THE GROUND STATE ENERGY OF HEAVY ATOMS
ACCORDING TO BROWN AND RAVENHALL: ABSENCE OF
RELATIVISTIC EFFECTS IN LEADING ORDER

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Abstract. It is shown that the ground state energy of heavy atoms is, to
leading order, given by the non-relativistic Thomas-Fermi energy. The proof is
based on the relativistic Hamiltonian of Brown and Ravenhall which is derived
from quantum electrodynamics yielding energy levels correctly up to order
$\alpha^2$Ry.

1. Introduction

The energy of heavy atoms has attracted considerable interest in the context of
nonrelativistic quantum mechanics. Lieb and Simon [20] proved that the leading
behavior of the ground state energy is given by the Thomas-Fermi energy which
decreases as $Z^{7/3}$. The leading correction to this behavior, the so called Scott
correction was established by Hughes [14, 15] (lower bound), and Siedentop and
Weikard [21, 22, 23, 24, 27, 28] (lower and upper bound). In fact even the existence
of the $Z^{5/3}$-correction conjectured by Schwinger was proven (Fefferman and Seco
[9, 10, 11, 12, 13, 14, 15]). Later these results where extended in various ways,
e.g., to ions and molecules.

Nevertheless, from a physical point of view, these considerations are questionable,
since large atoms force the innermost electrons on orbits that are close to the nucleus
where the electrons move with high speed which requires a relativistic treatment.
Our main goal in this paper is to show that the leading energy contribution is
unaffected by relativistic effects, i.e., the asymptotic results of Lieb and Simon [20]
remain also valid in the relativistic context, whereas the question mark behind the
quantitative correctness of the other corrections persists.

Sørensen [23] took a first step in this direction. He considered the Chandrasekhar
multi-particle operator and showed that the leading energy behavior is given by the
non-relativistic Thomas-Fermi energy in the limit of large $Z$ and large velocity of
light $c$. Nevertheless, a question from the physical point of view remains: Although
the Chandrasekhar model is believed to represent some qualitative features of rela-
tivistic systems, there is no reason to assume that it should give quantitative correct
results. Therefore, to obtain not only qualitatively correct results it is interesting,
in fact mandatory, to consider a Hamiltonian which – as the one by Brown and

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Ravenhall \[2\] – is derived from QED such that it yields the leading relativistic effects in a quantitative correct manner.

2. Definition of the Model

Brown and Ravenhall \[2\] describe two relativistic electrons interacting with an external potential. The model has an obvious generalization to the $N$-electron case. The energy in the state $\psi$ is defined as

$$E : \bigwedge_{\nu=1}^{N} (H^{1/2}(\mathbb{R}^3) \otimes \mathbb{C}^4) \rightarrow \mathbb{R}$$

$$\psi \mapsto (\psi, (\sum_{\nu=1}^{N} (D_{c,Z} - e^2)_{\nu} + \sum_{1 \leq \mu < \nu \leq N} |x_{\mu} - x_{\nu}|^{-1})\psi)$$

where

$$D_{c,Z} := c \cdot \hat{\nabla} + c^2 \beta - Z |\cdot|^{-1}$$

is the Dirac operator of an electron in the field of a nucleus of charge $Z$. As usual, the four matrices $\alpha_1, ..., \alpha_3$ and $\beta$ are the four Dirac matrices in standard representation. We are interested in the restriction $\mathcal{E}$ of this functional onto $\Omega_N := \bigwedge_{\nu=1}^{N} (H^{1/2}(\mathbb{R}^3) \otimes \mathbb{C}^4) \cap \mathfrak{H}_N$ where

$$\mathfrak{H}_N := \bigwedge_{\nu=1}^{N} \mathfrak{H}$$

the underlying one-particle Hilbert space is

$$\mathfrak{H} := \chi_{(0,\infty)}(D_{c,0})(L^2(\mathbb{R}^3) \otimes \mathbb{C}^4).$$

Note that we are using atomic units in this paper, i.e., $m_e = \hbar = e = 1$.

As an immediate consequence of the work of Evans et al. \[3\] this form is bounded from below, in fact it is positive (Tix \[29\] \[30\]), if $\kappa := Z/c \leq \kappa_{\text{crit}} := 2/(\pi/2 + 2/\pi)$. (In the following, we will assume that the ratio $\kappa \in [0, \kappa_{\text{crit}}]$ is fixed.) According to Friedrichs this allows us to define a self-adjoint operator $B_{c,N,Z}$ whose ground state energy

$$E(c, N, Z) := \inf \sigma(B_{c,N,Z}) = \inf \{\mathcal{E}(\psi) | \psi \in \Omega_N, ||\psi|| = 1\}$$

is of concern to us in this paper. In fact – denoting by $E_{\text{TF}}(Z, Z)$ the Thomas-Fermi energy of $Z$ electrons in the field of nucleus with atomic number $Z$ and $q = 2$ spin states per electron (see Equations \[17\] and \[18\] for more details) – our main result is

**Theorem 1.**

$$E(Z/\kappa, Z, Z) = E_{\text{TF}}(Z, Z) + o(Z^{7/3}).$$

This result, given here for the neutral atomic case, has obvious generalizations to ions and molecules. To keep the presentation short we refrain from presenting them here, as their treatment follows the same strategy.

The remaining paper is structured as follows: First we show how the treatment of the Brown-Ravenhall model can be reduced from Dirac spinor (4-spinors) to Pauli spinors (2-spinors). In Section \[3\] we prove the upper bound corresponding to Theorem \[1\] by rolling it back to Lieb’s upper bound in the non-relativistic case \[17\]. Section \[4\] reduces the lower bound to Sørensen’s lower bound \[23\]. Finally, in
the appendix we show that the correlation estimate using the exchange hole yields a pointwise lower bound with uniform error of order $Z$. This is interesting in itself since it allows to estimate the error purely by the particle number not using any kinetic energy.

We now indicate, how to reduce to Pauli spinors. To this end we parameterize the allowed states: Any $\psi \in \mathcal{H}$ can be written as

\[
\psi := \left( \frac{E_c(p) + c^2}{N_c(p)} u \right)
\]

for some $u \in \mathfrak{h} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$. Here, $\sigma$ are the three Pauli matrices,

\[
\hat{p} := -i\nabla, \quad E_c(p) := (c^2p^2 + c^4)^{1/2}, \quad N_c(p) := \left[ 2E_c(p)(E_c(p) + c^2)^{1/2} \right].
\]

In fact, the map

\[
\Phi : \mathfrak{h} \to \mathcal{H}
\]

embeds unitarily into $\mathcal{H}$ and its restriction onto $H^1(\mathbb{R}^3) \otimes \mathbb{C}^2$ is also unitary mapping to $\mathcal{H} \cap H^1(\mathbb{R}^3) \otimes \mathbb{C}^4$ (Evans et al. [3]).

It suffices to study the energy as function of $u$

\[
E \circ (\otimes_{\nu=1}^N \Phi) : \mathfrak{h} \to \mathbb{R}.
\]

The one-particle Brown-Ravenhall operator $B_\gamma$ for an electron the external electric potential of a point nucleus acting on Pauli spinors is then

\[
B_{c,Z} := E_c(\hat{p}) - Z\varphi_1 - Z\varphi_2
\]

where we have split the potential into

\[
\varphi_1 := \Phi_1^* \cdot |^{-1}\Phi_1, \quad \varphi_2 := \Phi_2^* \cdot |^{-1}\Phi_2.
\]

As we will see the first part $\varphi_1$ is contributing to the nonrelativistic limit whereas the second part turns out to give energy contribution that do not even affect the first correction term.

3. Upper Bound

3.1. Coherent States. The upper bound will be given by choosing a trial density matrix in the Hartree-Fock functional for the Brown-Ravenhall operator. To this end we introduce spinor valued function of $u$

\[
F_\alpha(x) := (\varphi_{p,q} \otimes e_{\tau})(x) := f(x - q) \exp(i p \cdot x) \delta_{\tau,\sigma},
\]

where $x = (x, \sigma) \in \mathbb{R}^3 \times \{1, 2\}$ and the vectors $e_\tau$ are the canonical basis vectors in $\mathbb{C}^2$ (see Lieb [17] and Evans et al. [3]). We will pick $f$ depending on a dilation parameter. More specifically we will choose

\[
f(x) := g_R(x) := R^{-3/2}g(R^{-1}x)
\]

where $R := Z^{-\delta}$ with $\delta \in (1/3, 2/3)$ and $g \in H^{3/2}$, spherically symmetric, normalized, and with support in the unit ball.
The natural measure on $\Gamma$ counting the number of electrons per phase space volume in the spirit of Planck is
\[
\int_{\Gamma} d\Omega(\alpha) := (2\pi)^{-3} \int dp \int dq \sum_{r=1}^{2} \tau^{2}.
\]
The essential properties needed are the following. For $A \in L^{1}(\Gamma, d\Omega)$
\[
\gamma := \int_{\Gamma} d\Omega(\alpha) A(\alpha) |F_{\alpha}/F_{\alpha}|.
\]
is a trace class operator and
\[
0 \leq A \leq 1 \implies 0 \leq \gamma \leq 1
\]
\[
\text{tr} \gamma = \int_{\Gamma} d\Omega(\alpha) A(\alpha).
\]
Using $\Phi$ we can lift any such operator $\gamma$ to an operator on $H$
\[
\gamma_{\Phi} := \Phi \gamma \Phi^{*}.
\]
We will pick
\[
A(\alpha) := \chi_{\{(\xi,x) \in \mathbb{R}^{3} : V_{Z}(x) \leq 0\}}(p,q)
\]
where $V_{Z} := Z/|\cdot| - |\cdot|^{-1} * \rho_{TF}$; here $\rho_{TF}$ is the unique minimizer of the Thomas-Fermi functional
\[
E_{TF}(\rho) := \int_{\mathbb{R}^{3}} \left[ \frac{3}{5} \gamma_{TF(\rho)}(x) \right]^{5/3} - \frac{Z}{|x|} \rho(x) \right] dx + D(\rho, \rho)
\]
where, for Fermions with $q$ spin states per particle, $\gamma_{TF} := (6\pi^{2}/q)^{2/3}h^{2}/(2m)$, i.e., in our units, $\gamma_{TF} = (3\pi^{2})^{2/3}/2$. Note that $\int d\Omega(\alpha) A(\alpha) = Z$ (Lieb and Simon [20]). Note also that $V_{Z}(q) := Z^{4/3}V_{1}(Z^{1/3}q)$ (see also Gombás [13] and [20]). Note also that the minimal energy $E_{TF}(N, Z)$ fulfills the scaling relation
\[
E_{TF}(N, Z) = E_{TF}(N/Z, 1)Z^{7/3}.
\]
Note, that we could restrict the minimization to $\int \rho \leq N$ without any problem. For $N \geq Z$ there would be no change in the minimizer; for $N < Z$ we would get a different minimizer. For notational convenience we will merely consider the neutral case $N = Z$ in the following.

3.2. Upper Bound. We begin by noting that the Hartree-Fock functional – with or without exchange energy – bounds $E(c, N, Z)$ from above. To be exact we introduce the set of density matrices
\[
S_{N} := \{ \gamma \in \mathfrak{S}^{1}(\mathfrak{h}) : E_{c}(\hat{p}) \gamma \in \mathfrak{S}^{1}(\mathfrak{h}), \ 0 \leq \gamma \leq 1, \ \text{tr} \gamma = N \}
\]
where $\mathfrak{S}^{1}(\mathfrak{h})$ denotes the trace class operators on $\mathfrak{h}$.
\[
\mathcal{E}_{HF} : S_{N} \to \mathbb{R}
\]
\[
\gamma \mapsto \text{tr}(E_{c}(\hat{p}) - c^{2} - Z/|x|) \gamma \Phi + D(\rho_{\gamma}, \rho_{\gamma})
\]
where – as usual – $\rho_{\gamma}$ is the density associated to $\gamma$ and $D$ is the Coulomb scalar product. By the analogon of Lieb’s result [13] [15] (see also Bach [1]) – which trivially transcribes from the Schrödinger setting to the present one – we have for all $\gamma \in S_{N}$
\[
E(c, N, Z) \leq \mathcal{E}_{HF}(\gamma).
\]
3.2.1. Kinetic Energy. By concavity we have
\[(22) \quad E_c(p) - c^2 \leq \frac{1}{2}p^2\]
which implies that the Brown-Ravenhall kinetic energy is bounded by the non-relativistic one, i.e., for all $\gamma \in S_N$ with $-\Delta \gamma \in G^1(h)$
\[(23) \quad \text{tr}[(E_c(p) - c^2)\gamma] \leq \text{tr}(-\frac{1}{2}\Delta \gamma)\]
Inserting our choice of $\gamma$ (see Equations 10, 11, 12, and 16) turns the right hand side into the Thomas-Fermi kinetic energy modulo the positive error $Z\|\nabla g\|R^{-\frac{3}{2}}$ (see Lieb [17] Formula (5.9)), i.e.,
\[(24) \quad \text{tr}[(E_c(p) - c^2)\gamma] \leq \frac{3}{5}\gamma TR \int \rho_{TF}^{\frac{5}{3}}(x)dx + ZR^{-2}\|\nabla g\|^2.

3.2.2. External Potential. Since $-Z\text{tr}(\varphi_2\gamma)$ is negative, we can and will estimate this term by zero. This estimate will be good, if this term is of smaller order. Although, logically unnecessary for the upper bound, it is, for pedagogical reasons, interesting to see that $\varphi_2$ does indeed not significantly contribute to the energy, if $\gamma$ is chosen as above. Moreover, the proof will be also useful for the proof of Lemma 2

**Lemma 1.** For our choice of $\gamma = \int d\Omega(\alpha)|F_\alpha\rangle\langle F_\alpha|$ and $\delta \in (1/3, 2/3)$ we have
\[(25) \quad 0 \leq Z\text{tr}(\varphi_2\gamma) \leq kZ \int d\Omega(\alpha)A(\alpha) \int d\xi d\xi' \frac{c^2|\xi||\xi'||\tilde{F}_\alpha(\xi)\tilde{F}_\alpha(\xi')|}{||\xi - \xi'||^2N_c(\xi)N_c(\xi')} = O(Z^{4/3+\delta}).

(In the following – throughout the paper – we use the letter $k$ for a constant independent of $c$, $N$, $R$, or $Z$.)

**Proof.** We begin by estimating the expectation of $\varphi_2$ in a coherent state.
\[(26) \quad 0 \leq (F_\alpha, \varphi_2 F_\alpha) \leq k \int d\xi d\xi' |\tilde{\varphi}(\xi)\tilde{\varphi}(\xi')| \frac{c^2|\xi||\xi'||\tilde{F}_\alpha(\xi)\tilde{F}_\alpha(\xi')|}{||\xi - \xi'||^2N_c(\xi)N_c(\xi')} \leq kc^{-2}R^{-3} \int d\xi d\xi' |\tilde{\varphi}(\xi)\tilde{\varphi}(\xi')| \frac{|\xi + Rp||\xi' + Rp|}{||\xi - \xi'||^2} \leq kc^{-2}R^{-3}(1 + R|p| + R^2|p|^2).

Here, we used that $N_c(\xi) \geq \sqrt{2c^2}$ and, in the last step, that
\[
|\tilde{\varphi}(\xi)\tilde{\varphi}(\xi')| \frac{1}{||\xi - \xi'||^2} \leq \frac{1}{||\xi'|| + ||\xi|| + 1}
\]
is integrable in $\xi$ and $\xi'$ because $g \in H^{3/2}(\mathbb{R}^3)$. Thus we get
\[(27) \quad 0 \leq Z\text{tr}(\varphi_2\gamma) = Z \int d\Omega(\alpha)A(\alpha)(F_\alpha, \varphi_2 F_\alpha)
\leq k \int d\Omega(\alpha)A(\alpha)(1 + R|p| + R^2|p|^2) \leq k \int d\Omega(\alpha)A(\alpha)(1 + R|p| + R^2|p|^2) \leq k \frac{Z^2}{c^2R^3} \left\{Z + R \int dq \left[Z^{4/3}V_1(Z^{1/3}q)\right]^2 + R^2 \left[Z^{4/3}V_1(Z^{1/3}q)\right]^{5/2}\right\} = O(Z^{3\delta} + Z^{2/3+2\delta} + Z^{4/3+\delta}).\]
\[\square\]
Lemma 2. For our choice of \( \gamma \) and \( \delta \in (1/3, 2/3) \) we have

\[
\left| Z \left( \left( \frac{1}{| \cdot |} \right) - \varphi_1 \right) g \right| \leq kZ \int d\Omega(\alpha)A(\alpha) \int \frac{d\xi d\xi'}{| \xi - \xi' |^2} \left( 1 - \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi)N_c(\xi')} \right) |\hat{F}_\alpha(\xi)||\hat{F}_\alpha(\xi')| = O(Z^{5/3 + \delta}).
\]

Proof. We first note that

\[
\left( 1 - \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi)N_c(\xi')} \right) \leq \frac{3E_c(\xi)E_c(\xi') - c^2(E_c(\xi) + E_c(\xi')) + c^2}{N_c(\xi)N_c(\xi')}.
\]

Then, noting that \( E_c(\xi) - c^2 \leq c|\xi| \), we obtain

\[
\left| 1 - \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi)N_c(\xi')} \right| \leq \frac{3c^2|\xi||\xi'| + 2c^3(\xi + \xi')}{N_c(\xi)N_c(\xi')} \leq \frac{3c^2|\xi||\xi'| + 2c^3(\xi + \xi')}{2c^4}.
\]

Using this last equation, we estimate

\[
\left| (F_\alpha, \left( \frac{1}{| \cdot |} \right) - \varphi_1 )g \right| \leq k \int \frac{d\xi d\xi'}{| \xi - \xi' |^2} \left( 1 - \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi)N_c(\xi')} \right) |\hat{F}_\alpha(\xi)||\hat{F}_\alpha(\xi')| \leq k \int \frac{d\xi d\xi'}{| \xi - \xi' |^2} \left( \frac{3c^2|\xi||\xi'| + 2c^3(\xi + \xi')}{N_c(\xi)N_c(\xi')} \right) \leq kc^{-2}R^{-3} \int \frac{d\xi d\xi'}{| \xi - \xi' |^2} \left( |\xi||\xi'| + cR |\xi + p| + cR |\xi| + cR |\xi' + p| \right) \leq kc^{-2}R^{-3} \left( 1 + cR |\xi + p| + cR |\xi' + p| \right).
\]

Thus

\[
Z \left( \left( \frac{1}{| \cdot |} \right) - \varphi_1 \right) g \left| \leq Z \int d\Omega(\alpha)A(\alpha) \left( \left( \frac{1}{| \cdot |} \right) - \varphi_1 \right) F_\alpha \right| \leq kZ \int \frac{d\xi d\xi'}{| \xi - \xi' |^2} \left( 1 - \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi)N_c(\xi')} \right) |\hat{F}_\alpha(\xi)||\hat{F}_\alpha(\xi')| \leq k(3^5 + Z^{2\delta + 2/3} + Z^{\delta + 4/3} + \delta Z^{\delta + 5/3})
\]

which yields the desired estimate.

3.2.3. The Electron-Electron Interaction. We will roll back the treatment of the electron-electron interaction to the treatment of nucleus-electron interaction.

Lemma 3. For our choice of \( \gamma \) and \( \delta \in (1/3, 2/3) \) we have

\[
D(\rho_{\gamma}, \rho_{\gamma'}) - D(\rho_{\gamma}, \rho_{\gamma}) = O(Z^{5/3 + \delta}),
\]

where \( \rho_\gamma \) is the density of \( \gamma \) and \( \rho_{\gamma \phi} \) is the density of \( \gamma \phi \).

**Proof.** We have

\[
|F[ (\rho_\gamma + \rho_{\gamma \phi}) \ast | \cdot |^{-1} ](\xi)| \leq \sqrt{2/\pi}||\rho_\gamma + \rho_{\gamma \phi}||_1 |\xi|^{-2} = 2^{3/2} \pi^{-1/2} Z |\xi|^{-2}.
\]

Now,

\[
|D(\rho_{\gamma \phi}, \rho_{\gamma}) - D(\rho_\gamma, \rho_\gamma)| = |D(\rho_{\gamma \phi} - \rho_\gamma, \rho_{\gamma \phi} + \rho_\gamma)|
\]

\[
\leq \frac{1}{2} \left| \int_{\mathbb{R}^3} (\rho_\gamma (x) - \rho_{\gamma \phi} (x))[(\rho_\gamma + \rho_{\gamma \phi}) \ast | \cdot |^{-1}](x) \, dx \right|
\]

\[
\leq \frac{1}{2} \int_G d \Omega(\alpha) A(\alpha)
\]

\[
\times \int \int d\xi d\xi' |F[(\rho_\gamma + \rho_{\gamma \phi}) \ast | \cdot |^{-1}](\xi - \xi')| K(\xi, \xi') |F_\alpha(\xi)||F_\alpha(\xi')| \, d\xi d\xi'
\]

\[
\leq \sqrt{\frac{2}{\pi}} Z \int_G d \Omega(\alpha) A(\alpha) \int \int d\xi d\xi' | \xi - \xi' |^{-2} K(\xi, \xi') |F_\alpha(\xi)||F_\alpha(\xi')| \, d\xi d\xi'
\]

where

\[
K(\xi, \xi') = \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi) N_c(\xi')} - 1 + \frac{c^2 |\xi| |\xi'|}{N_c(\xi) N_c(\xi')}
\]

and where we used (34) in the last step. Eventually, applying Lemmata 1 and 2 yields the desired result. \( \Box \)

**3.2.4. The Total Energy.** Gathering our above estimates allows us to reduce the problem to the non-relativistic result of Lieb [17].

**Theorem 2.** We have \( E(\kappa Z, Z, Z) \leq E_{\text{TF}}(1, 1) Z^{7/3} + k Z^{20/9} \).

**Proof.** Following Lieb [17] Section V.A.1 with the remainder terms given there (putting \( R = Z^{-\delta} \) as in our estimate), using the remainder terms obtained in Lemmata 1 through 3, and using (24) we get

\[
E(c, Z, Z) \leq E_{\text{HF}}(\gamma) \leq E_{\text{TF}}(Z, Z) + O(Z^{1+2\delta} + Z^{2-\delta/2} + Z^{2+\delta})
\]

which is optimized for \( \delta = 5/9 \) giving the claimed result. \( \Box \)

**4. Lower Bound**

The lower bound is – contrary to the usual folklore – easy. As we will see, it is a corollary of Sørensen’s [23] result for the Chandrasekhar operator and an estimate on the potential generated by the exchange hole [21]. The exchange hole of a density \( \sigma \) at a point \( x \in \mathbb{R}^3 \) is defined as the ball \( B_{R_\sigma}(x) \) of radius \( R_\sigma(x) \) centered at \( x \) where \( R_\sigma(x) \) is the smallest radius \( R \) fulfilling

\[
\frac{1}{2} = \int_{B_R} \sigma.
\]

The hole potential \( L_\sigma \) of \( \sigma \) is defined through

\[
L_\sigma(x) := \int_{|x-y|<R_\sigma(x)} \frac{\sigma(y)}{|x-y|} \, dy.
\]

Our second main result is the following lower bound.
Theorem 3.
\[ \liminf_{Z \to \infty} [E(c, Z, Z) - E_{\text{TF}}(Z, Z)] Z^{-7/3} \geq 0. \]

Proof. Pick \( \delta > 0 \) and set \( \rho_\delta \equiv \rho_{\text{TF}} * g_{2Z-\delta}^2 \). Then the exchange hole correlation bound \cite{21} Equation (14) implies the following pointwise estimate

\[ \sum_{1 \leq \mu < \nu \leq N} \frac{1}{|x_\mu - x_\nu|} \geq \sum_{\nu=1}^{N} [\rho_\delta * \cdot |^{-1}(x_\nu) - L_{\rho_\delta}(x_\nu)] - D(\rho_\delta, \rho_\delta). \]

Because of the spherical symmetry of \( g \) we can use Newton’s theorem \cite{22} and replace \( \rho_\delta \) by \( \rho_{\text{TF}} \) in the third summand of the right hand side of (38).

To count the number of spin states per electron correctly, i.e., two instead of the apparent four, we use an observation by Lieb et al. \cite{19, Appendix B}: Note that

\[ \Lambda_\delta = U^{-1} \Lambda_+ U, \quad \text{where} \quad U := \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \]

Indeed, we have

\[ \Lambda_\delta = \frac{1}{2} \left( 1 - \frac{D_0}{|D_0|} \right), \quad \Lambda_+ = \frac{1}{2} \left( 1 + \frac{D_0}{|D_0|} \right) \]

and

\[ U^{-1}D_0U = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \left( \begin{array}{cc} mc^2 & c\sigma \hat{p} \\ c\sigma \hat{p} & -mc^2 \end{array} \right) \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = -D_0. \]

We set \( X := (|D_0| - c^2 - V_\delta(x))I_2 \), and write

\[ \text{tr} \left[ \Lambda_\delta \begin{pmatrix} X & 0 \\ 0 & X \end{pmatrix} \Lambda_+ \right] \geq \text{tr} \left( \Lambda_\delta \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \Lambda_+ \right) = \text{tr} \left( \Lambda_\delta \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \right) \]

\[ \text{tr} \left( \Lambda_\delta \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \right) = \text{tr} \left( \Lambda_+ \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \right) \]

Thus

\[ 2 \text{tr} \left( \Lambda_\delta \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \right) = \text{tr} \left( \Lambda_+ \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \right) + \text{tr} \left( \Lambda_- \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \right) = 2 \text{tr}(X_-). \]

Since \( |D_0| = E_c(\hat{p}) \), we obtain

\[ E(\kappa Z, Z, Z) \geq 2 \text{tr} [E_c(\hat{p}) - c^2 - V_\delta(x)]_\delta - D(\rho_{\text{TF}}, \rho_{\text{TF}}) - kNZ \]

where the last trace is spinless. This connects to Sørensen’s Equation (3.2) from \cite{23}. The result then follows using his lower bound. \( \Box \)
APPENDIX A. \(L^\infty\)-BOUND ON THE EXCHANGE HOLE POTENTIAL

We begin the appendix with the following remark: the Thomas-Fermi potential
\(V_Z := Z/| \cdot | - \rho_{TF}*| \cdot |^{-1}\) can be written as

\[
\gamma_{TF}^{2/3} \rho_{TF} = V_Z
\]

(43)

(see, e.g., Gombás [13]). This equation yields immediately the upper bound

\[
\rho_{TF}(x) \leq (Z/\gamma_{TF})^{3/2}|x|^{-3/2}.
\]

This bound allows us to prove the following \(L^\infty\)-bounds on potentials of exchange holes.

**Lemma 4.**

\[\|L_{\rho_{TF}}\|_\infty = O(Z).\]

*Proof.* The function

\[
f : \mathbb{R}_+ \to \mathbb{R}
\]

\[
t \mapsto \sqrt{t} \int_{|y| < 1/t} |y|^{-1}|y + (0, 0, 1)|^{-3/2} dy
\]

(45)

is obviously continuous on \((0, \infty)\). Moreover, \(f(t)\) tends to a positive constant for \(t \to 0\) and to 0 for \(t \to \infty\). Thus, \(\|f\|_\infty < \infty\).

This allows us to obtain the desired estimate:

\[
L_{\rho_{TF}}(x) \leq A_1(x) + A_2(x)
\]

where

\[
A_1(x) := \int_{|y| \leq 1/Z} \frac{\rho_{TF}(x+y)}{|y|} dy \leq \left(\frac{Z}{\gamma_{TF}}\right)^{3/2} \int_{|y| \leq 1/Z} \frac{dy}{|y||y + x|^{3/2}}
\]

\[
= (Z/\gamma_{TF})^{3/2} Z^{-1/2} f(|x|Z) \leq \|f\|_\infty \gamma_{TF}^{-3/2} Z.
\]

(47)

and

\[
A_2(y) := \int_{\frac{1}{2} \leq |y| \leq R_{\rho_{TF}}(x)} \frac{\rho_{TF}(x+y)}{|y|} dy \leq Z \int_{\frac{1}{2} \leq |y| \leq R_{\rho_{TF}}(x)} \rho_{TF}(x+y) dy \leq \frac{Z}{2}.
\]

(48)

These two estimate proof the claim. \(\square\)

**Lemma 4** allow us already to estimate the \(N\) electron operator \(B_{e,N,Z}\) by the canonical one particle Brown-Ravenhall operator whose nuclear charge is screened by the the Thomas-Fermi potential. However, since we would like – because of mere convenience – to take advantage of Sørensen’s result [23], we derive an estimate on \(L_{\rho_{\delta}}\) (where \(\rho_{\delta} := \rho_{TF} * g_{Z-i}^2\)), i.e., the exchange hole potential of the density occurring in Sørensen’s proof.

**Lemma 5.**

\[\|L_{\rho_{\delta}}\|_\infty = O(Z).\]
Proof. We proceed analogously to the proof of Lemma 4:

\[
L_\rho_\delta(x) \leq \int \frac{\rho_\delta(x+y)}{|y|} \, dy + \int_{|y| \leq R_{\rho_\delta}(x)} \frac{\rho_\delta(x+y)}{|y|} \, dy
\]

\[
\leq \int \frac{d\Phi_{Z-\delta}(y)}{|y|} \int_{|y| \leq 1/Z} \frac{\rho_{TF}(x-z+y)}{|y|} \, dy + Z \int_{|y| \leq R_{\rho_\delta}(x)} \rho_\delta(x+y) \, dy
\]

\[
\leq \int d\Phi_{Z-\delta}(z) A_1(x-z) + \frac{Z}{2} \leq kZ
\]

where we used the definition of the radius of the exchange hole from first line to second line, the definition of \(A_1\) in the next step, and in the last step the \(L^\infty\)-estimate (47) on \(A_1\).

\[\square\]

REFERENCES

[1] Volker Bach. Error bound for the Hartree-Fock energy of atoms and molecules. *Comm. Math. Phys.*, 147:527–548, 1992.
[2] G. E. Brown and D. G. Ravenhall. On the interaction of two electrons. *Proc. Roy. Soc. London Ser. A.*, 208:552–559, 1951.
[3] William Desmond Evans, Peter Perry, and Heinz Siedentop. The spectrum of relativistic one-electron atoms according to Bethe and Salpeter. *Comm. Math. Phys.*, 178(3):733–746, July 1996.
[4] C. Fefferman and L. Seco. Eigenfunctions and eigenvalues of ordinary differential operators. *Adv. Math.*, 95(2):145–305, October 1992.
[5] C. Fefferman and L. Seco. The density of a one-dimensional potential. *Adv. Math.*, 107(2):187–364, September 1994.
[6] C. Fefferman and L. Seco. The eigenvalue sum of a one-dimensional potential. *Adv. Math.*, 108(2):263–335, October 1994.
[7] C. Fefferman and L. Seco. On the Dirac and Schwinger corrections to the ground-state energy of an atom. *Adv. Math.*, 107(1):1–188, August 1994.
[8] C. Fefferman and L. Seco. The density in a three-dimensional radial potential. *Adv. Math.*, 111(1):88–161, March 1995.
[9] C. L. Fefferman and L. A. Seco. An upper bound for the number of electrons in a large ion. *Proc. Nat. Acad. Sci. USA*, 86:3464–3465, 1989.
[10] C. L. Fefferman and L. A. Seco. Asymptotic neutrality of large ions. *Comm. Math. Phys.*, 128:109–130, 1990.
[11] C. L. Fefferman and L. A. Seco. On the energy of a large atom. *Bull. AMS*, 23(2):525–530, October 1990.
[12] Charles L. Fefferman and Luis A. Seco. Aperiodicity of the Hamiltonian flow in the Thomas-Fermi potential. *Revista Matemática Iberoamericana*, 9(3):409–551, 1993.
[13] P. Gombás. *Die statistische Theorie des Atoms und ihre Anwendungen*. Springer-Verlag, Wien, 1 edition, 1949.
[14] Webster Hughes. *An Atomic Energy Lower Bound that Gives Scott’s Correction*. PhD thesis, Princeton, Department of Mathematics, 1986.
[15] Webster Hughes. An atomic lower bound that agrees with Scott’s correction. *Adv. in Math.*, 79:213–270, 1990.
[16] Elliott H. Lieb. Erratum: “Variational principle for many-fermion systems” [Phys. Rev. Lett. 46 (1981), no. 7, 457–459; MR 81m:81083], *Phys. Rev. Lett.*, 47(1):69, 1981.
[17] Elliott H. Lieb. Thomas-Fermi and related theories of atoms and molecules. *Rev. Mod. Phys.*, 53(4):603–641, October 1981.
[18] Elliott H. Lieb. Variational principle for many-fermion systems. *Phys. Rev. Lett.*, 46(7):457–459, 1981.
[19] Elliott H. Lieb, Heinz Siedentop, and Jan Philip Solovej. Stability and instability of relativistic electrons in classical electromagnetic fields. *J. Statist. Phys.*, 89(1-2):37–59, 1997. Dedicated to Bernard Jancovici.
[20] Elliott H. Lieb and Barry Simon. The Thomas-Fermi theory of atoms, molecules and solids. *Adv. Math.*, 23:22–116, 1977.

[21] Paul Mancas, A. M. Klaus Müller, and Heinz Siedentop. The optimal size of the exchange hole and reduction to one-particle Hamiltonians. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, 111(1):49–53, February 2004.

[22] Isaac Newton. *Philosophiae naturalis principia mathematica*. Vol. I. Harvard University Press, Cambridge, Mass., 1972. Reprinting of the third edition (1726) with variant readings, Assembled and edited by Alexandre Koyré and I. Bernard Cohen with the assistance of Anne Whitman.

[23] Thomas Østergaard Sørensen. The large-$Z$ behavior of pseudorelativistic atoms. *J. Math. Phys.*, 46(5):052307, 24, 2005.

[24] Heinz Siedentop and Rudi Weikard. On the leading energy correction for the statistical model of the atom: Interacting case. *Comm. Math. Phys.*, 112:471–490, 1987.

[25] Heinz Siedentop and Rudi Weikard. Upper bound on the ground state energy of atoms that proves Scott’s conjecture. *Phys. Lett. A*, 120:341–342, 1987.

[26] Heinz Siedentop and Rudi Weikard. On the leading energy correction of the statistical atom: Lower bound. *Europhysics Letters*, 6:189–192, 1988.

[27] Heinz Siedentop and Rudi Weikard. On the leading correction of the Thomas-Fermi model: Lower bound – with an appendix by A. M. K. Müller. *Invent. Math.*, 97:159–193, 1989.

[28] Heinz Siedentop and Rudi Weikard. A new phase space localization technique with application to the sum of negative eigenvalues of Schrödinger operators. *Annales Scientifiques de l’École Normale Supérieure*, 24(2):215–225, 1991.

[29] C. Tix. Lower bound for the ground state energy of the no-pair Hamiltonian. *Phys. Lett. B*, 405(3-4):293–296, 1997.

[30] C. Tix. Strict positivity of a relativistic Hamiltonian due to Brown and Ravenhall. *Bull. London Math. Soc.*, 30(3):283–290, 1998.

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