A Statistical Theory of Heavy Atoms: Energy and Excess Charge

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The purpose of this note is to give an elementary derivation of a lower bound on the relativistic Thomas–Fermi–Weizsäcker–Dirac functional of Thomas-Fermi type and to apply it to get an upper bound on the excess charge of this model.

1. Introduction

The description of heavy atoms suffered for a long time from the fact that the naive adaptation of Thomas–Fermi theory to the relativistic setting leads to a functional that is unbounded from below (see Gombas [6, §14] and [7, Chapter III, Section 16] for reviews). As late as 1987 Engel and Dreizler [3] solved this problem deriving a relativistic Thomas–Fermi–Weizsäcker–Dirac functional $\mathcal{E}_Z^{\mathrm{TFWD}}$ from quantum electrodynamics. For atoms of atomic number Z, electron density ρ, and velocity of light c, the functional, written in Hartree units, is

$$\mathcal{E}_Z^{\mathrm{TFWD}}(\rho) := \mathcal{T}^{\mathrm{W}}(\rho) + \mathcal{T}^{\mathrm{TF}}(\rho) - \mathcal{X}(\rho) + \mathcal{V}(\rho). \tag{1.1}$$

The first summand on the right is an inhomogeneity correction of the kinetic energy generalizing the Weizsäcker correction. Using the abbreviation $p(x) := (3\pi^2\rho(x))^{1/3}$,

$$\mathcal{T}^{\mathrm{W}}(\rho) := \int_{\mathbb{R}^3} \mathrm{d}x\, \frac{3\lambda}{\pi^2}\big(\nabla p(x)\big)^2 c\, f\big(p(x)/c\big)^2 \tag{1.2}$$

with $f(t)^2 := t(t^2+1)^{-1/2} + 2t^2(t^2+1)^{-1}\mathfrak{Arsin}(t)$ where $\mathfrak{Arsin}$ is the inverse function of the hyperbolic sine and $\lambda \in \mathbb{R}_+$ is given by the gradient expansion as $1/9$ but in the non-relativistic analogue sometimes taken as an adjustable parameter (Weizsäcker [10], Yonei and Tomishima [11], Lieb [8, 9]). The second summand is the relativistic generalization of the Thomas–Fermi kinetic energy. It is

$$\mathcal{T}^{\mathrm{TF}}(\rho) := \int_{\mathbb{R}^3} \mathrm{d}x\, \frac{c^5}{8\pi^2} T^{\mathrm{TF}}\big(\tfrac{p(x)}{c}\big) \tag{1.3}$$

with $T^{\mathrm{TF}}(t) := t(t^2+1)^{3/2} + t^3(t^2+1)^{1/2} - \mathfrak{Arsin}(t) - \frac{8}{3}t^3$. The third summand is a relativistic generalization of the exchange energy. It is

$$\mathcal{X}(\rho) := \int_{\mathbb{R}^3} \mathrm{d}x\, \frac{c^4}{\pi^3} X\big(\tfrac{p(x)}{c}\big) \tag{1.4}$$

with $X(t) := 2t^4 - 3[t(t^2+1)^{\frac{1}{2}} - \mathfrak{Arsin}(t)]^2$, and, eventually, the last summand is the potential energy, namely the sum of the electron-nucleus energy and the electron-electron energy. It is

$$\mathcal{V}(\rho) := -Z\int_{\mathbb{R}^3} \mathrm{d}x\, \rho(x)|x|^{-1} + \underbrace{\tfrac{1}{2}\int_{\mathbb{R}^3}\mathrm{d}x \int_{\mathbb{R}^3}\mathrm{d}y\, \rho(x)\rho(y)|x-y|^{-1}}_{=:\mathcal{D}[\rho]}. \tag{1.5}$$

We note that, as $c \to \infty$, all integrands of $\mathcal{E}_Z^{\mathrm{TFWD}}$ tend pointwise to the corresponding part of the non-relativistic Thomas–Fermi–Weizsäcker–Dirac functional

$$\mathcal{E}_Z^{\mathrm{nr}}(\rho) = \int_{\mathbb{R}^3} \mathrm{d}x\, \Big(\tfrac{\lambda}{2}|\nabla\sqrt{\rho}(x)|^2 + \tfrac{3}{10}\gamma_{\mathrm{TF}}\rho(x)^{\frac{5}{3}} - \tfrac{3}{4}\big(\tfrac{3}{\pi}\big)^{\frac{1}{3}}\rho(x)^{\frac{4}{3}} - \tfrac{Z}{|x|}\rho(x)\Big) + \mathcal{D}[\rho] \tag{1.6}$$

with $\gamma_{\mathrm{TF}} := (3\pi^2)^{\frac{2}{3}}$ suggesting that we might expect a lower bound of Thomas–Fermi type when c is large. We will prove in Section 2 that this is indeed true. The bound will allow us to implement the method of [4] in the present context and give an improved bound on atomic excess charges. This is carried through in Section 3.

2. Bound on the Energy

2.1. *The Domain of* $\mathcal{E}_Z^{\mathrm{TFWD}}$

First we discuss the domain of the functional. To this end, we write $F(t) := \int_0^t f(s)\,\mathrm{d}s$ for the antiderivative of f. Then

$$\mathcal{T}^{\mathrm{W}}(\rho) = \frac{3\lambda c^3}{8\pi^2}\int_{\mathbb{R}^3}\mathrm{d}x\,\big|\nabla(F\circ(p/c)(x))\big|^2. \tag{2.1}$$

This allows to define $\mathcal{E}_Z^{\mathrm{TFWD}}$ on

$$P := \{\rho\in L^{\frac{4}{3}}(\mathbb{R}^3)|\rho\geq 0,\ \mathcal{D}[\rho]<\infty, F\circ p\in D^1(\mathbb{R}^3)\}. \tag{2.2}$$

2.2. *Lower Bound*

We turn to the lower bound itself and address the parts separately.

2.2.1. *The Weizsäcker Energy*

Since $F(t)\geq t\sqrt{\mathfrak{Arsin}(t)}/2$ (see [2, Formula (90)]), Hardy's inequality gives the lower bound

$$\begin{aligned}\mathcal{T}^{\mathrm{W}}(\rho) &\geq \frac{3\lambda c}{2^7\pi^2}\int_{\mathbb{R}^3}\mathrm{d}x\,\frac{p(x)^2\mathfrak{Arsin}(p(x)/c)}{|x|^2}\\ &= \frac{3^{\frac{5}{3}}\lambda c}{2^7\pi^{\frac{2}{3}}}\underbrace{\int_{\mathbb{R}^3}\mathrm{d}x\,\frac{\rho(x)^{\frac{2}{3}}\mathfrak{Arsin}\left(\frac{p(x)}{c}\right)}{|x|^2}}_{=:\mathcal{H}(\rho)}.\end{aligned} \tag{2.3}$$

2.2.2. *The Potential Energy*

Pick a density $\sigma\in P$ of finite mass and set $\varphi_\sigma := Z|\cdot|^{-1} - \sigma * |\cdot|^{-1}$. Since σ is nonnegative, we have $\varphi_\sigma(x)\leq Z/|x|$. Then

$$\begin{aligned}\mathcal{V}(\rho) &= -\int_{\mathbb{R}^3}\mathrm{d}x\,\varphi_\sigma(x)\rho(x) - 2\mathcal{D}(\sigma,\rho) + \mathcal{D}[\rho]\\ &\geq -\int_{\mathbb{R}^3}\mathrm{d}x\,\varphi_\sigma(x)\rho(x) - \mathcal{D}[\sigma].\end{aligned} \tag{2.4}$$

Splitting the integrals at s, using (2.4), and Schwarz's inequality yields

$$\begin{aligned}\mathcal{V}(\rho) \geq &-\int_{p(x)/c<s} \mathrm{d}x\, \varphi_\sigma(x)\rho(x) \\ &- Z\int_{p(x)/c\geq s} \mathrm{d}x\, \frac{\rho(x)^{\frac{1}{3}}}{|x|} \mathfrak{Arsin}\left(\tfrac{p(x)}{c}\right)^{\frac{1}{2}} \frac{\rho(x)^{\frac{2}{3}}}{\mathfrak{Arsin}\left(\frac{p(x)}{c}\right)^{\frac{1}{2}}} - \mathcal{D}[\sigma] \\ \geq &-\frac{Z}{\mathfrak{Arsin}(s)^{\frac{1}{2}}}\mathcal{H}(\rho)^{\frac{1}{2}}\mathcal{T}_>(\rho)^{\frac{1}{2}} - \int_{p(x)/c<s}\mathrm{d}x\, \varphi_\sigma(x)\rho(x) - \mathcal{D}[\sigma] \quad (2.5)\end{aligned}$$

with $\mathcal{T}_>(\rho) := \int_{p(x)/c>s} \mathrm{d}x\, \rho(x)^{\frac{4}{3}}$.

2.2.3. *The Thomas–Fermi Term*

First, we note that

$$\mathbb{R}_+ \to \mathbb{R}_+,\ t \mapsto T^{\mathrm{TF}}(t)/t^5, \tag{2.6}$$

is strictly monotone decreasing from 4/5 to 0 and

$$\mathbb{R}_+ \to \mathbb{R}_+,\ t \mapsto T^{\mathrm{TF}}(t)/t^4, \tag{2.7}$$

is strictly increasing from 0 to 2. Thus

$$\begin{aligned}\mathcal{T}^{\mathrm{TF}}(\rho) &= \int_{p(x)/c<s}\mathrm{d}x\, \frac{c^5}{8\pi^2}T^{\mathrm{TF}}\left(\tfrac{p(x)}{c}\right) + \int_{p(x)/c\geq s}\mathrm{d}x\, \frac{c^5}{8\pi^2}T^{\mathrm{TF}}\left(\tfrac{p(x)}{c}\right) \\ &\geq \int_{p(x)/c<s}\mathrm{d}x\, \frac{3}{10}\frac{5T^{\mathrm{TF}}(s)}{4s^5}\gamma_{\mathrm{TF}}\rho(x)^{\frac{5}{3}} \\ &\quad + \int_{p(x)/c\geq s}\mathrm{d}x\, \frac{T^{\mathrm{TF}}(s)}{s^4}\frac{3}{8}(3\pi^2)^{\frac{1}{3}}c\rho(x)^{\frac{4}{3}} \\ &= \frac{3}{10}\frac{5T^{\mathrm{TF}}(s)}{4s^5}\gamma_{\mathrm{TF}}\int_{p(x)/c<s}\mathrm{d}x\, \rho(x)^{\frac{5}{3}} + \frac{3}{8}\frac{T^{\mathrm{TF}}(s)}{s^4}\gamma_{\mathrm{TF}}{}^{\frac{1}{2}}c\mathcal{T}_>(\rho). \quad (2.8)\end{aligned}$$

2.2.4. *Exchange Energy*

Since X is bounded from above and $X(t) = O(t^4)$ at $t = 0$, we have that for every $\alpha \in [0, 4]$ there is a ξ_0 such that $X(t) \leq \xi_0 t^\alpha$. We pick $\alpha = 3$, in which case $\xi_0 \approx 1.15$. Thus

$$\mathcal{X}(\rho) \leq \frac{c\xi_0}{4\pi}N = \xi c N \tag{2.9}$$

with $\xi := \xi_0/(4\pi) \approx 0.0914$.

2.2.5. *The Total Energy*

Adding everything up yields

$$\begin{aligned}\mathcal{E}_Z^{\mathrm{TFWD}}(\rho) \geq & \frac{3^{\frac{5}{3}}\lambda c}{2^7\pi^{\frac{2}{3}}}\mathcal{H}(\rho) + \frac{3}{8}\frac{T^{\mathrm{TF}}(s)}{s^4}\gamma_{\mathrm{TF}}{}^{\frac{1}{2}}c\mathcal{T}_>(\rho) \\ & - \frac{Z}{\mathfrak{Arsin}(s)^{\frac{1}{2}}}\mathcal{H}(\rho)^{\frac{1}{2}}\mathcal{T}_>(\rho)^{\frac{1}{2}} \\ & + \int_{p(x)/c<s}\mathrm{d}x\left(\frac{3}{10}\underbrace{5\frac{T^{\mathrm{TF}}(s)}{4s^5}\gamma_{\mathrm{TF}}}_{=:\gamma_e(s)}\rho(x)^{\frac{5}{3}} - \varphi_\sigma(x)\rho(x)\right) \\ & - \mathcal{D}[\sigma] - \xi c N. \end{aligned} \tag{2.10}$$

We pick $s \in \mathbb{R}_+$ such that the sum of the first three summands of (2.10) is a complete square, i.e., fulfilling

$$\sqrt{\frac{3^{\frac{5}{3}}}{2^7\pi^{\frac{2}{3}}}\frac{3T^{\mathrm{TF}}(s)(3\pi^2)^{\frac{1}{3}}}{8s^4}} = \frac{Z}{c\sqrt{\lambda}}\frac{1}{2\mathfrak{Arsin}(s)^{\frac{1}{2}}}. \tag{2.11}$$

The solution is uniquely determined, since $T^{\mathrm{TF}}(s)/s^4$ is strictly monotone increasing from 0 to 2 and $\mathfrak{Arsin}(s)$ is also monotone increasing from 0 to ∞. Call the corresponding s s_0. Obviously, s_0 depends only on $\kappa := Z/(c\sqrt{\lambda})$ and is strictly monotone increasing from 0 to ∞.

Eventually we pick $\sigma(x) := \rho(x)\theta\big(sc - p(x)\big)$. Summing the first three terms of the second line of (2.10) yields the Thomas–Fermi functional with Thomas–Fermi constant $\gamma_e(s_0)$ evaluated at σ. Minimizing this functional and scaling in γ yields

$$\mathcal{E}_Z^{\mathrm{TFWD}}(\rho) \geq -\frac{4s_0^5}{5T^{\mathrm{TF}}(s_0)}e^{\mathrm{TF}}Z^{\frac{7}{3}} - \xi cN \tag{2.12}$$

where $-e^{\mathrm{TF}}$ is the Thomas–Fermi energy of hydrogen (with the physical value of the Thomas–Fermi constant, namely γ_{TF}).

The function s_0 tends exponentially to ∞ as $\kappa \to \infty$. Thus (2.12) is merely an exponential lower bound for large Z and fixed λ and c. However, if we fix $\kappa \in \mathbb{R}_+$, then we have a Thomas–Fermi type lower bound with a correction term linear in cN. In conclusion we have

Theorem 1: *For given $c, \lambda, Z \in \mathbb{R}_+$, set $\kappa := Z/(c\sqrt{\lambda})$. Define $s_0 : \mathbb{R}_+ \to \mathbb{R}_+$ by (2.11), set $\xi := \max\{X(t)/t^3 | t \in \mathbb{R}_+\}/(4\pi)$, and write $-e^{\mathrm{TF}}$ for the Thomas–Fermi energy of hydrogen. Then, for all $\rho \in P$ with $\int_{\mathbb{R}^3}\mathrm{d}x\,\rho(x) = N$,*

$$\mathcal{E}_Z^{\mathrm{TFWD}}(\rho) \geq -\frac{4s_0(\kappa)^5}{5T^{\mathrm{TF}}\big(s_0(\kappa)\big)}e^{\mathrm{TF}}Z^{\frac{7}{3}} - \xi cN. \tag{2.13}$$

Moreover, s_0 is strictly monotone increasing with $s_0(0) = 0$ and $s_0(\kappa) \to \infty$ as $\kappa \to \infty$.

3. Application on the Excess Charge Problem

In this section we will show that the bound (2.12) allows for an adaptation of the ideas of [4, 5] and show a bound on the excess charge of the relativistic Thomas-Fermi-Weizsäcker-Dirac atom which complements the bound obtained in [2] in the absence of the exchange term.

We define a monotone increasing function $\alpha : \mathbb{R} \to [0, \pi/2]$ by

$$\alpha(s) := \begin{cases} 0 & s \leq 0 \\ \frac{\pi}{2}s & s \in (0,1) \\ \frac{\pi}{2} & s \geq 1 \end{cases} . \tag{3.1}$$

We introduce two localization functions

$$R := \sin \circ \alpha \text{ and } L := \cos \circ \alpha, \tag{3.2}$$

and corresponding localization functions U and O on $\mathbb{R}^3$ defined by

$$U(x) := L\left(\frac{\omega \cdot x - l}{s}\right),\ O(x) := R\left(\frac{\omega \cdot x - l}{s}\right) \tag{3.3}$$

with the parameters $\omega \in \mathbb{S}^2$, $l \in \mathbb{R}_+$, and $s \in (0, \infty)$. For later use, we write $A := \mathrm{supp}(\nabla U)$ for the support of the gradient of U and O.

Assume ρ_N, with associated $p_N := (3\pi^2\rho_N)^{\frac{1}{3}}$, is a minimizer of $\mathcal{E}_Z^{\mathrm{TFWD}}$ under the constraint

$$\int_{\mathbb{R}^3} \mathrm{d}x\, \rho(x) = N. \tag{3.4}$$

In abuse of notation, we sometimes write the occurring energy functionals instead of depending on ρ as depending on p, i.e., p instead of $p^3/(3\pi^2)$.

Our starting point is the binding condition following directly from the variational principle by pushing the O-part away from the U-part

$$\mathcal{E}_Z^{\mathrm{TFWD}}(Up_N) + \mathcal{E}_0^{\mathrm{TFWD}}(Op_N) - \mathcal{E}_Z^{\mathrm{TFWD}}(p_N) \geq 0 \tag{3.5}$$

which is true, since

$$\begin{aligned} &\frac{1}{3\pi^2}\int_{\mathbb{R}^3} \mathrm{d}x\, \big(U(x)^3 + O(x)^3\big)p_N(x)^3 \\ \leq &\frac{1}{3\pi^2}\int_{\mathbb{R}^3} \mathrm{d}x\, \big(U(x)^2 + O(x)^2\big)p_N(x)^3 = \int_{\mathbb{R}^3} \mathrm{d}x\, \rho_N(x) = N \end{aligned} \tag{3.6}$$

and the infima under the constraint (3.4) and the constraint

$$3\pi^2 \int_{\mathbb{R}^3} \mathrm{d}x\, p(x)^3 = \int_{\mathbb{R}^3} \mathrm{d}x\, \rho(x) \leq N \tag{3.7}$$

agree by [1, Section 3.5]. The corresponding argument, namely pushing the charge difference between N and the charge of the minimizer to infinity, is a standard argument and works also when the Dirac term is included.

We also have by the product rule

$$\begin{aligned}
&\int_{\mathbb{R}^3} \mathrm{d}x \left[|\nabla(Up)(x)|^2 f(Up(x)/c)^2 + |\nabla(Op)(x)|^2 f(Op(x)/c)^2\right] \\
\leq &\int_{\mathbb{R}^3} \mathrm{d}x \left[|\nabla(Up)(x)|^2 + |\nabla(Op)(x)|^2\right] f(p(x)/c)^2 \\
= &\int_{\mathbb{R}^3} \mathrm{d}x \, |\nabla p(x)|^2 f(p(x)/c)^2 \\
&+ \int_{\mathbb{R}^3} \mathrm{d}x \, p(x)^2 \left[|\nabla U(x)|^2 + |\nabla O(x)|^2\right] f(p(x)/c)^2 \\
= &\int_{\mathbb{R}^3} \mathrm{d}x \, |\nabla p(x)|^2 f(p(x)/c)^2 \\
&+ s^{-2} \int_{\mathbb{R}^3} \mathrm{d}x \, \alpha'\big((\omega \cdot x - l)/s\big)^2 p(x)^2 f\big(p(x)/c\big)^2,
\end{aligned} \tag{3.8}$$

since f is monotone increasing.

An elementary calculation shows that there is a constant μ such for all $t \in \mathbb{R}_+$

$$f(t)^2 \leq \mu t. \tag{3.9}$$

The optimal constant, namely $\max\{f(t)^2/t | t > 0\}$, is $\mu \approx 1.66$ achieved at $t \approx 1.45$.

For $\alpha \in \mathbb{R}_+$ and $x \in \mathbb{R}^3$ we claim

$$\int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} (\omega \cdot x - \alpha)_+ = \frac{|x|}{4} \left[\left(1 - \frac{\alpha}{|x|}\right)_+\right]^2 \tag{3.10}$$

(see [4] for a related formula). Since the left side is independent of the direction of x and equals $|x| \int_{\mathbb{S}^2} \mathrm{d}\omega \, (4\pi)^{-1} (\omega \cdot x/|x| - \alpha/|x|)$, it suffices to show (3.10) for $x = \mathfrak{e}_3$:

$$\begin{aligned}
&\int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} (\omega \cdot \mathfrak{e}_3 - \alpha)_+ = \tfrac{1}{2} \int_0^\pi \mathrm{d}\vartheta \, \sin\vartheta (\cos\vartheta - \alpha)_+ \\
= &\tfrac{1}{2} \int_{\min\{1,\alpha\}}^1 \mathrm{d}u \, (u - \alpha) = \tfrac{1}{4} [(1-\alpha)_+]^2.
\end{aligned} \tag{3.11}$$

We estimate the various parts of (3.5) separately. We begin with the Weizsäcker terms and get using (3.8) and (3.9)

$$
\begin{aligned}
&\mathcal{T}^{\mathrm{W}}(Up_N)+\mathcal{T}^{\mathrm{W}}(Op_N)-\mathcal{T}^{\mathrm{W}}(p_N)\\
&\leq \frac{3\lambda}{8\pi^2 s^2}\int_{0<\omega\cdot x-l<s}\mathrm{d}x\,\alpha'\big((\omega\cdot x-l)/s\big)^2 p_N(x)^2 cf\big(p_N(x)/c\big)^2\\
&=\frac{3\lambda}{32s^2}\int_{0<\omega\cdot x-l<s}\mathrm{d}x\,p_N(x)^2 cf\big(p_N(x)/c\big)^2\\
&\leq \frac{3\lambda\mu}{32s^2}\int_{0<\omega\cdot x-l<s}\mathrm{d}x\,p_N(x)^3=\frac{9\pi^2\lambda\mu}{32s^2}\int_{0<\omega\cdot x-l<s}\mathrm{d}x\,\rho_N(x).
\end{aligned}
\tag{3.12}
$$

Integration over $l\in\mathbb{R}_+$ and $\omega\in\mathbb{S}^2$ and using (3.10) yields

$$
\begin{aligned}
&\int_{\mathbb{S}^2}\frac{\mathrm{d}\omega}{4\pi}\int_{\mathbb{R}_+}\mathrm{d}l\,\big(\mathcal{T}^{\mathrm{W}}(Up_N)+\mathcal{T}^{\mathrm{W}}(Op_N)-\mathcal{T}^{\mathrm{W}}(p_N)\big)\\
&\leq\frac{9\pi^2\lambda\mu}{128s^2}\int_{\mathbb{S}^2}\frac{\mathrm{d}\omega}{\pi}\int_{\mathbb{R}^3}\mathrm{d}x\,\big(\omega\cdot x-(\omega\cdot x-s)_+\big)_+\rho_N(x)\\
&=\frac{9\pi^2\lambda\mu}{128s^2}\int_{\mathbb{S}^2}\frac{\mathrm{d}\omega}{\pi}\int_{\mathbb{R}^3}\mathrm{d}x\,\big[(\omega\cdot x)_+-(\omega\cdot x-s)_+\big]\rho_N(x)\\
&=\frac{9\pi^2\lambda\mu}{128s^2}\int_{\mathbb{R}^3}\mathrm{d}x\,|x|\left[1-\left(1-\frac{s}{|x|}\right)_+^2\right]\rho_N(x)\\
&=\frac{9\pi^2\lambda\mu}{128s^2}\left(\int_{s<|x|}\mathrm{d}x\left(2s-\frac{s^2}{|x|}\right)\rho_N(x)+\int_{s>|x|}\mathrm{d}x\,|x|\rho_N(x)\right)\\
&\leq\frac{3^2\pi^2\lambda\mu}{2^6}\frac{N}{s}.
\end{aligned}
\tag{3.13}
$$

Next we estimate the combined Thomas–Fermi exchange part of (3.5). To this end we introduce the functions a and b on $\mathbb{R}_+$ defined by

$$
\begin{aligned}
a(t):=&\frac{c^5}{8\pi^2}T^{\mathrm{TF}}(t)+\frac{c^4}{8\pi^3}3\big[t(t^2+1)^{\frac{1}{2}}-\mathfrak{Arsin}(t)\big]^2,\\
b(t):=&\frac{c^4}{8\pi^3}2t^4.
\end{aligned}
\tag{3.14}
$$

Pick now $f_1,\ldots,f_n\in\mathbb{R}_+$ with $f_1^2+\cdots+f_n^2=1$. Since $a,\ldots,a^{(iv)}$ are all positive, we have

$$a'''(f_i t)\leq a'''(t) \tag{3.15}$$

because $f_i\leq 1$. Since also $a(0)=a'(0)=a''(0)=a'''(0)$, integration of (3.15) yields successively $a''(f_\nu t)\leq f_\nu a''(t)$, $a'(f_\nu t)\leq f_\nu^2 a'(t)$, and $a(f_\nu t)\leq f_\nu^3 a(t)$. (See [1, Formula 3.135] for a similar argument for $T^{\mathrm{TF}}(t)$.)

Thus, we get

$$
\begin{aligned}
&\mathcal{T}^{\rm TF}(Up_N) - \mathcal{X}(Up_N) + \mathcal{T}^{\rm TF}(Op_N) - \mathcal{X}(Op_N) - \big(\mathcal{T}^{\rm TF}(p_N) - \mathcal{X}(p_N)\big)\\
&= \int_{\mathbb{R}^3} \mathrm{d}x \Big[a\big(U(x)\tfrac{p_N(x)}{c}\big) + a\big(O(x)\tfrac{p_N(x)}{c}\big) - a\big(\tfrac{p_N(x)}{c}\big)\\
&\qquad + b\big(\tfrac{p_N(x)}{c}\big) - b\big(U(x)\tfrac{p_N(x)}{c}\big) - b\big(O(x)\tfrac{p_N(x)}{c}\big)\Big]\\
&\le \int_{\mathbb{R}^3} \mathrm{d}x \Big[\big(U(x)^3 + O(x)^3 - 1\big) a\big(\tfrac{p_N(x)}{c}\big) - \big(U(x)^4 + O(x)^4 - 1\big) b\big(\tfrac{p_N(x)}{c}\big)\Big]\\
&\le \frac{1}{4} \underbrace{\max\left\{ \frac{(1-\cos(t)^4 - \sin(t)^4)^2}{1 - \cos(t)^3 - \sin(t)^3} \middle| t \in [0, \pi/2] \right\}}_{=(2+\sqrt{2})/4} \int_A \mathrm{d}x\, \frac{b\big(\frac{p_N(x)}{c}\big)^2}{a\big(\frac{p_N(x)}{c}\big)}\\
&\le \ \frac{2+\sqrt{2}}{2^5} \frac{c^3}{\pi^4} \int_A \mathrm{d}x\, \frac{\big(\frac{p_N(x)}{c}\big)^8}{T^{\rm TF}\big(\frac{p_N(x)}{c}\big)}.
\end{aligned}
\tag{3.16}
$$

Using (2.6) and (2.7) we get for any $S \in \mathbb{R}_+$

$$
\begin{aligned}
&\mathcal{T}^{\rm TF}(Up_N) - \mathcal{X}(Up_N) + \mathcal{T}^{\rm TF}(Op_N) - \mathcal{X}(Op_N) - \big(\mathcal{T}^{\rm TF}(p_N) - \mathcal{X}(p_N)\big)\\
&\le \frac{2+\sqrt{2}}{2^5\pi^4} \int_{A, p_N(x)/c < S} \mathrm{d}x\, \frac{S^5}{T^{\rm TF}(S)} p_N(x)^3\\
&\quad + \frac{2+\sqrt{2}}{2^5\pi^4} \int_{A, p_N(x)/c \ge S} \mathrm{d}x\, \frac{S^4}{cT^{\rm TF}(S)} p_N(x)^4\\
&\le \frac{(2+\sqrt{2})3}{2^5\pi^2} \frac{S^5}{T^{\rm TF}(S)} N + \frac{(2+\sqrt{2})3^{\frac{4}{3}}}{2^5 \pi^{\frac{4}{3}} c} \frac{S^4}{T^{\rm TF}(S)} \int_{\mathbb{R}^3} \mathrm{d}x\, \rho_N(x)^{\frac{4}{3}}.
\end{aligned}
\tag{3.17}
$$

The external potential part yields

$$
-Z \int_{\mathbb{R}^3} \mathrm{d}x\, \frac{\big(U(x)^3 - 1\big)\rho_N(x)}{|x|} \le Z \int_{\omega\cdot x - l > 0} \mathrm{d}x\, \frac{\rho_N(x)}{|x|}. \tag{3.18}
$$

Integration over l and averaging over the sphere yields

$$
\begin{aligned}
&- Z \int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} \int_{\mathbb{R}_+} \mathrm{d}l \int_{\mathbb{R}^3} \mathrm{d}x\, \frac{(U(x)^3 - 1)\rho_N(x)}{|x|}\\
&\le Z \int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} \int_{\mathbb{R}_+} \mathrm{d}l \int_{\omega\cdot x - l > 0} \mathrm{d}x\, \frac{\rho_N(x)}{|x|}\\
&= Z \int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} \int_{\mathbb{R}^3} \mathrm{d}x\, \frac{(\omega\cdot x)_+ \rho_N(x)}{|x|} = \frac{Z}{4} \int_{\mathbb{R}^3} \mathrm{d}x\, \rho_N(x) = \frac{Z}{4} N.
\end{aligned}
\tag{3.19}
$$

Finally, we address the electron-electron repulsion in (3.5). We have

$$\begin{aligned} W(l,\omega) := {} & D(U^3\rho_N, U^3\rho_N) + D(O^3\rho_N, O^3\rho_N) \\ & - D\big((U^2+O^2)\rho_N, (U^2+O^2)\rho_N\big) \\ \leq {} & -2D(U^2\rho_N, O^2\rho_N) \\ \leq {} & -\int_{\omega\cdot x - l<0} \mathrm{d}x \int_{\omega\cdot y - l > s} \mathrm{d}y\, \frac{\rho_N(x)\rho_N(y)}{|x-y|}. \end{aligned} \tag{3.20}$$

Integration in l and ω and using (3.10) yields

$$\begin{aligned} & \int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} \int_{\mathbb{R}_+} \mathrm{d}l W(l,\omega) \\ \leq {} & -\int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} \int_{\mathbb{R}_+} \mathrm{d}l \int_{\omega\cdot x-l<0} \mathrm{d}x \int_{\omega\cdot y - l>s} \mathrm{d}y\, \frac{\rho_N(x)\rho_N(y)}{|x-y|} \\ = {} & -\int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{8\pi} \int_{\mathbb{R}_+} \mathrm{d}l \int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y\, \big[\theta(l-\omega\cdot x)\theta(\omega\cdot y - s - l) \\ & \qquad + \theta(l-(-\omega\cdot y))\theta(-\omega\cdot x - s - l)\big] \frac{\rho_N(x)\rho_N(y)}{|x-y|} \\ = {} & -\int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{8\pi} \int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y\, \frac{(\omega\cdot(y-x)-s)_+\rho_N(x)\rho_N(y)}{|x-y|}. \end{aligned} \tag{3.21}$$

Thus, with (3.10),

$$\begin{aligned} & \int_{\mathbb{S}^2} \frac{\mathrm{d}\omega}{4\pi} \int_{\mathbb{R}_+} \mathrm{d}l\, W(l,\omega) \\ \leq {} & -\frac{1}{8} \int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y\, \rho_N(x)\rho_N(y) \left(1 - \frac{s}{|x-y|}\right)_+^2 \\ = & -\frac{N^2}{8} + \frac{1}{8} \int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y\, \rho_N(x)\rho_N(y) \left[1 - \left(1 - \frac{s}{|x-y|}\right)_+^2\right] \\ = & -\frac{N^2}{8} + \frac{1}{8} \int_{\mathbb{R}^3} \mathrm{d}x \int_{\mathbb{R}^3} \mathrm{d}y\, \rho_N(x)\rho_N(y) \\ & \qquad \times \left\{ \begin{array}{cc} 1 & \text{if } s \geq |x-y| \\ \frac{2s}{|x-y|} - \left(\frac{s}{|x-y|}\right)^2 & \text{if } s < |x-y| \end{array} \right\} \\ \leq & -\frac{N^2}{8} + \frac{s}{2}\mathcal{D}[\rho_N]. \end{aligned} \tag{3.22}$$

Inserting these estimates in (3.5) gives

$$\frac{3^2\pi^2\lambda\mu}{2^6}\frac{N}{s} + \frac{ZN}{4} - \frac{N^2}{8} + c_1(S)N + \frac{c_2(S)}{c}\int_{\mathbb{R}^3} \mathrm{d}x\, \rho_N(x)^{\frac{4}{3}} + \frac{s}{2}\mathcal{D}[\rho_N] \geq 0 \tag{3.23}$$

or

$$N \leq 2Z + \frac{3^2\pi^2\lambda\mu}{2^3 s} + 2^2 s\frac{\mathcal{D}[\rho_N]}{N} + 8c_1(S) + \frac{8c_2(S)}{cN}\int_{\mathbb{R}^3} \mathrm{d}x\, \rho_N(x)^{\frac{4}{3}} \tag{3.24}$$

and after optimization in s

$$N \leq 2Z + 3\pi\sqrt{2}\sqrt{\frac{\lambda\mu\mathcal{D}[\rho_N]}{N}} + 8c_1(S) + \frac{8c_2(S)}{cN}\int_{\mathbb{R}^3} \mathrm{d}x\, \rho_N(x)^{\frac{4}{3}}. \tag{3.25}$$

Now, we assume $\kappa = Z/(c\sqrt{\lambda})$ fixed and apply Theorem 1 with a factor 2 in front of the exchange term and Z replaced by $2Z$. This gives (2.13) but with the corresponding replacements, namely Z by $2Z$ and a factor 2 in front of ξcN. Therefore we get

$$\begin{aligned} 0 \geq \mathcal{E}_Z^{\mathrm{TFWD}}(\rho_N) &= \frac{1}{2}\mathcal{T}^{\mathrm{W}}(\rho_N) + \frac{1}{2}\mathcal{T}^{\mathrm{TF}}(\rho_n) + \frac{1}{2}\mathcal{D}[\rho_N] \\ &+ \frac{1}{2}\left(\mathcal{T}^{\mathrm{W}}(\rho_N) + \mathcal{T}^{\mathrm{TF}}(\rho_N) + \mathcal{D}[\rho_N] - \int_{\mathbb{R}^3}\mathrm{d}x\,\frac{Z\rho_N(x)}{2|x|} - 2\mathcal{X}(\rho_N)\right) \\ &\geq \frac{1}{2}\mathcal{T}^{\mathrm{W}}(\rho_N) + \frac{1}{2}\mathcal{T}^{\mathrm{TF}}(\rho_N) + \frac{1}{2}\mathcal{D}[\rho_N] - C_\kappa Z^{7/3} - \xi cN. \end{aligned} \tag{3.26}$$

Thus, all three terms, $\mathcal{T}^{\mathrm{W}}(\rho_N)$, $\mathcal{T}^{\mathrm{TF}}(\rho_N)$, and $\mathcal{D}(\rho_N)$ are bounded by a constant times $Z^{7/3} + cN$.

Now, $T^{\mathrm{TF}}(t) \geq 2t^4 - (8/3)t^3$. Thus

$$\begin{aligned} &\int_{\mathbb{R}^3}\mathrm{d}x\,\rho_N(x)^{\frac{4}{3}} = \frac{c^4}{(2\pi^2)^{\frac{4}{3}}}\int_{\mathbb{R}^3}\mathrm{d}x\left(\frac{p_N(x)}{c}\right)^4 \\ &\leq \left(\frac{2}{\pi}\right)^{\frac{2}{3}}\frac{1}{c}\mathcal{T}^{\mathrm{TF}}(\rho_N) + \frac{2}{3}\left(\frac{2}{\pi}\right)^{\frac{2}{3}} cN \leq D_\kappa(Z^{\frac{4}{3}}\lambda^{\frac{1}{2}} + N + cN) \end{aligned} \tag{3.27}$$

with a κ-dependent constant D_κ. Thus, (3.25) yields the following bound on the excess charge.

Theorem 2: *Assume that $\rho \in P$ with $\mathcal{E}_Z^{\mathrm{TFWD}}(\rho) = \inf \mathcal{E}_Z^{\mathrm{TFWD}}(P)$, set $N := \int_{\mathbb{R}^3}\rho(x)\,\mathrm{d}x$, and assume κ and λ positive and fixed. Then, for large Z,*

$$N \leq 2Z + O(Z^{\frac{2}{3}}). \tag{3.28}$$

This should be compared to the bound $N \leq 2.56Z$ of [2, Formula (18)] for the relativistic Thomas–Fermi–Weizsäcker functional without exchange, i.e., even with exchange term included we are led to an improved leading order. Note, however, it comes at a price, namely the ratio Z/c and λ is now fixed.

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References

1. Hongshuo Chen, *On the Excess Charge Problem in Relativistic Quantum Mechanics*, PhD thesis, Ludwig-Maximilians-Universität München, 2019.
2. Hongshuo Chen and Heinz Siedentop, "On the excess charge of a relativistic statistical model of molecules with an inhomogeneity correction", *J. Phys. A: Math. Theor.* **53**, 395201 (2020).
3. E. Engel and R. M. Dreizler, "Field-theoretical approach to a relativistic Thomas–Fermi–Dirac–Weizsäcker model", *Phys. Rev. A* **35**, 3607–3618 (1987).
4. Rupert L. Frank, Phan Thành Nam, and Hanne Van Den Bosch, "The ionization conjecture in Thomas–Fermi–Dirac–von Weizsäcker theory", *Commun. Pure Appl. Math.* **71**, 577–614 (2018).
5. Rupert L. Frank, Phan Thành Nam, and Hanne Van Den Bosch, "The maximal excess charge in Müller density-matrix-functional theory", *Ann. Henri Poincaré*, 19(9):2839–2867, 2018.
6. P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen*, first edition, Springer-Verlag, Wien, Austria, 1949.
7. P. Gombás, "Statistische Behandlung des Atoms", In S. Flügge, editor, *Handbuch der Physik. Atome II*, vol. 36, Springer-Verlag, Berlin, Germany 1956; pp. 109–231.
8. Elliott H. Lieb, "Analysis of the Thomas–Fermi–von Weizsäcker equation for an infinite atom without electron repulsion", *Comm. Math. Phys.* **85**, 15–25 (1982).
9. Elliott H. Lieb and David A. Liberman, *Numerical calculation of the Thomas–Fermi-von Weizsäcker function for an infinite atom without electron repulsion*, Technical Report LA-9186-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, USA, 1982.

10. C. F. v. Weizsäcker, "Zur Theorie der Kernmassen", *Z. Phys.* **96**, 431–458 (1935).
11. Katsumi Yonei and Yasuo Tomishima, "On the Weizsäcker correction to the Thomas–Fermi theory of the atom", *J. Phys. Soc. Japan* **20**, 1051–1057 (1965).