THE LEADING BEHAVIOR OF THE GROUND-STATE ENERGY OF HEAVY IONS ACCORDING TO BROWN AND RAVENHALL

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ABSTRACT. In this article we prove the absence of relativistic effects in leading order for the ground-state energy according to Brown-Ravenhall operator. We obtain this asymptotic result for negative ions and for systems with the number of electrons proportional to the nuclear charge. In the case of neutral atoms the analogous result was obtained earlier by Cassanas and Siedentop [4].

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1. Introduction

Cassanas and Siedentop [4] have shown that the ground state energy of heavy atoms for the relativistic Hamiltonian of Brown and Ravenhall is, to leading order, given by the non-relativistic Thomas-Fermi energy. The relativistic Hamiltonian of Brown and Ravenhall is derived from quantum electrodynamics yielding energy levels correctly up to order $\alpha^2\text{Ry}$ [3]. However, only the case as $N = Z$ is considered in [4], where $N$ is the number of electrons and $Z$ is the nuclear charge. This thesis describes the other two cases: $N > Z$ and $N/Z = \lambda$ (constant).

2. Definition of The Model

Brown and Ravenhall [3] describe two relativistic electrons interacting with an external potential. The model has an obvious generalization to the $N$-electron case. First we define

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

is the Dirac operator of an electron in the field of a nucleus of charge $Z$. Note that we are using atomic units in this paper, i.e., $m_e = \hbar = e = 1$. As usual, the four matrices $\alpha_1, \alpha_2, \alpha_3$ and $\beta$ are the four Dirac matrices in standard representation, explicitly

$$ \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, $$

$\sigma$ denoting the three Pauli matrices

$$ \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, $$

and

$$ \beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. $$

Let $\Omega_N := \bigwedge_{\nu=1}^N (H^{1/2}(\mathbb{R}^3) \otimes \mathbb{C}^4) \cap \mathcal{H}_N$ where

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

the underlying one-particle Hilbert space is

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

where

$$ \chi_{(0,\infty)}(D_{c,0}) := \begin{cases} 1, & (\psi, D_{c,0}\psi) > 0; \\ 0, & (\psi, D_{c,0}\psi) \leq 0 \end{cases} $$

for any $\psi \in L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$, and

$$ D_{c,0} := \alpha \cdot \frac{c}{i} \nabla + c^2 \beta. $$
Now we define the model as
\[ E : \Omega_N \to \mathbb{R} \]
\[ \psi \mapsto (\psi, (\sum_{\nu=1}^{N} (D_{c,0} - c^2 - Z/|x_{\nu}|) \nu + \sum_{1 \leq \mu < \nu \leq N} |x_{\mu} - x_{\nu}|^{-1})\psi). \]

As an immediate consequence of the work of Evans et al. [5] quadratic form \( E \) is bounded from below, in fact it is positive (Tix [35, 36]), if \( \kappa := Z/c \leq \kappa_{\text{crit}} := 2/(\pi/2+2/\pi) \). According to Friedrichs this allows us to define a self-adjoint operator \( B_{c,N,Z} \) whose ground state energy
\[ E(c, N, Z) := \inf \sigma(B_{c,N,Z}) = \inf \{ E(\psi)|\psi \in \Omega_N, \|\psi\| = 1 \} \]
is of concern to us in this paper. In fact the main result of this article is

**Theorem 1.** When \( N > Z \) or \( N/Z = \lambda(\text{constant}) \), we have
\[ E(Z/\kappa, N, Z) = E_{\text{TF}}(N, Z) + o(Z^{7/3}) \]
where \( E_{\text{TF}}(N, Z) := \inf \{ E_{\text{TF}}(\rho)|\rho \geq 0, \int_{\mathbb{R}^3} \rho \leq N, \rho \in L^{5/3}(\mathbb{R}^3) \} \),
\[ E_{\text{TF}}(\rho) := \int_{\mathbb{R}^3} \left[ \frac{3}{5}\gamma_{\text{TF}} \rho(x)^{5/3} - \frac{Z}{|x|}\rho(x) \right] dx + D(\rho, \rho) \]
is the Thomas-Fermi functional, and \( \kappa := Z/c \leq \kappa_{\text{crit}} := 2/\pi \).

In the following, we will assume that the ratio \( \kappa \in [0, \kappa_{\text{crit}}] \) is fixed. Note that according to [24, Formula (9c)] the minimal energy \( E_{\text{TF}}(N, Z) \) fulfills the scaling relation
\[ E_{\text{TF}}(N, Z) = E_{\text{TF}}(N/Z, 1)Z^{7/3}. \]

The article is structured as follows: first we show how the treatment of the Brown-Ravenhall model can be reduced from Dirac spinors (4-spinors) to Pauli spinors (2-spinors). Then we separately give the upper and lower bounds for the case \( N > Z \) in Section 3 and for the case where \( N/Z \) is fixed in Section 4. Throughout the paper, we use the letter \( k \) for any constants independent of \( c, N, R, \) or \( Z \).

We now indicate, how to reduce to Pauli spinors. To this end we parameterize the allowed states: Any \( \psi \in \mathfrak{H} \) can be written as
\[ \psi := \left( \begin{array}{c} \frac{E_{\mathfrak{C}}(\mathfrak{p}) + c^2}{N_{\mathfrak{C}}(\mathfrak{p})} u \\ \frac{N_{\mathfrak{C}}(\mathfrak{p})}{\mathfrak{C}} u \end{array} \right) \]
for some \( u \in \mathfrak{h} := L^{2}(\mathbb{R}^3) \otimes \mathbb{C}^2 \). Here, \( \mathfrak{C} \) are the three Pauli matrices,
\[ \mathfrak{p} := -i\nabla, \quad E_{\mathfrak{C}}(\mathfrak{p}) := (c^2 \mathfrak{p}^2 + c^4)^{1/2}, \quad N_{\mathfrak{C}}(\mathfrak{p}) := [2E_{\mathfrak{C}}(\mathfrak{p})(E_{\mathfrak{C}}(\mathfrak{p}) + c^2)]^{1/2}. \]
In fact, the map
\[ \Phi : \mathfrak{h} \to \mathfrak{H} \]
\[ u \mapsto \left( \begin{array}{c} \Phi_1 u \\ \Phi_2 u \end{array} \right) := \left( \begin{array}{c} \frac{E_{\mathfrak{C}}(\mathfrak{p}) + c^2}{N_{\mathfrak{C}}(\mathfrak{p})} u \\ \frac{N_{\mathfrak{C}}(\mathfrak{p})}{\mathfrak{C}} u \end{array} \right) \]
embeds \( \mathfrak{h} \) unitarily into \( \mathfrak{H} \) and its restriction onto \( H^1(\mathbb{R}^3) \otimes \mathbb{C}^2 \) is also a unitary mapping to \( \mathfrak{H} \cap H^1(\mathbb{R}^3) \otimes \mathbb{C}^4 \) (Evans et al. [5]).
It suffices to study the energy as function of $u$

$$E \circ (\otimes_{\nu=1}^N \Phi): \bigwedge_{\nu=1}^N \mathfrak{h} \to \mathbb{R}. \quad (10)$$

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 (see Appendix [A])

$$B_{c,Z} = E_c(\hat{p}) - Z\varphi_1 - Z\varphi_2 \quad (11)$$

where

$$B_{c,Z} := \chi_{(0,\infty)}(D_{c,0})D_{c,Z} \quad (12)$$

and we have split the potential into

$$\varphi_1 := \Phi_1^* \cdot |^{-1}\Phi_1, \quad \varphi_2 := \Phi_2^* \cdot |^{-1}\Phi_2. \quad (13)$$

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

3. Case I: $N > Z$

In this section, we prove Theorem 1 for negatively charged atoms.

3.1. Coherent States. We obtain the upper bound by constructing a trial density matrix in the Hartree-Fock functional for the Brown-Ravenhall operator. To this end we introduce spinor valued coherent states.

Given functions $f, \tilde{f} \in H^{3/2}(\mathbb{R}^3)$ and an element $\alpha = (p, q, \tau)$ of the phase space $\Gamma := \mathbb{R}^3 \times \mathbb{R}^3 \times \{1, 2\}$, we define coherent states in $\hbar$ as

$$F_\alpha(x) := (\varphi_{p, q} \otimes e_\tau)(x) := f(x - q) \exp(i p \cdot x)\delta_{\tau, \sigma}, \quad (14)$$

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 [21] and Evans et al. [5]). We also define

$$\phi_k(x) := (2^k)^{-3/2}\tilde{f}(\frac{x}{2^k}), \quad (15)$$

where $k \in \mathbb{N}$. We will pick $f$ depending on a dilation parameter. More specifically, we will choose

$$f(x) := g_R(x) := R^{-3/2}g(R^{-1}x) \quad (16)$$

(see [3] Formula (11)),

$$\tilde{f}(x) := \begin{cases} (2\pi\tilde{R})^{-1/2} |x| - \tilde{R}^{-1} \sin(\pi |x| - \tilde{R} |/\tilde{R}), & \tilde{R} \leq |x| \leq 2\tilde{R}; \\ 0, & \text{otherwise}, \end{cases} \quad (17)$$

where $R := Z^{-\delta}$ with $\delta \in (1/3, 2/3)$, $\tilde{R} \in \mathbb{R}_+$ 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 $\int_\Gamma d\Omega(\alpha) := (2\pi)^{-1} \int dp \int dq \sum_{\tau=1}^2$. The essential properties needed are the following. For $A, \tilde{A} \in L^1(\Gamma, d\Omega)$, let

$$\tilde{\gamma}_1 := \int_\Gamma d\Omega(\alpha)\tilde{A}(\alpha)|F_\alpha|/|F_\gamma|,$$
\[
\gamma_2 := \sum_{k=K+1}^{K+N-Z} |\phi_k \rangle \langle \phi_k |,
\]

\[
\tilde{\gamma}_2 := \epsilon_R \sum_{k=K+1}^{K+Z} |\phi_{N-Z+k} \rangle \langle \phi_{N-Z+k} |, \quad \text{where} \quad \epsilon_R := 1 - \frac{\int_{\Gamma} d\Omega(\alpha) \tilde{A}(\alpha)}{Z}.
\]

Then

\[
\gamma := \gamma_1 + \gamma_2 + \tilde{\gamma}_2
\]

and

\[
(18) \quad \gamma_1 := \int_{\Gamma} d\Omega(\alpha) A(\alpha) |F_\alpha \rangle \langle F_\alpha |
\]

(see [11] Formula (12)) are trace class operators.

We will pick

\[
(19) \quad A(\alpha) := \chi_{\{ (p,q) \in \mathbb{R}^6 | p^2/2 - V_Z(q) \leq 0 \}} (p,q)
\]

(see [11] Formula (16)),

\[
(20) \quad \tilde{A}(\alpha) := \chi_{\{ (p,q) \in \mathbb{R}^6 | p^2/2 - V_Z(q) \leq 0, |q| \leq \tilde{R} - R \}} (p,q),
\]

where \( V_Z := Z/|\cdot| - |\cdot|^{-1} \ast \rho_{TF}^{(N,Z)} \); here \( \rho_{TF}^{(N,Z)} \) is the unique minimizer of the Thomas-Fermi functional

\[
(21) \quad \mathcal{E}_{TF}(\rho) := \int_{\mathbb{R}^3} \left[ \frac{3}{5} \gamma_{TF} \rho(x)^{5/3} - \frac{Z}{|x|} \rho(x) \right] dx + D(\rho,\rho)
\]

in the set of functions \( \rho \in \{ \rho | \rho \geq 0, \int_{\mathbb{R}^3} \rho \leq N, \rho \in L^{5/3}(\mathbb{R}^3) \} \). Here

\[
D(\rho,\rho) := \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \rho(x)|x-y|^{-1} \rho(y)dxdy
\]

is the Coulomb scalar product. For fermions with \( q \) spin states per particle, \( \gamma_{TF} := (6\pi^2/q)^{2/3}h^2/(2m) \) (see Lieb [21] Formula (2.6)), i.e., in our units, \( \gamma_{TF} = (3\pi^2)^{2/3}/2 \).

According to [25], \( E_{TF}(N,Z) := \inf \mathcal{E}_{TF}(\rho) \) is strictly monotone decreasing for \( N \leq Z \) and constant for \( N > Z \). Thus for \( N > Z \), the minimizer \( \rho \) of the Thomas-Fermi functional (21) coincides the minimizer in the case \( N = Z \), which we denote by \( \rho_Z \). Hence \( V_Z = Z/|\cdot| - |\cdot|^{-1} \ast \rho_Z \) for \( N > Z \).

By Lemma 18,

\[
(22) \quad 0 \leq A \leq 1 \implies 0 \leq \gamma_1 \leq 1,
\]

according to the definition of \( \tilde{A} \) and the support sets of \( \phi_k \),

\[
(23) \quad 0 \leq \tilde{A} \leq 1 \implies 0 \leq \gamma \leq 1;
\]

by Lemma 19,

\[
(24) \quad \text{tr} \, \gamma_1 = \int_{\Gamma} d\Omega(\alpha) A(\alpha) \leq N,
\]

\[
(25) \quad \text{tr} \, \gamma = \text{tr} \, \gamma_1 + \text{tr} \, \gamma_2 + \text{tr} \, \tilde{\gamma}_2 = N.
\]

Using \( \Phi \) we can lift \( \gamma \) to an operator on \( \mathcal{F} \)

\[
(26) \quad \gamma\Phi := \Phi \gamma \Phi^*.
\]
3.2. Upper Bound on $E_{\text{HF}}^R(\gamma)$. 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

$$S_{\partial N} := \{ \gamma \in \mathcal{S}^1(h) | E_c(\hat{\rho}) \gamma \in \mathcal{S}^1(h), \ 0 \leq \gamma \leq 1, \ \text{tr} \gamma = N \}$$

where $\mathcal{S}^1(h)$ denotes the trace class operators on $h$.

$$E_{\text{HF}}^R : S_{\partial N} \to \mathbb{R}$$

$$\gamma \mapsto \text{tr}[(E_c(\hat{\rho}) - c^2 - Z/|x|)\gamma] + D(\rho_x, \rho_{\gamma_x})$$

where – as usual $-\rho_x(x) := \gamma(x,x)$ is the density associated to $\gamma$ and $D$ is the Coulomb scalar product. By the analogue of Lieb’s result [22, Formula (9)] and [20] (see also Bach [1]) – which trivially transcribes from the Schrödinger setting to the present one – we have for all $\gamma \in S_{\partial N}$

$$E(c,N,Z) \leq E_{\text{HF}}^R(\gamma).$$

3.2.1. Kinetic Energy of $\gamma_1$. 

**Lemma 1.** The kinetic energy of $\hat{\gamma}_1$ does not exceed the kinetic energy of $\gamma_1$, i.e.,

$$\text{tr}[(E_c(\hat{\rho}) - c^2)\gamma_1] \leq \text{tr}[(E_c(\hat{\rho}) - c^2)\gamma_1].$$

**Proof.** According to

$$E_c(\hat{\rho}) - c^2 \geq 0,$$

we have

$$\text{tr}[(E_c(\hat{\rho}) - c^2)(\gamma_1 - \gamma_1)] = \int_{\Gamma} d\Omega(\alpha)|\tilde{A}(\alpha) - A(\alpha)||[E_c(\hat{\rho}) - c^2]F_\alpha(x)| \bar{F}_\alpha(x) dx$$

$$= \frac{1}{2} \int (2\pi)^{-3} \int_{p^2/2 - V_2(q) \leq 0} \sum_{\tau=1}^{2} dp dq |(E_c(\hat{\rho}) - c^2)^{1/2}F_\alpha(x)|[(E_c(\hat{\rho}) - c^2)^{1/2}F_\alpha(x)] dx$$

$$= - (2\pi)^{-3} \int \int |(E_c(\hat{\rho}) - c^2)^{1/2}F_\alpha(x)|^2 dx dp dq \leq 0.$$ 

Thus $\text{tr}[(E_c(\hat{\rho}) - c^2)\gamma_1] \leq \text{tr}[(E_c(\hat{\rho}) - c^2)\gamma_1]$. 

3.2.2. External Potential of $\gamma_1$.

**Lemma 2.** For any $\varepsilon > 0$, there exists $\bar{R}$ large enough such that

$$\text{tr}[-Z/|x|\gamma_1] \leq \text{tr}[-Z/|x|\gamma_1] + \varepsilon,$$

obviously for any fixed $\bar{R}$, we have

$$\text{tr}[-Z/|x|\gamma_1] \geq \text{tr}[-Z/|x|\gamma_1],\ \text{i.e.,}$$

$$\text{tr}[-Z/|x|\gamma_1] \to \text{tr}[-Z/|x|\gamma_1], \ \bar{R} \to \infty.$$
Lemma 3. According to Lieb [21, Formula (2.18)], we can write the Thomas-Fermi equation as
\[ \gamma_{TF} \rho_Z^{2/3}(x) = [V_Z(x) - u']_+, \]
where \( u' \geq 0 \) is some constant and for \( t \in \mathbb{R} \), we set \( \lfloor t \rfloor := \max \{ t, 0 \} \). Then for \( N > Z \), the Thomas-Fermi potential \( V_Z := \frac{Z}{|x|} - \rho_Z * \cdot |x|^{-1} \) can be written as
\[ \gamma_{TF} \rho_Z^{2/3} = V_Z \]
(see, e.g., Gombás [15]).

Using Kato’s inequality (see [16, Formula (2.9)]), passing from \( \xi \) to \( \frac{\xi}{R} + p \) and taking into account that
\[ |\hat{g}(\xi)|^2 \| \xi \|^2 + 2|\xi| + 1 \]
is integrable because \( g \in H^{3/2}(\mathbb{R}^3) \), we can get
\[
(37) \quad \text{tr}[(-Z/|x|)(\gamma_{1\Phi} - \gamma_{1\Phi})] \leq \frac{\pi}{2} Z \int \int_{\Gamma} d\Omega(\alpha) |A(\alpha) - \tilde{A}(\alpha)| \hat{F}_\alpha(\xi)^2 |\xi| d\xi
\]
\[
= \frac{\pi}{2} Z \int (2\pi)^{-3} \int_{\mathbb{R}^2} \sum_{q \geq 0} \sum_{|q| > R - R} dp d\xi |\hat{F}_\alpha(\xi)|^2 |\xi| d\xi
\]
\[
\leq kZ \int_{\Gamma} d\Omega(\alpha) |A(\alpha) - \tilde{A}(\alpha)| R^{-4} \int |\hat{g}(\xi)|^2 |\xi| + R p |d\xi|
\]
\[
\leq kZ \int_{\Gamma} d\Omega(\alpha) |A(\alpha) - \tilde{A}(\alpha)| R^{-4} (1 + R |p|)
\]
\[
\leq kZ^{1+4\delta} \int_{\mathbb{R}^2} dp d\xi (1 + R |p|)
\]
\[
\leq kZ^{1+4\delta} \int \rho_Z(q) + R \rho_Z^{4/3}(q) dq \rightarrow 0, \quad \text{when} \quad R \rightarrow \infty.
\]
The last step is according to absolute continuity of Lebesgue integral. Thus \( \text{tr}[(-Z/|x|)(\gamma_{1\Phi} - \gamma_{1\Phi})] \rightarrow \text{tr}[(-Z/|x|)(\gamma_{1\Phi})] \), when \( R \rightarrow \infty \). \( \square \)

3.2.3. The Electron-Electron Interaction of \( \gamma_1 \).

Lemma 3. The electron-electron interaction of \( \gamma_1 \) does not exceed the electron-electron interaction of \( \gamma_1 \), i.e.,
\[ D(\rho_{\gamma_{1\Phi}}, \rho_{\gamma_{1\Phi}}) \leq D(\rho_{\gamma_{1\Phi}}, \rho_{\gamma_{1\Phi}}). \]

Proof.
\[ D(\rho_{\gamma_{1\Phi}}, \rho_{\gamma_{1\Phi}})
\]
\[ = \frac{1}{2} \int \int_{\Gamma} d\Omega(\alpha) \tilde{A}(\alpha)|\Phi F_\alpha(x)^2| d\Omega(\alpha) \tilde{A}(\alpha)|\Phi F_\alpha(y)^2| d\xi dy
\]
\[ \leq \frac{1}{2} \int \int_{\Gamma} d\Omega(\alpha) A(\alpha)|\Phi F_\alpha(x)^2| d\Omega(\alpha) A(\alpha)|\Phi F_\alpha(y)^2| d\xi dy
\]
\[ = D(\rho_{\gamma_{1\Phi}}, \rho_{\gamma_{1\Phi}}). \]
3.2.4. Kinetic Energy of \( \gamma_2 \). We introduce the set of density matrices
\[
S_N := \{ \gamma_1 \in S^1(h) | E_c(\hat{p}) \gamma_1 \in S^1(h), \ 0 \leq \gamma_1 \leq 1, \ \text{tr} \gamma_1 \leq N \}
\]
where \( S^1(h) \) denotes the trace class operators on \( h \).

**Lemma 4.** For any \( \varepsilon > 0 \), there exists a large enough \( K \) such that
\[
\text{tr}[(E_c(\hat{p}) - c^2) \gamma_2 \Phi] \leq \varepsilon, \text{ i.e.,}
\]
\[
\text{tr}[(E_c(\hat{p}) - c^2) \gamma_2] \rightarrow 0, \ K \rightarrow \infty.
\]

**Proof.** By concavity we have
\[
E_c(\hat{p}) - c^2 \leq \frac{1}{2} \hat{p}^2 = -\frac{1}{2} \Delta,
\]
which implies that the Brown-Ravenhall kinetic energy is bounded by the non-relativistic one, i.e., for all \( \gamma_2 \in S_N \) with \( -\Delta \gamma_2 \in S^1(h) \)
\[
\text{tr}[(E_c(\hat{p}) - c^2) \gamma_2] \leq \text{tr}(-\frac{1}{2} \Delta \gamma_2).
\]
Then
\[
\text{tr}[(E_c(\hat{p}) - c^2) \gamma_2] \leq \text{tr}(-\frac{1}{2} \Delta \gamma_2) = \frac{1}{2} \sum_{k=K+1}^{K+N-Z} (2^k)^{-2} \| \nabla \hat{f} \|^2
\]
\[
\leq \frac{1}{2} \sum_{k=K+1}^{\infty} 4^{-k} \| \nabla \hat{f} \|^2 = \frac{1}{2} \left( \frac{1}{4} \right)^{K+1} \| \nabla \hat{f} \|^2
\]
\[
= \frac{2}{3} \left( \frac{1}{4} \right)^{K+1} \| \nabla \hat{f} \|^2 \rightarrow 0, \text{ when } K \rightarrow \infty.
\]
Thus \( \text{tr}[(E_c(\hat{p}) - c^2) \gamma_2] \rightarrow 0 \), when \( K \rightarrow \infty \). \( \square \)

3.2.5. External Potential of \( \gamma_2 \).

**Lemma 5.** The external potential of \( \gamma_2 \) does not exceed zero, i.e.,
\[
\text{tr}[-Z/|x| \gamma_2 \Phi] \leq 0.
\]

**Proof.**
\[
\text{tr}[-Z/|x| \gamma_2] = Z \sum_{k=K+1}^{K+N-Z} (\Phi_\phi_k, \frac{1}{|x|} \Phi_\phi_k) = Z \sum_{k=K+1}^{K+N-Z} \int \Phi_\phi_k(x) \frac{1}{|x|} |x| dx \geq 0.
\]

\( \square \)

3.2.6. The Electron-Electron Interaction of \( \gamma_2 \).

**Lemma 6.** For any \( \varepsilon > 0 \), there exists a large enough \( K \) such that
\[
D(\rho_{\gamma_2 \Phi}, \rho_{\gamma_2 \Phi}) \leq \varepsilon, \text{ i.e.,}
\]
\[
D(\rho_{\gamma_2 \Phi}, \rho_{\gamma_2 \Phi}) \rightarrow 0, \ K \rightarrow \infty.
\]
Proof. According to \([2, \text{Equation (12)}]\), we can get

\[
D(\rho_{\gamma_2\Phi}, \rho_{\gamma_2\Phi}) \leq \frac{\pi}{4} \text{tr} |\gamma_{2\Phi}| \text{tr} (\sqrt{-\Delta} |\gamma_{2\Phi}|)
\]

\[
\leq \frac{\pi}{4} (N - Z) \sum_{k=K+1}^{K+N-Z} (\Phi \delta_k, |\hat{p}| \Phi \delta_k)
\]

\[
\leq \frac{\pi}{4} (N - Z) \sum_{k=K+1}^{K+N-Z} |\hat{\phi}_k(\hat{p})|^2 |\hat{p}| d\hat{p}
\]

\[
\leq \sum_{k=K+1}^{\infty} \frac{\pi}{4} (N - Z) \int (2^k)^{-1} |\hat{f}(\xi)|^2 |\xi| d\xi
\]

\[
= \frac{\pi}{4} (N - Z) \left( \frac{1}{2} \right)^K \int |\hat{f}(\xi)|^2 |\xi| d\xi \to 0, \text{ when } K \to \infty.
\]

Thus \(D(\rho_{\gamma_2\Phi}, \rho_{\gamma_2\Phi}) \to 0\), when \(K \to \infty\). \(\square\)

3.2.7. The Total Energy of \(E_{RF}(\gamma)\). We define the reduced Hartree-Fock functional on \(\gamma_1\) as following

\[
E_{RF}^R : S_N \to \mathbb{R}
\]

\[
\gamma_1 \mapsto \text{tr} [(E_c(\hat{p}) - c^2 - Z/|x|) \gamma_1\Phi] + D(\rho_{\gamma_1\Phi}, \rho_{\gamma_1\Phi})
\]

where – as usual – \(\rho_{\gamma_1}\) is the density associated to \(\gamma_1\) and \(D\) is the Coulomb scalar product. Gathering our above estimates allows us to get Theorem 2.

**Theorem 2.** The reduced Hartree-Fock functional of \(\gamma\) does not exceed the reduced Hartree-Fock functional of \(\gamma_1\), i.e.,

\[
E_{RF}^R(\gamma) \leq E_{RF}^R(\gamma_1),
\]

when \(\tilde{R}\) and \(K\) are tending to infinity.

Proof. According to the definition of \(\hat{\gamma}_2\) and Appendix C we get that as \(\tilde{R}\) tends to infinity, \(\epsilon_R\) tends to zero, and thus \(E_{RF}^R(\hat{\gamma}_2)\) tends to zero. Using the results obtained in Lemmata 1 through 6 we get for any \(\varepsilon > 0\), there exist large enough \(\tilde{R}\) and \(K\) such that

\[
E_{RF}^R(\gamma) = \text{tr} [(E_c(\hat{p}) - c^2 - Z/|x|) \gamma_\Phi] + D(\rho_{\gamma_\Phi}, \rho_{\gamma_\Phi})
\]

\[
\leq \text{tr} [(E_c(\hat{p}) - c^2 - Z/|x|) \gamma_1\Phi] + D(\rho_{\gamma_1\Phi}, \rho_{\gamma_1\Phi}) + \varepsilon = E_{RF}^R(\gamma_1) + \varepsilon.
\]

\(\square\)

3.3. 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 \(\mathfrak{S}^1(\mathfrak{h})\), where \(\mathfrak{S}^1(\mathfrak{h})\) denotes the trace class operators on \(\mathfrak{h}\). We define the reduced Hartree-Fock functional of \(\gamma_1\) as \((49)\). By Theorem 2 and the analogon of Lieb’s result [22, 20] (see also Bach [1]) – which trivially transcribes from the Schrödinger setting to the present one – we have for all \(\gamma_1 \in S_N\)

\[
E(c, N, Z) \leq E_{HF}^R(\gamma) \leq E_{HF}^R(\gamma_1).
\]
3.3.1. Kinetic Energy. [12] implies that the Brown-Ravenhall kinetic energy is bounded by the non-relativistic one, i.e., for all $\gamma_1 \in S_N$ with $-\Delta \gamma_1 \in \mathfrak{S}^1(h)$

$$\text{(53)} \quad \text{tr}[(E_c(\mathbf{p}) - c^2)\gamma_1] \leq \text{tr}(-\frac{1}{2}\Delta \gamma_1).$$

Insertion of $\gamma_1$ (see Equations (14), (16), (18), and (19)) turns the right hand side into the Thomas-Fermi kinetic energy modulo the positive error $(\text{tr} \gamma_1)\|\nabla g\|^2R^{-2}$ (see Lieb [21] Formula (5.9)).

In fact, we choose

$$f(x) = (2\pi R)^{-1/2}|x|^{-1}\sin(\pi|x|/R)$$

(see Lieb [21] Formula (5.11)). Because of $f(x) = R^{-3/2}g(R^{-1}x)$, we know

$$g(x) = (2\pi)^{-1/2}|x|^{-1}\sin(\pi|x|).$$

Let $\eta = R^{-1}x$, we can calculate

$$\nabla f = R^{-3/2}\nabla g(R^{-1}x) = R^{-3/2}\nabla \eta g(\eta)\frac{\partial \eta}{\partial x} = R^{-3/2}\nabla \eta g(\eta)\frac{1}{R}\frac{x}{|x|},$$

$$|\nabla f| = R^{-5/2}|\nabla \eta g(\eta)|, \quad \int |\nabla f|^2d^3x = \int R^{-5}|\nabla \eta g(\eta)|^2(R^3d^3\eta) = R^{-2}\|\nabla g\|^2.$$

Thus we obtain

$$\text{(54)} \quad \text{tr}[(E_c(\mathbf{p}) - c^2)\gamma_1] \leq \frac{3}{5}\gamma_{TF}\int \rho_{Z}^{5/3}(x)dx + ZR^{-2}\|\nabla g\|^2.$$

3.3.2. External Potential. Since $-Z\text{tr}(\varphi_2\gamma_1)$ 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 interesting to see that $\varphi_2$ does indeed not significantly contribute to the energy, if $\gamma_1$ is chosen as above. Moreover, the proof will be also useful for the proof of Lemma 8.

Lemma 7. For our choice of $\gamma_1 = \int_{\Gamma} d\Omega(\alpha)A(\alpha)|F_\alpha\rangle\langle F_\alpha|$ and $\delta \in (1/3, 2/3)$ we have

$$\text{(55)} \quad 0 \leq Z \text{tr}(\varphi_2\gamma_1) \leq kZ \int_{\Gamma} d\Omega(\alpha)\text{A}(\alpha) \int d\xi d\xi' \frac{\varphi_2(\xi)\varphi_2(\xi')}{|\xi - \xi'|^2N_c(\xi)N_c(\xi')} = O(Z^{4/3+\delta}).$$

Proof. We begin by estimating the expectation of $\varphi_2$ on the coherent state [12].

$$\text{(56)} \quad 0 \leq (F_\alpha, \varphi_2 F_\alpha) \leq k \int d\xi d\xi' \frac{\varphi_2(\xi)\varphi_2(\xi')}{N_c(\xi)|\xi - \xi'|^2N_c(\xi')},$$

$$\leq kc^{-2}R^{-3} \int d\xi d\xi' \frac{|\varphi_2(\xi)|^2|\varphi_2(\xi')|^2}{|\xi - \xi'|^2} \leq kc^{-2}R^{-3}(1+R|R|+R^2|R|^2).$$

Here, we have used that $N_c(\xi) \geq \sqrt{Z}c^2$ and, at the last step, that

$$\frac{|\varphi_2(\xi)|^2|\varphi_2(\xi')|^2}{|\xi - \xi'|^2} \leq (4\xi + |\xi| + |\xi'| + 1).$$
is integrable in $\xi$ and $\xi'$ because $g \in H^{3/2}(\mathbb{R}^3)$. Thus according to (56), we get
\begin{equation}
0 \leq \text{tr}(\varphi_2 \gamma_1) = Z \int d\Omega(\alpha) A(\alpha)(F_\alpha, \varphi_2 F_\alpha)
\leq k \frac{Z}{c^2 R^3} \int d\Omega(\alpha) A(\alpha)(1 + R|p| + R^2|p|^2)
\leq k \frac{Z}{c^2 R^3} \left\{ Z + R \int dq \left| Z^{4/3} V_1(Z^{1/3} q) \right|^2 + R^2 \int dq \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})
\end{equation}
(see [3] Formula (27)).

**Lemma 8.** For our choice of $\gamma_1$ and $\delta \in (1/3, 2/3)$ we have
\begin{equation}
|Z \text{tr}(|\cdot|^1 - \varphi_1)\gamma_1| 
\leq k Z \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}).
\end{equation}

**Proof.** We first note that
\begin{equation}
1 - \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi) N_c(\xi')} 
\leq \frac{3E_c(\xi)E_c(\xi') - c^2(E_c(\xi) + E_c(\xi') + c^2)}{N_c(\xi) N_c(\xi')}
\end{equation}
Then, noting that $E_c(\xi) - c^2 \leq c|\xi|$, we obtain
\begin{equation}
1 - \frac{(E_c(\xi) + c^2)(E_c(\xi') + c^2)}{N_c(\xi) N_c(\xi')} 
\leq \frac{3E_c(\xi)|\xi'| + 2c^3(|\xi| + |\xi'|)}{N_c(\xi) N_c(\xi')}
\leq \frac{3c^2|\xi||\xi'| + 2c^3(|\xi| + |\xi'|)}{2c^4}
\end{equation}
Using this last equation, we estimate
\begin{equation}
|(F_\alpha, \frac{1}{|\cdot|} - \varphi_1)F_\alpha)|
\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_{\mathbb{R}^6} \frac{d\xi d\xi'}{|\xi - \xi'|^2} \left| \hat{g}_R(\xi - p) \right| \left| \hat{g}_R(\xi' - p) \right| (c^{-2} |\xi||\xi'| + c^{-1} (|\xi| + |\xi'|))
\leq kc^{-2} R^{-3} \int d\xi \int d\xi' \frac{|\hat{g}(\xi)||\hat{g}(\xi')|}{|\xi - \xi'|^2} (|\xi| + R|p||\xi'| + R|p| + cR|\xi| + cR|\xi'|)
\leq kc^{-2} R^{-3} \int d\xi \int d\xi' \frac{|\hat{g}(\xi)||\hat{g}(\xi')|}{|\xi - \xi'|^2} (|\xi||\xi'| + R|p||\xi| + |R|p| + R|\xi| + cR^2|p|)
\leq kc^{-2} R^{-3} (1 + R|p| + R^2|p|^2 + cR + cR^2|p|)
Theorem 3. There exist a constant $k$ such that for all $Z \geq 1$ we have

$$E(Z, N, Z) \leq E_{TF}(N/Z, 1)Z^{7/3} + kZ^{20/9}.$$
Proof. Following Lieb [21] 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 7 through [21] and applying (51) and (54) we get

\[
E(c,N,Z) \leq E_R^{HF}(\gamma) \leq E_R^{HF}(\gamma_1) \leq E_{TF}(N,Z) + O(Z^{1+2\delta} + Z^{2-2\delta} + Z^{2+\delta})
\]

(see [3] Formula (35)) which is optimized for \( \delta = 5/9 \) giving the claimed result. \( \square \)

3.4. Lower Bound. The lower bound is – contrary to the usual folklore – easy. As we will see, it is a corollary of Sørensen’s [28] result for the Chandrasekhar operator and an estimate on the potential generated by the exchange hole [26].

The exchange hole of a density \( \sigma \) at a point \( x \in \mathbb{R}^3 \) is defined as the ball \( B_{R_{\sigma}(x)}(x) \) 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

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

3.4.1. \( L^\infty \)-Bound on the Exchange Hole Potential. We begin with the following remark: the Thomas-Fermi potential \( V_Z := Z/|\cdot| - \rho_Z * |\cdot|^{-1} \) can be written as (36). This equation yields immediately the upper bound

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

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

Lemma 10.

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

Proof. The function

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

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

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:

(70) \[ L_{\rho_Z}(x) \leq A_1(x) + A_2(x) \]

(see [3] Formula (46)) where

(71) \[ A_1(x) := \int_{|y| \leq 1/Z} \frac{\rho_Z(x+y)}{|y|} dy \leq \left( \frac{Z}{\gamma_{TF}} \right)^{3/2} \int_{|y| \leq 1/Z} \frac{dy}{|y||y+x|^{3/2}} = (Z/\gamma_{TF})^{3/2}Z^{-1/2}f(|x|Z) \leq \|f\|_{\infty}^{-3/2}Z. \]

and

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

These two estimates prove the claim. \( \square \)
Indeed, we have − (76) Λ

\[\text{Lemma 10}\] allows us to estimate the \( N \) electron operator \( B_{c,N,Z} \) 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 [28], we derive an estimate on \( L_{\rho_\delta} \) (where \( \rho_\delta := \rho_Z \ast g_{Z-t}^2 \)), i.e., the exchange hole potential of the density occurring in Sørensen’s proof.

**Lemma 11.**

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

**Proof.** We proceed analogously to the proof of Lemma [10]

\[ L_{\rho_\delta}(x) \leq \int_{|y|\leq 1/2} \frac{\rho_\delta(x+y)}{|y|} dy + \int_{1/2 \leq |y| \leq R_N(x)} \frac{\rho_\delta(x+y)}{|y|} dy \]

\[ \leq \int d\eta^2_{Z-t}(z) \int_{|y|\leq 1/2} \frac{\rho_Z(x-z+y)}{|y|} dy + Z \int_{|y|\leq R_N(x)} \rho_\delta(x+y) dy \]

\[ \leq \int d\eta^2_{Z-t}(z) A_1(x-z) + \frac{Z}{2} \leq kZ \]

(see [4, Formula (49)]) where we used the definition of the radius of the exchange hole from the second line to the third line, the definition of \( A_1 \) in the next step, and in the last step the \( L^\infty \)-estimate [4] on \( A_1 \). □

3.4.2. Lower Bound.

**Theorem 4.**

\[ \lim_{Z \to \infty} \inf [E(c, N, Z) - E_{TF}(N, Z)] Z^{-7/3} \geq 0. \]

**Proof.** Pick \( \delta > 0 \) and set \( \rho_\delta := \rho_Z \ast g_{Z-t}^2 \). Then the exchange hole correlation bound [26, Equation (14)] implies the following pointwise estimate

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

Because of the spherical symmetry of \( g \) we can use Newton’s theorem [27] and replace \( \rho_\delta \) by \( \rho_Z \) in the third summand of the right hand side of (74). Then, by Lemma [41] we get that for all normalized \( \psi \in \Omega_N \)

\[ E(\psi) \geq \text{tr}[\Lambda_+(||D_0| - c^2 - V_6)\Lambda_-] - kNZ - D(\rho_Z, \rho_Z) \]

where, for \( t \in \mathbb{R} \), we set \( |t|_+ := \min\{t, 0\} \) and \( V_6 = Z/| \cdot | - \rho_\delta \ast | \cdot |^{-1} \).

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. [23, Appendix B]: Note that

\[ \Lambda_- = U^{-1} \Lambda_+ U, \quad \text{where} \quad U := \left( \begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \right). \]

Indeed, we have

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

and

\[ UD_0 U^{-1} = \left( \begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \right) \left( \begin{array}{cc} mc^2 & c \sigma \cdot \bar{p} \\ c \sigma \cdot \bar{p} & -mc^2 \end{array} \right) \left( \begin{array}{cc} 0 & -1 \\ 1 & 0 \end{array} \right) = -D_0. \]
We set $X := (|D_0| - c^2 - V_\delta(x))I_2$, and write
\[
\begin{align*}
\text{tr} \left[ \Lambda_+ \left( \begin{array}{cc} X & 0 \\ 0 & X \end{array} \right) \Lambda_+ \right] &\geq \text{tr} \left( \Lambda_+ \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right) \right) = \text{tr} \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right) \\
\text{tr} \left( \Lambda_- \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right) \right) &\geq \text{tr} \left( \Lambda_+ U \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right) U \right) = \text{tr} \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right)
\end{align*}
\]

Thus
\[
\begin{align*}
(77) \quad 2 \text{tr} \left( \Lambda_+ \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right) \right) &\geq \text{tr} \left( \Lambda_+ \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right) \right) + \text{tr} \left( \Lambda_- \left( \begin{array}{cc} X_- & 0 \\ 0 & X_- \end{array} \right) \right) = 2 \text{tr}(X_-).
\end{align*}
\]

Since $|D_0| = E_c(\hat{p})$ and $X$ is a 2 by 2 matrix, we obtain
\[
(78) \quad \text{tr} \left[ \Lambda_+ \left( |D_0| - c^2 - V_\delta(x) \right) \Lambda_+ \right] = \text{tr} \left[ \Lambda_+ \left( \begin{array}{cc} X & 0 \\ 0 & X \end{array} \right) \Lambda_+ \right] \geq \text{tr} \left( \Lambda_+ \left( \begin{array}{cc} X & 0 \\ 0 & X \end{array} \right) \right) = \text{tr} \left( E_c(\hat{p}) - c^2 - V_\delta(x) \right).
\]

Then
\[
(79) \quad E(Z/\kappa, N, Z) \geq 2 \text{tr} \left[ E_c(\hat{p}) - c^2 - V_\delta(x) \right] - D(\rho_Z, \rho_Z) - kNZ
\]

(see [4] Formula (42)) where the last trace is spinless. This connects to Sørensen’s Equation (3.2) from [28]. It is a fundamental result of [34] that $E(Z/\kappa, N, Z) = E(Z/\kappa, N_c(Z), Z)$, for any $N \geq N_c(Z)$, where $N_c$ is the number of negative particles that can be bound to an atom of nuclear charge $Z$. Considering $N_c < 2Z + 1$ (see [19] Formula (1.2)), when $Z \to \infty$, we can get
\[
(80) \quad E(Z/\kappa, N, Z) \geq 2 \text{tr} \left[ E_c(\hat{p}) - c^2 - V_\delta(x) \right] - D(\rho_Z, \rho_Z) - kO(Z).
\]

This result then follows using his lower bound. \hfill \Box

4. Case II: $N/Z = \lambda$ (Constant)

The case $\lambda > 1$ has been already solved in Section 3; $\lambda = 1$ is solved in [4], so it only remains to consider $\lambda < 1$.

4.1. Coherent States. This Section is analogous to 3.1

4.2. Upper Bound. This Division is similar to 3.2 and 3.3. Analogously to Formula (28), we introduce the set of density matrices
\[
(81) \quad S_{\partial N} := \{ \gamma \in \mathcal{S}^1(\mathfrak{h}) \mid E_c(\hat{p})\gamma \in \mathcal{S}^1(\mathfrak{h}), 0 \leq \gamma \leq 1, \text{tr} \gamma = N = \lambda Z, \}
\]

where $\mathcal{S}^1(\mathfrak{h})$ denotes the trace class operators on $\mathfrak{h}$; $\lambda$ is a number independent of $c, N, R, \text{or } Z$. Defining $E^R_{HF}$ as Formula (29), and as the same as above, for all $\gamma \in S_{\partial N}$, we have Formula (80).
4.2.1. Kinetic Energy. According to [25], we can write $\rho_{\text{TF}}^{(N, Z)}$ simply as $\rho_{\text{TF}}$ in the following. By concavity, and then analogously to Formula (53), we know

$$\text{tr}[(E_c(\rho) - c^2)\gamma] \leq \text{tr}(-\frac{1}{2}\Delta \gamma).$$

Similarly to Formula (53), we get

$$\text{tr}[(E_c(\rho) - c^2)\gamma] \leq \frac{3}{5} \gamma_{\text{TF}} \int \rho_{\text{TF}}(x) \, dx + (\text{tr} \gamma) R^{-2} \|\nabla g\|^2.$$  

4.2.2. External Potential. As the same as Part 5.3.2 we can obtain following two lemmata by the analogues of Lemmata 7 and 8.

Lemma 12. For our choice of $\gamma = \int_{\Gamma} d\Omega(\alpha) A(\alpha)|F_\alpha(\gamma)|$ and $\delta \in (1/3, 2/3)$ we have

$$0 \leq Z \text{tr}(\varphi_2\gamma) \leq kZ \int_{\Gamma} d\Omega(\alpha) A(\alpha) \int d\xi d\xi' c^2(\xi, \xi') \xi(\xi) N_c(\xi) N_c(\xi') = O(Z^{4/3+\delta}).$$

Lemma 13. For our choice of $\gamma$ and $\delta \in (1/3, 2/3)$ we have

$$\text{tr}((\gamma - 1 - \varphi_1)\gamma) \leq kZ \int_{\Gamma} d\Omega(\alpha) A(\alpha) \int d\xi d\xi' \xi(\xi) N_c(\xi) N_c(\xi') = O(Z^{5/3+\delta}).$$

4.2.3. The Electron-Electron Interaction. Similarly to Lemma 9 we get Lemma 14 below.

Lemma 14. For our choice of $\gamma$ and $\delta \in (1/3, 2/3)$ we have

$$D(\rho_{\gamma\Phi}, \rho_{\gamma}) - D(\rho_\gamma, \rho_\gamma) = O(Z^{5/3+\delta}),$$

where $\rho_\gamma$ is the density of $\gamma$ and $\rho_{\gamma\Phi}$ is the density of $\gamma_{\Phi}$.  

4.2.4. The Total Energy. By the analogue of Theorem 8 we obtain Theorem 5.

Theorem 5. There exist a constant $k$ such that we have for all $Z \geq 1$

$$E(Z/\kappa, N, Z) \leq E_{\text{TF}}(\lambda, 1) Z^{7/3} + kZ^{20/9}.$$  

4.3. Lower Bound. This Part is similar to 3.4.

4.3.1. $L^\infty$-Bound on the Exchange Hole Potential.

Lemma 15. $

\|L_{\rho_{\Phi}}\|_\infty = O(Z).$

Similarly to Lemma 11 since we would like to take advantage of Sørensen’s result [28], we derive an estimate on $L_{\rho_{\Phi}}$ (where $\rho_{\Phi} := \rho_{\text{TF}} * g_{Z^{-\delta}}^2$).

Lemma 16. \n
$\|L_{\rho_{\Phi}}\|_\infty = O(Z).$

4.3.2. Lower Bound.

Theorem 6. \n
$$\liminf_{Z \to \infty} [E(c, N, Z) - E_{\text{TF}}(N, Z)] Z^{-7/3} \geq 0.$$
Lemma 17. The one-particle Brown-Ravenhall operator $B_γ$ for an electron the external electric potential of a point nucleus acting on Pauli spinors is

$$B_{c,Z} = E_c(p) - Zφ_1 - Zφ_2.$$  

Proof. For any $ψ ∈ h$, we can get

$$(87) \quad \mathcal{E}(ψ) = (ψ, B_{c,Z}ψ) = (ψ, D_{c,Z}ψ)$$

$$= \left( \frac{E_c(p) + c^2}{N_c(p)} u \right) \left( \frac{c \sigma \cdot p}{N_c(p)} u \right) \left( \frac{c^2 - Z|\cdot|^{-1}}{c \sigma \cdot p} \right) \left( \frac{-c^2 - Z|\cdot|^{-1}}{\frac{c \sigma \cdot p}{N_c(p)} u} \right)$$

$$= (Φ_1 u \Phi_2 u) \left( \frac{(c^2 - Z|\cdot|^{-1}) Φ_1 u + c \sigma \cdot p Φ_2 u}{c \sigma \cdot p Φ_1 u + (-c^2 - Z|\cdot|^{-1}) Φ_2 u} \right)$$

$$= (u, (Φ_1 c^2 Φ_1 + Φ_1 c \sigma \cdot p Φ_2 + Φ_2 c \sigma \cdot p Φ_1 - Φ_2 c^2 Φ_2) u) - Ζ(u, φ_1 u) - Ζ(u, φ_2 u)$$

$$= (u, E_c(p) u) - Ζ(u, φ_1 u) - Ζ(u, φ_2 u).$$  

□

App. A. The Proof of $B_{c,Z} = E_c(p) - Zφ_1 - Zφ_2$  

Lemma 18.  

$0 ≤ γ_1 ≤ 1 \quad \text{and} \quad 0 ≤ γ ≤ 1.$

Proof. For any normalized $u ∈ h$, using Parseval’s equality, we get

$$(88) \quad (u, γ_1 u)$$

$$= (2π)^{-3} \int u(x) \int \frac{f(x - q)f(x' - q)}{A(α)} \exp(-iq⋅x') \int \overline{u(x')} dp dq dx'dx$$

$$= \int \overline{u(x)} f(x - q) dx A(α)$$

$$× \int \exp(-iq⋅x') u(x') f(x' - q) dx'dp dq$$

$$= \int |(2π)^{-3/2} \int \exp(-ip⋅x) u(x) f(x - q) dx|^2 A(α) dp dq$$

$$≤ \int |(2π)^{-3/2} \int \exp(-ip⋅x) u(x) f(x - q) dx|^2 dp dq$$

$$= \int |u(x)|^2 |f(x - q)|^2 dx dq$$

$$= \int |u(x)|^2 \left[ \int |f(x - q)|^2 dq \right] dx = ||u||^2 = 1,$$
and following [SS],

(89) \((u, \gamma u) = (u, \gamma_1 u) + (u, \gamma_2 u) + (u, \gamma_2 u)\)
\[
\leq \int_{|x| \leq R-R} |u(x)|^2 \, dx + \sum_{k=K+1}^{K+N-Z} \int_{x \in \text{supp}(\phi_k)} |u(x)|^2 \, dx
\]
\[
+ \sum_{k=K+N-Z+1}^{K+N} \int_{x \in \text{supp}(\phi_k)} |u(x)|^2 \, dx
\]
\[
\leq \|u\|^2 = 1.
\]

\[\square\]

**Appendix C. Checking of \(\text{tr} \gamma_1\) and \(\text{tr} \gamma\)**

**Lemma 19.** \n\(\text{tr} \gamma_1 \leq N\) and \(\text{tr} \gamma = N\).

**Proof.** Using formula (36), we can get

(90) \(\text{tr} \gamma_1 = \int_{\Gamma} d\Omega(\alpha) A(\alpha) = (2\pi)^{-3} \int_{\mathbb{R}^{2-\nu_2(q)}} \sum_{\tau=1}^{2} d\rho d\sigma\)
\[
= 2(2\pi)^{-3} \frac{4\pi}{3} (2\gamma_{TF})^{3/2} \int \rho_Z(\sigma) d\sigma = Z \leq N,
\]

and

(91) \(\text{tr} \gamma = \int_{\Gamma} d\Omega(\alpha) \tilde{A}(\alpha) + (N - Z) + \epsilon_R Z = N.\)

\[\square\]

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