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ABSTRACT

We bound the number of electrons Q that an atom can bind in excess of neutrality for density functionals generalizing the classical Thomas-Fermi-Weizsäcker functional: instead of the classical power $5/3$ more general powers p are considered. For $3/2 < p < 2$ we prove the excess charge conjecture, i.e., that Q is uniformly bounded in the atomic number Z. The case $p = 3/2$ is critical: the behavior changes from a uniform bound in Z to a linear bound at the critical coupling $4\sqrt{\pi}$ of the nonlinear term. We also improve the linear bound for all $p \geq 6/5$.

I. INTRODUCTION

Density functionals have been essential tools for analyzing the physical properties of atoms, molecules, and physics. In quantum mechanics, one can trace them back to Thomas[16] and Fermi.[6,7] Weizsäcker[17] added an inhomogeneity correction meant to improve the behavior of the density in regions of rapid change of the external potential. Benguria *et al.*[2] generalized the classical Thomas-Fermi-Weizsäcker functional to a more general functional and initiated its mathematical analysis. Written in the square root ψ of the electron density ρ it reads

$$\mathcal{E}_p : H^1(\mathbb{R}^3 : \mathbb{R}) \to \mathbb{R},$$
$$\psi \mapsto \underbrace{A\int_{\mathbb{R}^3}|\nabla\psi|^2}_{T[\psi]:=} + \underbrace{\frac{\gamma}{p}\int_{\mathbb{R}^3}|\psi|^{2p}}_{F[\psi]:=} - \underbrace{\int_{\mathbb{R}^3}V\psi^2}_{A[\psi]:=} + \underbrace{\frac{1}{2}\int_{\mathbb{R}^3}\mathrm{d}x\int_{\mathbb{R}^3}\mathrm{d}y\frac{\psi(x)^2\psi(y)^2}{|x-y|}}_{D[\psi^2]:=}, \tag{1}$$

with $p \geq 1$, $\gamma > 0$, and

$$V(x) = \sum_{k=1}^{K}\frac{Z_k}{|x-R_k|}, \tag{2}$$

where $\mathfrak{Z} := (Z_1,\ldots,Z_K) \in \mathbb{R}_+^K$ and $\mathfrak{R} := (R_1,\ldots,R_K) \in \mathbb{R}^{3K}$.

Note that we will not include Dirac-type terms. Functionals of this type have the peculiar property that the energy is—even with vanishing external potential—unbounded from below forming—poetically speaking—an neblua of self-attracting electrons. Thus the definition of the electron state of a saturated atom as the absolute minimizer is not true meaning that our line of attack would fail right from the beginning.

The generalized Thomas-Fermi term F arises by a semiclassical approximation from a many electron Hamiltonian with kinetic energy operator $|-\mathrm{i}\nabla|^{\alpha}$. The relation between the exponents is

$$p=\frac{\alpha+3}{3} \tag{3}$$

with the prefactor given by

$$\gamma=(3\pi^2)^{\frac{\alpha}{3}}. \tag{4}$$

The range $2>p>4/3$ corresponds to $3>\alpha>1$. [Note that the upper bound on p arises from the Proof of Lemma 2 and also later from bounding the potential φ uniformly in Z by Sommerfeld-type solutions: For $p\to 2$ the coefficients $b(p)$ and $\sigma(p)$ of the Sommerfeld solutions as defined in (A17) blow up.]

The Euler equation for the minimizer ψ reads

$$-A\Delta\psi+[\gamma|\psi|^{2p-2}-(\underbrace{V-|\psi|^2*|\cdot|^{-1}}_{\varphi:=})]\psi=0 \tag{5}$$

weakly in $H^1(\mathbb{R}^3:\mathbb{R}_+)$.

For $p>3/2$ we can scale the Euler equation by making the ansatz

$$\psi(x)=a_p\tilde{\psi}(b_p x),\ Z_k=c_p\tilde{Z}_k,\ R_k=\tilde{R}_k/b_p \tag{6}$$

with

$$a_p:=\frac{A^{\frac{1}{4p-6}}}{\gamma^{\frac{1}{2p-3}}},\ b_p:=\frac{A^{\frac{2-p}{4p-6}}}{\gamma^{\frac{1}{4p-6}}},\ c_p:=\frac{A^{\frac{3p-4}{4p-6}}}{\gamma^{\frac{1}{4p-6}}}. \tag{7}$$

Then

$$-\Delta\tilde{\psi}+[|\tilde{\psi}|^{2p-2}-(V_{\tilde{\mathfrak{R}},\tilde{\mathfrak{Z}}}-|\tilde{\psi}|^2*|\cdot|^{-1})]\tilde{\psi}=0. \tag{8}$$

Thus, we may assume for $p>3/2$ that $A=\gamma=1$ and retrieve the general case by (6).

If ψ minimizes $\mathcal{E}_p(H^1(\mathbb{R}^3:\mathbb{R}))$ then we write $N:=\int_{\mathbb{R}^3}\psi^2$ for its particle number $Z:=Z_1+\cdots+Z_K$ and

$$Q:=N-Z \tag{9}$$

for its excess charge. The excess charge has previously been studied. Lower bounds on the excess charge are $Q\geq 0$ for $p\geq 4/3$[2] (Lemma 12) and $Q>0$ for $p>5/3$ and $K=1$[2] (Lemma 13).

The following is known about upper bounds: In the classical case, Benguria and Lieb[3] [formula (43)] showed $Q\leq 270.74K$. Solovej[14] (Proposition 14) improved this value to $Q\leq 178.03$ K. Based on an immediate generalization of an argument of Lieb[10] it is clear that $Q<Z$ for all p.

The focus of this work will be on generalizing and sharpening those upper bounds. We will start in Sec. II with the improvement $Q\leq 0.5211Z$ for rather general p.

We will also generalize the bound uniform in the nuclear charge Z similar to Ref. 3 [formula (43)] and Solovej[14] (Proposition 14). We will carry these results through for $p\in(3/2,2)$ in Sec. IV.

The value $p=3/2$ is critical, since the energetic dominance shifts from the Thomas-Fermi term for $p>3/2$ to the Weizsäcker term for $p<3/2$. We will treat the critical case by different methods and will show for $\gamma<\gamma_c:=4\sqrt{\pi}$ a bound proportional to Z whereas for $\gamma\geq\gamma_c$ we have $Q=0$. This is done in Sec. V.

II. IMPROVING THE BOUND $Q\leq Z$ FOR EXPONENTS $p\geq 6/5$

We consider the atomic case, i.e., $K=1$. Because of translational invariance we can and will assume $R_1=0$ throughout this section. Following Benguria and Tubino[4] we will improve (A2). We begin with an inequality by Nam,[12]

$$\beta:=\inf\left\{\frac{\frac{1}{2}\int_{\mathbb{R}^3}\frac{|x|^2+|y|^2}{|x-y|}\ \psi(x)^2\psi(y)^2\ \mathrm{d}x\mathrm{d}y}{\int_{\mathbb{R}^3}\psi(x)^2\ \mathrm{d}x\int_{\mathbb{R}^3}|x|\ \psi(x)^2\ \mathrm{d}x}\middle|\, 0\neq\psi\in H^1(\mathbb{R}^3:\mathbb{R})\right\}\geq 0.8218. \tag{10}$$

Theorem 1. *Let ψ be a non-vanishing solution of (5) for $K=1$ in $H^1(\mathbb{R}^3)$. Then, for all $\gamma\geq 0$ and all $p\geq 6/5$,*

$$\int_{\mathbb{R}^3}\psi(x)^2\ \mathrm{d}x\leq\frac{5}{4\beta}Z\leq 1.5211\ Z. \tag{11}$$

Proof. Since the groundstate energy of hydrogen is $-1/4$ {Schrödinger[13] [Eq. (19)]}, we have for any positive nuclear charge $\tilde{Z}$,

$$\int_{\mathbb{R}^3} |\nabla f|^2 - \int_{\mathbb{R}^3} \frac{\tilde{Z}}{|x|} |f(x)|^2 \mathrm{d}x \geq -\frac{\tilde{Z}^2}{4} \int_{\mathbb{R}^3} |f|^2 \tag{12}$$

for any $f \in H^1(\mathbb{R}^3)$. Picking $f := \psi$ this can be recast as

$$\frac{1}{Z} A[\psi] \leq \frac{1}{\tilde{Z}} T[\psi] + \frac{\tilde{Z}}{4} N \tag{13}$$

using the notation for the various parts of the energy in (1). Optimizing in $\tilde{Z}$ yields

$$\left(\frac{A}{Z}\right)^2 \leq K\, N. \tag{14}$$

Now, from (A6) and (14) we get

$$A \leq \frac{1}{3} N\, Z^2. \tag{15}$$

If we define

$$I = \frac{\int_{\mathbb{R}^3} |x|\; \psi(x)^2\, \mathrm{d}x}{\int_{\mathbb{R}^3} \psi(x)^2\, \mathrm{d}x} = \frac{1}{N} \int_{\mathbb{R}^3} |x|\; \psi(x)^2\, \mathrm{d}x \tag{16}$$

and use the Schwarz inequality, we get

$$N^2 = \left(\int_{\mathbb{R}^3} \psi(x)^2\, \mathrm{d}x \right)^2 \leq \int_{\mathbb{R}^3} |x|\; \psi(x)^2\, \mathrm{d}x \int_{\mathbb{R}^3} \frac{\psi(x)^2}{|x|}\, \mathrm{d}x \leq (I\, N) \frac{A}{Z}. \tag{17}$$

Using (15) and (17) we finally get

$$I \geq \frac{3}{Z}. \tag{18}$$

To conclude we use Nam's method.[12] We multiply (5) by $\psi \cdot |x|^2$ and integrate over $\mathbb{R}^3$. From Nam's result we have

$$(-\Delta\psi, |x|^2 \psi) \geq -\frac{3}{4}\, (\psi, \psi) = -\frac{3}{4} N. \tag{19}$$

Also, $\gamma \int_{\mathbb{R}^3} |\psi(x)|^{2p-2} \psi(x)^2 |x|^2\, \mathrm{d}x \geq 0$. Hence,

$$\int_{\mathbb{R}^3} \varphi(x) |x|^2 \psi(x)^2\, \mathrm{d}x \geq -\frac{3}{4} N, \tag{20}$$

and using

$$\varphi(x) = \frac{Z}{|x|} - \int_{\mathbb{R}^3} \frac{\psi(y)^2}{|x-y|}\, \mathrm{d}y,$$

we get

$$Z \int_{\mathbb{R}^3} |x|\; \psi(x)^2\, \mathrm{d}x - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|x|^2 + |y|^2}{|x-y|}\; \psi(x)^2 \psi(y)^2\, \mathrm{d}x \mathrm{d}y \geq -\frac{3}{4} N, \tag{21}$$

where we did the standard symmetrization in the second integral. Moreover, from (16), the first term in (21) is given by ZNI.

From the definition of β, N, and I, we have

$$\frac{1}{2} \int_{\mathbb{R}^3} \frac{|x|^2 + |y|^2}{|x-y|}\; \psi(x)^2 \psi(y)^2\, \mathrm{d}x \mathrm{d}y \geq \beta N^2 I. \tag{22}$$

From (21), (22), and the definition of I, we get

$$ZNI \geq \beta N^2 I - \frac{3}{4} N \geq \beta N^2 I - \frac{1}{4} NZI, \tag{23}$$

where the last inequality follows from (18). Rearranging (23), we get

$$\frac{5}{4} ZNI \geq \beta N^2 I$$

yielding

$$N \leq \frac{5}{4\beta} Z. \tag{24}$$

Using Nam's numerical lower bound (10) on β in (24) gives

$$N \leq 1.5211 Z. \tag{25}$$

□

III. SOME PREPARATORY RESULTS

We start with a central observation keeping the constant γ in this section, since we will use the result also for $p = 3/2$ where it cannot be scaled out. Set

Definition 1.

$$\begin{aligned} P : \mathbb{R}^3 \backslash \{R_1, \ldots, R_K\} &\to \mathbb{R}_+, \\ x &\mapsto \sqrt{4\pi\psi(x)^2 + \varphi(x)^2}. \end{aligned} \tag{26}$$

The following allows us to bound the excess charge from above.

Lemma 1. The function P is subharmonic, and, for $K = 1$ and $R_1 = 0$, the function $rP(r)$ is convex, monotone decreasing in r, and $\lim_{r\to\infty} rP(r) = Q$. In particular, for all $r > 0$,

$$rP(r) \geq Q. \tag{27}$$

Note that we write – in abuse of notation – $P(r)$ instead of $P(x)$ in the radial case.

Proof. We compute

$$\begin{aligned} 2P\Delta P + 2(\nabla P)^2 = \Delta P^2 &= 8\pi\psi\Delta\psi + 8\pi(\nabla\psi)^2 + 2\varphi\Delta\varphi + 2(\nabla\varphi)^2 \\ &= 8\pi\psi^2(\gamma\psi^{2p-2} - \varphi) + 8\pi(\nabla\psi)^2 + 8\pi\varphi\psi^2 + 2(\nabla\varphi)^2 \\ &= 8\pi\psi^2\gamma\psi^{2p-2} + 8\pi(\nabla\psi)^2 + 2(\nabla\varphi)^2, \end{aligned} \tag{28}$$

where we used the TFW Eq. (5). By Schwarz's inequality $(\nabla P)^2 \leq 4\pi(\nabla\psi)^2 + (\nabla\varphi)^2$ and therefore (28) implies $\Delta P \geq 0$. This shows the subharmonicity.

Since

$$\Delta P(x) = \frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2} rP(r), \tag{29}$$

the convexity and monotonicity statements follow.

By Lemma 5 $r\psi(r) \to 0$ and by Newton's lemma $r\varphi(r) \to -Q$ as $r \to \infty$. This shows the limiting statement. – Inequality (27) is an immediate consequence of the monotonicity and the limiting statement. □

Lemma 2. For $\lambda \in (0,1)$ and $3/2 < p < 2$, every minimizer ψ of $\mathcal{E}_p$ with φ and V given by (1) and (2) respectively, satisfies

$$\lambda\gamma\psi^{2p-2} \leq \varphi + c_p(\lambda)\gamma^{1/(3-2p)}, \tag{30}$$

with

$$c_p(\lambda) = \frac{(2\pi)^{\frac{p-1}{2p-3}}}{\lambda^{\frac{p-1}{2p-3}}(1-\lambda)^{\frac{2-p}{2p-3}}}(2p-3)\frac{(2-p)^{\frac{2-p}{2p-3}}}{(p-1)^{\frac{2p-2}{2p-3}}}. \tag{31}$$

Note that when $p = 5/3$, i.e., in the case of non-relativistic TFW theory,

$$c_{\frac{5}{3}}(\lambda) = \frac{9}{4}\pi^2\frac{1}{\lambda^2(1-\lambda)} \tag{32}$$

as in Ref. 3 [formula (13)].

Proof. Put $u := \psi^{2p-2}$. Then (5) implies that

$$-\Delta u + (2p-2)(\gamma u - \varphi)u \leq 0, \tag{33}$$

provided $p \geq 3/2$. On the other hand, (2) and (5) imply

$$-\Delta\varphi = -4\pi\psi^2 = -4\pi u^{1/(p-1)}, \tag{34}$$

away from R_k, $k = 1, 2, \ldots K$. Now, set

$$v := \gamma\lambda u - \varphi - d, \tag{35}$$

with d a constant to be chosen later. Then, from (34) and (35) we get

$$-\Delta v = -\gamma\lambda\Delta u + \Delta\varphi \leq -\gamma\lambda(2p-2)(\gamma u - \varphi)u + 4\pi u^{\frac{1}{p-1}}. \tag{36}$$

Set $S = \{x | v > 0\}$. It follows from (35) and (2) that $R_k \notin S$, all $k = 1, 2, \ldots, K$. On S,

$$\varphi = \gamma\lambda\, u - d - v \leq -d + \gamma\lambda\, u, \tag{37}$$

and replacing in (36), on S,

$$-\Delta v \leq -\gamma\lambda(2p-2)\gamma(1-\lambda)u^2 - \gamma\lambda(2p-2)d\, u + 4\pi u^{\frac{1}{p-1}}.$$

Now, if $3/2 < p < 2$, then $1/2 < p - 1 < 1$, $1 < 1/(p-1) < 2$, and

$$4\pi u^{\frac{1}{p-1}} \leq \gamma^2 u^2 \lambda(1-\lambda)(2p-2) + b\, u,$$

i.e.,

$$4\pi u^{\frac{2-p}{p-1}} \leq \gamma^2 u\lambda(1-\lambda)(2p-2) + b.$$

Consider the function

$$f(u) = 4\pi u^{\frac{2-p}{p-1}} - \gamma^2 u\lambda(1-\lambda)(2p-2), \tag{38}$$

with $(2-p)/(p-1) < 1$, i.e., $p > 3/2$. Since $(2-p)/(p-1) < 1$, the function $f(u)$ for $u > 0$ has only one maximum, say $\hat{u}$, on the interval $(0, \infty)$. $\hat{u}$ is given by

$$\hat{u} = \left[\frac{\gamma^2(p-1)^2\lambda(1-\lambda)}{2\pi(2-p)}\right]^{(p-1)/(3-2p)}$$

and

$$f(\hat{u}) = (2\pi)^{\frac{p-1}{2p-3}}\left(\gamma^2\lambda(1-\lambda)\right)^{\frac{2-p}{3-2p}} 2(2p-3)(p-1)^{\frac{1}{3-2p}}(2-p)^{\frac{2-p}{2p-3}}.$$

Now choose $b = f(\hat{u})$, which in turn implies choosing $d = b/(\gamma\lambda(2p-2))$. With that choice of b, $-\Delta v \leq 0$ on S. Hence v is subharmonic on S. Since $v = 0$ on ∂S, we conclude that $v < 0$ on S. This in turn implies that S is empty and we are done. □

Corollay 1. For $3/2 < p < 2$ we have

$$-c_p(\lambda_0) = -\frac{2^{\frac{p-1}{2p-3}}\pi^{\frac{p-1}{2p-3}}(2p-3)}{(p-1)^{\frac{3(p-1)}{2p-3}}} < \varphi(x). \tag{39}$$

Moreover, if $\varphi(x) \leq 0$, then

$$\begin{aligned} \psi(x) &\leq \frac{2^{\frac{4p-3}{4p-6}}\pi^{\frac{p-1}{2p-3}}(2p-3)^{\frac{1}{2p-2}}}{(3p-4)^{\frac{3p-4}{2(p-1)(2p-3)}}}, \\ P(x) &\leq P_p^- := \sqrt{\max\left\{4\pi\left(\frac{c_p(\lambda_1)-c_p(\lambda_0)}{\lambda_1}\right)^{\frac{1}{p-1}} + c_p(\lambda_0)^2, 4\pi\left(\frac{c_p(\lambda_1)}{\lambda_1}\right)^{\frac{1}{p-1}}\right\}} \end{aligned} \tag{40}$$

with $\lambda_0 := p-1$ and $\lambda_1 := (3p-4)/(2p-2)$.

Proof. For the first claim, estimate the left side of (30) from below by zero and minimize in λ. The minimum occurs at $\lambda_0 = p - 1$.

To prove the claim on ψ drop φ in (30), move all λ to the right, and minimize the right side in λ. The minimum occurs at $\lambda_1 = (3p-4)/(2p-2)$. The minimal value is the right hand side of (40).

Finally, we pick $\lambda = \lambda_1$ in (30) and maximize over all possible negative values of $\varphi(x)$ given by (39). Since the function is convex, the maximum occurs at the boundary, i.e., $\varphi = 0$ or $\varphi = c_p(\lambda_0)$. □

We also have the bound

Lemma 3. For $p \geq 3/2$ and positive γ we have

$$\psi^{2p-2} \leq \gamma^{-1} V. \tag{41}$$

Proof. First we note that V is harmonic outside the positions of the nuclei $R_1, \ldots, R_K$. We set

$$f := \gamma^{-1} V - \psi^{2p-2}. \tag{42}$$

We wish to show that $f \geq 0$ and therefore consider the exceptional set

$$S := \{x \in \mathbb{R}^3 | f(x) < 0\}. \tag{43}$$

Certainly neither of the $R_1, \ldots, R_K$ is in S, since ψ is finite everywhere. On S we get from (5),

$$\begin{aligned}\Delta f &= -\Delta \psi^{2p-2} = -(2p-2)(2p-3)\psi^{2p-4}(\nabla\psi)^2 - (2p-2)\psi^{2p-3}\Delta\psi \\ &\leq (2p-2)\psi^{2p-3}(\varphi - \gamma\psi^{2p-2})\psi \leq (2p-2)\psi^{2p-2}(V - \gamma\psi^{2p-2}) < 0\end{aligned} \tag{44}$$

on S. Hence $\Delta f < 0$ on S, i.e., f is superharmonic on S. Since f vanishes on the boundary of S, the exceptional set S is empty which implies the claim. □

For $R > 0$ define D_R as the complement of the union of the balls of radius R around the positions of the nuclei $R_1, \ldots, R_K$, i.e., $B_R(R_1) \cup \cdots \cup B_R(R_K)$.

Lemma 4. For $3/2 < p < 2$, $\gamma > 0$ and $R > 0$, let ψ be the positive solution of (5) with V given by (2), φ by (5), and $S_{p,R}$ by (A26). Then for all $x \in D_R$,

$$\varphi(x) \leq \frac{\pi^2}{R^2} + \sum_{k=1}^{K} s_{p,R}(|x - R_k|). \tag{45}$$

Proof. Let $W = \gamma\rho^{p-1} - \varphi$, $\rho = \psi^2$ and consider the Hamiltonian $H = -\Delta + W$. The operator H is non-negative, since its ground state, the function ψ, has zero energy. In particular,

$$\int_{\mathbb{R}^3} \left(|\nabla e_{R,a}|^2 + W|e_{R,a}|^2\right) \geq 0, \tag{46}$$

where $e_{R,a}$ is the positive normalized groundstate of the Dirichlet Laplacian on $B_R(a)$, $a \in \mathbb{R}^3$, extended by 0 to the complement of $B_R(a)$, i.e.,

$$e_{R,a}(x) = \begin{cases} \dfrac{1}{R^{\frac{3}{2}}\sqrt{2\pi}} \dfrac{\sin(\pi|x-a|/R)}{|x-a|/R}, & |x-a| < R, \\ 0, & |x-a| \geq R. \end{cases} \tag{47}$$

Obviously $e_{R,a} \in H^1(\mathbb{R}^3)$, is spherically symmetric about a, is decreasing, and has compact support. With $g_{R,a} := e_{R,a}^2$ and $g_R := g_{R,0}$ we have

$$\int_{\mathbb{R}^3} |\nabla e_{R,x}|^2 = \left(\frac{\pi}{R}\right)^2. \tag{48}$$

Thus, (46) implies for all $R > 0$ and all $x \in \mathbb{R}^3$,

$$\int_{\mathbb{R}^3} W(y) e_{R,x}(y)\, \mathrm{d}y \geq -\left(\frac{\pi}{R}\right)^2. \tag{49}$$

Note that $\int_{\mathbb{R}^3} W(y) g_{R,x}(y)\, \mathrm{d}y = (g_R * W)(x)$ where $*$ denotes convolution. Define

$$\tilde{\phi} = \varphi * g_R - \left(\frac{\pi}{R}\right)^2. \tag{50}$$

Since $\varphi \in L^{3+\epsilon} + L^{3-\epsilon}$, $\epsilon > 0$ (Ref. 2, Proof of Lemma 7) and $g_R \in L^s$ for all $s \geq 1$, $\tilde{\phi}$ is continuous and tends to $-(\pi/R)^2$ at infinity (see Ref. 9, Lemma 3.1). Using Hölder's inequality, we have for all x,

$$(g_R * \rho^{p-1})(x) \leq [(g_R * \rho)(x)]^{p-1} \left(\int g_R(y)\, \mathrm{d}y\right)^{2-p} = [(g_R * \rho)(x)]^{p-1}, \tag{51}$$

provided $1 \leq p \leq 2$. Here we used $\int_{\mathbb{R}^3} g_R = 1$. Let us also define

$$\tilde{\rho} = g_R * \rho. \tag{52}$$

From Eqs. (49)–(52) we obtain for all x,

$$\left(\frac{\pi}{R}\right)^2 \geq (\varphi * g_R)(x) - \gamma\big(g_R * \rho^{p-1}\big)(x) \geq \tilde{\phi}(x) + \left(\frac{\pi}{R}\right)^2 - \gamma\tilde{\rho}(x)^{p-1}. \tag{53}$$

In other words,

$$\tilde{\phi} \leq \gamma\tilde{\rho}^{\ p-1}, \tag{54}$$

provided $1 \leq p \leq 2$. Notice that φ is subharmonic away from the nuclei and that $\tilde{\varphi} = g_R * \phi - (\pi/R)^2$ with g_R being spherically symmetric, positive, of total mass one, and having support in a ball of radius R. From this it follows that

$$\varphi(x) \leq \tilde{\phi}(x) + \left(\frac{\pi}{R}\right)^2, \tag{55}$$

for all x such that $|x - R_k| > R$, for all k. To prove (45) we need a bound on $\tilde{\phi}$. From (2) and (50), using the bound (54), and the fact that the Laplacian commutes with convolution, we compute

$$-\frac{1}{4\pi}\Delta\tilde{\phi} = \tilde{V} - \tilde{\rho} \leq \tilde{V} - \gamma^{-1/(p-1)}\big[\tilde{\phi}_+(x)\big]^{1/(p-1)} \tag{56}$$

with

$$\tilde{V} = V * g_R \tag{57}$$

and with $\tilde{\phi}_+(x) = \max\big(\tilde{\phi}(x), 0\big)$. Let $\hat{\phi}$ be the minimizer of the Thomas-Fermi functional with external potential $\tilde{V}$. It fulfills the equation

$$-\frac{1}{4\pi}\Delta\hat{\phi} = \tilde{V} - \left[\frac{\hat{\phi}_+(x)}{\gamma}\right]^{1/(p-1)}. \tag{58}$$

By the maximum principle we have for all x,

$$\tilde{\phi}(x) \leq \hat{\phi}(x). \tag{59}$$

The next step is to bound $\hat{\phi}$. We treat first the radial case with $V(x) = Z/|x|$. Since the Sommerfeld solution $S_{p,R}$ of the generalized TF model defined in (A26) fulfills for $p \in (3/2, 2)$,

$$\frac{1}{4\pi}\Delta S_{p,R} \leq \gamma^{-1/(p-1)}\ S_{p,R}^{1/(p-1)} \tag{60}$$

for $r > R$ and $\hat{\phi}$ satisfies there

$$\frac{1}{4\pi}\Delta\hat{\phi} = \gamma^{-1/(p-1)}\ \hat{\phi}^{\,1/(p-1)}. \tag{61}$$

We can again use a comparison argument. Since $s_{p,R}(R) - \hat{\phi}(R) = \infty$ we conclude that

$$\hat{\phi}(r) \leq s_{p,R}(r) \qquad \text{for } r > R. \tag{62}$$

This, together with (55) and (59), proves (45) in the radial case.

For the non radial case, let $\hat{\phi}_j(x)$ be the solution to (58) for an atom of smeared nuclear charge at R_j. By another comparison argument [see Lieb and Simon[11] (Theorem V.12) or Lieb[9] (Corollary 3.6)] we get

$$\hat{\phi}(x) \leq \sum_{j=1}^{K} \hat{\phi}_j(x).$$

This, together with the definition of $S_{p,R}$ in (A26) and (55) implies (45). □

IV. BOUND ON THE EXCESS CHARGE UNIFORM IN THE ATOMIC NUMBER FOR EXPONENTS $p \in (3/2, 2)$

Next we turn to bounds on Q that are uniform in the atomic number. That such bounds exist is the content of the excess charge conjecture. We will prove it for $p \in (3/2, 2)$ following Ref. 3 and start with the atomic case where we get

Theorem 2. *Assume $p \in (3/2, 2)$ and $B(p)$ as given in (66). Then the atomic excess charge Q of the generalized TFW functional is bounded as follows:*

$$0 \le Q \le B(p) \frac{A^{\frac{3p-4}{4p-6}}}{\gamma^{\frac{1}{4p-6}}}. \tag{63}$$

Proof. We recall that $\varphi = V - \rho * |\cdot|^{-1}$ with ρ the minimizer of $\mathcal{E}_p$ is the electric mean-field potential of the generalized TFW minimizer [see (5)]. Similarly we write

$$\hat{\phi} = \tilde{V} - \rho^{\mathrm{TF}} * |\cdot|^{-1}, \tag{64}$$

where ρ^{TF} is the minimizer of $\mathcal{E}_p^{\mathrm{TF}}$ with external potential $\tilde{V}$.

We have the following simple bound in terms of $s_{p,R}$,

$$\begin{aligned} Q &\overset{\varphi(r)\ge 0}{\le} r\sqrt{4\pi\left(\frac{\varphi + c_p(\lambda)}{\lambda}\right)^{\frac{1}{p-1}} + \varphi^2} \le r\sqrt{4\pi\left(\frac{\hat{\phi} + \frac{\pi^2}{R^2} + c_p(\lambda)}{\lambda}\right)^{\frac{1}{p-1}} + \left(\hat{\phi} + \frac{\pi^2}{R^2}\right)^2} \\ &\le r\sqrt{4\pi\left(\frac{s_{p,R}(r) + \frac{\pi^2}{R^2} + c_p(\lambda)}{\lambda}\right)^{\frac{1}{p-1}} + \left(s_{p,R}(r) + \frac{\pi^2}{R^2}\right)^2} =: F(p,\lambda,R,r), \\ Q &\overset{\varphi(r)<0}{\le} rP_p^- =: G(r,p). \end{aligned} \tag{65}$$

(Using Lemma 12 instead of Lemma 10 would improve the numerical result. However, to keep the numerical evaluation simple we refrain from doing so.) Thus, picking a triple λ, r, R such that $0 < \lambda < 1$ and $0 < R < r$ (which we numerically optimize) we have

$$Q \le B(p) := \max\{F(p,\lambda,R,r),\ G(r,p)\}. \tag{66}$$

The result is displayed in Fig. 1.

The parameters A and γ are restored by the scaling relations (6). □

The general case is more or less a corollary of the atomic case and merely yields a factor K, i.e.,

$$Q \le B(p) \frac{A^{\frac{3p-4}{4p-6}}}{\gamma^{\frac{1}{4p-6}}} K. \tag{67}$$

Technically it amounts to localized estimates around each nucleus which we accomplished above and patching them together in the same way as in the case $p = 5/3$ (see Ref. 3). We refrain from exhibiting the details again here.

V. THE CRITICAL EXPONENT $p = 3/2$

We turn to the critical exponent $p = 3/2$. We will keep the parameter γ in $\mathcal{E}_p$ in this section, since it cannot be scaled out in this case. In fact our result will depend on γ. Lemma 3 allows us to prove the following bound.

Theorem 3. *Let ψ be the positive solution of (5) for $p = 3/2$. Then*

$$Q \le \begin{cases} 0, & \gamma \ge \gamma_c := 4\sqrt{\pi}, \\ \frac{\gamma_c - \gamma}{\gamma} Z, & \gamma < \gamma_c. \end{cases} \tag{68}$$

Altough one might suspect that the linear growth of Q might be linear in Z, since the fermionic part of the kinetic energy is dominated by the bosonic part, our bound is not optimal: (i) In the purely bosonic case, i.e., $\gamma = 0$ it is known the $Q \to 0.21$ as $Z \to \infty$ (Baumgartner[1]). (ii) For all p we have $Q \le Z$ by adapting Lieb's argument.[10] Moreover, strictly speaking, it is not even clear that $Q > 0$ for $p < 5/3$.

Proof. We set

$$g := \varphi + aV - b\psi \tag{69}$$

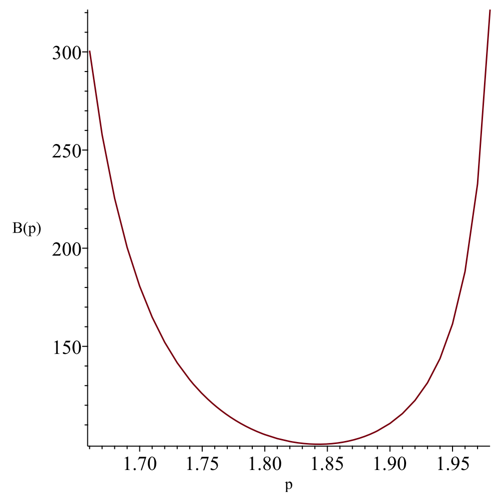

FIG. 1. Upper bound $B(p)$ on the excess charge. Minimum at $p_{\min} \approx 1.8431$ with $B(p_{\min}) \approx 100.14$.

with non-negative constants a and b to be suitably specified later. We want to show that g is nonnegative on all of $\mathbb{R}^3$. Again, we use a subharmonic argument and define an exceptional set

$$S := \{x \in \mathbb{R}^3 | g(x) < 0\}. \tag{70}$$

As in the Proof of Lemma 3, the positions of the nuclei $R_1, \ldots, R_K \notin S$. On S we have

$$\Delta g = 4\pi\psi^2 - b\Delta\psi = 4\pi\psi^2 + b\varphi\psi - b\gamma\psi^2. \tag{71}$$

Because of Lemma 3 we have on S,

$$\varphi < b\psi - aV \le b\psi - a\gamma\psi. \tag{72}$$

Combining this with (71) yields

$$\begin{aligned}\Delta g &\le 4\pi\psi^2 + b^2\psi^2 - ba\gamma\psi^2 - b\gamma\psi^2\\ &=\psi^2\left[4\pi + \left(b - \frac{\gamma}{2}(1+a)\right)^2 - \frac{\gamma^2}{4}(1+a)^2\right]\\ &=\psi^2(4\pi - \frac{\gamma^2}{4}(1+a)^2) = \frac{\psi^2}{4}(\gamma_c^2 - \frac{\gamma^2}{4}(1+a)^2),\end{aligned} \tag{73}$$

where we completed the square in b and picked $b = \gamma(1+a)/2$.

We will make different choices of a depending whether $\gamma \ge \gamma_c$ or $\gamma < \gamma_c$:

1. $\gamma \ge \gamma_c$: We chose $a = 0$ which implies that $\Delta g \le 0$, i.e., g is superharmonic, on S. Since g vanishes ∂S, $g \ge 0$ on S, eventually implying $S = \emptyset$. Thus,
$$\varphi \ge b\psi \tag{74}$$
and therefore
$$Q = N - Z = -\lim_{x\to\infty} |x|\varphi(x) \le 0, \tag{75}$$
yielding the first claim.
2. $0 \le \gamma < \gamma_c$ we pick $a := (\gamma_c - \gamma)/\gamma > 0$ and carry out the same subharmonic argument as before yielding
$$\varphi \ge b\psi - \frac{\gamma_c - \gamma}{\gamma} V. \tag{76}$$
Since $\psi(x)|x| \to 0$ as $x \to \infty$ by Lemma 5, we have
$$Q = -\lim_{x\to\infty} |x|\varphi(x) \le \frac{\gamma_c - \gamma}{\gamma} Z, \tag{77}$$
which proves the claimed inequality for $\gamma < \gamma_c$. □

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Rafael D. Benguria: Investigation (equal). **Heinz Siedentop**: Investigation (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX: MINIMIZERS OF GENERALIZED TF(W) FUNCTIONALS AND ASSOCIATED SOMMERFELD FORMULAE

We collect a few known facts for $\mathcal{E}_p$ mostly from Benguria *et al.*[2]) and generalize the Sommerfeld formula with a remainder term from $p = 5/3$ [see Solovej[15] (Lemma 4.4)] to $p \in (4/3, 2)$.

1. No sign change of minimizers

Since $T[\psi] \geq T[|\psi|]$ (Kato's inequality[8]) with equality, if and only if ψ does not change the sign, and since all other terms of $\mathcal{E}_p$ are unchanged under the substitution $\psi \to |\psi|$ any minimizer of the functional is either non-negative or non-positive.

2. Existence of TFW minimizers and strict positivity or negativity

By standard compactness methods one shows that $\mathcal{E}$ has a minimizer $\psi \in H^1(\mathbb{R}^3 : \mathbb{R})$. By unique continuation this implies that any minimizer of the functional is strictly positive or strictly negative. Conversely any positive solution of (5) minimizes $\mathcal{E}$.

3. Uniqueness of the minimizer and spherical symmetry for atoms

Since $\mathcal{E}_p(\psi) = \mathcal{E}_p(-\psi)$ it is enough to study on nonnegative functions. However, the functional restricted to nonnegative functions can be written in terms of the density ρ with $\sqrt{\rho} := \psi$ which makes it strictly convex. This implies uniqueness of the minimizer ψ among the non-negative functions (and also among the negative functions). Thus $\mathcal{E}_p$ has exactly two minimizers [and (5) has exactly two non-vanishing solutions] in $H^1(\mathbb{R}^3 : \mathbb{R})$, one positive and one negative. – Moreover in the atomic case, i.e., $K = 1$ and $R_1 = 0$, uniqueness implies that the minimizers are spherically symmetric.

4. Decay of the minimizers

Lemma 5. Suppose $p \in [1, 3]$ and $\psi \in H^1(\mathbb{R}^3 : \mathbb{R})$ is a nonnegative minimizer of $\mathcal{E}_p$ for the atomic case. Then $\psi(x)|x| \to 0$ as $x \to \infty$.

Proof. Lieb[9] (Theorem 2.12) shows that the atomic Thomas-Fermi energy decreases under spherically symmetric rearrangement. However, this is also true of $\rho^{\frac{5}{3}}$ is replaced by ρ^p, since all L^p-norms are invariant under spherical symmetric rearrangements and it also holds if $\int|\nabla\sqrt{\rho}|^2$ is added. Thus, by uniqueness ψ is spherically symmetric and decreasing. – In abuse of notation, we will write also $\psi(r)$ instead of $\psi(x)$ with $r := |x|$ in the remainder of this proof.

Now, suppose the claim would not be true. Then there exists a sequence $r_1, r_2, \ldots$ such $r_n \to \infty$ as $n \to \infty$ and $B := \lim_{n\to\infty} \psi(r_n) r_n > 0$. Thus there exists n_0 such that for all $n \geq n_0$ we have $\psi(r_n) r_n \geq B/2$. Thus we have

$$\begin{aligned}\infty > \int_{\mathbb{R}^3} |\psi|^2 &\geq \sum_{n=n_0}^{\infty} \frac{4\pi}{3}(r_n^3 - r_{n-1}^3)\psi(r_n)^2 \geq \pi B^2 \sum_{n=n_0}^{\infty} \frac{r_n^3 - r_{n-1}^3}{r_n^2} \\ &\geq \pi B^2 \sum_{n=n_0}^{\infty} (r_n - r_{n-1}) \frac{r_n^2 + r_n r_{n-1} + r_{n-1}^2}{r_n^2} = \infty,\end{aligned} \tag{A1}$$

where the first inequality uses that ψ is monotone decreasing. However, this is a contradiction. □

5. The excess charge

We know that $Q \in (-Z, \infty)$ for all $p \geq 1$. If $p \geq 4/3$, then $Q \in [Z, \infty)$, and if $p \geq 5/3$, i.e., the power of the classical Thomas-Fermi-Weizsäcker functional, then $Q > 0$ [Benguria *et al.*[2] (Theorem 1)].

Moreover, for all $\gamma \geq 0$ and $p > 1$,

$$Q < Z \tag{A2}$$

(see Lieb,[9] Theorem 7.23).

6. Virial theorems

There are two virial theorems that relate K, F, A, and R. Assume ψ to be a minimizer of $\mathcal{E}_p$. Then

$$T[\psi] + p\,F[\psi] - A[\psi] + 2R[\psi] = 0 \tag{A3}$$

and

$$T[\psi] + 3F[\psi] - 2A[\psi] + 5R[\psi] = 0. \tag{A4}$$

Multiplying (A3) by 5, (A4) by 2, and subtracting the results we obtain

$$0 = 3T[\psi] + (5p - 6)F[\psi] - A[\psi] \tag{A5}$$

and, if $p \geq 6/5$,

$$3T[\psi] \leq A[\psi]. \tag{A6}$$

To prove (A3) set $f(t) := \mathcal{E}_p(t\psi)$. Since f has a minimum at $t = 1$, we have $f'(1) = 0$. However, the left side of (A3) is simply $f'(1)/2$.

To prove (A4) introduce $g(t) := \mathcal{E}_p(\psi_t)$ with $\psi_t(x) := \psi(x/t)$. Again, g has a minimum for $t = 1$. Thus,

$$0 = g'(1) = T[\psi] + 3F[\psi] - 2A[\psi] + 5R[\psi], \tag{A7}$$

which proves (A4).

7. Basics on existence, uniqueness, and excess charge in generalized TF theory

In this section we are interested in the asymptotic behavior of the minimizing density of Thomas-Fermi type functionals, however, with a more general power p and also a more general external potential

$$V := |\cdot|^{-1} * \mu \tag{A8}$$

with $\mu \in M$ where we have the following.

Definition 2. M is the set of measures such that $\mathrm{supp}(\mu)$ *compact, and* $\mu(x) = \sum_{k=1}^{K} Z_k \delta(x - R_k)\mathrm{d}x + \sigma(x)\mathrm{d}x$ *with* $Z_1, \ldots, Z_k \geq 0$, $X_1, \ldots, X_k \in \mathbb{R}^3$, *and* $D[\sigma] < \infty$.

Note that the molecular case as defined in (2) is recovered by the choice $\sigma = 0$. The functional is defined as

$$\mathfrak{D}_p^{\mathrm{TF}} := \{\rho \in L^p(\mathbb{R}^3) | \rho \geq 0,\ D[\rho] := R[\sqrt{\rho}] < \infty\}. \tag{A9}$$

The generalized Thomas-Fermi functional is

$$\begin{aligned} &\mathcal{E}_p^{\mathrm{TF}} : \mathfrak{D}_p^{\mathrm{TF}} \to \mathbb{R}, \\ &\rho \mapsto \frac{1}{p}\int_{\mathbb{R}^3} \rho^p - \int_{\mathbb{R}^3} V\rho + D[\rho]. \end{aligned} \tag{A10}$$

Since in the atomic and molecular case the functional is unbounded from below for $p \leq 3/2$, we are mainly interested in $p > 3/2$. Before we continue, note that $D(\cdot,\cdot)$, the sesquilinear form associated with the quadratic form $D[\cdot]$, is a scalar product on the set of all tempered distributions μ for which $\int_{\mathbb{R}^3} \mathrm{d}\xi |\mathcal{F}(\mu)(\xi)|^2/|\xi|^2 < \infty$. In the following we will use $\eta := \delta(|x| - R)/(4\pi R^2)$. We also write $p' := p/(p-1)$ for the dual power of p. Then

Lemma 6. Assume $p > 3/2$, $\mu \in M$, and $V = \mu * |\cdot|^{-1}$. Then $\mathcal{E}_p^{TF}$ is bounded from below and coercive in the p-norm and the Coulomb norm. More precisely,

$$\mathcal{E}_p^{\mathrm{TF}}(\rho) \geq \frac{\gamma}{p}\|\rho\|_p^p - \frac{4\pi Z}{3 - p'}\|\rho_p\| - 2Z\sqrt{D[\rho]} + D[\rho]. \tag{A11}$$

Proof. Write $V_> := \eta * |\cdot|^{-1}$ and $V_< := |\cdot|^{-1} - V_>$. By Hölder's and Schwarz's inequality we have

$$\int_{\mathbb{R}^3} \mathrm{d}x V(x)\rho(x) = \sum_{k=1}^{K} Z_k \int_{\mathbb{R}^3} \mathrm{d}x (V_<(x-R_k)\rho(x) + V_>(x-R_k)\rho(x)) + 2D(\rho,\sigma)$$
$$\leq \sum_{k=1}^{K} Z_k \big(\|V_<\|_{p'} \|\rho\|_p + 2Z_k D(\eta,\rho) \big) + 2D(\sigma,\rho) \tag{A12}$$

and thus by the Schwarz inequality

$$\mathcal{E}_p^{\mathrm{TF}}(\rho) \geq \frac{\gamma}{p} \|\rho\|_p^p - Z\|V_<\|_{p'}\|\rho\|_p - Z\sqrt{D[\eta]D[\rho]} - \sqrt{D[\rho]D[\sigma]} + D[\rho] \tag{A13}$$

from which the claim follows, since $0 \leq V_<(x) \leq 1/|x|$, and therefore in $L^{p'}$. □

The Euler equation for the minimizer ρ^{TF} of (A10)—generalizing the classical Thomas-Fermi equation—reads

$$\rho^{p-1} = \phi_+,\ \ \phi = V - \rho * |\cdot|^{-1}. \tag{A14}$$

Lemma 7. Assume $p > 3/2$. *Then* $\mathcal{E}_p^{TF}$ *has a unique minimizer* ρ^{TF} *in* $\mathfrak{D}_p$. *The minimizer fulfills (A14). Moreover, any solution* $\rho^{TF} \in \mathfrak{D}_p$ *of (A14) minimizes* $\mathcal{E}_p^{TF}$.

As the proof is a standard compactness and convexity argument similar to the classical Thomas-Fermi case (Lieb and Simon[11]) we skip its proof and remark that it holds also for the molecular case.

Lemma 8. If ρ^{TF} *is a minimizer of* $\mathcal{E}_p^{TF}$ *for* $p > 3/2$. *Then* $\int_{\mathbb{R}^3} \rho^{TF} = Z$ *and* $\varphi \geq 0$. *Moreover* ρ^{TF} *is spherically symmetric in the atomic case.*

Proof. The well known proof of the classical case using subharmonicity transcribes to the general case. Instead we give a simple variational proof for the atomic case: Suppose $Q < 0$. Then, by (A14), there are $R, \epsilon > 0$ such that $\varphi(x) \geq \epsilon/|x|$ for $|x| \geq R$. Thus $\rho^{\mathrm{TF}}(x) \gtrsim \rho_R(x) := |x|^{-\frac{1}{p-1}}$ for $|x| > R$. But

$$D[\rho_R] \gtrsim \int_R^\infty \mathrm{d}r \int_R^\infty \mathrm{d}s \frac{r^2 s^2}{\max\{r^{\frac{1}{p-1}}, s^{\frac{1}{p-1}}\}} = \infty \tag{A15}$$

for $p \geq 4/3$.

Suppose $Q > 0$. Then, pick $R := \inf\{s \big| \int_{|x|<s} \mathrm{d}x \rho^{\mathrm{TF}}(x) \geq Z\}$. By assumption $R < \infty$. Now, define $\rho_R(x) := \rho^{\mathrm{TF}}(x)\theta(R - |x|)$ and $\rho_> := \rho^{\mathrm{TF}} - \rho_R$ which by uniqueness of ρ^{TF} are spherically symmetric. We compute

$$\mathcal{E}_p^{\mathrm{TF}}(\rho_R) - \mathcal{E}_p^{\mathrm{TF}}(\rho^{\mathrm{TF}}) < -\int_{\mathbb{R}^3} \mathrm{d}x \frac{\rho_>(x)}{|x|} + 2D(\rho_R,\rho_>) - D[\rho_>] = -D[\rho_>] < 0, \tag{A16}$$

where the last equality holds because of Newton's theorem. Thus ρ^{TF} cannot be a minimizer which is a contradiction.

By spherical symmetry and Newton's theorem it follows that $\varphi \geq 0$. □

Note that we proved Lemma 8 by a simple and direct variational argument using the spherical symmetry; however, the theorem can be also be proven in the molecular case using subharmonic estimates like Lieb and Simon[11] did. Since this amounts to a mere transcriptions we skip it here.

8. The Sommerfeld solution of generalized Thomas-Fermi theory and bounds on the physical solution

In this appendix we allow for more general external potentials than (2).

The classical atomic Sommerfeld solution $S_{\frac{5}{3}}(x) = 9\gamma^3/(\pi^2|x|^4)$ solves $\Delta S_{\frac{5}{3}} = 4\pi S_{\frac{5}{3}}^{\frac{3}{2}}$ on $\dot{\mathbb{R}}^3 := \mathbb{R}^3\setminus\{0\}$ and bounds the classical atomic Thomas-Fermi potential from above. This generalizes to more general p:

Lemma 9. Pick $p \in (3/2, 2)$,

$$b(p) := \left(\frac{(p-1)(3p-4)}{2\pi(2-p)^2}\right)^{\frac{p-1}{2-p}},\ \textit{and}\ \sigma := \frac{2(p-1)}{2-p}. \tag{A17}$$

Then

$$S_p(x) := s_p(|x|) := b(p)|x|^{-\sigma} \tag{A18}$$

solves the generalized differential Thomas-Fermi equation

$$\Delta S_p = 4\pi S_p^{\frac{1}{p-1}} \tag{A19}$$

on $\dot{\mathbb{R}}^3$ *and for the atomic case, i.e.,* $\mu = Z\delta$,

$$\phi \le S_p \tag{A20}$$

on $\dot{\mathbb{R}}^3$.

Proof. Inserting (A18) into (A19) yields

$$\frac{b(p)}{r^{\frac{2(p-1)+4-2p}{2-p}}}\left[\frac{2(p-1)}{2-p}\frac{2p-2+2-p}{2-p} - 2\frac{2(p-1)}{2-p}\right] = 4\pi b(p)^{\frac{1}{p-1}} r^{-\frac{2}{2-p}}, \tag{A21}$$

which is equivalent with

$$b(p)\left[\frac{2(p-1)}{2-p}\frac{p}{2-p} - 2\frac{2(p-1)}{2-p}\right] = 4\pi b(p)^{\frac{1}{p-1}} \tag{A22}$$

or

$$\frac{2(p-1)(3p-4)}{(2-p)^2} = 4\pi b(p)^{\frac{2-p}{p-1}}. \tag{A23}$$

Inserting the definition of $b(p)$ from (A18) gives identical left and right sides of (A19).

The bound (A20) follows then from the maximum principle, since the inequality is certainly true in a neighborhood of zero, since $\phi(x) \le Z/|x|$ and both $\phi(x), S_p(x) \to 0$ as $x \to \infty$. □

Lemma 10. Suppose $p \in (3/2, 2)$, *V as in Lemma* 6, ρ^{TF} *is the minimizer of* $\mathcal{E}_p^{TF}$, $\phi := V - \rho^{\mathrm{TF}} * |\cdot|^{-1}$, *and*

$$a(p) := \left(\frac{(p-1)p}{2\pi(2-p)^2}\right)^{\frac{p-1}{2-p}}, \text{ and } \sigma := \frac{2(p-1)}{2-p}. \tag{A24}$$

Then for $|x| > R$,

$$\Delta\phi = 4\pi\phi^{\frac{1}{p-1}} \tag{A25}$$

and

$$\phi(x) \le S_{p,R}(x) := s_{p,R}(|x|) := \frac{a(p)}{(|x| - R)^{\sigma}}. \tag{A26}$$

Proof. The generalized Thomas-Fermi Eq. (A14) and Poisson's equation $\Delta\varphi = 4\pi\rho^{\mathrm{TF}}$ imply (A25).

To show (A26) we first show that on the complement of $\overline{B_R(0)}$,

$$\Delta S_{p,R} \le 4\pi S_{p,R}^{\frac{1}{p-1}} : \tag{A27}$$

$$\begin{aligned} s''_{p,R}(r) + \frac{2}{r}s'_{p,R}(r) &= \sigma(\sigma+1)\frac{a(p)}{(r-R)^{\sigma+2}} - 2\sigma\frac{a(p)}{r(r-R)^{\sigma+1}} \\ &\le \frac{\sigma(\sigma+1)}{4\pi}a(p)^{-\frac{2-p}{p-1}}4\pi s_{p,R}(r)^{\frac{1}{p-1}} = 4\pi s_{p,R}(r)^{\frac{1}{p-1}} \end{aligned} \tag{A28}$$

and that the inequality is true on $\partial B_R(0)$ and both $S_{p,R}$ and ϕ tend to zero at infinity. Thus, the inequality follows for all $|x| > R$ by subharmonicity. □

Now we turn the Sommerfeld solution with a leading remainder term extending a result by Brezis and Lieb,[5] Solovej[14] (Lemma 11)[15] (Lemma 4.4). We will largely follow his proof.

Lemma 11. Pick $p \in (3/2, 2)$, *V as in Lemma* 6,

$$\zeta := \frac{-5p + 6 + \sqrt{p^2 + 20p - 28}}{2(2-p)}, \tag{A29}$$

and a smooth function π on $B_R(0)^c$ fulfilling

$$\Delta\phi = 4\pi\phi^{\frac{1}{p-1}}. \tag{A30}$$

Moreover, define

$$a(R) := \liminf_{r\searrow} \sup_{|x|=r} \left[\left(\frac{\phi(x)}{s_{p,\gamma}(|x|)}\right)^{-\frac{1}{2}} - 1\right]|x|^{\zeta}, \tag{A31}$$

$$A(R) := \liminf_{r\searrow} \sup_{|x|=r} \left[\frac{\phi(x)}{s_{p,\gamma}(|x|)} - 1\right]|x|^{\zeta}. \tag{A32}$$

Then on $B_R(0)^c$,

$$(1 + a(R)|x|^{-\zeta})^{-\frac{p-1}{p-2}} s_{p,\gamma}(|x|) \le \phi(x) \le (1 + A(R)|x|^{-\zeta}) s_{p,\gamma}(|x|). \tag{A33}$$

Note that for the classical exponent $p = 5/3$, $\zeta = (\sqrt{73} - 7)/2$ which agrees with[15] (Lemma 4.4).

Proof. We start by proving that ϕ tends to zero at infinity. To this end, pick $L > 4R$ and define the function $f(x) := C(s_{p,\gamma}(r - L/4) + s_{p,\gamma}(L - r))$ on $(L/4, L)$ writing $r := |x|$:

$$\begin{aligned}
\Delta f(x) &= C\Big(S''(r - L/4) + \frac{2}{r}S'(r - L/4) + S''(L - r) - \frac{2}{r}S'(L - r)\Big)\\
&= Cb(p)\gamma^{\frac{1}{2-p}}\Bigg[\frac{2(p-1)(2p-2+2-p)}{(2-p)^2}\frac{1}{(r-\frac{L}{4})^{\frac{2p-2+4-2p}{2-p}}} - \frac{2}{r}\frac{2(p-1)}{2-p}\frac{1}{(r-\frac{L}{4})^{\frac{p}{2-p}}}\\
&\qquad + \frac{2(p-1)(2p-2+2-p)}{(2-p)^2}\frac{1}{(L-r)^{\frac{2p-2+4-2p}{2-p}}} + \frac{2}{r}\frac{2(p-1)}{2-p}\frac{1}{(L-r)^{\frac{p}{2-p}}}\Bigg]\\
&= Cb(p)\gamma^{\frac{1}{2-p}}\frac{2(p-1)}{2-p}\\
&\qquad\times\left[\frac{p}{2-p}\frac{1}{(r-\frac{L}{4})^{\frac{2}{2-p}}} - \frac{2}{r}\frac{1}{(r-\frac{L}{4})^{\frac{p}{2-p}}} + \frac{p}{2-p}\frac{1}{(L-r)^{\frac{2}{2-p}}} + \frac{2}{r}\frac{1}{(L-r)^{\frac{p}{2-p}}}\right].
\end{aligned} \tag{A34}$$

We wish to estimate the sum of the second and fourth term of the last bracket by a multiple of the third one, i.e., show that

$$-\frac{2}{r}\frac{1}{(r-\frac{L}{4})^{\frac{p}{2-p}}} + \frac{2}{r}\frac{1}{(L-r)^{\frac{p}{2-p}}} \le D\frac{1}{(L-r)^{\frac{2}{2-p}}}. \tag{A35}$$

By scaling it is sufficient to show this for $L = 1$, i.e.,

$$-\frac{2}{r}\frac{1}{(r-\frac{1}{4})^{\frac{p}{2-p}}} + \frac{2}{r}\frac{1}{(1-r)^{\frac{p}{2-p}}} \le D\frac{1}{(1-r)^{\frac{2}{2-p}}}, \tag{A36}$$

which is equivalent with

$$-2(1-r)^{\frac{2}{2-p}} + 2(1-r)(r-\frac{1}{4})^{\frac{p}{2-p}} \le Dr(r-\frac{1}{4})^{\frac{p}{2-p}} \tag{A37}$$

or

$$-2(1-r)^{\frac{2}{2-p}} + 2(r-\frac{1}{4})^{\frac{p}{2-p}} \le (D-2)r(r-\frac{1}{4})^{\frac{p}{2-p}}, \tag{A38}$$

which is fulfilled if

$$-2(1-r)^{\frac{2}{2-p}} + 2(r-\frac{1}{4})^{\frac{p}{2-p}} \le \frac{D-2}{4}(r-\frac{1}{4})^{\frac{p}{2-p}} \tag{A39}$$

holds, since $r > L/4$. This is equivalent with

$$-2(1-r)^{\frac{2}{2-p}} \le \left(\frac{D}{4} - \frac{5}{2}\right)(r-\frac{1}{4})^{\frac{p}{2-p}} = 0, \tag{A40}$$

which is true, since we picked $D = 10$. Thus we get altogether

$$\Delta f(x) \le Cb(p)\gamma^{\frac{1}{2-p}}\frac{2(p-1)}{2-p}\left[\frac{p}{2-p}\frac{1}{(r-\frac{L}{4})^{\frac{2}{2-p}}} + \frac{20-10p+p}{2-p}\frac{1}{(L-r)^{\frac{2}{2-p}}}\right]$$
$$= Cb(p)\gamma^{\frac{1}{2-p}}\frac{2(p-1)}{(2-p)^2}\left[p\frac{1}{(r-\frac{L}{4})^{\frac{2}{2-p}}} + (20-9p)\frac{1}{(L-r)^{\frac{2}{2-p}}}\right]. \tag{A41}$$

Moreover, for $p \in (1,2)$,

$$f(r)^{\frac{1}{p-1}} \ge C^{\frac{1}{p-1}}\left(s_{p,\gamma}(r-L/4)^{\frac{1}{p-1}}\right). \tag{A42}$$

Thus, for each p and γ there is a constant C such that for all $L > 4R$ f is a supersolution of the generalized differential TF equation, i.e.,

$$\Delta f \le 4\pi f^{\frac{1}{p-1}} \tag{A43}$$

on $M_L := \overline{B_L(0)}\backslash B_{L/4}(0)$. Thus the maximum principle implies $f \ge \phi$ on A_L and $\sup_{|x|=L/2}\phi(x) \lesssim_p L^{\frac{2(p-1)}{2-p}}$. Thus $\phi(x)|x|^{\frac{2(p-1)}{2-p}}$ is bounded for $|x| > R$.

Next we turn to the main estimate. For any $k \in \mathbb{R}$ we define

$$\omega_k^+(x) := (1 + k|x|^{-\zeta})s_p(|x|), \tag{A44}$$

$$\omega_k^-(x) := (1 + k|x|^{-\zeta})^{-\frac{p-1}{p-2}}s_p(|x|). \tag{A45}$$

If we pick $R' > R$ and set $k = A' := A(R')$ and $k = a' := a(R')$ then $\omega_{A'}^+$ and $\omega_{a'}^+$ are right and left side of the main estimate (A33) but at R' instead of R.

We claim that

$$\Delta\omega_k^+ \le 4\pi(\omega_k^+/\gamma)^{\frac{1}{p-1}} \text{ and } \Delta\omega_k^- \ge 4\pi(\omega_k^-/\gamma)^{\frac{1}{p-1}}. \tag{A46}$$

[The first inequality for $p = 5/3$ was known to Brezis and Lieb (first inequality above Proposition A.5 in Ref. 5).]

Since $\omega_{A'}^+(R') = \phi(R') = \omega_{a'}^-(R')$ and since both functions tend to zero at infinity, this would imply the claim is true by a standard application of the maximum principle and taking the limit $R' \to R$.

Thus it remains to show that (A46) is really true. We compute starting with the supersolution:

$$\Delta\omega_k^+(x) = \left(S''(|x|) + \frac{2}{|x|}S'(|x|)\right)(1 + \frac{k}{|x|^\zeta}) - 2S'(|x|)k\frac{\zeta}{|x|^{\zeta+1}} + s_{p,\gamma}(|x|)k\frac{\zeta(\zeta+1)-2\zeta}{|x|^{\zeta+2}}$$
$$= 4\pi\left(\frac{s_{p,\gamma}(r)}{\gamma}\right)^{\frac{1}{p-1}}(1+\frac{k}{r^\zeta}) + s_{p,\gamma}(r)k\zeta r^{-\zeta-2}\left(2^2\frac{p-1}{p-2} + \zeta - 1\right)$$
$$= 4\pi\left(\frac{s_{p,\gamma}(r)}{\gamma}\right)^{\frac{1}{p-1}}(1+\frac{k}{r^\zeta}) + s_{p,\gamma}(r)k\zeta\left(\frac{s_{p,\gamma}(r)}{b(p)\gamma^{\frac{1}{2-p}}}\right)^{\frac{2-p}{p-1}}r^{-\zeta}\left(\frac{5p-6}{p-2}+\zeta\right)$$
$$= 4\pi\left(\frac{s_{p,\gamma}(r)}{\gamma}\right)^{\frac{1}{p-1}}\left[1 + \frac{k}{r^\zeta} + \frac{k\zeta}{4\pi b(p)^{\frac{2-p}{p-1}}r^\zeta}\left(\frac{5p-6}{p-2}+\zeta\right)\right]$$
$$= 4\pi\left(\frac{\omega_k^+}{\gamma}\right)^{\frac{1}{p-1}}\frac{1+\frac{k}{r^\zeta}\left[1+\frac{2\pi(p-2)^2\zeta}{4\pi(p-1)(3p-4)}\left(\frac{5p-6}{p-2}+\zeta\right)\right]}{(1+kr^{-\zeta})^{\frac{1}{p-1}}}. \tag{A47}$$

Thus, the claim would follow if the big fraction of the last line is not bigger than one. Since $p - 1 \le 1$, it suffices to show that

$$1 + \frac{k}{r^\zeta}\left[1 + \frac{(p-2)^2}{2(p-1)(3p-4)}\zeta\left(\frac{3p-2}{p-2}+\zeta\right)\right] \le 1 + (p-1)^{-1}kr^{-\zeta} \tag{A48}$$

or

$$\frac{(p-2)^2}{2(3p-4)}\zeta\left(\frac{5p-6}{p-2}+\zeta\right) \le 2-p, \tag{A49}$$

which is fulfilled, if

$$\zeta^2 + \frac{5p-6}{2-p}\zeta = 2\frac{3p-4}{2-p}, \tag{A50}$$

which true for the chosen ζ.

Next we treat the subsolution

$$\begin{aligned}
\Delta\omega^-_{a'}(x) \geq{}& \left(S''(r) + \frac{2}{|x|}S'(r)\right)\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{p-1}{2-p}} + 2S'(r)\frac{p-1}{2-p}\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta}{r^{\zeta+1}}\\
&+ s_{p,\gamma}(r)\frac{p-1}{2-p}\left[-\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta(\zeta+1)}{r^{\zeta+2}} + 2\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta}{r^{\zeta+2}}\right]\\
={}& \frac{4\pi}{\gamma^{\frac{1}{p-1}}}s_{p,\gamma}(r)^{\frac{1}{p-1}}\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{p-1}{2-p}}\\
&+ \frac{s_{p,\gamma}(r)}{r^2}\frac{(p-1)}{2-p}\left[-\frac{4(p-1)}{2-p}\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta}{r^\zeta} - \left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta(\zeta-1)}{r^\zeta}\right]\\
={}& \frac{4\pi}{\gamma^{\frac{1}{p-1}}}s_{p,\gamma}(r)^{\frac{1}{p-1}}\left\{\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{p-1}{2-p}} + \frac{2\pi(2-p)^2}{4\pi(p-1)(3p-4)}\frac{(p-1)}{2-p}\right.\\
&\left.\times\left[-\frac{4(p-1)}{2-p}\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta}{r^\zeta} - \left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta(\zeta-1)}{r^\zeta}\right]\right\}\\
={}& \frac{4\pi}{\gamma^{\frac{1}{p-1}}}s_{p,\gamma}(r)^{\frac{1}{p-1}}\left\{\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{p-1}{2-p}}\right.\\
&\left.+\frac{1}{2}\frac{2-p}{3p-4}\left[-\frac{4(p-1)}{2-p}\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta}{r^\zeta} - 2\left(1+\frac{a'}{r^\zeta}\right)^{-\frac{1}{2-p}}\frac{a'\zeta(\zeta-1)}{r^\zeta}\right]\right\}\\
={}& \frac{4\pi}{\gamma^{\frac{1}{p-1}}}\omega^-_{a'}(r)^{\frac{1}{p-1}}\left\{1+\left[1-2\frac{p-1}{3p-4}\zeta - \frac{1}{2}\frac{2-p}{3p-4}\zeta(\zeta-1)\right]\frac{a'}{r^\zeta}\right\} = \frac{4\pi}{\gamma^{\frac{1}{p-1}}}\omega^-_{a'}(r)^{\frac{1}{p-1}},
\end{aligned} \tag{A51}$$

where we drop a non-negative summand containing $(a'\zeta)^2$ in the first inequality and use (A29) in the last step. Thus $\omega^-_{a'}$ is indeed a subsolution. The result follows by taking the limits $\lim_{r'\searrow r} a(r')$ and $\lim_{r'\searrow r} A(r')$. □

Equipped with two atomic supersolutions, namely $S_{p,R}$ and ω^+_k, of the generalized Thomas-Fermi equation suggests that the pointwise minimum bounds ϕ from above. This would improve the bound for large r, since the coefficient $a(p)$ of the leading term of $S_{p,R}$ for large r is larger than the coefficient $b(p)$ of the leading term of ω^+_k. In fact this is true:

Lemma 12. Assume $p \in (3/2, 2)$, $r > R > 0$, $k \in \mathbb{R}^3$, ζ as in (A29), and ω^+_k as defined in (A44). Then

$$\phi(r) \leq \sigma_p(r) := \min\{s_{p,R}(r), \omega^+_k(r)\}. \tag{A52}$$

Proof. Both functions are supersolutions of the Thomas-Fermi equation and $s_{p,R}(r) \geq \phi(r)$. Moreover, the two function have exactly one point of intersection r_0 for $r > R$. Thus $\omega^+_k(r_0) = s_{p,R}(r_0) \geq \phi(r_0)$. Since $\omega^+_k(r) \to 0$ as $r \to \infty$ we have $\omega^+_k(r) \geq \phi(r)$ for $r \geq r_0$. □

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