ and $\Phi_R^{\rm TF}$ denote, respectively, its mean field and screened nuclear potential. With this notation

$$\mathcal{E}^{\rm TF}(\rho^{\rm TF}) = -e_0 Z^{\frac{7}{3}}, \tag{12}$$

where e_0 is the total binding energy of a neutral TF-atom of unit nuclear charge. We recall here a result due to Sommerfeld on the asymptotic behavior of the TF-mean field potential, see [23, Th. 4.6].

Theorem 1.11 (Sommerfeld asymptotics). *Assume that the potential* U *is continuous and harmonic for* $|\mathbf{x}|>R$ *and that it satisfies* $\lim_{|\mathbf{x}|\to\infty}U(\mathbf{x})=0$. *Consider the corresponding TF-mean field potential* $\varphi_U^{\rm TF}$ *and assume that* $\mu_U^{\rm TF} < \liminf\limits_{r\searrow R}\inf\limits_{|\mathbf{x}|=r}\varphi_U^{\rm TF}(\mathbf{x})$. *With* $\zeta=(-7+\sqrt{73})/2$ *define*

$$\begin{aligned} a(R) &:= \liminf_{r\searrow R}\sup_{|\mathbf{x}|=r}\Big[\Big(\frac{\varphi_U^{\rm TF}(\mathbf{x})}{3^4 2^{-1}q^{-2}\pi^2 r^{-4}}\Big)^{-\frac{1}{2}}-1\Big]r^{\zeta}\\ A(R,\mu_U^{\rm TF}) &:= \liminf_{r\searrow R}\sup_{|\mathbf{x}|=r}\Big[\frac{\varphi_U^{\rm TF}(\mathbf{x})-\mu_U^{\rm TF}}{3^4 2^{-1}q^{-2}\pi^2 r^{-4}}-1\Big]r^{\zeta}. \end{aligned}$$

Then we find for all $|\mathbf{x}|>R$

$$\begin{aligned} \varphi_U^{\rm TF}(\mathbf{x}) &\le \tfrac{3^4\pi^2}{2q^2}(1+A(R,\mu_U^{\rm TF})|\mathbf{x}|^{-\zeta})|\mathbf{x}|^{-4}+\mu_U^{\rm TF} \quad \textit{and}\\ \varphi_U^{\rm TF}(\mathbf{x}) &\ge \max\Big\{\tfrac{3^4\pi^2}{2q^2}(1+a(R)|\mathbf{x}|^{-\zeta})^{-2}|\mathbf{x}|^{-4},\nu(\mu_U^{\rm TF})|\mathbf{x}|^{-1}\Big\}, \end{aligned}$$

where

$$\nu(\mu_U^{\rm TF}) := \inf_{|\mathbf{x}|\ge R}\max\big\{\tfrac{3^4\pi^2}{2q^2}(1+a(R)|\mathbf{x}|^{-\zeta})^{-2}|\mathbf{x}|^{-3},\mu_U^{\rm TF}|\mathbf{x}|\big\}.$$

For easy reference we give here the estimate on the TF-mean field potential corresponding to the Coulomb potential.

Theorem 1.12 (Atomic Sommerfeld estimate, [23, Thm 5.2-5.4]). *The atomic TF-mean field potential satisfies the bound*

$$\frac{Z}{|\mathbf{x}|} - \min\left\{\frac{Z}{|\mathbf{x}|}, \frac{Z^{\frac{4}{3}}}{2\beta_0}\right\} \leq \varphi^{\mathrm{TF}}(\mathbf{x}) \leq \min\left\{\tfrac{3^4\pi^2}{2q^2}\frac{1}{|\mathbf{x}|^4}, \frac{Z}{|\mathbf{x}|}\right\}, \tag{13}$$

with $2\beta_0 = \pi^{\frac{2}{3}}3^{-\frac{5}{3}}2^{-\frac{1}{3}}q^{-\frac{2}{3}}$, *and for* $|\mathbf{x}| \geq R > 0$

$$\varphi^{\mathrm{TF}}(\mathbf{x}) \geq \tfrac{3^4\pi^2}{2q^2}(1 + a(R)|\mathbf{x}|^{-\zeta})^{-2}|\mathbf{x}|^{-4},$$

where ζ *and* $a(R)$ *are defined in Theorem 1.11.*

Corollary 1.13. *Let* ζ *and* β_0 *be defined as in Theorem 1.11 and 1.12 respectively. Then the TF-mean field potential satisfies the bound*

$$\varphi^{\mathrm{TF}}(\mathbf{x}) \geq \begin{cases} \dfrac{Z}{|\mathbf{x}|} - \dfrac{Z^{\frac{4}{3}}}{2\beta_0} & \text{if } |\mathbf{x}| \leq \beta_0 Z^{-\frac{1}{3}} \\ \dfrac{3^4\pi^2}{2q^2}(1 + aZ^{-\frac{\zeta}{3}}|\mathbf{x}|^{-\zeta})^{-2}|\mathbf{x}|^{-4} & \text{if } |\mathbf{x}| > \beta_0 Z^{-\frac{1}{3}}, \end{cases}$$

with $a = \beta_0^{\zeta}(3^2\pi/(q\beta_0^{\frac{3}{2}}) - 1)$.

Corollary 1.14. *The TF-screened nuclear potential satisfies*

$$\Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x}) \leq \tfrac{3^4 2\pi^2}{q^2}|\mathbf{x}|^{-4} \quad \text{for all } \mathbf{x} \in \mathbb{R}^3.$$

Corollary 1.15. *The following estimate holds*

$$\int_{\mathbb{R}^3} (\rho^{\mathrm{TF}}(\mathbf{x}))^{\frac{5}{3}} d\mathbf{x} \leq 4\tfrac{2^{\frac{2}{3}}}{\pi^2}\tfrac{5}{7}q^{\frac{4}{3}}Z^{\frac{7}{3}}.$$

Proof. By the TF-equation and since $\mu^{\mathrm{TF}} = 0$ we find

$$\int_{\mathbb{R}^3} (\rho^{\mathrm{TF}}(\mathbf{x}))^{\frac{5}{3}} d\mathbf{x} = 2^{\frac{5}{2}}(\tfrac{q}{6\pi^2})^{\frac{5}{3}} \int_{\mathbb{R}^3} (\varphi^{\mathrm{TF}}(\mathbf{x}))^{\frac{5}{2}} d\mathbf{x}.$$

The estimate follows from the atomic Sommerfeld upper bound. □

1.4 Construction and main results

We present the basic idea for the proof of Theorem 1.1. Let us consider an atomic system with $N \geq 2$ fermionic particles and a nucleus of charge $Z \geq 1$ with $Z\alpha = \kappa$ and $0 \leq \kappa < 2/\pi$. We assume that $N \geq Z$ and that N is such that a HF-minimizer exists. That is: there exists a density matrix $\gamma^{\mathrm{HF}} \in \mathcal{A}$ such that $\mathrm{Tr}[\gamma^{\mathrm{HF}}] = N$ and

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

Let ρ^{TF} be the TF-minimizer with potential $U(\mathbf{x}) = Z/|\mathbf{x}|$ and under the condition $\int \rho^{\mathrm{TF}} = Z$. We know that such a minimizer exists and that the corresponding chemical potential is zero (see Theorem 1.10).
Denoting by ρ^{HF} the density of the minimizer γ^{HF}, we find for all $r > 0$

$$\begin{aligned} N &= \int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x}) d\mathbf{x} \\ &= \int_{|\mathbf{x}|<r} \left[\rho^{\mathrm{HF}}(\mathbf{x}) - \rho^{\mathrm{TF}}(\mathbf{x})\right] d\mathbf{x} + \int_{|\mathbf{x}|<r} \rho^{\mathrm{TF}}(\mathbf{x})\, d\mathbf{x} + \int_{|\mathbf{x}|>r} \rho^{\mathrm{HF}}(\mathbf{x})\, d\mathbf{x}. \end{aligned}$$

By the equalities above and since $\int_{|\mathbf{x}|<r} \rho^{\mathrm{TF}}(\mathbf{x}) d\mathbf{x} \leq Z$, Theorem 1.1 follows from the following result.

Theorem 1.16. *There exist $r > 0$ and positive constants c_1 and c_2 independent of N and Z but possibly depending on κ such that*

$$\int_{|\mathbf{x}|<r} \left[\rho^{\mathrm{HF}}(\mathbf{x}) - \rho^{\mathrm{TF}}(\mathbf{x})\right] d\mathbf{x} \leq c_1 \text{ and } \int_{|\mathbf{x}|>r} \rho^{\mathrm{HF}}(\mathbf{x}) d\mathbf{x} \leq c_2.$$

The following theorem is the principal ingredient in the proof of the previous one and is the main technical estimate in the paper.

Theorem 1.17. *Let $Z\alpha = \kappa$, $0 \leq \kappa < 2/\pi$. Assume $N \geq Z \geq 1$.*
Then there exist universal constants $\alpha_0 > 0$, $0 < \varepsilon < 4$ and C_M and C_Φ depending on κ such that for all $\alpha \leq \alpha_0$

$$\left|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})\right| \leq C_\Phi |\mathbf{x}|^{-4+\varepsilon} + C_M.$$

This main estimate is proven by an iterative procedure. We first prove the estimate for small $\mathbf{x}$ (i.e. $|\mathbf{x}| \leq \beta_0 Z^{-\frac{1}{3}}$), then for intermediate $\mathbf{x}$ (i.e. up to a fixed distance independent of Z) and finally for big $\mathbf{x}$.
By proving Theorem 1.17 we also get the following interesting results. The proofs of those are given in Section 5.

Theorem 1.18 (Asymptotic formula for the radius). *Let $Z\alpha = \kappa$, $0 \leq \kappa < 2/\pi$. 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 behave asymptotically as*

$$3^{\frac{4}{3}} \frac{2^{\frac{1}{2}} \pi^{\frac{2}{3}}}{q^{\frac{2}{3}}} \nu^{-\frac{1}{3}} + o(\nu^{-\frac{1}{3}}) \text{ as } \nu \to \infty.$$

Theorem 1.19 (Bound on the ionization energy of a neutral atom). *Let $Z\alpha = \kappa$, $0 \leq \kappa < 2/\pi$ and $Z \geq 1$. The ionization energy of a neutral atom $E^{\mathrm{HF}}(Z-1, Z) - E^{\mathrm{HF}}(Z,Z)$ is bounded by a universal constant.*

Theorem 1.20 (Potential estimate). *Let $Z\alpha = \kappa$, $0 \leq \kappa < 2/\pi$. For all $Z \geq 1$ and N with $N \geq Z$ for which a HF minimizer exists with $\int \rho^{\mathrm{HF}} = N$, we have*

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

with A_0, A_1 and ε_0 universal constants.

2 Prerequisites

In this section we recall some results that will be used in the rest of the paper.
Localization of the kinetic energy. The following is the IMS formula corresponding to the operator $T(\mathbf{p})$.

Theorem 2.1 ([19]). *Let χ_i, $i = 0, \ldots, K$, be real valued Lipschitz continuous functions on $\mathbb{R}^3$ such that $\sum_{i=0}^K \chi_i^2(\mathbf{x}) = 1$ for all $\mathbf{x} \in \mathbb{R}^3$. Then for every $f \in H^{1/2}(\mathbb{R}^3)$*

$$\mathrm{t}(f,f) = \sum_{i=0}^{K} \mathrm{t}(\chi_i f, \chi_i f) - \alpha^{-1} \sum_{i=0}^{K} (f, L_i f),$$

where L_i is a bounded operator with kernel

$$L_i(\mathbf{x},\mathbf{y}) = \tfrac{\alpha^{-2}}{4\pi^2} \frac{|\chi_i(\mathbf{x}) - \chi_i(\mathbf{y})|^2}{|\mathbf{x}-\mathbf{y}|^2} K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|), \tag{14}$$

where K_2 is a modified Bessel function of the second kind.

Remark 2.2. *As in [24, App.A, pages 94–98] we use the following integral formula for the modified Bessel function*

$$K_2(t) = t \int_0^\infty e^{-t\sqrt{s^2+1}} s^2 \, ds\,, \quad t > 0.$$

We recall that this function is decreasing and smooth in $\mathbb{R}^+$. Moreover,

$$\int_0^{+\infty} t^2 K_2(t)\, dt = \tfrac{3\pi}{2} \quad \text{and} \quad K_2(t) \le 16\, t^{-2} e^{-\frac{1}{2}t} \text{ for } t > 0. \tag{15}$$

The integral is computed in [21, (A6)] while the estimate follows directly from the integral formula for K_2 by estimating $\sqrt{s^2+1} \ge \frac{1}{2} + \frac{1}{2}s$.

Generalization of the Lieb-Thirring inequality. This result due to Daubechies generalizes the Lieb-Thirring inequality to the pseudo-relativistic case.

Theorem 2.3 (Daubechies' inequality, [4]). *For $\gamma \in \mathcal{A}$*

$$\mathrm{Tr}[T(\mathbf{p})\gamma] \ge \int_{\mathbb{R}^3} G_\alpha(\rho_\gamma(\mathbf{x})) d\mathbf{x},$$

where $G_\alpha(\rho) = \frac{3}{8}\alpha^{-4} C g(\alpha(\rho/C)^{\frac{1}{3}}) - \alpha^{-1}\rho$ with $C = .163q$, q the number of spin states and $g(t) = t(1+t^2)^{\frac{1}{2}}(1+2t^2) - \ln(t + (1+t^2)^{\frac{1}{2}})$.

Remark 2.4. *The function G_α defined in the previous theorem is convex and it has the following behavior:*

$$\tfrac{9}{20} \min\left\{ \tfrac{1}{5}\alpha C^{-\frac{2}{3}} \rho^{\frac{5}{3}}, \tfrac{1}{2} C^{-\frac{1}{3}} \rho^{\frac{4}{3}} \right\} \le G_\alpha(\rho) \le \tfrac{3}{2} \min\left\{ \tfrac{1}{5}\alpha C^{-\frac{2}{3}} \rho^{\frac{5}{3}}, \tfrac{1}{2} C^{-\frac{1}{3}} \rho^{\frac{4}{3}} \right\}. \tag{16}$$

(The proof of the estimate above is in Appendix A.) Notice that when $\alpha \searrow 0$ then $\alpha^{-1}G_\alpha(\rho)$ tends to a constant times $\rho^{5/3}$.

Theorem 2.5 (Generalization of the Lieb-Thirring inequality, [4]). *Let f^{-1} be the inverse of the function $f(t) := \sqrt{t^2+\alpha^{-2}} - \alpha^{-1}$, $t \geq 0$, and define $F(s) = \int_0^s dt\ [f^{-1}(t)]^3$. Then for any density matrix γ it holds*

$$\mathrm{Tr}[(T(\mathbf{p}) - U)\gamma] \geq -Cq \int_{\mathbb{R}^3} F(|U(\mathbf{x})|) d\mathbf{x},$$

with $C \leq 0.163$.

Remark 2.6. *Since $f^{-1}(t) = (t^2 + 2\alpha^{-1}t)^{1/2}$ we find for F*

$$F(s) = 2^{\frac{3}{2}} \alpha^{-3/2} \int_0^s t^{3/2} \big(1 + \tfrac{1}{2}\alpha t\big)^{3/2}\, dt \quad \text{for } s \geq 0, \tag{17}$$

and since by convexity $(1 + \frac{1}{2}\alpha t)^{\frac{3}{2}} \leq \sqrt{2} + \frac{1}{2}(\alpha t)^{\frac{3}{2}}$ we have

$$F(s) \leq \tfrac{2^3}{5} \alpha^{-\frac{3}{2}} s^{\frac{5}{2}} + \tfrac{1}{2\sqrt{2}} s^4 \ \text{for } s \geq 0.$$

Hence for any density matrix γ and potential $U \in L^{\frac{5}{2}}(\mathbb{R}^3) \cap L^4(\mathbb{R}^3)$

$$\mathrm{Tr}[(T(\mathbf{p}) - U)\gamma] \geq -Cq \int_{\mathbb{R}^3} \Big(\tfrac{2^3}{5} \alpha^{-\frac{3}{2}} |U(\mathbf{x})|^{\frac{5}{2}} + \tfrac{1}{2\sqrt{2}} |U(\mathbf{x})|^4) d\mathbf{x}. \tag{18}$$

Coulomb norm estimate. We present here only the definition of Coulomb norm and the result we need. For a more complete presentation we refer to [23, Sec.9].

Definition 2.7. *For $f, g \in L^{\frac{6}{5}}(\mathbb{R}^3)$ we define the Coulomb inner product*

$$D(f,g) := \tfrac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f(\mathbf{x})\overline{g(\mathbf{y})}}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y},$$

and the corresponding norm $\|g\|_C := D(g,g)^{\frac{1}{2}}$.

In the following we write the direct term in the HF-energy functional using the Coulomb scalar product: i.e. $\mathcal{D}(\gamma) = D(\rho_\gamma, \rho_\gamma) = D(\rho_\gamma)$. Similarly, for $\rho \in L^1(\mathbb{R}^3) \cap L^{\frac{5}{3}}(\mathbb{R}^3)$ the term $D(\rho)$ denotes $D(\rho, \rho)$.
The next proposition follows as Corollary 9.3 in [23].

Proposition 2.8. *For $s > 0$, $\mathbf{x} \in \mathbb{R}^3$ and $f \in L^{\frac{6}{5}}(\mathbb{R}^3)$ it holds*

$$f * |\mathbf{x}|^{-1} \leq \int_{|\mathbf{x}-\mathbf{y}|<s} [f(\mathbf{y})]_+ \Big(\frac{1}{|\mathbf{x}-\mathbf{y}|} - \frac{1}{s} \Big) d\mathbf{y} + \sqrt{2}\, s^{-\frac{1}{2}} \|f\|_C.$$

Moreover, for $k > 0$

$$\int_{|\mathbf{y}|<|\mathbf{x}|} \frac{f(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \leq \int_{A(|\mathbf{x}|,k)} \frac{[f(\mathbf{y})]_+}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} + 2^{\frac{3}{2}} k^{-1} |\mathbf{x}|^{-\frac{1}{2}} \|f\|_C,$$

where $A(|\mathbf{x}|, k)$ denotes the annulus

$$A(|\mathbf{x}|, k) := \left\{ \mathbf{y} \in \mathbb{R}^3 : (1-2k)|\mathbf{x}| \leq |\mathbf{y}| \leq |\mathbf{x}| \right\}.$$

2.1 Improved relativistic Lieb-Thirring inequalities

A major difference between the pseudo-relativistic HF-model and the non-relativistic one studied in [23] is that the boundness of the functional does not yield a bound on the $L^{\frac{5}{3}}$ norm of the HF-density ρ^{HF} in the pseudo-relativistic case. By Theorem 2.3 and Remark 2.4 we see that we can control only the $L^{\frac{4}{3}}$-norm of ρ^{HF}. Therefore one cannot estimate the term $\rho^{\mathrm{HF}} * |\mathbf{x}|^{-1}$ in L^1-norm simply by Hölder's inequality with $p = 5/2$ and $q = 5/3$. To estimate it we are going to use a combined Daubechies-Lieb-Yau inequality.
The following lemma can be found in [24, pages 98–99][3].

Lemma 2.9. *For $f \in \mathcal{S}(\mathbb{R}^3)$,*

$$\int_{\mathbb{R}^3} \frac{e^{-\mu|\mathbf{x}|^2}}{|\mathbf{x}|}|f(\mathbf{x})|^2 d\mathbf{x} \leq \frac{\pi}{2}\frac{1}{\sqrt{2}-1}\,(f, T(\mathbf{p})f),$$

with $\mu = \pi^{-1}\alpha^{-2}$.

The following is a slight generalization of the Daubechies-Lieb-Yau inequality formulated in Theorem 2.8 in [24].

Theorem 2.10 (Daubechies-Lieb-Yau inequality). *Assume that the potential $U \in L^1_{loc}(\mathbb{R}^3)$ satisfies*

$$0 \geq -U(\mathbf{x}) \geq -\kappa|\mathbf{x}|^{-1} \quad \textit{for } |\mathbf{x}| < \max\{\alpha, R\}\,, \tag{19}$$

for $\alpha, R > 0$ and $0 \leq \kappa \leq 2/\pi$. Then we have

$$\begin{aligned}\mathrm{Tr}[T(\mathbf{p}) - U]_- \quad &\geq \quad -C\kappa^{5/2}\alpha^{-3/2}R^{1/2} - C\kappa^4\alpha^{-1} \\ &\quad\;\; -C\int_{|\mathbf{x}|>R}\left(\alpha^{-\frac{3}{2}}|U(\mathbf{x})|^{\frac{5}{2}} + |U(\mathbf{x})|^4\right)d\mathbf{x}.\end{aligned}$$

Proof. If $(\sqrt{2}-1)/\pi \leq \kappa \leq 2/\pi$ then $\kappa^{5/2}\alpha^{-3/2}R^{1/2} + \kappa^4\alpha^{-1} \geq C\kappa^{5/2}\alpha^{-1}$ and the result follows immediately from Theorem 2.8 in [24] observing that for $R > \alpha$ the two integrals of the potential on $\{\alpha < |\mathbf{x}| < R\}$ are bounded by the constants.
If $0 \leq \kappa < (\sqrt{2}-1)/\pi$ we write

$$U(x) = e^{-\mu|x|^2}U(x)\chi_{|\mathbf{x}|<R} + (1 - e^{-\mu|x|^2})U(x)\chi_{|\mathbf{x}|<R} + U(x)\chi_{|\mathbf{x}|>R}$$

with $\mu = \alpha^{-2}\pi^{-1}$. Using (19) and Lemma 2.9 we find that

$$T(\mathbf{p}) - U(\mathbf{x}) \geq \frac{1}{2}T(\mathbf{p}) - \kappa(1 - e^{-\mu|\mathbf{x}|^2})|\mathbf{x}|^{-1}\chi_{|\mathbf{x}|<R} - U(\mathbf{x})\chi_{|\mathbf{x}|>R}.$$

[3] The result of the lemma and the proof given in [24] are actually due to us, but we communicated the result to the authors of [24], where it is referred to as a a private communication.

Hence from the generalization of the Lieb-Thirring inequality Theorem 2.5 (see (18)) we obtain

$$\begin{aligned}\mathrm{Tr}[T(\mathbf{p})-U]_- \quad &\geq \quad -C\int_{|\mathbf{x}|<R}\alpha^{-\frac{3}{2}}\big(\kappa(1-e^{-\mu|\mathbf{x}|^2})|\mathbf{x}|^{-1})\big)^{\frac{5}{2}}\,d\mathbf{x}\\ &\quad -C\int_{|\mathbf{x}|<R}\big(\kappa(1-e^{-\mu|\mathbf{x}|^2})|\mathbf{x}|^{-1}\big)^4\,d\mathbf{x}\\ &\quad -C\int_{|\mathbf{x}|>R}\big(\alpha^{-\frac{3}{2}}|U(\mathbf{x})|^{\frac{5}{2}}+|U(\mathbf{x})|^4\big)\,d\mathbf{x}.\end{aligned}$$

Since the two first integrals above are estimated below by $-C\kappa^{5/2}\alpha^{-3/2}R^{1/2}-C\kappa^4\alpha^{-1}$ we get the result in the theorem. □

By Theorem 2.10 we find

$$\kappa\int_{|\mathbf{x}-\mathbf{y}|<R}\frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y}\leq \mathrm{Tr}[T(\mathbf{p})\gamma^{\mathrm{HF}}]+C_1\kappa Z^{\frac{3}{2}}R^{\frac{1}{2}}+C_2\kappa^3 Z, \tag{20}$$

with $\kappa\in[0,2/\pi]$, $\kappa=Z\alpha$ and $R>0$ parameters to be chosen. This is the inequality that we use to estimate $\rho^{\mathrm{HF}}*|\mathbf{x}|^{-1}$ (see proof of Lemma 3.2 below).

2.1.1 Bound on the Hartree-Fock energy

As a first application of Theorem 2.10 we can give a lower bound to the HF-energy.

Theorem 2.11 (Bound on the HF-energy). *Let $N>0$, $Z>0$ and such that $Z\alpha=\kappa$ with $0\leq\kappa\leq 2/\pi$. Then*

$$E^{\mathrm{HF}}(N,Z)\geq -2C^{\frac{2}{3}}Z^2N^{\frac{1}{3}}-C\kappa^2Z^2,$$

with C the constant in Theorem 2.10.

Proof. Let γ be a N-dimensional projection. Since the electron-electron interaction is positive we see that

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma) \quad &\geq \quad \alpha^{-1}\,\mathrm{Tr}[(T(\mathbf{p})-\frac{Z\alpha}{|\cdot|})\gamma]\\ &= \quad \alpha^{-1}\,\mathrm{Tr}[(T(\mathbf{p})-\frac{\kappa}{|\cdot|}\chi_{|\mathbf{x}|<R})\gamma]-\alpha^{-1}\,\mathrm{Tr}[\frac{\kappa}{|\cdot|}(1-\chi_{|\mathbf{x}|<R})\gamma]\end{aligned}$$

with $R>0$ a parameter to be chosen. By Theorem 2.10 we find

$$\mathcal{E}^{\mathrm{HF}}(\gamma) \quad \geq \quad -2C^{\frac{2}{3}}Z^2N^{\frac{1}{3}}-C\kappa^2Z^2,$$

using that $\kappa=Z\alpha$ and by choosing $R=C^{-\frac{2}{3}}Z^{-1}N^{\frac{2}{3}}$. □

3 Near the nucleus

In this section we prove the estimate in Theorem 1.17 in the region near the nucleus (i.e. at distance of $Z^{-\frac{1}{3}}$).
We again assume that $N \geq Z$ and that an HF-minimizer γ^{HF} exists for this N and Z. We denote the density of γ^{HF} by ρ^{HF}. We assume throughout that $\alpha Z = \kappa$ is fixed with $0 \leq \kappa < 2/\pi$ and $Z \geq 1$.

Lemma 3.1. *Let $Z\alpha = \kappa$ be fixed with $0 \leq \kappa < 2/\pi$ and $Z \geq 1$. Let G_α be the function defined in Theorem 2.3. Then, there exists $\alpha_0 > 0$ such that for all $\alpha \leq \alpha_0$*

$$\begin{gathered}\alpha^{-1}\int_{\mathbb{R}^3} G_\alpha(\rho^{\mathrm{HF}}(\mathbf{x}))d\mathbf{x} \leq CZ^{7/3}, \quad \alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma^{\mathrm{HF}}] \leq CZ^{7/3} \\ \textit{and} \quad \|\rho^{\mathrm{TF}} - \rho^{\mathrm{HF}}\|_C^2 \leq CZ^{2+\frac{3}{11}},\end{gathered} \tag{21}$$

with C a universal constant depending only on κ.

Proof. Let $\mu \in (0,1)$ be such that $\mu^{-1}\kappa < 2/\pi$. Notice that here we need $\kappa < 2/\pi$. Splitting the kinetic energy into two parts we find

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) &= (1-\mu)\alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma^{\mathrm{HF}}] + \mathcal{D}(\gamma^{\mathrm{HF}}) - \mathcal{E}x(\gamma^{\mathrm{HF}}) \\ &\quad + \mu\operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - \frac{Z}{\mu|\mathbf{x}|})\gamma^{\mathrm{HF}}] = \ldots,\end{aligned}$$

and introducing $\rho \in L^{\frac{5}{3}}(\mathbb{R}^3) \cap L^1(\mathbb{R}^3)$, $\rho \geq 0$, to be chosen

$$\begin{aligned}\ldots &= (1-\mu)\alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma^{\mathrm{HF}}] + \mu\|\rho - \rho^{\mathrm{HF}}\|_C^2 + (1-\mu)\mathcal{D}(\gamma^{\mathrm{HF}}) \\ &\quad - \mathcal{E}x(\gamma^{\mathrm{HF}}) - \mu D(\rho) + \mu\operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - (\frac{Z}{\mu|\mathbf{x}|} - \rho * \frac{1}{|\mathbf{x}|}))\gamma^{\mathrm{HF}}].\end{aligned} \tag{22}$$

Here $\|\cdot\|_C$ denotes the Coulomb norm defined in Definition 2.7 and we used that

$$\|\rho - \rho^{\mathrm{HF}}\|_C^2 = D(\rho) - \iint \frac{\rho^{\mathrm{HF}}(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} + \mathcal{D}(\gamma^{\mathrm{HF}}).$$

The estimates in the claim will follow from (22) with different choices of μ and ρ. The main idea is to relate, up to lower order term, the last term on the right hand side of (22) to the TF-energy of a neutral atom of nuclear charge $Z\mu^{-1}$. This has been done in [21]. For completeness and easy reference we repeat the reasoning in Propositions B.1 and B.2 in Appendix B.
To prove the first inequality in (21) we choose ρ as the minimizer of the TF-energy functional of a neutral atom with charge $\mu^{-1}Z$. Since the corresponding TF-mean field potential is $Z/(\mu|\mathbf{x}|) - \rho * 1/|\mathbf{x}|$ by Proposition B.2 in Appendix B we find

$$\operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - (\frac{Z}{\mu|\mathbf{x}|} - \rho * \frac{1}{|\mathbf{x}|}))\gamma^{\mathrm{HF}}] \geq -C_1 Z^{\frac{7}{3}} + D(\rho). \tag{23}$$

Here we use (12). Since $\mathcal{E}^{\rm HF}(\gamma^{\rm HF}) \leq 0$ from (22) and (23) leaving out the positive terms we find

$$0 \;\;\geq\;\; (1-\mu)\alpha^{-1}\,\mathrm{Tr}[T(\mathbf{p})\gamma^{\rm HF}] - \mathcal{E}x(\gamma^{\rm HF}) - C_1 Z^{\frac{7}{3}}. \tag{24}$$

From (24) and Theorem 2.3 we get

$$(1-\mu)\alpha^{-1}\int_{\mathbb{R}^3} G_\alpha(\rho^{\rm HF}(\mathbf{x}))\,d\mathbf{x} \leq (1-\mu)\alpha^{-1}\,\mathrm{Tr}[T(\mathbf{p})\gamma^{\rm HF}] \leq \mathcal{E}x(\gamma^{\rm HF}) + C_1 Z^{\frac{7}{3}}. \tag{25}$$

It remains to estimate the exchange term. By the exchange inequality (see [15])

$$\mathcal{E}x(\gamma^{\rm HF}) \;\;\leq\;\; 1.68\int_{\mathbb{R}^3}\big(\rho^{\rm HF}(\mathbf{x})\big)^{\frac{4}{3}}\,d\mathbf{x}.$$

To proceed we separate $\mathbb{R}^3$ into two regions. Let us define

$$\Sigma = \big\{\mathbf{x}\in\mathbb{R}^3 : \alpha\big(C^{-1}\rho^{\rm HF}(\mathbf{x})\big)^{\frac{1}{3}} \geq \tfrac{5}{2}\big\}, \tag{26}$$

with the same notation as in (16). By Remark 2.4, $G_\alpha(\rho^{\rm HF}(\mathbf{x})) \geq C_2(\rho^{\rm HF}(\mathbf{x}))^{\frac{4}{3}}$ in Σ and $\alpha^{-1}G_\alpha(\rho^{\rm HF}(\mathbf{x})) \geq C_3(\rho^{\rm HF}(\mathbf{x}))^{\frac{5}{3}}$ in $\mathbb{R}^3\setminus\Sigma$. Hence by Hölder's inequality we find

$$\begin{aligned}\mathcal{E}x(\gamma^{\rm HF}) \;\;\leq\;\; & 1.68\int_\Sigma(\rho^{\rm HF}(\mathbf{x}))^{\frac{4}{3}}\;d\mathbf{x}\\ & +1.68\Big(\int_{\mathbb{R}^3\setminus\Sigma}(\rho^{\rm HF}(\mathbf{x}))^{\frac{5}{3}}\,d\mathbf{x}\Big)^{\frac{1}{2}}\Big(\int_{\mathbb{R}^3\setminus\Sigma}\rho^{\rm HF}(\mathbf{x})\,d\mathbf{x}\Big)^{\frac{1}{2}}\\ \leq & C_4\int_{\mathbb{R}^3}G_\alpha(\rho^{\rm HF}(\mathbf{x}))\,d\mathbf{x} + C_5\Big(\int_{\mathbb{R}^3}\alpha^{-1}G_\alpha(\rho^{\rm HF}(\mathbf{x}))\,d\mathbf{x}\Big)^{\frac{1}{2}}N^{\frac{1}{2}}.\end{aligned} \tag{27}$$

Choosing α_0 such that $1-\mu > 2C_4\alpha$ for $\alpha\leq\alpha_0$, from (25) and (27) we find

$$\tfrac{1-\mu}{2}\alpha^{-1}\int_{\mathbb{R}^3}G_\alpha(\rho^{\rm HF}(\mathbf{x}))\,d\mathbf{x} \leq C_1Z^{\frac{7}{3}} + C_5\Big(\int_{\mathbb{R}^3}\alpha^{-1}G_\alpha(\rho^{\rm HF}(\mathbf{x}))\,d\mathbf{x}\Big)^{\frac{1}{2}}N^{\frac{1}{2}}.$$

The first estimate in (21) follows from the estimate above using that $x^2-bx-c\leq 0$ implies $x^2\leq b^2+2c$ and that $N\leq 2Z+1$ (Theorem 1.6). The second inequality in (21) follows then from (25) and the bound on the exchange term. To prove the third inequality in (21) we estimate from above and from below $\mathcal{E}^{\rm HF}(\gamma^{\rm HF})$. For the one from below we choose in (22) $\mu=1$ and $\rho=\rho^{\rm TF}$ the TF-minimizer of a neutral atom with nucleus of charge Z. We find

$$\mathcal{E}^{\rm HF}(\gamma^{\rm HF}) = \sum_{i=1}^N(u_i,(\alpha^{-1}T(\mathbf{p})-\varphi^{\rm TF})u_i) + \|\rho^{\rm HF}-\rho^{\rm TF}\|_C^2 - D(\rho^{\rm TF}) - \mathcal{E}x(\gamma^{\rm HF}). \tag{28}$$

From (28) and the proof of Proposition B.2 (see (B37)), we find

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) \quad \geq \quad & -\tfrac{2^{\frac{3}{2}}}{15\pi^2} q \int d\mathbf{q} (\varphi^{\mathrm{TF}}(\mathbf{q}))^{\frac{5}{2}} - CZ^{2+1/5} \\ & -D(\rho^{\mathrm{TF}}) + \|\rho^{\mathrm{HF}} - \rho^{\mathrm{TF}}\|_C^2 - \mathcal{E}x(\gamma^{\mathrm{HF}}).\end{aligned} \tag{29}$$

To estimate from above $\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})$ we may proceed exactly as in [23, page 543] using that $\alpha^{-1}T(\mathbf{p}) \leq \frac{1}{2}|\mathbf{p}|^2$. For completeness we repeat the main ideas. We consider γ the density matrix that acts identically on each of the spin components as

$$\gamma^j = \tfrac{1}{(2\pi)^3} \iint_{\frac{1}{2}|\mathbf{p}|^2 \leq \varphi^{\mathrm{TF}}(\mathbf{q})} \Pi_{\mathbf{p},\mathbf{q}} \, d\mathbf{q} d\mathbf{p} \text{ for } j = 1, \ldots, q.$$

Here $\Pi_{\mathbf{p},\mathbf{q}}$ is the projection onto the space spanned by $h_s^{\mathbf{p},\mathbf{q}}(\mathbf{x}) := h_s(\mathbf{x}-\mathbf{q})e^{i\mathbf{p}\cdot\mathbf{x}}$ where h_s is the ground state (normalized in $L^2(\mathbb{R}^3)$) for the Dirichlet Laplacian on the ball of radius Z^{-s} with $s \in (1/3, 2/3)$ to be chosen. One sees that $\mathrm{Tr}[\gamma] = Z \leq N$ since

$$\rho_\gamma(\mathbf{x}) = \tfrac{2^{3/2} q}{6\pi^2} (\varphi^{\mathrm{TF}})^{3/2} * h_s^2(\mathbf{x}) = \rho^{\mathrm{TF}} * h_s^2(\mathbf{x}),$$

where we have used the TF-equation. Hence $\mathcal{E}^{\mathrm{HF}}(\gamma) \geq \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}})$. Now we estimate from above $\mathcal{E}^{\mathrm{HF}}(\gamma)$. Since $\alpha^{-1}T(\mathbf{p}) \leq \frac{1}{2}|\mathbf{p}|^2$ and $\mathcal{E}x(\gamma) \geq 0$ we find

$$\mathcal{E}^{\mathrm{HF}}(\gamma) \leq \mathrm{Tr}[(-\tfrac{1}{2}\Delta - \frac{Z}{|\cdot|})\gamma] + D(\rho_\gamma) = \ldots,$$

and proceeding as in [23, page 543])

$$\cdots = \tfrac{q}{(2\pi)^3} \iint_{\frac{1}{2}|\mathbf{p}|^2 \leq \varphi^{\mathrm{TF}}(\mathbf{q})} \tfrac{1}{2}|\mathbf{p}|^2 \, d\mathbf{p} d\mathbf{q} - \tfrac{\pi^2}{2} Z^{2s} N - \int_{\mathbb{R}^3} \frac{Z}{|\mathbf{x}|} \rho_\gamma(\mathbf{x}) \, d\mathbf{x} + D(\rho_\gamma).$$

Computing the integral and summing and subtracting the term $\int \rho^{\mathrm{TF}} \varphi^{\mathrm{TF}}$ we get

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma) \quad \leq \quad & \tfrac{q 2^{\frac{1}{2}}}{5\pi^2} \int_{\mathbb{R}^3} (\varphi^{\mathrm{TF}}(\mathbf{q}))^{\frac{5}{2}} \, d\mathbf{q} - \tfrac{\pi^2}{2} Z^{2s} N - \int_{\mathbb{R}^3} \varphi^{\mathrm{TF}}(\mathbf{x}) \rho^{\mathrm{TF}}(\mathbf{x}) \, d\mathbf{x} \\ & - \int_{\mathbb{R}^3} \frac{Z}{|\mathbf{x}|} (\rho_\gamma(\mathbf{x}) - \rho^{\mathrm{TF}}(\mathbf{x})) d\mathbf{x} - 2D(\rho^{\mathrm{TF}}) + D(\rho_\gamma).\end{aligned} \tag{30}$$

By Newton's theorem one sees that $D(\rho_\gamma) \leq D(\rho^{\mathrm{TF}})$ and that

$$Z \int_{\mathbb{R}^3} \frac{\rho^{\mathrm{TF}}(\mathbf{x}) - \rho_\gamma(\mathbf{x})}{|\mathbf{x}|} \, d\mathbf{x} \leq Z \int_{|\mathbf{x}| \leq Z^{-s}} \frac{\rho^{\mathrm{TF}}(\mathbf{x})}{|\mathbf{x}|} \, d\mathbf{x} \leq CZ^{\frac{1}{5}(12-s)}.$$

In the last step we use Hölder's inequality and Corollary 1.15. From (30) using the TF-equation, that $N \leq 2Z + 1$ (Theorem 1.6) and optimizing in s we find

$$\mathcal{E}^{\mathrm{HF}}(\gamma) \leq -\tfrac{2^{\frac{3}{2}}}{15\pi^2} q \int_{\mathbb{R}^3} (\varphi^{\mathrm{TF}}(\mathbf{q}))^{\frac{5}{2}} \, d\mathbf{q} + CZ^{\frac{1}{5}(12 - \frac{7}{11})} - D(\rho^{\mathrm{TF}}). \tag{31}$$

Hence from (29) and (31) we obtain

$$\left\|\rho^{\mathrm{HF}} - \rho^{\mathrm{TF}}\right\|_C^2 \leq CZ^{2+\frac{3}{11}} + \mathcal{E}x(\gamma^{\mathrm{HF}}).$$

The last estimate in (21) follows from the estimate above since $\mathcal{E}x(\gamma^{\mathrm{HF}}) \leq CZ^{\frac{5}{3}}$ using (27) and the estimate just proved on $\alpha^{-1}\int G_\alpha(\rho^{\mathrm{HF}}(\mathbf{x}))\,d\mathbf{x}$. ☐

Lemma 3.2. *Let $Z\alpha = \kappa$ be fixed with $0 \leq \kappa < 2/\pi$ and $Z \geq 1$. Then, there exists an $\alpha_0 > 0$ such that for all $\alpha \leq \alpha_0$, $\mu > 0$ and $\mathbf{x} \in \mathbb{R}^3$ with $|\mathbf{x}| \leq \beta Z^{-\frac{1+\mu}{3}}$ we have*

$$|\Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C\beta^{\frac{4}{1+\mu}}(1 + \beta^{\frac{9}{22(1+\mu)}}|\mathbf{x}|^{\frac{2+11\mu}{22(1+\mu)}})|\mathbf{x}|^{-4+\frac{4\mu}{1+\mu}}.$$

Proof. By the definition of screened nuclear potential we have

$$\left|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})\right| \leq \int_{|\mathbf{y}|<|\mathbf{x}|} \frac{|\rho^{\mathrm{HF}}(\mathbf{y}) - \rho^{\mathrm{TF}}(\mathbf{y})|}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} = \dots$$

and for all $k > 0$ by Proposition 2.8

$$\dots \leq 2^{\frac{3}{2}} k^{-1} |\mathbf{x}|^{-\frac{1}{2}} \left\|\rho^{\mathrm{HF}} - \rho^{\mathrm{TF}}\right\|_C + \int_{A(|\mathbf{x}|,k)} \frac{\rho^{\mathrm{HF}}(\mathbf{y}) + \rho^{\mathrm{TF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y}. \quad (32)$$

Since $\|\rho^{\mathrm{TF}}\|_{L^{\frac{5}{3}}(\mathbb{R}^3)} \leq CZ^{\frac{7}{5}}$ (Corollary 1.15) and

$$\int_{A(|\mathbf{x}|,k)} \frac{1}{|\mathbf{x}-\mathbf{y}|^{\frac{5}{2}}} d\mathbf{y} \leq 8\pi |\mathbf{x}|^{\frac{1}{2}} (2k)^{\frac{1}{2}}. \quad (33)$$

(see [23] page 549) one finds

$$\int_{A(|\mathbf{x}|,k)} \frac{\rho^{\mathrm{TF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \leq CZ^{\frac{7}{5}} |\mathbf{x}|^{\frac{1}{5}} k^{\frac{1}{5}}. \quad (34)$$

The term with the HF-density has to be treated differently since we do not have a bound for the $L^{\frac{5}{3}}$-norm of ρ^{HF}. For a $R \in \mathbb{R}^+$ to be chosen later we consider the splitting

$$\int_{A(|\mathbf{x}|,k)} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} = \int_{\substack{A(|\mathbf{x}|,k)\\ |\mathbf{x}-\mathbf{y}|>R}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} + \int_{\substack{A(|\mathbf{x}|,k)\\ |\mathbf{x}-\mathbf{y}|<R}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y}. \quad (35)$$

We consider these two terms separately. Let Σ be defined as in (26); i.e. the region where $G_\alpha(\rho^{\mathrm{HF}})$ behaves like $(\rho^{\mathrm{HF}})^{\frac{4}{3}}$ (Remark 2.4). By Hölder's inequality we find

$$\begin{aligned}\int_{\substack{A(|\mathbf{x}|,k)\\ |\mathbf{x}-\mathbf{y}|>R}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \leq\ & \Big(\int_{\substack{A(|\mathbf{x}|,k)\\ |\mathbf{x}-\mathbf{y}|>R}} \frac{1}{|\mathbf{x}-\mathbf{y}|^4} d\mathbf{y}\Big)^{\frac{1}{4}} \Big(\int_{\mathbf{y}\in\Sigma} (\rho^{\mathrm{HF}}(\mathbf{y}))^{\frac{4}{3}} d\mathbf{y}\Big)^{\frac{3}{4}} \\ & + \Big(\int_{A(|\mathbf{x}|,k)} \frac{1}{|\mathbf{x}-\mathbf{y}|^{\frac{5}{2}}} d\mathbf{y}\Big)^{\frac{2}{5}} \Big(\int_{\mathbf{y}\in\mathbb{R}^3\setminus\Sigma} (\rho^{\mathrm{HF}}(\mathbf{y}))^{\frac{5}{3}} d\mathbf{y}\Big)^{\frac{3}{5}}.\end{aligned}$$

From the inequality above, Remark 2.4 and estimate (21) we get

$$\int_{\substack{A(|\mathbf{x}|,k)\\ |\mathbf{x}-\mathbf{y}|>R}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y} \quad \leq \quad CR^{-\frac{3}{8}}|\mathbf{x}|^{\frac{1}{8}}k^{\frac{1}{8}}Z + C|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}}Z^{\frac{7}{5}}. \tag{36}$$

On the other hand for the second term on the right hand side of (35) by (20) and Lemma 3.1 we find

$$\int_{|\mathbf{x}-\mathbf{y}|<R} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y} \leq C(Z^{\frac{4}{3}} + R^{\frac{1}{2}}Z^{\frac{3}{2}}). \tag{37}$$

Hence from (32), Lemma 3.1, (34), (36) and (37), we get

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C\big(\frac{Z^{1+\frac{3}{22}}}{|\mathbf{x}|^{1/2}k} + Z^{\frac{7}{5}}|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}} + R^{-\frac{3}{8}}|\mathbf{x}|^{\frac{1}{8}}k^{\frac{1}{8}}Z + R^{\frac{1}{2}}Z^{\frac{3}{2}} + Z^{\frac{4}{3}}\big). \tag{38}$$

Choosing k such that $Z^{\frac{4}{3}} = Z^{\frac{7}{5}}|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}}$, i.e. $k = |\mathbf{x}|^{-1}Z^{-\frac{1}{3}}$ and R such that $R^{-\frac{3}{8}}Z^{1-\frac{1}{24}} = Z^{\frac{4}{3}}$, i.e. $R = Z^{-1}$ we find

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C(|\mathbf{x}|^{\frac{1}{2}}Z^{\frac{4}{3}+\frac{3}{22}} + Z^{\frac{4}{3}}).$$

The claim follows using that $|\mathbf{x}| \leq \beta Z^{-\frac{1+\mu}{3}}$. □

Theorem 3.3. *Let $Z\alpha = \kappa$ be fixed with $0 \leq \kappa < 2/\pi$ and $Z \geq 1$. Then there exists an $\alpha_0 > 0$ such that for all $\alpha \leq \alpha_0$ and $\mathbf{x} \in \mathbb{R}^3$ with $|\mathbf{x}| \leq \beta Z^{-\frac{1}{3}}$ we have*

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C\beta^{2-\frac{1}{66}}(1 + \beta^2 + \beta^{\frac{5}{2}} + \beta^{2+\frac{789}{1936}}|\mathbf{x}|^{\frac{179}{1936}})|\mathbf{x}|^{-4+\frac{1}{66}}. \tag{39}$$

Moreover if $|\mathbf{x}| \leq \beta Z^{-\frac{1-\mu}{3}}$ for $\mu < \frac{2}{11}\frac{1}{49}$, then

$$|\Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C\beta^{2-a(\mu)}(1 + \beta^2 + \beta^{\frac{5}{2}} + \beta^{b(\mu)}|\mathbf{x}|^{c(\mu)})|\mathbf{x}|^{-4+a(\mu)}, \tag{40}$$

with $a(\mu) = \frac{1}{66(1-\mu)} - \frac{49\mu}{12(1-\mu)}$, $b(\mu) = 2 + \frac{3}{176}\frac{24-24\mu-\frac{1}{11}+\frac{49}{2}\mu}{1-\mu}$ and $c(\mu) = \frac{1}{11} - \frac{\frac{3}{11}-\frac{3}{2}49\mu}{22(8-8\mu)}$ strictly positive constants.

Proof. Proceeding as in the proof of Lemma 3.2 up to (36) we get

$$\begin{aligned} |\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \quad &\leq \quad C(k^{-1}|\mathbf{x}|^{-\frac{1}{2}}Z^{1+\frac{3}{22}} + Z^{\frac{7}{5}}|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}} + R^{-\frac{3}{8}}|\mathbf{x}|^{\frac{1}{8}}k^{\frac{1}{8}}Z) \\ &\quad + \int_{|\mathbf{x}-\mathbf{y}|\leq R} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y}, \end{aligned} \tag{41}$$

for $R \in \mathbb{R}^+$ to be chosen. It remains to estimate the last term on the right hand side of (41). For 'small' R which is relevant for small $\mathbf{x}$ we already did it in Lemma 3.2, for 'big' R which is relevant for big $\mathbf{x}$ we use Proposition B.1 in Appendix B.

Take $\gamma \leq 1/263$ to be chosen. If $|\mathbf{x}| \leq \beta Z^{-\frac{1+\gamma}{3}}$ then by Lemma 3.2

$$|\Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C\beta^{\frac{4}{1+\gamma}}(1+\beta^{\frac{9}{22(1+\gamma)}}|\mathbf{x}|^{\frac{2+11\gamma}{22(1+\gamma)}})|\mathbf{x}|^{-4+\frac{4\gamma}{1+\gamma}}. \tag{42}$$

If instead $|\mathbf{x}| > \beta Z^{-\frac{1+\gamma}{3}}$, let $H_{\mathbf{x}}$ be the Hamiltonian defined in (B2) with $\mathbf{P} = \mathbf{x}$ and $\nu = Z$. Then by the definition of $H_{\mathbf{x}}$ and taking the HF-minimizer as a trial wave function we have

$$\begin{aligned}\inf_{\substack{\psi\in\wedge_{i=1}^N L^2(\mathbb{R}^3)\\ \|\psi\|_2=1}} \langle \psi, H_{\mathbf{x}}\psi\rangle &\leq \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) - Z\int_{|\mathbf{x}-\mathbf{y}|<R} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y}\\ &= \inf_{\gamma\in\mathcal{A}} \mathcal{E}^{\mathrm{HF}}(\gamma) - Z\int_{|\mathbf{x}-\mathbf{y}|<R} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y} = \dots .\end{aligned}$$

Since $\frac{1}{2}|\mathbf{p}|^2 \geq \alpha^{-1}T(\mathbf{p})$, $\inf_{\gamma\in\mathcal{A}}\mathcal{E}^{\mathrm{HF}}(\gamma)$ is estimated from above by the HF-ground state energy of the non-relativistic model (i.e. when the kinetic energy is given by $-\frac{1}{2}\Delta$). Moreover, this last one can be estimated from above by $\mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}) + CN^{\frac{1}{5}}Z^2$ (see [18] and [11]). Hence we find

$$\dots \leq \mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}) + CN^{\frac{1}{5}}Z^2 - Z\int_{|\mathbf{x}-\mathbf{y}|<R} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y}.$$

On the other hand since $|\mathbf{x}| > \beta Z^{-\frac{1+\gamma}{3}}$ choosing for some $l > \frac{1+\gamma}{3}$, $R < \beta Z^{-l}/4$ from Proposition B.1 it follows that there exists a constant depending only on κ such that for $t \in ((1+\gamma)/3, \min\{l, 3/5\})$, and for every $\psi \in \wedge_{i=1}^N L^2(\mathbb{R}^3)$ with $\|\psi\|_2 = 1$ we have

$$\langle \psi, H_{\mathbf{x}}\psi\rangle \geq \mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}) - C(\beta^{1/2} + \beta^{-2})Z^{\frac{5}{2}-\frac{t}{2}},$$

Hence combining the two inequalities above we find

$$\int_{|\mathbf{x}-\mathbf{y}|\leq R} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y} \leq C(\beta^{1/2}+\beta^{-2})Z^{\frac{1}{2}(3-t)}. \tag{43}$$

From (41) and the inequality above we get

$$\begin{aligned}|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| &\leq Ck^{-1}|\mathbf{x}|^{-\frac{1}{2}}Z^{1+\frac{3}{22}} + CZ^{\frac{7}{5}}|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}}\\ &\quad + CR^{-\frac{3}{8}}|\mathbf{x}|^{\frac{1}{8}}k^{\frac{1}{8}}Z + C(\beta^{1/2}+\beta^{-2})Z^{\frac{1}{2}(3-t)}.\end{aligned}$$

Choosing k such that $Z^{\frac{1}{2}(3-t)} = Z^{\frac{7}{5}}|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}}$, i.e $k = |\mathbf{x}|^{-1}Z^{\frac{1}{2}(1-5t)}$ and R such that $Z^{\frac{1}{2}(3-t)} \sim R^{-\frac{3}{8}}Z^{1+\frac{1}{16}(1-5t)}$, i.e $R = \beta Z^{-\frac{7}{6}+\frac{1}{2}t}/4$ we find

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C(|\mathbf{x}|^{\frac{1}{2}}Z^{\frac{7}{11}+\frac{5}{2}t} + (\beta^{1/2}+\beta^{-2})Z^{\frac{1}{2}(3-t)}). \tag{44}$$

Notice that $R < \beta Z^{-l}/4$ is satisfied choosing $l = 4t/3$. Then for $\mathbf{x}$ such that $\beta Z^{-\frac{1+\gamma}{3}} \leq |\mathbf{x}| \leq \beta Z^{-\frac{1}{3}}$ we find

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C(|\mathbf{x}|^{-\frac{31}{22}-\frac{15}{2}t}\beta^{\frac{21}{11}+\frac{15}{2}t} + (\beta^{1/2}+\beta^{-2})\beta^{\frac{3}{2}(3-t)}|\mathbf{x}|^{-\frac{3}{2}(3-t)}).$$

Optimizing in t gives $t = 1/3 + 1/99$. For this value of t we get

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C(1+\beta^{\frac{5}{2}})\beta^{2-\frac{1}{66}}|\mathbf{x}|^{-4+\frac{1}{66}}. \tag{45}$$

Inequality (39) follows from (42) and (45) choosing γ such that $4\gamma/(1+\gamma) = 1/66$, i.e. $\gamma = 1/263$.
On the other hand from (44) for $\mathbf{x}$ such that $\beta Z^{-\frac{1+\gamma}{3}} \leq |\mathbf{x}| \leq \beta Z^{-\frac{1-\mu}{3}}$ we find

$$\begin{aligned} |\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \quad \leq \quad & C|\mathbf{x}|^{\frac{1}{2}-\frac{3}{1-\mu}(\frac{7}{11}+\frac{5}{2}t)}\beta^{\frac{3}{1-\mu}(\frac{7}{11}+\frac{5}{2}t)} \\ & +C(\beta^{1/2}+\beta^{-2})\beta^{\frac{3}{2(1-\mu)}(3-t)}|\mathbf{x}|^{-\frac{3}{2(1-\mu)}(3-t)}. \end{aligned}$$

Optimizing in t gives $t = 1/3 + 1/99 - \frac{1}{18}\mu$. For this value of t we get

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C(1+\beta^{\frac{5}{2}})\beta^{2-\frac{1}{66(1-\mu)}+\frac{49\mu}{12(1-\mu)}}|\mathbf{x}|^{-4+\frac{1}{66(1-\mu)}-\frac{49\mu}{12(1-\mu)}}.$$

Inequality (40) follows from the one above and (42) choosing γ such that $4\gamma/(1+\gamma) = \frac{1}{66(1-\mu)} - \frac{49\mu}{12(1-\mu)}$. □

4 The exterior part

In this section we complete the proof of Theorem 1.17. We first estimate the exterior integral of the density and study the minimization problem that the exterior part of the minimizer satisfies. Then we prove the main estimate in Theorem 1.17 in an intermediate zone, i.e. far from the nucleus but not further than a fixed distance independent of Z. To study this area we need first to construct a TF-model that gives a good approximation of the HF-density in this intermediate zone. By the estimate on the exterior integral of the density we can then also prove Theorem 1.17 in the region far away from the nucleus.

4.1 The exterior integral of the density

The main result of this section is the following lemma.

Lemma 4.1 (The exterior integral of the density). *Assume that for some* $R, \sigma, \varepsilon' > 0$

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq \sigma|\mathbf{x}|^{-4+\varepsilon'}, \tag{46}$$

holds for $|\mathbf{x}| \leq R$. *Then for* $0 < r \leq R$

$$\Big|\int_{|\mathbf{x}|<r}(\rho^{\mathrm{HF}}(\mathbf{x}) - \rho^{\mathrm{TF}}(\mathbf{x}))\,d\mathbf{x}\Big| \leq \sigma r^{-3+\varepsilon'} \tag{47}$$

and

$$\int_{|\mathbf{x}|>r}\rho^{\mathrm{HF}}(\mathbf{x})d\mathbf{x} \leq C(1+\sigma r^{\varepsilon'})(1+r^{-3}), \tag{48}$$

with C *a universal constant.*

We proceed similarly as in the proof of Lemma 10.5 in [23]. Since we need to localize we first present some technical lemmas that will take care of the error terms due to the localization. The localization error that will appear in the argument below (see (58)) will be in the form of an operator L similar to the error (14) in the IMS formula. We estimate this error in Lemma 4.3.

Remark 4.2. *Let $0 \le \beta_1 < .. < \beta_4$ be real numbers with possibly $\beta_4 = \infty$. Let us denote $\Sigma_r(\beta_i, \beta_j) = \{\mathbf{x} \in \mathbb{R}^3 : \beta_i r \le |\mathbf{x}| \le \beta_j r\}$. Then we have*

$$\iint_{\substack{\mathbf{x} \in \Sigma_r(\beta_1,\beta_2) \\ \mathbf{y} \in \Sigma_r(\beta_3,\beta_4)}} K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)^2 \, d\mathbf{x}d\mathbf{y} \le \tfrac{4^6\pi^2}{3} \frac{\beta_2^3 - \beta_1^3}{\beta_3 - \beta_2} \, \alpha^4 r^2 e^{-\alpha^{-1} r(\beta_3-\beta_2)} .$$

The proof of this estimate is given in Appendix A.

Lemma 4.3. *Let $r > 0$ and $\lambda, \nu \in (0,1)$. Let χ_- be the characteristic function of $B_{r(1-\nu)}(0)$ and χ_0 be the characteristic function of the sector $\{\mathbf{x} \in \mathbb{R}^3 : r(1-\nu) < |\mathbf{x}| < r(1+\nu)/(1-\lambda)\}$. Let η be a Lipschitz function such that $0 \le \eta(\mathbf{x}) \le 1$ for all $\mathbf{x} \in \mathbb{R}^3$, $\eta(\mathbf{x}) \equiv 0$ if $|\mathbf{x}| \le r$, $\eta(\mathbf{x}) \equiv 1$ if $|\mathbf{x}| \ge r(1-\lambda)^{-1}$ and $\|\nabla\eta\|_\infty$ is bounded. Let L denote the operator with integral kernel*

$$L(\mathbf{x},\mathbf{y}) = \frac{\alpha^{-2}}{4\pi^2} \frac{(\eta(\mathbf{x})-\eta(\mathbf{y}))(\eta(\mathbf{x})|\mathbf{x}| - \eta(\mathbf{y})|\mathbf{y}|)}{|\mathbf{x}-\mathbf{y}|^2} K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|). \tag{49}$$

Then for every function $f \in L^2(\mathbb{R}^3)$ we have

$$\alpha^{-1}|(f,Lf)| \le 3\,D(\eta,\lambda,r)\,\|\chi_0 f\|_2^2 + D(\eta,\lambda,r)e^{-\frac{1}{2}\alpha^{-1}r\nu}\|\chi_- f\|_2^2 + \alpha^{-1}|(f,Qf)|,$$

with $D(\eta,\lambda,r) := \|\nabla\eta\|_\infty\left(\frac{\|\nabla\eta\|_\infty r}{1-\lambda} + 1\right)$ and Q a positive semi-definite operator such that

$$\mathrm{Tr}[Q] \le C D(\eta,\lambda,r)\alpha^{-1} r^2 e^{-\frac{1}{2}\alpha^{-1}r\nu},$$

with C depending only on λ and ν.

Proof. As a first step we decompose the operator L. We introduce a third cut-off function χ_+ such that $1 = \chi_-(\mathbf{x}) + \chi_0(\mathbf{x}) + \chi_+(\mathbf{x})$ for all $\mathbf{x} \in \mathbb{R}^3$. We decompose the operator L with respect to these characteristic functions as follows:

$$L = \chi_- L(\chi_0 + \chi_+) + (\chi_0 + \chi_+)L\chi_- + \chi_0 L\chi_+ + \chi_+ L\chi_0 + \chi_0 L\chi_0.$$

We proceed similarly as in [24, Proof of Theorem 2.6 (Localization error)]. For Γ_1, Γ_2 bounded operators from $(\Gamma_1 - \Gamma_2)(\Gamma_1 - \Gamma_2)^* \ge 0$ it follows

$$\Gamma_1\Gamma_2^* + \Gamma_2\Gamma_1^* \le \Gamma_1\Gamma_1^* + \Gamma_2\Gamma_2^*. \tag{50}$$

We are going to use several times this inequality with different choices of Γ_1 and Γ_2.

As a first choice we consider $\Gamma_1 = \sqrt{\varepsilon_1}\chi_-$ and $\Gamma_2 = 1/\sqrt{\varepsilon_1}(\chi_0+\chi_+)L\chi_-$ with $\varepsilon_1 > 0$ to be chosen. Using (50) we get

$$|(f,(\chi_- L(\chi_0+\chi_+) + (\chi_0+\chi_+)L\chi_-)f)| \le \varepsilon_1\|\chi_- f\|_2^2 + \frac{1}{\varepsilon_1}(f,Q_1 f), \quad (51)$$

with $Q_1 = (\chi_0+\chi_+)L\chi_-^2 L(\chi_0+\chi_+)$. We estimate now the trace of Q_1. By the definition of η, χ_-, χ_0 and χ_+ it follows that

$$\mathrm{Tr}[Q_1] = \int_{|\mathbf{x}|\le r(1-\nu)}\int_{|\mathbf{y}|\ge r} L^2(\mathbf{x},\mathbf{y})\,d\mathbf{x}d\mathbf{y} \le \tfrac{(16)^2}{3\pi^2}\tfrac{(1-\nu)^3}{\nu}D(\eta,\lambda,r)^2 r^2 e^{-\alpha^{-1}r\nu}.$$

In the last step we use the definition of L, Remark 4.2 and the definition of the constant $D(\eta,\lambda,r)$ given in the statement of the lemma.
Now we choose $\Gamma_1 = \sqrt{\varepsilon_2}\chi_0$ and $\Gamma_2 = 1/\sqrt{\varepsilon_2}\chi_+ L\chi_0$ with $\varepsilon_2 > 0$ to be chosen. Proceeding as above we get

$$|(f,(\chi_+ L\chi_0 + \chi_0 L\chi_+)f)| \le \varepsilon_2\|\chi_0 f\|_2^2 + \frac{1}{\varepsilon_2}(f,Q_2 f), \quad (52)$$

with $Q_2 = \chi_+ L\chi_0^2 L\chi_+$ and such that

$$\mathrm{Tr}[Q_2] \le \tfrac{(16)^2}{3\pi^2}\tfrac{1-(1-\nu)^3(1-\lambda)^3}{\nu(1-\lambda)^2}D(\eta,\lambda,r)^2\; r^2 e^{-\alpha^{-1}r\frac{\nu}{1-\lambda}}.$$

It remains to study the term $\chi_0 L\chi_0$. This one has to be treated differently. By Schwartz's inequality one gets

$$|(f,\chi_0 L\chi_0 f)| \le \tfrac{3\alpha}{2}D(\eta,\lambda,r)\int_{\mathbb{R}^3}\chi_0(\mathbf{x})|f(\mathbf{x})|^2, \quad (53)$$

since $\int_{\mathbb{R}^3}|L(\mathbf{x},\mathbf{y})|d\mathbf{x}d\mathbf{y} \le \frac{3\alpha}{2}D(\eta,\lambda,r)$.
The claim follows from (51), (52) and (53) choosing $\varepsilon_1 = D(\eta,\lambda,r)\alpha e^{-\frac{1}{2}\alpha^{-1}r\nu}$, $\varepsilon_2 = \frac{3\alpha}{2}D(\eta,\lambda,r)$ and with $Q := \frac{1}{\varepsilon_1}Q_1 + \frac{1}{\varepsilon_2}Q_2$. ◻

DEFINITION 4.4 (The localization function). *Fix $0<\lambda<1$ and let $G:\mathbb{R}^3\to\mathbb{R}$ be given by*

$$G(\mathbf{x}) := \begin{cases} 0 & \text{if } |\mathbf{x}|\le 1,\\ \frac{\pi}{2}(|\mathbf{x}|-1)\frac{1}{(1-\lambda)^{-1}-1} & \text{if } 1\le|\mathbf{x}|\le(1-\lambda)^{-1},\\ \frac{\pi}{2} & \text{if } (1-\lambda)^{-1}\le|\mathbf{x}|.\end{cases}$$

Let $r>0$ and define the outside localization function $\theta_r(\mathbf{x}) := \sin(G(\frac{|\mathbf{x}|}{r}))$.

REMARK 4.5. *From the definition it follows that $\|\nabla\theta_r\|_\infty \le \frac{\pi}{2}\frac{1-\lambda}{\lambda}r^{-1}$.*

LEMMA 4.6. *For all $r>0$ and $\lambda,\nu\in(0,1)$ the density ρ^{HF} of the minimizer satisfies*

$$\int_{|\mathbf{x}|>r(1-\lambda)^{-1}}\rho^{\mathrm{HF}}(\mathbf{x})d\mathbf{x} \quad\le\quad 1+\tfrac{2}{\lambda}+2\sup_{|\mathbf{x}|=r(1-\lambda)}|\mathbf{x}|\Phi^{\mathrm{HF}}_{r(1-\lambda)}(\mathbf{x})+\mathcal{R}^{\frac{1}{2}}$$

with

$$\mathcal{R} = 6D(\lambda)r^{-1}\int_{r(1-\nu)<|\mathbf{x}|<r\frac{1+\nu}{1-\lambda}} \rho^{\mathrm{HF}}(\mathbf{x})\, d\mathbf{x} + 2D(\lambda)(r^{-1}N + Cr\alpha^{-2})e^{-\frac{1}{2}\alpha^{-1}r\nu},$$

with $D(\lambda) := (1+\pi/(2\lambda(1-\lambda)))\pi/(2\lambda)$ *and* $C = C(\lambda,\nu)$.

Proof. Let γ^{HF} be the minimizer. By the variational principle, γ^{HF} is a projection onto the subspace spanned by $u_1,\dots,u_N$. These functions u_i satisfy the Euler Lagrange equations $h_{\gamma^{\mathrm{HF}}}u_i = \varepsilon_i u_i$, $\varepsilon_i < 0$, for $i = 1,\dots,N$, with $h_{\gamma^{\mathrm{HF}}}$ defined in (11).
Given η a function in $C^1(\mathbb{R}^3)$ with support away from zero, we find

$$0 \geq \sum_{i=1}^N \varepsilon_i \int_{\mathbb{R}^3} |u_i(\mathbf{x})|^2|\mathbf{x}|\eta^2(\mathbf{x})d\mathbf{x} = \sum_{i=1}^N \int_{\mathbb{R}^3} u_i(\mathbf{x})^*|\mathbf{x}|\eta^2(\mathbf{x})\, h_{\gamma^{\mathrm{HF}}}u_i(\mathbf{x})d\mathbf{x}.$$

Since $\eta T(\mathbf{p})u_i \in L^2(\mathbb{R}^3)$ (Theorem 1.5, (3)), using the Euler-Lagrange equations and treating all the terms, except the kinetic energy, as in [23, Formula (63)] we get

$$\begin{aligned} 0 \quad \geq \quad & \alpha^{-1}\sum_{i=1}^N (u_i\eta|\cdot|, \eta T(\mathbf{p})u_i) - Z\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x} \\ & + \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \left[\rho^{\mathrm{HF}}(\mathbf{x})\rho^{\mathrm{HF}}(\mathbf{y}) - \mathrm{Tr}_{\mathbb{C}^q}|\gamma^{\mathrm{HF}}(\mathbf{x},\mathbf{y})|^2\right] \frac{|\mathbf{y}|(1-\eta^2(\mathbf{x}))\eta^2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\ & + \tfrac{1}{2}\Big(\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}\Big)^2 - \tfrac{1}{2}\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}. \end{aligned} \tag{54}$$

Now we look at the kinetic energy term. For each $i \in \{1,\dots,N\}$ we may write

$$\mathrm{Re}(u_i\eta|\cdot|, \eta T(\mathbf{p})u_i) = \mathrm{Re}(u_i\eta|\cdot|, T(\mathbf{p})(\eta u_i)) + \mathrm{Re}(u_i\eta|\cdot|, [\eta, T(\mathbf{p})]u_i), \tag{55}$$

where $[A,B]$ denotes the commutator of the operators A and B. The first term on the right hand side of (55) is non-negative by the result of Lieb in [13]. Notice that here we may use that $\eta u_i \in H^1(\mathbb{R}^3)$ (see Theorem 1.5, (3)).
Hence, from (54) and (55) we find

$$\begin{aligned} 0 \quad \geq \quad & \alpha^{-1}\sum_{i=1}^N \mathrm{Re}(u_i\eta|\cdot|, [\eta, T(\mathbf{p})]u_i) - Z\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x} \\ & + \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \left[\rho^{\mathrm{HF}}(\mathbf{x})\rho^{\mathrm{HF}}(\mathbf{y}) - \mathrm{Tr}_{\mathbb{C}^q}|\gamma^{\mathrm{HF}}(\mathbf{x},\mathbf{y})|^2\right] \frac{|\mathbf{y}|(1-\eta^2(\mathbf{x}))\eta^2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{x}d\mathbf{y} \\ & + \tfrac{1}{2}\Big(\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}\Big)^2 - \tfrac{1}{2}\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}. \end{aligned} \tag{56}$$

By a density argument we may choose $\eta = \theta_r$ the localization function defined in Definition 4.4. Reasoning as on page 541 of [23], we get

$$\begin{aligned} 0 \quad \geq \quad & \alpha^{-1}\sum_{i=1}^{N} \mathrm{Re}(u_i\eta|\cdot|, [\eta, T(\mathbf{p})]u_i) + \tfrac{1}{2}\Big(\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}\Big)^2 \\ & -\Big(\tfrac{1}{2} + \tfrac{1}{\lambda} + \sup_{|\mathbf{x}|=r(1-\lambda)} |\mathbf{x}|\Phi^{\mathrm{HF}}_{r(1-\lambda)}(\mathbf{x})\Big)\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}. \end{aligned} \tag{57}$$

It remains to estimate the first term on the right hand side of (57). With the same arguments used in the proof of the IMS formula, it can be rewritten as

$$\alpha^{-1}\sum_{i=1}^{N} \mathrm{Re}(u_i\eta|\cdot|, [\eta, T(\mathbf{p})]u_i) = -\alpha^{-1}\sum_{i=1}^{N}(u_i, Lu_i), \tag{58}$$

where L is the operator defined in (49). Using Lemma 4.3 and since $\|\nabla\eta\|_\infty = \|\nabla\theta_r\|_\infty \leq \pi/(2\lambda r)$ we find, with $D(\lambda)$ defined as in the statement,

$$\begin{aligned} \alpha^{-1}\Big|\sum_{i=1}^{N}(u_i, Lu_i)\Big| \quad \leq \quad & 3D(\lambda)r^{-1}\|\chi_0\rho^{\mathrm{HF}}\|_1 + D(\lambda)r^{-1}e^{-\frac{1}{2}\alpha^{-1}r\nu}\|\chi_-\rho^{\mathrm{HF}}\|_1 \\ & + CD(\lambda)r\alpha^{-2}e^{-\frac{1}{2}\alpha^{-1}r\nu}, \end{aligned} \tag{59}$$

where χ_0, χ_- and C are as defined in the statement of Lemma 4.3. Hence combining (57) with (59), using the definition of χ_0 and that $\|\chi_-\rho^{\mathrm{HF}}\|_1 \leq N$ we have

$$\begin{aligned} 0 \quad \geq \quad & -3D(\lambda)r^{-1}\int_{r(1-\nu)<|\mathbf{x}|<r\frac{1+\nu}{1-\lambda}} \rho^{\mathrm{HF}}(\mathbf{x})\,d\mathbf{x} - D(\lambda)r^{-1}e^{-\frac{1}{2}\alpha^{-1}r\nu}N \\ & -CD(\lambda)r\alpha^{-2}e^{-\frac{1}{2}\alpha^{-1}r\nu} + \tfrac{1}{2}\Big(\int_{\mathbb{R}^3}\rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}\Big)^2 \\ & -\Big(\tfrac{1}{2} + \tfrac{1}{\lambda} + \sup_{|\mathbf{x}|=r(1-\lambda)} |\mathbf{x}|\Phi^{\mathrm{HF}}_{r(1-\lambda)}(\mathbf{x})\Big)\int_{\mathbb{R}^3}\rho^{\mathrm{HF}}(\mathbf{x})\eta^2(\mathbf{x})d\mathbf{x}. \end{aligned}$$

The claim follows using that $x^2 - Bx - C \leq 0$ implies $x \leq B + \sqrt{C}$. □

Proof of Lemma 4.1. We proceed as in [23, page 551]. The first estimate follows directly from the equality

$$\int_{|\mathbf{x}|<r} (\rho^{\mathrm{HF}}(\mathbf{x}) - \rho^{\mathrm{TF}}(\mathbf{x}))\,d\mathbf{x} = \tfrac{1}{4\pi}r\int_{S^2}(\Phi^{\mathrm{HF}}_r(r\omega) - \Phi^{\mathrm{TF}}_r(r\omega))\,d\omega,$$

and (46). To prove (48) we use Lemma 4.6. We first notice that for $0 < \beta < \gamma$

and γ such that $r\gamma \leq R$

$$\begin{aligned}\int_{r\beta<|\mathbf{y}|<r\gamma} \rho^{\mathrm{HF}}(\mathbf{y})\, d\mathbf{y} &\leq \Big|\int_{|\mathbf{y}|<r\gamma} (\rho^{\mathrm{HF}}(\mathbf{y}) - \rho^{\mathrm{TF}}(\mathbf{y}))\, d\mathbf{y}\Big| \\ &\quad + \Big|\int_{|\mathbf{y}|<r\beta} (\rho^{\mathrm{HF}}(\mathbf{y}) - \rho^{\mathrm{TF}}(\mathbf{y}))\, d\mathbf{y}\Big| + \int_{|\mathbf{y}|>r\beta} \rho^{\mathrm{TF}}(\mathbf{y})\, d\mathbf{y} \\ &\leq Cr^{-3}\beta^{-3}(1+\sigma r^{\varepsilon'}). \end{aligned} \tag{60}$$

Here we used (47) and that by the TF-equation and (13)

$$\int_{|\mathbf{y}|>r\beta} \rho^{\mathrm{TF}}(\mathbf{y})\, d\mathbf{y} \leq \tfrac{3^4 2\pi^2}{q^2}\beta^{-3}r^{-3}.$$

Since $\int_{|\mathbf{x}|>r} \rho^{\mathrm{HF}} \leq \int_{|\mathbf{x}|>2r/3} \rho^{\mathrm{HF}}$ to prove the claim we estimate this second integral. By Lemma 4.6 with r replaced by $r/2$, $\lambda = \frac{1}{4}$ and $\nu = \frac{1}{2}$ we get

$$\int_{|\mathbf{x}|>2r/3} \rho^{\mathrm{HF}}(\mathbf{x}) d\mathbf{x} \leq 9 + \tfrac{3}{4} r \sup_{|\mathbf{x}|=3r/8} \Phi^{\mathrm{HF}}_{3r/8}(\mathbf{x}) + \mathcal{R}^{\frac{1}{2}},$$

with $\mathcal{R}$ defined as in the statement of Lemma 4.6. By (46) and Corollary 1.14 we find

$$\sup_{|\mathbf{x}|=3r/8} \Phi^{\mathrm{HF}}_{3r/8}(\mathbf{x}) \leq C\sigma r^{-4+\varepsilon'} + \sup_{|\mathbf{x}|=3r/8} \Phi^{\mathrm{TF}}_{3r/8}(\mathbf{x}) \leq C(1+\sigma r^{\varepsilon'})r^{-4}.$$

Moreover, from (60) with $\beta = 1/4$ and $\gamma = 1$, since $N < 2Z+1$ and the boundness of $\mathbb{R}^+ \ni x \mapsto x^p e^{-x}$ for all $p > 0$, we find

$$\mathcal{R} \leq C(r^{-4}(1+\sigma r^{\varepsilon'}) + r^{-1}).$$

The claim follows directly. □

4.2 Separating the inside from the outside

We consider the exterior part of the minimizer, i.e. the density matrix

$$\gamma_r^{\mathrm{HF}} := \theta_r \gamma^{\mathrm{HF}} \theta_r, \tag{61}$$

with θ_r as defined in Definition 4.4. This density matrix almost minimizes a new energy functional where there is no exchange term. Indeed sufficiently far away from the nucleus the electrons are far apart and hence their mutual interaction is small.

We define an auxiliary energy functional on $\mathcal{A}$ (see (8)) given by

$$\mathcal{E}^A(\gamma) := \mathrm{Tr}[(\alpha^{-1}T(\mathbf{p}) - \Phi_r^{\mathrm{HF}})\gamma] + D(\rho_\gamma). \tag{62}$$

Theorem 4.7. *Let $r > 0$ and $\lambda, \nu \in (0,1)$. Let χ_r^+ denote the characteristic function of $\mathbb{R}^3 \setminus B_r(0)$. The density matrix $\gamma_r^{\rm HF}$ defined in* (61) *satisfies*

$$\mathcal{E}^A(\gamma_r^{\rm HF}) \le \Big\{\mathcal{E}^A(\gamma) : \gamma \in \mathcal{A}, \operatorname{supp}(\rho_\gamma) \subset \mathbb{R}^3 \setminus B_r(0), \|\rho_\gamma\|_1 \le \|\rho^{\rm HF}\chi_r\|_1\Big\} + \mathcal{R},$$

where

$$\begin{aligned}\mathcal{R} \;=\;& (\tfrac{\pi}{2\lambda} + \tfrac{C}{\lambda^2} r^{-1}) r^{-1} \int_{r(1-\lambda)(1-\nu)\le|\mathbf{x}|} \rho^{\rm HF}(\mathbf{x})\, d\mathbf{x} + c'\alpha^{-2}(1+\alpha r^{-2}) e^{-\frac{1}{2}\alpha^{-1} r d} \\ & + \mathcal{E}x(\gamma_r^{\rm HF}) + C\int_{r(1-\lambda)\le|\mathbf{x}|\le\frac{r}{1-\lambda}} \Big[\big(\Phi^{\rm HF}_{r(1-\lambda)}(\mathbf{x})\big)^{\frac{5}{2}} + \alpha^3\big(\Phi^{\rm HF}_{r(1-\lambda)}(\mathbf{x})\big)^4\Big]\, d\mathbf{x},\end{aligned}$$

and c', d are positive constants depending only on ν and λ.

Proof. We proceed as in [23, pages 532-6]. The first step of the proof is a localization. Once again we have to treat carefully the localization error coming from the kinetic energy. This is the main difference with [23]. For completeness we repeat the main ideas of the reasoning.

We consider the following partition of unity of $\mathbb{R}^3$: $1 = \theta_r^2(\mathbf{x}) + \theta_0^2(\mathbf{x}) + \theta_-^2(\mathbf{x})$ with θ_r defined as in Definition 4.4 and

$$\theta_0(\mathbf{x}) := \big(\theta^2_{r(1-\lambda)}(\mathbf{x}) - \theta_r^2(\mathbf{x})\big)^{\frac{1}{2}} \text{ and } \theta_-(\mathbf{x}) := \big(1 - \theta^2_{r(1-\lambda)}(\mathbf{x})\big)^{\frac{1}{2}}.$$

Associated to this partition of unity we define

$$\gamma_0^{\rm HF} := \theta_0 \gamma^{\rm HF} \theta_0 \text{ and } \gamma_-^{\rm HF} := \theta_- \gamma^{\rm HF} \theta_-.$$

We prove the claim by showing that for all density matrices $\gamma \in \mathcal{A}$ such that $\operatorname{supp}(\rho_\gamma) \subset \mathbb{R}^3 \setminus B_r(0)$ and $\|\rho_\gamma\|_1 \le \|\rho^{\rm HF}\chi_r^+\|_1$ it holds that

$$\mathcal{E}^A(\gamma_r^{\rm HF}) + \mathcal{E}^{\rm HF}(\gamma_-^{\rm HF}) - \mathcal{R} \le \mathcal{E}^{\rm HF}(\gamma^{\rm HF}) \le \mathcal{E}^A(\gamma) + \mathcal{E}^{\rm HF}(\gamma_-^{\rm HF}). \tag{63}$$

The proof of the upper bound in (63) is as in [23, page 533].

To prove the lower bound as a first step we localize. By Theorem 2.1 we find

$$\begin{aligned}\alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma^{\rm HF}] \;=\;& \alpha^{-1}\operatorname{Tr}[T(\mathbf{p})(\gamma_r^{\rm HF} + \gamma_0^{\rm HF} + \gamma_-^{\rm HF})] \\ & -\alpha^{-1}\sum_{i=1}^N (u_i, (L_r + L_0 + L_-)u_i),\end{aligned}$$

where L_r, L_0 and L_- are defined as the L_i's in (14).

We first estimate the error term. The procedure is similar to the one used in the proof of Lemma 4.3. We introduce three cut-off functions: χ_- be the characteristic function of $B_{r(1-\lambda)(1-\nu)}(0)$, χ_r the characteristic function of $\mathbb{R}^3 \setminus B_{r\frac{1+\nu}{1-\lambda}}(0)$ and χ_0 defined by $\chi_0(\mathbf{x}) = 1 - \chi_r(\mathbf{x}) - \chi_-(\mathbf{x})$ for all $\mathbf{x} \in \mathbb{R}^3$. Notice that χ_- and χ_r are the characteristic functions of sets where θ_-, θ_0 and θ_r are constants. For $k \in \{-, 0, r\}$ we have the following splitting

$$L_k = \chi_- L_k(\chi_0 + \chi_r) + (\chi_0 + \chi_r) L_k \chi_- + \chi_r L_k \chi_0 + \chi_0 L_k \chi_r + \chi_0 L_k \chi_0,$$

and proceeding as in the proof of Lemma 4.3 with $\varepsilon_{1,k}, \varepsilon_{2,k}$ to be chosen we find

$$\begin{aligned}(f, L_k f) \quad \leq \quad & \varepsilon_{1,k}\|\chi_- f\|_2^2 + \varepsilon_{1,k}^{-1}(f, Q_1 f) + \varepsilon_{2,k}\|\chi_0 f\|_2^2 + \varepsilon_{2,k}^{-1}(f, Q_2 f) \\ & + \tfrac{3\alpha}{2}\|\nabla\theta_k\|_\infty^2 \|\chi_0 f\|_2^2.\end{aligned}$$

with operators Q_1 and Q_2 being positive semi-definite operators with

$$\begin{aligned}\mathrm{Tr}[Q_1] \quad \leq \quad & \tfrac{(16)^2}{3\pi^2}\tfrac{(1-\lambda)^2(1-\nu)^3}{\nu}\|\nabla\theta_k\|_\infty^4 r^2 e^{-\alpha^{-1}r\nu(1-\lambda)} \\ \mathrm{Tr}[Q_2] \quad \leq \quad & \tfrac{(16)^2}{3\pi^2}\tfrac{1}{\nu(1-\lambda)^2}\|\nabla\theta_k\|_\infty^4 r^2 e^{-\alpha^{-1}r\frac{\nu}{1-\lambda}}.\end{aligned}$$

Choosing then

$$\varepsilon_{2,k} = \tfrac{3\alpha}{2}\|\nabla\theta_k\|_\infty^2 \text{ and } \varepsilon_{1,k} = \alpha\|\nabla\theta_k\|_\infty^2 e^{-\frac{1}{2}\alpha^{-1}r\nu(1-\lambda)},$$

since $(\|\nabla\theta_r\|_\infty^2 + \|\nabla\theta_0\|_\infty^2 + \|\nabla\theta_-\|_\infty^2) \leq 3\pi^2/(4\lambda^2)r^{-2}$ and $\|\rho^{\mathrm{HF}}\chi_-\|_1 \leq N$ we get

$$\begin{aligned}\alpha^{-1}\sum_{i=1}^{N}(u_i, (L_r + L_0 + L_-)u_i) \quad \leq \quad & \tfrac{3\pi^2}{4\lambda^2}r^{-2}\|\rho^{\mathrm{HF}}\chi_0\|_1 + \tfrac{3\pi^2}{4\lambda^2}r^{-2}e^{-\frac{1}{2}\alpha^{-1}r\nu(1-\lambda)}N \\ + \quad & c\alpha^{-2}e^{-\frac{1}{2}\alpha^{-1}r\nu(1-\lambda)}.\end{aligned}$$

Here c is a constant that depends only on ν and λ.
Hence from (64), the inequality above and since $N \leq 2Z+1$ we find

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) \quad \geq \quad & \mathrm{Tr}\left[\Big(\alpha^{-1}T(\mathbf{p}) - \frac{Z}{|\cdot|}\Big)(\gamma_r^{\mathrm{HF}} + \gamma_0^{\mathrm{HF}} + \gamma_-^{\mathrm{HF}})\right] + \mathcal{D}(\gamma^{\mathrm{HF}}) \\ & -\mathcal{E}x(\gamma^{\mathrm{HF}}) - \tfrac{3\pi^2}{4\lambda^2}r^{-2}\|\rho^{\mathrm{HF}}\chi_0\|_1 - c'\alpha^{-2}(1+\alpha r^{-2})e^{-\frac{1}{2}\alpha^{-1}rd}.\end{aligned}$$

The constants c', d depend only on λ and ν. Proceeding as in [23] we get

$$\begin{aligned}\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) \quad \geq \quad & \mathcal{E}^{\mathrm{HF}}(\gamma_-^{\mathrm{HF}}) + \mathcal{E}^{A}(\gamma_r^{\mathrm{HF}}) - \mathcal{E}x(\gamma_r^{\mathrm{HF}}) - c'\alpha^{-2}(1+\alpha r^{-2})e^{-\frac{1}{2}\alpha^{-1}rd} \\ & + \mathrm{Tr}\left[\Big(\alpha^{-1}T(\mathbf{p}) - \Phi_{r(1-\lambda)}^{\mathrm{HF}}(\cdot)\Big)\gamma_0^{\mathrm{HF}}\right] \\ & -(\tfrac{\pi}{2\lambda} + \tfrac{3\pi^2}{4\lambda^2}r^{-1})r^{-1}\int_{|\mathbf{x}|\geq r(1-\lambda)(1-\nu)}\rho^{\mathrm{HF}}(\mathbf{x})\, d\mathbf{x}.\end{aligned}$$

The claim follows using Theorem 2.5. □

4.3 Comparing with an Outside Thomas Fermi

At this point we introduce an "Outside Thomas Fermi": a TF-energy functional whose minimizer approximates the HF-density at a certain distance from the nucleus.

Let $r>0$ such that

$$|\Phi^{\rm HF}_{|\mathbf{x}|}(\mathbf{x})-\Phi^{\rm TF}_{|\mathbf{x}|}(\mathbf{x})|\le\sigma|\mathbf{x}|^{-4+\varepsilon'}, \tag{64}$$

for all $|\mathbf{x}|\le r$ for some $\sigma>0$ and $\varepsilon'>0$. Let V_r be the potential defined by

$$V_r(\mathbf{x})=\chi_r^+(\mathbf{x})\Phi_r^{\rm HF}(\mathbf{x})=\begin{cases}0 & \text{if } |\mathbf{x}|<r,\\ \Phi_r^{\rm HF}(\mathbf{x}) & \text{if } |\mathbf{x}|\ge r.\end{cases} \tag{65}$$

Here and in the following $\chi_r^+(\mathbf{x}):=1-\chi_r(\mathbf{x})$, $\mathbf{x}\in\mathbb{R}^3$, where χ_r is the characteristic function of the ball of radius r centered at 0. Notice that $V_r\in L^{\frac52}(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)$ with

$$\inf\{\|W\|_\infty : V_r-W\in L^{\frac52}(\mathbb{R}^3)\}=0.$$

Let $\mathcal{E}_r^{\rm OTF}$ be the TF-functional $\mathcal{E}^{\rm TF}_{V_r}$ corresponding to the potential V_r defined in (65). Let $\rho_r^{\rm OTF}$ be the unique minimizer of $\mathcal{E}_r^{\rm OTF}$ under the condition

$$\int_{\mathbb{R}^3}\rho(\mathbf{x})d\mathbf{x}\le\int_{|\mathbf{y}|\ge r}\rho^{\rm HF}(\mathbf{y})d\mathbf{y},$$

(see Theorem 1.9). Then $\rho_r^{\rm OTF}$ is solution to the OTF-equation

$$\tfrac12\left(\tfrac{6\pi^2}{q}\right)^{\frac23}(\rho_r^{\rm OTF})^{\frac23}=[\varphi_r^{\rm OTF}-\mu_r^{\rm OTF}]_+\,, \tag{66}$$

where

$$\varphi_r^{\rm OTF}(\mathbf{x})=V_r(\mathbf{x})-\int_{\mathbb{R}^3}\frac{\rho_r^{\rm OTF}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y},$$

is the OTF-mean field potential and $\mu_r^{\rm OTF}$ is the corresponding chemical potential. From (66) (and $\mu_r^{\rm OTF}\ge0$) we see that the support of $\rho_r^{\rm OTF}$ is contained in $\mathbb{R}^3\setminus B_r(0)$.

In the intermediary zone instead of comparing directly $\Phi^{\rm HF}_{|\mathbf{x}|}$ and $\Phi^{\rm TF}_{|\mathbf{x}|}$ we compare first the HF-density with the OTF-density and then the OTF-density with the TF-density. When comparing the TF and OTF there is no difference with the non-relativistic case and for brevity we refer for the proofs to [23].

We start by studying the behavior of the minimizer and mean field potential of the OTF. The proof of the following bounds is in [23, page 557-558] in the case $q=2$ and it can be directly generalised to the other values of q.

Lemma 4.8 ([23, Lem.12.1]). *For all* $\mathbf{y}\in\mathbb{R}^3$ *we have*

$$\varphi^{\rm TF}(\mathbf{y})\le3^42^{-1}q^{-2}\pi^2|\mathbf{y}|^{-4}\ \textit{and}\ \rho^{\rm TF}(\mathbf{y})\le3^52^{-1}q^{-2}\pi|\mathbf{y}|^{-6}.$$

Let β_0 *be as defined in Theorem 1.12, then for all* $|\mathbf{y}|\ge\beta_0Z^{-\frac13}$ *we have*

$$\varphi^{\rm TF}(\mathbf{y})\ge C|\mathbf{y}|^{-4}\ \textit{and}\ \rho^{\rm TF}(\mathbf{y})\ge C|\mathbf{y}|^{-6}.$$

With r,σ,ε' *such that* (64) *holds and* $\sigma r^{\varepsilon'}\le1$ *we have for all* $|\mathbf{y}|\ge r$

$$\rho_r^{\rm OTF}(\mathbf{y})\le Cr^{-6}\ \textit{and}\ \varphi_r^{\rm OTF}(\mathbf{y})\le|V_r(\mathbf{y})|\le Cr^{-4}.$$

Lemma 4.9 ([23, Lem.12.2]). *With r, σ, ε' such that* (64) *holds for all* $|\mathbf{x}| \leq r$ *we have*

$$\int_{|\mathbf{y}|\geq r} (\rho^{\mathrm{TF}}(\mathbf{y}) - \rho^{\mathrm{HF}}(\mathbf{y}))d\mathbf{y} \leq \sigma r^{-3+\varepsilon'}.$$

For $\mathbf{x} \in \mathbb{R}^3$ with $|\mathbf{x}| > r$ we may write

$$\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x}) = \mathcal{A}_1(r,\mathbf{x}) + \mathcal{A}_2(r,\mathbf{x}) + \mathcal{A}_3(r,\mathbf{x}), \tag{67}$$

where

$$\begin{aligned} \mathcal{A}_1(r,\mathbf{x}) &= \varphi^{\mathrm{OTF}}_r(\mathbf{x}) - \varphi^{\mathrm{TF}}(\mathbf{x}), \\ \mathcal{A}_2(r,\mathbf{x}) &= \int_{|\mathbf{y}|>|\mathbf{x}|} \frac{\rho^{\mathrm{OTF}}_r(\mathbf{y}) - \rho^{\mathrm{TF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} \end{aligned}$$

and

$$\mathcal{A}_3(r,\mathbf{x}) = \int_{r<|\mathbf{y}|<|\mathbf{x}|} \frac{\rho^{\mathrm{OTF}}_r(\mathbf{y}) - \rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y}.$$

4.3.1 Estimate on $\mathcal{A}_1$ and $\mathcal{A}_2$

Lemma 4.10 ([23, Lem.12.4]). *Let $N \geq Z$. Given $\varepsilon', \sigma > 0$ there exists a constant $D > 0$ such that for all r with $\beta_0 Z^{-\frac{1}{3}} \leq r \leq D$ for which* (64) *holds for all $|\mathbf{x}| \leq r$, then $\mu^{\mathrm{OTF}}_r = 0$ and*

$$\tfrac{3^4\pi^2}{2q^2}|\mathbf{x}|^{-4}(1 + ar^{\zeta}|\mathbf{x}|^{-\zeta})^{-2} \leq \varphi^{\mathrm{OTF}}_r(\mathbf{x}) \leq \tfrac{3^4\pi^2}{2q^2}|\mathbf{x}|^{-4}(1 + Ar^{\zeta}|\mathbf{x}|^{-\zeta}) \ \textit{ for } |\mathbf{x}| > r,$$

where a, A are universal constants and $\zeta = (-7 + \sqrt{73})/2$.

Lemma 4.11 ([23, Lem.12.5]). *Let $N \geq Z$. Given $\varepsilon', \sigma > 0$ there exists a constant $D > 0$ depending only on ε', σ such that for all r with $\beta_0 Z^{-\frac{1}{3}} \leq r \leq D$ for which* (64) *holds for $|\mathbf{x}| \leq r$, then for all $|\mathbf{x}| \geq r$*

$$|\mathcal{A}_1(r,\mathbf{x})| \leq C|\mathbf{x}|^{-4-\zeta}r^{\zeta} \quad \textit{and} \quad |\mathcal{A}_2(r,\mathbf{x})| \leq C|\mathbf{x}|^{-4-\zeta}r^{\zeta},$$

with $\zeta = (-7 + \sqrt{73})/2$ and C a universal constant.

The proof of the previous lemmas is in [23, p. 558-564].

4.3.2 Estimate on $\|\chi^+_r \rho^{\mathrm{HF}} - \rho^{\mathrm{OTF}}_r\|_C$

Lemma 4.12. *Let G_α be the function defined in Theorem 2.3 and $\rho^{\mathrm{HF}}_r(\mathbf{x})$ be the one-particle density of the density matrix γ^{HF}_r defined in* (61). *Let $Z\alpha = \kappa$ fixed, $0 \leq \kappa < 2/\pi$ and $Z \geq 1$.*
Given constants $\varepsilon', \sigma > 0$ there exists $D < \frac{4}{5}$ such that for all r with $\beta_0 Z^{-\frac{1}{3}} \leq r \leq D$ for which (64) *holds for $|\mathbf{x}| \leq r$, it follows that*

$$\begin{aligned} \alpha^{-1}\int_{\mathbb{R}^3} G_\alpha(\rho^{\mathrm{HF}}_r(\mathbf{x}))\, d\mathbf{x} &\leq \alpha^{-1}\,\mathrm{Tr}[T(\mathbf{p})\gamma^{\mathrm{HF}}_r] \\ &\leq 2\mathcal{R} + Cr^{-7} + Cr^{-4}\int_{\mathbb{R}^3} \rho^{\mathrm{HF}}_r(\mathbf{x})\, d\mathbf{x}, \end{aligned}$$

with C a universal positive constant and $\mathcal{R}$ as defined in Theorem 4.7.

Proof. The first inequality follows directly from Theorem 2.3. To prove the second inequality we proceed as in Lemma 3.1. In this case we are interested only in the exterior part of the minimizer. Hence, instead of considering the HF-energy functional we consider the auxiliary functional $\mathcal{E}^A$, defined in (62), applied to the "exterior part of the minimizer" γ_r^{HF}.
Splitting the kinetic energy in two terms we find

$$\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) \geq \tfrac{1}{2}\alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma_r^{\mathrm{HF}}] + D(\rho_r^{\mathrm{HF}}) + \tfrac{1}{2}\operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - 2\Phi_r^{\mathrm{HF}})\gamma_r^{\mathrm{HF}}]. \quad (68)$$

Since $\Phi_r^{\mathrm{HF}}(\mathbf{x})$ is harmonic for $|\mathbf{x}| > r$ and going to zero at infinity

$$\Phi_r^{\mathrm{HF}}(\mathbf{x}) \leq \frac{r}{|\mathbf{x}|}\sup_{|\mathbf{y}|=r}\Phi_r^{\mathrm{HF}}(\mathbf{y}) \quad \text{for } |\mathbf{x}| > r.$$

Hence, since $\operatorname{supp}(\rho_r^{\mathrm{HF}}) \subset \mathbb{R}^3 \setminus B_r(0)$ we find

$$\operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - 2\Phi_r^{\mathrm{HF}})\gamma_r^{\mathrm{HF}}] \geq \operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - \frac{2r}{|\cdot|}\sup_{|\mathbf{y}|=r}\Phi_r^{\mathrm{HF}}(\mathbf{y}))\gamma_r^{\mathrm{HF}}] = \ldots .$$

Adding and subtracting $2D(\rho, \rho_r^{\mathrm{HF}})$ for $\rho \in L^1(\mathbb{R}^3) \cap L^{\frac{5}{3}}(\mathbb{R}^3)$, $\rho \geq 0$, to be chosen

$$\ldots = \operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - V_\rho)\gamma_r^{\mathrm{HF}}] - \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_r^{\mathrm{HF}}(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y}. \quad (69)$$

where for simplicity of notation here and in the following V_ρ is defined as $V_\rho(\mathbf{x}) := \frac{2r}{|\mathbf{x}|}\sup_{|\mathbf{y}|=r}\Phi_r^{\mathrm{HF}}(\mathbf{y}) - \rho * \frac{1}{|\mathbf{x}|}$.
From (69), (68) and the definition of the Coulomb norm and scalar product (Definition 2.7) we find

$$\begin{aligned}
\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) \geq\ & \tfrac{1}{2}\alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma_r^{\mathrm{HF}}] + \tfrac{1}{2}D(\rho_r^{\mathrm{HF}}) + \tfrac{1}{2}\|\rho_r^{\mathrm{HF}} - \rho\|_C^2 \\
& -\tfrac{1}{2}D(\rho) + \tfrac{1}{2}\operatorname{Tr}[(\alpha^{-1}T(\mathbf{p}) - V_\rho)\gamma_r^{\mathrm{HF}}] \qquad (70) \\
\geq\ & \tfrac{1}{2}\alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma_r^{\mathrm{HF}}] + \tfrac{1}{2}\sum_{i=1}^{N}(\theta_r u_i, (\alpha^{-1}T(\mathbf{p}) - V_\rho)\theta_r u_i) - \tfrac{1}{2}D(\rho),
\end{aligned}$$

denoting by u_i the HF-orbitals.
We now choose ρ as the minimizer of the TF-energy functional of a neutral atom with Coulomb potential and nuclear charge $2r\sup_{|\mathbf{y}|=r}\Phi_r^{\mathrm{HF}}(\mathbf{y})$. Then V_ρ is the corresponding TF-mean field potential and we see that the last two terms on the right hand side of (70) are like the ones in the claim of Proposition B.2. The only difference is due to the presence of the localization function θ_r. We now prove that these terms give the TF-energy modulo lower order terms. The method is the same as that of Proposition B.2. We repeat the main steps since in this case the scaling depends on r. Notice that since $r > \beta_0 Z^{-\frac{1}{3}}$ the contribution is coming only from the "outer zone".

Let $g \in C_0^\infty(\mathbb{R}^3)$ be spherically symmetric, normalized in $L^2(\mathbb{R}^3)$ and with support in $B_1(0)$. Let us define $g_r(\mathbf{x}) := r^{-3}g(\mathbf{x}r^{-2})$ and $\psi_r := g_r^2$. Since V_ρ is sub-harmonic on $|\mathbf{x}| > 0$, we see from the support properties of ψ_r and θ_r that

$$\sum_{i=1}^N (\theta_r u_i, (\alpha^{-1}T(\mathbf{p}) - V_\rho)\theta_r u_i) \geq \sum_{i=1}^N (\theta_r u_i, (\alpha^{-1}T(\mathbf{p}) - V_\rho * \psi_r)\theta_r u_i) = \dots.$$

For $\mathbf{p}, \mathbf{q} \in \mathbb{R}^3$ we define the coherent states $g_r^{\mathbf{p},\mathbf{q}}(\mathbf{x}) := g_r(\mathbf{x} - \mathbf{q})e^{i\mathbf{p}\cdot\mathbf{x}}$. By the formulas (B16) and (B17) with $L_\mathbf{q}$ the operator defined in the equation below (B17) we get

$$\begin{aligned} \dots \quad = \quad & \tfrac{1}{(2\pi)^3}\alpha^{-1} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} d\mathbf{p}d\mathbf{q}\, (T(\mathbf{p}) - \alpha V_\rho(\mathbf{q})) \sum_{i=1}^N \sum_{j=1}^q |(\theta_r u_i^j, g_r^{\mathbf{p},\mathbf{q}})|^2 \\ & - \alpha^{-1} \sum_{i=1}^N \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} d\mathbf{x}d\mathbf{q}\, \overline{(\theta_r u_i)}(\mathbf{x})(L_\mathbf{q}\theta_r u_i)(\mathbf{x}), \end{aligned} \tag{71}$$

where u_i^j denotes the j-th spin component of the orbital u_i. By the choice of the function g_r and with the same arguments that led to (B19) in the appendix we find

$$\begin{aligned} & \alpha^{-1} \sum_{i=1}^N \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} d\mathbf{x}d\mathbf{q}\, \overline{(\theta_r u_i)}(\mathbf{x})(L_\mathbf{q}\theta_r u_i)(\mathbf{x}) \\ \leq \quad & 3\sum_{i=1}^N \|\theta_r u_i\|_2^2 \|\nabla g_r\|_\infty^2 Vol(\mathrm{supp}(g_r)) \leq Cr^{-4}\|\rho_r^{\mathrm{HF}}\|_1. \end{aligned} \tag{72}$$

In the first term on the right hand side of (71) the integrand is zero if $|\mathbf{q}| < \frac{1}{4}r^2$ since in this case $\mathrm{supp}(\theta_r) \cap \mathrm{supp}(g_r^{\mathbf{q},\mathbf{p}}) = \emptyset$ (by the choice $D < 4/5$). To estimate it further from below we consider only the negative part of the integrand

$$\begin{aligned} & \tfrac{1}{(2\pi)^3}\alpha^{-1} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} d\mathbf{p}d\mathbf{q}\, (T(\mathbf{p}) - \alpha V_\rho(\mathbf{q})) \sum_{i=1}^N \sum_{j=1}^q |(\theta_r u_i^j, g_r^{\mathbf{p},\mathbf{q}})|^2 \\ \geq \quad & \tfrac{q}{(2\pi)^3}\alpha^{-1} \iint_{\substack{|\mathbf{q}| > \frac{1}{4}r^2 \\ T(\mathbf{p}) \leq \alpha V_\rho(\mathbf{q})}} d\mathbf{p}d\mathbf{q}\, (T(\mathbf{p}) - \alpha V_\rho(\mathbf{q})), \end{aligned} \tag{73}$$

where we have used that $0 \leq \sum_{i=1}^N |(\theta_r u_i^j, g_r^{\mathbf{p},\mathbf{q}})|^2 \leq 1$ (Bessel's inequality). We split the domain of integration in $\mathbf{p}$ as follows

$$\{\mathbf{p} \in \mathbb{R}^3 : T(\mathbf{p}) \leq \alpha V_\rho(\mathbf{q})\} = \Sigma_1 \cup \Sigma_2$$

with Σ_1, Σ_2 disjoint and $\Sigma_1 = \{\mathbf{p} \in \mathbb{R}^3 : \frac{1}{2}|\mathbf{p}|^2 \leq V_\rho(\mathbf{q})\}$. We treat these two contributions separately. We have

$$\alpha^{-1} \iint_{\substack{|\mathbf{q}| > \frac{1}{4}r^2 \\ \mathbf{p} \in \Sigma_2}} d\mathbf{p}d\mathbf{q}\, (T(\mathbf{p}) - \alpha V_\rho(\mathbf{q})) \geq -\iint_{\substack{|\mathbf{q}| > \frac{1}{4}r^2 \\ \mathbf{p} \in \Sigma_2}} d\mathbf{p}d\mathbf{q}\, [V_\rho(\mathbf{q})]_+ = \dots$$

and computing the integral, using that $(1+x)^{\frac{3}{2}} \leq 1 + \frac{3}{2}x + \frac{3}{8}x^2$

$$\cdots \geq -C \int_{|\mathbf{q}|>\frac{1}{4}r^2} d\mathbf{q}\, (\alpha^2 [V_\rho(\mathbf{q})]_+^{\frac{7}{2}} + \alpha^4 [V_\rho(\mathbf{q})]_+^{\frac{9}{2}}) \geq -C\alpha^2 r^{-\frac{23}{2}} - C\alpha^4 r^{-\frac{33}{2}}. \tag{74}$$

In the last step we used that $[V_\rho(\mathbf{q})]_+ \leq 2\frac{r}{|\mathbf{q}|} \sup_{|\mathbf{x}|=r} \Phi_r^{\rm HF}(\mathbf{x})$ and that by the hypothesis and Corollary 1.14

$$r \sup_{|\mathbf{x}|=r} \Phi_r^{\rm HF}(\mathbf{x}) \leq C r^{-3}, \tag{75}$$

choosing D such that $\sigma r^{\varepsilon'} \leq 1$.
Since $T(\mathbf{p}) \geq \frac{1}{2}\alpha|\mathbf{p}|^2 - \frac{1}{8}\alpha^3|\mathbf{p}|^4$ we find

$$\begin{aligned} &\alpha^{-1} \iint_{\substack{|\mathbf{q}|>\frac{1}{4}r^2 \\ \mathbf{p}\in\Sigma_1}} d\mathbf{p}d\mathbf{q}\, (T(\mathbf{p}) - \alpha V_\rho(\mathbf{q})) \\ \geq\ & \iint_{\substack{|\mathbf{q}|>\frac{1}{4}r^2 \\ \frac{1}{2}|\mathbf{p}|^2 \leq V_\rho(\mathbf{q})}} d\mathbf{p}d\mathbf{q}\, (\frac{1}{2}|\mathbf{p}|^2 - V_\rho(\mathbf{q})) - \tfrac{1}{8}\alpha^2 \iint_{\substack{|\mathbf{q}|>\frac{1}{4}r^2 \\ \frac{1}{2}|\mathbf{p}|^2 \leq V_\rho(\mathbf{q})}} d\mathbf{p}d\mathbf{q}\, |\mathbf{p}|^4. \end{aligned} \tag{76}$$

Computing the last integral we find

$$\alpha^2 \iint_{\substack{|\mathbf{q}|>\frac{1}{4}r^2 \\ \frac{1}{2}|\mathbf{p}|^2 \leq V_\rho(\mathbf{q})}} d\mathbf{p}d\mathbf{q}\, |\mathbf{p}|^4 \leq C\alpha^2 r^{-1} (2r \sup_{|\mathbf{x}|=r} \Phi_r^{\rm HF}(\mathbf{x}))^{\frac{7}{2}} \leq C\alpha^2 r^{-\frac{23}{2}}. \tag{77}$$

While for the first term on the right hand side of (76), computing the integral with respect to $\mathbf{p}$, we get

$$\iint_{\substack{|\mathbf{q}|>\frac{1}{4}r^2 \\ \frac{1}{2}|\mathbf{p}|^2 \leq V_\rho(\mathbf{q})}} d\mathbf{p}d\mathbf{q}\, (\tfrac{1}{2}|\mathbf{p}|^2 - V_\rho(\mathbf{q})) = -4\pi \frac{2^{\frac{5}{2}}}{15} \int_{|\mathbf{q}|>\frac{1}{4}r^2} d\mathbf{q}\, [V_\rho(\mathbf{q})]_+^{\frac{5}{2}}.$$

Hence collecting together (71), (72), (73) (74), (77) and the inequality above we find

$$\mathrm{Tr}[(\alpha^{-1}T(\mathbf{p}) - V_\rho)\gamma_r^{\rm HF}] \geq -\frac{2^{\frac{3}{2}}q}{15\pi^2} \int_{\mathbb{R}^3} d\mathbf{x}\, [V_\rho(\mathbf{x})]_+^{\frac{5}{2}} - Cr^{-4}\|\rho_r^{\rm HF}\|_1 - Cr^{-\frac{11}{2}} = \ldots.$$

since $\beta_0 Z^{-\frac{1}{3}} \leq r$ implies $\beta_0 \alpha^{\frac{1}{3}} \leq \kappa^{\frac{1}{3}} r$. From the TF-equation that ρ satisfies it follows that

$$\begin{aligned} \ldots &= \tfrac{3}{10}(\tfrac{6\pi^2}{q})^{\frac{2}{3}} \int_{\mathbb{R}^3} d\mathbf{x}\, \rho(\mathbf{x})^{\frac{5}{3}} - \int_{\mathbb{R}^3} \rho(\mathbf{x}) V_\rho(\mathbf{x})\, d\mathbf{x} - Cr^{-4}\|\rho_r^{\rm HF}\|_1 - Cr^{-\frac{11}{2}} \\ &= \mathcal{E}^{\rm TF}(\rho) + D(\rho) - Cr^{-4}\|\rho_r^{\rm HF}\|_1 - Cr^{-\frac{11}{2}}. \end{aligned}$$

Hence from (70) and the inequality above we get using (12) and (75)

$$\mathcal{E}^A(\gamma_r^{\rm HF}) \ \geq\ \tfrac{1}{2}\alpha^{-1}\,\mathrm{Tr}[T(\mathbf{p})\gamma^{\rm HF}] - Cr^{-7} - Cr^{-4}\|\rho_r^{\rm HF}\|_1.$$

The claim follows since $\mathcal{E}^A(\gamma_r^{\rm HF}) \leq \mathcal{R}$ by the result of Theorem 4.7 considering as a trial density matrix $\gamma \equiv 0$. □

Lemma 4.13. *Let $N' \in \mathbb{N}$ and $Z\alpha = \kappa$ be fixed, $0 \le \kappa < 2/\pi$ and $Z \ge 1$. Let e_j be the first N' negative eigenvalues of the operator $\alpha^{-1}T(\mathbf{p}) - \varphi_r^{\mathrm{OTF}}$ acting on functions with support on $\{\mathbf{x} \in \mathbb{R}^3 : |\mathbf{x}| \ge r\}$.*
Given constants $\varepsilon', \sigma > 0$ there exists $D < 4/5$ such that for all r with $\beta_0 Z^{-\frac{1}{3}} \le r \le D$ for which (64) holds for $|\mathbf{x}| \le r$, for all $\mu \in (0,1)$ and $s < r$ we have

$$\begin{aligned}\sum_{j=1}^{N'} e_j \quad &\ge \quad -(\tfrac{2}{1-\mu})^{\frac{3}{2}} \tfrac{1}{15\pi^2} \int_{|\mathbf{q}|>r} [\varphi_r^{\mathrm{OTF}}(\mathbf{q})]_+^{\frac{5}{2}}\, d\mathbf{q} - Cr^{-8} s\mu^{-\frac{3}{2}} - C\mu^{-3} r^{-5} s \\ &\quad -C(1-\mu)^{-\frac{7}{2}} r^{-5} - C(1-\mu) s^{-2} N',\end{aligned}$$

with C a positive constant.

Proof. Let f_j be the eigenfunctions (normalized in $L^2(\mathbb{R}^3, \mathbb{C}^q)$) corresponding to the eigenvalues e_j, $j = 1, .., N'$. Let $g \in C_0^\infty(\mathbb{R}^3)$ with support in $B_1(0)$ and define $g_s(\mathbf{x}) = s^{-\frac{3}{2}} g(\mathbf{x}/s)$ for a positive parameter s, $s < r$. We then write for $\mu \in (0,1)$

$$\sum_{j=1}^{N'} e_j = \sum_{j=1}^{N'} (f_j, (\alpha^{-1}T(\mathbf{p}) - \varphi_r^{\mathrm{OTF}}) f_j) = \mathcal{B}_1 + \mathcal{B}_2,$$

where

$$\begin{aligned}\mathcal{B}_1 \quad &= \quad \sum_{j=1}^{N'} (f_j, ((1-\mu)\alpha^{-1}T(\mathbf{p}) - \varphi_r^{\mathrm{OTF}} * g_s^2) f_j), \\ \mathcal{B}_2 \quad &= \quad \sum_{j=1}^{N'} (f_j, (\mu\alpha^{-1}T(\mathbf{p}) - \varphi_r^{\mathrm{OTF}} + \varphi_r^{\mathrm{OTF}} * g_s^2) f_j).\end{aligned}$$

We estimate these two terms separately. Considering for $\mathbf{p}, \mathbf{q} \in \mathbb{R}^3$ the coherent states $g_s^{\mathbf{p},\mathbf{q}}(\mathbf{x}) := e^{i\mathbf{p}\cdot\mathbf{x}} g_s(\mathbf{x} - \mathbf{q})$ using (B16) and (B17), we find

$$\begin{aligned}\mathcal{B}_1 \quad &= \quad \tfrac{1}{(2\pi)^3} \iint ((1-\mu)\alpha^{-1}T(\mathbf{p}) - \varphi_r^{\mathrm{OTF}}(\mathbf{q})) \sum_{j=1}^{N} |(f_j, g_s^{\mathbf{p},\mathbf{q}})|^2 \, d\mathbf{q} d\mathbf{p} \\ &\quad - (1-\mu)\alpha^{-1} \sum_{j=1}^{N'} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{x} d\mathbf{q} \overline{f_j(\mathbf{x})} (L_{\mathbf{q}} f_j)(\mathbf{x}) \,. \qquad (78)\end{aligned}$$

Estimating the error term as done in (B32) and previous inequalities we get

$$(1-\mu)\alpha^{-1} \sum_{j=1}^{N'} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{x} d\mathbf{q} \overline{f_j(\mathbf{x})} (L_{\mathbf{q}} f_j)(\mathbf{x}) \le C(1-\mu) s^{-2} N'.$$

Since we are interested in an estimate from below and $\varphi_r^{\mathrm{OTF}}(\mathbf{q}) \le 0$ for $|\mathbf{q}| < r$, from (78) we find

$$\begin{aligned}\mathcal{B}_1 &\geq \tfrac{1}{(2\pi)^3}\iint_{|\mathbf{q}|>r}((1-\mu)\alpha^{-1}T(\mathbf{p})-\varphi_r^{\rm OTF}(\mathbf{q}))\sum_{j=1}^{N}|(f_j,g_s^{\mathbf{p},\mathbf{q}})|^2\,d\mathbf{q}d\mathbf{p}\\ &\quad -C(1-\mu)s^{-2}N'. \end{aligned}\tag{79}$$

We estimate now the first term on the right hand side of (79). Considering only the negative part of the integrand and since $\sum_{j=1}^{N'}|(f_j,g_s^{\mathbf{p},\mathbf{q}})|^2\leq 1$ we get

$$\begin{aligned}&\tfrac{1}{(2\pi)^3}\iint_{|\mathbf{q}|>r}((1-\mu)\alpha^{-1}T(\mathbf{p})-\varphi_r^{\rm OTF}(\mathbf{q}))\sum_{j=1}^{N'}|(f_j,g_s^{\mathbf{p},\mathbf{q}})|\,d\mathbf{q}d\mathbf{p}\\ \geq\ &\tfrac{1}{(2\pi)^3}\iint_{\substack{|\mathbf{q}|>r,\\ (1-\mu)\alpha^{-1}T(\mathbf{p})\leq\varphi_r^{\rm OTF}(\mathbf{q})}}((1-\mu)\alpha^{-1}T(\mathbf{p})-\varphi_r^{\rm OTF}(\mathbf{q}))\,d\mathbf{p}d\mathbf{q}.\end{aligned}$$

Now we split the domain of integration in $\mathbf{p}$ as follows

$$\{\mathbf{p}\in\mathbb{R}^3:\alpha^{-1}(1-\mu)T(\mathbf{p})\leq\varphi_r^{\rm OTF}(\mathbf{q})\}=\Sigma_1\cup\Sigma_2,$$

with Σ_1,Σ_2 disjoint and $\Sigma_1=\{\mathbf{p}\in\mathbb{R}^3:(1-\mu)|\mathbf{p}|^2/2\leq\varphi_r^{\rm OTF}(\mathbf{q})\}$. We treat these two contributions separately. Then

$$\begin{aligned}&\tfrac{1}{(2\pi)^3}\iint_{\substack{|\mathbf{q}|>r,\\ \mathbf{p}\in\Sigma_2}}((1-\mu)\alpha^{-1}T(\mathbf{p})-\varphi_r^{\rm OTF}(\mathbf{q}))d\mathbf{p}d\mathbf{q}\\ \geq\ &-\tfrac{1}{(2\pi)^3}\iint_{\substack{|\mathbf{q}|>r,\\ \mathbf{p}\in\Sigma_2}}[\varphi_r^{\rm OTF}(\mathbf{q})]_+d\mathbf{p}d\mathbf{q}=\ldots\end{aligned}$$

and since in the domain of integration

$$\tfrac{2}{1-\mu}[\varphi_r^{\rm OTF}(\mathbf{q})]_+\leq|\mathbf{p}|^2\leq\tfrac{2}{1-\mu}[\varphi_r^{\rm OTF}(\mathbf{q})]_+(1+\tfrac{1}{2(1-\mu)}\alpha^2[\varphi_r^{\rm OTF}(\mathbf{q})]_+)$$

we get

$$\begin{aligned}\ldots &\geq -\tfrac{C}{(1-\mu)^{\frac52}}\alpha^2\int_{|\mathbf{q}|>r}d\mathbf{q}\,([\varphi_r^{\rm OTF}(\mathbf{q})]_+^{\frac72}+\tfrac{\alpha^2}{8(1-\mu)}[\varphi_r^{\rm OTF}(\mathbf{q})]_+^{\frac92})\\ &\geq -\tfrac{C}{(1-\mu)^{\frac52}}\alpha^2(r^{-11}+\tfrac{\alpha^2}{1-\mu}r^{-15}),\end{aligned}\tag{80}$$

using Lemma 4.10 in the last step.
Since $\sqrt{1+t^2}\geq 1+(1/2)t^2-(1/8)t^4$, we get

$$\begin{aligned}&\tfrac{1}{(2\pi)^3}\iint_{\substack{|\mathbf{q}|>r,\\ \mathbf{p}\in\Sigma_1}}((1-\mu)\alpha^{-1}T(\mathbf{p})-\varphi_r^{\rm OTF}(\mathbf{q}))d\mathbf{p}d\mathbf{q}\\ \geq\ &\tfrac{1}{(2\pi)^3}\iint_{\substack{|\mathbf{q}|>r,\\ \mathbf{p}\in\Sigma_1}}((1-\mu)\tfrac12|\mathbf{p}|^2-\varphi_r^{\rm OTF}(\mathbf{q})-\tfrac18(1-\mu)\alpha^2|\mathbf{p}|^4)d\mathbf{p}d\mathbf{q}.\end{aligned}$$

The last term gives by Lemma 4.10

$$\alpha^2 \iint_{\substack{|\mathbf{q}|>r\\ \mathbf{p}\in\Sigma_1}} d\mathbf{p}d\mathbf{q}\, |\mathbf{p}|^4 = \alpha^2 \tfrac{4\pi}{7} \int_{|\mathbf{q}|>r} d\mathbf{q}\, (\tfrac{2}{1-\mu})^{\frac{7}{2}} [\varphi_r^{\mathrm{OTF}}(\mathbf{q})]_+^{\frac{7}{2}} \leq C\alpha^2 (\tfrac{2}{1-\mu})^{\frac{7}{2}} r^{-11}. \tag{81}$$

While for the other terms computing the integral with respect to $\mathbf{p}$, we get

$$\begin{aligned} &\tfrac{1}{(2\pi)^3} \iint_{\substack{|\mathbf{q}|>r,\\ \mathbf{p}\in\Sigma_1}} ((1-\mu)\tfrac{1}{2}|\mathbf{p}|^2 - \varphi_r^{\mathrm{OTF}}(\mathbf{q})) d\mathbf{p}d\mathbf{q} \\ &= -(\tfrac{2}{1-\mu})^{\frac{3}{2}} \tfrac{1}{15\pi^2} \int_{|\mathbf{q}|>r} d\mathbf{q}\, [\varphi_r^{\mathrm{OTF}}(\mathbf{q})]_+^{\frac{5}{2}}. \end{aligned} \tag{82}$$

For the term $\mathcal{B}_2$ using Theorem 2.5 and Remark 2.6 we find

$$\mathcal{B}_2 \geq -Cq(\mu^{-\frac{3}{2}} \|[\varphi_r^{\mathrm{OTF}} - \varphi_r^{\mathrm{OTF}} * g_s^2]_+\|_{\frac{5}{2}}^{\frac{5}{2}} + \alpha^3\mu^{-3} \|[\varphi_r^{\mathrm{OTF}} - \varphi_r^{\mathrm{OTF}} * g_s^2]_+\|_4^4).$$

From the choice of g_s it follows that $\varphi_r^{\mathrm{OTF}} - \varphi_r^{\mathrm{OTF}} * g_s^2 \leq V_r - V_r * g_s^2$ and the term $V_r - V_r * g_s^2$ is non-zero only for $r - s \leq |\mathbf{x}| \leq r + s$. Hence by Lemma 4.8 and since $s < r$

$$\|[\varphi_r^{\mathrm{OTF}} - \varphi_r^{\mathrm{OTF}} * g_s^2]_+\|_{\frac{5}{2}}^{\frac{5}{2}} \leq \int_{r-s\leq|\mathbf{x}|\leq r+s} [V_r(\mathbf{x}) - V_r * g^2(\mathbf{x})]_+^{\frac{5}{2}} d\mathbf{x} \leq Cr^{-8}s, \tag{83}$$

and similarly $\|[\varphi_r^{\mathrm{OTF}} - \varphi_r^{\mathrm{OTF}} * g_s^2]_+\|_4^4 \leq Cr^{-14}s$. The claim follows from (79), (80), (81), (82) and (83) using that $\beta_0\alpha^{\frac{1}{3}} \leq \kappa^{\frac{1}{3}} r$. □

Lemma 4.14. *Let G_α be the function defined in Theorem 2.3 and $\rho_r^{\mathrm{HF}}(\mathbf{x})$ the one-particle density of the density matrix γ_r^{HF} defined in* (61). *Let $Z\alpha = \kappa$ be fixed, $0 \leq \kappa < 2/\pi$ and $Z \geq 1$.*
There exists $\alpha_0 > 0$ such that given $\varepsilon', \sigma > 0$ there exists $D < 1/4$ such that for all $\alpha \leq \alpha_0$ and r with $\beta_0 Z^{-\frac{1}{3}} \leq r \leq D$ for which (64) *holds for $|\mathbf{x}| \leq r$, we have*

$$\begin{aligned} &\|\chi_r^+\rho^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_C \leq Cr^{-\frac{7}{2}+\frac{1}{6}} \qquad \textit{and} \\ &\alpha^{-1}\int_{\mathbb{R}^3} G_\alpha(\chi_r^+\rho^{\mathrm{HF}}(\mathbf{x}))d\mathbf{x} \leq Cr^{-7}, \quad \alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma_r^{\mathrm{HF}}] \leq Cr^{-7}, \end{aligned} \tag{84}$$

with C a universal positive constant.

Proof. The idea of the proof is the same as that of Lemma 3.1. In this case we are interested only in the exterior part of the minimizer. Hence, instead of considering the HF-energy functional we estimate from above and below the auxiliary one $\mathcal{E}^A$, defined in (62), applied on the "exterior part of the minimizer" γ_r^{HF}.
Step I. Estimate from above on $\mathcal{E}^A(\gamma_r^{\mathrm{HF}})$. Let us consider γ the density matrix that acts identically on the spin components and on each as

$$\gamma^j = \tfrac{1}{(2\pi)^3} \iint_{\frac{1}{2}|\mathbf{p}|^2 \leq \varphi_r^{\mathrm{OTF}}(\mathbf{q})} \Pi_{\mathbf{p},\mathbf{q}}\, d\mathbf{p}d\mathbf{q},$$

where $j \in \{1, \ldots, q\}$ is the spin index, $\Pi_{\mathbf{p},\mathbf{q}}$ is the projection onto the space spanned by $h_s^{\mathbf{p},\mathbf{q}}(\mathbf{x}) = h_s(\mathbf{x}-\mathbf{q})e^{i\mathbf{p}\cdot\mathbf{x}}$ where h_s is the ground state for the Dirichlet Laplacian on the ball of radius s for $0 < s < r$. By the OTF-equation (66) and since $\mu_r^{\mathrm{OTF}} = 0$ (see Lemma 4.10) we see that $\rho_\gamma(\mathbf{x}) = \rho_r^{\mathrm{OTF}} * |h_s|^2(\mathbf{x})$. Moreover, by Lemma 4.10

$$\mathrm{Tr}[-\tfrac{1}{2}\Delta\gamma] = \tfrac{3}{10}(\tfrac{6\pi^2}{q})^{\frac{2}{3}} \int_{\mathbb{R}^3} (\rho_r^{\mathrm{OTF}}(\mathbf{x}))^{\frac{5}{3}}\, d\mathbf{x} + Cs^{-2}r^{-3}. \tag{85}$$

Since $[\Phi_r^{\mathrm{HF}}]_+ \in L_{loc}^{\frac{5}{2}}(\mathbb{R}^3)$, by [23, Lemma 8.5] for $\lambda' \in (0,1)$ we may find $\tilde{\gamma}$ such that $\mathrm{supp}(\rho_{\tilde{\gamma}}) \subset \{\mathbf{x} : |\mathbf{x}| \geq r\}$, $\rho_{\tilde{\gamma}}(\mathbf{x}) \leq \rho_\gamma(\mathbf{x})$ for $\mathbf{x} \in \mathbb{R}^3$ and

$$\begin{aligned}\mathrm{Tr}[(-\tfrac{1}{2}\Delta - \Phi_r^{\mathrm{HF}})\tilde{\gamma}] \quad &\leq \quad \mathrm{Tr}[(-\tfrac{1}{2}\Delta - \chi_r^+\Phi_r^{\mathrm{HF}})\gamma] + L_1 \int_{|\mathbf{x}| \leq \frac{r}{1-\lambda'}} [V_r(\mathbf{x})]_+^{\frac{5}{2}}\, d\mathbf{x} \\ &\quad + \tfrac{1}{2}(\tfrac{\pi}{2\lambda' r})^2 \int_{|\mathbf{x}| \leq \frac{r}{1-\lambda'}} \rho_\gamma(\mathbf{x})\, d\mathbf{x}.\end{aligned} \tag{86}$$

Since $\int \rho_{\tilde{\gamma}} \leq \int \rho_\gamma = \int \rho_r^{\mathrm{OTF}} \leq \int \chi_r^+ \rho^{\mathrm{HF}}$ we may choose $\tilde{\gamma}$ as a trial density matrix in Theorem 4.7 and we find for λ, ν to be chosen

$$\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) \leq \mathcal{E}^A(\tilde{\gamma}) + \mathcal{R} \leq \mathrm{Tr}[(-\tfrac{1}{2}\Delta - \Phi_r^{\mathrm{HF}})\tilde{\gamma}] + \mathcal{R} + D(\rho_{\tilde{\gamma}}),$$

since $\alpha^{-1}T(\mathbf{p}) \leq \frac{1}{2}|\mathbf{p}|^2$. Notice that $\mathcal{R}$ depends on λ and ν. From (86) it follows that

$$\begin{aligned}\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) \quad &\leq \quad \mathrm{Tr}[(-\tfrac{1}{2}\Delta - \chi_r^+\Phi_r^{\mathrm{HF}})\gamma] + L_1 \int_{|\mathbf{x}| \leq \frac{r}{1-\lambda'}} [V_r(\mathbf{x})]_+^{\frac{5}{2}}\, d\mathbf{x} \\ &\quad + \tfrac{1}{2}(\tfrac{\pi}{2\lambda' r})^2 \int_{|\mathbf{x}| \leq \frac{r}{1-\lambda'}} \rho_\gamma(\mathbf{x})\, d\mathbf{x} + \mathcal{R} + D(\rho_{\tilde{\gamma}}).\end{aligned} \tag{87}$$

From the OTF-equation (66) and Lemma 4.10 we get

$$\int_{|\mathbf{x}| \leq \frac{r}{1-\lambda'}} \rho_\gamma(\mathbf{x})\, d\mathbf{x} \leq \int_{|\mathbf{x}| \leq \frac{2-\lambda'}{1-\lambda'} r} \rho_r^{\mathrm{OTF}}(\mathbf{x})\, d\mathbf{x} \leq Cr^{-3}.$$

While since $V_r(\mathbf{y}) \leq Cr^{-4}$ (Lemma 4.8) and is non-zero only for $|\mathbf{y}| > r$

$$\int_{|\mathbf{x}| \leq \frac{r}{1-\lambda'}} [V_r(\mathbf{x})]_+^{\frac{5}{2}}\, d\mathbf{x} \leq Cr^{-7} \tfrac{\lambda'}{(1-\lambda')^3}.$$

Hence, from (85) and (87) and the inequalities above we find choosing $\lambda' = r^{\frac{2}{3}}$

$$\begin{aligned}\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) \quad &\leq \quad \tfrac{3}{10}(\tfrac{6\pi^2}{q})^{\frac{2}{3}} \int_{\mathbb{R}^3} (\rho_r^{\mathrm{OTF}}(\mathbf{x}))^{\frac{5}{3}}\, d\mathbf{x} - \int_{\mathbb{R}^3} V_r(\mathbf{x})\rho_\gamma(\mathbf{x})\, d\mathbf{x} + Cs^{-2}r^{-3} \\ &\quad + Cr^{-7+\frac{2}{3}} + \mathcal{R} + D(\rho_{\tilde{\gamma}}) = \ldots.\end{aligned}$$

Here we used that $\lambda' \le 1/2$ which follows by the bound on D. Since $\rho_{\tilde{\gamma}} \le \rho_\gamma$, $D(\rho_{\tilde{\gamma}}) \le D(\rho_\gamma)$. Moreover by Newton's Theorem $D(\rho_\gamma) \le D(\rho_r^{\mathrm{OTF}})$. Hence we get

$$\begin{aligned} \dots \quad \le \quad & \mathcal{E}^{\mathrm{OTF}}(\rho_r^{\mathrm{OTF}}) + \int_{\mathbb{R}^3} V_r(\mathbf{x})(\rho_r^{\mathrm{OTF}}(\mathbf{x}) - \rho_\gamma(\mathbf{x}))\, d\mathbf{x} + Cs^{-2}r^{-3} \\ & + Cr^{-7+\frac{2}{3}} + \mathcal{R}. \end{aligned} \tag{88}$$

We study now the second term on the right hand side of (88). Since $\rho_\gamma = \rho^{\mathrm{OTF}} * |h_s|^2$, rewriting

$$\int_{\mathbb{R}^3} V_r(\mathbf{x})(\rho_r^{\mathrm{OTF}}(\mathbf{x}) - \rho_\gamma(\mathbf{x}))\, d\mathbf{x} = \int_{\mathbb{R}^3} \rho_r^{\mathrm{OTF}}(\mathbf{x})(V_r(\mathbf{x}) - V_r * |h_s|^2(\mathbf{x}))\, d\mathbf{x}.$$

Since $s < r$, V_r is harmonic on $|\mathbf{x}| > r$ and ρ_r^{OTF} vanishes for $|\mathbf{x}| < r$ one sees that the integrand on the right hand side of the equation above is non-zero only for $r < |\mathbf{x}| < r + s$. Hence by Lemma 4.8

$$\int_{\mathbb{R}^3} V_r(\mathbf{x})(\rho_r^{\mathrm{OTF}}(\mathbf{x}) - \rho_\gamma(\mathbf{x}))\, d\mathbf{x} \le \int_{r<|\mathbf{x}|<r+s} \rho_r^{\mathrm{OTF}}(\mathbf{x}) V_r(\mathbf{x})\, d\mathbf{x} \le Cr^{-8}s.$$

Choosing $s = r^{\frac{5}{3}}$ we find from (88) that

$$\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) \le \mathcal{E}^{\mathrm{OTF}}(\rho_r^{\mathrm{OTF}}) + Cr^{-7+\frac{2}{3}} + \mathcal{R}. \tag{89}$$

It remains to estimate $\mathcal{R}$. From Lemma 4.1, choosing $\lambda, \nu \le 1/2$ and D such that $\sigma r^{\varepsilon'} \le 1$ we find

$$\left(\tfrac{\pi}{2\lambda r} + \tfrac{C}{\lambda^2 r^2}\right) \int_{|\mathbf{x}| \ge r(1-\lambda)(1-\nu)} \rho^{\mathrm{HF}}(\mathbf{x})\, d\mathbf{x} \le Cr^{-5}\lambda^{-2}.$$

By Lemma 4.8, (65) and since $\lambda \le 1/2$ we get

$$\int_{r(1-\lambda) \le |\mathbf{x}| \le \frac{r}{1-\lambda}} (\Phi^{\mathrm{HF}}_{r(1-\lambda)}(\mathbf{x}))^{\frac{5}{2}}\, d\mathbf{x} \le Cr^{-7}\lambda,$$

and similarly

$$\alpha^3 \int_{r(1-\lambda) \le |\mathbf{x}| \le \frac{r}{1-\lambda}} (\Phi^{\mathrm{HF}}_{r(1-\lambda)}(\mathbf{x}))^4\, d\mathbf{x} \le Cr^{-4}\lambda,$$

since $r \ge \beta_0 Z^{-\frac{1}{3}}$ implies $\alpha r^{-3} \le \beta_0^{-3}\kappa$. Hence from the expression of $\mathcal{R}$ and the boundness of $t^p e^{-t}$ for $t > 0$, we find

$$\mathcal{R} \le \mathcal{E}x(\gamma_r^{\mathrm{HF}}) + Cr^{-5}\lambda^{-2} + Cr^{-7}\lambda. \tag{90}$$

We estimate now the exchange term. By the exchange inequality ([15] or [23, Th.6.4]) and proceeding as in (27) we find by Lemma 4.1 and Lemma 4.12

$$\begin{aligned} \mathcal{E}x(\gamma_r^{\rm HF}) &\leq C\int_{\mathbb{R}^3} G_\alpha(\rho_r^{\rm HF}(\mathbf{x}))d\mathbf{x} + Cr^{-\frac{3}{2}}\Big(\alpha^{-1}\int_{\mathbb{R}^3} G_\alpha(\rho_r^{\rm HF}(\mathbf{x}))d\mathbf{x}\Big)^{\frac{1}{2}} \\ &\leq C\alpha\mathcal{R} + C\alpha r^{-7} + Cr^{-\frac{3}{2}}(\mathcal{R}+r^{-7})^{\frac{1}{2}}. \end{aligned}$$

Hence choosing α_0 such that $1 - C\alpha \geq 1/2$ for all $\alpha \leq \alpha_0$ we get from the inequality above and (90)

$$\tfrac{1}{2}\mathcal{R} \leq Cr^{-\frac{3}{2}}(\mathcal{R}+r^{-7})^{\frac{1}{2}} + Cr^{-5}\lambda^{-2} + Cr^{-7}\lambda\,,$$

that gives

$$\mathcal{R} \leq C(r^{-5}\lambda^{-2} + \lambda r^{-7})\,. \tag{91}$$

The second two inequalities in (84) follow from the estimate above and lemmas 4.1 and 4.12 choosing $\lambda = 1/2$ and replacing r with $r/2$.

Step II. Estimate from below on $\mathcal{E}^A(\gamma_r^{\rm HF})$. Adding and subtracting $D(\rho_r^{\rm OTF})$ and $\mathrm{Tr}[\rho_r^{\rm OTF} * \frac{1}{|\cdot|}\gamma_r^{\rm HF}]$ we write

$$\mathcal{E}^A(\gamma_r^{\rm HF}) = \mathrm{Tr}[(\alpha^{-1}T(\mathbf{p}) - \varphi_r^{\rm OTF})\gamma_r^{\rm HF}] + \|\rho_r^{\rm OTF} - \rho_r^{\rm HF}\|_C^2 - D(\rho_r^{\rm OTF}), \tag{92}$$

using that $V_r = \Phi_r^{\rm HF}$ on the support of $\rho_r^{\rm HF}$. The first term on the right hand side of (92) is estimated from below by the sum of the first N' eigenvalues of the operator $\alpha^{-1}T(\mathbf{p}) - \varphi_r^{\rm OTF}$ acting on the functions with support on $\{\mathbf{x} : |\mathbf{x}| \geq r\}$. Here N' denotes the smallest integer bigger than $\mathrm{Tr}[\gamma_r^{\rm HF}]$. Hence by Lemma 4.13 we find for $\mu \in (0,1)$ and $s < r$

$$\begin{aligned} \mathcal{E}^A(\gamma_r^{\rm HF}) \;\geq\; & -(\tfrac{2}{1-\mu})^{\frac{3}{2}}\tfrac{q}{15\pi^2}\int_{\mathbb{R}^3}[\varphi_r^{\rm OTF}(\mathbf{q})]_+^{\frac{5}{2}}\,d\mathbf{q} - Cr^{-8}s\mu^{-\frac{3}{2}} - C\mu^{-3}r^{-5}s \\ & -C(1-\mu)^{-\frac{7}{2}}r^{-5} - C(1-\mu)s^{-2}\Big(\int_{\mathbb{R}^3}\rho_r^{\rm HF}(\mathbf{x})\,d\mathbf{x} + 1\Big) \\ & +\|\rho_r^{\rm OTF} - \rho_r^{\rm HF}\|_C^2 - D(\rho_r^{\rm OTF}) = \ldots, \end{aligned}$$

Notice the factor q due to spin. Choosing D such that $\sigma r^{\varepsilon'} \leq 1$, by lemmas 4.1 and 4.10 we find

$$\int_{\mathbb{R}^3}\rho_r^{\rm HF}(\mathbf{x})\,d\mathbf{x} \leq Cr^{-3} \text{ and } \int_{\mathbb{R}^3}[\varphi_r^{\rm OTF}(\mathbf{q})]_+^{\frac{5}{2}}\,d\mathbf{q} \leq Cr^{-7}.$$

Hence considering $\mu \leq 1/2$

$$\begin{aligned} \ldots \;\geq\; & -2^{\frac{3}{2}}\tfrac{q}{15\pi^2}\int_{\mathbb{R}^3}[\varphi_r^{\rm OTF}(\mathbf{q})]_+^{\frac{5}{2}}\,d\mathbf{q} - Cr^{-7} - Cr^{-8}s\mu^{-\frac{3}{2}} - C\mu^{-3}r^{-5}s \\ & -Cs^{-2}r^{-3} + \|\rho_r^{\rm OTF} - \rho_r^{\rm HF}\|_C^2 - D(\rho_r^{\rm OTF}) = \ldots. \end{aligned}$$

By the OTF-equation (66) and since $\rho_r^{\rm OTF}$ has support where $\varphi_r^{\rm OTF} \geq 0$ we find

$$\cdots = \mathcal{E}^{\rm OTF}(\rho_r^{\rm OTF}) - Cr^{-7+\frac{1}{3}} + \|\rho_r^{\rm OTF} - \rho_r^{\rm HF}\|_C^2,$$

choosing $\mu = \frac{1}{2}r^{-\frac{2}{5}}s^{\frac{2}{5}}$ and $s = r^{\frac{11}{6}}$.
Hence combining the inequality above with (89) and (91) we find

$$\|\rho_r^{\mathrm{OTF}} - \rho_r^{\mathrm{HF}}\|_C^2 \le Cr^{-7+\frac{1}{3}} + C(r^{-5}\lambda^{-2} + \lambda r^{-7}). \tag{93}$$

We study now $\|\chi_r^+\rho^{\mathrm{HF}} - \rho_r^{\mathrm{HF}}\|_C$. By Hardy-Littlewood-Sobolev inequality we find

$$\|\chi_r^+\rho^{\mathrm{HF}} - \rho_r^{\mathrm{HF}}\|_C \le C\|\chi_r^+\rho^{\mathrm{HF}} - \rho_r^{\mathrm{HF}}\|_{\frac{6}{5}} \le C\Big(\int_{r\le|\mathbf{x}|\le\frac{r}{1-\lambda}} \rho^{\mathrm{HF}}(\mathbf{x})^{\frac{6}{5}}\,d\mathbf{x}\Big)^{\frac{5}{6}}. \tag{94}$$

To estimate the last term in (94) we are going to use the second estimate in (84) that we have just proved. With Σ defined as in (26) we find by Hölder's inequality

$$\begin{aligned}\int_{r\le|\mathbf{x}|\le\frac{r}{1-\lambda}} \rho^{\mathrm{HF}}(\mathbf{x})^{\frac{6}{5}}\,d\mathbf{x} \quad &\le \quad \Big(\int_{\substack{r\le|\mathbf{x}|,\\ \mathbf{x}\in\Sigma}} \rho^{\mathrm{HF}}(\mathbf{x})^{\frac{4}{3}}\,d\mathbf{x}\Big)^{\frac{9}{10}}\Big(\int_{r\le|\mathbf{x}|\le\frac{r}{1-\lambda}} 1\,d\mathbf{x}\Big)^{\frac{1}{10}} \\ &\quad + \Big(\int_{\substack{r\le|\mathbf{x}|,\\ \mathbf{x}\in\mathbb{R}^3\setminus\Sigma}} \rho^{\mathrm{HF}}(\mathbf{x})^{\frac{5}{3}}\,d\mathbf{x}\Big)^{\frac{18}{25}}\Big(\int_{r\le|\mathbf{x}|\le\frac{r}{1-\lambda}} 1\,d\mathbf{x}\Big)^{\frac{7}{25}} \\ &\le \quad Cr^{-\frac{33}{10}}\lambda^{\frac{1}{10}} + Cr^{-\frac{21}{5}}\lambda^{\frac{7}{25}}.\end{aligned}$$

From the estimate above, (93) and (94) it then follows

$$\begin{aligned}\|\chi_r^+\rho^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_C \quad &\le \quad \|\chi_r^+\rho^{\mathrm{HF}} - \rho_r^{\mathrm{HF}}\|_C + \|\rho_r^{\mathrm{HF}} - \rho_r^{\mathrm{OTF}}\|_C \\ &\le Cr^{-\frac{7}{2}+\frac{1}{6}} + C(r^{-5}\lambda^{-2} + \lambda r^{-7})^{\frac{1}{2}} + C(r^{-\frac{11}{4}}\lambda^{\frac{1}{12}} + r^{-\frac{7}{2}}\lambda^{\frac{7}{30}}),\end{aligned}$$

that gives the claim choosing $\lambda = r^{\frac{5}{7}}$ □

4.3.3 Estimate on $\mathcal{A}_3$

Lemma 4.15. *Let G_α be the function defined in Theorem 2.3. Let $Z\alpha = \kappa$ fixed, $0 \le \kappa < 2/\pi$ and $Z \ge 1$.*
There exists $\alpha_0 > 0$ such that given $\varepsilon', \sigma > 0$ there exists a constant $D < 1/4$ depending only on ε' and σ such that if (64) holds for all $|\mathbf{x}| \le D$, then for all $\alpha \le \alpha_0$

$$\alpha^{-1}\int_{|\mathbf{y}|\ge|\mathbf{x}|} G_\alpha(\rho^{\mathrm{HF}}(\mathbf{y}))d\mathbf{y} \le C|\mathbf{x}|^{-7} \text{ for all } |\mathbf{x}| \le D,$$

with C a universal positive constant.

Proof. If $|\mathbf{x}| < \beta_0 Z^{-\frac{1}{3}}$ we find by Lemma 3.1

$$\alpha^{-1}\int_{|\mathbf{y}|>|\mathbf{x}|} G_\alpha(\rho^{\mathrm{HF}}(\mathbf{y}))d\mathbf{y} \le \alpha^{-1}\int_{\mathbb{R}^3} G_\alpha(\rho^{\mathrm{HF}}(\mathbf{y}))d\mathbf{y} \le CZ^{\frac{7}{3}} \le C|\mathbf{x}|^{-7}.$$

While if $D \ge |\mathbf{x}| \ge \beta_0 Z^{-\frac{1}{3}}$ the claim follows from the second estimate in (84). □

Lemma 4.16. *Let $Z\alpha = \kappa$ fixed, $0 \le \kappa < 2/\pi$, $Z \ge 1$ and $0 < \mu < \frac{1}{109}$. There exists α_0 such that given $\varepsilon', \sigma > 0$ there exists a constant $D < 1/4$ depending only on ε' and σ such that for all $\alpha \le \alpha_0$ and for all r with $\beta_0 Z^{-\frac{1-\mu}{3}} \le r \le D$ for which (64) holds for $|\mathbf{x}| \le r$, then for all $\mathbf{x}$ with $|\mathbf{x}| \ge r$*

$$|\mathcal{A}_3(r,\mathbf{x})| \le C\Big(\frac{|\mathbf{x}|}{r}\Big)^{\frac{1}{12}} r^{-4+\frac{3\mu}{1-\mu}},$$

with $C > 0$ a universal constant.

Proof. We proceed similarly as in Theorem 3.3. By the formula for $\mathcal{A}_3$, Proposition 2.8 and Lemma 4.14 we get

$$|\mathcal{A}_3(r,\mathbf{x})| \le \int_{A(|\mathbf{x}|,k)} \chi_r^+(\mathbf{y}) \frac{|\rho_r^{\mathrm{OTF}}(\mathbf{y}) - \rho^{\mathrm{HF}}(\mathbf{y})|}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} + Ck^{-1}|\mathbf{x}|^{-\frac{1}{2}} r^{-\frac{7}{2}+\frac{1}{6}}. \quad (95)$$

By Hölder's inequality, Lemma 4.10, the OTF-equation (66) and (33) we find

$$\int_{A(|\mathbf{x}|,k)} \frac{\rho_r^{\mathrm{OTF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} \le Cr^{-\frac{21}{5}} |\mathbf{x}|^{\frac{1}{5}} k^{\frac{1}{5}}. \quad (96)$$

Once again, to estimate $\int_{A(|\mathbf{x}|,k)} \frac{\chi_r^+(\mathbf{y})\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y}$ we have to proceed differently than in [23, Lem.12.7] since ρ^{HF} is not in $L^{\frac{5}{3}}(\mathbb{R}^3)$. We consider the following splitting

$$\int_{A(|\mathbf{x}|,k)} \chi_r^+(\mathbf{y}) \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} = \int_{\substack{A(|\mathbf{x}|,k)\\ |\mathbf{x}-\mathbf{y}|>R, |\mathbf{y}|>r}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} + \int_{\substack{|\mathbf{y}|>r,\\ |\mathbf{x}-\mathbf{y}|<R}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y}, \quad (97)$$

for $R > 0$ to be chosen. By Hölder's inequality, Theorem 2.3, Remark 2.4, (33) and Lemma 4.14 we get

$$\int_{\substack{A(|\mathbf{x}|,k)\\ |\mathbf{x}-\mathbf{y}|>R, |\mathbf{y}|>r}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} \le C\alpha^{\frac{3}{4}} R^{-\frac{3}{8}} |\mathbf{x}|^{\frac{1}{8}} k^{\frac{1}{8}} r^{-\frac{21}{4}} + Cr^{-\frac{21}{5}} |\mathbf{x}|^{\frac{1}{5}} k^{\frac{1}{5}}. \quad (98)$$

It remains to study the second term on the right hand side of (97). Let $\nu \in \mathbb{R}^+$ be such that $\nu\alpha \le 2/\pi$. We consider the density matrix $\gamma_{r/2}^{\mathrm{HF}}$ defined in (61) with $\lambda = 1/2$. From Theorem 2.10 it follows that for $\mathbf{x}$ such that $|\mathbf{x}| \ge r$

$$\mathrm{Tr}[(\alpha^{-1}T(\mathbf{p}) - \frac{\nu}{|\cdot - \mathbf{x}|}\chi_{B_R(\mathbf{x})}(\cdot))\gamma_{r/2}^{\mathrm{HF}}] \ge -C(\nu^{\frac{5}{2}} R^{\frac{1}{2}} + \nu^4\alpha^2).$$

Hence we find

$$\begin{aligned} \nu \int_{|\mathbf{y}-\mathbf{x}|<R} \chi_r^+(\mathbf{y}) \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \quad &\le \quad \nu \int_{|\mathbf{y}-\mathbf{x}|<R} \frac{\rho_{r/2}^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \\ &\le \quad \mathrm{Tr}[\alpha^{-1}T(\mathbf{p})\gamma_{r/2}^{\mathrm{HF}}] + C(\nu^{\frac{5}{2}} R^{\frac{1}{2}} + \nu^4\alpha^2) \end{aligned}$$

and by Lemma 4.14

$$\int_{|\mathbf{y}-\mathbf{x}|<R} \chi_r^+(\mathbf{y}) \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|} d\mathbf{y} \leq C\nu^{-1} r^{-7} + C(\nu^{\frac{3}{2}} R^{\frac{1}{2}} + \nu^3 \alpha^2). \tag{99}$$

Hence from (95), (96), (98) and (99) it follows that

$$\begin{aligned} |\mathcal{A}_3(r,\mathbf{x})| \quad \leq \quad & C\nu^{-1}r^{-7} + C(\nu^{\frac{3}{2}}R^{\frac{1}{2}} + \nu^3\alpha^2) + C\alpha^{\frac{3}{4}}R^{-\frac{3}{8}}|\mathbf{x}|^{\frac{1}{8}}k^{\frac{1}{8}}r^{-\frac{21}{4}} \\ & + Cr^{-\frac{21}{5}}|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}} + Ck^{-1}|\mathbf{x}|^{-\frac{1}{2}}r^{-\frac{7}{2}+\frac{1}{6}}. \end{aligned}$$

So choosing $\nu = 1/2(\beta_0 r^{-1})^{\frac{3}{1-\mu}}$ (that gives $\nu\alpha < 2/\pi$), k such that $r^{-\frac{21}{5}}|\mathbf{x}|^{\frac{1}{5}}k^{\frac{1}{5}} = k^{-1}|\mathbf{x}|^{-\frac{1}{2}}r^{-\frac{7}{2}+\frac{1}{6}}$, i.e. $k = |\mathbf{x}|^{-\frac{7}{12}}r^{\frac{13}{18}}$ and R such that $\alpha^{\frac{3}{4}}R^{-\frac{3}{8}}|\mathbf{x}|^{\frac{1}{8}\frac{5}{12}}r^{-\frac{21}{4}+\frac{1}{8}\frac{13}{18}} = r^{-4-\frac{1}{18}}|\mathbf{x}|^{\frac{1}{12}}$, i.e. $R = \alpha^2|\mathbf{x}|^{-\frac{1}{12}}r^{-\frac{5}{18}}$

$$|\mathcal{A}_3(r,\mathbf{x})| \leq C(r^{-4+\frac{3\mu}{1-\mu}} + |\mathbf{x}|^{-\frac{1}{24}}r^{-\frac{5}{36}-\frac{9}{2(1-\mu)}}\alpha + r^{-\frac{9}{1-\mu}}\alpha^2 + |\mathbf{x}|^{\frac{1}{12}}r^{-4-\frac{1}{18}}).$$

Finally since $r^{-1}\alpha^{\frac{1-\mu}{3}} \leq \beta_0^{-1}\kappa^{\frac{1-\mu}{3}}$, the claim follows for $|\mathbf{x}| \geq r$ and $\mu < 1/(109)$. □

4.4 The intermediate region

Here we prove the main estimate in Theorem 1.17 up to a fixed distance independent of Z.

Lemma 4.17 (Iterative step). *Let $Z\alpha = \kappa$ fixed with $0 \leq \kappa < 2/\pi$. Consider $\mu = \frac{1}{11}\frac{1}{49}$ and assume $N \geq Z \geq 1$.*
Then there exists $\alpha_0 > 0$ such that for all $\delta, \varepsilon', \sigma > 0$ with $\delta < \delta_0$, where δ_0 is some universal constant, there exists constants $\varepsilon_2, C'_\phi > 0$ depending only on δ and a constant $D = D(\varepsilon', \sigma) > 0$ depending only on ε', σ with the following property. For all $\alpha \leq \alpha_0$ and $R_0 < D$ satisfying that $\beta_0 Z^{-\frac{1-\mu}{3}} \leq R_0^{1+\delta}$ and that (64) holds for all $|\mathbf{x}| \leq R_0$, there exists $R'_0 > R_0$ such that

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C'_\Phi |\mathbf{x}|^{-4+\varepsilon_2}$$

for all $\mathbf{x}$ with $R_0 < |\mathbf{x}| < R'_0$.

Proof. Let $D > 0$ depending on σ, ε' be the smaller of the values of D occurring in Lemma 4.11 and Lemma 4.16. Given $\delta > 0$. We consider $R_0 < D$ satisfying $\beta_0 Z^{-\frac{1-\mu}{3}} \leq R_0^{1+\delta}$ and such that (64) holds for all $|\mathbf{x}| \leq R_0$.
Set $R'_0 = R_0^{1-\delta}$ and $r = R_0^{1+\delta}$. Then we have $\beta_0 Z^{-\frac{1}{3}} \leq \beta_0 Z^{-\frac{1-\mu}{3}} \leq r \leq R_0 < D$ we can therefore apply Lemma 4.11 and Lemma 4.16. From (67) we obtain that for all $|\mathbf{x}| \geq r$ and all $\alpha \leq \alpha_0$

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C|\mathbf{x}|^{-4-\zeta}r^{\zeta} + C\Big(\frac{|\mathbf{x}|}{r}\Big)^{\frac{1}{12}} r^{-4+\frac{3\mu}{1-\mu}}.$$

Since for $R_0 < |\mathbf{x}| < R_0'$ we have

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

and thus

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \le C|\mathbf{x}|^{-4+\delta\zeta} + C|\mathbf{x}|^{-4+3\frac{\mu}{1-\mu}}|\mathbf{x}|^{-\frac{\delta}{1-\delta}(8+\frac{1}{6}-\frac{6\mu}{1-\mu})}.$$

Hence choosing δ_0 sufficiently small there are C'_Φ and ε_2 such that the claim holds. □

Lemma 4.18. *Let $Z\alpha = \kappa$ fixed with $0 \le \kappa < 2/\pi$. Assume $N \ge Z \ge 1$. Then there exist universal constants α_0, $\varepsilon \in (0,4)$ and $D, C_\Phi > 0$, $D < 1/4$, such that for all $\alpha \le \alpha_0$ and $\mathbf{x}$ with $|\mathbf{x}| \le D$ we have*

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \le C_\Phi|\mathbf{x}|^{-4+\varepsilon}.$$

Proof. We fix $\mu = \frac{1}{11}\frac{1}{49}$ as in Lemma 4.17. Since $\mu < \frac{2}{11}\frac{1}{49}$, by Theorem 3.3 we know that there exists constants $a, b, c > 0$ such that for all $|\mathbf{x}| \le \beta Z^{-\frac{1-\mu}{3}}$

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \le C(1+\beta^2+\beta^{5/2}+\beta^b|\mathbf{x}|^c)\beta^{2-a}|\mathbf{x}|^{-4+a}. \tag{100}$$

We first show that we may choose δ small enough such that if we choose $\tilde{R}^{1+\delta} = \beta_0 Z^{-\frac{1-\mu}{3}}$ we have for all $|\mathbf{x}| < \tilde{R}$ that

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \le C''_\Phi|\mathbf{x}|^{-4+\frac{a}{2}}. \tag{101}$$

Let $\beta > 0$ be such that $(\beta Z^{-\frac{1-\mu}{3}})^{1+\delta} = \beta_0 Z^{-\frac{1-\mu}{3}}$, i.e. $\beta^{1+\delta} = \beta_0 Z^{\delta\frac{1-\mu}{3}}$. Hence from (100) we find for all $|\mathbf{x}| \le \beta Z^{-\frac{1-\mu}{3}}$

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \le C(1+\beta^2+\beta^{5/2}+\beta^b|\mathbf{x}|^c)\beta^{2-\frac{a}{2}}Z^{-\frac{a}{2}\frac{1-\mu}{3}}|\mathbf{x}|^{-4+\frac{a}{2}},$$

and by the choice of β (and $\beta_0 < 1$)

$$\begin{aligned}|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \quad \le \quad & C(1+Z^{2\frac{\delta}{1+\delta}\frac{1-\mu}{3}}+Z^{\frac{5}{2}\frac{\delta}{1+\delta}\frac{1-\mu}{3}}+Z^{\frac{\delta}{1+\delta}\frac{1-\mu}{3}(b+c)}Z^{-c\frac{1-\mu}{3}})\\ & Z^{(2-\frac{a}{2})\frac{1-\mu}{3}\frac{\delta}{1+\delta}}Z^{-\frac{a}{2}\frac{1-\mu}{3}}|\mathbf{x}|^{-4+\frac{a}{2}}.\end{aligned}$$

Hence if δ is small enough we may choose a universal constant C''_Φ such that (101) holds.

Let now δ be small enough so that we may apply Lemma 4.17. This give constant ε_2 and C'_Φ (depending only on δ) and for all $\sigma, \varepsilon' > 0$ a constant $D < 1/4$. Now choose $\sigma = \max\{C'_\Phi, C''_\Phi\}$ and $\varepsilon' = \min\{a/2, \varepsilon_2\}$. Now σ, ε' and D are universal constants. To prove the claim we shall prove that for all $|\mathbf{x}| \le D$

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \le \sigma|\mathbf{x}|^{-4+\varepsilon'}. \tag{102}$$

We have to prove that D belongs to the set

$$\mathcal{M} = \{0 < R \leq 1/4 : \text{ Inequality (102) holds for all } |\mathbf{x}| \leq R\}.$$

We reason by contradiction. If this was not true then $D > R_0 = \sup \mathcal{M}$ and in particular $R_0 < 1/4$. From (101) and the choice of σ and ε' it follows that either $\tilde{R} > 1/4$ or $\tilde{R} \in \mathcal{M}$. In the first case then $R_0 = \sup \mathcal{M} = 1/4 > D$ that contradicts our hypothesis. On the other hand if $\tilde{R} \in \mathcal{M}$, then $R_0^{1+\delta} \geq \tilde{R}^{1+\delta} = \beta_0 Z^{-\frac{1-\mu}{3}}$. It then follows from Lemma 4.17 that there exists $R_0' \in \mathcal{M}$ with $R_0' > R_0$. This contradicts also our hypothesis. ☐

4.5 The outer zone and proof of Theorem 1.17

The proof of Theorem 1.17 follows directly from Lemma 4.18 and the following result.

Lemma 4.19. *Let $Z\alpha = \kappa$, $0 \leq \kappa < 2/\pi$. Assume $N \geq Z \geq 1$. Let D, ε and C_Φ be the constants introduced in Lemma 4.18.*
Then there exist $\alpha_0 > 0$ and a universal constant $C_M > 0$ such that for all $\alpha \leq \alpha_0$ and $\mathbf{x}$ with $|\mathbf{x}| \geq D$ we have

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq C_M.$$

Proof. Here C_i, $i = 1, \ldots, 6$ denote positive universal constants. We write

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})| \leq |\Phi^{\mathrm{HF}}_{D}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{D}(\mathbf{x})| + \int_{D<|\mathbf{y}|<|\mathbf{x}|} \frac{\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y}. \tag{103}$$

Since $\Phi^{\mathrm{HF}}_{D}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{D}(\mathbf{x})$ is harmonic for $|\mathbf{x}| > D$ and tends to zero at infinity we have by Lemma 4.18

$$|\Phi^{\mathrm{HF}}_{D}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{D}(\mathbf{x})| \leq \sup_{|\mathbf{x}|=D} |\Phi^{\mathrm{HF}}_{D}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{D}(\mathbf{x})| \leq C_\phi D^{-4+\varepsilon}. \tag{104}$$

For the second term on the right hand side of (103) we write

$$\begin{aligned} &\int_{D<|\mathbf{y}|<|\mathbf{x}|} \frac{\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} \\ &\leq \int_{\substack{|\mathbf{x}-\mathbf{y}|<D/4 \\ |\mathbf{y}|>D}} \frac{\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, d\mathbf{y} + \frac{4}{D} \int_{D<|\mathbf{y}|} (\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y}))\, d\mathbf{y}. \end{aligned} \tag{105}$$

By Lemma 4.1, Lemma 4.18, estimate (13) and the TF-equation we find

$$\int_{D<|\mathbf{y}|} (\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y}))\, d\mathbf{y} \leq C_1(1 + C_\Phi D^{\varepsilon})(1 + D^{-3}) + C_1 D^{-3}. \tag{106}$$

It remains to estimate the first term on the right hand side of (105). By Hölder's inequality, estimate (13) and the TF-equation we get

$$\int_{\substack{|\mathbf{x}-\mathbf{y}|<D/4\\|\mathbf{y}|>D}} \frac{\rho^{\mathrm{TF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y} \le C_2\Big(\int_{|\mathbf{y}|>D} (\rho^{\mathrm{TF}}(\mathbf{y}))^{\frac{5}{3}}\,d\mathbf{y}\Big)^{\frac{3}{5}} D^{\frac{1}{5}} \le C_3 D^{-4}. \quad (107)$$

To estimate the term with the HF-density we use Theorem 2.10. Let γ_D^{HF} be the exterior HF-density matrix as defined in (61) with $r = D/2$ and $\lambda = 1/2$. Then by Theorem 2.10 with $\nu = \beta_0^3 D^{-3}$

$$\alpha^{-1}\operatorname{Tr}[(T(\mathbf{p}) - \frac{\nu\alpha}{|\mathbf{x}-\cdot|}\chi_{B_{\frac{D}{4}}(\mathbf{x})}(\cdot))\gamma_{D/2}^{\mathrm{HF}}] \ge -C_4(D^{\frac{1}{2}}\nu^{\frac{5}{2}} + \nu^4\alpha^2),$$

and thus

$$\int_{|\mathbf{x}-\mathbf{y}|<D/4} \frac{\rho_{D/2}^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y} \le C_5 D^3\alpha^{-1}\operatorname{Tr}[T(\mathbf{p})\gamma_{D/2}^{\mathrm{HF}}] + C_6 D^{-4},$$

Here we use that $D > 2\beta_0 Z^{-\frac{1}{3}}$ (for $\alpha \le \alpha_0$) and $D < 1/4$. By Lemma 4.14 we conclude

$$\int_{|\mathbf{x}-\mathbf{y}|<D/4} \chi_D^+(\mathbf{y})\frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y} \le \int_{|\mathbf{x}-\mathbf{y}|<D/4} \frac{\rho_{D/2}^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y} \le C_7 D^{-4}. \quad (108)$$

The claim follows collecting together formula (103) to formula (108). □

5 Proofs of Theorems 1.1, 1.18, 1.19 and 1.20

In this section we always assume the following: $Z\alpha = \kappa$ with $0 \le \kappa < 2/\pi$ and $N \ge Z \ge 1$.

Proof of Theorem 1.1. Assume that a HF-minimizer exists with $\int \rho^{\mathrm{HF}} = N$. Let ρ^{TF} be the minimizer of the TF-energy functional of the neutral atom with nuclear charge Z. Then for $R > 0$ to be chosen

$$N = \int_{|\mathbf{x}|<R} \rho^{\mathrm{TF}}(\mathbf{x})\,d\mathbf{x} + \int_{|\mathbf{x}|<R} (\rho^{\mathrm{HF}}(\mathbf{x}) - \rho^{\mathrm{TF}}(\mathbf{x}))\,d\mathbf{x} + \int_{|\mathbf{x}|>R} \rho^{\mathrm{HF}}(\mathbf{x})\,d\mathbf{x}. \quad (109)$$

By Theorem 1.17 we know that there exist universal positive constants $\varepsilon, \alpha_0, C_M$ and C_Φ such that for all $\alpha \le \alpha_0$ and $\mathbf{x} \in \mathbb{R}^3$

$$|\Phi_{|\mathbf{x}|}^{\mathrm{HF}}(\mathbf{x}) - \Phi_{|\mathbf{x}|}^{\mathrm{TF}}(\mathbf{x})| \le C_\Phi|\mathbf{x}|^{-4+\varepsilon} + C_M. \quad (110)$$

Let Z_0 be such that $Z_0\alpha_0 = \kappa$. Then $\alpha \le \alpha_0$ corresponds to $Z \ge Z_0$. Let us choose R such that $C_\Phi R^{-4+\varepsilon} = C_M$. Then from (109), (110) and Lemma 4.1 for all $Z \ge Z_0$ we find

$$N \le \int_{|\mathbf{x}|<R} \rho^{\mathrm{TF}}(\mathbf{x})\,d\mathbf{x} + 2C_\Phi R^{-3+\varepsilon} + C(1 + C_\Phi R^\varepsilon)(R^{-3} + 1) < Z + \tilde{Q}.$$

The claim follows choosing $Q = \max\{\tilde{Q}, Z_0 + 1\}$. □

Proof of Theorem 1.18. Let $\rho^{\rm HF}$ be the density of the HF-minimizer in the neutral case $N = Z$. We have

$$\begin{aligned}\Big|\int_{|\mathbf{x}|>R}(\rho^{\rm HF}(\mathbf{x})-\rho^{\rm TF}(\mathbf{x}))d\mathbf{x}\Big| &= \Big|\int_{|\mathbf{x}|<R}(\rho^{\rm HF}(\mathbf{x})-\rho^{\rm TF}(\mathbf{x}))d\mathbf{x}\Big| \\ &= \Big|\frac{R}{4\pi}\int_{S^2}d\omega(\Phi_R^{\rm HF}(R\omega)-\Phi_R^{\rm TF}(R\omega))\Big| \\ &\leq C_\Phi R^{-3+\varepsilon}+C_M R,\end{aligned}$$

where in the last step we have used Theorem 1.17. Notice that for Z sufficiently big $\alpha \leq \alpha_0$ where α_0 is the constant given in Theorem 1.17. By the TF-equation, Theorem 1.12 we then find

$$\begin{aligned}3^4\frac{2\pi^2}{q^2}R^{-3}-C_\Phi R^{-3+\varepsilon}-C_M R &\leq \int_{|\mathbf{x}|>R}\rho^{\rm HF}(\mathbf{x})d\mathbf{x} \\ &\leq 3^4\frac{2\pi^2}{q^2}R^{-3}+C_\Phi R^{-3+\varepsilon}+C_M R,\end{aligned}$$

from which the claim follows directly by the definition of HF-radius. □

Proof of Theorem 1.19. Since $E^{\rm HF}(Z-1,Z) \geq E^{\rm HF}(Z,Z)$ the ionization energy is bounded from below by zero. If Z is smaller than a universal constant then we can also bound the ionization energy with a universal constant using Theorem 2.11.

It remains to estimate from above the ionization energy when Z is larger than a universal constant. We first construct a density matrix γ such that $\mathrm{Tr}[\gamma] \leq Z-1$. Let $\theta_- := (1-\theta^2_{r(1-\lambda)})^{\frac{1}{2}}$ for r, λ positive parameters and θ_r defined in Definition 4.4. We consider the density matrix $\gamma_-^{\rm HF} := \theta_-\gamma^{\rm HF}\theta_-$ where $\gamma^{\rm HF}$ is the HF-minimizer in the neutral case. By an opportune choice of r we will then have $\mathrm{Tr}[\gamma_-^{\rm HF}] \leq Z-1$. Indeed,

$$\mathrm{Tr}[\gamma_-^{\rm HF}] = \int_{\mathbb{R}^3}\rho^{\rm HF}(\mathbf{x})\,d\mathbf{x}-\int_{\mathbb{R}^3}\theta^2_{r(1-\lambda)}(\mathbf{x})\rho^{\rm HF}(\mathbf{x})\,d\mathbf{x} \leq Z-\int_{|\mathbf{x}|>r}\rho^{\rm HF}(\mathbf{x})\,d\mathbf{x}.$$

We now choose $\lambda = \frac{1}{2}$. Let $R > 0$ be such that $C_M = C_\Phi R^{-4+\varepsilon}$ where C_M, C_Φ, ε are the constants in Theorem 1.17. Then R is a universal constant. We consider Z large enough so that $\beta_0 Z^{-\frac{1}{3}} < R$ where β_0 is the constant in Theorem 1.12. This gives that Z has to be larger than some universal constant. For r such that $\beta_0 Z^{-\frac{1}{3}} < r < R$ by Theorem 1.17 we find

$$|\Phi^{\rm HF}_{|\mathbf{x}|}(\mathbf{x})-\Phi^{\rm TF}_{|\mathbf{x}|}(\mathbf{x})| \leq 2C_\Phi|\mathbf{x}|^{-4+\varepsilon} \text{ for all } |\mathbf{x}| \leq r.$$

Since $\int\rho^{\rm TF} = \int\rho^{\rm HF}$, by the choice of r and Lemma 4.1 we get

$$\begin{aligned}\int_{|\mathbf{x}|>r}\rho^{\rm HF}(\mathbf{x})\,d\mathbf{x} &= \int_{|\mathbf{x}|>r}\rho^{\rm TF}(\mathbf{x})\,d\mathbf{x}+\int_{|\mathbf{x}|<r}(\rho^{\rm TF}(\mathbf{x})-\rho^{\rm HF}(\mathbf{x}))\,d\mathbf{x} \\ &\geq \int_{|\mathbf{x}|>r}\rho^{\rm TF}(\mathbf{x})\,d\mathbf{x}-2C_\Phi r^{-3+\varepsilon} \geq Cr^{-3}-2C_\Phi r^{-3+\varepsilon}. \quad (111)\end{aligned}$$

In the last step we used the TF-equation, Corollary 1.13 and that $r > \beta_0 Z^{-\frac{1}{3}}$. Finally, it follows from (111) by choosing r sufficiently small that $\int_{|\mathbf{x}|>r} \rho^{\mathrm{HF}} > 1$ and hence that $\mathrm{Tr}[\gamma_-^{\mathrm{HF}}] \leq Z - 1$. We may choose r sufficiently small by taking Z large enough. Notice that r can be chosen universally and so Z has to be larger than some universal constant.
By the last estimate in the proof of Theorem 4.7 we find

$$\mathcal{E}^{\mathrm{HF}}(\gamma_-^{\mathrm{HF}}) \leq \mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) - \mathcal{E}^A(\gamma_r^{\mathrm{HF}}) + \mathcal{R},$$

with $\mathcal{R}$ and γ_r^{HF} as defined in the statement of Theorem 4.7. Since $\mathcal{E}^{\mathrm{HF}}(\gamma_-^{\mathrm{HF}}) \geq E^{\mathrm{HF}}(Z-1, Z)$ and $\mathcal{E}^{\mathrm{HF}}(\gamma^{\mathrm{HF}}) = E^{\mathrm{HF}}(Z, Z)$ it remains to prove that $-\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) + \mathcal{R}$ is bounded from above by some universal constant. Here we use repeteadly that r is a universal constant. By estimate (91) we see that $\mathcal{R} \leq Cr^{-7}$ a universal constant. To estimate from below $\mathcal{E}^A(\gamma_r^{\mathrm{HF}})$ we first leave out the kinetic energy term and the direct term since these are positive. Moreover, since Φ_r^{HF} is harmonic for $|\mathbf{x}| > r$ and tends to zero at infinity we see that

$$\Phi_r^{\mathrm{HF}}(\mathbf{x}) \leq \frac{r}{|\mathbf{x}|} \sup_{|\mathbf{y}|=r} \Phi_r^{\mathrm{HF}}(\mathbf{y}) \leq \frac{r}{|\mathbf{x}|} \sup_{|\mathbf{y}|=r} \Phi_r^{\mathrm{TF}}(\mathbf{y}) + \frac{r}{|\mathbf{x}|} \sup_{|\mathbf{y}|=r} |\Phi_r^{\mathrm{TF}}(\mathbf{y}) - \Phi_r^{\mathrm{HF}}(\mathbf{y})|,$$

which is bounded by $C'/|\mathbf{x}|$, C' a universal constant, by Theorem 1.17 and Corollary 1.14. It then follows that

$$\mathcal{E}^A(\gamma_r^{\mathrm{HF}}) \geq -\mathrm{Tr}[\frac{C'}{|\cdot|}\gamma_r^{\mathrm{HF}}] \geq -\frac{C'}{r}\int_{|\mathbf{x}|>r} \rho^{\mathrm{HF}}(\mathbf{x})\, d\mathbf{x},$$

that is bounded from below by a universal constant using Lemma 4.1. □

Proof of Theorem 1.20. Let α_0 be the constant appearing in Theorem 1.17 and Z_0 be such that $\alpha_0 Z_0 = \kappa$. The claim follows directly for $Z \leq Z_0$ since both functions are bounded for $|\mathbf{x}|$ large, while for $|\mathbf{x}|$ small the functions are bounded by a constant times $|\mathbf{x}|^{-1}$.
The case $Z > Z_0$ corresponds to $\alpha < \alpha_0$ and for such values of α we can use the result in Theorem 1.17. We separate the case small $\mathbf{x}$, intermediate $\mathbf{x}$ and large $\mathbf{x}$. Once again, comparing with the proof in the non-relativistic case ([23]) we have to do an extra splitting for small $\mathbf{x}$.
By the definition of the mean field potential and Proposition 2.8 we find

$$\begin{aligned} |\varphi^{\mathrm{TF}}(\mathbf{x}) - \varphi^{\mathrm{HF}}(\mathbf{x})| \;\leq\; & \int_{|\mathbf{x}-\mathbf{y}|<s} (\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y}))\Big(\frac{1}{|\mathbf{x}-\mathbf{y}|} - \frac{1}{s}\Big) \\ & + \frac{\sqrt{2}}{s^{\frac{1}{2}}} \|\rho^{\mathrm{TF}} - \rho^{\mathrm{HF}}\|_C. \end{aligned}$$

Since ρ^{TF} is bounded in $L^{\frac{5}{3}}$-norm, we find using Hölder's inequality, Corollary 1.15 and Lemma 3.1 that

$$|\varphi^{\mathrm{TF}}(\mathbf{x}) - \varphi^{\mathrm{HF}}(\mathbf{x})| \leq \int_{|\mathbf{x}-\mathbf{y}|<s} \rho^{\mathrm{HF}}(\mathbf{y})\Big(\frac{1}{|\mathbf{x}-\mathbf{y}|} - \frac{1}{s}\Big) + C(s^{\frac{1}{5}} Z^{\frac{7}{5}} + s^{-\frac{1}{2}} Z^{1+\frac{3}{22}}). \tag{112}$$

For the integral with the HF-density we need to split the region where the HF-density is bounded in $L^{\frac{4}{3}}$-norm from the one where it is bounded in $L^{\frac{5}{3}}$-norm. Proceeding as in the proof of Lemma 3.2 (from (35) to (37) replacing the integrals on $A(|\mathbf{x}|,k)$ with integrals on $|\mathbf{x}-\mathbf{y}|<s$) using the results of Lemma 3.1 we get with $R\in(0,s)$ to be chosen

$$\int_{|\mathbf{x}-\mathbf{y}|<s}\rho^{\mathrm{HF}}(\mathbf{y})\Big(\frac{1}{|\mathbf{x}-\mathbf{y}|}-\frac{1}{s}\Big)\leq C(Z^{\frac{7}{5}}s^{\frac{1}{5}}+R^{-\frac{1}{4}}(\alpha Z^{\frac{7}{3}})^{\frac{3}{4}}+Z^{\frac{4}{3}}+R^{\frac{1}{2}}Z^{\frac{3}{2}}). \quad (113)$$

Recall that $Z\alpha=\kappa$ is fixed. Choosing s such that $Z^{\frac{7}{5}}s^{\frac{1}{5}}=Z^{\frac{4}{3}}$ (i.e. $s=Z^{-\frac{1}{3}}$) and R such that $R^{-\frac{1}{4}}Z=R^{\frac{1}{2}}Z^{\frac{3}{2}}$ (i.e $R=Z^{-\frac{2}{3}}$; notice that $R<s$) we get from (112) and (113)

$$|\varphi^{\mathrm{TF}}(\mathbf{x})-\varphi^{\mathrm{HF}}(\mathbf{x})|\leq C(Z^{\frac{4}{3}}+Z^{\frac{7}{6}}).$$

The claim follows from this inequality for $\mathbf{x}\in\mathbb{R}^3$ such that $|\mathbf{x}|\leq\beta_0 Z^{-\frac{1+\gamma}{3}}$ for $\gamma>0$. We consider $\gamma<\frac{1}{263}$.

If $|\mathbf{x}|\geq\beta_0 Z^{-\frac{1+\gamma}{3}}$ then proceeding as for very small $\mathbf{x}$ and as in the proof of Theorem 3.3 up to inequality (43) we get for $t\in(\frac{1+\gamma}{3},\frac{3}{5})$, $l>t$ and $R<\beta_0 Z^{-l}$

$$|\varphi^{\mathrm{TF}}(\mathbf{x})-\varphi^{\mathrm{HF}}(\mathbf{x})|\leq C(s^{\frac{1}{5}}Z^{\frac{7}{5}}+s^{-\frac{1}{2}}Z^{1+\frac{3}{22}}+R^{-\frac{3}{8}}s^{\frac{1}{8}}Z+Z^{\frac{1}{2}(3-t)}).$$

Here we have also used that $Z\alpha$ is a constant. So choosing s such that $s^{\frac{1}{5}}Z^{\frac{7}{5}}=Z^{\frac{1}{2}(3-t)}$ (i.e. $s=Z^{\frac{1}{2}-\frac{5}{2}t}$), R such that $R^{-\frac{3}{8}}Z^{1+\frac{1}{16}-\frac{5}{16}t}=Z^{\frac{1}{2}(3-t)}$ (i.e. $R=Z^{-\frac{7}{6}+\frac{1}{2}t}$) and optimizing in t (i.e. $t=\frac{1}{3}+\frac{4}{3}\frac{1}{77}$) we obtain

$$|\varphi^{\mathrm{TF}}(\mathbf{x})-\varphi^{\mathrm{HF}}(\mathbf{x})|\leq CZ^{\frac{4}{3}-\frac{2}{3}\frac{1}{77}}. \quad (114)$$

Notice that $t>\frac{1+\gamma}{3}$, $R<s$ by the choice of t and that R satisfies the condition $R<\beta_0 Z^{-l}$, $l>t$, for Z sufficiently big. The claim then follows from (114) for $\mathbf{x}\in\mathbb{R}^3$ such that $|\mathbf{x}|^{1+\delta}\leq\beta_0 Z^{-\frac{1}{3}}$ for $\delta<\frac{1}{153}$. We fix $\delta=\frac{1}{2}\frac{1}{153}$.

We turn now to study intermediate $\mathbf{x}$. Let $D\leq 1$ be such that $C_M\leq C_\Phi D^{-4+\varepsilon}$ with C_M, C_Φ, ε the constants in Theorem 1.17. Then for all $\mathbf{x}$ such that $|\mathbf{x}|\leq D$

$$|\Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x})-\Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x})|\leq 2C_\Phi|\mathbf{x}|^{-4+\varepsilon}.$$

Moreover we choose D such that Lemma 4.11 holds. Let $\mathbf{x}$ be such that $\beta_0 Z^{-\frac{1}{3}}\leq|\mathbf{x}|^{1+\delta}\leq D^{\frac{1+\delta}{1+\mu}}$ with $0<\mu\leq\delta$. We set $r=|\mathbf{x}|^{1+\mu}$. Then $\beta_0 Z^{-\frac{1}{3}}\leq r\leq D$. We write $\varphi^{\mathrm{TF}}(\mathbf{x})-\varphi^{\mathrm{HF}}(\mathbf{x})=\varphi^{\mathrm{TF}}(\mathbf{x})-\varphi_r^{\mathrm{OTF}}(\mathbf{x})+\varphi_r^{\mathrm{OTF}}(\mathbf{x})-\varphi^{\mathrm{HF}}(\mathbf{x})$ with φ_r^{OTF} the mean field potential of the OTF-problem defined in Subsection 4.3. By the choice of r and D and Lemma 4.11 we get since $|\mathbf{x}|\geq r=|\mathbf{x}|^{1+\mu}$

$$|\varphi^{\mathrm{TF}}(\mathbf{x})-\varphi_r^{\mathrm{OTF}}(\mathbf{x})|\leq C|\mathbf{x}|^{-4-\zeta}r^{\zeta}, \quad (115)$$

for $|\mathbf{x}|\geq r$ with $\zeta=(7+\sqrt{73})/2$. For the other two terms we see

$$\varphi^{\mathrm{HF}}(\mathbf{x})-\varphi_r^{\mathrm{OTF}}(\mathbf{x})=\int\frac{\rho_r^{\mathrm{OTF}}(\mathbf{y})-\chi_r^+(\mathbf{y})\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{y},$$

and proceeding as for small $\mathbf{x}$ with the Coulomb-norm estimate Proposition 2.8, by Lemma 4.14 and inequality (99)

$$|\varphi^{\mathrm{HF}}(\mathbf{x})-\varphi_r^{\mathrm{OTF}}(\mathbf{x})| \leq C\Big(\frac{s^{\frac{1}{5}}}{r^{\frac{21}{5}}}+\frac{r^{-\frac{7}{2}+\frac{1}{6}}}{s^{\frac{1}{2}}}+R^{-\frac{1}{4}}(\alpha r^{-7})^{\frac{3}{4}}+\nu^{-1}r^{-7}+\nu^{\frac{3}{2}}R^{\frac{1}{2}}+\nu^3\alpha^2\Big).$$

Choosing $\nu = \beta_0^3 r^{-3\frac{1+\delta}{1+\mu}}$, so that $\nu\alpha \leq \kappa < 2/\pi$, s such that $s^{\frac{1}{5}}r^{-\frac{21}{5}} = r^{-\frac{7}{2}+\frac{1}{6}}s^{-\frac{1}{2}}$ (i.e. $s = r^{1+\frac{5}{21}}$), and choosing R such that the two terms where it appears are equal (i.e. $R = r^{2+9\frac{\delta-\mu}{1+\mu}}$; notice that $R < s$) we get

$$|\varphi^{\mathrm{HF}}(\mathbf{x}) - \varphi_r^{\mathrm{OTF}}(\mathbf{x})| \leq C(r^{-4+\frac{1}{21}} + r^{-4+3\frac{\delta-\mu}{1+\mu}}),$$

since $\alpha r^{-3\frac{1+\delta}{1+\mu}}$ is bounded and $r \leq 1$. Collecting together the inequality above and (115) and using that $r = |\mathbf{x}|^{1+\mu}$ the claim follows for $\beta_0 Z^{-\frac{1}{3}} \leq |\mathbf{x}|^{1+\delta} \leq D^{\frac{1+\delta}{1+\mu}}$. We fix $\mu = \delta/2$.

It remains to study the case of large $\mathbf{x}$, i.e. $|\mathbf{x}| \geq D^{\frac{1+\delta}{1+\mu}}$ with D, δ, μ universal constants. For simplicity of notation we fix the universal constant $A := D^{\frac{1+\delta}{1+\mu}}$. We first notice that

$$\varphi^{\mathrm{HF}}(\mathbf{x}) - \varphi^{\mathrm{TF}}(\mathbf{x}) = \Phi^{\mathrm{HF}}_{|\mathbf{x}|}(\mathbf{x}) - \Phi^{\mathrm{TF}}_{|\mathbf{x}|}(\mathbf{x}) + \int_{|\mathbf{y}|>|\mathbf{x}|} \frac{\rho^{\mathrm{TF}}(\mathbf{y}) - \rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y}.$$

The difference of the first two terms is bounded by a universal constant for $|\mathbf{x}| \geq A$ by the result in Theorem 1.17. To estimate the last integral we split it as follows

$$\begin{aligned}\int_{|\mathbf{y}|>|\mathbf{x}|} \frac{|\rho^{\mathrm{TF}}(\mathbf{y}) - \rho^{\mathrm{HF}}(\mathbf{y})|}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y} \quad &\leq \quad \int_{\substack{|\mathbf{y}|>|\mathbf{x}|\\|\mathbf{x}-\mathbf{y}|<1}} \frac{\rho^{\mathrm{TF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y} + \int_{\substack{|\mathbf{y}|>|\mathbf{x}|\\|\mathbf{x}-\mathbf{y}|<1}} \frac{\rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y}\\ &\quad + \int_{|\mathbf{y}|>|\mathbf{x}|} (\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y}))\, d\mathbf{y}.\end{aligned}$$

Since $|\mathbf{x}| \geq A$ the third term on the right hand side is bounded by a universal constant by Lemma 4.1 (for ρ^{HF}) and Corollary 1.13 (for ρ^{TF}). We estimate the first term by Hölder's inequality and Corollary 1.15. We get a bound on the second term proceeding as in (99) (using Theorem 2.10) and choosing $\nu = \frac{1}{2}$ and $R = 1$. We obtain

$$\int_{\substack{|\mathbf{y}|>|\mathbf{x}|\\|\mathbf{x}-\mathbf{y}|<1}} \frac{\rho^{\mathrm{TF}}(\mathbf{y}) + \rho^{\mathrm{HF}}(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{y} \leq C(A^{-\frac{21}{5}} + A^{-7} + \alpha^2).$$

Then there exists a universal contant A' such that $|\varphi^{\mathrm{HF}}(\mathbf{x}) - \varphi^{\mathrm{TF}}(\mathbf{x})| \leq A'$ for $|\mathbf{x}| \geq A$. □

A Technical lemmas

Proof of (16) By the definition of the function G_α the inequalities in (16) are equivalent to the following ones

$$\tfrac{3}{5}t^4\min\{\tfrac{2}{5}t,1\} \le g(t) - \tfrac{8}{3}t^3 \le 2t^4\min\{\tfrac{2}{5}t,1\} \text{ for } t \ge 0. \tag{A1}$$

As before we use the substitution $t = \alpha(\rho/C)^{\frac{1}{3}}$.
The estimates in (A1) follow directly from the study of the function g separating the cases $t < \frac{5}{2}$ and $t \ge \frac{5}{2}$.
Proof of Remark 4.2 Using the estimate on K_2 given in (15) we find

$$\begin{aligned} &\iint_{\substack{\mathbf{x}\in\Sigma_r(\beta_1,\beta_2)\\ \mathbf{y}\in\Sigma_r(\beta_3,\beta_4)}} K_2(\alpha^{-1}|\mathbf{x}-\mathbf{y}|)^2\, d\mathbf{x}d\mathbf{y} \\ \le\ & (16)^2\alpha^4 \iint_{\substack{\mathbf{x}\in\Sigma_r(\beta_1,\beta_2)\\ \mathbf{y}\in\Sigma_r(\beta_3,\beta_4)}} \frac{e^{-\alpha^{-1}|\mathbf{x}-\mathbf{y}|}}{|\mathbf{x}-\mathbf{y}|^4}\, d\mathbf{x}d\mathbf{y} \\ \le\ & (16)^2\alpha^4 e^{-\alpha^{-1}r(\beta_3-\beta_2)} 4\pi \int_{r(\beta_3-\beta_2)}^{\infty} \rho^{-2}d\rho \int_{\Sigma_r(\beta_1,\beta_2)} d\mathbf{x}, \end{aligned}$$

since $|\mathbf{x}-\mathbf{y}| \ge (\beta_3-\beta_2)r$. The claim follows computing the two integrals.

A.1 Fourier transform

In the present sub-section we present our notation for the Fourier transform (as in [20]). Given $f \in L^2(\mathbb{R}^3)$ we denote its Fourier transform by

$$\hat{f}(\mathbf{p}) = \mathcal{F}(f)(\mathbf{p}) := \tfrac{1}{(2\pi)^{\frac{3}{2}}} \int_{\mathbb{R}^3} e^{i\mathbf{p}\cdot x} f(\mathbf{x})d\mathbf{x}.$$

Let $f, g \in L^2(\mathbb{R}^3)$. The following formulas hold:

1. $\mathcal{F}(f*g)(\mathbf{p}) = (2\pi)^{\frac{3}{2}}\hat{f}(\mathbf{p})\hat{g}(\mathbf{p})$;
2. $\mathcal{F}(fg)(\mathbf{p}) = (2\pi)^{-\frac{3}{2}}(\hat{f}*\hat{g})(\mathbf{p})$;
3. if $g(\mathbf{x}) = e^{-\lambda|\mathbf{x}|^2}$ then $\hat{g}(\mathbf{p}) = (2\lambda)^{-\frac{3}{2}}e^{-|\mathbf{p}|^2/(4\lambda)}$;
4. $|\mathbf{x}|^{-\alpha} = \pi^{\frac{\alpha}{2}}(\Gamma(\frac{\alpha}{2}))^{-1}\int_0^{+\infty} e^{-\pi|\mathbf{x}|^2\lambda}\lambda^{\frac{\alpha}{2}-1}d\lambda$ for $0 < \alpha < n$ (see [14, page 130]).

Moreover,

$$\mathcal{F}\Big(\frac{f(\mathbf{x})}{|\mathbf{x}|}\Big)(\mathbf{k}) = \tfrac{1}{2\pi^2}\int_{\mathbb{R}^3} \frac{\hat{f}(\mathbf{p})}{|\mathbf{k}-\mathbf{p}|^2}d\mathbf{p}.$$

B Large Z-behavior of the energy

In [21] the author studies the large Z-behavior of the ground state energy for problem (1). In this work we are going to use the same construction in several points (Lemmas 3.1, 4.12, Theorem 3.3, ...) and with, in certain cases, a slightly different Hamiltonian. For convenience we repeat here the main ideas of the proof. We do it as it is needed in the proof of Theorem 3.3 since in this case the proof is more involved. We remark that in our proof we use a localisation less than in [21]. Thanks to Theorem 2.10 and [24, Theorem 2.8] it is sufficient to consider the region near the nuclei and the one far away from the nuclei. There is no need for an intermediate region.

Proposition B.1. *Let $Z\alpha = \kappa$ be fixed with $0 \le \kappa < 2/\pi$ and $Z \ge 1$. Let us consider $\mathbf{P} \in \mathbb{R}^3$, with $|\mathbf{P}| \ge \beta Z^{-\frac{1+\mu}{3}}$ for $\beta > 0$ and $\mu \in (0, 4/5)$. Let $Z \ge \nu > 0$ and $R > 0$ be such that $R < \beta Z^{-l}/4$ for some $\frac{1+\mu}{3} < l$. Moreover, let $\rho^{\rm TF}$ denote the minimizer of the TF-energy functional of a neutral atom with nucleus of charge Z. Consider the Hamiltonian*

$$H_{\mathbf{P}} := \sum_{i=1}^{N} \left(\alpha^{-1}T(\mathbf{p}_i) - \frac{Z}{|\mathbf{x}_i|} - \frac{\nu}{|\mathbf{x}_i - \mathbf{P}|}\chi_{B_R(\mathbf{P})}(\mathbf{x}_i)\right) + \sum_{i<j}\frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}, \qquad \text{(B2)}$$

acting on $\wedge_{i=1}^N L^2(\mathbb{R}^3;\mathbb{C}^q)$.
Then for all $t \in (\frac{1+\mu}{3}, \min\{l, \frac{3}{5}\})$ and $\psi \in \wedge_{i=1}^N L^2(\mathbb{R}^3)$, with $\|\psi\|_2 = 1$,

$$\langle \psi, H_{\mathbf{p}}\psi\rangle \ge \mathcal{E}^{\rm TF}(\rho^{\rm TF}) - C(\beta^{\frac{1}{2}} + \beta^{-2})Z^{\frac{5}{2}-\frac{1}{2}t},$$

with C depending only on q and κ.

Proof. Since $\mathcal{E}^{\rm TF}(\rho^{\rm TF}) = -e_0 Z^{\frac{7}{3}}$ (see (12)) to prove the claim it is sufficient to show that the TF-energy gives a lower bound to the quantum energy modulo lower order terms. In the proof we first reduce to a one-particle operator. Then we localize the energy separating the contribution from the regions near the nuclei from the contribution from the region far away from them. Finally we study the contribution of each of these terms. The main contribution to the energy is given by the region far away from the nuclei. This region will give the TF-energy.
In the following, $s = (3-t)/4$ ($t < s < 2/3$).
In the proof C denotes a generic positive constant depending only on q and κ.
Reduction to a one-particle problem. We are going to estimate from below $H_{\mathbf{P}}$ by a one-particle operator. This allows us to consider only Slater determinants when minimizing the energy.
Let $g \in C_0^\infty(\mathbb{R}^3)$, $g \ge 0$ be spherically symmetric with $\mathrm{supp}(g) \subset B_1(0)$ and such that $\|g\|_2 = 1$. Starting from these g we define $\Phi_s(\mathbf{x}) :=$

$(\beta/(8Z^s))^{-3}g^2(8Z^s\mathbf{x}/\beta)$. Then by Newton's theorem

$$\begin{aligned}\sum_{i<j}\frac{1}{|\mathbf{x}_i-\mathbf{x}_j|} &\geq \sum_{i<j}\iint\frac{\Phi_s(\mathbf{x}_i-\mathbf{x})\Phi_s(\mathbf{x}_j-\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} = \\ &= \tfrac{1}{2}\sum_{i,j=1}^{N}\iint\frac{\Phi_s(\mathbf{x}_i-\mathbf{x})\Phi_s(\mathbf{x}_j-\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} - \tfrac{N}{2}\iint\frac{\Phi_s(\mathbf{x})\Phi_s(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} = \dots\end{aligned}$$

and introducing $\rho\in L^1(\mathbb{R}^3)\cap L^{\frac{5}{3}}(\mathbb{R}^3)$, $\rho\geq 0$, to be chosen

$$\begin{aligned}\dots &= \tfrac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{(\sum_{i=1}^N\Phi_s(\mathbf{x}_i-\mathbf{x})-\rho(\mathbf{x}))(\sum_{j=1}^N\Phi_s(\mathbf{x}_j-\mathbf{y})-\rho(\mathbf{y}))}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} \\ &+ \sum_{i=1}^N\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\Phi_s(\mathbf{x}_i-\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} - D(\rho) - \tfrac{N}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\Phi_s(\mathbf{x})\Phi_s(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} \\ &\geq \sum_{i=1}^N\rho*\Phi_s*\frac{1}{|\mathbf{x}_i|} - D(\rho) - C\|g^2\|^2_{\frac{6}{5}}N\beta^{-1}Z^s. \qquad \text{(B3)}\end{aligned}$$

In the last inequality we use that the first term on the left hand side of (B3) is non-negative and that

$$\begin{aligned}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\Phi_s(\mathbf{x})\Phi_s(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} &= C\beta^{-1}Z^s\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{g^2(\mathbf{x})g^2(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} \\ &\leq C\beta^{-1}Z^s\|g^2\|^2_{6/5},\end{aligned}$$

by definition of Φ_s and Hardy-Littlewood-Sobolev's inequality. Hence

$$\begin{aligned}H_{\mathbf{P}} \geq& \sum_{i=1}^N\big(\alpha^{-1}T(\mathbf{p}_i) - \frac{Z}{|\mathbf{x}_i|} - \frac{\nu}{|\mathbf{x}_i-\mathbf{P}|}\chi_{B_R(\mathbf{P})}(\mathbf{x}_i) + \rho*\Phi_s*\frac{1}{|\mathbf{x}_i|}\big) \\ &-D(\rho) - C\|g^2\|^2_{\frac{6}{5}}N\beta^{-1}Z^s. \qquad \text{(B4)}\end{aligned}$$

Choice of the localization. The localization will be given by the following functions $\chi_1,\chi_2\in C_0^\infty(\mathbb{R}^3)$:

$$\chi_1(\mathbf{x}) := \begin{cases} 1 & \text{if } |\mathbf{x}|<\frac{1}{4}\beta Z^{-t}, \\ 0 & \text{if } |\mathbf{x}|>\frac{1}{2}\beta Z^{-t},\end{cases} \quad \chi_2(\mathbf{x}) := \begin{cases} 1 & \text{if } |\mathbf{x}-\mathbf{P}|<\frac{1}{4}\beta Z^{-t}, \\ 0 & \text{if } |\mathbf{x}-\mathbf{P}|>\frac{1}{2}\beta Z^{-t}\end{cases} \qquad \text{(B5)}$$

and $\chi_3\in C^\infty(\mathbb{R}^3)$ such that $\sum_{i=1}^3\chi_i^2(\mathbf{x})=1$ for all $\mathbf{x}\in\mathbb{R}^3$. Moreover we ask that

$$\|\nabla\chi_1\|_\infty, \|\nabla\chi_2\|_\infty, \|\nabla\chi_3\|_\infty \leq 2^5\beta^{-1}Z^t. \qquad \text{(B6)}$$

Here t is the parameter given in the statement of the proposition. Notice that by the assumptions on R and $\mathbf{P}$ the functions defined above give a well defined partition of unity of $\mathbb{R}^3$. Moreover, $B_R(\mathbf{P})$ is a subset of $\{\mathbf{x}\in\mathbb{R}^3 : \chi_2(\mathbf{x})=1\}$.

The localization in the energy expectation. We insert now the localization in the energy expectation. As already observed, since we reduced the operator to a one-particle operator in the energy expectation it is sufficient to consider Slater determinants: i.e. $\psi = u_1 \wedge \cdots \wedge u_N$ with $\{u_i\}_{i=1}^N$ orthonormal functions in $L^2(\mathbb{R}^3, \mathbb{C}^q)$. We may assume that $u_i \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C}^q)$ for $i = 1, \ldots, N$.
From (B4) and Theorem 2.1 we find with $\psi = u_1 \wedge \cdots \wedge u_N$

$$\begin{aligned} \langle \psi, H_{\mathbf{P}} \psi \rangle \quad \geq \quad & \sum_{i=1}^N \sum_{j=1}^3 (\chi_j u_i, h \chi_j u_i) - D(\rho) - C \|g^2\|_{\frac{6}{5}}^2 N \beta^{-1} Z^s \\ & - \alpha^{-1} \sum_{i=1}^N \sum_{j=1}^3 (u_i, L_j u_i), \end{aligned} \tag{B7}$$

with

$$h := \alpha^{-1} T(\mathbf{p}) - \frac{Z}{|\cdot|} - \frac{\nu \, \chi_{B_R(\mathbf{P})}(\cdot)}{|\cdot - \mathbf{P}|} + \rho * \Phi_s * \frac{1}{|\cdot|},$$

and L_j is the operator (defined in Theorem 2.1) that gives the error due to the localization in the kinetic energy. We first estimate this error term. Using the definition of L_j we find for all $j \in \{1, 2, 3\}$, $i \in \{1, \ldots, N\}$

$$(u_i, L_j u_i) \leq \frac{\alpha^{-2}}{4\pi^2} \|\nabla \chi_j\|_\infty^2 \iint K_2(\alpha^{-1}|\mathbf{x} - \mathbf{y}|) |u_i(\mathbf{y})| |u_i(\mathbf{x})| \, d\mathbf{x} d\mathbf{y}.$$

We then obtain by using Schwarz's inequality

$$\alpha^{-1} \sum_{i=1}^N \sum_{j=1}^3 (u_i, L_j u_i) \leq \frac{\alpha^{-3}}{4\pi^2} \sum_{j=1}^3 \|\nabla \chi_j\|_\infty^2 \sum_{i=1}^N \int K_2(\alpha^{-1}|\mathbf{z}|) d\mathbf{z} \leq C N \beta^{-2} Z^{2t}, \tag{B8}$$

since from (15)

$$\int_{\mathbb{R}^3} K_2(\alpha^{-1}|\mathbf{z}|) \, d\mathbf{z} = \alpha^3 \int_{\mathbb{R}^3} K_2(|\mathbf{z}|) \, d\mathbf{z} = 4\pi \alpha^3 \int_0^\infty t^2 K_2(t) \, dt = 6\pi^2 \alpha^3. \tag{B9}$$

Collecting together (B7) and (B8) we get

$$\langle \psi, H_{\mathbf{P}} \psi \rangle \geq \sum_{i=1}^N \sum_{j=1}^3 (\chi_j u_i, h \chi_j u_i) - D(\rho) - C \beta^{-2} Z^{1+2t} - C \beta^{-1} Z^{7/4 - t/4}. \tag{B10}$$

Here we used that $N \leq 2Z + 1$, the choice of s and that we may choose g such that $\|\nabla g\|_2^2 \leq 2\pi$.
Near the nuclei. When $j = 1$ in the summation in the first term on the right hand side of (B10) we find

$$\sum_{i=1}^N (\chi_1 u_i, h \chi_1 u_i) \geq \sum_{i=1}^N (\chi_1 u_i, (\alpha^{-1} T(\mathbf{p}) - \frac{Z}{|\cdot|}) \chi_1 u_i),$$

since $\chi_{B_R(\mathbf{P})}\chi_1 \equiv 0$ by the choice of χ_1, and the term $\Phi_s * \rho * \frac{1}{|\cdot|}$ is non-negative. Then by Theorem 2.10 we find

$$\begin{aligned}\sum_{i=1}^{N}(\chi_1 u_i, h\chi_1 u_i) &\geq \operatorname{Tr}[\alpha^{-1}T(\mathbf{p}) - \frac{Z}{|\cdot|}\chi_{|\mathbf{x}|<\frac{1}{2}\beta Z^{-t}}]_- \\ &\geq -C\beta^{1/2}Z^{5/2-t/2} - C\kappa^2 Z^2. \end{aligned} \tag{B11}$$

To estimate from below the term corresponding to $j = 2$ in the sum on the right hand side of (B10) we use [24, Theorem 2.8]. Here we need the result in [24] (instead of Theorem 2.10) because of the presence of the two nuclei. Notice that Theorem 2.10 can be extended to include also different nuclei. We have

$$\begin{aligned}\sum_{i=1}^{N}(\chi_2 u_i, h\chi_2 u_i) &\geq \sum_{i=1}^{N}(\chi_2 u_i, (\alpha^{-1}T(\mathbf{p}) - \frac{Z}{|\mathbf{x}|} - \frac{\nu}{|\mathbf{x}-\mathbf{P}|}\chi_{B_R(\mathbf{P})})\chi_2 u_i) \\ &\geq \operatorname{Tr}[\alpha^{-1}T(\mathbf{p}) - \frac{Z}{|\mathbf{x}|}\chi_{|\mathbf{x}-\mathbf{P}|<\frac{1}{2}\beta Z^{-t}} - \frac{\nu}{|\mathbf{x}-\mathbf{P}|}\chi_{B_R(\mathbf{P})}]_-,\end{aligned}$$

and by [24, Theorem 2.8] we get

$$\begin{aligned}\sum_{i=1}^{N}(\chi_2 u_i, h\chi_2 u_i) &\geq -CZ^{5/2}\alpha^{1/2} - C\int_{\frac{1}{2}\beta Z^{-t}>|\mathbf{x}-\mathbf{P}|>\alpha}\left(\frac{Z^{5/2}}{|\mathbf{x}|^{5/2}} + \alpha^3\frac{Z^4}{|\mathbf{x}|^4}\right)d\mathbf{x} \\ &\quad -C\int_{R>|\mathbf{x}-\mathbf{P}|>\alpha}\left(\frac{\nu^{5/2}}{|\mathbf{x}-\mathbf{P}|^{5/2}} + \alpha^3\frac{\nu^4}{|\mathbf{x}-\mathbf{P}|^4}\right)d\mathbf{x} \\ &\geq -C\kappa^{1/2}Z^2 - C\beta^{1/2}Z^{5/2-t/2} - C\kappa^2 Z^2. \end{aligned} \tag{B12}$$

Here we used that $t < l$ and $Z\alpha = \kappa$.

The outer zone. This region gives the main contribution to the energy. The term in (B10) that we still have to study is

$$\sum_{i=1}^{N}(\chi_3 u_i, h\chi_3 u_i) - D(\rho) \tag{B13}$$

We start by estimating the first term in (B13) using coherent states.

We consider again the function $g \in \mathcal{C}_0^\infty(\mathbb{R}^3)$ introduced at the beginning of the proof and we define the function

$$g_s(\mathbf{x}) := (\beta/(8Z^s))^{-\frac{3}{2}}g(8Z^s\mathbf{x}/\beta) = \Phi_s^{\frac{1}{2}}(\mathbf{x}), \tag{B14}$$

with s the same parameter as before. For simplicity of notation we write $\tilde{V} := Z/|\mathbf{x}| - \rho * 1/|\mathbf{x}|$. Then

$$\frac{Z}{|\mathbf{x}|} - \rho * \Phi_s * \frac{1}{|\mathbf{x}|} = \tilde{V} * \Phi_s - Z\Phi_s * \frac{1}{|\mathbf{x}|} + \frac{Z}{|\mathbf{x}|}.$$

Since $\mathrm{supp}(g_s) \cap \mathrm{supp}(\chi_3) = \emptyset$ by Newton's Theorem we find

$$\sum_{i=1}^{N} (\chi_3 u_i, h\chi_3 u_i) = \sum_{i=1}^{N} (\chi_3 u_i, (\alpha^{-1} T(\mathbf{p}) - \tilde{V} * \Phi_s)\chi_3 u_i). \tag{B15}$$

We consider the coherent states $g_s^{\mathbf{p},\mathbf{q}}$ defined for $\mathbf{p}, \mathbf{q} \in \mathbb{R}^3$ by

$$g_s^{\mathbf{p},\mathbf{q}}(\mathbf{x}) = g_s(\mathbf{x} - \mathbf{q}) e^{-i\mathbf{p}.\mathbf{x}}.$$

The following formulas hold for $f \in H^{\frac{1}{2}}(\mathbb{R}^3, \mathbb{C})$

$$\begin{aligned} (f, f) &= \tfrac{1}{(2\pi)^3} \int_{\mathbb{R}^3} d\mathbf{p} \int_{\mathbb{R}^3} d\mathbf{q}\, (f, g_s^{\mathbf{p},\mathbf{q}})\, (g_s^{\mathbf{p},\mathbf{q}}, f), \\ (f, V * g_s^2 f) &= \tfrac{1}{(2\pi)^3} \int_{\mathbb{R}^3} d\mathbf{p} \int_{\mathbb{R}^3} d\mathbf{q}\, V(\mathbf{q})\, (f, g_s^{\mathbf{p},\mathbf{q}})\, (g_s^{\mathbf{p},\mathbf{q}}, f) \end{aligned} \tag{B16}$$

and

$$\begin{aligned} (f, T(\mathbf{p}) f) &= \tfrac{1}{(2\pi)^3} \int_{\mathbb{R}^3} d\mathbf{p} \int_{\mathbb{R}^3} d\mathbf{q}\, T(\mathbf{p})\, (f, g_s^{\mathbf{p},\mathbf{q}})\, (g_s^{\mathbf{p},\mathbf{q}}, f) \\ &\quad - \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{q} \overline{f(\mathbf{x})} (L_q f)(\mathbf{x}), \end{aligned} \tag{B17}$$

where L_q has integral kernel

$$L_q(\mathbf{x}, \mathbf{y}) = \frac{\alpha^{-2}}{4\pi^2} |g_s(\mathbf{x} - \mathbf{q}) - g_s(\mathbf{y} - \mathbf{q})|^2 \frac{K_2(\alpha^{-1}|\mathbf{x} - \mathbf{y}|)}{|\mathbf{x} - \mathbf{y}|^2}.$$

Using these formulas we can rewrite (B15) as follows

$$\begin{aligned} &\sum_{i=1}^{N} (\chi_3 u_i, (\alpha^{-1} T(\mathbf{p}) - \tilde{V} * \Phi_s)\chi_3 u_i) \\ = \; &\tfrac{1}{(2\pi)^3} \alpha^{-1} \int_{\mathbb{R}^3} d\mathbf{p} \int_{\mathbb{R}^3} d\mathbf{q} (T(\mathbf{p}) - \alpha \tilde{V}(\mathbf{q})) \sum_{j=1}^{q} \sum_{i=1}^{N} |(\chi_3 u_i^j, g_s^{\mathbf{p},\mathbf{q}})|^2 \\ &- \alpha^{-1} \sum_{i=1}^{N} \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{q}\, \overline{\chi_3 u_i(\mathbf{x})} (L_{\mathbf{q}} \chi_3 u_i)(\mathbf{x}), \end{aligned} \tag{B18}$$

Here u_i^j is the j-th spin component of u_i. We start by estimating the error term, the last term on the right hand side of (B18). From the definition of $L_{\mathbf{q}}$ it follows

$$L_q(\mathbf{x}, \mathbf{y}) \le \frac{\alpha^{-2}}{4\pi^2} \|\nabla g_s\|_\infty^2 K_2(\alpha^{-1}|\mathbf{x} - \mathbf{y}|)(\chi_{\mathrm{supp}(g_s)}(\mathbf{x} - \mathbf{q}) + \chi_{\mathrm{supp}(g_s)}(\mathbf{y} - \mathbf{q})),$$

and by the definition of the function g_s

$$\int_{\mathbb{R}^3} L_q(\mathbf{x}, \mathbf{y})\, d\mathbf{q} \le C \|\nabla g\|_\infty^2 \alpha^{-2} \beta^{-2} Z^{2s} K_2(\alpha^{-1}|\mathbf{x} - \mathbf{y}|).$$

By the estimate above, Schwarz's inequality, (B9) and the choice of s we find

$$\alpha^{-1}\sum_{i=1}^{N}\int_{\mathbb{R}^3}d\mathbf{x}\int_{\mathbb{R}^3}d\mathbf{q}\,\overline{\chi_3 u_i(\mathbf{x})}(L_{\mathbf{q}}\chi_3 u_i)(\mathbf{x})\leq C\|\nabla g\|_\infty^2\beta^{-2}Z^{3/2-t/2}N. \quad \text{(B19)}$$

It remains to study the first term on the right hand side of (B18). In order to get an estimate from below we consider only the negative part of the integrand. Moreover, since if $|\mathbf{q}|<\beta Z^{-t}/8$ then $\operatorname{supp}(\chi_3 g_s^{\mathbf{p},\mathbf{q}})=\emptyset$ (because $Z^{-t}>Z^{-s}$ since $s>t$) we find

$$\begin{aligned}
&\tfrac{1}{(2\pi)^3}\alpha^{-1}\int_{\mathbb{R}^3}d\mathbf{p}\int_{\mathbb{R}^3}d\mathbf{q}\,(T(\mathbf{p})-\alpha\tilde V(\mathbf{q}))\sum_{j=1}^{q}\sum_{i=1}^{N}|(\chi_3 u_i^j,g_s^{\mathbf{p},\mathbf{q}})|^2\\
\geq\;&\tfrac{q}{(2\pi)^3}\alpha^{-1}\int_{|\mathbf{q}|\geq\frac18\beta Z^{-t}}d\mathbf{q}\int_{T(\mathbf{p})-\alpha\tilde V(\mathbf{q})\leq 0}d\mathbf{p}\,(T(\mathbf{p})-\alpha\tilde V(\mathbf{q}))=\ldots,
\end{aligned} \quad \text{(B20)}$$

where we also use that $\sum_{i=1}^N|(\chi_3 u_i^j,g_s^{\mathrm{P},\mathrm{Q}})|^2\leq 1$ (Bessel's inequality). We split now the integral as a sum of two terms

$$\begin{aligned}
\ldots\;=\;&\tfrac{q}{(2\pi)^3}\alpha^{-1}\iint_{\substack{\frac12|\mathbf{p}|^2-\tilde V(\mathbf{q})\leq 0\\ |\mathbf{q}|\geq\frac18\beta Z^{-t}}}d\mathbf{q}d\mathbf{p}\,(T(\mathbf{p})-\alpha\tilde V(\mathbf{q}))\\
+\;&\tfrac{q}{(2\pi)^3}\alpha^{-1}\iint_{\substack{\frac{\alpha}{2}|\mathbf{p}|^2\geq\alpha\tilde V(\mathbf{q})\geq T(\mathbf{p})\\ |\mathbf{q}|\geq\frac18\beta Z^{-t}}}d\mathbf{q}d\mathbf{p}\,(T(\mathbf{p})-\alpha\tilde V(\mathbf{q})).
\end{aligned} \quad \text{(B21)}$$

We consider these two terms separately. The second term in (B21) gives a lower order contribution. Indeed

$$\begin{aligned}
&\tfrac{q}{(2\pi)^3}\alpha^{-1}\iint_{\substack{\frac{\alpha}{2}|\mathbf{p}|^2\geq\alpha\tilde V(\mathbf{q})\geq T(\mathbf{p})\\ |\mathbf{q}|\geq\frac18\beta Z^{-t}}}d\mathbf{q}d\mathbf{p}\,(T(\mathbf{p})-\alpha\tilde V(\mathbf{q}))\\
\geq\;&-\tfrac{q}{(2\pi)^3}\iint_{\substack{(\alpha^2[\tilde V(\mathbf{q})]_+^2+2[\tilde V(\mathbf{q})]_+)^{\frac12}\geq|\mathbf{p}|\geq(2[\tilde V(\mathbf{q})]_+)^{\frac12}\\ |\mathbf{q}|\geq\frac18\beta Z^{-t}}}d\mathbf{q}d\mathbf{p}\,[\tilde V(\mathbf{q})]_+=\ldots,
\end{aligned}$$

and computing the $\mathbf{p}$-integral

$$\cdots=-C\int_{|\mathbf{q}|\geq\frac18\beta Z^{-t}}d\mathbf{q}\,[\tilde V(\mathbf{q})]_+^{\frac52}((1+\frac{\alpha^2}{2}[\tilde V(\mathbf{q})]_+)^{\frac32}-1)=\ldots.$$

Using $(1+x)^{\frac32}\leq 1+\frac32 x+\frac38 x^2$ and that $[\tilde V(\mathbf{q})]_+\leq Z/|\mathbf{q}|$ we get computing the integral

$$\begin{aligned}
\ldots\;=\;&-C\alpha^2\int_{|\mathbf{q}|\geq\frac18\beta Z^{-t}}d\mathbf{q}\,[\tilde V(\mathbf{q})]_+^{\frac72}(1+\tfrac{\alpha^2}{8}[\tilde V(\mathbf{q})]_+)\\
\geq\;&-C\beta^{-\frac12}\kappa^2 Z^{3/2+t/2}-C\kappa^4\beta^{-\frac32}Z^{1/2+3t/2}.
\end{aligned} \quad \text{(B22)}$$

Here we use that $Z\alpha = \kappa$.
Since $\sqrt{1+x} \geq 1 + x/2 - x^3/8$ for all $x > 0$, we have

$$T(\mathbf{p}) \geq \alpha \tfrac{1}{2}|\mathbf{p}|^2 - \alpha^3 \tfrac{1}{8}|\mathbf{p}|^4,$$

and, for the first term on the right hand side of (B21), we obtain

$$\begin{aligned} &\tfrac{q}{(2\pi)^3}\alpha^{-1} \iint_{\substack{\frac{1}{2}|\mathbf{p}|^2 - \tilde{V}(\mathbf{q}) \leq 0 \\ |\mathbf{q}| \geq \frac{1}{8}\beta Z^{-t}}} d\mathbf{q}d\mathbf{p}\, (T(\mathbf{p}) - \alpha\tilde{V}(\mathbf{q})) \geq \\ \geq\ & \tfrac{q}{(2\pi)^3} \iint_{\substack{\frac{1}{2}|\mathbf{p}|^2 - \tilde{V}(\mathbf{q}) \leq 0 \\ |\mathbf{q}| \geq \frac{1}{8}\beta Z^{-t}}} d\mathbf{q}d\mathbf{p}\, (\tfrac{1}{2}|\mathbf{p}|^2 - \tfrac{1}{8}\alpha^2|\mathbf{p}|^4 - \tilde{V}(\mathbf{q})) = \ldots . \end{aligned}$$

Computing now the integral with respect to $\mathbf{p}$, we find

$$\cdots = -\tfrac{2^{\frac{3}{2}}q}{15\pi^2} \int_{|\mathbf{q}| > \frac{1}{8}\beta Z^{-t}} [\tilde{V}(\mathbf{q})]_+^{\frac{5}{2}}\, d\mathbf{q} - C\alpha^2 \int_{|\mathbf{q}| > \frac{1}{8}\beta Z^{-t}} [\tilde{V}(\mathbf{q})]_+^{\frac{7}{2}}\, d\mathbf{q}. \tag{B23}$$

We see that the second term on the right hand side of (B23) gives a lower order contribution since it is of the same order as the one in (B22).
Collecting together (B10), (B11), (B12), (B15), (B18), (B19), (B22) and (B23)

$$\langle\psi, H_{\mathbf{P}}\psi\rangle \geq -C(\beta^{\frac{1}{2}} + \beta^{-2})Z^{5/2-t/2} - \tfrac{2^{\frac{3}{2}}q}{15\pi^2} \int_{\mathbb{R}^3} [\tilde{V}(\mathbf{q})]_+^{\frac{5}{2}}\, d\mathbf{q} - D(\rho)\,. \tag{B24}$$

Here we used also that $N < 2Z+1$, the choice of s and that $t \leq 3/5$.
Now we choose $\rho = \rho^{\mathrm{TF}}$ the minimizer of the TF-energy functional of a neutral atom with Coulomb potential and nuclear charge Z. Hence ρ^{TF} satisfies the TF-equation

$$\tfrac{1}{2}\left(\tfrac{6\pi^2}{q}\right)^{\frac{2}{3}} \rho^{\mathrm{TF}}(\mathbf{x})^{\frac{2}{3}} = [\tilde{V}(\mathbf{x})]_+,$$

since $\tilde{V}$ is the TF-mean field potential. Notice that here we use that the chemical potential of a neutral atom is zero. By the choice of ρ from the TF-equation it follows from (B24) that

$$\begin{aligned} \langle\psi, H_{\mathbf{P}}\psi\rangle &\geq -C(\beta^{\frac{1}{2}} + \beta^{-2})Z^{5/2-t/2} + \tfrac{3}{10}\left(\tfrac{6\pi^2}{q}\right)^{\frac{2}{3}} \int_{\mathbb{R}^3} d\mathbf{x}\, \rho^{\mathrm{TF}}(\mathbf{x})^{\frac{5}{3}} \\ &\quad -Z\int_{\mathbb{R}^3} \frac{\rho^{\mathrm{TF}}(\mathbf{x})}{|\mathbf{x}|}\, d\mathbf{x} + D(\rho^{\mathrm{TF}}) \\ &= \mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}) - C(\beta^{\frac{1}{2}} + \beta^{-2})Z^{5/2-t/2}\,. \end{aligned}$$

The claim follows. □

Proposition B.2. *Let ρ^{TF} be the minimizer of the TF-energy functional of a neutral atom with nuclear charge Z. Let $Z\alpha = \kappa$ be fixed with $0 \leq \kappa < 2/\pi$ and $Z \geq 1$.*

Then there is a constant depending only on κ and q such that for all $\{u_i\}_{i=1}^N \subset H^{\frac{1}{2}}(\mathbb{R}^3;\mathbb{C}^q)$ orthonormal in $L^2(\mathbb{R}^3)$ we have

$$\sum_{i=1}^N (u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}})u_i) - D(\rho^{\mathrm{TF}}) \geq \mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}) - CZ^{2+\frac{1}{5}}\,,$$

with $D(\cdot) = D(\cdot,\cdot)$ the Coulomb scalar product.

Proof. Since $\mathcal{E}^{\mathrm{TF}}(\rho^{\mathrm{TF}}) = -e_0 Z^{\frac{7}{3}}$ (see (12)) to prove the claim it is sufficient to show that the TF-energy gives a lower bound to the quantum energy modulo lower order terms. In the proof we localize the energy separating the contribution from the region near the nucleus to the one far away. The region far away from the nuclei will give the TF-energy.

In the proof C denotes a generic universal positive constant.

Choice of the localization. The localization will be given by the functions $\chi_1 \in C_0^\infty(\mathbb{R}^3)$ and $\chi_2 \in C^\infty(\mathbb{R}^3)$ such that: $0 \leq \chi_1, \chi_2 \leq 1$, $\chi_1^2 + \chi_2^2 = 1$ in $\mathbb{R}^3$,

$$\chi_1(\mathbf{x}) := \begin{cases} 1 & \text{if } |\mathbf{x}| < 2Z^{-3/5}, \\ 0 & \text{if } |\mathbf{x}| > 3Z^{-3/5}. \end{cases} \tag{B25}$$

Moreover we ask that

$$\|\nabla\chi_1\|_\infty, \|\nabla\chi_2\|_\infty \leq 2^2 Z^{3/5}. \tag{B26}$$

The localization in the energy expectation. We insert now the localization in the energy expectation. From Theorem 2.1 we find

$$\begin{aligned} &\sum_{i=1}^N (u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}})u_i) - D(\rho^{\mathrm{TF}}) \qquad\qquad \text{(B27)} \\ \geq\ & \sum_{i=1}^N \sum_{j=1}^2 (\chi_j u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}})\chi_j u_i) - D(\rho^{\mathrm{TF}}) - \alpha^{-1}\sum_{i=1}^N \sum_{j=1}^2 (u_i, L_j u_i), \end{aligned}$$

with L_j is the operator (defined in Theorem 2.1) that gives the error due to the localization in the kinetic energy. We first estimate this error term. Since $N \leq 2Z+1$ we find as in (B8) that

$$\alpha^{-1}\sum_{i=1}^N \sum_{j=1}^2 (u_i, L_j u_i) \leq CZ^{6/5}N \leq CZ^{2+1/5}\,. \tag{B28}$$

Near the nucleus. Since

$$\sum_{i=1}^N (\chi_1 u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}})\chi_1 u_i) \geq \mathrm{Tr}[\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}}\chi_{|\mathbf{x}|<3Z^{-3/5}}]_-,$$

by Theorem 2.10 with $R = 3Z^{-3/5}$ we find

$$\sum_{i=1}^{N} (\chi_1 u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}})\chi_1 u_i) \geq -CZ^{2+1/5} - C\kappa^2 Z^2. \tag{B29}$$

Here we use that $Z\alpha = \kappa$.

The outer zone. This region gives the main contribution to the energy.

Let $g \in C_0^\infty(\mathbb{R}^3)$, $g \geq 0$ be spherically symmetric with $\operatorname{supp}(g) \subset B_1(0)$ and such that $\|g\|_2 = 1$. Starting from these g we define $\Phi_Z(\mathbf{x}) := (Z^{-3/5})^{-3} g^2(\mathbf{x}Z^{3/5})$ and

$$g_Z(\mathbf{x}) := (Z^{-3/5})^{-\frac{3}{2}} g(\mathbf{x}Z^{3/5}) = \Phi_Z^{\frac{1}{2}}(\mathbf{x}).$$

Since $\operatorname{supp}(g_Z) \cap \operatorname{supp}(\chi_2) = \emptyset$ by Newton's Theorem we find

$$\sum_{i=1}^{N} (\chi_2 u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}})\chi_2 u_i) = \sum_{i=1}^{N} (\chi_2 u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}} * \Phi_Z)\chi_2 u_i). \tag{B30}$$

We consider the coherent states $g_Z^{\mathbf{p},\mathbf{q}}$ defined for $\mathbf{p}, \mathbf{q} \in \mathbb{R}^3$ by

$$g_Z^{\mathbf{p},\mathbf{q}}(\mathbf{x}) = g_Z(\mathbf{x} - \mathbf{q}) e^{-i\mathbf{p}.\mathbf{x}}.$$

Using formulas (B16) and (B17) we can rewrite (B30) as follows

$$\begin{aligned} &\sum_{i=1}^{N} (\chi_2 u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}} * g_Z^2)\chi_2 u_i) \\ = \; & \tfrac{1}{(2\pi)^3}\alpha^{-1} \int_{\mathbb{R}^3} d\mathbf{p} \int_{\mathbb{R}^3} d\mathbf{q} (T(\mathbf{p}) - \alpha\varphi^{\mathrm{TF}}(\mathbf{q})) \sum_{j=1}^{q} \sum_{i=1}^{N} |(\chi_2 u_i^j, g_Z^{\mathbf{p},\mathbf{q}})|^2 \\ & - \alpha^{-1} \sum_{i=1}^{N} \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{q} \, \overline{\chi_2 u_i(\mathbf{x})} (L_{\mathbf{q}} \chi_2 u_i)(\mathbf{x}), \end{aligned} \tag{B31}$$

Here u_i^j is the j-th spin component of u_i. We start by estimating the error term, the last term on the right hand side of (B31). We find as in (B19) that

$$\alpha^{-1} \sum_{i=1}^{N} \int_{\mathbb{R}^3} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{q} \, \overline{\chi_2 u_i(\mathbf{x})} (L_{\mathbf{q}} \chi_2 u_i)(\mathbf{x}) \leq C \|\nabla g\|_\infty^2 Z^{6/5} N. \tag{B32}$$

It remains to study the first term on the right hand side of (B31). In order to get an estimate from below we consider only the negative part of the integrand. Moreover, since if $|\mathbf{q}| < Z^{-3/5}$ then $\operatorname{supp}(\chi_2 g_Z^{\mathbf{p},\mathbf{q}}) = \emptyset$ we find

$$\begin{aligned} &\tfrac{1}{(2\pi)^3}\alpha^{-1} \int_{\mathbb{R}^3} d\mathbf{p} \int_{\mathbb{R}^3} d\mathbf{q} \, (T(\mathbf{p}) - \alpha\varphi^{\mathrm{TF}}(\mathbf{q})) \sum_{j=1}^{q} \sum_{i=1}^{N} |(\chi_2 u_i^j, g_Z^{\mathbf{p},\mathbf{q}})|^2 \\ \geq \; & \tfrac{q}{(2\pi)^3}\alpha^{-1} \int_{|\mathbf{q}| \geq Z^{-3/5}} d\mathbf{q} \int_{T(\mathbf{p}) - \alpha\varphi^{\mathrm{TF}}(\mathbf{q}) \leq 0} d\mathbf{p} \, (T(\mathbf{p}) - \alpha\varphi^{\mathrm{TF}}(\mathbf{q})) = \ldots, \end{aligned} \tag{B33}$$

where we also use that $\sum_{i=1}^N |(\chi_3 u_i^j, g_Z^{\mathrm{P,Q}})|^2 \le 1$ (Bessel's inequality). We split now the integral as a sum of two terms

$$\begin{aligned}\cdots &= \tfrac{q}{(2\pi)^3}\alpha^{-1}\iint_{\substack{\frac12|\mathbf{p}|^2-\varphi^{\mathrm{TF}}(\mathbf{q})\le 0\\ |\mathbf{q}|\ge Z^{-3/5}}} d\mathbf{q}d\mathbf{p}\,(T(\mathbf{p})-\alpha\varphi^{\mathrm{TF}}(\mathbf{q}))\\ &+ \tfrac{q}{(2\pi)^3}\alpha^{-1}\iint_{\substack{\frac{\alpha}{2}|\mathbf{p}|^2\ge\alpha\varphi^{\mathrm{TF}}(\mathbf{q})\ge T(\mathbf{p})\\ |\mathbf{q}|\ge Z^{-3/5}}} d\mathbf{q}d\mathbf{p}\,(T(\mathbf{p})-\alpha\varphi^{\mathrm{TF}}(\mathbf{q})). \quad \text{(B34)}\end{aligned}$$

We consider these two terms separately. The second term in (B34) gives a lower order contribution. Indeed

$$\begin{aligned}&\tfrac{q}{(2\pi)^3}\alpha^{-1}\iint_{\substack{\frac{\alpha}{2}|\mathbf{p}|^2\ge\alpha\varphi^{\mathrm{TF}}(\mathbf{q})\ge T(\mathbf{p})\\ |\mathbf{q}|\ge Z^{-3/5}}} d\mathbf{q}d\mathbf{p}\,(T(\mathbf{p})-\alpha\varphi^{\mathrm{TF}}(\mathbf{q}))\\ \ge\ & -\tfrac{q}{(2\pi)^3}\iint_{\substack{(\alpha^2[\varphi^{\mathrm{TF}}]_+^2+2[\varphi^{\mathrm{TF}}]_+)^{\frac12}\ge|\mathbf{p}|\ge(2[\varphi^{\mathrm{TF}}(\mathbf{q})]_+)^{\frac12}\\ |\mathbf{q}|\ge Z^{-3/5}}} d\mathbf{q}d\mathbf{p}\,[\varphi^{\mathrm{TF}}(\mathbf{q})]_+ = \ldots,\end{aligned}$$

and computing the integral in $\mathbf{p}$

$$\cdots = -C\int_{|\mathbf{q}|\ge Z^{-3/5}} d\mathbf{q}\,[\varphi^{\mathrm{TF}}(\mathbf{q})]_+^{\frac52}((1+\frac{\alpha^2}{2}[\varphi^{\mathrm{TF}}(\mathbf{q})]_+)^{\frac32}-1) = \ldots.$$

Using $(1+x)^{\frac32}\le 1+\frac32 x+\frac38 x^2$ and that $[\varphi^{\mathrm{TF}}(\mathbf{q})]_+\le Z/|\mathbf{q}|$ we get computing the integral

$$\begin{aligned}\cdots &= -C\alpha^2\int_{|\mathbf{q}|\ge Z^{-3/5}} d\mathbf{q}\,[\varphi^{\mathrm{TF}}]_+^{\frac72}(1+\frac{\alpha^2}{8}[\varphi^{\mathrm{TF}}(\mathbf{q})]_+)\\ &\ge -C\kappa^2 Z^{2-\frac15}-C\kappa^4 Z^{\frac75}.\end{aligned} \quad \text{(B35)}$$

Since $\sqrt{1+x}\ge 1+x/2-x^3/8$ for all $x\ge 0$, we have

$$T(\mathbf{p})\ge \alpha\tfrac12|\mathbf{p}|^2-\alpha^3\tfrac18|\mathbf{p}|^4,$$

and, for the first term on the right hand side of (B34), we obtain

$$\begin{aligned}&\tfrac{q}{(2\pi)^3}\alpha^{-1}\iint_{\substack{\frac12|\mathbf{p}|^2-\varphi^{\mathrm{TF}}(\mathbf{q})\le 0\\ |\mathbf{q}|\ge Z^{-3/5}}} d\mathbf{q}d\mathbf{p}\,(T(\mathbf{p})-\alpha\varphi^{\mathrm{TF}}(\mathbf{q}))\ge\\ \ge\ & \tfrac{q}{(2\pi)^3}\iint_{\substack{\frac12|\mathbf{p}|^2-\varphi^{\mathrm{TF}}(\mathbf{q})\le 0\\ |\mathbf{q}|\ge Z^{-3/5}}} d\mathbf{q}d\mathbf{p}\,(\tfrac12|\mathbf{p}|^2-\tfrac18\alpha^2|\mathbf{p}|^4-\varphi^{\mathrm{TF}}(\mathbf{q})) = \ldots.\end{aligned}$$

Computing now the integral with respect to $\mathbf{p}$, we find

$$\cdots = -\tfrac{2^{\frac32}q}{15\pi^2}\int_{|\mathbf{q}|>Z^{-3/5}}[\varphi^{\mathrm{TF}}(\mathbf{q})]_+^{\frac52}\,d\mathbf{q} - C\alpha^2\int_{|\mathbf{q}|>Z^{-3/5}}[\varphi^{\mathrm{TF}}(\mathbf{q})]_+^{\frac72}\,d\mathbf{q}. \quad \text{(B36)}$$

We see that the second term on the right hand side of (B36) gives a lower order contribution since it is of the same order as the one in (B35).
Starting from (B27), by (B28), (B29), (B32), (B35) and (B36) we find

$$\sum_{i=1}^{N}(u_i, (\alpha^{-1}T(\mathbf{p}) - \varphi^{\mathrm{TF}})u_i) - D(\rho^{\mathrm{TF}}) \tag{B37}$$
$$\geq -C(Z^{2+1/5} + Z^2 + Z^{2-1/5} + Z^{7/5}) - \tfrac{2^{\frac{3}{2}}q}{15\pi^2}\int_{\mathbb{R}^3}[\varphi^{\mathrm{TF}}(\mathbf{q})]_+^{\frac{5}{2}}\,d\mathbf{q} - D(\rho^{\mathrm{TF}}).$$

The result follows from the TF-equation. □

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