On the excess charge of a relativistic statistical model of molecules with an inhomogeneity correction

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Abstract
We show that the molecular relativistic Thomas–Fermi–Weizsäcker functional consisting of atoms of atomic numbers \( Z_1, \ldots, Z_K \) has a minimizer, if the particle number \( N \) is constrained to a number less or equal to the total nuclear charge \( Z := Z_1 + \cdots + Z_K \). Moreover, there is no minimizer, if the particle number exceeds \( 2.56Z \). This gives lower and upper bounds on the maximal ionization of heavy atoms.

Keywords: excess charge, relativistic Thomas–Fermi–Weizsäcker functional, existence of minimizers

1. Introduction

Shortly after the advent of quantum mechanics it became clear that the many particle problem of interacting quantum systems cannot be solved exactly much like in classical quantum mechanics. Thomas [27] and Fermi [9, 10] developed a density functional theory that turned out to describe atoms of large atomic numbers \( Z \) asymptotically correct as far as the energy and the density on the scale \( Z^{-1/3} \) is concerned (Lieb and Simon [23]). Thomas and Fermi assumed in their intuitive derivation that the potential would be locally constant. Their functional (Lenz [18]) generalized to molecules with atomic nuclei of atomic number \( Z_k \) situated at \( R_k \) reads

\[
E^{n\text{TF}}(\rho) := \int_{\mathbb{R}^3} dx \left( \frac{3}{10} \gamma \rho^5(x) - \frac{1}{3} \sum_{k=1}^{K} Z_k \rho(x) \frac{x_k}{|x - R_k|} \right) + D[\rho] + \sum_{1 \leq k < l \leq K} \frac{Z_k Z_l}{|R_k - R_l|} \tag{1}
\]
where \( D[\rho] := D(\rho, \rho) \) is the quadratic form associated with the Hermitian form

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

(2)

The functional is naturally defined on all nonnegative \( \rho \in L^{5/3}(\mathbb{R}^3) \) with finite Coulomb energy \( D[\rho] \). The positive constant \( \gamma \) is physically \( (3\pi^2)^{2/3} \). In the following we will write \( Z \) for the sum of the nuclear charges, i.e.,

\[
Z := Z_1 + \cdots + Z_K.
\]

By Teller’s lemma (Teller [26], see also Simon [24], section 3.9) the infimum of this functional taken over the densities \( \rho \) in the above set and all pairwise different nuclear positions \( R_1, \ldots, R_K \in \mathbb{R}^3 \) is the sum of the infima of the atomic functional (no binding) and scales in \( \gamma \) and \( Z_k \):

\[
\mathcal{E}^{\text{TF}}(\rho) \geq -\gamma^{-1} e_{\text{TF}} \sum_{k=1}^K Z_k^{2/3}
\]

(3)

where \( -e_{\text{TF}} \) is the infimum of the Thomas–Fermi functional with \( K = 1, Z = Z_1 = 1, \) and \( \gamma = 1 \).

Later Weizsäcker added a correction accounting for rapidly changing potentials. The resulting functional of the density, the nonrelativistic TFW-functional, for atom with \( q \) spin states per electron is

\[
\int_{\mathbb{R}^3} \frac{1}{2} |\nabla \sqrt{\rho(x)}|^2 + \mathcal{E}^{\text{TF}}(\rho).
\]

(4)

Note that 1/2 in front of the gradient term is the original constant used by Weizsäcker. However, there are also other constants discussed, e.g., 1/18 emanating from the gradient expansion (Kirzhnits [17], Hodges [16]), or 1/10 adapting the Scott correction of the TFW functional to its physical value (Yonei and Tomishima [28], see also Lieb and Liberman [21] for a slightly different numerical value).

This so called inhomogeneity correction yields an exponential decay of the atomic density as opposed the power decay of TF-theory and makes the potential finite at the nucleus as opposed to the pure Thomas–Fermi case which has a \(|x|^{-3/2}\) singularity at the nucleus. Also the excess charge \( Q := N - Z \), where \( N \) is the maximal number of electrons that the atom can bind, is raised from 0 to a positive number which Benguria and Lieb [4] bound by a constant of order one. This reflects the experimental fact, that for real atoms there are no doubly charged negative atomic ions.

From the physical point of view, however, the description of large atoms with nonrelativistic theories is of limited interest, since large atomic numbers result in velocities of the innermost electrons that require a relativistic description. This has well known consequence to the quantum energy (Solovej et al [25], Frank et al [11, 13], and Handrek and Siedentop [15]) and for the density (Frank et al [12]).

A generalization to relativistic density functionals, however, suffered from the fact that the naive generalization leads to an energy functional that is unbounded from below and yields a relativistic TF-equation whose solution has necessarily infinitely many particles because of a \(|x|^{-3}\) singularity at the origin. (For a review see Gombas [14], section 14.1.)

Dreizler and Engel [7] offered a solution to this problem: they derived a relativistic functional from quantum electrodynamics and later solved it numerically for atoms (Dreizler and
Engel [8]). Following Engel and Dreizler we write it in terms of the Fermi momentum \( p \) given by

\[
p(x) := (3\pi^2 \rho(x))^{1/3}, \tag{5}\]

instead of the density \( \rho \). The TFW part (dropping the Dirac term and an overall trivial factor of \( mc^2 \)) reads in the case of molecules consisting of \( K \) atoms of atomic numbers \( Z_1, \ldots, Z_K \) located at positions \( R_1, \ldots, R_K \)

\[
\mathcal{E}_{\text{TFW}}(p) := \mathcal{T}_{\text{W}}(p) + \mathcal{T}_{\text{TF}}(p) - \sum_{k=1}^{K} \frac{\alpha_S Z_k}{3\pi^2} \int_{\mathbb{R}^3} \frac{p^3(x)}{|x - R_k|} + \frac{\alpha_S}{9\pi^2} D[p^3] + \sum_{1 \leq k < j \leq K} \frac{\alpha_S Z_k Z_j}{|R_k - R_j|} \tag{6}\]

where \( \alpha_S \) is the Sommerfeld fine structure constant, which is \( 1/c \) in Hartree units and has the physical value of about \( 1/137 \). (The atomic case is \( K = 1 \) in which case we can assume \( R_1 = 0 \). Of course, then \( Z_1 = Z \).) The Thomas–Fermi part of the kinetic energy is

\[
\mathcal{T}_{\text{TF}}(p) := \frac{1}{8\pi^2} \int_{\mathbb{R}^3} \, dx \, t_{\text{TF}}(p(x)) \tag{7}\]

with

\[
t_{\text{TF}}(s) := s(s^2 + 1)^{1/2} + s^3 + 1)^{1/2} - \text{arsinh}(s) - \frac{8}{3}s^3. \tag{8}\]

The Weizsäcker part of the kinetic energy is

\[
\mathcal{T}_{\text{W}}(p) := \frac{3\lambda}{8\pi^2} \int_{\mathbb{R}^3} \, dx \, (\nabla p(x))^2 f(p(x))^2 \tag{9}\]

with

\[
f(t) := \sqrt{\frac{t}{\sqrt{t^2 + 1} + 2} \, t^2 + 1 \, \text{arsinh}(t)}. \tag{10}\]

The constant \( \lambda \) is positive.

We note that the ultrarelativistic limit of this functional—dropping the regularizing \( \text{arsinh} \) in the Weizsäcker term—has been considered before by Benguria et al [5]; it turns out that stability of matter holds for small enough \( Z \), whereas the functional is unbounded from below, if the \( Z \) is large. A preliminary investigation of the massive functional appeared in [6].

In this paper we consider the massive case. As opposed to the above case and many other relativistic models, we will show that \( \mathcal{E}_{\text{TFW}} \) is bounded from below for all \( Z_1, \ldots, Z_K, R_1, \ldots, R_K \) and \( N \), in fact, we will show that the bound can be uniform in \( R_1, \ldots, R_K \) and \( N \). This will be achieved by showing an upper bound on the number of particles that can be bounded in terms of the nuclear charge \( Z \).

Next we specify the space of allowed Fermi momenta \( p \). To this end we introduce the antiderivative

\[
F(t) := \int_0^t ds \, f(s). \tag{11}\]

We define

\[
P := \{ p \in L^4(\mathbb{R}^3) | p \geq 0, \ D[p^3] < \infty, \ F \circ p \in D^1(\mathbb{R}^3) \} \tag{12}\]
where $D^1(\mathbb{R}^3)$ is the space of all locally integrable functions on $\mathbb{R}^3$ which decay at infinity and have a square integrable gradient (Lieb and Loss [[22], section 8.2]). For later purposes we also introduce for $N \geq 0$

$$P_N := \{ \rho | \sqrt{\rho} \in P, \int_{\mathbb{R}^3} dx \rho(x) \leq N \}.$$  \hspace{1cm} (13)

It turns out that all terms occurring in the TFW functional are well defined on $P_N$ as we shall see in the proof of theorem 1. In particular the Weizsäcker term becomes simply

$$T^W(F \circ p) := \int_{\mathbb{R}^3} dx |\nabla (F \circ p)|^2(x).$$

For the proof on the excess charge, it will be convenient to write the energy functional in terms of $\chi := F \circ p$.

Our first results are:

**Theorem 1.** (Stability) For any $Z_\infty > 0$, and any $K \in \mathbb{N}$ there exists a constant $c(Z_\infty^{2/3} \cdot K)$ depending only on $Z_\infty^{2/3} \cdot K$ such for all $N \in \mathbb{R}_+, Z_1, \ldots, Z_k \in [0, Z_\infty]$, and pairwise different $R_1, \ldots, R_k \in \mathbb{R}^3$

$$\inf E^{TFW}(P_N) \geq -N - c(Z_\infty^{2/3} \cdot K).$$  \hspace{1cm} (14)

Note the surprising fact that—unlike in many other relativistic models of Coulomb systems—there is no critical nuclear charge beyond which the energy is unbounded from below. As the proof will show this is due to the occurrence of the arsinh in the Weizsäcker term making it logarithmically stronger than the Coulomb singularity.—In Engel and Dreizler’s formal derivation of the functional from quantum electrodynamics this occurrence is a consequence of the necessary renormalization.

Furthermore, we remark that—unlike the case treated here—a lower bound which is linear in $N$ and even in $K$—of the nonrelativistic TFW-functional is obvious, since it is bounded from below by the nonrelativistic TF-functional. The stability of the TF-functional follows then by Teller’s no-binding theorem and the fact that the excess charge of atoms is zero. The same is true here. However, the relativistic TF kinetic energy is not strong enough to prevent collapse: its infimum is $-\infty$ (Gombas [[14], chapter III, section 14]).

**Theorem 2.** (Existence of minimizers) For any $N, Z_1, \ldots, Z_k \geq 0$, the functional $E^{TFW}$ has a minimizer $p_N$ on $P_N$, and, moreover, if $p_N$ is a minimizer on $P_N$ for $N \leq Z$, then its particle number $\int_{\mathbb{R}^3} dx p_N(x)^3/(3\pi^2)$ is equal to $N$, i.e., the minimizer occurs on the boundary of $P_N$.

Note that we do not claim uniqueness of the minimizer: unlike the nonrelativistic TFW functional, the relativistic Weizsäcker correction is not a convex functional of the density $\rho$, i.e., the standard tool for showing uniqueness of minimizers is not available.

To formulate the next theorem we introduce the function $H$ on the positive real line by

$$H(s) := F(s)/(sF(s))$$  \hspace{1cm} (15)

and write for its minimum and maximum

$$a := \inf_{\mathbb{R}_+} H(x) \text{ and } b := \sup_{\mathbb{R}_+} H(x).$$  \hspace{1cm} (16)
Numerically $a = 0.6116832747$.

**Theorem 3.** (Bound on the excess charge) For all $N \in \mathbb{R}_+$, all $K \in \mathbb{N}$, all $Z_1, \ldots, Z_K \in \mathbb{R}_+$, and all pairwise different $R_1, \ldots, R_K \in \mathbb{R}^3$ the minimizer $\rho$ of $E_{\text{TFW}}$ on $P_N$ fulfills

$$\int_{\mathbb{R}^3} \rho(x) \, dx < \frac{2}{\sqrt{a}} Z.$$

(17)

Note that inserting the numerical value of $a$ gives

$$\int_{\mathbb{R}^3} \rho(x) \, dx < 2.56Z.$$  

(18)

This result shows in particular that the relativistic TFW functional cannot bind infinitely many electrons. Of course one should—presumably—regard this only as a first step, since one might conjecture also here that the maximal excess charge $Q$ is—like in the nonrelativistic case—bounded by one $[4]$.

Finally, we note the following immediate consequence of theorems 1 and 3: by theorem 3 inf$_{N \in \mathbb{R}_+} \inf \ E_{\text{TFW}}(P_N) \geq \inf \ E_{\text{TFW}}(P_{2a^{-1/2}Z})$. Thus, when minimizing $E_{\text{TFW}}$, we might, right from the beginning, restrict to the case that $N \leq 2a^{-1/2}Z$. Moreover, $Z = Z_1 + \cdots + Z_K \leq Z_\infty K$. Inserting this in (19) gives the following corollary:

**Corollary 1.** For any $Z_\infty \geq 1$, and any $K \in \mathbb{N}$ there exists a constant $d(Z_\infty^{1/3} \cdot K)$ such for all $N \in \mathbb{R}_+, Z_1, \ldots, Z_K \in [0, Z_\infty]$, and pairwise different $R_1, \ldots, R_k \in \mathbb{R}^3$

$$\inf \ E_{\text{TFW}}(P_N) \geq -d(Z_\infty^{1/3} \cdot K).$$

(19)

Note that physics suggests that $Z_\infty$ can be chosen uniformly in $K$, since there are no elements known with a nuclear charge higher than 119, i.e., $Z_\infty = 119$ is a reasonable assumption. Assuming such a uniform bound on $Z_1, \ldots, Z_K$ yields a lower bound on the energy which depends only on the number of nuclei which are present in the Coulomb system at hand.  

The structure of the remaining part is basically structured according to our three main results: in section 2 we prove the stability result theorem 1. The main part is a detailed lower bound on the energy. The essential input is an estimate on the potential energies using the nonrelativistic TF-theory and an involved estimate of the resulting negative nonrelativistic TF kinetic energy in terms of relativistic Weizsäcker term and the massless relativistic TF kinetic energy. Section 3 contains the existence result which is inspired by Benguria et al [2]. Sections 4 and 5 show the bounds on the ionization. Although the upper bound is inspired by Benguria’s early unpublished proof of the bound $N < 2Z$ for the excess charge of the Thomas–Fermi model, namely to integrate the Euler equation against a suitable weight. (See also the application of this idea by Lieb [19] for the Schrödinger equation and Benguria et al [3] for the Hellmann–Weizsäcker functional.) However, it cannot be applied in a straightforward manner in the present context. We need to transform the functional and estimate the resulting functional using some estimates on the function $F$ of (11) and its inverse. We are able to control the errors so that we loose only slightly compared to the above mentioned nonrelativistic results [3, 19].

Finally, we collect some basic facts needed throughout the proves in the appendix: appendix A gives some results that are a consequence of the phase space representation of the kinetic energy of the relativistic TF-functional. Appendix B gives the needed basic properties of $F$.  

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2. Proof of stability

In this section we will show that the infimum of the energy functional is bounded from below by a bound that is linear in the number of involved electrons $N$ plus a constant depending on the number of nuclei $K$ and the maximal occurring atomic number $Z_{\infty}$.

We begin with the definition of two cut-off radii $R$ and $\tilde{R}$ depending on parameters $\alpha$ and $\beta$. These are defined as minimizers of two functions $F_\beta$ and $\tilde{F}_{\alpha,\beta}$.

**Definition 1.** We define the function $R$:

$$R : \mathbb{R}_+ \to \mathbb{R}_+$$

$$\beta \mapsto R_\beta \quad (20)$$

where, given $\beta \in \mathbb{R}_+$, $R_\beta$ is the unique minimizer of $F_\beta$ given by

$$F_\beta(r) := \frac{1}{r \arcsinh(r)^3} + \frac{r}{\beta}$$

in the variable $r \in \mathbb{R}_+$.

Furthermore, we define the function $\tilde{R}$:

$$\tilde{R} : \mathbb{R}_+^2 \to \mathbb{R}_+$$

$$(\alpha, \beta) \mapsto \tilde{R}_{\alpha,\beta} \quad (21)$$

where, given $(\alpha, \beta) \in \mathbb{R}_+^2$, $\tilde{R}_{\alpha,\beta}$ is the unique minimizer of

$$\tilde{F}_{\alpha,\beta}(r) := \begin{cases} 
\frac{1}{r \arcsinh(R_\beta)^3} + \frac{r}{\alpha} & r \geq R_\beta \\
\frac{1}{r^3} \left( \frac{R_\beta}{\arcsinh(R_\beta)} \right)^3 + \frac{r}{\alpha} & r < R_\beta 
\end{cases} \quad (22)$$

in the variable $r \in \mathbb{R}_+$.

That these definitions are meaningful is a consequence of lemma 1 below; because the function $F_\beta$ with $\beta \in \mathbb{R}_+$ fixed, is continuous and diverges to $+\infty$ for $R \to 0$ or $R \to \infty$, its infimum on $\mathbb{R}_+$ is attained. Because of the strict convexity of $F_\beta$ its minimizer $R_\beta$ is uniquely defined. Thus $R$ is well defined.

Since $R_\beta$ is well defined, it follows that $\tilde{F}_{\alpha,\beta}$ is well defined. Now, we repeat the above argument to define $\tilde{R}_{\alpha,\beta}$ again using lemma 1.

**Lemma 1.** The functions $F_\beta$ and $\tilde{F}_{\alpha,\beta}$ are continuous, diverge to $+\infty$ at 0 and $\infty$, and are strictly convex.

**Proof.** Obviously $F_\beta$ is continuous and has the stated behavior at 0 and $\infty$. That it is strictly convex follows from the fact that it is twice differentiable (even real analytic) on $\mathbb{R}_+$ and the second derivative is positive, since its first derivative

$$F_\beta'(r) = -\frac{1}{r^2 \arcsinh(r)^3} - \frac{3}{r \arcsinh(r)^3 \sqrt{1 + r^2}} + \frac{1}{\beta}$$

is obviously strictly increasing.
The functions $\tilde{F}_{\alpha,\beta}$ are, by inspection, also continuous and diverge to $\infty$ at $0$ and $\infty$. Outside $r = R_{\beta}$ they are also twice differentiable (in fact again real analytic) and have the derivative

$$
\tilde{F}'_{\alpha,\beta}(r) = \begin{cases} 
-\frac{1}{r^2 \text{arsinh}(R_{\beta})^3} + \frac{1}{\alpha} & r > R_{\beta} \\
\frac{4}{r^3} \left( \frac{R_{\beta}}{\text{arsinh}(R_{\beta})} \right)^3 + \frac{1}{\alpha} & r < R_{\beta}.
\end{cases}
$$

(24)

Outside $R_{\beta}$ these functions are monotone increasing. In addition at $R_{\beta}$ we have a jump of positive height, namely

$$
\lim_{r \to R_{\beta}^-} \tilde{F}'_{\alpha,\beta}(r) - \lim_{r \to R_{\beta}^+} \tilde{F}'_{\alpha,\beta}(r) = \frac{3}{R_{\beta}^3 \text{arsinh}(R_{\beta})} > 0,
$$

(25)

which shows strict convexity.

We need the following basic properties of the functions $R$ and $\tilde{R}$.

**Lemma 2.** The following properties hold:

(a) For all $\beta \in \mathbb{R}_+$ we have $R(\beta) = \tilde{R}(\beta, \beta)$.

(b) The functions $R$ and $\tilde{R}(\cdot, \beta)$ (with $\beta \in \mathbb{R}_+$ fixed) are monotone increasing maps onto $\mathbb{R}_+$.

**Proof.** (1) For all $\alpha, \beta \in \mathbb{R}_+$ we have directly from the definitions of the functions $\tilde{F}_{\alpha,\beta}$ and $F_{\beta}$ that $\tilde{F}_{\alpha,\beta}(r) \geq F_{\beta}(r)$ and $\tilde{F}_{\alpha,\beta}(R_{\beta}) = F_{\beta}(R_{\beta})$. Thus, $R_{\beta}$ does not only minimize $F_{\beta}$ but also $\tilde{F}_{\alpha,\beta}$. However, the minimizer of $\tilde{F}_{\alpha,\beta}$ is uniquely determined. Thus, $R_{\alpha,\beta} = \tilde{R}_{\alpha,\beta}$.

(2) $\tilde{R}(\beta)$ solves the equation $F_{\beta}(r) = 0$. From (23) it is obvious that the function $R$ is monotone increasing. It is also obvious from (23) that $R_{\beta} \to 0$ as $\beta \to 0$ and $R_{\beta} \to \infty$ as $r \to \infty$. This shows the claim on $R$.

By strict convexity, $\tilde{F}'_{\alpha,\beta}(r) < 0$ for $r < \tilde{R}_{\alpha,\beta}$ and $\tilde{F}'_{\alpha,\beta}(r) > 0$ for $r > \tilde{R}_{\alpha,\beta}$ holding for all $\alpha, \beta \in \mathbb{R}_+$, holding in particular for $\alpha = \beta$. Moreover, for $\alpha > \beta$ and $r < R_{\beta}$ we have

$$
\tilde{F}'_{\alpha,\beta}(r) = -\frac{4}{r^3} \left( \frac{R_{\beta}}{\text{arsinh}(R_{\beta})} \right)^3 + \frac{1}{\alpha} < \tilde{F}'_{\beta,\beta}(r) < 0,
$$

(26)

i.e., $\tilde{R}_{\alpha,\beta} \geq R_{\beta}$ for $\alpha > \beta$. Away from $R_{\beta}$ we can use again the Euler equation: suppose that there is a $\alpha' \in \mathbb{R}_+$ such that $\tilde{R}_{\alpha',\beta} > R_{\beta}$. Then $\tilde{R}_{\alpha',\beta}$ fulfills

$$
\tilde{F}'_{\alpha',\beta}(\tilde{R}_{\alpha',\beta}) = \frac{1}{\tilde{R}_{\alpha',\beta}^3 \text{arsinh}(R_{\beta})^3} + \frac{1}{\alpha'} = 0.
$$

Thus, we have for any $\alpha'' > \alpha'$, an $r' > \tilde{R}_{\alpha'',\beta} > R_{\beta}$ solving the equation

$$
\tilde{F}'_{\alpha'',\beta}(r') = \frac{1}{r'^3 \text{arsinh}(R_{\beta})^3} + \frac{1}{\alpha''} = 0.
$$

Since $\tilde{R}_{\alpha',\beta} > R_{\beta}$, we have $r' = \tilde{R}_{\alpha',\beta}$. Thus $\tilde{R}_{\alpha',\beta} > \tilde{R}_{\alpha'',\beta}$ for $\alpha'' > \alpha' > \beta$. This implies the monotony in $\alpha$ for $\alpha > \beta$. Similar arguments yield the monotony in $\alpha$ for $\alpha \leq \beta$.

**Proof of theorem 1.** The condition $\nabla(F \circ p) \in L^2(\mathbb{R}^3)$ is a mere rewriting of the finiteness condition of the Weizsäcker term. Similarly $D[p^3] < \infty$ is equivalent to the finiteness of the electron–electron repulsion.
Next we look at the Thomas–Fermi term. Obviously the massive Thomas–Fermi term is bounded above by the massless one. It is also bounded from below by the massless Thomas–Fermi term minus the particle number (see (87)), i.e.,

\[ \mathcal{T}^{\text{TF}}(p) \geq \frac{1}{4\pi^2} \int_{\mathbb{R}^3} dx \ p(x)^4 - N. \]  

(27)

Both bounds are obvious from the representation of \( \mathcal{T}^{\text{TF}} \) as phase space integral.

Since \( p \in L^4(\mathbb{R}^3) \), \( p \) decays at infinity and therefore also \( F \circ p \). Thus, we may employ the Sobolev inequality yielding \( F \circ p \in L^6(\mathbb{R}^3) \) and estimate \( F \) from below using (90) from the appendix. We get

\[
\int_{\mathbb{R}^3} dx \ |\nabla(F \circ p)(x)|^2 \geq c_s \left( \int_{\mathbb{R}^3} dx \ |F \circ p(x)|^6 \right)^{1/3} \geq \frac{c_s}{4} \left( \int_{\mathbb{R}^3} dx \ p(x)^6 \arcsinh(p(x))^3 \right)^{1/3} =: \frac{c_s}{4} W(p)^{1/3}
\]  

(28)

where \( c_s \) is the Sobolev constant. Thus, using (28), (3), and (27) we get

\[
\mathcal{E}^{\text{TFW}}(p) \geq \frac{3c_s^3 \lambda}{32\pi^2} W(p)^{1/3} + \frac{1}{4\pi^2} T(p) - N - \frac{3}{10} \gamma \alpha_S \int_{\mathbb{R}^3} dx \ p(x)^5 - \frac{\alpha_S}{\gamma} A
\]  

(29)

with \( T(p) := \int_{\mathbb{R}^3} dx \ p(x)^4 \). We pick

\[
\gamma = \sqrt{\frac{A}{10 \int_{\mathbb{R}^3} dx \ p(x)^5}}
\]

and get

\[
\mathcal{E}^{\text{TFW}}(p) \geq \frac{3\lambda c_s^3}{32\pi^2} W(p)^{1/3} + \frac{1}{4\pi^2} T(p) - N - 2\alpha_S \sqrt{\frac{3A}{10} \int_{\mathbb{R}^3} dx \ p(x)^5}.
\]  

(30)

We pick \( \beta \in \mathbb{R}_+ \) to be specified later but independently of \( p \) and estimate

\[
\int_{\mathbb{R}^3} dx \ p(x)^5 \leq \frac{1}{\beta} \int_{|p(x)| > \beta} dx \ p(x)^5 \arcsinh(p(x))^3 + \beta \int_{|p(x)| \leq \beta} dx \ p(x)^4 \leq \frac{1}{\beta} \arcsinh(\beta)^3 W(p) + \beta T(p) \leq \begin{cases} \frac{1}{\beta} \arcsinh(R_\beta)^3 W(p) + \beta T(p) & r \geq R_\beta \\ \frac{1}{\beta} W(p)(R_\beta/\arcsinh(R_\beta))^3 + \beta T(p) & r < R_\beta \end{cases}
\]  

(34)

where \( R_\beta \) is the unique minimizer of the function \( F_\beta \) defined in (21). Using (22) allows us to rewrite (34) so that we get

\[
\int_{\mathbb{R}^3} dx \ p(x)^5 \leq W(p) \tilde{F}_{Q,\beta}(r)
\]  

(35)

in the variable \( r \). Here we use the abbreviation \( Q := W(p)/T(p) \). The resulting minimizer \( \tilde{R}_{Q,\beta} \)
exists uniquely for each \( p \) and \( \beta \) by lemma 1. Inserting it into (35) gives

\[
\int_{\mathbb{R}^3} dx \ p(x)^5 \leq W(p) \tilde{F}_{Q,\beta}(\tilde{R}_{Q,\beta})
\]

(36)

\[
= \begin{cases} 
\frac{1}{R_{Q,\beta} \text{arsinh}(R_{\beta})} W(p) + \tilde{R}_{Q,\beta} T(p) & Q \geq \beta \\
\frac{1}{R_{Q,\beta}^4} W(p)(R_{\beta}/\text{arsinh}(R_{\beta}))^3 + R_{Q,\beta} T(p) & Q < \beta 
\end{cases}
\]

(37)

In the last step we used that \( \tilde{R}_{Q,\beta} \) is bounded from below—independently of \( \alpha \) and \( \tilde{R}_{\beta,\beta} = R_{\beta} \).

The optimizer of the first line is

\[
\tilde{R}_{Q,\beta} = \sqrt[4]{\frac{W(p)}{T(p) \text{arsinh}(R_{\beta})}}.
\]

The second line is minimized for

\[
\tilde{R}_{Q,\beta} = \sqrt[4]{\frac{4W(p)R_{\beta}^3}{\text{arsinh}(R_{\beta})^4 T(p)}}.
\]

Thus,

\[
\int_{\mathbb{R}^3} dx \ p(x)^5 \leq \begin{cases} 
2 \sqrt{\frac{W(p)T(p)}{\text{arsinh}(R_{\beta})^5}} & W(p) \geq \beta T(p) \\
\frac{5}{4^4 \sqrt{2}} (W(p)(R_{\beta}/\text{arsinh}(R_{\beta}))^{1/5} T(p)^{4/5}) & W(p) < \beta T(p) 
\end{cases}
\]

(38)

We insert this bound in (30) and obtain

\[
E_{\text{TFW}}(p) \geq \frac{3 \lambda_3}{32 \pi^2} W(p)^{1/3} + \frac{1}{4 \pi^2} T(p) - N
\]

\[
- 2\alpha_S \begin{cases} 
\sqrt{\frac{3A}{5 \sqrt{2 \text{arsinh}(R_{\beta})}}} \left( \frac{W(p)^{1/3}}{4} + \frac{T(p)}{4} \right) & W(p) \geq \beta T(p) \\
\sqrt{\frac{3A}{2 \sqrt{2}}} (\beta R_{\beta}^3/\text{arsinh}(R_{\beta})^{1/5} T(p)) & W(p) < \beta T(p).
\end{cases}
\]

(39)

Now, we pick \( \beta \) such that

\[
\min \left\{ \frac{\lambda_3}{8 \pi^2}, \frac{1}{4 \pi^2} \right\} = \sqrt{\frac{3A}{5 \sqrt{2 \text{arsinh}(R_{\beta})}}}. 
\]

(40)

This bounds the case of the first line from below by \(-N\).

The second line is bounded from below—indeed, independently of \( p \), since the leading power in \( T(p) \) has a positive coefficient. To make this quantitative, we write \( a \) for the coefficient of \( T(p) \).
and $b$ for the coefficient of $T(p)$ in the second case of (39). Now $aT(p) - b\sqrt{T(p)}$ is minimized for $T(p) = b^2/(4a^2)$ implying

$$aT(p) - b\sqrt{T(p)} \geq -b^2/(4a) =: C(A)$$

independently of $p$.

Since (40) implies that $R_\beta$ is increasing in $A$, we find that $C(A)$ is increasing. Moreover by the definition of $A$ in (3), we can estimate $A \leq \epsilon_T Z_{\infty}^2 \cdot K$. Thus, the second case of (39) is bounded from below by $-N = C(\epsilon_T Z_{\infty}^2 \cdot K)$. Writing the latter constant as $c(Z_{\infty}^2 \cdot K)$ yields (19).

3. Proof of the existence of minimizers (theorem 2)

Since $E_{\text{TFW}}$ is bounded from below on $P_N$, we will now address the question whether the infimum is attained. It is convenient, to regard the functional as function of the density $\rho$ instead of the Fermi momentum $p$ and similarly for other parts of the energy functional. In abuse of notation we write $E_{\text{TFW}}(\rho)$ instead of $E_{\text{TFW}}(\sqrt{T(p)})$, i.e.,

$$E_{\text{TFW}}(\rho) = \frac{3\lambda}{8\pi^2} \int_{\mathbb{R}^3} d^3x \left| \nabla (F \circ \sqrt{3\pi^2 \rho}) \right|^2 + T_{\text{TF}}(\rho) = \alpha S \sum_{k=1}^{K} \int_{\mathbb{R}^3} dx \frac{Z_k \rho(x)}{|x - R_k|} + \alpha S D(\rho)$$

(42)

Theorem 4. For every $N, Z_1, \ldots, Z_K \in \mathbb{R}_+ \text{ and } R_1, \ldots, R_K \in \mathbb{R}^3$ there exists $\rho \in P_N$ such that

$$E_{\text{TFW}}(\rho) = \inf E_{\text{TFW}}(P_N).$$

(43)

Since $E_{\text{TFW}}$ has a lower bound, there is a minimizing sequence $\rho_j$, such that

$$\lim_{j \to \infty} E_{\text{TFW}}(\rho_j) = \inf E_{\text{TFW}}(P_N).$$

(44)

However (39) shows not only boundedness from below but also that $E_{\text{TFW}}(\rho_j) \to \infty$ as either of the norms $\|\rho_j\|_{L^4(\mathbb{R}^3)}$, $\|F \circ \sqrt{3\pi^2 \rho_j}\|_{D^{1/2}(\mathbb{R}^3)}$, or $\|\rho_j\|_{L^\infty} = \sqrt{D[\rho]}$ tend to infinity. By the Banach–Alaoglu theorem we can pick a subsequence, such that we have weak convergence in all of these norms. We now imagine that we started already with this subsequence to avoid a new notation. We have $\chi \in D^{1}(\mathbb{R}^3)$, $\zeta_2 \in L^{4/3}(\mathbb{R}^3)$, $\zeta_3 \in L^2(\mathbb{R}^3)$ with $D[\zeta_3] < \infty$, and $\zeta_4 \in L^{5/3}(\mathbb{R})$ such that, as $j \to \infty$,

$$\int_{\mathbb{R}^3} dx \nabla f(x) \nabla (F \circ \sqrt{3\pi^2 \rho_j} - \chi) \to 0 \quad \forall f \in D^{1}(\mathbb{R}^3),$$

(45)

$$\int_{\mathbb{R}^3} dx f(x)(\rho_j - \zeta_2) \to 0 \quad \forall f \in L^2(\mathbb{R}^3),$$

(46)

$$D(f, \rho_j - \zeta_4) \to 0 \quad \forall f \text{ with } D[f] < \infty,$$

(47)

$$\int_{\mathbb{R}^3} dx f(x)(\rho_j - \zeta_4) \to 0 \quad \forall f \in L^{5/2}(\mathbb{R}^3)$$

(48)

using the abbreviation (2). The convergence (48) holds, since by (38), $\|\rho_j\|_{L^{5/3}(\mathbb{R}^3)}$ is also bounded.
To prove the existence of the minimizer, we prove the lower semicontinuity of each term of $E^{TFW}$.

We begin with the Weizsäcker term. Since the norm on $D^1(\mathbb{R}^3)$ is lower continuous (Lieb and Loss [22], section 8.2), we immediately have

$$T^W(\zeta) \leq \liminf_{j \to \infty} T^W(\rho_j)$$

(49)

with $\zeta := (3\pi^2)^{-1}(F^{-1}(\chi))^3$.

Next we consider the $T^{TF}$ which obviously is a convex functional with a derivative $d$ at $\rho$ (see also appendix A)

$$[d(T^{TF})(\rho)] : L^{4/3} \to \mathbb{R}$$

(50)

$$\eta \mapsto \int_{\mathbb{R}^3} dx \left( \sqrt{(3\pi^2\rho)^{2/3} + 1} - 1 \right) \eta(x).$$

(51)

Since $d(T^{TF})(\rho)$ is in the dual space of $L^{4/3}$. Therefore, we get by convexity

$$\liminf_{j \to \infty} T^{TF}(\rho_j) \geq T^{TF}(\zeta_2) + \liminf_{j \to \infty} d(T^{TF})(\eta_2)(\rho_j - \zeta_2) = T^{TF}(\zeta_2).$$

(52)

The third term, the external potential, is actually weakly continuous at the limiting element. Because of linearity and translational invariance it suffices to show this for the Coulomb potential of a unit point charge at the origin. We decompose it into a singular and a long range part

$$1/|x| := l(x) + r(x)$$

(53)

with

$$r(|x|) := \int_{|y| < 1} dy \frac{\mu(y)}{|x-y|},$$

where we pick some spherically symmetric charge distribution supported in the unit ball centered at the origin with $D[\mu] < \infty$. Whereas $l \in L^{5/2}$, since $\text{supp}(l) \subset B_1(0)$ and $l(x) \leq 1/|x|$ because of Newton’s theorem (see [24], section 3.9).

Thus

$$\lim_{j \to \infty} \int_{\mathbb{R}^3} dx \ r(x) \rho_j(x) = 2 \lim_{j \to \infty} D(\mu, \rho_j) = 2D(\mu, \zeta_3) = \int_{\mathbb{R}^3} dx \ r(x) \zeta_3(x).$$

Since $l \in L^{5/2}(\mathbb{R}^3)$ we have

$$\lim_{j \to \infty} \int_{\mathbb{R}^3} dx \ l(x) \rho_j(x) = \lim_{j \to \infty} \int_{\mathbb{R}^3} dx \ l(x) \zeta_4(x).$$

Eventually we consider the electron–electron repulsion. By the Schwarz inequality

$$D(\zeta_3, \zeta_3) = \lim_{j \to \infty} D(\rho_j, \zeta_3) \leq \liminf_{j \to \infty} \sqrt{D[\rho_j]D[\zeta_3]}$$

and thus

$$D[\zeta_3] \leq \liminf_{j \to \infty} D[\rho_j].$$

Thus all the terms are lower continuous at the corresponding limiting points. To conclude the proof, we wish to show that $\zeta = \zeta_2 = \zeta_3 = \zeta_4$ and that the limiting point is in $P_N$. 
Since \( C_0^\infty(\mathbb{R}^3) \subset L^4(\mathbb{R}^3) \cap L^{5/2}(\mathbb{R}^3) \) we have for all \( f \in C_0^\infty(\mathbb{R}^3) \) the two equalities
\[
\int_{\mathbb{R}^3} dx \ f(x) \zeta_2 = \lim_{j \to \infty} \int_{\mathbb{R}^3} dx \ f(x) \rho_j(x) = \int_{\mathbb{R}^3} dx \ f(x) \zeta_4,
\]
i.e., \( \zeta_2 = \zeta_4 \).

Next we take \( -(4\pi)^{-1} \Delta f \) with \( f \in C_0^\infty(\mathbb{R}^3) \). Then
\[
\int_{\mathbb{R}^3} dx \ f(x) \zeta_3(x) = D(-(4\pi)^{-1} \Delta f , \zeta_3) = \lim_{j \to \infty} D(-(4\pi)^{-1} \Delta f , \rho_j)
\]
\[
= \lim_{j \to \infty} \int_{\mathbb{R}^3} dx \ f(x) \rho_j(x) = \int_{\mathbb{R}^3} dx \ f(x) \zeta_2(x). \quad (54)
\]

Thus \( \zeta_2 = \zeta_3 \).

By [[22], theorem 8.7] we can also assume that \( \chi_j := F(\sqrt{3\pi^2 \rho_j}) \to \chi \|_A \) converges in \( L^6(\mathbb{A}) \) strongly on sets \( A \subset \mathbb{R}^3 \) of finite measure. We will show now, that \( \rho_j \) converges strongly in \( L^{3/2}(\mathbb{A}) \) to \( \chi \|_A \) and thus \( \zeta = \zeta_2 \), since \( A \) is arbitrary. To do this we will use an estimate on the inverse of \( F \) that follows from lemma 3 of appendix B.

\[
(3\pi^2)^{4/3} \int_A dx \ |\rho_j(x) - \chi(x)|^{4/3}
\]
\[
= \int_A dx \ |(F^{-1}(\chi_j(x)))^3 - (F^{-1}(\chi(x)))^3|^{4/3}
\]
\[
\leq 8 \int_A dx \ \left| \chi_j(x)^2(\chi_j(x)+1) - \chi(x)^2(\chi(x)+1) \right|^{4/3}
\]
\[
\leq 8 \int_A dx \ \left| (\chi_j(x)-\chi(x))(\chi_j(x)^2 + \chi_j(x)\chi(x) + \chi(x)^2 + \chi_j(x) + \chi(x)) \right|^{4/3}
\]
\[
\leq 8 \left( \int_A dx \ |\chi_j(x) - \chi(x)|^{9/2} \right)^{2/9} \left( \int_A dx \ \left| \chi_j^2 + \chi_j\chi + \chi^2 + \chi_j + \chi \right|^{12/7} \right)^{7/9}
\]
which tends to zero, since the last factor is uniformly bounded in \( j \).

Finally, \( \zeta \in P_N \), since otherwise this would lead to immediate contradictions to \( \zeta \geq 0 \) or \( \int_{\mathbb{R}^3} dx \ \zeta(x) \leq N \).

4. Proof of a lower bound on the maximal ionization

**Proof.** We will now assume that \( N \leq Z \) and—contradictory to the assumption of the theorem that the minimizer has a particle number that is strictly less than \( N \), i.e., \( \int_{\mathbb{R}^3} dx \ p_N(x)^3/3\pi^2 < N \).

If this is the case, then \( p_N \) fulfills the Thomas–Fermi–Weizsäcker equation
\[
8\pi \int_0^\infty \frac{p_N^2(x)(\sqrt{p_N^2(x)+1} - 1)}{F(p_N(x))} - 6\lambda \Delta F(p_N)(x) - \sum_{k=1}^K \frac{8\alpha Z_k p_N^2(x)}{|x-R_k|^2 F(p_N(x))} + \frac{8\alpha S^3}{3\pi^2} \int_{\mathbb{R}^3} dy \frac{p_N^2(x)p_N^2(y)}{|x-y|F(p_N(x))} = 0.
\]

The following is inspired by an idea of Benguria, Brézis, and Lieb [2]. We choose \( \zeta_0 \in C_0^\infty \) the same as in Benguria, Brézis, and Lieb [2]. It is a spherically symmetric function such that
supp(ζ₀) ⊂ B₂(0) \ B₁(0). Set ζ_n(x) = ζ_0(x/n). By (56) we have,

\[ \int_{\mathbb{R}^3} dx \, \zeta_n^2(x) \left( 8(\sqrt{p_n^0(x)} + 1) - \frac{6\lambda F'(p_n)(x)\Delta F(p_n)(x)}{p_n^0(x)} \right) - \sum_{k=1}^K \frac{8\alpha \zeta_k}{|x - R_k|} + \frac{8\alpha \zeta}{3\pi^2} \int_{\mathbb{R}^3} dy \, \frac{\zeta_n^2(y)}{|x - y|} = 0. \]  
(57)

Integrating by parts and using the Schwarz inequality, we have

\[ \int_{\mathbb{R}^3} dx \, \zeta_n^2 \frac{F'(p_n)\Delta F(p_n)}{p_n^0} = \int_{\mathbb{R}^3} dx \left( 2\zeta_n \nabla \zeta_n \frac{F'(p_n)}{p_n^0} + \zeta_n^2 \frac{F'(p_n)}{p_n^0} \nabla p_n \right) \frac{F'(p_n)}{p_n^0} \nabla p_n \]
\[ \leq \frac{1}{\epsilon} \int_{\mathbb{R}^3} dx \, |\nabla \zeta_n|^2 + \frac{1}{\epsilon} \int_{\mathbb{R}^3} dx \left( \epsilon \frac{F^2(p_n)}{p_n^0} \right)^2 
\]
\[ + \left( \frac{F'(p_n)}{p_n^0} \right)' \frac{F'(p_n)}{p_n^0} \zeta_n^2 |\nabla p_n|^2. \]
(58)

Using the definition of F(p_n), we get

\[ \left( \frac{F'(p_n)}{p_n^0} \right)' = - \frac{(2p_n^0 + 3)\sqrt{p_n^0 + 1} + 4(2p_n^0 + 1)p_n \arcsin(p_n)}{2p_n^0(p_n^0 + 1)^2\sqrt{p_n^0 + 1} + 2p_n \arcsin(p_n)} < 0. \]
(59)

Define

\[ g(s) := - \left( \frac{F'(s)}{F^2(s)} \right)' \frac{F'(s)}{F^2(s)} > 0 g(s) > 0. \]
(60)

We easily get g(0+) = 3/2 and lim s→∞ g(s) = ∞. So c₂ := min \{s g(s) : s > 0\} > 0. Choose ε = c₂. Then

\[ \int_{\mathbb{R}^3} dx \, \zeta_n^2 \frac{F'(p_n)\Delta F(p_n)}{p_n^0} \leq \frac{1}{c_2} \int_{\mathbb{R}^3} dx \, |\nabla \zeta_n|^2 \leq Cn. \]
(61)

Next, we compute

\[ \int_{\mathbb{R}^3} dx \, \zeta_n^2 \sqrt{p_n^0 + 1 - 1} < \int_{\mathbb{R}^3} dx \, \zeta_n^2 p_n \leq c_0 n^2, \]
(62)

where c_0 → 0 as n → ∞. The last inequality is proved by Benguria, Brézis, and Lieb [2]. About the external potential term, since ζ_n(x) = 0 for |x| < n, we have

\[ \int_{\mathbb{R}^3} dx \, \zeta_n^2(x) \sum_{k=1}^K 8\alpha \zeta_k \frac{1}{|x - R_k|} = \int_{\mathbb{R}^3} dx \, \zeta_n^2(x) \sum_{k=1}^K 8\alpha \zeta_k \left( \frac{1}{|x|} + \frac{|x| - |x - R_k|}{|x||x - R_k|} \right) 
\]
\[ \geq \int_{\mathbb{R}^3} dx \, \zeta_n^2(x) \sum_{k=1}^K 8\alpha \zeta_k \left( \frac{1}{|x|} - \frac{\max \{|R_k|\}}{|x|(|n - \max \{|R_k|\})} \right) 
\]
\[ \geq \left( 1 - \frac{c_0}{n} \right) \frac{8\alpha \zeta}{n} \int_{\mathbb{R}^3} dx \, \zeta_n^2(x) \frac{1}{|x|} \]
(63)
for large $n$. We now address the remaining term: since $\zeta_n$ is spherically symmetric, by a result of Lieb and Simon ([23], equation (35)) we have

$$\int_{\mathbb{R}^3} dx \, \zeta^2_n(x) \frac{8 \alpha \omega}{3 \pi^2} \int_{\mathbb{R}^3} dy \, \frac{p^2_n(y)}{|x - y|} = \int_{\mathbb{R}^3} dx \, \zeta^2_n(x) \frac{8 \alpha \omega}{3 \pi^2} \int_{\mathbb{R}^3} dy \, \frac{p^2_n(y)}{|x - y|}$$

$$= \int_{\mathbb{R}^3} dx \, \zeta^2_n(x) \frac{8 \alpha \omega}{3 \pi^2} \int_{\mathbb{R}^3} dy \, \frac{p^2_n(y)}{\max(|x|, |y|)}$$

$$\leq 8 \alpha \omega N \int_{\mathbb{R}^3} dx \, \frac{\zeta^2_n(x)}{|x|}, \tag{64}$$

where $[\varphi]$ denotes the spherical average of $\varphi$, i.e.,

$$[\varphi](x) = \frac{1}{4\pi} \int_{\mathbb{S}^2} d\Omega \, \varphi(|x|\Omega).$$

Thus, for large $n$, we find

$$\int_{\mathbb{R}^3} dx \, \zeta^2_n(x) \left( - \sum_{k=1}^K \frac{8 \alpha \omega Z_k}{|x - R_k|} + \frac{8 \alpha \omega}{3 \pi^2} \int_{\mathbb{R}^3} dy \, \frac{p^2_n(y)}{|x - y|} \right) \leq c(N - Z)n^2 + cn. \tag{65}$$

Combining (57), (61), (62), and (65), we find

$$\epsilon_n n^2 + Cn + c(N - Z)n^2 \geq 0. \tag{66}$$

As $n \to \infty$, we have that $Z \leq N$ which contradicts the assumption that $N < Z$. \hfill $\square$

5. Proof of the upper bound on the maximal ionization

**Proof of $N \leq \text{const} Z$.** It will be convenient to express the TFW functional in terms of

$$\chi := F \circ p \tag{67}$$

which is guided by the idea to make the dominating term in the energy simple. Obviously $F$ is strictly monotone and $F(\mathbb{R}_+) = \mathbb{R}_+$. We get

$$\mathcal{E}^{\text{TFW}}(\chi) := \mathcal{E}^{\text{TFW}}(F^{-1} \circ \chi) = \frac{3 \lambda}{8 \pi^2} \int_{\mathbb{R}^3} dx \, |\nabla \chi(x)|^2 + \frac{1}{8 \pi^2} \int_{\mathbb{R}^3} dx \, T^{\text{TF}}(F^{-1} \circ \chi(x))$$

$$- \sum_{k=1}^K \frac{\alpha \omega Z_k}{3 \pi^2} \int_{\mathbb{R}^3} dx \, \frac{(F^{-1}(\chi(x)))^3}{|x - R_k|} + \frac{\alpha \omega}{9 \pi^2} D_{\text{TF}}[(F^{-1} \circ \chi)^3] + \sum_{l \leq k < j \leq k} \frac{\alpha \omega Z_k Z_l}{|R_k - R_l|}. \tag{68}$$

Suppose that $\chi$ minimizes the TFW functional on $F(P_\delta)$. Then it satisfies

$$- \frac{3 \lambda}{4 \pi^2} \Delta \chi + \frac{1}{8 \pi^2} T'(F^{-1}(\chi))(F^{-1})' \chi$$

$$- \sum_{k=1}^K \frac{Z_k \alpha \omega}{\pi^2} \frac{(F^{-1}(\chi)(F^{-1})(\chi))^2}{|x - R_k|} + \frac{\alpha \omega}{3 \pi^2} (F^{-1})' \chi(F^{-1})(\chi) \int_{\mathbb{R}^3} dy \, \frac{(F^{-1}(\chi(y)))^3}{|x - y|} = 0, \tag{69}$$

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Following the spirit of Lieb [20], we multiply by $\chi/\phi(x)$ and integrate. The function $\phi$ is defined as
$$\phi(x) := \sum_{k=1}^{K} \frac{R_k}{|x - R_k|}. \quad (70)$$

The coefficients $R_k > 0$ will be given later. Due to our transform the Weizsäcker term becomes easy. We can follow Lieb’s argument [[20], equation (3.17)] step by step to see that it is positive.

Since $F$ is the antiderivative of a positive expression, $F'$ is positive and thus also the derivative of $F^{-1}$. Therefore
$$\int_{\mathbb{R}} dx \frac{\chi(x)}{\phi(x)} F^{-1}(\chi(x))(F^{-1})'(\chi(x)) > 0$$
when $\chi$ does not vanish almost everywhere.

Thus we have the inequality
$$-\sum_{k=1}^{K} Z_k \int_{\mathbb{R}} dx \frac{\chi(x)}{\phi(x)|x - R_k|} (F^{-1})'(\chi(x))(F^{-1}(\chi(x))^2 + \frac{1}{3\pi^2} \int_{\mathbb{R}} dx \int_{\mathbb{R}} dy \frac{\chi(x)(F^{-1})'(\chi(x))(F^{-1}(\chi(y)))^2}{\phi(x)|x - y|} < 0 \quad (71)$$
where we assumed that $\chi$ is not vanishing almost everywhere, which we may, since otherwise the claim is trivial. Rewriting this in $p$ it becomes
$$-3\pi^2 \sum_{k=1}^{K} Z_k \int_{\mathbb{R}} dx \frac{F(p(x))/F'(p(x))p(x)^2}{\phi(x)|x - R_k|} + \int_{\mathbb{R}} dx \int_{\mathbb{R}} dy \frac{F(p(x))/F'(p(x))p(x)^2p(y)^3}{\phi(x)|x - y|} < 0. \quad (72)$$

We now analyze the minimum $a$ and maximum $b$ of the function $H$ (see (15) and (16)). That $b = 1$ is easily seen from the fact, that $f'(t) > 0$ for all $t > 0$ which implies that $F(t) := \int_{0}^{t} dx \ f(s) \leq f(t)$. That $a > 0$ follows from the bounds given in lemma 3 of appendix B. Then (72) is equivalent to
$$-3\pi^2 \sum_{k=1}^{K} Z_k \int_{\mathbb{R}} dx \frac{H(x)p(x)^3}{\phi(x)|x - R_k|} + \int_{\mathbb{R}} dx \int_{\mathbb{R}} dy \frac{H(x)p(x)^3p(y)^3}{\phi(x)|x - y|} < 0. \quad (73)$$

This and symmetrizing the second integrand in $x$ allows us to turn (72) into two new inequalities
$$\frac{a}{2} \int_{\mathbb{R}} dx \int_{\mathbb{R}} dy \frac{\phi(x)^{-1} + \phi(y)^{-1}}{|x - y|} p(x)^3p(y)^3 < 3\pi^2 \sum_{k=1}^{K} Z_k \int_{\mathbb{R}} dx \ g_k(x)H(x)p(x)^3 \quad (74)$$
and
$$\frac{1}{2} \int_{\mathbb{R}} dx \int_{\mathbb{R}} dy \frac{\phi(x)^{-1} + \phi(y)^{-1}}{|x - y|}\ H(x)p(x)^3H(y)p(y)^3 < 3\pi^2 \sum_{k=1}^{K} Z_k \int_{\mathbb{R}} dx \ g_k(x)H(x)p(x)^3, \quad (75)$$
where \( g_k(x) := (\phi(x)|x - R_k|)^{-1} \). Following an idea of Baumgartner [1] and using the triangular inequality, we have

\[
\frac{\phi(x)^{-1} + \phi(y)^{-1}}{|x - y|} = \sum_{k=1}^{K} \kappa_k \frac{|x - R_k| + |y - R_k|}{|x - y|} g_k(x) g_k(y) \geq \sum_{k=1}^{K} \kappa_k g_k(x) g_k(y).
\]

(76)

Therefore, applying (76) on the left side of (74) and (75) yields

\[
\frac{a}{2} \sum_{k=1}^{K} \kappa_k \left( \int_{\mathbb{R}^3} dx \ g_k(x)p(x)^3 \right)^2 < 3 \pi^2 \sum_{k=1}^{K} Z_k \int_{\mathbb{R}^3} dx \ g_k(x)H(x)p(x)^3, \]

(77)

\[
\frac{1}{2} \sum_{k=1}^{K} \kappa_k \left( \int_{\mathbb{R}^3} dx \ g_k(x)H(x)p(x)^3 \right)^2 < 3 \pi^2 \sum_{k=1}^{K} Z_k \int_{\mathbb{R}^3} dx \ g_k(x)H(x)p(x)^3.
\]

(78)

Adding the two inequalities, we have

\[
6 \pi^2 \sum_{k=1}^{K} Z_k \int_{\mathbb{R}^3} dx \ \mathbf{g}_k(x)H(x)p(x)^3
\]

\[
\geq \sum_{k=1}^{K} \kappa_k \left( \frac{a}{2} \left( \int_{\mathbb{R}^3} dx \ g_k(x)p(x)^3 \right)^2 + \frac{1}{2} \left( \int_{\mathbb{R}^3} dx \ g_k(x)H(x)p(x)^3 \right)^2 \right)
\]

\[
\geq \sum_{k=1}^{K} \kappa_k \sqrt{a} \left( \int_{\mathbb{R}^3} dx \ g_k(x)p(x)^3 \right) \left( \int_{\mathbb{R}^3} dx \ g_k(x)H(x)p(x)^3 \right).
\]

(79)

This is equivalent to

\[
\left( \sum_{k=1}^{K} \int_{\mathbb{R}^3} dx \ g_k(x)H(x)p(x)^3 \right) \left( 6 \pi^2 Z_k - \sqrt{a} \kappa_k \int_{\mathbb{R}^3} dx \ g_k(x)p(x)^3 \right) > 0.
\]

(80)

Following Lieb’s [20] setting, let

\[
\delta_k := \kappa_k \frac{3 \pi^2 N}{\sqrt{a}}, \quad \nu_k := Z_k / Z_k.
\]

(81)

Note that

\[
\sum_{k=1}^{K} \delta_k = \sum_{k=1}^{K} \nu_k = 1.
\]

(82)

It is proved by Lieb [[20], appendix B] that we can choose \( \kappa_k \) such that

\[
\delta_k = \nu_k, \quad k = 1, \ldots, K.
\]

(83)

Then the left-hand side of (80) becomes

\[
3 \pi^2 (2Z - \sqrt{a}N) \sum_{k=1}^{K} \int_{\mathbb{R}^3} dx \ g_k(x)H(x)p(x)^3 \delta_k > 0.
\]

(84)
The sum is positive, so this yields
\[ N < \frac{2}{\sqrt{a}} Z \]  
(85)
or, numerically \( N < 2.557 \times 10^7 Z \). Recall that by definition \( a := \inf H(\mathbb{R}_+) \) (see (15) and the line below) and thus depends only on \( f \).

\[ \square \]

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Appendix A. On the semiclassical nature of the Thomas–Fermi term

Note that the Thomas–Fermi \( T^{TF} \) can be rewritten to emphasize its semiclassical nature
\[ T^{TF}[p] = 2 \int_{\mathbb{R}^3} dx \int_{|\xi| < p(x)} \frac{d\xi}{(2\pi)^3} (\sqrt{|\xi|^2 + 1} - 1). \]  
(86)
Writing it this way is not only mere curiosity but also shows the convexity of \( T^{TF} \) and the bound
\[ \frac{1}{4\pi^2} \int_{\mathbb{R}^3} dx \rho(x)^{4/3} \geq T^{TF}(\sqrt{3\pi^2} \rho) \geq \frac{1}{4\pi^2} \int_{\mathbb{R}^3} dx \rho(x)^{4/3} \rho \rho \rho \rho. \]  
(87)
This also allows to read off its derivative:
\[ (dT^{TF})(\rho)(\eta) = \frac{1}{\pi^2} \int_{\mathbb{R}^3} dx \rho(x)^2 (\sqrt{\rho(x)^2 + 1} - 1) \eta(x) \]  
(88)
with \( \eta \in L^4(\mathbb{R}^3) \). Obviously, \((dT^{TF})(\rho)\) can be identified with an element in \( L^{4/3}(\mathbb{R}^3) \).

Writing the TF functional in \( \rho \) yields
\[ (dT^{TF} \circ \sqrt{3\pi^2})\rho)(\eta) = \int_{\mathbb{R}^3} dx (\sqrt{3\pi^2} \rho(x)^{2/3} + 1 - 1) \eta(x). \]  
(89)
for \( \eta \in L^{4/3}(\mathbb{R}^3) \). Obviously this derivative can be identified with an element in \( L^4(\mathbb{R}^3) \).

Appendix B. Bound on the function \( F \), its derivative, and the Thomas–Fermi energy

Lemma 3. For all \( s, t > 0 \)
\[ F(s) > \tilde{F}(s) := s \sqrt{\text{arsinh}(s)}/2, \]  
(90)
\[ f(s) > \tilde{f}(s) := \sqrt{\text{arsinh}(s)}, \]  
(91)
\[ T^{TF}(s) > \tilde{T}^{TF}(s) := \frac{s^4}{1 + 1/(s/2)}, \]  
(92)
\[ F(s) > G(s) := \frac{s^{3/2}}{2\sqrt{1+s}}, \quad (93) \]
\[ G^{-1}(t) < 2t^{2/3} \sqrt[3]{1+t}. \quad (94) \]

Moreover, \( \tilde{f} \) is monotone increasing and concave.

**Proof.** The monotony and concavity of \( \tilde{f}(s) \) follows immediately by taking the derivatives
\[
\frac{d}{ds} \tilde{f}(s) = \frac{1}{2\sqrt{(s^2+1)}\text{arsinh}(s)} > 0
\]
and
\[
\frac{d^2}{ds^2} \tilde{f}(s) = -\frac{s}{2\sqrt{(s^2+1)^3}\text{arsinh}(s)} - \frac{1}{4(s^2+1)\text{arsinh}(s)^{3/2}} < 0.
\]

The inequality (91) is equivalent to
\[
\frac{s}{\sqrt{1+s^2}} + \frac{2s^2}{1+s^2} \text{arsinh}(s) > \text{arsinh}(s)
\]
or
\[
s\sqrt{1+s^2} > (1-s^2)\text{arsinh}(s).
\]
This, however, is clear, since \( s > \text{arsinh}(s) \).

The claim (90) follows from (91) and the concavity of \( \tilde{f}(s) \). We have
\[
F(t) = \int_0^t ds \ f(s) > \int_0^t ds \ \tilde{f}(s) = \int_0^{t/2} ds \ (\tilde{f}(s) + \tilde{f}(t-s))
\]
\[
> \int_0^{t/2} ds \ (\tilde{f}(0) + \tilde{f}(t)) = t\sqrt{\text{arsinh}(t)/2}.
\]

Next we treat (92). To this end we remark that \( tF(0) = \tilde{t}F(0) = 0 \). Moreover, the derivative of the difference is
\[
\frac{d}{ds} \left( tF(s) - \tilde{t}F(s) \right) = \frac{128 \left( (p + \frac{5}{2})^2 (p^2 + 1) - \left( \frac{4}{3}p^3 + \frac{57}{32}p^2 + \frac{5}{2}p + \frac{25}{16} \right) \sqrt{p^2 + 1} \right) p^2}{(4p + 5)^2 \sqrt{p^2 + 1}} > 0,
\]
which proves the result.

The inequality (93) is equivalent to the fact \( \text{arsinh}(s) > \frac{1}{1+s} \). Using the monotony of \( G(s) \) and \( G(2t^{2/3} \sqrt[3]{1+t}) = \frac{s^{3/2} \sqrt{1+s}}{2\sqrt{1+2s^{3/2} \sqrt{1+t}}} > t = G(G^{-1}(t)) \), the inequality (94) follows. \( \square \)

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