The Energy of Heavy Atoms According to Brown and Ravenhall: The Scott Correction

Rupert L. Frank, Heinz Siedentop, and Simone Warzel

Received: March 9, 2009

Communicated by Alfred K. Louis

Abstract. We consider relativistic many-particle operators which – according to Brown and Ravenhall – describe the electronic states of heavy atoms. Their ground state energy is investigated in the limit of large nuclear charge and velocity of light. We show that the leading quasi-classical behavior given by the Thomas-Fermi theory is raised by a subleading correction, the Scott correction. Our result is valid for the maximal range of coupling constants, including the critical one. As a technical tool, a Sobolev-Gagliardo-Nirenberg-type inequality is established for the critical atomic Brown-Ravenhall operator. Moreover, we prove sharp upper and lower bounds on the eigenvalues of the hydrogenic Brown-Ravenhall operator up to and including the critical coupling constant.

2000 Mathematics Subject Classification: Primary 81V45; Secondary 81V55, 35Q40, 46N50, 47N50.
Keywords and Phrases: Heavy atoms, ground state energy, relativistic Coulomb system, Scott correction, Brown-Ravenhall operator.

Contents

1 Introduction and main result

The description of atoms and molecules, in particular of their energies, has been a primer for the development of quantum mechanics. However, it became soon clear that atoms with more than one electron are not accessible to explicit solutions. This motivated the development of approximate models for large Coulomb systems. One of the most simple and – simultaneously – the most fundamental models was introduced by Thomas [73], Fermi [27, 28], and Lenz [41] who proposed the energy functional which we will also use here. It predicts that the ground state energy of atoms would decrease with the atomic number Z to leading order as $Z^{7/3}$. In order to get a refined description, Scott [54] conjectured that the electrons close to the nucleus should raise the energy by $Z^2/2$. Considerably later Schwinger [52] argued also for Scott's prediction; Schwinger [53] and Englert and Schwinger [13, 14, 15] even refined these considerations by adding more lower order terms [53] (see also Englert [12]). In fact, a contribution to the $Z^{5/3}$-term can be traced back to Dirac [10]. — The challenge to address the question whether the predicted formulae would yield asymptotically correct results when compared with the N-particle Schrödinger theory was for a long time unsuccessful. It was Lieb and Simon who proved in their seminal paper [44] that the prediction of Thomas, Fermi, and Lenz is indeed asymptotically correct. However, establishing the Scott correction resisted the mathematical efforts and became Problem 10B of Simon's 15 Problems in Mathematical Physics [62]. Eventually, the Scott correction was established mathematically by Hughes [37, 38] (lower bound), and Siedentop and Weikard [55, 56, 57, 58, 59] (lower and upper bound). In fact, even the existence of the $Z^{5/3}$-correction conjectured by Schwinger was proved by Fefferman and Seco [23, 24, 25, 18, 26, 21, 19, 20, 22]. Later these results were extended in various ways, e.g., to ions and molecules [1, 39, 66, 4].

Despite of the mathematical success in establishing the large Z asymptotics of the Schrödinger theory, these considerations remain questionable from a physical point of view, since large atoms force electrons into orbits that are close to the nucleus where the electrons move with high speed which should require a relativistic treatment. The atom is shrinking with increasing Z: already in non-relativistic quantum mechanics the bulk of the electrons has a distance $Z^{-1/3}$ from the nucleus; the electrons contributing to the Scott correction even live on the scale Z^{-1}. Schwinger [53] has estimated these effects concluding that a correction to the Scott correction occurs whereas the leading term should be unaffected by the change of model. Sørensen [51] was the first who proved that the latter is indeed the case for a simplified ad hoc naive relativistic model, the Chandrasekhar multi-particle operator, in the limit of large Z and large velocity of light c. The value of the Scott correction is again of order Z^2, a result which was announced [64] and proven [65] by Solovej, Sørensen, and Spitzer (see also Sørensen [50] for the non-interacting case). In a previous paper [31] we gave a short alternative proof, roling the problem back to the non-relativistic Scott correction. 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 quantitatively 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 [6] – is derived from QED such that it yields the leading relativistic effects in a quantitative correct manner. (See also Sucher [69, 70, 71].) The first step in this direction was taken by Cassanas and Siedentop [7] who showed that, similarly to the Chandrasekhar case, the leading energy is not affected. To show in which way the Scott correction is changed for this model is our concern in this paper.

1.1 Relativistic energy form

According to Brown and Ravenhall [6] the energy of an atom with N electrons in a state $\psi \in \mathfrak{Q}_N^B$ is given by

$$\begin{aligned}&\mathcal{E}_N^B(\psi)\\ &:= \left\langle \psi, \left[\sum_{\nu=1}^N \left(c\,\boldsymbol{\alpha}_\nu \cdot \mathbf{p}_\nu + c^2\beta_\nu - c^2 - \frac{Z}{|\mathbf{x}_\nu|}\right) + \sum_{1\leq\mu<\nu\leq N} \frac{1}{|\mathbf{x}_\mu - \mathbf{x}_\nu|}\right] \psi \right\rangle.\end{aligned} \tag{1.1}$$

This involves the free Dirac operator reduced by the rest mass, acting in $L^2(\mathbb{R}^3, \mathbb{C}^4)$, with the four Dirac matrices in standard representation,

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

where $\boldsymbol{\sigma}$ are the three Pauli matrices in standard representation, i.e.,

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

We use atomic units in which $m = e^2 = \hbar = 1$. The parameter Z is the atomic number and c the velocity of light.
The Hilbert space of an electron is chosen as the positive spectral subspace of the Dirac operator,

$$\mathfrak{H}^B := \chi_{[c^2,\infty)}(c\,\boldsymbol{\alpha}\cdot\mathbf{p} + c^2\beta)\left(L^2(\mathbb{R}^3, \mathbb{C}^4)\right),$$

and, correspondingly, the Hilbert space of N electrons $\mathfrak{H}_N^B$ is the antisymmetric tensor product of the one-particle space, i.e., $\mathfrak{H}_N^B := \bigwedge_{\nu=1}^N \mathfrak{H}^B$. Finally, the form domain of (1.1) is $\mathfrak{Q}_N^B := \mathfrak{H}_N^B \cap \mathfrak{S}(\mathbb{R}^{3N}, \mathbb{C}^{4^N})$ with $\mathfrak{S}$ the Schwartz space of rapidly decreasing functions. As is shown in [17], the Brown-Ravenhall form $\mathcal{E}_N^B$ is closable and bounded from below if and only if

$$\kappa := \frac{Z}{c} \leq \kappa^B := \frac{2}{2/\pi + \pi/2}. \tag{1.2}$$

(See also Tix [74, 76], who improved the bound given in [17] to an explicit positive bound.) For the physical value, about 1/137, of the Sommerfeld fine structure, which equals $1/c$ in atomic units used here, the critical atomic number Z exceeds 124 slightly. This includes all known elements.

In the following we will assume that the atom described by (1.1) is neutral, i.e., $Z = N$, an assumption that we make mainly for the sake of brevity and clarity of presentation, since the Scott correction is independent of the ionization degree $N/Z \geq$ const > 0. Similarly, it might seem that our treatment is restricted to spherically symmetric systems (atoms). However, on the energy scale considered here, molecular Hamiltonians essentially separate – in nature the distances between nuclei with charges $ZZ_1, ..., ZZ_K$ remain on a scale much larger than $Z^{-1/3}$ – into spherically symmetric one-center problems (atoms). Therefore, the molecular case follows from the atomic case by additional localization. However, for the sake of brevity and clarity, we will spare the reader the corresponding tedious technicalities, restrict to the atomic case, and freely use the resulting symmetry.
Thus, according to Friedrichs, the one-particle form $\mathcal{E}_1^B$ defines for $\kappa \leq \kappa^B$ a distinguished self-adjoint operator in $\mathfrak{H}^B$. Through a unitary transformation it may be represented as a self-adjoint operator in the Hilbert space $\mathfrak{H} := L^2(\mathbb{R}^3, \mathbb{C}^2)$ of two-spinors. More precisely, using the notation $p := |\mathbf{p}|$, $\boldsymbol{\omega}_\mathbf{p} := \mathbf{p}/p$ we set

$$E(p) := \sqrt{\mathbf{p}^2 + 1}, \qquad \phi_\nu(p) := \sqrt{\frac{E(p) + (-1)^\nu}{2E(p)}},\ \nu = 0, 1, \tag{1.3}$$

and introduce the following bounded operators on $\mathfrak{H}$,

$$\Phi_0(\mathbf{p}) := \phi_0(p), \quad \Phi_1(\mathbf{p}) := \phi_1(p)\ \boldsymbol{\sigma} \cdot \boldsymbol{\omega}_\mathbf{p}. \tag{1.4}$$

The operator $\boldsymbol{\Phi}_c : \mathfrak{H} \to \mathfrak{H}^B$, $\psi \mapsto (\Phi_0(\mathbf{p}/c)\,\psi, \Phi_1(\mathbf{p}/c)\,\psi)$, maps $\mathfrak{H}$ unitarily onto $\mathfrak{H}^B$ [7]. Therefore, the form $\mathcal{E}_1^B$ defines the (two-spinor) Brown-Ravenhall operator in $\mathfrak{H}$,

$$\begin{aligned} B_c[Z/|\mathbf{x}|] :=& \boldsymbol{\Phi}_c^{-1} \left(c\boldsymbol{\alpha} \cdot \mathbf{p} + c^2\beta - c^2 - Z/|\mathbf{x}|\right) \boldsymbol{\Phi}_c \\ =& c^2 E(p/c) - c^2 - \mathcal{U}_c(Z/|\mathbf{x}|), \end{aligned} \tag{1.5}$$

where $\mathcal{U}_c(A) := \Phi_0(\mathbf{p}/c)\,A\,\Phi_0(\mathbf{p}/c) + \Phi_1(\mathbf{p}/c)\,A\,\Phi_1(\mathbf{p}/c)$. In the case $c = 1$ we denote this operator by B_Z. Further properties of B_Z and its relation to the corresponding Chandrasekhar operator and Schrödinger operator

$$C_Z := (\mathbf{p}^2 + 1)^{1/2} - 1 - Z/|\mathbf{x}|, \qquad S_Z := \tfrac{1}{2}\mathbf{p}^2 - Z/|\mathbf{x}| \tag{1.6}$$

all realized in $\mathfrak{H}$, can be found in Sections 2 and 3 below and in Appendix C.

1.2 Main result

We are interested in the ground state energy

$$E_c^B(Z) := \inf\{\mathcal{E}_Z^B(\psi) \,|\, \psi \in \mathfrak{Q}_Z^B,\ \|\psi\| = 1\}$$

of the energy form (1.1) for large atomic number Z and large velocity of light c satisfying (1.2). Note that we picked $N = Z$. It was shown in [7], that similarly to the Chandrasekhar case [51], the leading behavior of $E_c^B(Z)$ is not affected by relativistic effects and is, as in the Schrödinger case [44], given by the minimal Thomas-Fermi energy

$$E_{\rm TF}(Z) := \inf\{\mathcal{E}_{\rm TF}(\rho) \,|\, \rho \in L^{5/3}(\mathbb{R}^3),\ \rho \geq 0,\ D(\rho,\rho) < \infty\}. \tag{1.7}$$

The latter is defined in terms of the Thomas-Fermi energy functional

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

where, in our units, $\gamma_{\rm TF} = (3\pi^2)^{2/3}/2$ and

$$D(\rho,\sigma) := \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\overline{\rho(\mathbf{x})}\sigma(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{y}$$

is the Coulomb scalar product. By scaling, one finds $E_{\rm TF}(Z) = E_{\rm TF}(1)\,Z^{7/3}$. This paper concerns the correction to the leading behavior. For the formulation of the main result, we abbreviate the negative part of an operator by $A_- := -A\chi_{(-\infty,0)}(A)$ and introduce for $0 < \kappa \leq \kappa^B$ the spectral shift

$$s(\kappa) := \kappa^{-2}\,\mathrm{tr}_{\mathfrak{H}}\left[(B_\kappa)_- - (S_\kappa)_-\right]. \tag{1.8}$$

(We use the term "spectral shift" for s for convenience although it is used in slightly different meaning otherwise.) It describes the shift of the Brown-Ravenhall bound state energies compared to those of the Schrödinger operator. In Section 3 we show that s is well-defined and discuss some of its properties. In particular, we prove that the function s is non-negative on the interval $(0,\kappa^B]$ and can be continuously extended to zero where it satisfies

$$s(\kappa) = \mathcal{O}(\kappa^2) \qquad \text{as } \kappa \to 0. \tag{1.9}$$

We are now ready to state our main result.

Theorem 1.1 (Scott correction). *There exists a constant $C > 0$ such that for all $Z \geq 1$ and all $c \geq Z/\kappa^B$ one has*

$$\left|E_c^B(Z) - E_{\rm TF}(Z) - \left(\tfrac{1}{2} - s(Z/c)\right)Z^2\right| \leq CZ^{47/24}. \tag{1.10}$$

Put differently, Theorem 1.1 asserts that in the limit $Z \to \infty$ we have uniformly in the quotient $\kappa = Z/c \in (0,\kappa^B]$

$$E_c^B(Z) = E_{\rm TF}(Z) + \left(\tfrac{1}{2} - s(\kappa)\right)Z^2 + o(Z^2). \tag{1.11}$$

(We do not claim that the error $Z^{47/24}$ in (1.10) is sharp, so we only write $o(Z^2)$ here.) The second term $\left(\frac{1}{2} - s(\kappa)\right)Z^2$ in (1.11) is the so-called Scott correction in the Brown-Ravenhall model. It does not exceed the Scott correction $Z^2/2$ in the non-relativistic model [55]. Indeed, if $\kappa = Z/c$ stays away from zero then there is a relativistic lowering of the ground state energy at order Z^2. On the other hand, in the non-relativistic limit $c \to \infty$ with $\kappa = Z/c \to 0$, one recovers – non-surprisingly – the value of the Schrödinger case. In this case (1.9) implies

$$E_c^B(Z) = E_{\mathrm{TF}}(Z) + \tfrac{1}{2}Z^2 + \mathcal{O}(c^{-2}Z^4 + Z^{47/24}). \tag{1.12}$$

The Scott correction in the Brown-Ravenhall model, however, exceeds the Scott correction predicted by the naive Chandrasekhar model treated in [65] and [31]. This follows from the fact that sums of bound state energies of the atomic Chandrasekhar operator are dominated by those of the Brown-Ravenhall operator, cf. the proof of Theorem 3.1 below.

1.3 Outline of the paper

The central strategy of our paper is to compare the ground state energy of the Brown-Ravenhall operator with that of the Schrödinger operator. The latter is known up to the required accuracy $o(Z^2)$ and the leading contribution agrees with the Brown-Ravenhall energy. The subtraction of the corresponding ground state energies results in a renormalized effective model which accurately describes the energy differences and is amenable to analysis. The germ of this idea has been presented in the simpler context of the Chandrasekhar model [31]. The full blown renormalization required is developed in this paper. A virtue of our approach is that it leads to an explicit formula for the spectral shift which can be evaluated numerically. We believe it would be interesting to compare this formula with experimental data.

We show that the difference between the Brown-Ravenhall and Schrödinger ground state energies on the multi-particle level coincides, up to the required accuracy, with a spectral shift on the one-particle level. A crucial step in our analysis is therefore a bound on the corresponding spectral shift for rather general spherically symmetric potentials. This is presented in Section 3, where we show that sums of differences of Brown-Ravenhall and Schrödinger eigenvalues decay rather rapidly as the angular momentum increases.

In Section 2 we address various aspects of hydrogenic Brown-Ravenhall operators. An essential feature and source of difficulties, which does not occur in the naive Chandrasekhar model, is the non-locality of the potential energy. In particular, instead of the usual Coulomb potential $|\mathbf{x}|^{-1}$ we face the 'twisted' non-local operator $\mathcal{U}_c(|\mathbf{x}|^{-1})$. Estimating the difference between the corresponding potential energies is the topic in Subsection 2.3. Since, in contrast to the Schrödinger case, the eigenvalues of the hydrogenic Brown-Ravenhall operator are not known explicitly, we prove upper and lower bounds in Subsection 2.1. Our bounds are sharp with respect to their dependence on the quantum numbers n and l. An upper bound is given by the Dirac eigenvalues, a consequence of the mini-max principle for eigenvalues in the gap. For the lower bound we overcome the non-locality of the potential by a non-trivial comparison argument with a super-critical Chandrasekhar operator. In Subsection 2.2 we prove a new Sobolev-type inequality, from which we derive estimates on the eigenfunctions of the hydrogenic Brown-Ravenhall operator. The technical challenge here is to prove such a result up to and including the critical coupling constant.

Finally, we present the proof of our main result, Theorem 1.1, in Section 4.

For the readers' convenience we collect various facts in the appendices. Appendix A recalls the partial wave decomposition of the Hilbert space of two-spinors, Appendix B establishes some useful properties of the twisting operators, and Appendix C collects basic facts on hydrogenic Brown-Ravenhall and Chandrasekhar operators. Appendix D fills in some details in the proof of Theorem 2.2 and, eventually, Appendix E defines the one-particle density matrix giving the main contribution of the energy.

2 The hydrogenic Brown-Ravenhall operator

In this section we set $c = 1$ and investigate the Brown-Ravenhall operator with Coulomb potential

$$B_\kappa = \sqrt{\mathbf{p}^2 + 1} - 1 - \kappa \mathcal{U}(|\mathbf{x}|^{-1}) \tag{2.1}$$

in the Hilbert space $\mathfrak{H} = L^2(\mathbb{R}^3, \mathbb{C}^2)$ of two-spinors, where we recall that

$$\mathcal{U}(|\mathbf{x}|^{-1}) = \Phi_0(\mathbf{p})|\mathbf{x}|^{-1}\Phi_0(\mathbf{p}) + \Phi_1(\mathbf{p})|\mathbf{x}|^{-1}\Phi_1(\mathbf{p}) \tag{2.2}$$

with Φ_ν defined in (1.4). In Subsection 2.1 we prove sharp upper and lower bounds on the eigenvalues of B_κ. In Subsection 2.2 we prove L^p estimates on the eigenfunctions of this operator. Technically, this is expressed as a Sobolev-type inequality for the massless version of B_κ, which is a non-negative operator. Finally, in Subsection 2.3 we compare the potential energy of the operator B_κ, namely $\langle \psi, \mathcal{U}(|\mathbf{x}|^{-1})\psi\rangle$, with the corresponding local potential energy $\langle \psi, |\mathbf{x}|^{-1}\psi\rangle$. For comparison purpose also the corresponding Chandrasekhar and Schrödinger operator C_κ and S_κ occur (see (1.6)).

According to [17] and [40] the operators B_κ and C_κ are well-defined for all $\kappa \leq \kappa^\#$ with $\# = B, C$ and

$$\kappa^B = \frac{2}{2/\pi + \pi/2}, \qquad \kappa^C := 2/\pi; \tag{2.3}$$

see also Appendix C. Of course, for the Schrödinger operator no upper bound on κ is needed.

2.1 Estimates on eigenvalues of the hydrogen atom

In contrast to the Schrödinger or Dirac models, the eigenvalues of B_κ and C_κ are not known explicitly. In order to obtain upper and lower bounds on these eigenvalues, we use that the spectra of B_κ, C_κ and S_κ may be classified in terms of angular momenta.

As usual write $\mathbf{L} := \mathbf{x} \times \mathbf{p}$ for the operators of orbital angular momentum and $\mathbf{J} := \mathbf{L} + \frac{1}{2}\boldsymbol{\sigma}$ for the operators of total angular momentum. The four operators

B_κ, $\mathbf{J}^2$, J_3, $\mathbf{L}^2$ commute pairwise, and this also holds, if C_κ or S_κ replace B_κ. This allows us to decompose the Hilbert space $\mathfrak{H}$ into orthogonal subspaces which reduce such a quadruple of operators, i.e.,

$$\mathfrak{H} = \bigoplus_{j\in\mathbb{N}_0+\frac{1}{2}} \bigoplus_{l=j\pm1/2} \mathfrak{H}_{j,l}, \qquad \mathfrak{H}_{j,l} := \bigoplus_{m=-j}^{j} \mathfrak{H}_{j,l,m}. \tag{2.4}$$

Here $\mathfrak{H}_{j,l,m}$ is the maximal joint eigenspace of $\mathbf{J}^2$ with eigenvalues $j(j+1)$, of $\mathbf{L}^2$ with eigenvalue $l(l+1)$, and J_3 with eigenvalue m. More details concerning the partial wave decomposition (2.4) can be found in Appendix A.

We denote by $b_{j,l}(\kappa)$, $c_l(\kappa)$, and $s_l(\kappa)$ the reduced operators corresponding to fixed angular momenta j and l, where, strictly speaking, we consider $b_{j,l}(\kappa)$ and $c_l(\kappa)$ in momentum space whereas $s_l(\kappa)$ in position space. We refer to Appendix C for precise definitions of $b_{j,l}(\kappa)$ and $c_l(\kappa)$ and for further discussion. Of course, $s_l(\kappa) = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2} - \frac{\kappa}{r}$.

The main result of this subsection is that for large quantum numbers n, j, and l, the eigenvalues of $b_{j,l}(\kappa)$ and $c_l(\kappa)$ behave similarly to the explicitly known ones of the Schrödinger operator $s_l(\kappa)$.

THEOREM 2.1 (ENERGIES OF BROWN-RAVENHALL HYDROGEN). *There is a constant $C < \infty$ such that for all $j \in \mathbb{N}_0 + \frac{1}{2}$, and $l = j \pm \frac{1}{2}$, $n \in \mathbb{N}$ and $\kappa \in (0, \kappa^B]$ one has*

$$-C\frac{\kappa^2}{(n+l)^2} \leq \lambda_n(b_{j,l}(\kappa)) \leq -\frac{\kappa^2}{2(n+l)^2}. \tag{2.5}$$

Here and below, we denote by $\lambda_1(A) \leq \lambda_2(A) \leq \ldots$ the eigenvalues, repeated according to multiplicities, below the bottom of the essential spectrum of the self-adjoint, lower semi-bounded operator A. Note that $-\kappa^2(2(n+l)^2)^{-1} = \lambda_n(s_l(\kappa))$ on the right hand side of (2.5) is the n-th eigenvalue of the Schrödinger operator corresponding to angular momentum l. In particular, we conclude from (2.5) that the partial traces in $\mathfrak{H}_{j,l}$ (cf. (3.1)) satisfy

$$0 \leq \mathrm{tr}_{j,l}\left([B_\kappa + \mu]_- - [S_\kappa + \mu]_-\right) < \infty \tag{2.6}$$

for all $\mu \geq 0$. In the proof of Theorem 2.1 we use heavily the corresponding result for the Chandrasekhar case, which we state next.

THEOREM 2.2 (ENERGIES OF CHANDRASEKHAR HYDROGEN). *There is a constant $C < \infty$ such that for all $l \in \mathbb{N}_0$, $n \in \mathbb{N}$ and $\kappa \in (0, \kappa^C]$ one has*

$$-C\frac{\kappa^2}{(n+l)^2} \leq \lambda_n(c_l(\kappa)) \leq -\frac{\kappa^2}{2(n+l)^2}. \tag{2.7}$$

We break the proofs of Theorems 2.1 and 2.2 into three parts, corresponding to the upper bound and the lower bound for subcritical and, respectively, critical values of the coupling constant.

2.1.1 Upper bound on hydrogen eigenvalues

We begin with the Chandrasekhar case.

Proof of Theorem 2.2. Upper bound. The second inequality in (2.7) is an immediate consequence of the inequality $\sqrt{p^2+1}-1 \leq p^2/2$ and the known form of the Schrödinger eigenvalues in the subspace corresponding to fixed angular momentum l. $\square$

Next, we turn to the Brown-Ravenhall case.

Proof of Theorem 2.1. Upper bound. We first recall some facts about the eigenvalues of the hydrogenic Dirac operator $D_\kappa := \boldsymbol{\alpha}\cdot\mathbf{p} + \beta - \kappa|\mathbf{x}|^{-1}$; see Darwin [8], Gordon [32] and also Bethe and Salpeter [5] for a textbook presentation. The following subspaces of $L^2(\mathbb{R}^3,\mathbb{C}^4)$,

$$\tilde{\mathfrak{H}}_{j,l,m} = \left\{\mathbf{x} \mapsto \begin{pmatrix} ir^{-1}f(r)\Omega_{j,l,m}(\omega_{\mathbf{x}}) \\ -r^{-1}g(r)\Omega_{j,2j-l,m}(\omega_{\mathbf{x}})\end{pmatrix} :\ f,g \in L^2(\mathbb{R}_+)\right\},$$

reduce the Dirac operator D_κ with $\kappa\in(0,1)$. Under the natural identification of $\tilde{\mathfrak{H}}_{j,l,m}$ with $L^2(\mathbb{R}_+,\mathbb{C}^2)$ the part of D_κ in $\tilde{\mathfrak{H}}_{j,l,m}$ is unitarily equivalent to

$$d_{j,l}(\kappa) = \begin{pmatrix} 1-\frac{\kappa}{r} & -\frac{\mathrm{d}}{\mathrm{d}r} - \frac{(j-l)(2j+1)}{r} \\ \frac{d}{dr} - \frac{(j-l)(2j+1)}{r} & -1-\frac{\kappa}{r}\end{pmatrix}.$$

The non-decreasing sequence $\lambda_n(d_{j,l}(\kappa))$ of eigenvalues of $d_{j,l}(\kappa)$ in the gap $(-1,1)$ is independent of l and given explicitly by

$$\lambda_n(d_{j,l}(\kappa)) = \left(1 - \frac{\kappa^2}{\left(n-1+\sqrt{(j+1/2)^2-\kappa^2}\right)^2+\kappa^2}\right)^{1/2}, \quad n\in\mathbb{N}. \tag{2.8}$$

The Dirac eigenvalues reduced by the rest energy are bounded from above by the Schrödinger eigenvalues: for all n, l, j, and $\kappa\in(0,1)$

$$1-\lambda_n(d_{j,l}(\kappa)) \geq \tfrac{\kappa^2}{2(n+l)^2} = -\lambda_n(s_l(\kappa)). \tag{2.9}$$

To show (2.9), we use

$$\sqrt{(j+1/2)^2-\kappa^2} \leq \sqrt{(l+1)^2-\kappa^2} \leq \sqrt{(n+l)^2-\kappa^2}+1-n$$

and expand the outer square root in (2.8) up to first order which gives an upper bound.

Hence the upper bound in Theorem 2.1 will follow if we can show that

$$\lambda_n(b_{j,l}(\kappa)) \leq -1+\lambda_n(d_{j,l}(\kappa)). \tag{2.10}$$

To prove this, we fix (j, l) and abbreviate $\Lambda_+ := \chi_{[1,\infty)}(d_{j,l}(0))$ and $\Lambda_- := 1 - \Lambda_+$. It follows from the definition of the Brown-Ravenhall operator that $b_{j,l}(\kappa)$ is unitarily equivalent to the operator $\Lambda_+(d_{j,l} - 1)\Lambda_+$ in the Hilbert space $\Lambda_+(L^2(\mathbb{R}_+, \mathbb{C}^2))$. The variational principle for eigenvalues in gaps by Griesemer et al. [34, 35] under the weakened hypotheses of Dolbeault et al. [11] states that

$$\lambda_n(d_{j,l}(\kappa)) = \inf_{\substack{V\subset\Lambda_+(L^2(\mathbb{R}_+,\mathbb{C}^2)),\\ \dim V = n}} \sup\left\{\frac{(f, d_{j,l}(\kappa)f)}{\|f\|^2} :\ 0 \neq f \in V \oplus \Lambda_-(L^2(\mathbb{R}_+, \mathbb{C}^2))\right\}.$$

Since the supremum decreases when restricted to $0 \neq f \in V$, one obtains (2.10). □

2.1.2 Lower bounds on hydrogen eigenvalues. Subcritical case

Proof of Theorem 2.2. Subcritical case. Since we will reduce the Brown-Ravenhall case in Theorem 2.1 to the Chandrasekhar case, we actually prove a slightly stronger statement. As explained in (C.8), the operators $c_l(\kappa)$ are lower bounded for all $l \geq 1$ up to $\kappa_l^C > \kappa^B$.

We assume that either $l \geq 1$ and $0 < \kappa \leq \kappa^B$ or else that $l = 0$ and $0 < \kappa \leq \kappa^B\kappa^C/\kappa_1^C$. For any $0 < \delta < 1$ there exist $M_\delta > 0$ and $c_\delta > 0$ such that

$$\sqrt{p^2 + 1} - 1 \geq \begin{cases} (1 - \delta)p & \text{if } p \geq M_\delta \\ c_\delta\, p^2/2 & \text{if } p \leq M_\delta. \end{cases}.$$

Denoting by χ_i the characteristic function of the centered ball in $\mathbb{R}^3$ with radius M_δ, and putting $\chi_o := 1 - \chi_i$, the Schwarz inequality implies the operator inequality

$$|\mathbf{x}|^{-1} \leq (1 + \delta^{-1})\chi_i(\mathbf{p})|\mathbf{x}|^{-1}\chi_i(\mathbf{p}) + (1 + \delta)\chi_o(\mathbf{p})|\mathbf{x}|^{-1}\chi_o(\mathbf{p}),$$

and hence

$$\begin{aligned}\sqrt{\mathbf{p}^2 + 1} - 1 - \kappa|\mathbf{x}|^{-1} \geq & \chi_i(\mathbf{p})\left(c_\delta\mathbf{p}^2/2 - (1 + \delta^{-1})\kappa|\mathbf{x}|^{-1}\right)\chi_i(\mathbf{p}) \\ & + \chi_o(\mathbf{p})\left((1 - \delta)|\mathbf{p}| - (1 + \delta)\kappa|\mathbf{x}|^{-1}\right)\chi_o(\mathbf{p})\,.\end{aligned} \tag{2.11}$$

Now choose δ as the the unique solution of the equation $(1+\delta)/(1-\delta) = \kappa_1^C/\kappa^B$ in the interval $(0, 1)$. Then the restrictions on κ imply that $(1 + \delta)\kappa \leq (1 - \delta)\kappa_1^C \leq (1 - \delta)\kappa_l^C$ for $l \geq 1$ and $(1 + \delta)\kappa \leq (1 - \delta)\kappa^C$ for $l = 0$. In any case, the second operator in the above sum is non-negative. The variational principle hence implies that the n-th eigenvalue of $c_l(\kappa)$ is greater or equal to the n-th eigenvalue of $\chi_i(\mathbf{p})\left(c_\delta\mathbf{p}^2/2 - (1 + \delta^{-1})\kappa|\mathbf{x}|^{-1}\right)\chi_i(\mathbf{p})$. Again by the variational principle, the latter is greater or equal to the n-th eigenvalue of $c_\delta\mathbf{p}^2/2 - (1 + \delta^{-1})\kappa|\mathbf{x}|^{-1}$, which is $-\text{const}\,\kappa^2(n + l)^{-2}$. □

Proof of Theorem 2.1. Subcritical case. We assume that either $j \geq 3/2$ and $0 < \kappa \leq \kappa^B$ or else that $j = 1/2$ and $0 < \kappa \leq \kappa^B \kappa^C / \kappa_1^C$. We claim that

$$\lambda_n(c_l(\kappa)) = \lambda_{2n-1}(c_l(\kappa) \otimes 1_{\mathbb{C}^2}) \leq \lambda_{2n-1}(b_{j,l}(\kappa)) \,. \tag{2.12}$$

Once we have proved this, the assertion follows easily from what we have shown in the proof of Theorem 2.2 above.
To establish (2.12) we use the same notation as in the proof of the upper bound in Theorem 2.1. By the variational principle,

$$\begin{aligned}
&\lambda_n(b_{j,l}(\kappa)) \\
&= \sup_{\substack{f_1,\ldots,f_{n-1}\in \\ \Lambda_+(L^2(\mathbb{R}_+,\mathbb{C}^2))}} \inf\{\langle f, (d_{j,l}(\kappa) - 1) f\rangle : \ \|f\| = 1, f \in \Lambda_+(L^2(\mathbb{R}_+, \mathbb{C}^2)), f \perp f_\nu\} \\
&= \sup_{\substack{f_1,\ldots,f_{n-1}\in \\ L^2(\mathbb{R}_+,\mathbb{C}^2)}} \inf\{\langle \mathcal{F}_l f, c_l(\kappa) \mathcal{F}_l f\rangle : \ \|f\| = 1, f \in \Lambda_+(L^2(\mathbb{R}_+, \mathbb{C}^2)), f \perp f_\nu\}
\end{aligned}$$

with $\mathcal{F}_l$ the Fourier-Bessel transform, see (A.5). The infimum does not increase if the condition $f \in \Lambda_+(L^2(\mathbb{R}_+, \mathbb{C}^2))$ is relaxed to $f \in L^2(\mathbb{R}_+, \mathbb{C}^2)$. This gives the eigenvalues of the operator $c_l(\kappa) \otimes 1_{\mathbb{C}^2}$, proving (2.12). $\square$

2.1.3 Lower bounds on hydrogen eigenvalues. Critical case

Proof of Theorem 2.2. Critical case. It remains to prove that

$$\lambda_n(c_0(\kappa)) \geq -\text{const}\, \kappa^2 n^{-2}$$

for $\kappa^B \kappa^C / \kappa_1^C \leq \kappa \leq \kappa^C$. We may assume that $\kappa = \kappa^C$ and will prove that for all $\tau > 0$

$$N(-\tau, c_0(\kappa^C)) := \operatorname{tr} \chi_{(-\infty,-\tau)}(c_0(\kappa^C)) \leq \text{const}\, \tau^{-1/2}. \tag{2.13}$$

Let $\chi_i^2 + \chi_o^2 = 1$ be a smooth radial quadratic partition of unity with χ_i supported in the unit ball and χ_o supported outside the ball of radius $1/2$ about the origin. It was shown in [31, Eq. (19)] that the localization error can be estimated by a bounded exponentially decaying potential $v(r) \leq \text{const}\, e^{-r}$, i.e.,

$$\begin{aligned}
\sqrt{\mathbf{p}^2+1} - 1 - \kappa^C |\mathbf{x}|^{-1} \geq \chi_i &\left(\sqrt{\mathbf{p}^2+1} - 1 - \kappa^C|\mathbf{x}|^{-1} - v(|\mathbf{x}|)\right)\chi_i \\
&+ \chi_o \left(\sqrt{\mathbf{p}^2+1} - 1 - \kappa^C|\mathbf{x}|^{-1} - v(|\mathbf{x}|)\right)\chi_o.
\end{aligned}$$

By the variational principle it suffices to consider the eigenvalue counting function corresponding to the interior and exterior term separately. The interior term is further estimated according to

$$\begin{aligned}
&\chi_i \left(\sqrt{\mathbf{p}^2+1} - 1 - \kappa^C|\mathbf{x}|^{-1} - v(|\mathbf{x}|)\right)\chi_i \\
&\geq \chi_i \left(|\mathbf{p}| - \kappa^C|\mathbf{x}|^{-1} - \text{const}\ \right)\chi_i.
\end{aligned}$$

As shown by Lieb and Yau [46] and explained in Corollary D.1, the number of negative eigenvalues of the latter operator acting in the subspace corresponding to $l=0$ is finite, i.e., for all $\tau>0$

$$N_{l=0}\left(-\tau,\chi_i\left(|\mathbf{p}|-\kappa^C|\mathbf{x}|^{-1}-\text{const}\ \right)\chi_i\right)\leq \text{const}\ . \tag{2.14}$$

For the exterior problem, we note that by the variational principle

$$\begin{aligned} &N_{l=0}\left(-\tau,\chi_o\left(\sqrt{\mathbf{p}^2+1}-1-\kappa^C|\mathbf{x}|^{-1}-v(|\mathbf{x}|)\right)\chi_o\right)\\ &\qquad\leq N_{l=0}\left(-\tau,\sqrt{\mathbf{p}^2+1}-1-\chi(\mathbf{x})(\kappa^C|\mathbf{x}|^{-1}+v(|\mathbf{x}|))\right) \end{aligned}\tag{2.15}$$

where χ denotes the characteristic function of the support of χ_o. With the singularity gone, the result follows as in the subcritical case. Namely, similarly as in (2.11) we cut in momentum space according to small and large momenta. Again, by the variational principle, the right-hand side of (2.15) is then bounded from above by

$$N_{l=0}(-\text{const}\ \tau,|\mathbf{p}|-w(|\mathbf{x}|))+N_{l=0}(-\text{const}\ \tau,p^2-w(|\mathbf{x}|)),$$

where $w(r)=\text{const}\ \chi(r)(\kappa^C r^{-1}+v(r))$. The first term is estimated with the help of Daubechies' inequality [9]

$$\begin{aligned} N_{l=0}(-\tau,|\mathbf{p}|-w(|\mathbf{x}|))&\leq \tau^{-1/2}\operatorname{tr}_{l=0}(|\mathbf{p}|-w(|\mathbf{x}|))_-^{1/2}\\ &\leq \text{const}\ \tau^{-1/2}\int_0^\infty w(r)^{3/2}\,dr \end{aligned}$$

with the latter integral being finite. For the second term we estimate $w(r)\leq$ const r^{-1} and use that

$$N_{l=0}(-\tau,p^2-\text{const}\ |\mathbf{x}|^{-1})\leq \text{const}\ \tau^{-1/2}.$$

This concludes the proof of Theorem 2.2. □

Our proof of Theorem 2.1 in the critical Brown-Ravenhall case is based on a reduction to the Chandrasekhar case. The next lemma compares the number of eigenvalues of the critical operators $b_{1/2,l}(\kappa^B)$ with those of the two operators $c_{l'}(\kappa^C_{l'})$ with $l'=0,1$ and critical coupling constants $\kappa^C_0=2/\pi$ and $\kappa^C_1=\pi/2$, cf. (C.8).

Lemma 2.3. *There is a constant such that for $l=0,1$ and all $\tau>0$ one has*

$$N\left(-\tau,b_{1/2,l}(\kappa^B)\right)\leq \text{const}\ \left[N\left(-\tfrac{\tau}{\text{const}},c_0(\kappa^C_0)\right)+N\left(-\tfrac{\tau}{\text{const}},c_1(\kappa^C_1)\right)\right].$$

Proof. We start with the observation that $(\kappa^C_0)^{-1}+(\kappa^C_1)^{-1}=2(\kappa^B)^{-1}$. Using the explicit form of the reduced operators (cf. Appendix C), this implies the identities

$$\begin{aligned} b_{1/2,0}(\kappa^B)&=\kappa^B\left((\kappa^C_0)^{-1}\phi_0\tilde b_{0,0}\phi_0+(\kappa^C_1)^{-1}\phi_1\tilde b_{1,1}\phi_1\right),\\ b_{1/2,1}(\kappa^B)&=\kappa^B\left((\kappa^C_0)^{-1}\phi_1\tilde b_{0,1}\phi_1+(\kappa^C_1)^{-1}\phi_0\tilde b_{1,0}\phi_0\right), \end{aligned}\tag{2.16}$$

where the operators $\tilde{b}_{l,\nu}$ are defined in $L^2(\mathbb{R}_+)$ through quadratic forms

$$\langle f, \tilde{b}_{l,\nu} f\rangle := \int_0^\infty \frac{E(p)-1}{2\phi_\nu(p)^2} |f(p)|^2 \,\mathrm{d}p - \kappa_l^C \int_0^\infty \int_0^\infty \overline{f(p)} k_l^C(p,q) f(q) \,\mathrm{d}p \,\mathrm{d}q.$$

In case $\nu = 1$ it hence follows from $2\phi_1(p)^2 \le 1$ that $\langle f, \tilde{b}_{l,1} f\rangle \ge \langle f, c_l(\kappa_l^C) f\rangle$. In case $\nu = 0$ we use the inequality

$$(E(p)-1)\phi_0(p)^{-2} \ge \sqrt{p^2+4} - 2 = 2(E(p/2)-1) \tag{2.17}$$

which is most easily seen by writing both sides in terms of $E(p)$. It implies

$$\langle f, \tilde{b}_{l,0} f\rangle \ge 2\langle uf, c_l(\kappa_l^C)\, uf\rangle$$

where the unitary scaling transformation u is defined through $(uf)(p) := \sqrt{2} f(2p)$. The proof is completed by the variational principle. $\square$

We are now ready to give a

Proof of Theorem 2.1. Critical case. The previous lemma implies that it suffices to show that for $l = 0, 1$

$$N\left(-\tau, c_l(\kappa_l^C)\right) \le \text{const}\ \tau^{-1/2}.$$

In case $l = 0$ this was established in (2.13), and the case $l = 1$ follows similarly with the analogue of (2.14) given in Corollary D.1. $\square$

2.2 Sobolev inequality for the critical Brown-Ravenhall operator

Having studied the eigenvalues of B_κ in the previous subsection, we now turn to integrability properties of its eigenfunctions. The L^q-norm of two-spinors ψ is given by

$$\|\psi\|_q := \left(\int_{\mathbb{R}^3} |\psi(\mathbf{x})|^q \mathrm{d}\mathbf{x}\right)^{1/q},$$

where the modulus, $|\cdot|$, refers to the Euclidean norm in $\mathbb{C}^2$. For $q = 2$ we drop the subscript. We aim at proving the following

Theorem 2.4 (L^q-properties of eigenfunctions). *Let $2 \le q < 3$. There exists a constant $C_q < \infty$ such that for any $\kappa \in (0, \kappa^B]$ and all $\psi \in \mathfrak{Q}(B_\kappa)$ with $\langle \psi, B_\kappa \psi\rangle \le 0$ one has $\psi \in L^q$ with*

$$\|\psi\|_q \le C_q \|\psi\|. \tag{2.18}$$

Note that (2.18) applies, in particular, to eigenfunctions of B_κ corresponding to negative eigenvalues. The proof of Theorem 2.4, which is spelled out below, relies on a Sobolev inequality for the massless atomic Brown-Ravenhall operator in $\mathfrak{H}$ given by

$$B_\kappa^{(0)} := |\mathbf{p}| - \frac{\kappa}{2}\left(|\mathbf{x}|^{-1} + \omega_{\mathbf{p}}\cdot\boldsymbol{\sigma}\ |\mathbf{x}|^{-1}\ \omega_{\mathbf{p}}\cdot\boldsymbol{\sigma}\right).$$

This operator is bounded below (in fact, non-negative) if and only if $\kappa \leq \kappa^B$.

Theorem 2.5 (Sobolev inequality). *For any $2 \leq q < 3$ there exists a constant $C_q > 0$ such that for all $\psi \in \mathfrak{Q}(B_{\kappa^B}^{(0)})$,*

$$\|\psi\|_q^2 \leq C_q \left\langle \psi, B_{\kappa^B}^{(0)}\psi\right\rangle^\theta \|\psi\|^{2(1-\theta)}, \qquad \theta = 6(\tfrac{1}{2} - \tfrac{1}{q}). \tag{2.19}$$

It is illustrative to compare (2.19) with the 'standard' Sobolev-Gagliardo-Nirenberg inequalities,

$$\|\psi\|_q^2 \leq C_q' \left\langle \psi, |\mathbf{p}|\psi\right\rangle^\theta \|\psi\|^{2(1-\theta)}, \qquad \theta = 6(\tfrac{1}{2} - \tfrac{1}{q}), \qquad 2 \leq q \leq 3, \tag{2.20}$$

see, e.g., [43, Thm. 8.4]. Hence Theorem 2.5 says that, if the endpoint $q = 3$ is avoided, an inequality of the same form remains true after subtracting the maximal possible multiple of $\frac{1}{2}\left(|\mathbf{x}|^{-1} + \omega_{\mathbf{p}}\cdot\boldsymbol{\sigma}\ |\mathbf{x}|^{-1}\ \omega_{\mathbf{p}}\cdot\boldsymbol{\sigma}\right)$ from $|\mathbf{p}|$. Moreover, one can show that (2.19) does not hold with $q = 3$, not even if the L^3-norm is replaced by the weak L^3-norm.

Note that if $\kappa < \kappa^B$ then (2.19) with $B_\kappa^{(0)}$ instead of $B_{\kappa^B}^{(0)}$ follows from (2.20) – but with a constant that deteriorates as $\kappa \to \kappa^B$. The main point is to derive an inequality which holds uniformly in κ up to and including the critical constant. Our proof is based on the somewhat surprising fact that the Brown-Ravenhall operator with coupling constant κ^B can be bounded from below by the Chandrasekhar operator with *smaller* coupling constant κ^C.

Before we start the proof of (2.19), we provide the

Proof of Theorem 2.4. The Sobolev inequality (2.19) implies

$$\begin{aligned}\|\psi\|_q^2 &\leq C_q \left\langle \psi, B_\kappa^{(0)}\psi\right\rangle^\theta \|\psi\|^{2(1-\theta)} \leq C_q\left\langle\psi, \left[B_\kappa^{(0)} - B_\kappa\right]\psi\right\rangle^\theta \|\psi\|^{2(1-\theta)} \\ &\leq C_q \|B_\kappa^{(0)} - B_\kappa\|^\theta \|\psi\|^2.\end{aligned}$$

Tix showed [75, Thm. 1] (see also Balinsky and Evans [3]) that the difference $B_\kappa^{(0)} - B_\kappa$ extends to a bounded operator with norm uniformly bounded for any $\kappa \in (0, \kappa^B]$. □

2.2.1 Comparison of critical operators

The first step in the proof of the Sobolev inequality (2.19) is a comparison of $B_\kappa^{(0)}$ with the massless atomic Chandrasekhar operator in $\mathfrak{H}$, which is given by

$$C_\kappa^{(0)} := |\mathbf{p}| - \kappa|\mathbf{x}|^{-1}.$$

It is bounded below if and only if $\kappa \leq \kappa^C$. As discussed in Appendix C the parts of $B^{(0)}_\kappa$ and $C^{(0)}_\kappa$ in the subspace $\mathfrak{H}_{j,l,m}$ are unitarily equivalent to operators $b^{(0)}_j(\kappa)$ and $c^{(0)}_l(\kappa)$ in $L^2(\mathbb{R}_+)$, which depend only on j in the Brown-Ravenhall case and only on l in the Chandrasekhar case. For the comparison argument it is important to note that the reduced operators $b^{(0)}_j(\kappa)$ and $c^{(0)}_l(\kappa)$ are lower bounded for κ up to and including the critical coupling constants κ^B_j and κ^C_l respectively. They are defined in (C.7) and, as is explained there, exceed κ^B and κ^C, if $j \geq 3/2$ or $l \geq 1$.

We begin by observing that all the critical operators $b^{(0)}_j(\kappa^B_j)$ and $c^{(0)}_l(\kappa^C_l)$ have the same 'generalized ground state', namely p. The corresponding ground state representation formula (in momentum space) is given in

Lemma 2.6 (Ground state representation). *If $f \in \mathfrak{Q}(b^{(0)}_j(\kappa^B_j))$ and $g(p) = pf(p)$, then*

$$\langle f, b^{(0)}_j(\kappa^B_j) f\rangle = \frac{\kappa^B_j}{2} \int_0^\infty \int_0^\infty |g(p) - g(q)|^2 k^B_j(p,q)\, \frac{\mathrm{d}p}{p} \frac{\mathrm{d}q}{q}. \tag{2.21}$$

Similarly, if $f \in \mathfrak{Q}(c^{(0)}_l(\kappa^C_l))$ and $g(p) = pf(p)$, then

$$\langle f, c^{(0)}_l(\kappa^C_l) f\rangle = \frac{\kappa^C_l}{2} \int_0^\infty \int_0^\infty |g(p) - g(q)|^2 k^C_l(p,q)\, \frac{\mathrm{d}p}{p} \frac{\mathrm{d}q}{q}. \tag{2.22}$$

where k^B_j and k^C_l are defined in (C.4).

Proof. We write k for one of the functions k^B_j or k^C_l and κ for the corresponding constant κ^B_j or κ^C_l. Expanding the square and using $k(p,q) = k(q,p)$, we find

$$\begin{aligned}
&\frac{1}{2} \int_0^\infty \int_0^\infty |g(p) - g(q)|^2 k(p,q)\, \frac{\mathrm{d}p}{p} \frac{\mathrm{d}q}{q} \\
&= \int_0^\infty |g(p)|^2 \left(\int k(p,q)\, \frac{\mathrm{d}q}{q} \right) \frac{\mathrm{d}p}{p} - \int_0^\infty \int_0^\infty \overline{g(p)} k(p,q) g(q) \frac{\mathrm{d}p}{p} \frac{\mathrm{d}q}{q} \\
&= \int_0^\infty p|f(p)|^2 \left(\int k(p,q)\, \frac{\mathrm{d}q}{q} \right) \mathrm{d}p - \int_0^\infty \int_0^\infty \overline{f(p)} k(p,q) f(q)\, \mathrm{d}p\, \mathrm{d}q.
\end{aligned}$$

By definitions (C.7) and (C.8) of κ we have

$$\int_0^\infty k(p,q)\, \frac{\mathrm{d}q}{q} = \kappa^{-1},$$

which implies the assertion. □

Next, we bound $B^{(0)}_{\kappa^B}$ from below by $C^{(0)}_{\kappa^C}$.

Lemma 2.7 (Comparison of critical operators). *There is a positive constant such that for any $\psi \in \mathfrak{Q}(B^{(0)}_{\kappa^B}) \cap \mathfrak{H}^\perp_{1/2,1}$*

$$\left\langle \psi, B^{(0)}_{\kappa^B} \psi \right\rangle \geq \text{const } \left\langle \psi, C^{(0)}_{\kappa^C} \psi \right\rangle. \tag{2.23}$$

An inequality of the form (2.23) cannot hold for $\psi \in \mathfrak{H}_{1/2,1}$, since the right hand side is bounded from below by a constant times $\langle\psi, |\mathbf{p}|\psi\rangle$ while the left hand side is not.

Proof. By orthogonality it suffices to prove the inequality on each subspace $\mathfrak{H}_{j,l}$. First let $(j,l) = (1/2, 0)$. We may also fix $m = \pm 1/2$ and choose $\psi \in \mathfrak{H}_{1/2,0,m}$. Its Fourier transform is of the form $\hat{\psi}(\mathbf{p}) = p^{-1} f(p) \Omega_{\frac{1}{2},0,m}(\omega_{\mathbf{p}})$, see Appendix A. Setting $f(p) =: p g(p)$ one finds using (C.2) and Lemma 2.6

$$\langle\psi, B^{(0)}_{\kappa^B}\psi\rangle = \langle f, b^{(0)}_{1/2}(\kappa^B) f\rangle = \frac{\kappa^B}{2}\int_0^\infty\int_0^\infty |g(p)-g(q)|^2\, k^B_{1/2}(p,q)\,\frac{\mathrm{d}p}{p}\frac{\mathrm{d}q}{q}.$$

Similarly, using (C.3)

$$\langle\psi, C^{(0)}_{\kappa^C}\psi\rangle = \langle f, c^{(0)}_{0}(\kappa^C) f\rangle = \frac{\kappa^C}{2}\int_0^\infty\int_0^\infty |g(p)-g(q)|^2\, k^C_{0}(p,q)\,\frac{\mathrm{d}p}{p}\frac{\mathrm{d}q}{q}.$$

Recalling the explicit expressions (C.4) and (C.5) for $k^B_{1/2}$ and k^C_0 and estimating $Q_1 \geq 0$ we conclude that

$$\langle\psi, B^{(0)}_{\kappa^B}\psi\rangle \geq (1+(2/\pi)^2)^{-1}\langle\psi, C^{(0)}_{\kappa^C}\psi\rangle,$$

which proves the assertion on the subspace $\mathfrak{H}_{1/2,0}$. Now assume that $\psi \in \left(\mathfrak{H}_{1/2,0}\oplus\mathfrak{H}_{1/2,1}\right)^\perp$. Since κ^B_j is monotone increasing in j, see Appendix C, we have on that subspace

$$|\mathbf{p}| \geq \frac{\kappa^B_{3/2}}{2}\left(|\mathbf{x}|^{-1} + \omega_{\mathbf{p}}\cdot\boldsymbol{\sigma}\ |\mathbf{x}|^{-1}\ \omega_{\mathbf{p}}\cdot\boldsymbol{\sigma}\right).$$

We conclude that

$$\langle\psi, B^{(0)}_{\kappa^B}\psi\rangle \geq \frac{\kappa^B_{3/2}-\kappa^B_{1/2}}{\kappa^B_{3/2}}\langle\psi, |\mathbf{p}|\psi\rangle \geq \frac{\kappa^B_{3/2}-\kappa^B_{1/2}}{\kappa^B_{3/2}}\langle\psi, C^{(0)}_{\kappa^C}\psi\rangle,$$

proving the assertion. □

2.2.2 Proof of the Sobolev inequality

We are now ready to give a

Proof of Theorem 2.5. By scaling, (2.19) is equivalent to the inequality

$$\|\psi\|_q^2 \leq C'_q\ \left(\left\langle\psi, B^{(0)}_{\kappa^B}\psi\right\rangle + \|\psi\|^2\right).$$

This, together with the triangle inequality, shows that it is enough to prove the inequality separately on the subspaces $\mathfrak{H}_{1/2,1}$ and $\mathfrak{H}^\perp_{1/2,1}$. On the latter subspace, the claim follows immediately from Lemma 2.7 above and the Sobolev inequality for the critical Chandrasekhar operator [30, Corollary 2.5]. We now reduce the claim for the subspace $\mathfrak{H}_{1/2,1}$ to that for $\mathfrak{H}_{1/2,0}$. For this purpose, we note that the helicity operator $\mathrm{H} = \omega_{\mathbf{p}} \cdot \boldsymbol{\sigma}$, cf. (B.1), commutes with $B_\kappa^{(0)}$ and, by (B.2), maps $\mathfrak{H}_{j,l}$ into $\mathfrak{H}_{j,2j-l}$. Hence if $\psi \in \mathfrak{H}_{1/2,1}$ then by the Sobolev inequality on $\mathfrak{H}_{1/2,0}$

$$\left\langle \psi, B_{\kappa^B}^{(0)} \psi \right\rangle + \|\psi\|^2 = \left\langle \mathrm{H}\psi, B_{\kappa^B}^{(0)} \mathrm{H}\psi \right\rangle + \|\mathrm{H}\psi\|^2 \geq \mathrm{const}\, \|\mathrm{H}\psi\|_q^2.$$

By Lemma B.1 the helicity $\mathrm{H} = \mathrm{H}^{-1}$ is bounded on $L^q(\mathbb{R}^3, \mathbb{C}^2)$. □

2.3 Estimates on the electric potential

The goal of this subsection is to compare twisted and untwisted electric potentials. We begin with an estimates for point charges and then turn to smeared out charges.

Lemma 2.8. *Let $l \geq 1$ and $\psi \in \mathfrak{H}_{j,l}$. Then*

$$\left|\left\langle \psi, \left(|\mathbf{x}|^{-1} - \mathcal{U}(|\mathbf{x}|^{-1})\right) \psi \right\rangle\right| \leq \frac{\mathrm{const}}{l^2} \langle \psi, \mathbf{p}^2 \psi \rangle. \tag{2.24}$$

Proof. By orthogonality it suffices to prove the assertion for $\psi \in \mathfrak{H}_{j,l,m}$. Its Fourier transform is of the form $\hat\psi(\mathbf{p}) = f(p)p^{-1}\Omega_{j,l,m}(\omega_{\mathbf{p}})$, cf. Appendix A, and we compute similarly as in (C.11)

$$\begin{aligned}
&\langle \psi, \left(|\mathbf{x}|^{-1} - \mathcal{U}(|\mathbf{x}|^{-1})\right) \psi \rangle \\
&= \frac{1}{\pi} \int_0^\infty \mathrm{d}p\, \overline{f(p)} \int_0^\infty \mathrm{d}q\, f(q) \Big\{ [1 - \phi_0(p)\phi_0(q)]\, Q_l\left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right) \\
&\qquad\qquad\qquad\qquad\qquad - \phi_1(p)\phi_1(q) Q_{2j-l}\left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right)\Big\} \\
&= \frac{1}{2\pi}(A_1 + A_2)
\end{aligned}$$

with

$$\begin{aligned}
A_1 :=& \int_0^\infty \mathrm{d}p\, \overline{f(p)} \int_0^\infty \mathrm{d}q\, f(q) \sum_{\nu=0}^{1} \left(\phi_\nu(p) - \phi_\nu(q)\right)^2 Q_l\left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right), \\
A_2 :=& 2\int_0^\infty \mathrm{d}p\, \overline{f(p)} \int_0^\infty \mathrm{d}q\, f(q)\phi_1(p)\phi_1(q) \\
&\qquad \times \left[Q_l\left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right) - Q_{2j-l}\left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right)\right].
\end{aligned}$$

We estimate these terms separately. For the first term we use (B.5) and (B.6) together with Abel's argument to turn Hermitian integral operators into multiplication operators by means of the Schwarz inequality (see also [46, Ineq.

(6.9)]). Since the Q_l are positive, we obtain

$$\begin{aligned}A_1 \leq& \int_0^\infty \mathrm{d}p \frac{|f(p)|^2}{E(p)^4} \int_0^\infty \mathrm{d}q \left(\frac{p}{q}\right)^2 E(p)^2 \\ &\times \sum_{\nu=0}^{1} (\phi_\nu(p) - \phi_\nu(q))^2 E(q)^2 Q_l \left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right) \\ \leq& \frac58 \int_0^\infty \mathrm{d}p \frac{|f(p)|^2}{E(p)^4} \int_0^\infty \mathrm{d}q \left(\frac{p}{q}\right)^2 (p-q)^2 Q_l \left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right) \\ =& \frac58 \int_0^\infty \mathrm{d}p \frac{|f(p)|^2}{E(p)^4} p^3 \int_0^\infty \frac{\mathrm{d}q}{q^2} (1-q)^2 Q_l \left(\tfrac12 \left(q + q^{-1}\right)\right).\end{aligned}$$

We now use the bounds $p^3/E(p)^4 \leq p^2$ and, for $q \geq 1$, $(1-q)^2 \leq q^2 - 1$ which yield

$$\begin{aligned}\int_0^\infty \frac{\mathrm{d}q}{q^2}(1-q)^2 Q_l\left(\tfrac12\left(q+q^{-1}\right)\right) &= 2\int_1^\infty \frac{\mathrm{d}q}{q^2}(1-q)^2 Q_l\left(\tfrac12\left(q+q^{-1}\right)\right) \\ &\leq 4\int_1^\infty \mathrm{d}x\, Q_l(x) = \frac{4}{l(l+1)},\end{aligned}$$

where the last step involved [16, 324(18)]. Thus,

$$A_1 \leq \frac{5}{2l(l+1)} \int_0^\infty \mathrm{d}p\, p^2 |f(p)|^2 = \frac{5}{2l(l+1)} \langle \psi, \mathbf{p}^2 \psi \rangle.$$

We estimate the term A_2 similarly by the Schwarz inequality,

$$\begin{aligned}A_2 \leq& 2\int_0^\infty \mathrm{d}p |f(p)|^2 \, |\phi_1(p)|^2 \\ &\times \int_0^\infty \mathrm{d}q \, \frac{p}{q} \left| Q_l \left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right) - Q_{2j-l} \left(\tfrac12 \left(\tfrac{q}{p} + \tfrac{p}{q}\right)\right)\right| \\ \leq& 4\int_0^\infty \mathrm{d}p |f(p)|^2 p^2 \\ &\times \int_1^\infty \frac{\mathrm{d}q}{q} \left| Q_l\left(\tfrac12\left(q+q^{-1}\right)\right) - Q_{2j-l}\left(\tfrac12\left(q+q^{-1}\right)\right)\right|.\end{aligned}$$

Due to the pointwise monotonicity (C.10) the difference inside the modulus is of definite sign. Without loss of generality, we may therefore assume $2j = 2l+1$. Using the integral representation (C.1) we can bound

$$\begin{aligned}&\int_1^\infty \frac{\mathrm{d}q}{q} \left[Q_l\left(\tfrac12\left(q+q^{-1}\right)\right) - Q_{l+1}\left(\tfrac12\left(q+q^{-1}\right)\right)\right] \\ =& \int_1^\infty \mathrm{d}z z^{-l-2}(z-1) \int_1^{\frac12(z+z^{-1})} \frac{\mathrm{d}x}{\sqrt{x^2-1}} \frac{1}{\sqrt{1-2xz+z^2}} \\ \leq& \frac{\pi}{\sqrt2} \int_1^\infty \mathrm{d}z z^{-l-5/2}(z-1) = \frac{\pi}{\sqrt2 (l+\frac12)(l+\frac32)}.\end{aligned}$$

Adding the estimates for A_1 and A_2 we arrive at (2.24). $\square$

Note that our proof shows that one can choose different powers of $|\mathbf{p}|$ on the right hand side of (2.24).

Lemma 2.9. *There exists a constant such that for any electric potential v of a spherically symmetric non-negative charge density*

$$|\langle\psi, (v - \mathcal{U}(v))\,\psi\rangle| \le \text{const}\ v(0)\,\langle\psi, \mathbf{p}^2\psi\rangle.$$

Proof. We denote by $\tau : \mathbb{R}^3 \to [0,\infty)$ the spherically symmetric, non-negative charge density corresponding to v, i.e., $v(\mathbf{x}) = \int \tau(\mathbf{x}-\mathbf{y})\,|\mathbf{y}|^{-1}\mathrm{d}\mathbf{y}$. The Fourier transform of τ obeys the estimates

$$|\hat\tau(\mathbf{p})| = \sqrt{\frac{2}{\pi\,\mathbf{p}^2}}\left|\int_0^\infty r\,\sin(|\mathbf{p}|r)\,\tau(r)\mathrm{d}r\right| \le \frac{v(0)}{(2\pi)^{3/2}\,|\mathbf{p}|}.$$

By Fourier transform the scalar product on the left side of the assertion becomes

$$\begin{aligned}&\langle\psi, (v - \mathcal{U}(v))\,\psi\rangle\\ &\quad= \sqrt{\frac{2}{\pi}}\iint \hat\psi(\mathbf{p})^*\frac{\hat\tau(\mathbf{p}-\mathbf{q})}{|\mathbf{p}-\mathbf{q}|^2}\,(1 - \Phi_0(\mathbf{p})\Phi_0(\mathbf{q}) - \Phi_1(\mathbf{p})\Phi_1(\mathbf{q}))\,\hat\psi(\mathbf{q})\mathrm{d}\mathbf{p}\mathrm{d}\mathbf{q}.\end{aligned}$$

Using Lemma B.2 we estimate the absolute value of the preceding expression from above by the sum of two terms, B_1 and B_2. The first term can be further bounded as follows,

$$\begin{aligned}B_1 &= \text{const}\iint |\hat\tau(\mathbf{p}-\mathbf{q})||\hat\psi(\mathbf{p})||\hat\psi(\mathbf{q})|\,\mathrm{d}\mathbf{p}\mathrm{d}\mathbf{q}\\ &\le \text{const}\ v(0)\int \mathrm{d}\mathbf{p}\,|\hat\psi(\mathbf{p})|^2\int\left(\frac{|\mathbf{p}|}{|\mathbf{q}|}\right)^{5/2}\frac{1}{|\mathbf{p}-\mathbf{q}|}\,\mathrm{d}\mathbf{q}\\ &\le \text{const}\ v(0)\int |\hat\psi(\mathbf{p})|^2\mathbf{p}^2\,\mathrm{d}\mathbf{p},\end{aligned}$$

where we use the Schwarz inequality in the second step. The second term is estimated similarly

$$\begin{aligned}B_2 &= \text{const}\iint |\hat\tau(\mathbf{p}-\mathbf{q})|\frac{\sqrt{|\mathbf{p}|\,|\mathbf{q}|}}{|\mathbf{p}-\mathbf{q}|}|\hat\psi(\mathbf{p})||\hat\psi(\mathbf{q})|\,\mathrm{d}\mathbf{p}\mathrm{d}\mathbf{q}\\ &\le \text{const}\ v(0)\int \mathrm{d}\mathbf{p}\,|\hat\psi(\mathbf{p})|^2\int\left(\frac{|\mathbf{p}|}{|\mathbf{q}|}\right)^{2}\frac{\sqrt{|\mathbf{p}|\,|\mathbf{q}|}}{|\mathbf{p}-\mathbf{q}|^2}\,\mathrm{d}\mathbf{q}\\ &\le \text{const}\ v(0)\int |\hat\psi(\mathbf{p})|^2|\mathbf{p}|^2\,\mathrm{d}\mathbf{p}.\end{aligned}$$

This proves the assertion. $\square$

3 Spectral shift from Schrödinger to Brown-Ravenhall operators

The main theme of this section is the (integrated) spectral shift, i.e., the difference of sums of eigenvalues of the Brown-Ravenhall or Chandrasekhar operator

$$B[v] := \sqrt{\mathbf{p}^2+1} - 1 - \mathcal{U}(v), \qquad C[v] := \sqrt{\mathbf{p}^2+1} - 1 - v,$$

(cf. (2.2)) and the Schrödinger operator $S[v] := \frac{1}{2}\mathbf{p}^2 - v$, all acting in the Hilbert space $\mathfrak{H} = L^2(\mathbb{R}^3, \mathbb{C}^2)$ of two-spinors. We have set $c = 1$.
Concerning the potential $v : \mathbb{R}^3 \to \mathbb{R}$ we will always assume that the above operators can be defined through the Friedrichs extension starting from $\mathfrak{S}(\mathbb{R}^3, \mathbb{C}^2)$. For example, the condition $0 \le v(\mathbf{x}) \le \kappa^{\#} |\mathbf{x}|^{-1}$ with $\# = B,\, C$ (cf. (2.3)) ensures that the Brown-Ravenhall, respectively the Chandrasekhar operator are well-defined and bounded from below (see [17] and [40]).
We assume throughout that the potential v is radially symmetric which allows us to investigate the spectral shift on each subspace $\mathfrak{H}_{j,l}$ in the decomposition (2.4) separately. We write $\Lambda_{j,l}$ for the orthogonal projection onto $\mathfrak{H}_{j,l}$. For the reduced traces we use the notations

$$\operatorname{tr}_{j,l}(A) := \operatorname{tr}(\Lambda_{j,l}A), \qquad \operatorname{tr}_j(A) := \operatorname{tr}_{j,j+1/2}(A) + \operatorname{tr}_{j,j-1/2}(A). \tag{3.1}$$

3.1 Estimate on the spectral shift

One of the key observations in our proof of the Scott correction is that the spectral shift between the one-particle Brown-Ravenhall and the Schrödinger operator decreases sufficiently fast for high angular momenta.

Theorem 3.1 (Spectral shift: Brown-Ravenhall case). *There exists a constant $C < \infty$ such that for any $\kappa \le \kappa^B$, any $v : [0,\infty) \to [0,\infty)$ satisfying*

$$v(r) \le \kappa\, r^{-1}, \tag{3.2}$$

any $\mu > 0$ and any $j \in \mathbb{N}_0 + 1/2$ one has

$$\operatorname{tr}_j\big([B[v]+\mu]_- - [S[v]+\mu]_-\big) \le C\,\kappa^4\, j^{-2}. \tag{3.3}$$

We derive this result from a corresponding theorem for the Chandrasekhar operator. For a proof of the latter we need to strengthen [31, Thm. 2]. In particular, we need to consider $C[v]$ for potentials v satisfying (3.2) also in case $\kappa^C < \kappa \le \kappa^B$. Those operators are *not* densely defined in the Hilbert space $\mathfrak{H}$. However, according to (C.8) below, they *are* densely defined in the subspaces $\mathfrak{H}_{j,l}$ with $j \ge 3/2$. Another new aspect is that we trace the dependence on the coupling constant.

Theorem 3.2 (Spectral shift: Chandrasekhar case). *There exists a constant $C < \infty$ such that for all $l \in \mathbb{N}_0$, $j = l \pm \frac{1}{2}$, for all κ satisfying*

$$\kappa \le \begin{cases} \kappa^C & \text{if } l = 0, \\ \kappa^B & \text{if } l \ge 1, \end{cases}$$

for all $\mu \geq 0$ *and for all* $v : [0, \infty) \to [0, \infty)$ *satisfying* (3.2)*, one has*

$$0 \leq \mathrm{tr}_{j,l} \left([C[v] + \mu]_- - [S[v] + \mu]_- \right) \leq C \frac{\kappa^4}{(l + \frac{1}{2})^2}. \tag{3.4}$$

One of the key points to be appreciated in the above theorems is an effective cancellation in the differences in (3.4) and (3.3). This can already be seen for Coulomb potentials $v(r) = \kappa r^{-1}$, where

$$\mathrm{tr}_{j,l} \left[S_\kappa \right]_- = (2j + 1) \frac{\kappa^2}{2} \sum_{n=1}^{\infty} \frac{1}{(n + l)^2},$$

which does not decay at all as $j \to \infty$. Moreover, for fixed j and l the above trace vanishes only like κ^2 as $\kappa \to 0$. It is rather remarkable that such cancellations occur uniformly for all attractive potential v satisfying (3.2).

The following proof of Theorem 3.2 follows the ideas of [31, Thm. 2]. It is not only included to render the paper self-contained, but also to establish the above mentioned improvement, which is important for the present paper.

Proof of Theorem 3.2. We note that both traces $\mathrm{tr}_{j,l} \left[C[v] + \mu \right]_-$ and $\mathrm{tr}_{j,l} \left[S[v] + \mu \right]_-$ are finite. This follows by the variational principle from the case $v(r) = \kappa r^{-1}$, cf. Theorem 2.2 in the Chandrasekhar case. Thus, for $l < 3$ say, it is enough to show the claim for κ in a neighborhood of 0. More precisely, we can assume $\kappa \leq \frac{1}{\sqrt{8}}(l + \frac{1}{2})$ which covers all $\kappa \leq \kappa^B$ for $l \geq 3$.

Moreover, by an approximation argument it is sufficient to consider $\mu > 0$ and bounded potentials v, cf. [31].

We denote by $\gamma_{j,l}$ the orthogonal projection onto the eigenspace of $C[v]$ corresponding to angular momenta j, l and eigenvalues less or equal than $-\mu$. The identity

$$\tfrac{1}{2} p^2 = C_0 + \tfrac{1}{2} C_0^2 \tag{3.5}$$

and the variational principle (cf. [43, Thm. 12.1]) imply

$$0 \leq 2 \, \mathrm{tr}_{j,l} \left([C[v] + \mu]_- - [S[v] + \mu]_- \right) \leq \mathrm{tr} \left[C_0^2 \gamma_{j,l} \right]. \tag{3.6}$$

Using the eigenvalue equation and the bound (3.2) on the potential we estimate this term further as follows.

$$\mathrm{tr} \left[C_0^2 \gamma_{j,l} \right] \leq \mathrm{tr}_{j,l} \left[C[v] \right]_-^2 + \mathrm{tr} \left[v^2 \gamma_{j,l} \right] \leq \mathrm{tr}_{j,l} \left[C_\kappa \right]_-^2 + \kappa^2 \, \mathrm{tr} \left[|\mathbf{x}|^{-2} \gamma_{j,l} \right].$$

Using Hardy's inequality and (3.5)

$$\begin{aligned} \mathrm{tr} \left[|\mathbf{x}|^{-2} \gamma_{j,l} \right] &\leq \left(l + \tfrac{1}{2} \right)^{-2} \mathrm{tr} \left[\mathbf{p}^2 \gamma_{j,l} \right] \\ &= \left(l + \tfrac{1}{2} \right)^{-2} \left(\mathrm{tr} \left[C_0^2 \gamma_{j,l} \right] + 2 \, \mathrm{tr} \left[C_0 \gamma_{j,l} \right] \right). \end{aligned}$$

Since $\kappa < l + \frac{1}{2}$, the last two estimates may be summarized as

$$\mathrm{tr} \left[C_0^2 \gamma_{j,l} \right] \leq \left(1 - \frac{\kappa^2}{(l + \frac{1}{2})^2} \right)^{-1} \left(\mathrm{tr}_{j,l} \left[C_\kappa \right]_-^2 + \frac{2\kappa^2}{(l + \frac{1}{2})^2} \, \mathrm{tr} \left[C_0 \gamma_{j,l} \right] \right). \tag{3.7}$$

We shall estimate the two terms on the right hand side separately. From [31, Lemma 3] we recall the following angular momentum barrier inequality on $\mathfrak{H}_{j,l}$,

$$C_0 \geq 2\kappa r^{-1}\chi_{\{r\leq R_l(\kappa)\}}, \qquad R_l(\kappa) = \tfrac{1}{8\kappa}(l+\tfrac{1}{2})^2. \tag{3.8}$$

(Here we use that $\kappa \leq \frac{1}{\sqrt{8}}(l+\frac{1}{2})$.) This implies

$$\begin{aligned}\operatorname{tr}[C_0\gamma_{j,l}] &\leq \kappa \operatorname{tr}\left[|\mathbf{x}|^{-1}\gamma_{j,l}\right] \leq \frac{1}{2}\operatorname{tr}[C_0\gamma_{j,l}] + \frac{1}{4}\operatorname{tr}[w_l\gamma_{j,l}] \\ &= \frac{3}{4}\operatorname{tr}[C_0\gamma_{j,l}] - \frac{1}{4}\operatorname{tr}[C[w_l]\gamma_{j,l}]\end{aligned}$$

where $w_l(r) := 4\kappa r^{-1}\chi_{\{r\geq R_l(\kappa)\}}$. Hence, using the variational principle followed by Daubechies' inequality [9] (cf. also [31, Prop. 1])

$$\begin{aligned}&\operatorname{tr}[C_0\gamma_{j,l}] \leq \operatorname{tr}_{j,l}[C[w_l]]_- \\ &\quad\leq \text{const}\,(2l+1)\left(\int_0^\infty w_l(r)^{3/2}\,dr + \int_0^\infty w_l(r)^2\,dr\right) \leq \text{const}\,\kappa^2.\end{aligned} \tag{3.9}$$

In order to estimate the first term on the right hand side of (3.7) we use (3.8) to obtain on $\mathfrak{H}_{j,l}$

$$C_\kappa \geq \tfrac{1}{2}C_0 - \kappa r^{-1}\chi_{\{r\geq R_l(\kappa)\}} \geq \tfrac{1}{2}C[w_l].$$

with w_l as above. Hence again by Daubechies' inequality

$$\begin{aligned}\operatorname{tr}_{j,l}[C_\kappa]_-^2 &\leq \text{const}\,(2l+1)\left(\int_0^\infty w_l(r)^{5/2}\,dr + \int_0^\infty w_l(r)^3\,dr\right) \\ &\leq \text{const}\,\kappa^4(l+\tfrac{1}{2})^{-2}.\end{aligned}$$

Combing this with (3.9), (3.7), and (3.6) completes the proof. □

Having finished the proof of Theorem 3.2 it is easy to give the

Proof of Theorem 3.1. Since the trace $\operatorname{tr}_j[B[v]+\mu]_-$ is finite according to Theorem 2.1 we may assume that either $\kappa \leq \kappa^C$ and $j = 1/2$, or else that $j \geq 3/2$. In this case, the claim essential boils down to Theorem 3.2. To see this, we note the identity

$$B[v] = \mathcal{U}(C[v]) = \tfrac{1}{2}\left(U(\mathbf{p})^* C[v] U(\mathbf{p}) + U(\mathbf{p}) C[v] U(\mathbf{p})^*\right) \tag{3.10}$$

involving the unitary operator $U(\mathbf{p}) := \Phi_0(\mathbf{p}) + i\Phi_1(\mathbf{p})$ (see also (2.1)). Equality (3.10) as well as the unitarity of $U(\mathbf{p})$ are easily derived from the fact that $\Phi_0^2(\mathbf{p}) + \Phi_1^2(\mathbf{p}) = 1$.
Even if v satisfies (3.2) only with a $\kappa^C < \kappa \leq \kappa^B$, identity (3.10) remains valid on all subspaces $\mathfrak{H}_j$ with $j \geq 3/2$. Hence by the concavity of the sum of

negative eigenvalues [72] of $B[v]+\mu$ one has for any $\mu \geq 0$

$$\begin{aligned}
&\operatorname{tr}_j [B[v]+\mu]_- \\
\leq &\frac{1}{2}\operatorname{tr}_j [U^*(\mathbf{p})C[v]U(\mathbf{p})+\mu]_- + \frac{1}{2}\operatorname{tr}_j [U(\mathbf{p})C[v]U^*(\mathbf{p})+\mu]_- \\
= &\operatorname{tr}_j [C[v]+\mu]_- .
\end{aligned} \tag{3.11}$$

By (3.4) the trace in (3.3) is thus bounded from above by

$$\operatorname{tr}_j \left([C[v]+\mu]_- - [S[v]+\mu]_-\right) \leq \text{const}\, \kappa^4 j^{-2},$$

as claimed. □

3.2 Properties of the spectral shift

In this subsection we discuss some properties of the spectral shift $s(\kappa)$ defined in (1.8).

Lemma 3.3 (Properties of the spectral shift). *The spectral shift s is a continuous, non-negative function on $(0,\kappa^B]$ satisfying $s(\kappa)=\mathcal{O}(\kappa^2)$ as $\kappa \downarrow 0$.*

Proof. According to (2.6) and Theorem 3.1 one has

$$0 \leq s_j(\kappa) := \kappa^{-2}\operatorname{tr}_j \left([B_\kappa]_- - [S_\kappa]_-\right) \leq \text{const}\, \kappa^2 j^{-2}.$$

Therefore the sum $s(\kappa) = \sum_j s_j(\kappa)$ converges, is non-negative and satisfies the claimed asymptotic estimate as $\kappa \downarrow 0$. By the min-max principle each eigenvalue depends continuously on κ. Thus the continuity of their sum follows from the estimates in Theorem 2.1 and the Weierstraß criterion for uniform convergence. □

4 Proof of the Scott correction

The strategy of the proof of the main results is similar to the one used for the Chandrasekhar operator [31]. We employ the Schrödinger operator as a regularization for the relativistic problem, i.e., we will use it to eliminate the main contribution to the energy (the Thomas-Fermi energy) and focus only on the energy shift of the low lying states. For these the electron-electron interaction plays no role and the unscreened problem remains. We define

$$E^S(Z) := \inf\{\mathcal{E}_Z^S(\psi)\,|\,\psi \in \mathfrak{Q}_Z^S, \|\psi\|=1\}$$

to be the ground state energy in the Schrödinger case,

$$\mathcal{E}_N^S(\psi) := \left\langle \psi, \left[\sum_{\nu=1}^N \left(\frac{1}{2}\mathbf{p}_\nu^2 - Z|\mathbf{x}_\nu|^{-1}\right) + \sum_{1\leq\mu<\nu\leq N} |\mathbf{x}_\mu - \mathbf{x}_\nu|^{-1}\right]\psi\right\rangle.$$

It is defined on $\mathfrak{Q}_N^S := \mathfrak{H}_N^S \cap \mathfrak{S}(\mathbb{R}^{3N}, \mathbb{C}^{2^N})$, where $\mathfrak{H}_N^S := \bigwedge_{\nu=1}^N \mathfrak{H}$ is the Hilbert space of anti-symmetric two-spinors. We recall that we suppose neutrality, i.e., $N = Z$.

The asymptotics of the Schrödinger ground-state energy up to Scott correction reads [55]

$$E^S(Z) = E_{\mathrm{TF}}(Z) + \tfrac{1}{2} Z^2 + \mathcal{O}(Z^{47/24}). \tag{4.1}$$

For our purpose this remainder estimate is sufficient. However, even the coefficient of the $Z^{5/3}$-term in the asymptotic expansion is known [23, 24, 25, 18, 26, 21, 19, 20, 22].

Our main result, Theorem 1.1, will follow from (4.1) if we can show that in the limit $Z \to \infty$ the difference of the Schrödinger and Brown-Ravenhall ground-state energy satisfies

$$E^S(Z) - E_c^B(Z) = s(Z/c)\, Z^2 + \mathcal{O}(Z^{47/24}) \tag{4.2}$$

uniformly in $\kappa = Z/c \in (0, \kappa^B]$. We break the proof of this assertion into an upper and lower bound.

4.1 Upper bound on the energy difference

The Thomas-Fermi functional (1.7) has a unique minimizer ϱ_Z, the Thomas-Fermi density (Lieb and Simon [44]). It scales as $\varrho_Z(\mathbf{x}) := Z^2 \varrho_1(Z^{1/3}\mathbf{x})$. We set

$$\phi_{\mathrm{TF}}(\mathbf{x}) := Z|\mathbf{x}|^{-1} - \int_{\mathbb{R}^3} \frac{\varrho_Z(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, \mathrm{d}\mathbf{y}, \tag{4.3}$$

the Thomas-Fermi potential, and

$$L_{\mathrm{TF}}(\mathbf{x}) := \int_{|\mathbf{x}-\mathbf{y}|<R_Z(\mathbf{x})} \frac{\varrho_Z(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\, \mathrm{d}\mathbf{y},$$

the exchange hole potential. Here $R_Z(\mathbf{x})$ is defined as the (unique) minimal radius for which $\int_{|\mathbf{x}-\mathbf{y}|\le R_Z(\mathbf{x})} \varrho_Z(\mathbf{y})\mathrm{d}\mathbf{y} = \frac{1}{2}$. The corresponding one-particle operators – self-adjointly realized in $\mathfrak{H}$ – are

$$S_{\mathrm{TF}} = S[\phi_{\mathrm{TF}} + L_{\mathrm{TF}}], \qquad B_{\mathrm{TF}} = B_c[\phi_{\mathrm{TF}} + L_{\mathrm{TF}}].$$

Here we use a notation analogous to that in (1.5).

We shall express the many-particle ground-state energies $E^S(Z)$ and $E_c^B(Z)$ in terms of quantities involving the above one-particle operators. In the Schrödinger case, this was achieved in [55, 58] in terms of the Thomas-Fermi potential ϕ_{TF}. Our point in the proof of the following proposition is to replace ϕ_{TF} by the exchange hole reduced potential $\phi_{\mathrm{TF}} + L_{\mathrm{TF}}$.

Proposition 4.1. *Let* $J := \left[Z^{1/9}\right] + \frac{1}{2}$. *Then, as* $Z \to \infty$,

$$E^S(Z)$$
$$= - \sum_{j=1/2}^{J-1} \mathrm{tr}_j \left[S[Z|\mathbf{x}|^{-1}]\right]_- - \sum_{j=J}^{Z+1/2} \mathrm{tr}_j \left[S_{\mathrm{TF}}\right]_- - D(\varrho_Z, \varrho_Z) + O(Z^{47/24}). \tag{4.4}$$

Since $\phi_{\mathrm{TF}} + L_{\mathrm{TF}}$ has a Coulomb tail, the trace $\mathrm{tr}_j \left[S_{\mathrm{TF}}\right]_-$ is finite for each j, but not summable with respect to j. It is therefore essential to restrict the second sum to a finite number of angular momenta. However, the value of the cut-off, $j \leq Z + 1/2$, is not chosen optimally here, since for our argument it is largely arbitrary.

Proof of Proposition 4.1. According to the correlation inequality [47]

$$E^S(Z) \geq - \sum_{j=1/2}^{Z+1/2} \mathrm{tr}_j \left[S_{\mathrm{TF}}\right]_- - D(\varrho_Z, \varrho_Z).$$

Note that the Z electrons can certainly be accommodated in the first Z angular momentum channels (which is a very crude bound). Estimating $\phi_{\mathrm{TF}} + L_{\mathrm{TF}}$ from above by the Coulomb potential for small angular momenta, we obtain

$$E^S(Z) \geq - \sum_{j=1/2}^{J-1} \mathrm{tr}_j \left[S[Z|\mathbf{x}|^{-1}]\right]_- - \sum_{j=J}^{Z+1/2} \mathrm{tr}_j \left[S_{\mathrm{TF}}\right]_- - D(\varrho_Z, \varrho_Z). \tag{4.5}$$

Moreover, see [55, 58],

$$E^S(Z)$$
$$\leq - \sum_{j=1/2}^{J-1} \mathrm{tr}_j \left[S[Z|\mathbf{x}|^{-1}]\right]_- - \sum_{j=J}^{\infty} \mathrm{tr}_j \left[S[\phi_{\mathrm{TF}}]\right]_- - D(\varrho_Z, \varrho_Z) + \mathrm{const}\, Z^{47/24}.$$

Hence it suffices to prove that

$$- \sum_{j=J}^{Z+1/2} \mathrm{tr}_j \left[S_{\mathrm{TF}}\right]_- \geq - \sum_{j=J}^{\infty} \mathrm{tr}_j \left[S[\phi_{\mathrm{TF}}]\right]_- - \mathrm{const}\, Z^{5/3} \tag{4.6}$$

(Note that the lower bound in [31] contains an error by estimating [31, Equation (43)] too generously. Really, only the first Z lowest negative eigenvalues need to occur on the right hand side instead of all. In particular, there will be never more than Z total angular momentum channels occupied. This fact is taken into account here yielding a suitable lower bound. The problem in [31] can be circumvented in exactly the same way.) We decompose $L_{\mathrm{TF}} = L_< + L_>$ where

$$L_< = \chi_{\{|\mathbf{x}|<R\}} L_{\mathrm{TF}}, \qquad L_> = \chi_{\{|\mathbf{x}|\geq R\}} L_{\mathrm{TF}},$$

with a constant R (independent of Z) to be chosen below. For $\varepsilon > 0$ to be specified later we estimate using the variational principle for sums of eigenvalues

$$\begin{aligned}&\mathrm{tr}_j\,[S_{\mathrm{TF}}]_- \\ &\le \mathrm{tr}_j(\tfrac12(1-2\varepsilon^2)p^2-\phi_{\mathrm{TF}})_- + \varepsilon^2\,\mathrm{tr}_j(\tfrac12 p^2-\varepsilon^{-2}L_<)_- + \varepsilon^2\,\mathrm{tr}_j(\tfrac12 p^2-\varepsilon^{-2}L_>)_- .\end{aligned} \tag{4.7}$$

By the subsequent lemma the first (and main) term is bounded according to

$$\begin{aligned}&\sum_{j=J}^{Z+1/2}\mathrm{tr}_j(\tfrac12(1-2\varepsilon^2)p^2-\phi_{\mathrm{TF}})_- - \sum_{j=J}^{\infty}\mathrm{tr}_j(\tfrac12 p^2-\phi_{\mathrm{TF}})_- \\ &\le \mathrm{tr}(\tfrac12(1-2\varepsilon^2)p^2-\phi_{\mathrm{TF}})_- - \mathrm{tr}(\tfrac12 p^2-\phi_{\mathrm{TF}})_- \le \mathrm{const}\,\varepsilon^2 Z^{7/3}.\end{aligned}$$

For the second term on the right side of (4.7) we use the Lieb-Thirring inequality [45] to obtain

$$\begin{aligned}&\varepsilon^2\sum_{j=J}^{Z+1/2}\mathrm{tr}_j(\tfrac12 p^2-\varepsilon^{-2}L_<)_- \le \varepsilon^2\,\mathrm{tr}(\tfrac12 p^2-\varepsilon^{-2}L_<)_- \\ &\le \mathrm{const}\,\varepsilon^{-3}\int L_<(\mathbf{x})^{5/2}\,\mathrm{d}\mathbf{x} \le \mathrm{const}\,\varepsilon^{-3}Z^{2/3}.\end{aligned}$$

In the last inequality we used a bound of Siedentop and Weikard [58, Proof of Lemma 2]. It is at this point that R is chosen. The penultimate inequality in [58, Proof of Lemma 2] asserts after scaling that $L_>(\mathbf{x}) \le \mathrm{const}\,|\mathbf{x}|^{-1}$. Hence by comparison with the exact hydrogen solution

$$\begin{aligned}&\varepsilon^2\sum_{j=J}^{Z+1/2}\mathrm{tr}_j(\tfrac12 p^2-\varepsilon^{-2}L_>)_- \le \varepsilon^2\sum_{j=1/2}^{Z+1/2}\mathrm{tr}_j(\tfrac12 p^2-\varepsilon^{-2}\mathrm{const}\,|\mathbf{x}|^{-1})_- \\ =&\mathrm{const}\,\varepsilon^{-2}\sum_{j=1/2}^{Z+1/2}\sum_{n=1}^{\infty}\frac{2j+1}{(n+j-1/2)^2} \le \mathrm{const}\,\varepsilon^{-2}Z.\end{aligned}$$

Choosing $\varepsilon = Z^{-1/3}$ all the error terms are $\mathcal{O}(Z^{5/3})$, proving (4.6). □

In the previous proof we used

Lemma 4.2. *For all* $0 < \varepsilon \le 1/2$, *as* $Z \to \infty$,

$$\mathrm{tr}(\tfrac12(1-\varepsilon^2)p^2-\phi_{\mathrm{TF}})_- \le \mathrm{tr}(\tfrac12 p^2-\phi_{\mathrm{TF}})_- + \mathrm{const}\,\varepsilon^2 Z^{7/3}. \tag{4.8}$$

Note that there are only a finite number of eigenvalues, since ϕ_{TF} decays like $|\mathbf{x}|^{-4}$.

Proof. Let $d^\varepsilon_{\mathrm{TF}}$ be the projection onto the negative eigenvalues of $\frac{1}{2}(1-\epsilon^2)p^2 - \phi_{\mathrm{TF}}$. Then, by the variational principle

$$\begin{aligned}&\mathrm{tr}(\tfrac{1}{2}(1-\varepsilon^2)p^2 - \phi_{\mathrm{TF}})_- - \mathrm{tr}(\tfrac{1}{2}p^2 - \phi_{\mathrm{TF}})_- \\ &\quad \leq -\,\mathrm{tr}\, d^\varepsilon_{\mathrm{TF}}(\tfrac{1}{2}(1-\varepsilon^2)p^2 - \phi_{\mathrm{TF}}) + \mathrm{tr}\, d^\varepsilon_{\mathrm{TF}}(\tfrac{1}{2}p^2 - \phi_{\mathrm{TF}}) = \tfrac{\varepsilon^2}{2}\,\mathrm{tr}\, d^\varepsilon_{\mathrm{TF}} p^2. \end{aligned} \tag{4.9}$$

Hence the claim will follow, if we show that $\mathrm{tr}\, d^\varepsilon_{\mathrm{TF}} p^2 \leq \mathrm{const}\ Z^{7/3}$. Note that $d^\varepsilon_{\mathrm{TF}}$ depends on both ε and Z, and by rescaling one may get rid of the ε dependence at the expense of changing Z. We may therefore assume that $\varepsilon = 0$ and write $d_{\mathrm{TF}} = d^0_{\mathrm{TF}}$.
Thus, it remains to prove

$$\mathrm{tr}\, d_{\mathrm{TF}} p^2 \leq \mathrm{const}\ Z^{7/3}. \tag{4.10}$$

Note that this says that the *kinetic* energy is bounded by the order of the *total* energy $\mathrm{tr}\, d_{\mathrm{TF}}(\frac{1}{2}p^2 - \phi_{\mathrm{TF}})$, which is well-known to be of order $Z^{7/3}$. Using that ϕ_{TF} is bounded by a constant times $\min\{Z|\mathbf{x}|^{-1}, |\mathbf{x}|^{-4}\}$ (see [44]) we get for any $R > 0$

$$\begin{aligned}&\tfrac{1}{2}\,\mathrm{tr}\, d_{\mathrm{TF}} p^2 \leq \mathrm{tr}\, d_{\mathrm{TF}}\phi_{\mathrm{TF}} \\ &\quad \leq \mathrm{const}\ \Bigg(\left(\int_{\{|\mathbf{x}|<R\}} (Z|\mathbf{x}|^{-1})^{5/2}\,\mathrm{d}\mathbf{x} \right)^{2/5} \left(\int d_{\mathrm{TF}}(\mathbf{x},\mathbf{x})^{5/3}\,\mathrm{d}\mathbf{x} \right)^{3/5} \\ &\qquad\qquad + R^{-4} \int d_{\mathrm{TF}}(\mathbf{x},\mathbf{x})\,\mathrm{d}\mathbf{x} \Bigg). \end{aligned}$$

The Cwikel-Lieb-Rozenblum inequality (for a textbook presentation, see, e.g., [63]) guarantees that

$$\int d_{\mathrm{TF}}(\mathbf{x},\mathbf{x})\,\mathrm{d}\mathbf{x} \leq \mathrm{const}\ \int \phi_{\mathrm{TF}}(\mathbf{x})^{3/2}\mathrm{d}\mathbf{x} = \mathrm{const}\ Z.$$

Moreover, by the Lieb-Thirring inequality [45]

$$\int d_{\mathrm{TF}}(\mathbf{x},\mathbf{x})^{5/3}\,\mathrm{d}\mathbf{x} \leq \mathrm{const}\ \mathrm{tr}\, d_{\mathrm{TF}} p^2.$$

We can estimate for any $\delta > 0$

$$\begin{aligned}&\left(\int_{\{|\mathbf{x}|<R\}} (Z|\mathbf{x}|^{-1})^{5/2}\,\mathrm{d}\mathbf{x} \right)^{2/5} \left(\int d_{\mathrm{TF}}(\mathbf{x},\mathbf{x})^{5/3}\,\mathrm{d}\mathbf{x} \right)^{3/5} \\ &\quad \leq \mathrm{const}\ Z R^{1/5} \left(\mathrm{tr}\, d_{\mathrm{TF}} p^2\right)^{3/5} \\ &\quad \leq \delta\,\mathrm{tr}\, d_{\mathrm{TF}} p^2 + \mathrm{const}\ \delta^{-3/2} Z^{5/2} R^{1/2}. \end{aligned}$$

In summary, we have shown that

$$\left(\tfrac{1}{2} - \mathrm{const}\,\delta\right) \mathrm{tr}\, d_{\mathrm{TF}} p^2 \le \mathrm{const}\,\left(\delta^{-3/2} Z^{5/2} R^{1/2} + R^{-4} Z\right).$$

Choosing δ small (of order one) and $R = Z^{-1/3}$ we obtain (4.10). □

Next, we bound the many-particle ground state energy of the Brown-Ravenhall operator from below by one-body quantities which match the corresponding quantities in the Schrödinger case (4.4).

Lemma 4.3. *For all $J \in \mathbb{N}_0 + 1/2$ and $Z \in \mathbb{N}$*

$$E_c^B(Z) \ge -\sum_{j=1/2}^{J-1} \mathrm{tr}_j \left[B_c[Z|\mathbf{x}|^{-1}]\right]_- - \sum_{j=J}^{Z+1/2} \mathrm{tr}_j \left[B_{\mathrm{TF}}\right]_- - D(\varrho_Z, \varrho_Z).$$

Proof. This follows by the same argument leading to (4.5). □

We are now ready to give a

Proof of Theorem 1.1 – first part. Choosing $J = \left[Z^{1/9}\right] + \frac{1}{2}$ and combining Proposition 4.1 and Lemma 4.3 we obtain

$$\begin{aligned} E^S(Z) - E_c^B(Z) \le &\sum_{j=1/2}^{J-1} \mathrm{tr}_j \left(\left[B_c[Z|\mathbf{x}|^{-1}]\right]_- - \left[S[Z|\mathbf{x}|^{-1}]\right]_-\right) \\ &+ \sum_{j=J}^{Z+1/2} \mathrm{tr}_j \left([B_{\mathrm{TF}}]_- - [S_{\mathrm{TF}}]_-\right) + \mathcal{O}(Z^{47/24}). \end{aligned} \tag{4.11}$$

We note that by scaling $\mathbf{x} \mapsto \mathbf{x}/c$, the operators $S[Z|\mathbf{x}|^{-1}]$ and $B_c[Z|\mathbf{x}|^{-1}]$ are unitarily equivalent to the operators $Z^2\kappa^{-2}S_\kappa$ and $Z^2\kappa^{-2}B_\kappa$ where $\kappa = Z/c$. Similarly, S_{TF} and B_{TF} are unitarily equivalent to the operators $Z^2\kappa^{-2}S[\kappa|\mathbf{x}|^{-1} - \chi_c]$ and $Z^2\kappa^{-2}B[\kappa|\mathbf{x}|^{-1} - \chi_c]$ acting in $\mathfrak{H}$, where

$$\chi_c(\mathbf{x}) := c^{-4} \int_{|\mathbf{x}-\mathbf{y}|>cR_Z(c^{-1}\mathbf{x})} \frac{\varrho_Z(c^{-1}\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,\mathrm{d}\mathbf{y}.$$

This implies that the first two terms on the right-hand side of (4.11), which we denote by $\Sigma_1(Z,c)$ and $\Sigma_2(Z,c)$, can be rewritten as

$$\begin{aligned} \Sigma_1(Z,c) &= Z^2\kappa^{-2} \sum_{j=1/2}^{J-1} \mathrm{tr}_j \left([B_\kappa]_- - [S_\kappa]_-\right), \\ \Sigma_2(Z,c) &= Z^2\kappa^{-2} \sum_{j=J}^{Z+1/2} \mathrm{tr}_j \left(\left[B[\kappa|\mathbf{x}|^{-1} - \chi_c]\right]_- - \left[S[\kappa|\mathbf{x}|^{-1} - \chi_c]\right]_-\right). \end{aligned}$$

Inequality (2.6) and Theorem 3.1 guarantee that the terms in the first sum are non-negative and that the terms in both sums are bounded from above by a constant times $\kappa^4 j^{-2}$ independently of Z and c. Therefore, the first sum can be bounded from above by an absolutely convergent series,

$$\Sigma_1(Z,c) \le Z^2\kappa^{-2} \sum_{j=1/2}^{\infty} \mathrm{tr}_j \left([B_\kappa]_- - [S_\kappa]_-\right) = Z^2\, s(\kappa).$$

By the same token

$$\Sigma_2(Z,c) \le \text{const } Z^2\kappa^2 \sum_{j=J}^{\infty} j^{-2} = \mathcal{O}(Z^{17/9}),$$

uniformly in c. This concludes the proof of the upper bound on the energy difference. $\square$

4.2 Lower bound on the energy difference

Similarly to [55] we define one-particle density matrices d^S and d^B on $\mathfrak{H}$ as sums

$$d^\# = d^\#_< + d_>, \quad \# = S, B. \tag{4.12}$$

The contribution of small total angular momenta, $d^\#_< = \sum_{l<L} d^\#_l$, is defined in Appendix E.1. It comes from the eigenspinors of the atomic problems. The contribution of large angular momentum, $d_> = \sum_{l=L}^\infty d_l$, is defined in Appendix E.2. It corresponds to the Macke orbitals of [55] and, in particular, coincides for the Schrödinger and Brown-Ravenhall case. The angular-momentum cut-off L will be chosen in a Z-dependent way, namely,

$$L := [Z^{1/12}].$$

Important properties of the density matrices, whose construction is explained in more detail in Appendix E, are:

- The densities
$$\rho^\#(\mathbf{x}) := \mathrm{tr}_{\mathbb{C}^2}\left(d^\#(\mathbf{x},\mathbf{x})\right), \quad \rho^\#_l(\mathbf{x}) := \mathrm{tr}_{\mathbb{C}^2}\left(d^\#_l(\mathbf{x},\mathbf{x})\right),$$
$$\rho^\#_<(\mathbf{x}) := \sum_{l<L} \rho^\#_l(\mathbf{x}), \quad \rho_>(\mathbf{x}) := \sum_{l\ge L} \rho_l(\mathbf{x}).$$
of $d^\#$, $d^\#_l$, and $d_>$ are all spherically symmetric.
- The dimension of the ranges of the density matrices d^S and d^B is at most Z, in particular $\mathrm{tr}\, d^\# \le Z$. Moreover,
$$\mathrm{tr}\, d^\#_l = \int \rho^\#_l(\mathbf{x})\,\mathrm{d}\mathbf{x} = 2(2l+1)(K-l), \qquad 0 \le l < L, \tag{4.13}$$
with $K = [\text{const } Z^{1/3}]$ and a suitable constant.

For a lower bound on the ground state energy in the Schrödinger case, we recall from [55] and [31, Proposition 4] the following

Proposition 4.4. *For large Z,*

$$E^S(Z) = \mathrm{tr}\left[S[Z|\mathbf{x}|^{-1}]\, d^S\right] + D(\rho^S,\rho^S) + \mathcal{O}(Z^{47/24}).$$

To obtain an upper bound on the ground state energy in the Brown-Ravenhall case, we use the reduced Hartree-Fock variational principle. It involves the density

$$\rho_U^B(\mathbf{x}) := \mathrm{tr}_{\mathbb{C}^2}\left(\mathcal{U}_c(d^B)(\mathbf{x},\mathbf{x})\right)$$

of the twisted density matrix $\mathcal{U}_c(d^B)$.
For further reference, we also set

$$\rho_{U,l}^B(\mathbf{x}) := \mathrm{tr}_{\mathbb{C}^2}\left(\mathcal{U}_c(d_l^B)(\mathbf{x},\mathbf{x})\right), \quad \rho_{U,<}^B(\mathbf{x}) := \sum_{l<L}\rho_{U,l}^B(\mathbf{x}),$$

$$\rho_{U,>}(\mathbf{x}) := \sum_{l\geq L}\rho_{U,l}(\mathbf{x}).$$

Applying to (1.1) the Hartree-Fock variational principle – in the strengthened version of Lieb [42] (see also Bach [2]) – and omitting the manifestly negative exchange energy we arrive at

Proposition 4.5. *For all Z and c,*

$$E_c^B(Z) \leq \mathrm{tr}[B_c[Z|\mathbf{x}|^{-1}]\, d^B] + D(\rho_U^B,\rho_U^B).$$

Combining Propositions 4.4 and 4.5 we find

$$\begin{aligned}&E_c^B(Z) - E^S(Z)\\ &\leq \mathrm{tr}[B_c[Z|\mathbf{x}|^{-1}]d^B] - \mathrm{tr}[S[Z|\mathbf{x}|^{-1}]d^S] + D(\rho_U^B-\rho^S,\rho_U^B+\rho^S) + \mathrm{const}\ Z^{47/24}.\end{aligned}$$

Now we use the inequality $\mathbf{p}^2 \geq 2c^2(E(p/c)-1)$ for the kinetic energy corresponding to $d_>$. Moreover, we write

$$\begin{aligned}D(\rho_U^B-\rho^S,\rho_U^B+\rho^S) = &D(\rho_{U,>}-\rho_>,\rho_{U,>}+\rho_>) + 2\,D(\rho_{U,<}^B,\rho_U^B+\rho^S)\\ &- D(\rho_{U,<}^B+\rho_<^S,\rho_{U,<}^B+\rho_<^S) - 2\,D(\rho_{U,<}^B+\rho_<^S,\rho_>)\end{aligned}$$

and drop the two negative terms on the right hand side. We arrive at

$$\begin{aligned}E_c^B(Z) - E^S(Z) \leq\ &\mathrm{tr}\left[B_c[\tfrac{Z}{|\mathbf{x}|}]d_<^B\right] - \mathrm{tr}\left[S[\tfrac{Z}{|\mathbf{x}|}]d_<^S\right] + \underbrace{\mathrm{tr}\left[\left(\tfrac{Z}{|\mathbf{x}|} - \mathcal{U}_c(\tfrac{Z}{|\mathbf{x}|})\right)d_>\right]}_{=:\mathcal{R}_1}\\ &+ \underbrace{D(\rho_{U,>}-\rho_>,\rho_{U,>}+\rho_>)}_{=:\mathcal{R}_2} + 2\underbrace{D(\rho_{U,<}^B,\rho_U^B+\rho^S)}_{=:\mathcal{R}_3} + \mathrm{const}\ Z^{47/24}.\end{aligned} \tag{4.14}$$

As we shall see, the first two terms will yield the Scott correction. In the following subsections we prove that $\mathcal{R}_1$, $\mathcal{R}_2$, and $\mathcal{R}_3$ are relatively small remainder terms. Hence, we wish to control the effects of the twisting operation $\mathcal{U}_c$, which stems from the electronic projection, on the electrostatic Coulomb energy.

4.2.1 Controlling the electron projection for high angular momenta

Our task in this subsection is to prove that for large angular momenta, the twisted and untwisted electrostatic energy are asymptotically equal.
We start by comparing the electric potential energy with or without electron projection for large angular momentum. This will imply that the term $\mathcal{R}_1$ in (4.14) is relatively small.

Lemma 4.6. *In the limit $Z \to \infty$ one has uniformly in $\kappa = Z/c \in (0, \kappa^B]$*

$$\int (\rho_>(\mathbf{x}) - \rho_{U,>}(\mathbf{x})) \frac{\mathrm{d}\mathbf{x}}{|\mathbf{x}|} = \mathrm{tr}\left[\left(|\mathbf{x}|^{-1} - \mathcal{U}_c(|\mathbf{x}|^{-1})\right) d_>\right] = \mathcal{O}(Z^{11/12}).$$

Proof. Let $\{\psi_\alpha\}$ stand for the Macke orbitals building up $d_>$ which we label by $\alpha = (j, l, m, n)$; see (E.1) and preceding equations in Appendix E.2. By the scaling $\mathbf{x} \mapsto \mathbf{x}/c$ one has the relation

$$\left\langle \psi_\alpha, \left[|\mathbf{x}|^{-1} - \mathcal{U}_c(|\mathbf{x}|^{-1})\right] \psi_\alpha \right\rangle = c \left\langle \psi_\alpha^{(c)}, \left[|\mathbf{x}|^{-1} - \mathcal{U}_1(|\mathbf{x}|^{-1})\right] \psi_\alpha^{(c)} \right\rangle$$

where $\psi_\alpha^{(c)}(\mathbf{x}) := c^{-3/2}\psi_\alpha(\mathbf{x}/c)$. Assuming that α corresponds to a fixed (large) (j, l) we may use Lemma 2.8 to estimate the right-hand side by a constant times

$$\frac{c}{l^2} \left\langle \psi_\alpha^{(c)}, \mathbf{p}^2 \psi_\alpha^{(c)} \right\rangle = \frac{1}{l^2\, c} \left\langle \psi_\alpha, \mathbf{p}^2 \psi_\alpha \right\rangle .$$

Using that $Z/c \le \kappa^B$ we obtain the estimate

$$\mathrm{tr}\left[\left(|\mathbf{x}|^{-1} - \mathcal{U}_c(|\mathbf{x}|^{-1})\right) d_>\right] \le \mathrm{const}\, \frac{\kappa^B}{Z} \sum_{l=L}^{\infty} \frac{1}{l^2} \sum_{j=l\pm 1/2} \mathrm{tr}_{j,l}\left[\mathbf{p}^2 d_>\right] .$$

The proof is completed using Lemma E.1 from Appendix E.3. $\square$

Next, we estimate the difference of Coulomb energies corresponding to large total angular momenta. This shows that the term $\mathcal{R}_2$ in (4.14) may be neglected.

Lemma 4.7. *In the limit $Z \to \infty$,one has uniformly in $\kappa = Z/c \in (0, \kappa^B]$*

$$\mathcal{R}_2 = D(\rho_{U,>} - \rho_>, \rho_> + \rho_{U,>}) = \mathcal{O}(Z^{5/3}).$$

Proof. We define $v := (\rho_> + \rho_{U,>}) * |\cdot|^{-1}$ to be the electric potential generated by $\rho_> + \rho_{U,>}$ which is obviously spherically symmetric and obeys

$$\begin{aligned} v(0) &= \mathrm{tr}\left[d_> \left(|\mathbf{x}|^{-1} + \mathcal{U}_c(|\mathbf{x}|^{-1})\right)\right] \\ &= 2\,\mathrm{tr}\left[d_> |\mathbf{x}|^{-1}\right] - \mathrm{tr}\left[d_> \left(|\mathbf{x}|^{-1} - \mathcal{U}_c(|\mathbf{x}|^{-1})\right)\right] . \end{aligned}$$

According to [55] (see also (E.8)) the first term on the right side is $\mathcal{O}(Z^{4/3})$. Moreover the second term is $\mathcal{O}(Z^{11/12})$ by Lemma 4.6, hence much smaller than the first term. Now,

$$D(\rho_> - \rho_{U,>}, \rho_> + \rho_{U,>}) = \tfrac{1}{2} \operatorname{tr}\left[d_> \left(v - \mathcal{U}_c(v)\right)\right]. \tag{4.15}$$

Decomposing the trace in (4.15) into the orbitals contributing to $d_>$ and scaling $\mathbf{x} \mapsto \mathbf{x}/c$ enables us to employ Lemma 2.9 to obtain the bound

$$\operatorname{tr}\left[d_> \left(v - \mathcal{U}_c(v)\right)\right] \leq \frac{\text{const}}{c^2} v(0) \operatorname{tr}\left[d_> \mathbf{p}^2\right].$$

This concludes the proof, since again from [55] (see (E.8)) we conclude that the trace on the right-hand side is $\mathcal{O}(Z^{7/3})$. ☐

4.2.2 Contribution from low angular momenta to the Coulomb energy

We now show that the term $\mathcal{R}_3$ in (4.14) is negligible.

Lemma 4.8. *In the limit $Z \to \infty$ one has uniformly in $\kappa = Z/c \in (0, \kappa^B]$*

$$\mathcal{R}_3 = D(\rho^B_{U,<}, \rho^B_U + \rho^S) = \mathcal{O}(Z^{11/6} \log Z).$$

Proof. We first treat the term $D(\rho^B_{U,<}, \rho_{U,>} + \rho_>)$. By construction the densities $\rho^B_{U,j}$ are spherically symmetric and satisfy according to (4.13)

$$\int \rho^B_{U,l}(\mathbf{x})\, \mathrm{d}\mathbf{x} = \int \rho^B_l(\mathbf{x})\, \mathrm{d}\mathbf{x} = 2(2l+1)(K-l), \quad 0 \leq l < L. \tag{4.16}$$

Recalling the choice of K and L we see that

$$\int \rho^B_{U,<}(\mathbf{x})\, \mathrm{d}\mathbf{x} = \mathcal{O}(Z^{1/2}). \tag{4.17}$$

It follows from (E.8) and Lemma 4.6 that

$$\int \frac{\rho_{U,>}(\mathbf{x}) + \rho_>(\mathbf{x})}{|\mathbf{x}|} \mathrm{d}\mathbf{x} = \mathcal{O}(Z^{4/3}).$$

Hence Newton's theorem [49] yields

$$D(\rho^B_{U,<}, \rho_{U,>} + \rho_>) \leq \frac{1}{2} \int \rho^B_{U,<}(\mathbf{x}) \mathrm{d}\mathbf{x} \int \frac{\rho_{U,>}(\mathbf{y}) + \rho_>(\mathbf{y})}{|\mathbf{y}|} \mathrm{d}\mathbf{y} = \mathcal{O}(Z^{11/6}).$$

In the remainder of the proof we are concerned with the term $D(\rho^B_{U,<}, \rho^B_{U,<} + \rho^S_<)$. Noting that

$$D(\rho^B_{U,<}, \rho^B_{U,<} + \rho^S_<) \leq \frac{3}{2} D(\rho^B_{U,<}, \rho^B_{U,<}) + \frac{1}{2} D(\rho^S_<, \rho^S_<).$$

and that according to [55, Prop. 3.5] $D(\rho^S_<, \rho^S_<) = \mathcal{O}(Z^{11/6})$, it suffices to consider $D(\rho^B_{U,<}, \rho^B_{U,<})$. We split the lowest angular momentum corresponding to $l \leq 2Z/c - 1/4 =: l_0$ off and define

$$d^B_\vdash := \sum_{l \leq l_0} d^B_l, \qquad d^B_\dashv := \sum_{l > l_0}^{L-1} d^B_l,$$

and

$$\rho^B_{U,\vdash} := \mathrm{tr}_{\mathbb{C}^2} \left(\mathcal{U}_c(d^B_\vdash)(\mathbf{x},\mathbf{x})\right), \qquad \rho^B_{U,\dashv} := \mathrm{tr}_{\mathbb{C}^2} \left(\mathcal{U}_c(d^B_\dashv)(\mathbf{x},\mathbf{x})\right).$$

Note that in case $l_0 < 0$ there is no need for this procedure. Accordingly, we estimate

$$D(\rho^B_{U,<}, \rho^B_{U,<}) \leq 2\, D(\rho^B_{U,\vdash}, \rho^B_{U,\vdash}) + 2\, D(\rho^B_{U,\dashv}, \rho^B_{U,\dashv}).$$

For an estimate of the second part corresponding to $l_0 < l < L$, we apply the following angular momentum barrier inequality

$$B_c[0] \geq \mathcal{U}_c\left(\frac{2Z}{|\mathbf{x}|}\,\chi_{\{|\mathbf{x}|\leq r_l\}}\right) \tag{4.18}$$

on $\mathfrak{H}_{j,l}$, where $r_l = \left((l+1/2)^2c^2 - 4Z^2\right)/(4Zc^2)$ and $l > 2Z/c$. This bound follows by applying $\mathcal{U}_1$ to the inequality in [31, Lemma 2.6] with $R_l = [(l+1/2)^2 - 4\kappa^2]/(4\kappa)$ and scaling $\mathbf{x} \mapsto \mathbf{x}/c$.
Inequality (4.18) implies

$$\begin{aligned}\mathrm{tr}\left[\mathcal{U}_c\left(|\mathbf{x}|^{-1}\right) d^B_l\right] &\leq \frac{1}{2Z}\,\mathrm{tr}\left[B_c[0]\, d^B_l\right] + \mathrm{tr}\left[\mathcal{U}_c\left(|\mathbf{x}|^{-1}\chi_{\{|\mathbf{x}|>r_l\}}\right) d^B_l\right]\\ &\leq \frac{1}{2}\,\mathrm{tr}\left[\mathcal{U}_c\left(|\mathbf{x}|^{-1}\right) d^B_l\right] + \frac{4Z}{(l+1/2)^2 - 4Z^2/c^2}\ \mathrm{tr}[d^B_l].\end{aligned}$$

Here the last inequality used the fact that eigenfunctions of d^B_l are eigenfunctions of $B_c[Z|\mathbf{x}|^{-1}]$ with negative eigenvalue. Now, note that

$$(l+1/2)^2 - 4Z^2/c^2 = (l+1/2+2Z/c)(l+1/2-2Z/c) \geq \mathrm{const}\ (l+1/2)^2$$

for $l \geq l_0$. Hence, using (4.16) and summing over l we obtain

$$\begin{aligned}\int \frac{\rho^B_{U,\dashv}(x)}{|\mathbf{x}|}\mathrm{d}\mathbf{x} &= \sum_{l>l_0}^{L-1} \mathrm{tr}\left[\mathcal{U}_c(|\mathbf{x}|^{-1})d^B_l\right]\\ &\leq \mathrm{const}\ Z\sum_{l=0}^{L-1}(l+1/2)^{-2}\int \rho^B_l(\mathbf{x})\,\mathrm{d}\mathbf{x} = \mathcal{O}(Z^{4/3}\log Z).\end{aligned}$$

Accordingly, Newton's theorem and (4.17) yield

$$D(\rho^B_{U,\dashv}, \rho^B_{U,\dashv}) \leq \frac{1}{2}\int \rho^B_{U,\dashv}(\mathbf{x})\,\mathrm{d}\mathbf{x}\int \frac{\rho^B_{U,\dashv}(\mathbf{x})}{|\mathbf{x}|}\,\mathrm{d}\mathbf{x} = \mathcal{O}(Z^{11/6}\log Z).$$

Finally, we consider the contribution from $l \leq l_0$. Note that then $l \leq 2\kappa^B - 1/4 < 2$. We claim that the electrostatic energy corresponding to the electrons in this subspace is bounded by

$$D\big(\rho^B_{U,\vdash}, \rho^B_{U,\vdash}\big) \leq \text{const}\ cK^2. \tag{4.19}$$

Since by the choice of l_0 one has $2Z/c \geq l + 1/4 \geq 1/4$, estimate (4.19) will imply that $D\big(\rho^B_{U,\vdash}, \rho^B_{U,\vdash}\big) \leq \text{const}\ ZK^2 = \mathcal{O}(Z^{5/3})$ and hence complete the proof of Lemma 4.8. By scaling it suffices to prove (4.19) for $c = 1$, which we will assume in the sequel. The Hardy-Littlewood-Sobolev inequality (see, e.g., [43, Thm. 4.3]) implies that

$$D\big(\rho^B_{U,\vdash}, \rho^B_{U,\vdash}\big) \leq \text{const}\ \big\|\rho^B_{U,\vdash}\big\|^2_{6/5}. \tag{4.20}$$

The triangle inequality together with the definition of $\mathcal{U}$ and (B.2) yields

$$\|\rho_{U,\vdash}\|_{6/5} \leq \sum_{\alpha\in\mathcal{A}} \sum_{\nu=0,1} \|\Phi_\nu \psi_\alpha\|^2_{12/5}, \tag{4.21}$$

where $\{\psi_\alpha | \alpha \in \mathcal{A}\}$ stands for the collection of normalized eigenfunctions building up $d^B_\vdash$, i.e., the corresponding sum ranges over all indices (j, l, m, n). We further estimate with the help of Lemma B.1 and Theorem 2.4,

$$\|\Phi_\nu \psi_\alpha\|^2_{12/5} \leq \text{const}\ \|\psi_\alpha\|^2_{12/5} \leq \text{const}\ .$$

This, together with (4.20), (4.21) and the fact that the number of indices in $\mathcal{A}$ is bounded by a constant times K proves (4.19). $\square$

4.2.3 Finishing the proof

We repeat (4.14),

$$E^S(Z) - E^B_c(Z) \geq \operatorname{tr}[S[\tfrac{Z}{|\mathbf{x}|}]d^S_<] - \operatorname{tr}[B_c[\tfrac{Z}{|\mathbf{x}|}]d^B_<] - \mathcal{R}_1 - \mathcal{R}_2 - \mathcal{R}_3 - \text{const}\ Z^{\frac{47}{24}}.$$

By Lemmata 4.6, 4.7, and 4.8 we have uniformly in $\kappa = Z/c \in (0, \kappa^B]$

$$\mathcal{R}_1 = \mathcal{O}(Z^{23/12}), \quad \mathcal{R}_2 = \mathcal{O}(Z^{5/3}), \quad \mathcal{R}_3 = \mathcal{O}(Z^{11/6}\log Z),$$

so these terms are of lower order than $Z^{47/24}$. Next, we scale $\mathbf{x} \mapsto \mathbf{x}/c$ and obtain

$$\operatorname{tr}[S[Z|\mathbf{x}|^{-1}]d^S_<] - \operatorname{tr}[B_c[Z|\mathbf{x}|^{-1}]d^B_<] = Z^2 s(\kappa) - \mathcal{R}_4$$

where $s(\kappa)$ is introduced in (1.8) and

$$\mathcal{R}_4 := Z^2\kappa^{-2} \sum_{l=0}^{L-1} (2l+1) \sum_{j=l\pm 1/2} \sum_{n=K-l+1}^{\infty} \left(\lambda_n(s_l(\kappa)) - \lambda_n(b_{j,l}(\kappa))\right).$$

By Theorem 2.1 there is a constant such that for all $0 < \kappa \leq \kappa^B$

$$\begin{aligned} 0 \leq \mathcal{R}_4 &\leq Z^2 \kappa^{-2} \sum_{l=0}^{L-1} (2l+1) \sum_{j=l\pm 1/2} \sum_{n=K-l+1}^{\infty} |\lambda_n(b_{j,l}(\kappa)| \\ &\leq \text{const } Z^2 \sum_{l=0}^{L-1} (2l+1) \sum_{n=K-l+1}^{\infty} (n+l)^{-2} \\ &\leq \text{const } Z^2 L^2 K^{-1} = \mathcal{O}(Z^{11/6}). \end{aligned}$$

This concludes the proof of the lower bound and hence of our main result. □

Acknowledgments. We thank Elliott Lieb and Robert Seiringer for supportive discussions. H.S. thanks the Departments of Mathematics and Physics of Princeton University and R.F. and S.W. thank the Department of Mathematics of LMU Munich for hospitality while parts of this work were done. We also thank Volker Bach for stimulating questions resulting in several improvements. The work has been partially supported by the Deutscher Akademischer Austauschdienst, grant D/06/49117 (R.F.), the U.S. National Science Foundation, grant PHY 01 39984 (H.S.), the Deutsche Forschungsgemeinschaft, grant SI 348/13-1 (H.S.), and a Sloan Fellowship (S.W.).

Note added in proof. After this paper has been submitted, one of us (R. F.) found an easier proof of a stronger inequality than (2.19). This proof is based on an inequality from [65] as well as Lemma 2.6 in the present paper; see [29].

A Partial wave analysis

For the convenience of the reader and for normalization of the notation we gather some fact on the partial wave analysis of the Brown-Ravenhall operator. We denote by $Y_{l,m}$ the normalized spherical harmonics on the unit sphere $\mathbb{S}^2$ (see, e.g., [48], p. 421) with the convention that $Y_{l,m} \equiv 0$ if $|m| > l$, and we define for $j \in \mathbb{N}_0 + \frac{1}{2}$, $l \in \mathbb{N}_0$, and $m = -j, \ldots, j$ the spherical spinors

$$\Omega_{j,l,m}(\omega) := \begin{cases} \begin{pmatrix} \sqrt{\frac{j+m}{2j}}\, Y_{l,m-\frac{1}{2}}(\omega) \\ \sqrt{\frac{j-m}{2j}}\, Y_{l,m+\frac{1}{2}}(\omega) \end{pmatrix} & \text{if } j = l + \frac{1}{2}, \\ \begin{pmatrix} -\sqrt{\frac{j-m+1}{2j+2}}\, Y_{l,m-\frac{1}{2}}(\omega) \\ \sqrt{\frac{j+m+1}{2j+2}}\, Y_{l,m+\frac{1}{2}}(\omega) \end{pmatrix} & \text{if } j = l - \frac{1}{2}. \end{cases} \tag{A.1}$$

The set of admissible indices is $\mathcal{I} := \{(j,l,m) : j \in \mathbb{N} - 1/2,\ l = j \pm 1/2,\ m = -j, ..., j\}$. It is known that the functions $\Omega_{j,l,m}$, $(j,l,m) \in \mathcal{I}$, form an orthonormal basis of the Hilbert space $L^2(\mathbb{S}^2; \mathbb{C}^2)$. They are joint eigenfunctions of $\mathbf{J}^2$,

J_3, and $\mathbf{L}^2$ with eigenvalues given by $j(j+1)$, $l(l+1)$, and m. The subspace $\mathfrak{H}_{j,l,m}$ corresponding to the joint eigenspace of total angular momentum $\mathbf{J}^2$ with eigenvalue $j(j+1)$ and angular momentum $\mathbf{L}^2$ with eigenvalue $l(l+1)$ is then given by

$$\mathfrak{H}_{j,l,m} = \mathrm{span}\{\mathbf{x} \mapsto |\mathbf{x}|^{-1} f(|\mathbf{x}|)\,\Omega_{j,l,m}(\omega_{\mathbf{x}}) \mid f \in L^2(\mathbb{R}_+)\}$$

where $\omega_{\mathbf{x}} := \mathbf{x}/|\mathbf{x}|$. This leads to the orthogonal decomposition

$$\mathfrak{H} = \bigoplus_{j\in\mathbb{N}_0+\frac{1}{2}} \bigoplus_{l=j\pm 1/2} \mathfrak{H}_{j,l}, \qquad \mathfrak{H}_{j,l} = \bigoplus_{m=-j}^{j} \mathfrak{H}_{j,l,m}, \tag{A.2}$$

of the Hilbert space of two spinors.
We note that the Fourier transform,

$$\hat\psi(\mathbf{p}) := (2\pi)^{-3/2} \int_{\mathbb{R}^3} e^{-i\mathbf{p}\cdot\mathbf{x}} \psi(\mathbf{x})\,\mathrm{d}\mathbf{x}, \tag{A.3}$$

leaves the spaces $\mathfrak{H}_{j,l}$ invariant. Namely, if we decompose ψ according to (A.2),

$$\psi(\mathbf{x}) = \sum_{(j,l,m)\in\mathcal{I}} r^{-1}\psi_{j,m,l}(r)\,\Omega_{j,l,m}(\omega_{\mathbf{x}}),$$

then

$$\hat\psi(\mathbf{p}) = \sum_{(j,l,m)\in\mathcal{I}} p^{-1}\left(\mathcal{F}_l\psi_{j,m,l}\right)(p)\,\Omega_{j,l,m}(\omega_{\mathbf{p}}) \tag{A.4}$$

with the Fourier-Bessel transform

$$(\mathcal{F}_l f)(p) = i^{-l}\sqrt{\frac{2}{\pi}} \int_0^\infty f(r) j_l(rp) rp\,\mathrm{d}r. \tag{A.5}$$

Here j_l is a spherical Bessel function. Moreover,

$$\|\psi\|^2 = \sum_{(j,l,m)\in\mathcal{I}} \int_0^\infty |\psi_{j,m,l}(r)|^2 \mathrm{d}r = \sum_{(j,l,m)\in\mathcal{I}} \int_0^\infty |(\mathcal{F}_l\psi_{j,m,l})(p)|^2 \mathrm{d}p = \|\hat\psi\|^2.$$

B Properties of the twisting operators

We define the helicity operator $\mathrm{H} = \omega_{\mathbf{p}} \cdot \boldsymbol{\sigma}$ on $\mathfrak{H}$ by

$$\widehat{\mathrm{H}\psi}(\mathbf{p}) := \boldsymbol{\sigma}\cdot\boldsymbol{\omega}_{\mathbf{p}}\hat\psi(\mathbf{p}). \tag{B.1}$$

It follows from the pointwise identity

$$(\omega_{\mathbf{p}}\cdot\boldsymbol{\sigma})\Omega_{j,l,m}(\omega_{\mathbf{p}}) = -\Omega_{j,2j-l,m}(\omega_{\mathbf{p}}), \tag{B.2}$$

see, e.g., Greiner [33, p. 171, (12)], that H is an isomorphism between $\mathfrak{H}_{j,l}$ and $\mathfrak{H}_{j,2j-l}$. Moreover, since $(\boldsymbol{\sigma}\cdot\boldsymbol{a})\,(\boldsymbol{\sigma}\cdot\boldsymbol{b}) = \boldsymbol{a}\cdot\boldsymbol{b} + i\boldsymbol{\sigma}\cdot(\boldsymbol{a}\times\boldsymbol{b})$ for any $\boldsymbol{a},\boldsymbol{b}\in\mathbb{R}^3$, we infer that H is an involution on $\mathfrak{H}$, i.e., $\mathrm{H}=\mathrm{H}^{-1}$.
We shall need to consider H on L^p spaces with $p\neq 2$. The relevant properties are summarized in the next lemma, together with those of the operators

$$\widehat{\Phi_\nu\psi}(\mathbf{p}) := \Phi_\nu(\mathbf{p})\,\hat\psi(\mathbf{p}), \tag{B.3}$$

introduced in (1.4). Note that while Φ_0 acts trivially on the spin, Φ_1 involves the helicity H.

Lemma B.1 (L^p-properties of H and Φ_ν). *The operators* H *and* Φ_ν, $\nu = 0,1$, *extend to bounded operators from* $L^p(\mathbb{R}^3,\mathbb{C}^2)$ *to* $L^p(\mathbb{R}^3,\mathbb{C}^2)$ *for any* $p\in(1,\infty)$.

Proof. The L^p-boundedness of H follows from that of the Riesz transformation, see [68, Ch. II-III]. Therefore, to prove the statement about the operators Φ_ν, it suffices to consider the operators ϕ_ν defined analogously as in (B.3) on $L^2(\mathbb{R}^3)$. Since $\mathbf{p}\mapsto\phi_\nu(p)$ is smooth away from the origin and $p^k\partial^k\phi_\nu$ is bounded for $k=0,1,2$, the Hörmander-Mihlin multiplier theorem [68, Thm. IV.3] implies that ϕ_ν extend to bounded operators from $L^p(\mathbb{R}^3)$ to $L^p(\mathbb{R}^3)$ for any $p\in(1,\infty)$. ∎

Lemma B.2. *For all* $\mathbf{p},\mathbf{q}\in\mathbb{R}^3$

$$\begin{aligned}1 &- \Phi_0(\mathbf{p})\Phi_0(\mathbf{q}) - \Phi_1(\mathbf{p})\Phi_1(\mathbf{q})\\ &= \frac12\sum_{\nu=0}^{1}(\Phi_\nu(\mathbf{p})-\Phi_\nu(\mathbf{q}))^2 + \frac12\left(\Phi_1(\mathbf{q})\Phi_1(\mathbf{p}) - \Phi_1(\mathbf{p})\Phi_1(\mathbf{q})\right).\end{aligned} \tag{B.4}$$

and furthermore

$$\begin{aligned}|\Phi_0(\mathbf{p})-\Phi_0(\mathbf{q})|^2 &\le \frac{|\mathbf{p}-\mathbf{q}|^2}{8E(\mathbf{p})^2E(\mathbf{q})^2}\\ |\Phi_1(\mathbf{p})-\Phi_1(\mathbf{q})|^2 &\le \frac{|\mathbf{p}-\mathbf{q}|^2}{E(\mathbf{p})E(\mathbf{q})}\\ |\Phi_1(\mathbf{q})\Phi_1(\mathbf{p})-\Phi_1(\mathbf{p})\Phi_1(\mathbf{q})| &\le \frac{\sqrt{|\mathbf{p}||\mathbf{q}|}\,|\mathbf{p}-\mathbf{q}|}{E(\mathbf{p})E(\mathbf{q})}\end{aligned}$$

Proof. The first equality is an immediate consequence of the definition of Φ_0 and Φ_1. From this definition we also conclude by an explicit calculation that

$$|\Phi_0(\mathbf{p})-\Phi_0(\mathbf{q})|^2 = (\phi_0(\mathbf{p})-\phi_0(\mathbf{q}))^2 \le \frac{|\mathbf{p}-\mathbf{q}|^2}{8E(\mathbf{p})^2E(\mathbf{q})^2}. \tag{B.5}$$

Moreover, for a proof of the next inequality we write

$$|\Phi_1(\mathbf{p})-\Phi_1(\mathbf{q})|^2 = (\phi_1(\mathbf{p})-\phi_1(\mathbf{q}))^2 + \phi_1(\mathbf{p})\phi_1(\mathbf{q})|\omega_{\mathbf{p}}-\omega_{\mathbf{q}}|^2,$$

and estimate the last two terms with the help of the inequalities

$$(\phi_1(\mathbf{p}) - \phi_1(\mathbf{q}))^2 \leq \frac{(|\mathbf{p}| - |\mathbf{q}|)^2}{2E(\mathbf{p})^2 E(\mathbf{q})^2} \leq \frac{|\mathbf{p} - \mathbf{q}|^2}{2E(\mathbf{p})^2 E(\mathbf{q})^2}, \tag{B.6}$$

and

$$\phi_1(\mathbf{p}) \leq \frac{1}{\sqrt{2}} \frac{|\mathbf{p}|}{E(\mathbf{p})} \quad \text{and} \quad |\omega_{\mathbf{p}} - \omega_{\mathbf{q}}|^2 \leq \frac{|\mathbf{p} - \mathbf{q}|^2}{|\mathbf{p}||\mathbf{q}|}. \tag{B.7}$$

Finally, for a proof of the last inequality we use

$$\begin{aligned} |\Phi_1(\mathbf{q})\Phi_1(\mathbf{p}) - \Phi_1(\mathbf{p})\Phi_1(\mathbf{q})| &= 2\phi_1(\mathbf{p})\phi_1(\mathbf{q})\, |\boldsymbol{\sigma} \cdot (\omega_{\mathbf{p}} \times \omega_{\mathbf{q}})| \\ &\leq 2\phi_1(\mathbf{p})\phi_1(\mathbf{q}) |\omega_{\mathbf{p}} - \omega_{\mathbf{q}}|. \end{aligned}$$

Using again (B.7) concludes the proof of the third inequality. □

C Basics of relativistic hydrogenic operators

In this section we collect – following [17] – some basic properties of the operators B_κ and C_κ which describe hydrogenic atoms in the Brown-Ravenhall respectively Chandrasekhar model. For pedagogical reasons we first discuss their massless analogues,

$$B_\kappa^{(0)} := |\mathbf{p}| - \frac{\kappa}{2} \left(|\mathbf{x}|^{-1} + \omega_{\mathbf{p}} \cdot \boldsymbol{\sigma}\, |\mathbf{x}|^{-1}\, \omega_{\mathbf{p}} \cdot \boldsymbol{\sigma} \right), \quad C_\kappa^{(0)} := |\mathbf{p}| - \kappa |\mathbf{x}|^{-1}. \tag{C.1}$$

C.1 Massless case

Expanding $\hat{\psi}$ as in (A.4) and using (B.2) yields [17] the following partial diagonalization of the massless operators,

$$\langle \psi, B_\kappa^{(0)} \psi \rangle = \sum_{(l,m,s) \in \mathcal{I}} \langle \mathcal{F}_l \psi_{j,m,l}, b_j^{(0)}(\kappa)\, \mathcal{F}_l \psi_{j,m,l} \rangle, \tag{C.2}$$

$$\langle \psi, C_\kappa^{(0)} \psi \rangle = \sum_{(l,m,s) \in \mathcal{I}} \langle \mathcal{F}_l \psi_{j,m,l}, c_l^{(0)}(\kappa)\, \mathcal{F}_l \psi_{j,m,l} \rangle. \tag{C.3}$$

Here the operators $b_j^{(0)}(\kappa)$ and $c_l^{(0)}(\kappa)$ are densely defined in $L^2(\mathbb{R}_+)$ through their quadratic forms,

$$\begin{aligned} \langle f, b_j^{(0)}(\kappa) f \rangle &:= \int_0^\infty p\, |f(p)|^2 \mathrm{d}p - \kappa \int_0^\infty \int_0^\infty \overline{f(p)}\, k_j^B(p,q)\, f(q)\, \mathrm{d}q\, \mathrm{d}p, \\ \langle f, c_l^{(0)}(\kappa) f \rangle &:= \int_0^\infty p\, |f(p)|^2 \mathrm{d}p - \kappa \int_0^\infty \int_0^\infty \overline{f(p)}\, k_l^C(p,q)\, f(q)\, \mathrm{d}q\, \mathrm{d}p, \end{aligned}$$

with maximal form domain denoted by $\mathfrak{Q}(b_j^{(0)}(\kappa))$ and $\mathfrak{Q}(c_l^{(0)}(\kappa))$. In the above expression, the integral kernels k_j^B and k_l^C are given by

$$k_j^B(p,q) := \frac{1}{2\pi} \left[Q_{j-1/2} \left(\tfrac{1}{2} \left(\tfrac{p}{q} + \tfrac{q}{p} \right) \right) + Q_{j+1/2} \left(\tfrac{1}{2} \left(\tfrac{p}{q} + \tfrac{q}{p} \right) \right) \right], \tag{C.4}$$

$$k_l^C(p,q) := \frac{1}{\pi} Q_l \left(\tfrac{1}{2} \left(\tfrac{p}{q} + \tfrac{q}{p} \right) \right), \tag{C.5}$$

where Q_l are the Legendre functions of the second kind, i.e.,

$$Q_l(z) = \tfrac{1}{2}\int_{-1}^{1} P_l(t)(z-t)^{-1}\mathrm{d}t \tag{C.6}$$

with P_l standing for Legendre polynomials; see Stegun [67] for the notation and some properties of these special functions.
It was proved in [17] and [40, Eq. (5.33)] that the operators (C.1) are self-adjoint and lower bounded if and only if $\kappa \leq \kappa^{\#}$, $\# = B, C$, cf. (2.3). More can be said about the reduced operators $b_j^{(0)}(\kappa)$ and $c_l^{(0)}(\kappa)$. They are lower bounded (in fact, non-negative) if and only if

$$\frac{1}{\kappa} \geq \frac{1}{\kappa_j^B} := \int_0^\infty k_j^B(1,t)\,\frac{\mathrm{d}t}{t}, \tag{C.7}$$

$$\frac{1}{\kappa} \geq \frac{1}{\kappa_l^C} := \int_0^\infty k_l^C(1,t)\,\frac{\mathrm{d}t}{t}. \tag{C.8}$$

This follows by the same lines of reasoning as in [17].
Since [67, (8.4)] $P_0(t) = 1$, $P_1(t) = t$, we have

$$Q_0(t) = \frac{1}{2}\log\frac{t+1}{t-1}, \quad Q_1(t) = \frac{t}{2}\log\frac{t+1}{t-1} - 1, \tag{C.9}$$

such that $\kappa_0^C = 2/\pi$, $\kappa_1^C = \pi/2$ and thus $\kappa_{1/2}^B = 2/(2/\pi + \pi/2)$.
The critical coupling constants κ_j^B and κ_l^C are strictly increasing in j and l and, in particular, $\kappa_{1/2}^B = \kappa^B$ and $\kappa_0^C = \kappa^C$. This follows from the pointwise monotonicity

$$Q_l(t) \geq Q_{l'}(t) \qquad \text{for } l' \geq l \text{ and } t > 1 \tag{C.10}$$

which, in turn, is evident from the integral representation

$$Q_l(x) = \int_{x+\sqrt{x^2-1}}^\infty \frac{z^{-l-1}}{\sqrt{1-2xz+z^2}}\mathrm{d}z, \qquad x > 1;$$

see Whittaker and Watson [77, p. 334, Chap. X, Sec. 3.2].

C.2 Massive case

Similarly as in the previous subsection, one obtains the following partial diagonalization of the massive hydrogenic Brown-Ravenhall and Chandrasekhar operators,

$$\langle \psi, B_\kappa\,\psi\rangle = \sum_{(l,m,s)\in\mathcal{I}} \langle \mathcal{F}_l\psi_{j,m,l}, b_{j,l}(\kappa)\,\mathcal{F}_l\psi_{j,m,l}\rangle, \tag{C.11}$$

$$\langle \psi, C_\kappa\psi\rangle = \sum_{(j,l,m)\in\mathcal{I}} \langle \mathcal{F}_l\psi_{j,m,l}, c_l(\kappa)\,\mathcal{F}_l\psi_{j,m,l}\rangle. \tag{C.12}$$

Here the operators $b_{j,l}(\kappa)$ and $c_l(\kappa)$ are densely defined in $L^2(\mathbb{R}_+)$ through their quadratic forms,

$$\begin{aligned}&\langle f, b_{j,l}(\kappa) f\rangle \\ &:= \int_0^\infty (E(p)-1)|f(p)|^2 \mathrm{d}p - \kappa \int_0^\infty \int_0^\infty \overline{f(p)}\, k^B_{j,l}(p,q)\, f(q)\,\mathrm{d}q\,\mathrm{d}p, \qquad \text{(C.13)}\\ &\langle f, c_l(\kappa) f\rangle \\ &:= \int_0^\infty (E(p)-1)|f(p)|^2 \mathrm{d}p - \kappa \int_0^\infty \int_0^\infty \overline{f(p)}\, k^C_{l}(p,q)\, f(q)\,\mathrm{d}q\,\mathrm{d}p \qquad \text{(C.14)}\end{aligned}$$

with maximal form domain denoted by $\mathfrak{Q}(b_{j,l}(\kappa))$ and $\mathfrak{Q}(c_l(\kappa))$, cf. [17]. In the above expression, the integral kernel $k^B_{j,l}$ depends, in contrast to the massless case, on both j and l and is given by

$$\begin{aligned}&k^B_{j,l}(p,q)\\ &\quad := \frac{1}{\pi}\left[\phi_0(p) Q_l\left(\tfrac{1}{2}\left(\tfrac{p}{q}+\tfrac{q}{p}\right)\right)\phi_0(q) + \phi_1(p) Q_{2j-l}\left(\tfrac{1}{2}\left(\tfrac{p}{q}+\tfrac{q}{p}\right)\right)\phi_1(q)\right].\end{aligned}$$

The form (C.13) defines a self-adjoint semi-bounded operator $b_{j,l}(\kappa)$ if and only if $\kappa \le \kappa^B_j$ (Evans et al. [17]). A trivially modified argument shows that (C.14) defines a self-adjoint semi-bounded operator $c_l(\kappa)$ if and only if $\kappa \le \kappa^C_l$. In fact, the semiboundedness of the massive cases and the massless cases are equivalent, since the differences of the massive and massless forms are bounded (Tix [75, Thm. 1]). (One even knows that $b_{j,l}(\kappa)+1$ is non-negative (Tix [76]).)

D Critical Chandrasekhar operator on a finite domain

Lieb and Yau [46] have shown that the critical Chandrasekhar operator $|\mathbf{p}| - \kappa^C|\mathbf{x}|^{-1}$ when restricted to a ball has only discrete spectrum with eigenvalues accumulating at infinity at the rate predicted by the semiclassical result for $|\mathbf{p}|$ alone. This is remarkable since the semiclassical phase-space volume corresponding to $|\mathbf{p}| - \kappa|\mathbf{x}|^{-1}$ is infinite.

We aim at proving an analogous result for the Chandrasekhar operator restricted to a ball and restricted to the subspace of fixed angular momentum. In the proof of Theorem 2.1 it is essential to handle coupling constants which are larger than κ^C, all the way up to and including κ^C_1.

In order to define the above operator we consider for $R > 0$ and $l \in \mathbb{N}$ the Hilbert space

$$\mathfrak{F}_l(R) := \left\{ f \in L^2(0,\infty) \,\middle|\, \left(\mathcal{F}_l^{-1} f\right)(r) = 0 \text{ for all } r \ge R \right\},$$

where $\mathcal{F}_l$ denotes the Fourier-Bessel transformation, cf. (A.5). The quadratic form given by $\langle f, c^{(0)}_l(\kappa) f\rangle$ with domain $\mathfrak{F}_l(R) \cap \mathfrak{Q}(c^{(0)}_l(\kappa))$ defines for all $\kappa \le \kappa^C_l$ a self-adjoint, non-negative operator in $\mathfrak{F}_l(R)$ which we will denote by $c^{(0)}_l(\kappa, R)$.

Lemma D.1. *Let $l \in \mathbb{N}$. There is a constant such that for all $R > 0$, $\mu > 0$, and $\kappa \leq \kappa_l^C$*

$$\operatorname{tr}\left(c_l^{(0)}(\kappa, R) - \mu\right)_- \leq \text{const } \mu^2 R. \tag{D.1}$$

We have not tried to track the l-dependence of the constant, since the cases $l = 0, 1$ will be enough for our purpose.

Proof. For a proof of (D.1) we basically follow the argument in [46]. The starting point is the following reduction to a simpler variational problem involving only functions. Namely, for any non-negative function $h : \mathbb{R}_+ \to \mathbb{R}_+$, let

$$t(p) := \frac{\kappa_l^C}{\pi h(p)} \int_0^\infty Q_l\big(\tfrac{1}{2}(\tfrac{p}{q} + \tfrac{q}{p})\big) h(q)\, \mathrm{d}q\,.$$

Then

$$-\operatorname{tr}\left(c_l(\kappa_l^C, R) - \mu\right)_- \geq \inf\left\{\int_0^\infty \sigma(p)\,(p - \mu - t(p))\,\mathrm{d}p \,\middle|\, 0 \leq \sigma \leq M_l\right\} \tag{D.2}$$

where $M_l := R \sup_{r>0}(2/\pi) r^2 j_l^2(r)$. The proof of (D.2) is analogous to the one of [46, Eq. (7.8)]. We merely replace the Fourier transformation in $\mathbb{R}^3$ by the Fourier-Bessel transformation $\mathcal{F}_l$ in $\mathbb{R}_+$.

From now on we assume that $l \geq 1$ and comment on the necessary changes in case $l = 0$ at the end. We choose h of the form

$$h(p) = \begin{cases} p^{-1} - (A/2)p^{-2} & \text{if } p > A, \\ (2A)^{-1} & \text{if } p \leq A. \end{cases}$$

Below we shall show that the constant A can be picked in such a way that for some $\delta > 0$

$$p - \mu - t(p) \geq \begin{cases} 0 & \text{if } p \geq \delta^{-1}A, \\ -\text{const } A^{-1}\mu^2 & \text{if } p < \delta^{-1}A. \end{cases} \tag{D.3}$$

In view of (D.2) this will prove the result, since then

$$\begin{aligned} &\inf\left\{\int_0^\infty \sigma(p)\,(p - \mu - t(p))\,\mathrm{d}p \,\middle|\, 0 \leq \sigma \leq M_l\right\} \\ &\geq -\text{ const } A^{-1}\mu^2 M_l \int_0^{\delta^{-1}A} \mathrm{d}p = -\text{const } \delta^{-1}\mu^2 M_l. \end{aligned}$$

To prove (D.3) we recall that $\int_0^\infty Q_l\big(\frac{1}{2}(t + \frac{1}{t})\big)\,\frac{dt}{t} = \pi(\kappa_l^C)^{-1}$, cf. (C.8), and hence by a straightforward calculation

$$\begin{aligned} p - t(p) &= p\,\frac{\kappa_l^C}{\pi} \int_0^\infty Q_l\big(\tfrac{1}{2}(t + \tfrac{1}{t})\big)\left(\tfrac{1}{t} - \tfrac{h(tp)}{h(p)}\right)\mathrm{d}t \\ &= p\,\frac{\kappa_l^C}{\pi} \begin{cases} \frac{A/2p}{1 - A/2p}\,(F(1) - F(A/p)) & \text{if } p \geq A, \\ (-F(1) + F(p/A)) & \text{if } p < A. \end{cases} \end{aligned}$$

Here for $0 < s \leq 1$ we have set

$$F(s) := \int_0^s Q_l\big(\tfrac{1}{2}(t + \tfrac{1}{t})\big)\,\big(\tfrac{1}{t} - \tfrac{1}{s}\big)^2\,\mathrm{d}t\,.$$

Since $Q_l(\tau) \leq Q_1(\tau)$, which vanishes like a constant times τ^{-2} as $\tau \to \infty$, one has $F(s) \to 0$ as $s \to 0$. Choosing $\delta \in (0,1)$ such that $F(s) \leq \frac{1}{2}F(1)$ for all $0 < s \leq \delta$, we have shown that for all $p \geq \delta^{-1}A$ one has

$$p - t(p) \geq \frac{A\;F(1)}{8(1 - A/2p)} \geq A\;\frac{F(1)}{8}\,.$$

For $A \leq p < \delta^{-1}A$ we use the monotonicity, $dF/ds \geq 0$, to bound

$$p - t(p) \geq 0.$$

Finally, for $0 \leq p < A$ we drop the term $F(p/A) \geq 0$ to obtain

$$p - t(p) \geq -\frac{p}{2}F(1) \geq -A\frac{F(1)}{2}.$$

Choosing $A := 8\mu/F(1)$ yields the claimed inequality (D.3).
In case $l = 0$, the function h can be chosen as before. However, the corresponding expressions $F(1) - F(s)$ should be interpreted as a single integral, and estimated with slightly more care. □

Corollary D.2. *Let $l \in \mathbb{N}$. Then there is a constant such that for all $0 < \kappa \leq \kappa_l^C$, all $\mu > 0$ and all functions χ on $\mathbb{R}_+$ with $\chi = 0$ on $[R,\infty)$ for some $R > 0$ one has*

$$N_l(0, \chi\left(|\mathbf{p}| - \kappa|\mathbf{x}|^{-1} - \mu\right)\chi) \leq \mathrm{const}\;\mu R.$$

Proof. The variational principle implies that

$$N_l(0, \chi\left(|\mathbf{p}| - \kappa|\mathbf{x}|^{-1} - \mu\right)\chi) \leq N(\mu, c_l^{(0)}(\kappa, R)).$$

Indeed, if $\mathcal{V}_l$ is the negative spectral subspace of $\chi\left(|\mathbf{p}| - \kappa|\mathbf{x}|^{-1} - \mu\right)\chi$ with fixed l, then any $f \in \mathcal{F}_l\chi\mathcal{V}_l \subset \mathfrak{F}_l(R)$ satisfies $\langle f, (c_l^{(0)}(\kappa, R) - \mu)\,f\rangle < 0$.
Hence, in order to prove the assertion, it suffices to show that

$$N(\mu, c_l^{(0)}(\kappa, R)) \leq \mathrm{const}\;\mu R.$$

For a proof, we note that the elementary inequality $\chi_{(-\infty,\mu)}(E) \leq \frac{(E-\lambda)_-}{\lambda-\mu}$, valid for any $\mu < \lambda$, together with Lemma D.1 implies that

$$N(\mu, c_l^{(0)}(\kappa, R)) \leq (\lambda - \mu)^{-1}\,\mathrm{tr}(c_l^{(0)}(\kappa, R) - \lambda)_- \leq \mathrm{const}\;(\lambda - \mu)^{-1}\lambda^2 R.$$

The proof is completed by optimizing over λ. □

E The trial density matrix

In this section we define the density matrices d^S and d^B that we use to bound the Schrödinger energy, respectively the Brown-Ravenhall energy, from above. Both density matrices are split into two parts corresponding to low and high angular momenta

$$d^S := d^S_< + d_>, \qquad d^B := d^B_< + d_>.$$

Low angular momenta correspond to orbits whose perinucleon is close to the nucleus, while high angular momenta ensure that the orbits are never close to the nucleus. We will cut between these two at $L := [Z^{1/12}]$.

E.1 Low angular momenta

In the vicinity of the nucleus the nuclear attraction dominates the interaction with the other electrons. This motivates to choose the orbitals as the ones of the Bohr atom, i.e., as the eigenfunctions of the unscreened operator with nuclear charge Z. The corresponding density matrices $d^\#_<$ are of the form

$$d^\#_< = \sum_{l=0}^{L-1} d^\#_j, \qquad d^\#_l = \sum_{j=l\pm 1/2,\ j\geq 1/2} d^\#_{j,l}$$

and

$$d^\#_{j,l} = \sum_{m=-j}^{j} \sum_{n=1}^{K-l} |\psi^\#_{j,l,m,n}\rangle\langle\psi^\#_{j,l,m,n}|.$$

Here $K = [\text{const } Z^{1/3}]$ with some positive constant, i.e., on the order of the last occupied shell of the Bohr atom. We now turn to the definition of the orbitals $\psi^\#_{j,l,m,n}$ for which we consider the cases $\# = B, S$ separately.
In the Brown-Ravenhall case we choose $\psi^B_{j,l,m,n}$ such that its Fourier transform is

$$\hat\psi^B_{j,l,m,n}(\mathbf{p}) = p^{-1} f^B_{j,l,n}(p)\Omega_{j,l,m}(\omega_\mathbf{p}),$$

where $f^B_{j,l,n}$ is the n-th eigenfunction of the operator $V_c\, b_{j,l}(Z/c)\, V_c^*$ in $L^2(\mathbb{R}_+)$. Here the unitary scaling operator V_c is defined by $(V_c f)(p) := c^{-1/2} f(p/c)$ and we recall that the operator $b_{j,l}(\kappa)$ was defined in Subsection C.2. The operators $V_c\, b_{j,l}(Z/c)\, V_c^*$ appear as the angular momentum reductions of $B_c[Z|\mathbf{x}|^{-1}]$. Indeed, by (C.11) and scaling one has

$$\langle\psi, B_c[Z|\mathbf{x}|^{-1}]\,\psi\rangle = c^2 \sum_{(j,l,m)\in\mathcal{I}} \langle\hat\psi_{j,m,l}, V_c\, b_{j,l}(Z/c)\, V_c^*\, \hat\psi_{j,m,l}\rangle.$$

In the Schrödinger case we choose

$$\psi^S_{j,l,m,n}(\mathbf{x}) = r^{-1} f^S_{l,n}(r)\Omega_{j,l,m}(\omega_\mathbf{x}),$$

where $f^S_{l,n}$ is the n-th eigenfunction of $-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}$ in $L^2(\mathbb{R}_+)$ with Dirichlet boundary conditions.

E.2 High angular momenta

For large angular momenta, the electrons are sufficiently far from the center moving – classically speaking – slowly. This motivates to pick non-relativistic orbitals in both in the relativistic and non-relativistic case. Moreover, for large quantum numbers the correspondence principle would predict quasi-classical behavior (in the quantum sense) as well. This motivates the following choice which we take – with slight modifications – from [55]:

$$d_> := \sum_{l\geq L} d_l, \quad d_l := \sum_{j=l\pm 1/2} \sum_{m=-j}^{j} \sum_{n\in\mathbb{Z}} w_{n,l} |\varphi_{n,l}\Omega_{j,l,m}\rangle\langle\varphi_{n,l}\Omega_{j,l,m}|. \tag{E.1}$$

We repeat at this point the construction of the Macke orbitals $\varphi_{n,l}$ and their weights $w_{n,l}$. We will also present a new estimate not directly given in that paper.

The semi-classical mean-field in which the electrons move is the Thomas-Fermi potential ϕ_{TF} (see (4.3)). According to Hellmann [36] the semi-classical electron density for fixed angular momentum is

$$\sigma_l^H(r) := \frac{2(2l+1)}{\pi}\sqrt{2\left[n_Z\phi_{\mathrm{TF}}(r) - \frac{(l+\frac{1}{2})^2}{2r^2}\right]_+}, \tag{E.2}$$

where we added the factor $n_Z = (1 - aZ^{-1/2})^{2/3}$ for normalization purposes with some fixed positive a and where we replaced the self-generated field of the sum of the radial densities σ_l by the Thomas-Fermi potential. We will write ρ_l^H for the functions σ_l^H when $a = 0$, i.e., no normalization factor occurs. In passing we note that the densities ρ_l^H are the minimizers of the Hellmann functional with external potential given by the Thomas-Fermi density and no other interaction between the electrons (see [61]).

The functions σ_l^H vanish for large l and we define

$$k' := \min\{l \in \mathbb{N} \,|\, \sigma_l^H \equiv 0\}.$$

By scaling, k' is of the order $Z^{1/3}$. Moreover, since the function $r \mapsto \phi_{\mathrm{TF}}(r)r^2$ has exactly one maximum, the support of σ_l^H is an interval $[r_1(l), r_2(l)]$.

We cannot use the density σ_l^H directly in defining semi-classical orbitals, since the derivative of its square root is not square integrable. Thus we pick two points,

$$x_1(l) := r_1(l) + T(l+\tfrac{1}{2})Z^{-1}, \; x_2(l) := r_2(l) - SZ^{-2/3} \tag{E.3}$$

for some positive S and $T \in (0,4)$, and set

$$\rho_l(r) := \begin{cases} 2(2l+1)\alpha^2 r^{2l+2}, & r \in [0, x_1(l)], \\ \sigma_l^H(r), & r \in [x_1(l), x_2(l)], \\ 2(2l+1)\beta^2 \exp(-2^{3/2}Z^{2/3}r), & r \in [x_2(l), \infty). \end{cases} \tag{E.4}$$

The constants α and β are chosen such that ρ_l is continuous. We suppress their dependence on l in the notation.
Next, we define for $l < k'$ and $n \in \mathbb{Z}$ the Macke orbitals

$$\varphi_{n,l}(r) := \frac{\sqrt{\zeta_l'(r)}}{r} e^{\mathrm{i}\pi k_{n,l}\zeta_l(r)} \tag{E.5}$$

where $\zeta_l : [0,\infty) \to [0,1)$ is the Macke transform

$$\zeta_l(r) := \frac{\int_0^r \rho_l(t)\mathrm{d}t}{\int_0^\infty \rho_l(t)\mathrm{d}t}. \tag{E.6}$$

For $l \geq k'$ we set $\varphi_{n,l} :\equiv 0$. The integral

$$N_{j,l,m} := \frac{1}{2(2l+1)} \int_0^\infty \rho_l(r)\mathrm{d}r,$$

which is independent of j and m, will represent the number of electrons in the angular momentum channel (j,l,m). Moreover, we set $\varepsilon_l := N_{j,l,m} - [N_{j,l,m}]$. If $[N_{j,l,m}]$ is odd, we pick $k_{n,l} = 2n$, otherwise $k_{n,l} = 2n-1$. The weights are chosen as

$$w_{n,l} := \begin{cases} 1 & |k_{n,l}| \leq [N_{j,l,m}] - 1 \\ \varepsilon_l/2 & |k_{n,l}| = [N_{j,l,m}] + 1 \\ 0 & \text{otherwise} \end{cases} \tag{E.7}$$

which guarantees that $\sum_{n\in\mathbb{Z}} w_{n,l} = N_{j,l,m}$.
Strictly speaking, our trial density matrix differs from the one used in [55], since we label the orbitals by the modulus of total angular momentum, by the third component of total angular momentum, and by the orbital angular momentum. This, however, is merely a minor rearrangement of terms.
We also adapt to atomic units used in this paper which changes the value of the Thomas-Fermi constant and gives a factor 1/2 in front of all three kinetic energy terms in the Hellmann-Weizsäcker functional.

E.3 Energy estimates for high angular momenta

For the convenience of the reader, we gather from [55] (based on the construction in [60]) two estimates on the order of the average kinetic and potential energy of the Schrödinger operator associated with the semi-classical density matrix $d_>$,

$$\operatorname{tr}(\mathbf{p}^2 d_>) = \mathcal{O}(Z^{7/3}), \qquad \operatorname{tr}(|\mathbf{x}|^{-1} d_>) = \mathcal{O}(Z^{4/3}). \tag{E.8}$$

We also need a more detailed estimate on the kinetic energy.

Lemma E.1. *Let $L = [Z^{1/12}]$. Then for large Z,*

$$\sum_{l=L}^{\infty} l^{-2} \operatorname{tr}(\mathbf{p}^2 d_l) = \mathcal{O}(Z^2/L). \tag{E.9}$$

Proof. The definition of d_l implies (cf. [55, (2.3)]) that for angular momenta $l < k'$ one has

$$\operatorname{tr}(\mathbf{p}^2 d_l) = \int_0^\infty \left[\sqrt{\rho_l}\;'^2 + \frac{\alpha_l}{3}\rho_l^3 + \frac{l(l+1)}{r^2}\rho_l \right] \mathrm{d}r + F_l \tag{E.10}$$

where we set

$$\begin{aligned} F_l &:= \frac{\alpha_l}{3} \left(\frac{-1+6\varepsilon_l - 3\varepsilon_l^2}{N_{j,l,m}^2} + \frac{2\varepsilon_l^3 - 6\varepsilon_l^2 + 4\varepsilon_l}{N_{j,l,m}^3} \right) \int_0^\infty \rho_l^3 \mathrm{d}r, \\ \alpha_l &:= \frac{\pi^2}{4(2l+1)^2}, \end{aligned}$$

and emphasize that α_l should not be confused with α from (E.4). According to [55, Proposition 3.6]

$$\sum_{l=L}^\infty l^{-2}\, F_l \le \sum_{l=L}^\infty F_l \le \text{const } Z^{5/3}$$

where $L = [Z^{1/12}]$. The first term on the right-hand side of (E.10) is estimated according to

$$\begin{aligned} &\int_0^\infty \left[\sqrt{\rho_l}\;'^2 + \frac{\alpha_l}{3}\rho_l^3 + \frac{l(l+1)}{r^2}\rho_l \right] \mathrm{d}r \\ &\le \int_0^\infty \left[\frac{\alpha_l}{3}\rho_l^H(r)^3 + \frac{(l+\frac12)^2}{r^2}\rho_l^H(r) \right] \mathrm{d}r + G_l + H_l + I_l. \end{aligned} \tag{E.11}$$

with

$$\begin{aligned} G_l &:= \int_0^{x_1(l)} \left[\sqrt{\rho_l}\;'^2 + \frac{\alpha_l}{3}\rho_l^3 + \frac{\left(l+\frac12\right)^2}{r^2}\rho_l \right] \mathrm{d}r \le \text{const } Z^2 \left(l+\frac12\right)^{-3/2}, \\ H_l &:= \int_{x_2(l)}^\infty \left[\sqrt{\rho_l}\;'^2 + \frac{\alpha_l}{3}\rho_l^3 + \frac{\left(l+\frac12\right)^2}{r^2}\rho_l \right] \mathrm{d}r \le \text{const } Z^{7/6} \left(l+\frac12\right) \end{aligned}$$

where the inequalities were obtained by integration as in [55, (3.4)]. Inequality [55, (3.9)] for the gradient term in the middle region reads

$$\begin{aligned} I_l := \int_{x_1(l)}^{x_2(l)} \sqrt{\rho_l}\;'^2 \mathrm{d}r &\le \text{const } \left(l+\frac12\right) \\ &\times \left[Z^2 \left(l+\frac12\right)^{-3} + Z + Z^2 \left(l+\frac12\right)^{-5/2} + \frac{Z^{5/3}\left(l+\frac12\right)^{-1/2}}{\min\{l+\frac12, Z^{1/4}\}} \right]. \end{aligned}$$

This implies

$$\begin{aligned}
&\sum_{l=L}^{\infty} l^{-2}\,G_l \le \text{const } Z^2 \sum_{l=L}^{\infty} l^{-7/2} \le \text{const } Z^2 L^{-5/2},\\
&\sum_{l=L}^{\infty} l^{-2}\,H_l \le \sum_{l=L}^{k'} l^{-2}\,H_l \le \text{const } Z^{7/6}\log k' \le \text{const } Z^{7/6}\log Z\\
&\sum_{l=L}^{\infty} l^{-2}\,I_l \le \text{const } \left[Z^2L^{-3} + Z\log Z + Z^2 L^{-5/2} + Z^{5/3}L^{-3/2}\right]\\
&\qquad\qquad \le \text{const } Z^{43/24}.
\end{aligned}$$

It thus remains to estimate the sum of the first terms on the right-hand side of (E.11). We begin with the first summand,

$$\begin{aligned}
&\sum_{l=L}^{\infty} \frac{1}{l^2}\int_0^\infty \frac{\alpha_l}{3}\rho_l^H(r)^3 \mathrm{d}r \le \text{const } \sum_{l=L}^{\infty} \frac{1}{l}\int_0^\infty (Z/r - l^2/r^2)_+^{3/2}\mathrm{d}r\\
=&\text{const } Z^2 \sum_{l\ge L} \frac{1}{l^2}\int_0^\infty r^{-3/2}(1-r^{-1})_+^{3/2}\mathrm{d}r = \mathcal{O}(Z^2/L)
\end{aligned}$$

where we used that the Thomas-Fermi potential is bounded from above by Z/r. This leaves the second summand,

$$\begin{aligned}
&\sum_{l=L}^{\infty} \frac{1}{l^2}\int_0^\infty \frac{\left(l+\frac12\right)^2}{r^2}\rho_l^H(r)\mathrm{d}r \le \text{const } \sum_{l=L}^{\infty} l\int_0^\infty r^{-2}(Z/r - l^2/r^2)_+^{1/2}\mathrm{d}r\\
=&\text{ const } Z^2 \sum_{l=L}^{\infty} \frac{1}{l^2}\int_0^\infty r^{-5/2}(1-r^{-1})_+^{1/2}\mathrm{d}r = \mathcal{O}(Z^2/L),
\end{aligned}$$

which completes the proof of Lemma E.1. □

References

[1] Volker Bach. A proof of Scott's conjecture for ions. *Rep. Math. Phys.*, 28(2):213–248, October 1989.

[2] Volker Bach. Error bound for the Hartree-Fock energy of atoms and molecules. *Comm. Math. Phys.*, 147:527–548, 1992.

[3] A. A. Balinsky and W. D. Evans. On the virial theorem for the relativistic operator of Brown and Ravenhall, and the absence of embedded eigenvalues. *Lett. Math. Phys.*, 44(3):233–248, 1998.

[4] Pedro Balodis. A proof of Scott's correction for matter. *Comm. Math. Phys.*, 249(1):79–132, 2004.

[5] Hans A. Bethe and Edwin E. Salpeter. Quantum mechanics of one- and two-electron atoms. In S. Flügge, editor, *Handbuch der Physik, XXXV*, pages 88–436. Springer, Berlin, 1 edition, 1957.

[6] G. E. Brown and D. G. Ravenhall. On the interaction of two electrons. *Proc. Roy. Soc. London Ser. A.*, 208:552–559, 1951.

[7] Roch Cassanas and Heinz Siedentop. The ground-state energy of heavy atoms according to Brown and Ravenhall: absence of relativistic effects in leading order. *J. Phys. A*, 39(33):10405–10414, 2006.

[8] Charles G. Darwin. The wave equation of the electron. *Proc. Roy. Soc. (London)*, 1928.

[9] Ingrid Daubechies. An uncertainty principle for Fermions with generalized kinetic energy. *Comm. Math. Phys.*, 90:511–520, September 1983.

[10] Paul A. M. Dirac. Note on exchange phenomena in the Thomas-Fermi atom. *Proc. Cambridge Philos. Soc.*, 26:376–385, 1931.

[11] Jean Dolbeault, Maria J. Esteban, and Eric Séré. On the eigenvalues of operators with gaps. Application to Dirac operators. *J. Funct. Anal.*, 174(1):208–226, 2000.

[12] Berthold-Georg Englert. *Semiclassical Theory of Atoms.* Number 300 in Lecture Notes in Physics. Springer-Verlag, Berlin, 1 edition, 1988.

[13] Berthold-Georg Englert and Julian Schwinger. Statistical atom: Handling the strongly bound electrons. *Phys. Rev. A*, 29(5):2331–2338, 1984.

[14] Berthold-Georg Englert and Julian Schwinger. Statistical atom: Some quantum improvements. *Phys. Rev. A*, 29(5):2339–2352, 1984.

[15] Berthold-Georg Englert and Julian Schwinger. Atomic-binding-energy oscillations. *Phys. Rev. A*, 32:47–63, 1985.

[16] A. Erdélyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi. *Tables of integral transforms. Vol. II.* McGraw-Hill Book Company, Inc., New York-Toronto-London, 1954. Based, in part, on notes left by Harry Bateman.

[17] 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.

[18] C. Fefferman and L. Seco. Eigenfunctions and eigenvalues of ordinary differential operators. *Adv. Math.*, 95(2):145–305, October 1992.

[19] C. Fefferman and L. Seco. The density of a one-dimensional potential. *Adv. Math.*, 107(2):187–364, September 1994.

[20] C. Fefferman and L. Seco. The eigenvalue sum of a one-dimensional potential. *Adv. Math.*, 108(2):263–335, October 1994.

[21] 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.

[22] C. Fefferman and L. Seco. The density in a three-dimensional radial potential. *Adv. Math.*, 111(1):88–161, March 1995.

[23] 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.

[24] C. L. Fefferman and L. A. Seco. Asymptotic neutrality of large ions. *Comm. Math. Phys.*, 128:109–130, 1990.

[25] C. L. Fefferman and L. A. Seco. On the energy of a large atom. *Bull. AMS*, 23(2):525–530, October 1990.

[26] Charles L. Fefferman and Luis A. Seco. Aperiodicity of the Hamiltonian flow in the Thomas-Fermi potential. *Revista Mathemática Iberoamericana*, 9(3):409–551, 1993.

[27] E. Fermi. Un metodo statistico per la determinazione di alcune proprietá dell'atomo. *Atti della Reale Accademia Nazionale dei Lincei, Rendiconti, Classe di Scienze Fisiche, Matematiche e Naturali*, 6(12):602–607, 1927.

[28] E. Fermi. Eine statistische Begründung zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendungen auf die Theorie des periodischen Systems der Elemente. *Z. Phys.*, 48:73–79, 1928.

[29] Rupert L. Frank. A simple proof of Hardy-Lieb-Thirring inequalities. *Comm. Math. Phys.*, 290(2):789–800, 2009.

[30] Rupert L. Frank, Elliott H. Lieb, and Robert Seiringer. Hardy-Lieb-Thirring inequalities for fractional Schrödinger operators. *J. Amer. Math. Soc.*, 21(4):925–950, 2008.

[31] Rupert L. Frank, Heinz Siedentop, and Simone Warzel. The ground state energy of heavy atoms: relativistic lowering of the leading energy correction. *Comm. Math. Phys.*, 278(2):549–566, 2008.

[32] Walter Gordon. Die Energieniveaus des Wasserstoffatoms nach der Diracschen Quantentheorie. *Z. Phys.*, 48:11–14, 1928.

[33] Walter Greiner. *Relativistic Quantum Mechanics*, volume 3 of *Theoretical Physics – Text and Excercise Books*. Springer, Berlin, 1 edition, 1990.

[34] Marcel Griesemer, Roger T. Lewis, and Heinz Siedentop. A minimax principle for eigenvalues in spectral gaps: Dirac operators with Coulomb potential. *Doc. Math.*, 4:275–283, 1999.

[35] Marcel Griesemer and Heinz Siedentop. A minimax principle for the eigenvalues in spectral gaps. *J. London Math. Soc. (2)*, 60(2):490–500, 1999.

[36] Heinrich Hellmann. Ein kombiniertes Näherungsverfahren zur Energieberechnung im Vielelektronenproblem. II. *Acta Physicochim. U.S.S.R.*, 4:225–244, 1936.

[37] Webster Hughes. *An Atomic Energy Lower Bound that Gives Scott's Correction*. PhD thesis, Princeton, Department of Mathematics, 1986.

[38] Webster Hughes. An atomic lower bound that agrees with Scott's correction. *Adv. in Math.*, 79:213–270, 1990.

[39] V. Ja. Ivrii and I. M. Sigal. Asymptotics of the ground state energies of large Coulomb systems. *Annals of Math.*, 138(2):243–335, 1993.

[40] Tosio Kato. *Perturbation Theory for Linear Operators*, volume 132 of *Grundlehren der mathematischen Wissenschaften*. Springer-Verlag, Berlin, 1 edition, 1966.

[41] W. Lenz. Über die Anwendbarkeit der statistischen Methode auf Ionengitter. *Z. Phys.*, 77:713–721, 1932.

[42] Elliott H. Lieb. Variational principle for many-fermion systems. *Phys. Rev. Lett.*, 46(7):457–459, 1981.

[43] Elliott H. Lieb and Michael Loss. *Analysis*, volume 14 of *Graduate Studies in Mathematics*. American Mathematical Society, Providence, RI, second edition, 2001.

[44] Elliott H. Lieb and Barry Simon. The Thomas-Fermi theory of atoms, molecules and solids. *Adv. Math.*, 23:22–116, 1977.

[45] Elliott H. Lieb and Walter E. Thirring. Inequalities for the moments of the eigenvalues of the Schrödinger Hamiltonian and their relation to Sobolev inequalities. In Elliott H. Lieb, Barry Simon, and Arthur S. Wightman, editors, *Studies in Mathematical Physics: Essays in Honor of Valentine Bargmann*. Princeton University Press, Princeton, 1976.

[46] Elliott H. Lieb and Horng-Tzer Yau. The stability and instability of relativistic matter. *Comm. Math. Phys.*, 118:177–213, 1988.

[47] 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.

[48] Albert Messiah. *Mécanique Quantique*, volume 1. Dunod, Paris, 2 edition, 1969.

[49] 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.

[50] Thomas Østergaard Sørensen. *Towards a Relativistic Scott Correction.* PhD thesis, Aarhus Universitet, http://www.imf.au.dk/cgi-bin/viewers/viewpublications.cgi?id=79, October 1998.

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

[52] Julian Schwinger. Thomas-Fermi model: The leading correction. *Phys. Rev. A*, 22(5):1827–1832, 1980.

[53] Julian Schwinger. Thomas-Fermi model: The second correction. *Phys. Rev. A*, 24(5):2353–2361, 1981.

[54] J. M. C. Scott. The binding energy of the Thomas-Fermi atom. *Phil. Mag.*, 43:859–867, 1952.

[55] 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.

[56] 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.

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

[58] 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.

[59] 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.

[60] Heinz K. H. Siedentop. On the relation between the Hellmann energy functional and the ground state energy of an N-Fermion system. *Z. Phys. A*, 302:213–218, 1981.

[61] Heinz K. H. Siedentop and Rudi Weikard. On the leading energy correction for the statistical model of the atom: Non-interacting case. *Abh. Braunschweig. Wiss. Ges.*, 38:145–158, 1986.

[62] B. Simon. Fifteen problems in mathematical physics. In *Perspectives in Mathematics*. Birkhäuser, 1984.

[63] Barry Simon. *Functional Integration and Quantum Physics*. Academic Press Inc. [Harcourt Brace Jovanovich Publishers], New York, 1979.

[64] Jan Philip Solovej. The relativistic Scott correction. In Maria J. Esteban, Claude Le Bris, and Gustavo Scuseria, editors, *Mathematical and Numerical Aspects of Quantum Chemistry Problems*, volume 47/2006 of *Oberwolfach Report*, pages 52–53. Mathematisches Forschungsinstitut Oberwolfach, European Mathematical Society, September 2006.

[65] Jan Philip Solovej, Thomas Østergaard Sørensen, and Wolfgang L. Spitzer. The relativistic Scott correction for atoms and molecules, *Commun. Pure Appl. Math.*, 63:39–118, 2010.

[66] Jan Philip Solovej and Wolfgang L. Spitzer. A new coherent states approach to semiclassics which gives Scott's correction. *Comm. Math. Phys.*, 241(2-3):383–420, 2003.

[67] Irene A. Stegun. Legendre functions. In Milton Abramowitz and Irene A. Stegun, editors, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, chapter 8, pages 331–353. Dover Publications, New York, 1965.

[68] Elias M. Stein. *Singular integrals and differentiability properties of functions*. Princeton Mathematical Series, No. 30. Princeton University Press, Princeton, N.J., 1970.

[69] J. Sucher. Foundations of the relativistic theory of many-electron atoms. *Phys. Rev. A*, 22(2):348–362, August 1980.

[70] J. Sucher. Foundations of the relativistic theory of many-electron bound states. *International Journal of Quantum Chemistry*, 25:3–21, 1984.

[71] J. Sucher. Relativistic many-electron Hamiltonians. *Phys. Scripta*, 36:271–281, 1987.

[72] Walter Thirring. *Lehrbuch der Mathematischen Physik 3: Quantenmechanik von Atomen und Molekülen*. Springer-Verlag, Wien, New York, 1 edition, 1979.

[73] L. H. Thomas. The calculation of atomic fields. *Proc. Camb. Phil. Soc.*, 23:542–548, 1927.

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

[75] C. Tix. Self-adjointness and spectral properties of a pseudo-relativistic Hamiltonian due to Brown and Ravenhall. *Preprint*, mp-arc: 97-441, 1997.

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

[77] E. T. Whittaker and G. N. Watson. *A Course of Modern Analysis; An Introduction to the General Theory of Infinite Processes and of Analytic Functions, with an Account of the Principal Transcendental Functions.* Cambridge University Press, Cambridge, 4 edition, 1927.

Rupert L. Frank
Dept. of Mathematics,
Princeton University,
Princeton, NJ 08544-1000,
USA
rlfrank@math.princeton.edu

Heinz Siedentop
Mathematisches Institut
LMU München
Theresienstraße 39
80333 München, Germany
h.s@lmu.de

Simone Warzel
TU München
Zentrum Mathematik - M7
Boltzmannstraße 3
85747 Garching, Germany
warzel@ma.tum.de