A STATISTICAL THEORY OF HEAVY ATOMS:
ENERGY AND EXCESS CHARGE

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Abstract. 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 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 $E_{TFWD}^Z$ from quantum electrodynamics. For atoms of atomic number $Z$ and electron density $\rho$ and velocity of light $c$ the functional, written in Hartree units, is

$$E_{TFWD}^Z(\rho) := T^W(\rho) + T^{TF}(\rho) - X(\rho) + V(\rho).$$

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

$$T^W(\rho) := \int_{\mathbb{R}^3} \frac{3\lambda}{8\pi^2} (\nabla p(x))^2 c f(p(x)/c)^2$$

with $f(t) := t(t^2 + 1)^{-\frac{3}{2}} + 2\lambda(t^2 + 1)^{-1}\text{arsin}(t)$ where $\text{arsin}$ 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 [9, 8]). The second summand is the relativistic generalization of the Thomas-Fermi kinetic energy. It is

$$T^{TF}(\rho) := \int_{\mathbb{R}^3} \frac{c^5}{8\pi^2} T^{TF}(\frac{p(x)}{c})$$

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

$$X(\rho) := \int_{\mathbb{R}^3} \frac{c^4}{8\pi^2} X(\frac{p(x)}{c})$$

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

$$V(\rho) := -Z \int_{\mathbb{R}^3} d\rho(x)|x|^{-1} + \frac{1}{2} \int_{\mathbb{R}^3} dx \int_{\mathbb{R}^3} dg(x) \rho(x)|x-y|^{-1} =: D[\rho].$$
We note that, as \( c \to \infty \), all integrands of \( E_{Z}^{\text{TFWD}} \) tend pointwise to the corresponding part of the non-relativistic Thomas-Fermi-Weizsäcker-Dirac functional

\[
E_{Z}^{\mu}(\rho) = \int_{R^3} dx \left( \frac{1}{2} |\nabla \sqrt{\rho}(x)|^2 + \frac{\gamma}{4} TF \rho(x) \frac{3}{9} \rho(x)^{1/3} - \frac{Z}{|x|} \rho(x) \right) + D[\rho]
\]

with \( \gamma_{TF} := (3\pi^2)^{3/2} \) suggesting that we might expect a lower bound of Thomas-Fermi type when \( c \) is large. We will prove in Section 2.2 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 \( E_{Z}^{\text{TFWD}} \). First we discuss the domain of the functional. To this end, we write \( F(t) := \int_{0}^{t} f(s) ds \) for the antiderivative of \( f \). Then

\[
T^{W}(\rho) = \frac{3\lambda c^2}{8\pi^2} \int_{R^3} dx |\nabla (F \circ (p/c))(x)|^2.
\]

This allows to define \( E_{Z}^{\text{TFWD}} \) on

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

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

2.2.1. The Weizsäcker Energy. Since \( F(t) \geq t \sqrt{\text{arsin}(t)} / 2 \) (see [2] Formula (90))), Hardy’s inequality gives the lower bound

\[
T^{W}(\rho) \geq \frac{3\lambda c}{2\pi^2} \int_{R^3} dx \frac{p(x)^2 \text{arsin}(p(x)/c)}{|x|^2} = \frac{3\lambda c}{2\pi^2} \int_{R^3} dx \frac{p(x)^2 \text{arsin}(\frac{p(x)}{c})}{|x|^2} =: \mathcal{H}(\rho).
\]

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

\[
\mathcal{V}(\rho) = -\int_{R^3} dx \varphi_{\sigma}(x) \rho(x) - 2D(\sigma, \rho) + D[\rho] \geq -\int_{R^3} dx \varphi_{\sigma}(x) \rho(x) - D[\sigma].
\]

Splitting the integrals at \( s \), using (9), and Schwarz’s inequality yields

\[
\mathcal{V}(\rho) \geq -\int_{p(x)/c < s} dx \varphi_{\sigma}(x) \rho(x) - Z \int_{p(x)/c \geq s} dx \frac{p(x)^2}{|x|} \frac{\text{arsin}(\frac{p(x)}{c})}{\text{arsin}(\frac{p(x)}{c})} - D[\sigma] \geq -\int_{p(x)/c \geq s} \frac{Z}{\text{arsin}(s)^{2/3}} \mathcal{H}(\rho)^{2/3} T_{s}(\rho)^{2/3} - D[\sigma],
\]

with \( T_{s}(\rho) := \int_{p(x)/c < s} dx \rho(x)^{2/3} \).

2.2.3. The Thomas-Fermi Term. First, we note that

\[
\mathbb{R}_{+} \to \mathbb{R}_{+}, \ t \mapsto T^{TF}(t)/t^{5},
\]

is strictly monotone decreasing from 4/5 to 0 and

\[
\mathbb{R}_{+} \to \mathbb{R}_{+}, \ t \mapsto T^{TF}(t)/t^{4},
\]
is strictly increasing from 0 to 2. Thus
\[
\mathcal{T}^{TF}(\rho) = \int_{p(x) \leq s} \frac{e^5}{8\pi^2} \sqrt{5\mathcal{T}^{TF}(\rho(x))} + \int_{p(x) > s} \frac{e^5}{8\pi^2} \sqrt{\mathcal{T}^{TF}(\rho(x))}
\]
(13) \geq \int_{p(x) \leq s} \frac{3}{10} \frac{5^{TS}(s)}{4s^3} \gamma_{\mathcal{T}^{TF}}(\rho(x)) \frac{1}{2} + \int_{p(x) > s} \frac{5^{TS}(s)}{8s^4} \gamma_{\mathcal{T}^{TF}}^{\frac{1}{2}} c_{\mathcal{T}_{\geq}}(\rho).

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 \( \xi_0 \) such that \( X(t) \leq \xi_0 t^\alpha \). We pick \( \alpha = 3 \) in which case \( \xi_0 \approx 1.15 \). Thus
\[
\mathcal{X}(\rho) \leq \frac{c_{\xi_0}}{4\pi} N = \xi cN.
\]
with \( \xi := \xi_0/(4\pi) \approx 0.0914 \).

2.2.5. The Total Energy. Adding everything up yields
\[
\mathcal{E}_Z^{TFWD}(\rho) \geq \frac{3\pi^2 \xi c}{2\sqrt{\pi}} H(\rho) + \frac{3}{8s^4} 5^{TS}(s) \gamma_{\mathcal{T}^{TF}}^{\frac{1}{2}} c_{\mathcal{T}_{\geq}}(\rho) - \frac{Z}{\mathcal{R}(\mathcal{X}(\rho))} \gamma_{\mathcal{T}^{TF}}^{\frac{1}{2}} \mathcal{R}(\mathcal{X}(\rho)) \frac{1}{2}
\]
(15) + \int_{p(x) < s} \frac{5^{TS}(s)}{8s^4} \gamma_{\mathcal{T}^{TF}}^{\frac{1}{2}} \varphi(x) \rho(x) - \varphi(x) \rho(x) \right) - D[\sigma] - \xi cN.

We pick \( s \in \mathbb{R}_+ \) such that the sum of the first three summands of (15) is a complete square, i.e., fulfilling
\[
\sqrt{\frac{3\pi^2}{2\sqrt{\pi}} 5^{TS}(s)(3\pi^2)^{\frac{1}{2}}} = \frac{Z}{\xi cN} 2\sqrt{\pi}.
\]
(16)

The solution is uniquely determined, since \( 5^{TS}(s)/s^4 \) is strictly monotone increasing from 0 to 2 and \( \sqrt{\mathcal{R}(\mathcal{X}(\rho))} \) is also monotone increasing from 0 to \( \infty \). 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 \( \infty \).

Eventually we pick \( \sigma(x) := \rho(x) \theta(s - p(x)) \). Summing the first three terms of the second line of (15) yields the Thomas-Fermi functional with Thomas-Fermi constant \( \gamma_{c}(s_0) \) evaluated at \( \sigma \). Minimizing this functional and scaling in \( \gamma \) yields
\[
\mathcal{E}_Z^{TFWD}(\rho) \geq - \frac{4s_0^5}{5^{TS}(s_0)} e^{TF} Z^\frac{1}{2} - \xi cN
\]
(17)
where \( -e^{TF} \) is the Thomas-Fermi energy of hydrogen (with the physical value of the Thomas-Fermi constant, namely \( \gamma_{TF} \)).

The function \( s_0 \) tends exponentially to \( \infty \) as \( \kappa \to \infty \). Thus (17) is merely an exponential lower bound for large \( Z \) and fixed \( \lambda \) 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 \( (16) \), set \( \xi := \max\{X(t)/t^4/t \in \mathbb{R}_+\}/(4\pi) \), and write \( -e^{TF} \) for the Thomas-Fermi energy of hydrogen. Then, for all \( \rho \in P \) with \( \int \rho = N \),
\[
\mathcal{E}_Z^{TFWD}(\rho) \geq - \frac{4s_0^5}{5^{TS}(s_0)} e^{TF} Z^\frac{1}{2} - \xi cN.
\]
(18)
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 \([17]\) allows for an adaptation of the ideas of \([11, 13]\) 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
\[
\alpha(s) := \begin{cases} 
0 & s \leq 0 \\
\frac{3}{8} s & s \in (0, 1) \\
\frac{\pi}{2} & s \geq 1
\end{cases}
\]

We introduce two localization functions
\[
R := \sin \alpha s \quad \text{and} \quad L := \cos \alpha s,
\]
and corresponding localization functions \(U\) and \(O\) on \(\mathbb{R}^3\) defined by
\[
U(x) := L \left( \frac{\omega \cdot x - l}{s} \right), \quad O(x) := R \left( \frac{\omega \cdot x - l}{s} \right)
\]
with the parameters \(\omega \in \mathbb{S}^2\), \(l \in \mathbb{R}_+\), and \(s \in (0, \infty)\). For later use, we write \(A := \text{supp}(\nabla U)\) for the support of the gradient of \(U\) and \(O\).

Assume \(\rho_N\), with associated \(p_N := (3\pi^2 \rho_N)^{\frac{1}{2}}\), is a minimizer of \(E^{\text{TFWD}}_Z\) under the constraint
\[
\int_{\mathbb{R}^3} \rho(x) dx = N.
\]

In abuse of notation, we sometimes write the occurring energy functionals instead of depending on \(\rho\) as depending on \(p\), i.e., \(p\) instead of \(p^1/(3\pi^2)\).

Our starting point is the binding condition following directly from the variational principle by pushing the \(O\)-part away from the \(U\)-part
\[
E^{\text{TFWD}}_Z(U p_N) + E^{\text{TFWD}}_0(O p_N) - E^{\text{TFWD}}_Z(p_N) \geq 0
\]
which is true, since
\[
\frac{1}{3\pi^2} \int_{\mathbb{R}^3} (U(x)^3 + O(x)^3)p_N(x)^3 dx \leq \frac{1}{3\pi^2} \int_{\mathbb{R}^3} (U(x)^2 + O(x)^2)p_N(x)^3 dx
\]
\[
= \int_{\mathbb{R}^3} \rho_N(x) dx = N
\]
and the infima under the constraint \([22]\) and the constraint
\[
3\pi^2 \int_{\mathbb{R}^3} p(x)^3 dx = \int_{\mathbb{R}^3} \rho(x) dx \leq N
\]
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
\[
\int_{\mathbb{R}^3} dx |\nabla(U p)(x)|^2 f(U p(x)/c)^2 + |\nabla(O p)(x)|^2 f(O p(x)/c)^2
\]
\[
\leq \int_{\mathbb{R}^3} dx |\nabla(U p)(x)|^2 + |\nabla(O p)(x)|^2 f(p(x)/c)^2
\]
\[
= \int_{\mathbb{R}^3} dx |\nabla p(x)|^2 f(p(x)/c)^2 + \int_{\mathbb{R}^3} dx p(x)^2 |\nabla U(x)|^2 + |\nabla O(x)|^2 f(p(x)/c)^2
\]
\[
= \int_{\mathbb{R}^3} dx |\nabla p(x)|^2 f(p(x)/c)^2 + s^{-2} \int_{\mathbb{R}^3} dx |\alpha'(\omega \cdot x - l)/s| f(p(x)/c)^2,
\]
since \( f \) is monotone increasing.

An elementary calculation shows that there is a constant \( \mu \) such for all \( t \in \mathbb{R}_+ \)
\[
(27) \quad f(t)^2 \leq \mu t.
\]
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
\[
(28) \quad \int_{S^2} \frac{d\omega}{4\pi} (\omega \cdot x - \alpha) = \frac{|x|}{4} [(1 - \alpha/|x|^2)]^2
\]
(see [4] for a related formula). Since the left side is independent of the direction of \( x \) and equals \( |x| \int_{S^2} d\omega (4\pi)^{-1} (\omega \cdot x/|x| - \alpha/|x|) \), it suffices to show (28) for \( x = e_3 \):
\[
\int_{S^2} \frac{d\omega}{4\pi} (\omega \cdot e_3 - \alpha) = \frac{1}{2} \int_0^\pi d\theta \sin \theta (\cos \theta - \alpha) = \frac{1}{2} \int_{\min(1,\alpha)}^1 d\alpha (u - \alpha)
\]
\[
= \frac{1}{4} [(1 - \alpha)^2 + \alpha].
\]

We estimate the various parts of (23) separately. We begin with the Weizsäcker terms and get using (26) and (27)
\[
\tau^W(U\rho_N) + \tau^W(O\rho_N) - \tau^W(p_N)
\]
\[
\leq \frac{3\lambda}{8\pi^2s^2} \int_{0 < \omega \cdot x < t < \infty} dx \alpha'((\omega \cdot x - t)/s) p_N(x)^2 \rho_N(x)\leq \frac{3\lambda\mu}{32s^2} \int_{0 < \omega \cdot x < t < \infty} dx p_N(x)^3
\]
\[
(29) = \frac{9\pi^2\lambda\mu}{32s^2} \int_{0 < \omega \cdot x < t < \infty} dx p_N(x).
\]
Integration over \( t \in \mathbb{R}_+ \) and \( \omega \in \mathbb{S}^2 \) and using (25) yields
\[
\int_{S^2} \frac{d\omega}{4\pi} \int_{\mathbb{R}_+} dt \left( \tau^W(U\rho_N) + \tau^W(O\rho_N) - \tau^W(p_N) \right)
\]
\[
\leq \frac{9\pi^2\mu}{128s^2} \int_{S^2} \frac{d\omega}{\pi} \int_{\mathbb{R}_+} dx (\omega \cdot x - (\omega \cdot x - s)_+) p_N(x)
\]
\[
= \frac{9\pi^2\mu}{128s^2} \int_{S^2} \frac{d\omega}{\pi} \int_{\mathbb{R}_+} dx [(\omega \cdot x)_+ - (\omega \cdot x - s)_+] p_N(x)
\]
\[
= \frac{9\pi^2\mu}{128s^2} \int_{\mathbb{R}_+} dx |x|[1 - ((1 - \frac{s}{|x|})^2)] p_N(x)
\]
\[
= \frac{9\pi^2\mu}{128s^2} \left( \int_{s < |x|} dx 2s^2 \frac{x^2}{|x|^2} p_N(x) + \int_{|x| > s} dx p_N(x) \right) \leq \frac{3\pi^2\mu N}{2s^2}.
\]

Next we estimate the combined Thomas-Fermi-Exchange part of (23). To this end we introduce the functions \( a \) and \( b \) on \( \mathbb{R}_+ \) defined by
\[
(31) \quad a(t) := \frac{c^5}{8\pi^2} T^F(t) + \frac{c^4}{8\pi^3} \frac{1}{2} [t(t^2 + 1)^{1/2} - \frac{At}{2}]^2.
\]
\[
(32) \quad b(t) := \frac{c^4}{8\pi^3} 2^4 t^4.
\]
Pick now \( f_1, \ldots, f_n \in \mathbb{R}_+ \) with \( f_1^2 + \ldots + f_n^2 = 1 \). Since \( a, \ldots, a^{(n)} \) are all positive, we have
\[
(33) \quad a''(f_i t) \leq a''(t)
\]
because \( f_1 \leq 1 \). Since also \( a(0) = a'(0) = a''(0) = a'''(0) \), integration of (33) yields successively \( a''(f,t) \leq f_a a''(t), a'(f,t) \leq f_a^2 a'(t), \) and \( a(f,t) \leq f_a^3 a(t) \). (See [11] Formula 3.135 for a similar argument for \( T_{TF} \).)

Thus, we get

\[
T_{TF}(u_{PN}) - \mathcal{X}(u_{PN}) + T_{TF}(O_{PN}) - \mathcal{X}(O_{PN}) - (T_{TF}(p_N) - \mathcal{X}(p_N))
\]

\[
= \int_{\mathbb{R}^3} dx [a(U(x)\frac{p_N(x)}{c}) + a(O(x)\frac{p_N(x)}{c}) - a(\frac{p_N(x)}{c})]
\]

\[
+ b(\frac{p_N(x)}{c}) - b(U(x)\frac{p_N(x)}{c}) - b(O(x)\frac{p_N(x)}{c})]
\]

\[
\leq \int_{\mathbb{R}^3} dx [(U(x)^3 + O(x)^3) - (U(x)^4 + O(x)^4) - (p_N(x)^3)]
\]

\[
\leq \frac{1}{4} \max \left\{ \frac{1 - \cos(t)^4 - \sin(t)^4}{1 - \cos(t)^3 - \sin(t)^3} \middle| t \in [0, \pi/2] \right\} \int_A dx \left( \frac{p_N(x)^3}{(a(\frac{p_N(x)}{c}))^2} \right)
\]

\[
\leq \frac{2 + \sqrt{2}}{2\pi} \int_A dx \left( \frac{p_N(x)^3}{T_{TF}(\frac{p_N(x)}}{c}) \right).
\]

Using (11) and (12) we get for any \( S \in \mathbb{R}_+ \)

\[
T_{TF}(u_{PN}) - \mathcal{X}(u_{PN}) + T_{TF}(O_{PN}) - \mathcal{X}(O_{PN}) - (T_{TF}(p_N) - \mathcal{X}(p_N))
\]

\[
\leq \frac{2 + \sqrt{2}}{2\pi} \int_{A_{p_N(x)/c} \leq S} dx \left( \frac{S^5}{T_{TF}(S)} p_N(x)^3 \right)
\]

\[
+ \frac{2 + \sqrt{2}}{2\pi} \int_{A_{p_N(x)/c} \leq S} dx \left( \frac{S^4}{cT_{TF}(S)} p_N(x)^4 \right)
\]

\[
\leq \frac{(2 + \sqrt{2})^3}{2\pi} \frac{S^5}{T_{TF}(S)} N + \frac{(2 + \sqrt{2})^4}{2\pi} \frac{S^4}{T_{TF}(S)} \int_{\mathbb{R}^3} dx \rho_N(x)^2.
\]

The external potential part yields

\[
- Z \int_{\mathbb{R}^3} dx \left( \frac{U(x)^3 - 1}{|x|} \right) \rho_N(x) \leq Z \int_{\omega x \leftarrow l > 0} dx \rho_N(x) |x|.
\]

Integration over \( l \) and averaging over the sphere yields

\[
- Z \int_{\mathbb{R}^3} \frac{d\omega}{4\pi} \int_{\mathbb{R}_+} dl \int_{\mathbb{R}^3} dx \left( \frac{U(x)^3 - 1}{|x|} \right) \rho_N(x)
\]

\[
\leq Z \int_{\mathbb{R}^3} \frac{d\omega}{4\pi} \int_{\mathbb{R}_+} dl \int_{\omega x \leftarrow l > 0} dx \rho_N(x) |x|
\]

\[
= Z \int_{\mathbb{R}^3} \frac{d\omega}{4\pi} \int_{\mathbb{R}^3} dx \rho_N(x) \left( \frac{\omega \cdot x}{|x|} + \rho_N(x) \right) = Z \int_{\mathbb{R}^3} dx \rho_N(x) = Z \frac{4}{N}.
\]

Finally, we address the electron-electron repulsion in (29). We have

\[
W(l, \omega) := D(U^3 \rho_N, U^3 \rho_N) + D(O^3 \rho_N, O^3 \rho_N)
\]

\[
- D((U^2 + O^2) \rho_N, (U^2 + O^2) \rho_N)
\]

\[
\leq - 2D(U^2 \rho_N, O^2 \rho_N) \leq \int_{\omega x \leftarrow l < 0} dx \int_{\omega y \leftarrow l > 0} \frac{\rho_N(x) \rho_N(y)}{|x - y|}.
\]
Integration in $l$ and $\omega$ and using (28) yields

$$
\int_{\mathbb{R}^3} \frac{d\omega}{4\pi} \int_{\mathbb{R}_+} dl W(l, \omega) \leq \int_{S^2} \frac{d\omega}{4\pi} \int_{\mathbb{R}_+} dl \int_{|x-l|<0} dx \int_{|x-y|>l} dy \frac{\rho_N(x)\rho_N(y)}{|x-y|}
$$

$$
= - \int_{S^2} \frac{d\omega}{8\pi} \int_{\mathbb{R}_3} dl \int_{\mathbb{R}_3} dx \int_{\mathbb{R}_3} dy \left[ \theta(l-\omega \cdot x)\theta(\omega \cdot y-s-l) + \theta(l-(\omega \cdot y))\theta(-\omega \cdot x-s-l) \right] \frac{\rho_N(x)\rho_N(y)}{|x-y|}
$$

$$
= - \int_{S^2} \frac{d\omega}{8\pi} \int_{\mathbb{R}_3} dl \int_{\mathbb{R}_3} dy \left( \omega \cdot (y-x)-s \right) \rho_N(x)\rho_N(y) \frac{\rho_N(x)\rho_N(y)}{|x-y|}
$$

Thus, with (28),

$$
\int_{S^2} \frac{d\omega}{4\pi} \int_{\mathbb{R}_+} dl W(l, \omega) \leq - \frac{1}{8} \int_{\mathbb{R}_3} dx \int_{\mathbb{R}_3} dy \rho_N(x)\rho_N(y) \left[ \left( 1 - \frac{s}{|x-y|} \right)^2 + \right]
$$

$$
= - \frac{N^2}{8} + \frac{1}{8} \int_{\mathbb{R}_3} dx \int_{\mathbb{R}_3} dy \rho_N(x)\rho_N(y) \left\{ 1 - \left( 1 - \frac{s}{|x-y|} \right)^2 \right\}
$$

$$
= - \frac{N^2}{8} + \frac{1}{8} \int_{\mathbb{R}_3} dx \int_{\mathbb{R}_3} dy \rho_N(x)\rho_N(y) \times \left\{ \frac{1}{2s} - \left( \frac{s}{|x-y|} \right)^2 \right\} \quad s \geq |x-y|
$$

$$
\leq - \frac{N^2}{8} + \frac{s}{2} D[\rho_N]
$$

Inserting these estimates in (23) gives

$$
\frac{3\pi^2\lambda_N N}{8} + \frac{Z N}{4} - \frac{N^2}{8} + c_1(N) + \frac{c_2(S)}{c} \int_{\mathbb{R}^3} dx \rho_N(x)^{\frac{2}{3}} + \frac{s}{2} D[\rho_N] \geq 0
$$

or

$$
N \leq 2Z + \frac{3\pi^2\lambda_N N}{24s} + 2^2 \frac{D[\rho_N]}{N} + 8c_1(S) + \frac{8c_2(S)}{cN} \int_{\mathbb{R}^3} dx \rho_N(x)^{\frac{2}{3}}
$$

and after optimization in $s$

$$
N \leq 2Z + 3\pi\sqrt{2} \sqrt{\frac{\lambda_N D[\rho_N]}{N}} + 8c_1(S) + \frac{8c_2(S)}{cN} \int_{\mathbb{R}^3} dx \rho_N(x)^{\frac{2}{3}}.
$$

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 (13) but with the corresponding replacements, namely $Z$ by $2Z$ and a factor 2 in front of $\xi cN$. Therefore we get

$$
0 \geq \mathcal{F}_Z^{\text{FWD}}(\rho_N) = \frac{1}{2} T^W(\rho_N) + \frac{1}{2} T^{\text{TF}}(\rho_N) + \frac{1}{2} D[\rho_N]
$$

$$
+ \frac{1}{2} \left( T^W(\rho_N) + T^{\text{TF}}(\rho_N) + D[\rho_N] - \int_{\mathbb{R}^3} dx \frac{Z\rho_N(x)}{2|x|} - 2\mathcal{A}(\rho_N) \right) \geq \frac{1}{2} T^W(\rho_N) + \frac{1}{2} T^{\text{TF}}(\rho_N) + \frac{1}{2} D[\rho_N] - C\kappa Z^{7/3} - \xi cN.
$$

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


Now, $T^{\text{TF}}(t) \geq 2t^4 - (8/3)t^3$. Thus
\begin{equation}
\int_{\mathbb{R}^3} \rho_N(x)^{\frac{4}{3}} = \frac{c^4}{(2\pi^2)^{\frac{3}{2}}} \int_{\mathbb{R}^3} dx \left( \frac{\rho_N(x)}{c} \right)^{\frac{4}{3}} \leq \left( \frac{2}{\pi} \right)^{\frac{3}{2}} \left( e^{-1} T^{\text{TF}}(\rho_N) + cN \right) \leq D_\kappa (Z^\frac{4}{3} \lambda^\frac{1}{2} + N + cN)
\end{equation}
with a $\kappa$-dependent constant $D_\kappa$. Thus, (43) yields the following bound on the excess charge.

**Theorem 2.** Assume that $\rho \in P$ with $E_Z^{\text{TPWD}}(\rho) = \inf E_Z^{\text{TFWD}}(P)$, set $N := \int_{\mathbb{R}^3} \rho(x) dx$, and assume $\kappa$ and $\lambda$ positive and fixed. Then, for large $Z$,
\begin{equation}
N \leq 2Z + O(Z^{\frac{2}{3}}).
\end{equation}
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 lead to an improved leading order. Note, however, it comes at a price, namely the ratio $Z/c$ and $\lambda$ is now fixed.

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