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Bound on the Ionization Energy of Large Atoms

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Abstract. We present a simple argument which gives a bound on the ionization energy of large atoms that implies the bound on the excess charge of Fefferman and Seco [2].

1. Introduction

A system consisting of a nucleus of charge Z and N electrons is described by the Schrödinger operator

$$H_{N,Z} = \sum_{i}^{N}\left(-\Delta_i - \frac{Z}{|x_i|}\right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \tag{1}$$

acting on the antisymmetric space $\mathscr{H}_F = \bigwedge_{i=1}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^2)$. Here we have assumed for simplicity that the nucleus is infinitely heavy. We call such a system an atom.

The **ground state energy** of the atom is

$$E(N,Z) = \inf \operatorname{spec}_{\mathscr{H}_F} H_{N,Z} \tag{2}$$

and the **ionization energy** is defined as

$$I(N,Z) = E(N-1,Z) - E(N,Z). \tag{3}$$

This is the energy which binds the atom together. It is well known that there is a critical number of electrons $N_c(Z)$ such that

$$I(N_c, Z) > 0 \quad \text{and} \quad I(N,Z) = 0 \quad \text{if} \quad N > N_c$$

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(see [11, 12, 15, 16]). Using a variational estimate one can derive the lower bound $N_c(Z) \geqq Z$ ([20]). It was shown in [8] and [17] (for large Z) that $N_c(Z) < 2Z + 1$. Define the **excess charge** as

$$Q_c(Z) = N_c(Z) - Z. \tag{4}$$

For $N \leqq N_c$ the operator $H_{N,Z}$ has a ground state $\psi_{N,Z} \in \mathscr{H}_F$.

We define the **radius** $R(N, Z)$ of the atom by

$$\int_{|x| \leqq R(N,Z)} \rho_{N,Z} dx = N - 1, \tag{5}$$

where $\rho_{N,Z}$ is the **one-electron density**

$$\rho_{N,Z}(x) = N \sum_{\sigma = 1,2} \int |\psi_{N,Z}(x, \sigma; x_2, \sigma_2; \cdots; x_N, \sigma_N)|^2 d(x_2, \sigma_2) \cdots d(x_N, \sigma_N),$$

x_i are the space variables and σ_i the spin variables, $\int d(x, \sigma) = \sum_\sigma \int dx$. (Throughout most of the paper explicit mention of the spin variables will be omitted.) Outside $R(N, Z)$ there is an average of one electron.

It is expected that as $Z \to \infty$

$$Q_c(Z), I(Z, Z), R(Z, Z) = O(1). \tag{6}$$

In Thomas–Fermi theory it has been known for some time that as $Z \to \infty$ the atomic structure shows a universal behavior, which is to say that the quantities in (6) actually converge to non-zero values as $Z \to \infty$ (see [7]). In the present paper we will indeed compare with TF theory. In the Thomas–Fermi–von Weizsäcker theory universality was recently proved in [18].

It follows from [8, 17] that

$$Q_c(Z) \leqq CZ, \quad I(Z, Z) \leqq CZ^{4/3} \quad \text{and} \quad R(Z, Z) \geqq CZ^{-1/3}. \tag{7}$$

In [9] it was proved that $Q_c(Z) = o(Z)$. This has recently been improved in [2] (an announcement was made in [3]) to $Q_c(Z) \leqq CZ^{1-\alpha}$ with $\alpha = 9/56$.

Our main result is

Theorem 1. *For $Z \leqq N \leqq N_c$ and with $\alpha = 9/56$,*

$$I(N, Z) \leqq C_1 Z^{(4/3)(1-\alpha)} - C_2 (N - Z) Z^{(1/3)(1-\alpha)}. \tag{8}$$

We get as an immediate consequence

Corollary 2.

$$Q_c(Z) \leqq CZ^{1-\alpha},$$

and for $N \geqq Z$,

$$I(N, Z) \leqq CZ^{(4/3)(1-\alpha)}.$$

As a very easy consequence of the proof of Theorem 1 we also find (see Lemma 7)

Theorem 3. *For $N \geqq Z$,*

$$R(N, Z) \geqq CZ^{-(1/3)(1-\alpha)}. \tag{9}$$

We prove Theorem 1 by first proving a general estimate on $I(N,Z)$ which for an arbitrary radius R bounds I in terms of quantities we call the screening charge at radius R, the excess charge at radius R, and the 2-point correlation outside R. This general bound is given in Sect. 2. In Sect. 4 we estimate the above quantities.

Our method emphasizes the importance of controlling the 2-point correlation function

$$\rho^{(2)}(x,y) = N(N-1) \sum_{\sigma_1,\sigma_2} \int |\psi(x,\sigma_1; y,\sigma_2; \cdots; x_N,\sigma_N)|^2 d(x_3,\sigma_3)\cdots d(x_N,\sigma_N),$$

(we will often omit the subscripts N,Z). In fact the key step is to estimate the truncated correlation function

$$\rho^{(2)}(x,y) - \rho(x)\rho(y),$$

where $\rho = \rho_{N,Z}$, this is done in Sect. 3 Lemma 5.

Now we explain the origin of the number α in (8). Define the effective particle (or quasiparticle in physicists' terminology) Hamiltonian

$$H^{\mathrm{ind}}_{N,Z} = \sum_{i=1}^{N} (-\Delta_i - \phi(x_i)) - D_{\mathrm{TF}}$$

acting on $\mathscr{H}_F$. Here ϕ is the smeared Thomas–Fermi potential

$$\phi(x) = \frac{Z}{|x|} - \frac{1}{|x|} * \rho_{\mathrm{TF}}(x), * \varphi,$$

with a C_0^∞ cut-off function φ introduced in (12) below, where ρ_{TF} is the Thomas–Fermi density for a neutral atom with nuclear charge Z (see [7] for a review of Thomas–Fermi theory), and

$$D_{\mathrm{TF}} = \iint \frac{\rho_{\mathrm{TF}}(x)\rho_{\mathrm{TF}}(y)}{|x-y|}.$$

It is a fundamental result of Lieb and Simon ([10], see also [7] and [19] for a proof) that there exists $0 < b$ such that for $N \geqq Z - \text{const}$,

$$H^{\mathrm{ind}}_{N,Z} \geqq E(N,Z) - CZ^{7/3-b} \tag{10}$$

for some constant C. Finding the optimal b is a hard problem requiring an understanding of the ground state structure. Presently the best known result is $b \geqq 3/8$ ([4, 13, 14] the previous result in [7], was $b \geqq 1/30$). This estimate involves the proof of the Scott conjecture. It is believed that the optimal value for b is $2/3$. Our arguments hold as long as $b \leqq 2/3$.

Note that in the result of [2] as well as in our result $\alpha = 3b/7$.

2. General Argument

Given δ, choose $\theta_1 \in C^\infty(\mathbb{R}_+)$ with $0 \leqq \theta_0 \leqq 1$, and $\theta_1(t) = 0$ if $t \leqq 1-\delta$, $\theta_1(t) = 1$ if $t \geqq 1$.

For all R, let θ_R and $\lambda_R: \mathbb{R}^3 \mapsto \mathbb{R}^3$ be given by

$$\theta_R(x) = \theta_1(|x|/R)^2 \quad \text{and} \quad \lambda_R(x) = (1 - \theta_R(x)).$$

We define (δ is fixed):

the excess charge at radius R,

$$Q(R)=\int \rho(x)\theta_R(x)dx,$$

the screening charge at radius R,

$$v(R)=Z-\frac{1}{Q(R)}\int \rho^{(2)}(x,y)\frac{|x|}{|x-y|}\theta_R(x)\lambda_R(y)dx\,dy,$$

the normalized 2-point correlation outside R,

$$K(R)=\frac{1}{Q(R)}\int \rho^{(2)}(x,y)\theta_R(x)\theta_R(y)dx\,dy.$$

We will prove an upper bound to the ionization energy in terms of these quantities by using a very simple trick which goes back to Benguria (see [7]) and was used in [8] to prove $N_c<2Z+1$. The idea here is to use the trick on the outside problem ($|x|>R$). The same method was used in [18]. Below, $\delta>0$ is fixed and the dependence on δ of quantities of interest and constants is not displayed.

Theorem 4. *For all* $\delta>0$ *and* $R>0$,

$$I\leqq[v(R)-\tfrac{1}{2}K(R)]R^{-1}+X(R), \tag{11}$$

where the error term is bounded by

$$X\leqq cR^{-2}\frac{Q(R(1-\delta))}{Q(R)}.$$

Proof. From the IMS formula (see *e.g.* [1]) we find

$$\begin{aligned}E_{N,Z}\int \rho(x)|x|\theta_R(x)dx&=\sum_i\langle\psi_{N,Z}|\theta_R(x_i)|x_i|H_{N,Z}|\psi_{N,Z}\rangle\\&=\sum_i\langle\psi_{N,Z}|\theta_R(x_i)^{1/2}|x_i|^{1/2}H_{N,Z}\theta_R(x_i)^{1/2}|x_i|^{1/2}|\psi_{N,Z}\rangle\\&\quad-\sum_i\langle\psi_{N,Z}||\nabla(\theta_R(x_i)^{1/2}|x_i|^{1/2})|^2|\psi_{N,Z}\rangle.\end{aligned}$$

Isolating the contribution of the i^{th} electron in the i^{th} term in the first sum on the right-hand side, we obtain

$$\begin{aligned}E_{N,Z}\int\rho(x)|x|\theta_R(x)dx&\geqq E_{N-1,Z}\int\rho(x)|x|\theta_R(x)dx\\&\quad+\sum_i\left\langle\psi_{N,Z}\left|\theta_R(x_i)|x_i|\left(-\frac{Z}{|x_i|}+\sum_{j,j\neq i}\frac{1}{|x_j-x_i|}\right)\right|\psi_{N,Z}\right\rangle\\&\quad-\sum_i\int|\nabla(\theta_R(x_i)^{1/2}|x_i|^{1/2})|^2|\psi|^2dx.\end{aligned}$$

Using $|\nabla(\theta_R(x)^{1/2}|x|^{1/2})|\leqq cR^{-1}\theta_{(1-\delta)R}(x)$ and $\int\rho(x)|x|\theta_R(x)dx\geqq RQ(R)$, we rewrite this inequality as

$$-RIQ(R)\geqq -ZQ(R)+\int\rho^{(2)}(x,y)\frac{|x|}{|x-y|}\theta_R(x)dx\,dy-cQ(R(1-\delta))R^{-1}.$$

In [8] the error term (the last term above) could be ignored by use of the uncertainty principle: $\int(\nabla u)^2 \geqq (1/4)\int u^2/|x|^2$. Here the uncertainty principle can be used to improve c, but this is not necessary.

The trick is now to symmetrize and use the triangle inequality

$$RIQ(R) \leqq v(R)Q(R) - \int \rho^{(2)}(x,y)\frac{|x|}{|x-y|}\theta_R(x)\theta_R(y)dx\,dy + cQ(R(1-\delta))R^{-1}$$

$$= v(R)Q(R) - \tfrac{1}{2}\int \rho^{(2)}(x,y)\frac{|x|+|y|}{|x-y|}\theta_R(x)\theta_R(y)dx\,dy + cQ(R(1-\delta))R^{-1}$$

$$\leqq v(R)Q(R) - \tfrac{1}{2}K(R)Q(R) + cQ(R(1-\delta))R^{-1}. \quad \blacksquare$$

3. Estimates on the Density and Correlation Function

The idea of comparing the exact charge distribution with the Thomas–Fermi one goes back to [10] with an effective estimate derived in [2]. We extend this idea and, in particular, the method of [2] further to estimates of the 2-point correlation. Choose $\varphi_1 \in C_0^\infty(\mathbb{R}^3)$ radially symmetric, positive and with $\int \varphi_1 = 1$. Let

$$\varphi(x) = \varphi_Z(x) = Z^2\varphi_1(Z^{2/3}x), \tag{12}$$

then $\int \varphi = 1$. With ρ_{TF} the Thomas–Fermi density for a neutral atom with nuclear charge Z, we define a function $K_N:\mathbb{R}^{3N}\to\mathbb{R}_+$ by

$$K_N(x_1,\dots,x_N) = D\left(\sum_{i=1}^N \varphi(\cdot - x_i) - \rho_{\mathrm{TF}}, \sum_{i=1}^N \varphi(\cdot - x_i) - \rho_{\mathrm{TF}}\right), \tag{13}$$

where

$$D(f,g) = \tfrac{1}{2}\iint f(x)|x-y|^{-1}g(x)dx\,dy.$$

We derive the key inequality from [2], i.e., (15) below, which also plays an essential role in our analysis. Main steps in this derivation go back to [6]. The first step is to smear the point charges. Namely using Newton's screening Theorem, one obtains

$$\sum_{1\leqq i<j\leqq N} |x_i - x_j|^{-1} \geqq D(\rho_{\underline{x}}, \rho_{\underline{x}}) - cZ^{5/3}, \tag{14}$$

where

$$\rho_{\underline{x}} = \sum_{i=1}^N \varphi(x - x_i), \quad \underline{x} = (x_1,\dots,x_N),$$

is the random variable for the smeared charge density and the last term in (14) comes from the self-energy, $D(\varphi,\varphi)$ of the smeared charges.

The next idea is that in the ground state $\rho_{\underline{x}}$ must look essentially as ρ_{TF}. With this in mind we write

$$D(\rho_{\underline{x}}, \rho_{\underline{x}}) = \int \rho_{\underline{x}}(|x|^{-1} * \rho_{\mathrm{TF}})dx + K_N(\underline{x}) - 2D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}).$$

The last two relations lead to the representation

$$H_{N,Z} \geqq H_{N,Z}^{\mathrm{ind}} + K_N(\underline{x}) + O(Z^{5/3}).$$

Combining this with (10), we arrive at the desired operator estimate

$$H_{N,Z} \geqq E(N,Z) + K_N(x_1,\dots,x_N) - C_0 Z^{7/3-b}. \tag{15}$$

As with (10) this estimate is proven only for N with $Z - \text{const} \leqq N$.

Our main estimate is

Lemma 5. *Given* $\sqrt{\theta} \in C^\infty(\mathbb{R}^3)$ *with* $0 \leqq \theta \leqq 1$, $\operatorname{supp}\theta \subset \{|x| \geqq R\}$ *and* $|\nabla\sqrt{\theta}| < c_1 R^{-1}$ *and* $\chi \in C^\infty(\mathbb{R}^3 \times \mathbb{R}^3)$ *with* $0 \leqq \chi$ *and* $\chi_x = \chi(x,\cdot)$ *compactly supported. Then for all* N *with* $Z \leqq N \leqq N_c(Z)$,

$$\begin{aligned}&\left|\int [\rho^{(2)}(x,y) - \rho_{\mathrm{TF}}(y)\rho(x)]\theta(x)\chi(x,y)\,dx\,dy\right| \\ &\leqq C \sup_x \|\nabla_y \chi_x\|_{L^2(\mathbb{R}^3)} \{(Z^{(7/3-b)} + ZR^{-1})\textstyle\int \rho(x)\theta(x)dx + ZR^{-2}\}^{1/2} \\ &\quad \cdot \{\textstyle\int \rho(x)\theta(x)dx\}^{1/2} + CZ^{1/3}\|\nabla_y\chi\|_{L^\infty}\textstyle\int\rho(x)\theta(x)dx,\end{aligned} \tag{16}$$

where ρ *and* $\rho^{(2)}$ *are the ground state density and correlation function.* C *depends only on* C_0 *and* φ_1.

Remark. The reason for the rather peculiar cutoff in (16) will be clear in Lemma 8 below.

Proof. Define the particle number random variables $N_x : \mathbb{R}^{N-1} \to \mathbb{R}_+$ and $N_x^{\mathrm{TF}} \in \mathbb{R}_+$ by

$$N_x(x_2,\dots,x_N) = \sum_{i=2}^N \chi_x * \varphi(x_i) \quad \text{and} \quad N_x^{\mathrm{TF}} = \int \rho_{\mathrm{TF}}(y)\chi_x(y)\,dy. \tag{17}$$

Then

$$\begin{aligned}&\left|\int [\rho^{(2)}(x,y) - \rho_{\mathrm{TF}}(y)\rho(x)]\theta(x)\chi(x,y)\,dx\,dy\right| \\ &\quad \leqq \int \rho^{(2)}(x,y)|\chi_x * \varphi(y) - \chi_x(y)|\theta(x)\,dx\,dy \\ &\qquad + N\left|\int |\psi(x,x_2,\dots,x_N)|^2 (N_x(x_2,\dots,x_N) - N_x^{\mathrm{TF}})\,dx_2\cdots dx_N \theta(x)\,dx\right| \\ &\quad \leqq C_2 Z^{1/3}\|\nabla_y\chi\|_{L^\infty}\textstyle\int\rho(x)\theta(x)dx \\ &\qquad + \{N|\textstyle\int|\psi(x,x_2,\dots,x_N)|^2|N_x - N_x^{\mathrm{TF}}|^2\theta(x)\,dx\,dx_2\cdots dx_N\}^{1/2} \\ &\qquad \cdot\{\textstyle\int\rho(x)\theta(x)dx\}^{1/2},\end{aligned} \tag{18}$$

where we have used Cauchy–Schwarz inequality.

Since

$$N_x(x_2,\dots,x_N) - N_x^{\mathrm{TF}} = \int\left(\sum_{i=2}^N \varphi(y - x_i) - \rho_{\mathrm{TF}}(y)\right)\chi(x,y)\,dy,$$

we get again from Cauchy–Schwarz

$$\begin{aligned}|N_x - N_x^{\mathrm{TF}}|^2 &\leqq \int|\hat{\chi}_x(\xi)|^2|\xi|^2 d\xi \int\left|\left(\sum_{i=2}^N \varphi(y - x_i) - \rho_{\mathrm{TF}}(y)\right)^{\wedge}(\xi)\right|^2 |\xi|^{-2} d\xi \\ &\leqq C\|\nabla\chi_x\|^2_{L^2(\mathbb{R}^3)} K_{N-1}(x_2,\dots,x_N),\end{aligned} \tag{19}$$

where ^ denotes Fourier transform. From (15) we find using IMS,

$$
\begin{aligned}
E_{N-1,Z}\int\rho(x)\theta(x)dx &\geqq E_{N,Z}\int\rho(x)\theta(x)dx\\
&\geqq \sum_{i=1}^{N}\left\{\langle\psi|\sqrt{\theta(x_i)}H_{N-1,Z}\sqrt{\theta(x_i)}|\psi\rangle-\langle\psi|(\nabla\sqrt{\theta(x_i)})^2|\psi\rangle\right.\\
&\quad\left.+\left\langle\psi\left|-\theta(x_i)\frac{Z}{|x_i|}+\sum_{j,j\neq i}\frac{\theta(x_i)}{|x_i-x_j|}\right|\psi\right\rangle\right\}\\
&\geqq E_{N-1,Z}\int\rho(x)\theta(x)dx+N\int|\psi|^2K_{N-1}\theta(x)dx\,dx_2\cdots dx_N\\
&\quad+C_0Z^{7/3-b}\int\rho(x)\theta(x)dx-cNR^{-2}-R^{-1}Z\int\rho(x)\theta(x)dx.
\end{aligned}
$$

Thus

$$
\begin{aligned}
&N\int|\psi|^2\|\nabla\chi_x\|_{L^2}^2K_{N-1}\theta(x)dx\,dx_2\cdots dx_N\\
&\leqq C\sup_x\|\nabla\chi_x\|_{L^2}^2((Z^{(7/3-b)}+R^{-1}Z)\int\rho\theta dx+ZR^{-2}).
\end{aligned}
\tag{20}
$$

Putting together (18),(19) and (20) gives (16). ■

A simplification of the above proof gives

Lemma 6. *With the notation of Sect. 2,*

$$
|\int(\rho(x)-\rho_{\mathrm{TF}}(x))\lambda_R(x)dx|\leqq C(R^{1/2}Z^{(7/6-b/2)}+R^{-1}Z^{1/3}).
\tag{21}
$$

4. Estimates on Q, v and K

Estimate on Q. Using that $\rho_{\mathrm{TF}}(x)=Z^2\rho_{\mathrm{TF}}^{(Z=1)}(Z^{1/3}x)$, and

$$
|x|\geqq 1\Rightarrow C_-|x|^{-6}\leqq\rho_{\mathrm{TF}}^{(1)}(x)\leqq C_+|x|^{-6},
$$

gives

$$
|x|\geqq Z^{-1/3}\Rightarrow C_-|x|^{-6}\leqq\rho_{\mathrm{TF}}(x)\leqq C_+|x|^{-6}.
\tag{22}
$$

Furthermore $\int\rho_{\mathrm{TF}}dx=Z$. Thus

$$
\begin{aligned}
Q(R)&=N-\int\rho(x)\lambda_R(x)dx\\
&=N-\int\rho_{\mathrm{TF}}(x)\lambda_R(x)dx-\int(\rho(x)-\rho_{\mathrm{TF}}(x))\lambda_R(x)dx\\
&=N-Z+\int\rho_{\mathrm{TF}}(x)\theta_R(x)dx-\int(\rho(x)-\rho_{\mathrm{TF}}(x))\lambda_R(x)dx.
\end{aligned}
$$

Choose

$$
R=\gamma Z^{-1/3+b/7}.
\tag{23}
$$

From

$$
C_1R^{-3}\leqq\int\rho_{\mathrm{TF}}(x)\theta_R(x)dx\leqq C_2R^{-3},
\tag{24}
$$

and from Lemma 6 we then find

$$
(C_1\gamma^{-3}-C\gamma^{1/2})Z^{(1-3b/7)}\leqq Q(R)-(N-Z)\leqq(C_2\gamma^{-3}+C\gamma^{1/2})Z^{(1-3b/7)}.
$$

Choosing γ appropriately ($\gamma\leqq(1/2)(C_1/C)^{2/7}$ we have proved

Lemma 7. *With $\alpha=3b/7$ and for $R=\gamma Z^{(1/3)(1-\alpha)}$ with γ sufficiently small,*

$$
0<cZ^{1-\alpha}\leqq Q(R)-(N-Z)\leqq CZ^{1-\alpha}.
\tag{25}
$$

From the lower bound in (25) we get the result in Theorem 3 with $\alpha = 3b/7$.

Estimate on ν.

Lemma 8. *For* α *and* R *as in Lemma* γ,

$$\nu(R) \leqq CZ^{1-\alpha}. \tag{26}$$

Proof. In (16) we choose $\theta(x) = \theta_R(x)$ and

$$\chi(x, y) = \frac{|x|}{|x-y|}\lambda_{R(1-2\delta)}(y).$$

For $(x, y) \in \operatorname{supp}\chi$ and $x \in \operatorname{supp}\theta_R$ we have $|x - y| > \delta R$. It is then easy to see that for $x \in \operatorname{supp}\theta_R$ we have

$$\|\nabla_y \chi_x\|_{L^2(\mathbf{R}^3)} \leqq cR^{1/2} \quad \text{and} \quad \|\nabla \chi_x\|_{L^\infty} \leqq cR^{-1}.$$

Taking this into account and remembering that $R = \gamma Z^{-(1/3)(1-\alpha)}$, we obtain from (16),

$$\begin{aligned}
&\left| \int [\rho^{(2)}(x, y) - \rho_{\mathrm{TF}}(y)\rho(x)]\theta_R(x)\frac{|x|}{|x-y|}\lambda_{R(1-2\delta)}(y)dx\,dy \right| \\
&\leqq C_\delta(Q(R)Z^{1-\alpha} + Q(R)^{1/2}Z^{(2/3-\alpha/6)} + Q(R)Z^{(2/3-\alpha/3)}) \\
&\leqq C_\delta(Q(R)Z^{1-\alpha} + Q(R)^{1/2}Z^{(2/3-\alpha/6)}),
\end{aligned}$$

where we have used that $b \leqq 2/3$ implies $\alpha \leqq 2/7$. From $\lambda_R \geqq \lambda_{(1-2\delta)R}$ and Lemma 7 we can now conclude

$$\nu(R) \leqq Z - \frac{1}{Q(R)}\int \rho_{\mathrm{TF}}(y)\rho(x)\theta_R(x)\frac{|x|}{|x-y|}\lambda_{R(1-2\delta)}(y)dx\,dy + C_\delta Z^{1-\alpha}.$$

Since $|x - y|^{-1}$ is the harmonic potential, $\lambda_{R(1-2\delta)}$ and ρ_{TF} are spherically symmetric and $\lambda_{R(1-2\delta)}$ is supported disjointly from θ_R we obtain

$$\nu(R) \leqq Z - \int \rho_{\mathrm{TF}}(y)\lambda_{R(1-2\delta)}(y)dy + C_\delta Z^{1-\alpha}.$$

Recalling (22) we get

$$\nu(R) \leqq \int \rho_{\mathrm{TF}}(y)\theta_{R(1-2\delta)}(y)dy + CZ^{1-\alpha} \leqq CZ^{1-\alpha}. \quad \blacksquare$$

Estimate on K

Lemma 9. *For* R *as in Lemma* 7,

$$K(R) \geqq CQ(R) \quad \text{with} \quad C > 0. \tag{27}$$

Proof. This can be done without the use of Lemma 5. Indeed notice that the inequality $\langle F^2 \rangle - \langle F \rangle^2 \geqq 0$ used on $F = \sum_{i=1}^{N} f(x_i)$ implies

$$\int \rho^{(2)}(x, y)f(x)f(y)dx\,dy \geqq \left(\int \rho(x)f(x)dx\right)^2 - \int \rho(x)f(x)^2dx.$$

Hence since $\theta_R \leqq 1$,

$$K(R) \geqq \frac{1}{Q(R)}(Q(R)^2 - Q(R)),$$

and the result follows from Lemma 7. ■

Proof of Theorem 1. Inserting the bounds from Lemmas 7–9 into the inequality of Theorem 4 gives the result of Theorem 1.

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Note added in proof. It has recently been shown (Fefferman, C. L., Seco, L. A.: The Ground State Energy of a Large Atom (To appear) that we can take the parameter b equal to the optimal value $\frac{2}{3}$. This allows us to take $\alpha = \frac{2}{7}$.