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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 α^2Ry.

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1. Introduction

The energy of heavy atoms has attracted considerable interest in the context of non-relativistic quantum mechanics. Lieb and Simon [20] proved that the leading behaviour of the ground-state energy is given by the Thomas–Fermi energy which decreases as $Z^{7/3}$. The leading correction to this behaviour, the so-called Scott correction was established by Hughes [14, 15] (lower bound) and Siedentop and Weikard [24–28] (lower and upper bound). In fact even the existence of the $Z^{5/3}$-correction conjectured by Schwinger was proven [4–12]. Later these results were 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 behaviour 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 relativistic 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 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 ψ is defined as

$$\begin{aligned} &\bigwedge_{\nu=1}^{N}(H^{1/2}(\mathbb{R}^3)\otimes\mathbb{C}^4)\to\mathbb{R} \\ &\psi\mapsto\left(\psi,\left(\sum_{\nu=1}^{N}(D_{c,Z}-c^2)_\nu+\sum_{1\leqslant\mu<\nu\leqslant N}|\mathbf{x}_\mu-\mathbf{x}_\nu|^{-1}\right)\psi\right)\end{aligned}\tag{1}$$

where

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

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

$$\mathfrak{H}_N:=\bigwedge_{\nu=1}^{N}\mathfrak{H},\tag{2}$$

the underlying one-particle Hilbert space is

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

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 [29, 30], if $\kappa:=Z/c\leqslant\kappa_{\mathrm{crit}}:=2/(\pi/2+2/\pi)$. (In the following, we will assume that the ratio $\kappa\in[0,\kappa_{\mathrm{crit}})$ is fixed.) According to Friedrichs, this allows us to define a self-adjoint operator $B_{c,N,Z}$ whose ground-state energy

$$E(c,N,Z):=\inf\sigma(B_{c,N,Z})=\inf\{\mathcal{E}(\psi)|\psi\in\mathfrak{Q}_N,\|\psi\|=1\}\tag{4}$$

is of concern to us in this paper. In fact, denoting by $E_{\mathrm{TF}}(Z,Z)$ 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.

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

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 us 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 $\psi \in \mathfrak{H}$ can be written as

$$\psi := \begin{pmatrix} \frac{E_c(\hat{\mathbf{p}})+c^2}{N_c(\hat{\mathbf{p}})} u \\ \frac{c\hat{\mathbf{p}}\cdot\boldsymbol{\sigma}}{N_c(\hat{\mathbf{p}})} u \end{pmatrix} \tag{5}$$

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

$$\hat{\mathbf{p}} := -\mathrm{i}\nabla, \qquad E_c(\mathbf{p}) := (c^2\mathbf{p}^2 + c^4)^{1/2}, \qquad N_c(\mathbf{p}) := [2E_c(\mathbf{p})(E_c(\mathbf{p}) + c^2)]^{1/2}.$$

In fact, the map

$$\begin{aligned} &\Phi : \mathfrak{h} \to \mathfrak{H} \\ &u \mapsto \begin{pmatrix} \Phi_1 u \\ \Phi_2 u \end{pmatrix} := \begin{pmatrix} \frac{E_c(\hat{\mathbf{p}})+c^2}{N_c(\hat{\mathbf{p}})} u \\ \frac{c\hat{\mathbf{p}}\cdot\boldsymbol{\sigma}}{N_c(\hat{\mathbf{p}})} u \end{pmatrix} \end{aligned} \tag{6}$$

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

It suffices to study the energy as a function of u,

$$\mathcal{E} \circ \left(\otimes_{\nu=1}^N \Phi\right) : \bigwedge_{\nu=1}^N \mathfrak{h} \to \mathbb{R}. \tag{7}$$

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

$$B_{c,Z} := E_c(\hat{\mathbf{p}}) - Z\varphi_1 - Z\varphi_2, \tag{8}$$

where we have split the potential into

$$\varphi_1 := \Phi_1^* |\cdot|^{-1} \Phi_1, \qquad \varphi_2 := \Phi_2^* |\cdot|^{-1} \Phi_2. \tag{9}$$

As we will see, the first part φ_1 contributes to the non-relativistic limit whereas the second part turns out to give energy contribution that does 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 coherent states.

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

$$F_\alpha(x) := (\varphi_{\mathbf{p},\mathbf{q}} \otimes e_\tau)(x) := f(\mathbf{x} - \mathbf{q}) \exp(\mathrm{i}\mathbf{p} \cdot \mathbf{x}) \delta_{\tau,\sigma}, \tag{10}$$

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

$$f(\mathbf{x}) := g_R(\mathbf{x}) := R^{-3/2} g(R^{-1}\mathbf{x}) \tag{11}$$

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 Γ counting the number of electrons per phase space volume in the spirit of Planck is $\int_\Gamma đ\Omega(\alpha) := (2\pi)^{-3} \int \mathrm{d}\mathbf{p} \int \mathrm{d}\mathbf{q} \sum_{\tau=1}^{2}$. The essential properties needed are the following. For $A \in L^1(\Gamma, đ\Omega)$

$$\gamma := \int_\Gamma đ\Omega(\alpha) A(\alpha) |F_\alpha\rangle\langle F_\alpha| \tag{12}$$

is a trace class operator and

$$0 \leqslant A \leqslant 1 \implies 0 \leqslant \gamma \leqslant 1 \tag{13}$$

$$\operatorname{tr} \gamma = \int_\Gamma đ\Omega(\alpha) A(\alpha). \tag{14}$$

Using Φ we can lift any such operator γ to an operator on $\mathfrak{H}$

$$\gamma_\Phi := \Phi \gamma \Phi^*. \tag{15}$$

We will pick

$$A(\alpha) := \chi_{\{(\boldsymbol{\xi}, \mathbf{x}) \in \mathbb{R}^6 | \boldsymbol{\xi}^2/2 - V_Z(\mathbf{x}) \leqslant 0\}}(\mathbf{p}, \mathbf{q}) \tag{16}$$

where $V_Z := Z/|\cdot| - |\cdot|^{-1} * \rho_{\mathrm{TF}}$; here ρ_{TF} is the unique minimizer of the Thomas–Fermi functional

$$\mathcal{E}_{\mathrm{TF}}(\rho) := \int_{\mathbb{R}^3} \left[\frac{3}{5} \gamma_{\mathrm{TF}} \rho(\mathbf{x})^{5/3} - \frac{Z}{|\mathbf{x}|} \rho(\mathbf{x}) \right] \mathrm{d}\mathbf{x} + D(\rho, \rho) \tag{17}$$

where, for fermions with q spin states per particle, $\gamma_{\mathrm{TF}} := (6\pi^2/q)^{2/3} \hbar^2/(2m)$, i.e., in our units, $\gamma_{\mathrm{TF}} = (3\pi^2)^{2/3}/2$. Note that $\int đ\Omega(\alpha) A(\alpha) = Z$ [20]. Note also that $V_Z(\mathbf{q}) := Z^{4/3} V_1(Z^{1/3}\mathbf{q})$ (see also [13, 20]). Note also that the minimal energy $E_{\mathrm{TF}}(N, Z)$ fulfils the scaling relation

$$E_{\mathrm{TF}}(N, Z) = E_{\mathrm{TF}}(N/Z, 1) Z^{7/3}. \tag{18}$$

Note that we could restrict the minimization to $\int \rho \leqslant N$ without any problem. For $N \geqslant Z$ 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

$$S_N := \{\gamma \in \mathfrak{S}^1(\mathfrak{h}) \mid E_c(\hat{\mathbf{p}})\gamma \in \mathfrak{S}^1(\mathfrak{h}), 0 \leqslant \gamma \leqslant 1, \operatorname{tr}\gamma = N\}, \tag{19}$$

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

$$\begin{aligned} &\mathcal{E}_{\mathrm{HF}} : S_N \to \mathbb{R} \\ &\gamma \mapsto \operatorname{tr}[(E_c(\hat{\mathbf{p}}) - c^2 - Z/|\mathbf{x}|)\gamma_\Phi] + D\big(\rho_{\gamma_\Phi}, \rho_{\gamma_\Phi}\big) \end{aligned} \tag{20}$$

where, as usual, ρ_γ is the density associated with γ and D is the Coulomb scalar product. By the analogon of Lieb's result [16, 18] (see also [1])—which trivially transcribes from the Schrödinger setting to the present one—we have for all $\gamma \in S_N$

$$E(c, N, Z) \leqslant \mathcal{E}_{\mathrm{HF}}(\gamma). \tag{21}$$

3.2.1. Kinetic energy. By concavity we have

$$E_c(\mathbf{p}) - c^2 \leqslant \tfrac{1}{2}\mathbf{p}^2 \tag{22}$$

which implies that the Brown–Ravenhall kinetic energy is bounded by the non-relativistic one, i.e., for all $\gamma \in S_N$ with $-\Delta\gamma \in \mathfrak{S}^1(\mathfrak{h})$

$$\operatorname{tr}[(E_c(\hat{\mathbf{p}}) - c^2)\gamma] \leqslant \operatorname{tr}\left(-\tfrac{1}{2}\Delta\gamma\right). \tag{23}$$

Inserting our choice of γ (see equations (10), (11), (12) and (16)) turns the right-hand side into the Thomas–Fermi kinetic energy modulo the positive error $Z\|\nabla g\|^2 R^{-2}$ (see [17, formula (5.9)]), i.e.,

$$\operatorname{tr}[(E_c(\hat{\mathbf{p}}) - c^2)\gamma] \leqslant \frac{3}{5}\gamma_{\mathrm{TF}} \int \rho_{\mathrm{TF}}^{5/3}(\mathbf{x})\,\mathrm{d}\mathbf{x} + ZR^{-2}\|\nabla g\|^2. \tag{24}$$

3.2.2. External potential. Since $-Z\operatorname{tr}(\varphi_2\gamma)$ 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 φ_2 does indeed not significantly contribute to the energy, if γ is chosen as above. Moreover, the proof will be also useful for the proof of lemma 2.

Lemma 1. *For our choice of* $\gamma = \int_\Gamma đ\Omega(\alpha)|F_\alpha\rangle\langle F_\alpha|$ *and* $\delta \in (1/3, 2/3)$ *we have*

$$0 \leqslant Z\operatorname{tr}(\varphi_2\gamma) \leqslant kZ\int_\Gamma đ\Omega(\alpha)A(\alpha)\iint \mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}' \frac{c^2|\boldsymbol{\xi}||\boldsymbol{\xi}'||\hat{F}_\alpha(\boldsymbol{\xi})||\hat{F}_\alpha(\boldsymbol{\xi}')|}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2 N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')} = O(Z^{4/3+\delta}). \tag{25}$$

(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 φ_2 in a coherent state:

$$\begin{aligned} 0 &\leqslant (F_\alpha, \varphi_2 F_\alpha) \leqslant k\iint \mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}' \frac{c^2|\boldsymbol{\xi}||\boldsymbol{\xi}'||\hat{F}_\alpha(\boldsymbol{\xi})\hat{F}_\alpha(\boldsymbol{\xi}')|}{N_c(\boldsymbol{\xi})|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2 N_c(\boldsymbol{\xi}')} \\ &\leqslant kc^{-2}R^{-3}\iint \mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}' \frac{|\hat{g}(\boldsymbol{\xi})\hat{g}(\boldsymbol{\xi}')|}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}|\boldsymbol{\xi}+R\mathbf{p}||\boldsymbol{\xi}'+R\mathbf{p}| \leqslant kc^{-2}R^{-3}(1+R|\mathbf{p}|+R^2|\mathbf{p}|^2). \end{aligned} \tag{26}$$

Here, we used that $N_c(\boldsymbol{\xi}) \geqslant \sqrt{2}c^2$ and, in the last step, that

$$\frac{|\hat{g}(\boldsymbol{\xi})\hat{g}(\boldsymbol{\xi}')|}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}[|\boldsymbol{\xi}||\boldsymbol{\xi}'| + |\boldsymbol{\xi}| + |\boldsymbol{\xi}'| + 1]$$

is integrable in $\boldsymbol{\xi}$ and $\boldsymbol{\xi}'$ because $g \in H^{3/2}(\mathbb{R}^3)$. Thus we get

$$\begin{aligned} 0 \leqslant Z\operatorname{tr}(\varphi_2\gamma) &= Z\int đ\Omega(\alpha)A(\alpha)(F_\alpha, \varphi_2 F_\alpha) \\ &\leqslant k\frac{Z}{c^2R^3}\int đ\Omega(\alpha)A(\alpha)(1+R|\mathbf{p}|+R^2|\mathbf{p}|^2) \\ &\leqslant k\frac{Z}{c^2R^3}\left\{Z + R\int \mathrm{d}\mathbf{q}[Z^{4/3}V_1(Z^{1/3}\mathbf{q})]^2 + R^2[Z^{4/3}V_1(Z^{1/3}\mathbf{q})]^{5/2}\right\} \\ &= O(Z^{3\delta} + Z^{2/3+2\delta} + Z^{4/3+\delta}). \end{aligned} \tag{27}$$

□

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

$$\begin{aligned}
\left|Z\,\mathrm{tr}[(|\cdot|^{-1} - \varphi_1)\gamma]\right| &\leqslant kZ \int \text{đ}\Omega(\alpha)A(\alpha) \\
&\quad \times \iint \frac{\mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}'}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}\left(1 - \frac{(E_c(\boldsymbol{\xi})+c^2)(E_c(\boldsymbol{\xi}')+c^2)}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}\right)|\hat{F}_\alpha(\boldsymbol{\xi})||\hat{F}_\alpha(\boldsymbol{\xi}')| \\
&= O(Z^{5/3+\delta}).
\end{aligned} \tag{28}$$

Proof. We first note that

$$\left|1 - \frac{(E_c(\boldsymbol{\xi})+c^2)(E_c(\boldsymbol{\xi}')+c^2)}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}\right| \leqslant \frac{|3E_c(\boldsymbol{\xi})E_c(\boldsymbol{\xi}') - c^2(E_c(\boldsymbol{\xi})+E_c(\boldsymbol{\xi}')) - c^4|}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}. \tag{29}$$

Then, noting that $E_c(\boldsymbol{\xi}) - c^2 \leqslant c|\boldsymbol{\xi}|$, we obtain

$$\left|1 - \frac{(E_c(\boldsymbol{\xi})+c^2)(E_c(\boldsymbol{\xi}')+c^2)}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}\right| \leqslant \frac{3c^2|\boldsymbol{\xi}||\boldsymbol{\xi}'| + 2c^3|\boldsymbol{\xi}+\boldsymbol{\xi}'|}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')} \leqslant \frac{3c^2|\boldsymbol{\xi}||\boldsymbol{\xi}'| + 2c^3|\boldsymbol{\xi}+\boldsymbol{\xi}'|}{2c^4}. \tag{30}$$

Using this last equation, we estimate

$$\begin{aligned}
\left|\left(F_\alpha, \left(\frac{1}{|\cdot|} - \varphi_1\right)F_\alpha\right)\right| &\leqslant k \iint \frac{\mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}'}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}\left(1 - \frac{(E_c(\boldsymbol{\xi})+c^2)(E_c(\boldsymbol{\xi}')+c^2)}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}\right)|\hat{F}_\alpha(\boldsymbol{\xi})||\hat{F}_\alpha(\boldsymbol{\xi}')| \\
&\leqslant k\int_{\mathbb{R}^6} \mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}' \frac{|\hat{g}_R(\boldsymbol{\xi}-\mathbf{p})\hat{g}_R(\boldsymbol{\xi}'-\mathbf{p})|}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}(c^{-2}|\boldsymbol{\xi}||\boldsymbol{\xi}'| + c^{-1}(|\boldsymbol{\xi}| + |\boldsymbol{\xi}'|)) \\
&\leqslant kc^{-2}R^{-3}\int \mathrm{d}\boldsymbol{\xi}\int \mathrm{d}\boldsymbol{\xi}' \frac{|\hat{g}(\boldsymbol{\xi})\hat{g}(\boldsymbol{\xi}')|}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}(|\boldsymbol{\xi}+R\mathbf{p}||\boldsymbol{\xi}'+R\mathbf{p}| + cR|\boldsymbol{\xi}+R\mathbf{p}|) \\
&\leqslant kc^{-2}R^{-3}\int \mathrm{d}\boldsymbol{\xi}\int \mathrm{d}\boldsymbol{\xi}' \frac{|\hat{g}(\boldsymbol{\xi})\hat{g}(\boldsymbol{\xi}')|}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}(|\boldsymbol{\xi}||\boldsymbol{\xi}'| + R|\mathbf{p}||\boldsymbol{\xi}| + |R\mathbf{p}|^2 + cR|\boldsymbol{\xi}| + cR^2|\mathbf{p}|) \\
&\leqslant kc^{-2}R^{-3}(1 + R|\mathbf{p}| + R^2|\mathbf{p}|^2 + cR + cR^2|\mathbf{p}|).
\end{aligned} \tag{31}$$

Thus

$$\begin{aligned}
Z|\,\mathrm{tr}[(|\cdot|^{-1} - \varphi_1)\gamma] &\leqslant Z\left|\int_\Gamma \text{đ}\Omega(\alpha)A(\alpha)(F_\alpha, (|\cdot|^{-1} - \varphi_1)F_\alpha)\right| \\
&\leqslant kZ\int \text{đ}\Omega(\alpha)A(\alpha) \\
&\quad \times \iint \frac{\mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}'}{|\boldsymbol{\xi}-\boldsymbol{\xi}'|^2}\left(1 - \frac{(E_c(\boldsymbol{\xi})+c^2)(E_c(\boldsymbol{\xi}')+c^2)}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}\right)|\hat{F}_\alpha(\boldsymbol{\xi})||\hat{F}_\alpha(\boldsymbol{\xi}')| \\
&\leqslant k(Z^{3\delta} + Z^{2\delta+2/3} + +Z^{\delta+4/3} + Z^{2\delta} + Z^{\delta+5/3})
\end{aligned} \tag{32}$$

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 the nucleus–electron interaction.

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

$$D(\rho_{\gamma_\Phi}, \rho_{\gamma_\Phi}) - D(\rho_\gamma, \rho_\gamma) = O(Z^{5/3+\delta}), \tag{33}$$

where ρ_γ is the density of γ and ρ_{γ_Φ} is the density of γ_Φ.

Proof. We have

$$\left|\mathcal{F}\left[(\rho_\gamma + \rho_{\gamma_\Phi}) * |\cdot|^{-1}\right](\boldsymbol{\xi})\right| \leqslant \sqrt{2/\pi}\,\|\rho_\gamma + \rho_{\gamma_\Phi}\|_1|\boldsymbol{\xi}|^{-2} = 2^{3/2}\pi^{-1/2}Z|\boldsymbol{\xi}|^{-2}. \tag{34}$$

Now,

$$\begin{aligned}
\left|D\left(\rho_{\gamma_\Phi},\rho_{\gamma_\Phi}\right)-D\left(\rho_\gamma,\rho_\gamma\right)\right| &= \left|D\left(\rho_{\gamma_\Phi}-\rho_\gamma,\rho_{\gamma_\Phi}+\rho_\gamma\right)\right| \\
&\leqslant \frac{1}{2}\left|\int_{\mathbb{R}^3}\left(\rho_\gamma(\mathbf{x})-\rho_{\gamma_\Phi}(\mathbf{x})\right)\left[\left(\rho_\gamma+\rho_{\gamma_\Phi}\right)*|\cdot|^{-1}\right](\mathbf{x})\,\mathrm{d}\mathbf{x}\right| \\
&\leqslant \frac{1}{2}\int_\Gamma \text{đ}\Omega(\alpha)A(\alpha) \\
&\quad\times\iint \mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}'\left|\mathcal{F}\left[\left(\rho_\gamma+\rho_{\gamma_\Phi}\right)*|\cdot|^{-1}\right](\boldsymbol{\xi}-\boldsymbol{\xi}')|K(\boldsymbol{\xi},\boldsymbol{\xi}')|\hat{F}_\alpha(\boldsymbol{\xi})||\hat{F}_\alpha(\boldsymbol{\xi}')|\,\mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}'\right. \\
&\leqslant \sqrt{\frac{2}{\pi}}Z\int_\Gamma \text{đ}\Omega(\alpha)A(\alpha)\iint \mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}'||\boldsymbol{\xi}-\boldsymbol{\xi}'|^{-2}K(\boldsymbol{\xi},\boldsymbol{\xi}')|\hat{F}_\alpha(\boldsymbol{\xi})||\hat{F}_\alpha(\boldsymbol{\xi}')|\,\mathrm{d}\boldsymbol{\xi}\,\mathrm{d}\boldsymbol{\xi}'
\end{aligned}$$

where

$$K(\boldsymbol{\xi},\boldsymbol{\xi}')=\left|\frac{(E_c(\boldsymbol{\xi})+c^2)(E_c(\boldsymbol{\xi}')+c^2)}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}-1\right|+\frac{c^2|\boldsymbol{\xi}||\boldsymbol{\xi}'|}{N_c(\boldsymbol{\xi})N_c(\boldsymbol{\xi}')}$$

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

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. *There exist a constant k such that we have for all* $Z \geqslant 1$

$$E(Z/\kappa, Z, Z) \leqslant E_{\mathrm{TF}}(1,1)Z^{7/3} + kZ^{20/9}.$$

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 lemmas 1 through 3, and using (24), we get

$$E(c,Z,Z) \leqslant \mathcal{E}_{\mathrm{HF}}(\gamma) \leqslant E_{\mathrm{TF}}(Z,Z) + O(Z^{1+2\delta} + Z^{\frac{5}{2}-\frac{\delta}{2}} + Z^{\frac{5}{3}+\delta}) \tag{35}$$

which is optimized for $\delta = 5/9$ giving the claimed result. □

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 σ at a point $\mathbf{x} \in \mathbb{R}^3$ is defined as the ball $B_{R_\sigma(\mathbf{x})}(\mathbf{x})$ of radius $R_\sigma(\mathbf{x})$ centred at $\mathbf{x}$ where $R_\sigma(\mathbf{x})$ is the smallest radius R fulfilling

$$\frac{1}{2} = \int_{B_R} \sigma. \tag{36}$$

The hole potential L_σ of σ is defined through

$$L_\sigma(\mathbf{x}) := \int_{|\mathbf{x}-\mathbf{y}|<R_\sigma(\mathbf{x})} \frac{\sigma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{y}. \tag{37}$$

Our second main result is the following lower bound.

Theorem 3.

$$\liminf_{Z\to\infty}[(E(Z/\kappa,Z,Z) - E_{\mathrm{TF}}(Z,Z)]Z^{-7/3} \geqslant 0.$$

Proof. Pick $\delta > 0$ and set $\rho_\delta := \rho_{\mathrm{TF}} * g^2_{Z^{-\delta}}$. Then the exchange hole correlation bound [21, equation (14)] implies the following pointwise estimate:

$$\sum_{1\leqslant\mu<\nu\leqslant N} \frac{1}{|\mathbf{x}_\mu - \mathbf{x}_\nu|} \geqslant \sum_{\nu=1}^{N} [\rho_\delta * |\cdot|^{-1}(\mathbf{x}_\nu) - L_{\rho_\delta}(\mathbf{x}_\nu)] - D(\rho_\delta, \rho_\delta). \tag{38}$$

Because of the spherical symmetry of g we can use Newton's theorem [22] and replace ρ_δ by ρ_{TF} in the third summand of the right-hand side of (38). Then, by lemma 5, we get that for all normalized $\psi \in \mathfrak{Q}_N$

$$\mathcal{E}(\psi) \geqslant \mathrm{tr}[\Lambda_+(|D_0| - c^2 - V_\delta)\Lambda_+]_- - kNZ - D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) \tag{39}$$

where, for $t \in \mathbb{R}$, we set $[t]_- := \min\{t, 0\}$ and $V_\delta = Z/|\cdot| - \rho_\delta * |\cdot|^{-1}$. (We remind the reader that k is independent of Z.)

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* [19, appendix B]. Note that

$$\Lambda_- = U^{-1}\Lambda_+ U, \qquad \text{where} \quad U := \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \tag{40}$$

Indeed, we have

$$\Lambda_- = \frac{1}{2}\left(1 - \frac{D_0}{|D_0|}\right), \qquad \Lambda_+ = \frac{1}{2}\left(1 + \frac{D_0}{|D_0|}\right)$$

and

$$U D_0 U^{-1} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} c^2 & c\boldsymbol{\sigma}\cdot\hat{\mathbf{p}} \\ c\boldsymbol{\sigma}\cdot\hat{\mathbf{p}} & -c^2 \end{pmatrix} \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} = -D_0.$$

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

$$\mathrm{tr}\left[\Lambda_+ \begin{pmatrix} X & 0 \\ 0 & X \end{pmatrix} \Lambda_+\right]_- \geqslant \mathrm{tr}\left(\Lambda_+ \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} \Lambda_+\right) = \mathrm{tr}\left(\Lambda_+ \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix}\right)$$

$$\mathrm{tr}\left(\Lambda_- \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix}\right) = \mathrm{tr}\left(\Lambda_+ U \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix} U\right) = \mathrm{tr}\left(\Lambda_+ \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix}\right).$$

Thus

$$2\,\mathrm{tr}\left(\Lambda_+ \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix}\right) = \mathrm{tr}\left(\Lambda_+ \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix}\right) + \mathrm{tr}\left(\Lambda_- \begin{pmatrix} X_- & 0 \\ 0 & X_- \end{pmatrix}\right) = 2\,\mathrm{tr}(X_-). \tag{41}$$

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

$$E(Z/\kappa, Z, Z) \geqslant 2\,\mathrm{tr}[E_c(\hat{\mathbf{p}}) - c^2 - V_\delta(\mathbf{x})]_- - D(\rho_{\mathrm{TF}}, \rho_{\mathrm{TF}}) - kNZ \tag{42}$$

where the last trace is spinless. This connects to Sørensen's equation (3.2) from [23]. The result then follows using his lower bound. □

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Appendix. L^∞-bound on the exchange hole potential

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

$$\gamma_{\mathrm{TF}}\rho_{\mathrm{TF}}^{2/3} = V_Z \tag{A.1}$$

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

$$\rho_{\mathrm{TF}}(\mathbf{x}) \leqslant (Z/\gamma_{\mathrm{TF}})^{3/2}|\mathbf{x}|^{-3/2}. \tag{A.2}$$

This bound allows us to prove the following L^∞-bounds on potentials of exchange holes.

Lemma 4.

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

Proof. The function

$$\begin{aligned} &f : \mathbb{R}_+ \to \mathbb{R} \\ &t \mapsto \sqrt{t}\int_{|\mathbf{y}|<1/t} |\mathbf{y}|^{-1}|\mathbf{y} + (0, 0, 1)|^{-3/2}\,\mathrm{d}\mathbf{y} \end{aligned} \tag{A.3}$$

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:

$$L_{\rho_{\mathrm{TF}}}(\mathbf{x}) \leqslant A_1(\mathbf{x}) + A_2(\mathbf{x}), \tag{A.4}$$

where

$$\begin{aligned} A_1(\mathbf{x}) &:= \int_{|y|\leqslant 1/Z} \frac{\rho_{\mathrm{TF}}(\mathbf{x}+\mathbf{y})}{|\mathbf{y}|}\,\mathrm{d}\mathbf{y} \leqslant \left(\frac{Z}{\gamma_{\mathrm{TF}}}\right)^{3/2} \int_{|y|\leqslant 1/Z} \frac{\mathrm{d}\mathbf{y}}{|\mathbf{y}||\mathbf{y}+\mathbf{x}|^{3/2}} \\ &= (Z/\gamma_{\mathrm{TF}})^{3/2} Z^{-1/2} f(|\mathbf{x}|Z) \leqslant \|f\|_\infty \gamma_{\mathrm{TF}}^{-3/2} Z \end{aligned} \tag{A.5}$$

and

$$A_2(\mathbf{y}) := \int_{\frac{1}{Z}\leqslant|\mathbf{y}|\leqslant R_{\rho_{\mathrm{TF}}}(\mathbf{x})} \frac{\rho_{\mathrm{TF}}(\mathbf{x}+\mathbf{y})}{|\mathbf{y}|}\,\mathrm{d}\mathbf{y} \leqslant Z\int_{\frac{1}{Z}\leqslant|\mathbf{y}|\leqslant R_{\rho_{\mathrm{TF}}}(\mathbf{x})} \rho_{\mathrm{TF}}(\mathbf{x}+\mathbf{y})\,\mathrm{d}\mathbf{y} \leqslant \frac{Z}{2}. \tag{A.6}$$

These two estimates prove the claim. □

Lemma 4 allow us already 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 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_{ρ_δ} (where $\rho_\delta := \rho_{\mathrm{TF}} * g^2_{Z^{-\delta}}$), 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:

$$\begin{aligned} L_{\rho_\delta}(\mathbf{x}) &\leqslant \int_{|\mathbf{y}|\leqslant 1/Z} \frac{\rho_\delta(\mathbf{x}+\mathbf{y})}{|\mathbf{y}|}\,\mathrm{d}\mathbf{y} + \int_{1/Z\leqslant|\mathbf{y}|\leqslant R_{\rho_\delta}(\mathbf{x})} \frac{\rho_\delta(\mathbf{x}+\mathbf{y})}{|\mathbf{y}|}\,\mathrm{d}\mathbf{y} \\ &\leqslant \int \mathrm{d}\mathbf{z}\, g^2_{Z^{-\delta}}(\mathbf{z}) \int_{|\mathbf{y}|\leqslant 1/Z} \frac{\rho_{\mathrm{TF}}(\mathbf{x}-\mathbf{z}+\mathbf{y})}{|\mathbf{y}|}\,\mathrm{d}\mathbf{y} + Z\int_{|\mathbf{y}|\leqslant R_{\rho_\delta}(\mathbf{x})} \rho_\delta(\mathbf{x}+\mathbf{y})\,\mathrm{d}\mathbf{y} \\ &\leqslant \int \mathrm{d}\mathbf{z}\, g^2_{Z^{-\delta}}(\mathbf{z}) A_1(\mathbf{x}-\mathbf{z}) + \frac{Z}{2} \leqslant kZ \end{aligned} \tag{A.7}$$

where we used the definition of the radius of the exchange hole from the first line to the second line, the definition of A_1 in the next step and in the last step the L^∞-estimate (A.5) on A_1.

$\square$

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