The Ground State Energy of Heavy Atoms: 
The Leading Correction

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Abstract: For heavy atoms (large atomic number \( Z \)) described by no-pair operators in the Furry picture, we find the ground state’s leading energy correction. We compare the result with (semi-)empirical values and Schwinger’s prediction showing more than qualitative agreement.

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1. Introduction

Since the advent of quantum mechanics the description of heavy atoms and molecules, in particular their energies, has been of considerable interest in physics, quantum chemistry, and mathematics. However, as in classical mechanics, an explicit treatment beyond one-electron systems is elusive. This spurred the development of effective models of large Coulomb systems starting with Thomas [79], Fermi [29,30], and Lenz [46], who formulated the Thomas–Fermi model in the appropriate language of energy functionals. It asserts that in terms of the nuclear charge $Z$, the ground state energy of an atom is of leading order $Z^{7/3}$. That this is only an approximation was clear since the beginning. But it was even doubted that the leading behavior for large $Z$ was correct. In fact, Foldy [31] claimed a $Z^{12/5}$ behavior for large $Z$ based on numerical computations. Scott [64] offered a refined physical argument yielding a positive, additive correction of order $Z^{2}$. The correction originates from the strongly bound electrons, which are ill-represented semi-classically. Later Schwinger [62] and Bander [5] gave additional arguments for the validity of the Scott correction. Schwinger [63], and Englert and Schwinger [13–15] even argued for a $Z^{5/3}$ that can be partially traced back to Dirac [12].

The question whether the conjectured formula for the ground state energy holds asymptotically for the $N$-electron Schrödinger theory was left unanswered until Lieb and Simon’s seminal paper [48], which successfully established the asymptotic correctness of Thomas’, Fermi’s, and Lenz’s prediction. Later the Scott correction for atoms was mathematically confirmed by Hughes [41,42] (lower bound), and Siedentop and Weikard [66–68] (lower and upper bound). Eventually, even the existence of a $Z^{5/3}$-term, the so-called Dirac–Schwinger correction, was proved by Fefferman and Seco in a tour de force [21–28]. These results were extended in various ways to, e.g., ions and molecules [1,4,43]. However, from a physical point of view, it is questionable how these mathematical results reflect reality. It is expected that electrons located close to the nucleus will move at high velocities, thus requiring a relativistic treatment. Already in non-relativistic quantum mechanics the bulk of the electrons are forced on orbits of distances on order $Z^{-1/3}$; the electrons contributing to the Scott correction even live on the scale $Z^{-1}$. Thus, it is expected that only the latter will generate the leading correction to the non-relativistic ground state energy. Already Schwinger [62] estimated this effect and illustrated that the leading term remains unaffected. Sørensen [57] was the first to put Schwinger’s prediction on mathematical ground by showing that the leading Thomas–Fermi term is indeed left unchanged in the limit of large nuclear charge $Z$ and large speed of light $c$ when replacing the non-relativistic Hamiltonian by the Chandrasekhar (or pseudo-relativistic) Hamiltonian. Subsequently, the Scott correction for the Chandrasekhar model was again proved to be of order $Z^{2}$ by Sørensen [56] (non-interacting case) and Solovej, Sørensen and Spitzer [71] (molecular interacting case). A short, alternative proof was given by Frank, Siedentop, and Warzel [34] in the atomic case. By going from the non-relativistic Schrödinger theory to the pseudo-relativistic Chandrasekhar theory one observes a lowering of the leading energy correction.

Despite the mathematical success in establishing the large $Z$-asymptotics for this simplified relativistic model, it is still desirable to examine models that not only rep-
resent qualitative features of relativistic systems but are also expected to be quantitatively correct. In particular, the pseudo-relativistic theory fails to reproduce the energies of hydrogen-like atoms. In fact, it predicts collapse of the innermost electron for Ra ($Z = 88$) and beyond, i.e., it does not even allow one to treat very large atoms. For this matter it is believed to be necessary to study Hamiltonians that are derived directly from QED, among them the so called no-pair operators [75–77]. The most simple of those models has been introduced by Brown and Ravenhall [7]. In analogy to the Schrödinger and Chandrasekhar theory, Cassanas and Siedentop [9] proved that to leading order this model has no effect on the energy asymptotics. In a further step Frank, Siedentop, and Warzel [35] established the Scott correction for this model as well. However, although the Brown–Ravenhall model raises the energies of the Chandrasekhar model, it nevertheless—even in the one-particle picture—predicts still too low energies. In consequence, the Scott correction, which is determined by the pure unscreened Coulomb potential, is too small. In fact, the energy becomes unbounded from below at about $Z = 124$, which is higher than any known element, but nevertheless lower than the expected value 137.

In passing we would like to mention two recent results on the inclusion of the self-generated magnetic field (quantized or not): it turns out that it does not affect the leading order (Erdős and Solovej [19]). In fact the Scott term is not affected in the Chandrasekhar model either whereas in the non-relativistic setting—which is expected to be unphysical because of the argument mentioned above—the Scott term would be changed [16–18]. This and corresponding numerical results motivate us to drop the self-generated magnetic fields in this paper.

Despite the shortcomings of the original Brown–Ravenhall model, it is known that no-pair operators reproduce relativistic effects in a quantitative correct manner [40] when taking into account the external potential in determining the electron space (Furry picture) [40,59]. Physically this is reasonable since the first order correction stemming from the innermost electrons is now derived from the Dirac equation with the unscreened Coulomb potential. This is actually the underlying physical argument for Schwinger’s [62] relativistic correction.

1.1. The energy form. The relativistic description of an electron moving in the potential of a static nucleus of charge $Z$ and a mean-field potential $\chi$ is given by the Dirac operator

$$D_{\gamma,\chi} = \alpha \cdot p + \beta - \frac{\gamma}{|x|} + \chi$$  \hspace{1cm} (1)

with $\gamma = Z/c$ in units of $mc^2$ and $p := (1/i)\nabla$. This operator is self-adjointly realized in $L^2(\mathbb{R}^3 : \mathbb{C}^4)$. Here

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$  \hspace{1cm} (2)

where $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ are the three Pauli matrices in standard representation. A physical example for $\chi$ would be the screening mean-field potential of the electrons. We will assume that $\chi$ is a bounded operator. Assuming $\gamma := Z/c \in (-1, 1)$, Nenciu [55] showed that $D_{\gamma,\chi}$ defined on $\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4)$ has a distinguished self-adjoint extension whose domain includes $H^1(\mathbb{R}^3 : \mathbb{C}^4)$ and whose form domain is $H^{1/2}(\mathbb{R}^3 : \mathbb{C}^4)$. By the usual abuse of notation we do no longer distinguish notationally between the original operator and its extension. Moreover, we write $D_\gamma := D_{\gamma,0}$ for the pure Coulomb–Dirac operator without screening.
The energy form $\mathcal{E}^N$ on $\mathcal{S}(\mathbb{R}^{3N} : \mathbb{C}^{4N})$ is

$$\mathcal{E}^N[\Psi] := e^2 \left\langle \Psi, \left( \sum_{v=1}^{N} (D_\gamma - 1)_{\nu} + \sum_{1 \leq \mu < \nu \leq N} \frac{\alpha}{|\mathbf{x}_\nu - \mathbf{x}_\mu|} \right) \Psi \right\rangle = \left\langle V_c \Psi, \left( \sum_{v=1}^{N} (c\alpha_v \cdot \mathbf{p}_v + c^2 \beta_v - \frac{Z}{|\mathbf{x}_v|} - e^2) + \sum_{1 \leq \mu < \nu \leq N} \frac{1}{|\mathbf{x}_\nu - \mathbf{x}_\mu|} \right) V_c \Psi \right\rangle$$

(3)

where $\alpha := e^2/(\hbar c)$, i.e., $\alpha = 1/c$ in our units, is the Sommerfeld fine structure constant. The scaling map $V_c$ will be defined in Sect. 1.2.

Since electrons are fermions, we will restrict the domain to antisymmetric spinors $\Psi$. Moreover, in the spirit of Dirac’s postulate of a filled Dirac sea, Brown and Ravenhall [7] and later Sucher [76, 77], extending this idea, formulated this mathematically by requiring that the one-electron space is given by the positive spectral subspace of a suitable Dirac operator. Typical choices for such operators:

**Free picture (Brown and Ravenhall [7])** The free Dirac operator, i.e., $D_0$ with

$$\mathcal{E}_0 := \Lambda_0(L^2(\mathbb{R}^3 : \mathbb{C}^4)) := \mathbb{1}_{(0, \infty)}(D_0)(L^2(\mathbb{R}^3 : \mathbb{C}^4)).$$

**Furry picture (Furry and Oppenheimer [36])** The Dirac operator with the external potential, i.e., $D_\gamma$ with

$$\mathcal{E}_\gamma := \Lambda_\gamma(L^2(\mathbb{R}^3 : \mathbb{C}^4)) := \mathbb{1}_{(0, \infty)}(D_\gamma)(L^2(\mathbb{R}^3 : \mathbb{C}^4)).$$

**Intermediate or Fuzzy picture (Mittleman [54])** The intermediate picture with some screening potential $\chi$, e.g. it may be picked as the mean-field potential of the Dirac–Hartree–Fock equations. An optimal choice, which depends on the two-particle density matrix, was suggested by Mittleman. This leads to a non-linear equation, which has been studied numerically with great success in quantum chemistry, see, e.g., Saue [60].

We will pick $\chi$ to be the rescaled Thomas–Fermi screening potential reduced by the exchange hole (see (20)), i.e., $D_{\gamma, \chi}$, with the corresponding one-particle Hilbert space

$$\mathcal{E}_{\gamma, \chi} := \Lambda_{\gamma, \chi}(L^2(\mathbb{R}^3 : \mathbb{C}^4)) := \mathbb{1}_{(0, \infty)}(D_{\gamma, \chi})(L^2(\mathbb{R}^3 : \mathbb{C}^4)).$$

The corresponding $N$ particle Hilbert spaces are $\mathcal{E}^N_{\#} := \bigwedge_{\nu=1}^{N} \mathcal{E}_{\#}$ where # either denotes the free picture, i.e., # = 0, the Furry picture, i.e., # = $\gamma$, or our choice of the intermediate picture, i.e., # = ($\gamma$, $\chi$). Because of Nenciu’s result as described above [55],

$$\Lambda_\#(\mathcal{S}(\mathbb{R}^3 : \mathbb{C}^4)) \subset H^{1/2}(\mathbb{R}^3 : \mathbb{C}^4)$$

and dense in $\Lambda_\#(L^2(\mathbb{R}^3 : \mathbb{C}^4))$. Thus, the functional $\mathcal{E}^N_{\#} := \mathcal{E}^N|_{\bigwedge_{\nu=1}^{N}(\Lambda_\#(\mathcal{S}(\mathbb{R}^3 ; \mathbb{C}^4)))}$ is well defined for $\gamma \in [0, 1)$ and bounded screening potential, i.e., in particular for our choice.

The above quadratic forms are bounded from below under suitable constraints on $\gamma$, and thus define according to Friedrichs a distinguished self-adjoint operator. In particular this holds, if

**Brown–Ravenhall** $\gamma \leq \frac{\gamma_{\text{crit}}}{2}$ (Evans et al. [20]).

**Furry and Intermediate** $\gamma < 1$ (Nenciu [55]).

Matte and Stockmeyer [51] have worked out the detailed structure of the spectrum of such no-pair operators.
1.2. Scaling and units. The technical necessity of the limit $Z \to \infty$ only being possible in the simultaneous limit $c \to \infty$ such that $\gamma = \frac{Z}{c} \to C < 1$ suggests that the appropriate units are chosen as in (1). To draw a connection to the usual Schrödinger operator of hydrogen

$$\frac{\mathbf{p}^2}{2} - \frac{Z}{|\mathbf{x}|}$$

it will be useful to consider the unitary scaling operator $V_c$ on $L^2(\mathbb{R}^3 : \mathbb{C}^4)$ defined by

$$(V_c \psi)(x) := c^\frac{3}{2} \Psi(c x)$$

such that

$$c^2 \langle \psi, (\alpha \cdot \mathbf{p} + \beta - \frac{\gamma}{|\mathbf{x}|}) \psi \rangle = \langle V_c \psi, (c \alpha \cdot \mathbf{p} + c^2 \beta - \frac{Z}{|\mathbf{x}|}) V_c \psi \rangle.$$  \hspace{1cm} (6)

1.3. Main result. Ground state energies of neutral atoms in no-pair pictures are given by

$$E_\#(Z) := \inf \{E_Z[\psi] | \psi \in Q^Z_\#, \|\psi\| = 1\}$$

where $Q^Z_\# := \tilde{\mathcal{F}}^Z_\# \cap \bigwedge_{\nu=1}^Z (\Lambda_{\#}(\mathbb{S}(\mathbb{R}^3 : \mathbb{C}^4))).$

For the Brown–Ravenhall operator, i.e., # set to 0, Cassanas and Siedentop [9] proved that the leading order term is given by the Thomas–Fermi energy $E^{TF}$ (see Appendix 6), i.e.,

$$E_0(Z) = E^{TF}(1)Z^{7/3} + o(Z^{7/3}).$$  \hspace{1cm} (8)

Furthermore, Frank et al. [35] found the leading correction. It is given by the spectral shift function $s^B(\gamma)$ for $\gamma \in (0, \gamma^B_{crit}]$, i.e., the difference of bound state energies of the one-particle Brown–Ravenhall operator and Schrödinger operator.

This paper concerns the analogous result in the case of the Furry picture, i.e., # replaced by $\gamma$. In this case we are in the fortunate situation that the eigenvalues of the one-particle Furry operator are explicitly known. They are identical to the eigenvalues $\lambda^D_n$ (labeled in increasing order) of the Dirac–Coulomb operator $D_Y - 1$. Likewise, denoting the eigenvalues of the hydrogen Schrödinger operator $(\mathbf{p}^2/2 - \gamma/|\mathbf{x}|) \otimes 1_{\mathbb{C}^2}$ in $L^2(\mathbb{R}^3 : \mathbb{C}^2)$ by $\lambda^S_n$, we can write down rather explicitly a new spectral shift function

$$s^D(\gamma) := \frac{1}{\gamma^2} \sum_{n=1}^{\infty} (\lambda^D_n - \lambda^S_n)$$

for $\gamma \in (0, 1)$.

We are now ready to state the main theorem.

**Theorem 1** (Scott correction). There exists a constant $C > 0$ such that for all $Z > 0$ and $\gamma = \frac{Z}{c} < 1$ one has

$$\left| E_\gamma(Z) - E^{TF}(Z) - \left(\frac{1}{2} + s^D(\gamma)\right)Z^2 \right| \leq CZ^{47/24}. \hspace{1cm} (10)$$
Put differently, Theorem 1 asserts that in the limit $Z \to \infty$ one has

$$E_\gamma(Z) = E_{\text{TF}}(Z) + \left( \frac{1}{2} + s^D(\gamma) \right) Z^2 + o(Z^2)$$  \hfill (11)

uniformly in $\gamma = \frac{Z}{c} < 1$.

2. The Scott Correction of the Hydrogenic Atom: The Shift from Schrödinger to Dirac Energies

Since the Scott correction results from the innermost electrons, it is not only intuitively obvious that the Scott corrections can be computed for atoms whose electrons do not interact with each other; it is also important for obtaining the Scott correction in the interacting case. To turn this intuition into a proof, we will estimate the difference of Dirac and Schrödinger eigenvalues for hydrogenic atoms and exhibit the leading correction to the non-relativistic correction $Z^2/2$.

2.1. Bounds on the energy shift. We denote by $\lambda_{\gamma,n,l,j}^D$ the $n^{th}$ eigenvalue of the operator $D_\gamma - 1$ for $0 \leq \gamma < 1$ restricted to the angular momentum subspace $H_{j,l,m}$ (note that the eigenvalue does not depend on the azimuthal quantum number $m$). The corresponding eigenfunction is denoted by $\psi_{n,l,j,m}$. We write $\lambda_{\gamma,n,l}^S$ and $\psi_{n,l,m}$ for the $n^{th}$ eigenvalue and corresponding eigenfunction of the operator $p^2/2 - \gamma/|x|$ restricted to $|Y_{l,m}\rangle\langle Y_{l,m}|L^2(\mathbb{R}^3)$. The Dirac eigenvalues of the Kepler problem are well known (Gordon [37] and Darwin [10]), in fact they were already anticipated by Sommerfeld in his famous fine structure formula (Sommerfeld [72]) before the Dirac operator was written down. Even earlier the non-relativistic eigenvalues of the Kepler problem were found by Schrödinger [61] and yet even earlier anticipated by Balmer [3]. See, e.g., Bethe [6], for a textbook treatment.

$$\lambda_{\gamma,n,l,j}^D = \left( 1 - \frac{\gamma^2}{(n+l-(j+\frac{1}{2})) + \sqrt{(j+\frac{1}{2})^2 - \gamma^2} + \gamma^2} \right)^{\frac{1}{2}} - 1$$

$$\lambda_{\gamma,n,l}^S = -\frac{\gamma^2}{2(n+l)^2}. \hfill (12)$$

Expanding the square root in (12) and using the fact that $\sqrt{1-x} < 1-x/2$ for $x \in (0, 1]$ we have

$$\lambda_{\gamma,n,l,j}^D < \lambda_{\gamma,n,l}^S < 0. \hfill (13)$$

Moreover, for fixed $l$ and $n$ the dimension of the Dirac eigenspace is $2(2l+1)$ (see (94)) and the dimension of the Schrödinger eigenspace is $2l+1$. 
Lemma 1. Assume $\gamma_0 < 1$. Then there exists a constant $C \in \mathbb{R}$ such that for all $l \in \mathbb{N}$, $j = l \pm 1/2$, $j \geq 1/2$, and $\gamma \in [0, \gamma_0)$

\[ |\lambda^D_{\gamma,n,l,j} - \lambda^S_{\gamma,n,l,j} + \frac{\gamma^4}{2(n+l)^3} \left( \frac{1}{j + \frac{1}{2}} - \frac{3}{4n+l} \right) | \leq C\gamma^6 \frac{n}{(n+l)^4l}. \]  

(14)

Proof. Note that

\[ \frac{1}{2}(n+l)^2 \leq (n+l)^2 - 2(n+l - (j + \frac{1}{2}))(j + \frac{1}{2} - \sqrt{(j + \frac{1}{2})^2 - \gamma^2}) \leq (n+l)^2. \]  

(15)

Expanding the square root gives sufficient error estimates:

\[
\begin{align*}
&\left( 1 - \frac{\gamma^2}{(n+l)^2 - 2(n+l - (j + \frac{1}{2}))(j + \frac{1}{2} - \sqrt{(j + \frac{1}{2})^2 - \gamma^2})} \right)^{\frac{1}{2}} \\
&= 1 - \frac{\gamma^2}{2 \left( (n+l)^2 - 2(n+l - (j + \frac{1}{2}))(j + \frac{1}{2} - \sqrt{(j + \frac{1}{2})^2 - \gamma^2}) \right)} - \frac{\gamma^4}{8 \left( (n+l)^2 - 2(n+l - (j + \frac{1}{2}))(j + \frac{1}{2} - \sqrt{(j + \frac{1}{2})^2 - \gamma^2}) \right)^2} + O\left( \frac{\gamma^6}{(n+l)^6} \right) \\
&= 1 - \frac{\gamma^2}{2(n+l)^2} - \frac{\gamma^4}{2(n+l)^4} \frac{n+l - (j + \frac{1}{2})}{j + \frac{1}{2}} \\
&\quad - \frac{\gamma^4}{8(n+l)^2} + O\left( \frac{\gamma^6n}{(n+l)^4(l+1)^2} \right) \\
&= 1 - \frac{\gamma^2}{2(n+l)^2} - \frac{\gamma^4}{2(n+l)^4} \frac{n+l - (j + \frac{1}{2})}{j + \frac{1}{2}} \\
&\quad - \frac{\gamma^4}{8(n+l)^2} + O\left( \frac{\gamma^6n}{(n+l)^4(l+1)} \right). \\
\end{align*}
\]

For our application it is convenient to simplify the estimate.

Corollary 1. Under the assumptions of Lemma 1 we have

\[ 0 \leq \lambda^S_{\gamma,n,l} - \lambda^D_{\gamma,n,l,j} \leq \frac{C\gamma^4}{(n+l)^3l}. \]  

(16)
2.2. Expectation of the electric potential. We will need an estimate on the expectation value of the Coulomb potential in eigenstates of the Coulomb–Dirac operator. In the non-relativistic case the virial theorem yields immediately

\[ \langle \psi_{n,l,m} \mid \gamma \mid \psi_{n,l,m} \rangle = \gamma^2 (n + l)^{-2}. \]

In the relativistic case explicit computation (Burke and Grant [8]) yields

\[ \langle \psi_{n,l,j,m} \mid \gamma \mid \psi_{n,l,j,m} \rangle \]

This formula would also follow from hypervirial theorems (see, e.g., [65]). The following lemma simplifies the Eq. (17) and gives an estimate similar to the non-relativistic case.

**Lemma 2.** Pick \( \gamma_0 \in (0, 1) \). Given \( n \in \mathbb{N}, j \in \mathbb{N} - 1/2, l \neq j \pm 1/2, m = -j, \ldots, j, \) and \( \gamma \in (0, \gamma_0] \). Then there is a constant \( C_{\gamma_0} \) such that

\[ \langle \psi_{n,l,j,m} \mid \gamma \mid \psi_{n,l,j,m} \rangle \leq \frac{C_{\gamma_0} \gamma^2}{(n + l)^2}. \]

**Proof.** The claim follows by applying the following crude estimates to Eq. (18),

\[ \frac{1}{\sqrt{(j + \frac{1}{2})^2 - \gamma^2}} \leq \frac{1}{j + \frac{1}{2} - \gamma} \leq \frac{1}{(1 - \gamma)(j + \frac{1}{2})}, \]

\[ \frac{1}{(\sqrt{(j + \frac{1}{2})^2 - \gamma^2} + n + l - (j + \frac{1}{2}))^2 + \gamma^2} \leq \frac{1}{(n + l - \gamma)^2 + \gamma^2} \]

\[ \leq \frac{2}{(n + l)^2 - 2(n + l - 1)} \leq \frac{2}{(n + l)^2} (j + \frac{1}{2})^2 + (n + l - (j + \frac{1}{2})) \sqrt{(j + \frac{1}{2})^2 - \gamma^2} \]

\[ = (n + l)(j + \frac{1}{2}) - (n + l - (j + \frac{1}{2}))(j + \frac{1}{2} - \sqrt{(j + \frac{1}{2})^2 - \gamma^2}) \leq (n + l)(j + \frac{1}{2}). \]

Note that the restriction \( \gamma \leq \gamma_0 \) is only relevant for \( j = \frac{1}{2} \).

3. Lower Bound on the Energy

To prove a lower bound on the energy we will reduce the multi-particle operator to an effective one-particle operator via the pointwise correlation inequality of Mancas et al. [50]

\[ c^{-1} \sum_{1 \leq \nu < \mu \leq N} \frac{1}{|x_\nu - x_\mu|} \geq \frac{1}{c} \sum_{\nu=1}^N \chi(x_\nu) - c^{-2} D[\rho_{Z}^{\text{TF}}]. \]

Here \( \chi \) denotes the rescaled screening part of the Thomas–Fermi potential reduced by the exchange hole, i.e.,

\[ \chi(x) = c^{-4} \int_{|x-y| > c R_Z(x/c)} \frac{\rho_{Z}^{\text{TF}}(y/c)}{|x-y|} \, dy. \]
with $R_Z$ being the unique minimal radius such that
\[ \int_{|x-y| \leq R_Z(x)} \rho_Z^{TF}(y) dy = \frac{1}{2}, \] (21)
and
\[ D[\rho] := \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|} dx dy \] (22)
is the classical energy of a charge density $\rho$. (The corresponding sesquilinear form is denoted by $D(\rho, \sigma)$.) Of course,
\[ 0 < \chi(x) < \frac{1}{c^2} \int_{\mathbb{R}^3} dy \frac{\rho_Z^{TF}(y)}{|c^{-1}x-y|} \] (23)
and in particular
\[ \|\chi\|_{\infty} \leq CZ^4 c^{-2} \] (24)
for some constant $C > 0$. Thus, to estimate the form $E_N^\gamma$ from below, it suffices to bound
\[ \mathcal{F}(d) := \text{tr}((D_\gamma, \chi - 1)d) - c^{-2} D[\rho_Z^{TF}] \] (25)
with $d$ a one-particle density matrix on $\mathfrak{h}_\gamma$ of particle number not exceeding $N$, and of finite kinetic energy, i.e., $0 \leq d \leq 1$, $\text{tr}d \leq N$, and $\text{tr}(|p|d) < \infty$.

We now use that $\chi$ is spherically symmetric and therefore $D_\gamma, \chi$ commutes with the total angular momentum $J$ and we split the trace into angular momentum channels, i.e.,
\[ \mathcal{F}(d) \geq \sum_{l,j,l} \text{tr}_{j,l}((D_\gamma - 1)d) + \sum_{l,j,l} \text{tr}_{j,l}((D_\gamma, \chi - 1)d)) - c^{-2} D[\rho_Z^{TF}] \] (26)
where $\text{tr}_{j,l}$ denotes the trace in $\mathfrak{h}_{j,l}$ (see Appendix 6). This is true, since the projections $\Lambda_\#$ commute with the projections $\Pi_{j,l}$ onto $\mathfrak{h}_{j,l}$, i.e.,
\[ \Pi_{j,l} \Lambda_\# = \Lambda_\# \Pi_{j,l}. \] (27)
We will make use of the parameter $L$ later so that we get the desired lower bound.

### 3.1. Shift from Furry to Thomas–Fermi picture.

To prove a lower bound we use a uniform estimate on the difference between the Furry and the Thomas–Fermi picture.

**Lemma 3.** Assume $\gamma < 1$. Then for every state $\psi \in \Lambda_\gamma H^1(\mathbb{R}^3, \mathbb{C}^4)$
\[ 0 \geq \langle \psi, [D_\gamma, \chi - 1 - \Lambda_\gamma, \chi (D_\gamma, \chi - 1) \Lambda_\gamma, \chi] \psi \rangle \geq -\frac{\pi^2 + B(\frac{1}{4}, \frac{1}{2})^2}{4\pi^2 (1 - \gamma^2)} \|\chi\|_2^2 \|\psi\|^2 \] (28)

Note that the lemma generalizes to more general positive operators $\chi$. Note also that we give an explicit constant in terms of the Beta function although the specific value is not relevant for our purposes.
Proof. The expression to be estimated can be written as a manifestly negative term
\[ 0 \geq \langle \psi, (D_{r,\chi} - \Lambda_{r,\chi}^+) \psi \rangle = \langle \psi, (\Lambda_{r} - \Lambda_{r,\chi}^+)(D_{r,\chi} - \Lambda_{r,\chi}^+) (\Lambda_{r} - \Lambda_{r,\chi}^+) \psi \rangle. \]
(In our convention the negative part \( A_- \) of a self-adjoint operator \( A \) is negative.) By the usual integral representation for \( \text{sgn}(x) \), the resolvent identity, and the spectral theorem we get
\[
\langle \psi, (\Lambda_{r} - \Lambda_{r,\chi}^+)(D_{r,\chi} - \Lambda_{r,\chi}^+) (\Lambda_{r} - \Lambda_{r,\chi}^+) \psi \rangle
= \frac{1}{4\pi^2} \int_{\mathbb{R}^2} d\mu \, d\nu \langle \psi, \frac{1}{D_{r} + i\mu} \chi \frac{1}{D_{r,\chi} - + i\nu} \chi \frac{1}{D_{r} + i\nu} \rangle
\leq \left( \frac{1}{2\pi} \int_{\mathbb{R}} d\nu \, \|D_{r,\chi} - \chi\| \chi \| \Lambda_{r} \psi \| \right)^2 \leq \left( \frac{1}{2\pi} \int_{\mathbb{R}} d\nu \, \| \chi \| \| \psi \| \right)^2 \leq \left( \frac{1 - \gamma^2}{2\pi} \int_{\mathbb{R}} d\nu \, \| \chi \| \| \psi \| \right)^2 \leq (1 - \gamma^2)^{-1/2} \| \chi \|_{\infty} \| \psi \|^2
\]
using the Schwarz inequality in the first estimate.
A similar estimate yields
\[
\langle \psi, (\Lambda_{r} - \Lambda_{r,\chi}^+)\Lambda_{r,\chi}^+ (\Lambda_{r} - \Lambda_{r,\chi}^+) \psi \rangle \leq \frac{1}{4} (1 - \gamma^2)^{-1} \| \chi \|^2_{\infty}.
\]
\[\square\]

3.2. Lower bound in the Thomas–Fermi picture. Lemma 3 and (26) allow to write
\[
\mathcal{E}_r^N[\psi]/c^2 \geq \sum_{l=0}^{L-1} \sum_{j=l+\frac{1}{2}, j \geq 0} \text{tr}_{j,l}(\Lambda_{r} (D_{r} - 1) \Lambda_{r}) - C \frac{Z^{8/3} N}{c^4}
+ \sum_{l=L}^{N} \sum_{j=l+\frac{1}{2}, j \geq 0} \text{tr}_{j,l}(\Lambda_{r,\chi} (D_{r,\chi} - 1) \Lambda_{r,\chi}) - c^{-2} D(\rho_{r,\chi}^{\text{TF}}, \rho_{r}^{\text{TF}}).
\]
By the min-max principle for operators with spectral gaps [39], we have
\[
\lambda_{n,j,l,m}(\Lambda_{r,\chi} (D_{r,\chi} - 1) \Lambda_{r,\chi}) \geq \lambda_{n,j,l,m}(\Lambda_{0} (D_{r,\chi} - 1) \Lambda_{0})
\]
for \( l \geq 1 \) and \( \gamma < 1 \). This holds, since the variational principle of Griesemer et al. [39, Theorem 1] is applicable to Dirac operators with radial potential with Coulomb singularities restricted to angular momentum channels. In fact the critical condition
\[
\| (|D_{0}| + 1)^{1/2} \Lambda_{0} \Lambda_{r,\chi} (|D_{0}| + 1)^{-1/2} \|_{j,l} < 1
\]
of [39, Theorem 1] is true for an increasing range of coupling constants as the angular momentum \( j \) increases where \( \| \cdot \|_{j,l} \) denotes the operator norm in angular momentum channel \( j, l \). For our purposes it is enough to note that it is true, if \( j \geq \frac{3}{2} \), which is readily seen copying the proof of [39, Theorem 2] and replacing the usual Hardy inequality
\[
p^2 \geq \frac{1}{4|x|^2}
\]
(30)
by Hardy’s inequality for eigenfunctions of the angular momentum operator $\mathbf{L}$ with eigenvalue $l'$,

$$ p^2 \geq \frac{(l' + \frac{1}{2})^2}{|x|^2}, \quad (31) $$

i.e.

$$ p^2 \geq \frac{j^2}{|x|^2}, \quad (32) $$

in the subspaces $\mathfrak{h}_{j,l}$. Note that although the subspaces $\mathfrak{h}_{j,l}$ are not eigenspaces of $\mathbf{L}$, they only contain functions with orbital angular momentum larger than $j - \frac{1}{2}$.

Therefore,

$$ E_{N}^N[\psi]/c^2 \geq \sum_{l=0}^{L-1} \sum_{j=\pm \frac{1}{2}, j \geq 0} \text{tr}_{j,l}[\Lambda_\gamma(D_\gamma - 1)\Lambda_\gamma] - C\frac{Z^{8/3}N}{c^4} \quad + \sum_{l=L}^{N} \sum_{j=\pm \frac{1}{2}, j \geq 0} \text{tr}_{j,l}[\Lambda_0(D_\gamma + \chi - 1)\Lambda_0] - c^{-2}D[\rho^\text{TF}\!_Z]. \quad (33) $$

Note that the detour via the projections $\Lambda_\gamma,\chi$ was central to our argument, since although we have

$$ \lambda_{n,j,l,m}(\Lambda_\gamma(D_\gamma - 1)\Lambda_\gamma) \geq \lambda_{n,j,l,m}(\Lambda_0(D_\gamma - 1)\Lambda_0). \quad (34) $$

by the same arguments as above, it is however not clear whether

$$ \lambda_{n,j,l,m}(\Lambda_\gamma(D_\gamma,\chi - 1)\Lambda_\gamma) \geq \lambda_{n,j,l,m}(\Lambda_0(D_\gamma,\chi - 1)\Lambda_0), \quad (35) $$

because of the (albeit small) perturbation $\chi$.

### 3.3. Difference between Schrödinger and Brown–Ravenhall energies

We now compare the lower bound in (33) with the non-relativistic atomic energy, which as the proof of the Scott correction for the Brown–Ravenhall operator in [35] shows, is given—for $N = Z$ and $L = [Z^{1/9}]$—by

$$ E_S(Z) = -2 \sum_{l=0}^{L-1} (2l + 1) \sum_{n=1}^\infty \frac{Z^2}{2(n+l)^2} - D[\rho^\text{TF}\!_Z] \quad + c^2 \sum_{l=L}^{Z} \sum_{j=\pm \frac{1}{2}, j \geq 0} \text{tr}_{j,l}[\Lambda_0(D_\gamma,\chi - 1)\Lambda_0] + O(Z^{5/3}), \quad (36) $$

i.e., replacing for large angular momenta $l \geq L$ the non-relativistic, screened one-particle operator in [35, Proposition 4.1] with the corresponding Brown–Ravenhall operator does not give a significant contribution to the total energy [35, Theorem 3.1]. Again note that although [35, Theorem 3.1] was formulated only for coupling constants $\gamma \leq \gamma^B_{\text{crit}}$, for all angular momenta higher than the lowest one it holds for all $\gamma < 1$. This is easily verified by copying the proof using (32) instead of the classical Hardy inequality. Thus
Theorem 2 [35, Theorem 3.1]. There exists a constant $C < \infty$ such that for any $\gamma \leq 1$ $v : [0, \infty) \to [0, \infty)$, satisfying
\[
v(r) \leq \frac{\gamma}{r}, \tag{37}\]
any $\mu > 0$ and any $l \in \mathbb{N}$, $j = l \pm \frac{1}{2}$ one has
\[
\text{tr}_{j,l} \left[ \Lambda_0 (D_0 - v(|x|)) \Lambda_0 - 1 + \mu \right] - \text{tr}_{l} \left[ \frac{p^2}{2} - v(|x|) + \mu \right] \leq C \frac{\gamma^4}{j^2}. \tag{38}\]

Combining (33) (with $N$ set to $Z$) and (36) with the known asymptotic expansion of the non-relativistic ground state energy gives the desired lower bound for the Furry Hamiltonian,
\[
E_{\gamma}^{Z}[\psi] - E_{S}(Z) \geq c^2 \sum_{l=0}^{L-1} \sum_{j=l \pm \frac{1}{2}, j \geq 0} \text{tr}_{j,l} \left[ (\Lambda_\gamma (D_\gamma - 1) \Lambda_\gamma ) \right] - \sum_{l=0}^{L-1} \sum_{n=1}^{\infty} \frac{(2l+1)Z^2}{(n+l)^2} - CZ^{5/3}
\]
\[
= c^2 \sum_{l=0}^{L-1} \sum_{j=l \pm \frac{1}{2}, j \geq 0} (2j+1) \sum_{n=1}^{\infty} (\lambda_{\gamma,n,l,j} - \lambda_{\gamma,n,l,j}^{S}) - CZ^{5/3}
\]
\[
= c^2 \sum_{l=0}^{\infty} \sum_{j=l \pm \frac{1}{2}, j \geq 0} (2j+1) \sum_{n=1}^{\infty} (\lambda_{\gamma,n,l,j} - \lambda_{\gamma,n,l,j}^{S}) - CZ^2 L^{-1}.
\]

In particular, we see that large angular momenta do not contribute to the change of the $Z^2$ correction. This is a direct consequence of the fact that the differences are absolutely summable by Lemma 1. The only change comes from the low lying eigenvalues of low angular momenta. Their difference is—to leading order—the renormalized energy, i.e., the change of the total energy from the non-relativistic to the relativistic ground state energy.

4. Upper Bound on the Energy

In this section we will derive a sufficient decay of the difference of the Furry and Brown–Ravenhall operators when restricted to angular momentum $l$. For high angular momenta, up to an error of lower order the Furry picture will then be replaced by the Brown–Ravenhall picture which in turn was shown to give the correct upper bound in [35]. We will frequently use the following inequality.

Lemma 4. Assume $j \geq \frac{3}{2}$ and $\gamma \leq 1$. By $\| \cdot \|_{j,l}$ we denote the operator norm in $\mathcal{F}_{j,l}$. Then we have
\[
\left\| |D_0|^{-\frac{1}{2}} |D_\gamma|^{-\frac{1}{2}} \right\|_{j,l} \leq \sqrt{\frac{j}{j - \gamma}}. \tag{39}\]
\textbf{Proof.} Note that \(|D_0| = \sqrt{p^2 + 1}\) and

\[
\left\| D_0^{1/2} D_\gamma^{-1/2} \right\|_{j,l} = \sup_{\psi \in \Pi_{j,l} C_0^\infty(\mathbb{R}^3, \mathbb{C}^4)} \frac{\left\| D_0^{1/2} \psi \right\|_2}{\left\| D_\gamma^{-1/2} \psi \right\|_2}.
\]  

(40)

Squaring the operators and using (32) yields

\[
\left\| D_\gamma \psi \right\| = \left\| (D_0 - \frac{\gamma}{|x|}) \psi \right\| \geq \left\| D_0 \psi \right\| - \left\| \frac{\gamma}{|x|} \psi \right\| \geq (1 - \frac{\gamma}{j}) \left\| D_0 \psi \right\|.
\]  

(41)

The claim follows from the operator monotony of the square root. \(\Box\)

4.1. Estimate on the electric potential. We will now show that for high angular momenta the expectation value of the potential in the Furry picture is close to that in the Brown–Ravenhall picture.

\textbf{Lemma 5.} Let \(j \geq \frac{3}{2}\), \(\psi \in \Pi_{j,l} H^1(\mathbb{R}^3, \mathbb{C}^4), -\frac{1}{|x|} \leq \phi(x) \leq \frac{1}{|x|}, \gamma < 1\). Then

\[
|\langle \psi, (\Lambda_\gamma \phi \Lambda_\gamma - \Lambda_0 \phi \Lambda_0) \psi \rangle| \leq \frac{C}{l^{1/2}} \langle \psi, p^2 \psi \rangle.
\]  

(42)

\textbf{Proof.} The proof follows loosely the arguments found in [39].

One has

\[
\left| \langle \psi, (\Lambda_\gamma \phi \Lambda_\gamma - \Lambda_0 \phi \Lambda_0) \psi \rangle \right| \\
\leq \frac{2}{l} \left| \langle \psi, (\Lambda_\gamma - \Lambda_0 \phi \Lambda_0) \psi \rangle \right| + \left| \langle \psi, (\Lambda_\gamma - \Lambda_0) \phi (\Lambda_\gamma - \Lambda_0) \psi \rangle \right|. 
\]  

(43)

The second resolvent identity gives

\[
\Lambda_0 - \Lambda_\gamma = -\frac{\gamma}{2\pi} \int_{-\infty}^{\infty} dz \frac{1}{D_0 - iz} \frac{1}{|x|} \frac{1}{D_\gamma - iz} \\
= -\frac{\gamma}{\pi} \int_{0}^{\infty} dz \frac{1}{D_0^2 + z^2} \left( D_0 \frac{1}{|x|} D_\gamma - \frac{z^2}{|x|} \right) \frac{1}{D_\gamma^2 + z^2}.
\]  

(44)

Term I:

\[
\left| \langle \psi, (\Lambda_\gamma - \Lambda_0) \phi \Lambda_0 \psi \rangle \right| \\
= \left| \langle \psi, \frac{\gamma}{\pi} \int_{0}^{\infty} dz \frac{1}{D_0^2 + z^2} \left( D_0 \frac{1}{|x|} D_\gamma - \frac{z^2}{|x|} \right) \frac{1}{D_\gamma^2 + z^2} \phi \Lambda_0 \psi \rangle \right|. 
\]  

(45)
The first summand on the right side of (45) is estimated as follows
\[
\left| \frac{\psi}{\pi} \int_0^\infty dz \frac{1}{D_0^2 + z^2} D_0 \frac{1}{|x|} D_\gamma \frac{1}{D_\gamma^2 + z^2} \phi \Lambda_0 \psi \right|
\leq \frac{\gamma}{\pi} \left[ \int_0^\infty dz \left| \frac{1}{|x|} D_0 \frac{1}{D_0^2 + z^2} \psi \right|^2 \right]^{1/2} \left[ \int_0^\infty dz \left| D_\gamma \frac{1}{D_\gamma^2 + z^2} \phi \Lambda_0 \psi \right|^2 \right]^{1/2}. \tag{46}
\]

Note that
\[
\int_0^\infty dz \frac{1}{(1 + z^2)^2} = \int_0^\infty dz \frac{z^2}{(1 + z^2)^2} = \frac{\pi}{4}. \tag{47}
\]

Thus, using (32)
\[
\left[ \int_0^\infty dz \left| \frac{1}{|x|} D_0 \frac{1}{D_0^2 + z^2} \psi \right|^2 \right]^{1/2} \leq \frac{1}{j^2} \left[ \int_0^\infty dz \left| \psi \right|^2 \right]^{1/2} \leq \frac{\pi}{4j^2} \left\| \psi \right\|^2. \tag{48}
\]

Similarly,
\[
\left[ \int_0^\infty dz \left| D_\gamma \frac{1}{D_\gamma^2 + z^2} \phi \Lambda_0 \psi \right|^2 \right]^{1/2} \leq \frac{\pi}{4j^2} \left\| \phi \Lambda_0 \psi \right\|^2. \tag{49}
\]

where the last line uses Hardy’s inequality.

The second summand of (45)
\[
\left| \frac{\psi}{\pi} \int_0^\infty dz \frac{1}{D_0^2 + z^2} \frac{z^2}{|x|} D_\gamma \frac{1}{D_\gamma^2 + z^2} \phi \Lambda_0 \psi \right|
\leq \frac{\gamma}{\pi} \left[ \int_0^\infty dz \left| \frac{z^2}{|x|} D_\gamma \frac{1}{D_\gamma^2 + z^2} \psi \right|^2 \right]^{1/2} \left[ \int_0^\infty dz \left| D_\gamma \frac{1}{D_\gamma^2 + z^2} \phi \Lambda_0 \psi \right|^2 \right]^{1/2} \tag{50}
\]

The first factor on the right side is estimated similarly as in (48); the second factor is estimated similarly as in (49) with the same results. Putting everything together gives
\[
I \leq \frac{\gamma}{2j(j - 1)} \left\| \psi \right\|^2. \tag{51}
\]

Term II: The square root of II is
\[
\left| \frac{\psi}{\pi} \int_0^\infty dz \frac{1}{D_0^2 + z^2} \frac{z^2}{|x|} D_\gamma \frac{1}{D_\gamma^2 + z^2} \phi \Lambda_0 \psi \right|
\leq \frac{1}{j^2} \sup_{h \in \beta_{j,l}} \left| \int_0^\infty dz \left| p \right|^2 \left( \frac{1}{|\lambda_\gamma - \Lambda_0|} \left| \frac{D_\gamma}{|x|} D_0 - \frac{z^2}{|x|} \right| \right) \frac{1}{D_0^2 + z^2} \psi \right|. \tag{52}
\]
using (44) in the last step. The second term of the right side yields

\[
\left| \langle h, \int_0^\infty dz |p|^{1/2} \frac{1}{D_\gamma^2 + z^2} |x| D_0^2 + z^2 \psi \rangle \right|
\]

\[
\leq \left[ \int_0^\infty \left\| \frac{z}{D_\gamma^2 + z^2} |p|^{1/2} h \right\|^2 \frac{1}{|x| D_0^2 + z^2} \psi \right]^{1/2} \left[ \int_0^\infty \left\| \frac{1}{|x| D_0^2 + z^2} \psi \right\|^2 \frac{1}{D_\gamma^2 + z^2} \right]^{1/2}
\]

\[
\leq \frac{\sqrt{\pi}}{2j} \left\| \frac{1}{|D_\gamma|^2} |p|^{1/2} h \right\| \left[ \int_0^\infty \left\| \frac{z}{D_\gamma^2 + z^2} \psi \right\|^2 \frac{1}{D_0^2 + z^2} \psi \right]^{1/2}
\]

\[
\leq \frac{\pi}{4\sqrt{j}(j-1)} \|h\| \left\| \frac{1}{|D_0|^2} |p| \psi \right\| \leq \frac{\pi}{4\sqrt{j}(j-1)} \|p\| \psi .
\] (53)

The first term can be treated analogously.

Summing I and II yields the claimed estimate since \( j + \frac{1}{2} \geq l \geq j - \frac{1}{2} \) in \( \mathcal{H}_{j,l} \).

4.2. Estimate on the projected Dirac–Coulomb operator. We will need a similar estimate for the expectation value of the Dirac operator \( D_\gamma \).

**Lemma 6.** Assume \( \gamma \in [0, 1], j \geq \frac{3}{2} \) and \( \psi \in \Pi_{l,j} \Lambda_0 H^1(\mathbb{R}^3, \mathbb{C}^4) \). Then

\[
0 \leq \langle \psi, \Lambda_\gamma(D_\gamma - 1)\Lambda_\gamma \psi \rangle - \langle \psi, (D_\gamma - 1)\Lambda_\gamma \psi \rangle \leq \frac{C}{2l^2} \langle \psi, p^2 \psi \rangle.
\] (54)

**Proof.** Observe that

\[
\langle \psi, \Lambda_\gamma(D_\gamma - 1)\Lambda_\gamma \psi \rangle = \langle \psi, \Lambda_0 \Lambda_\gamma(D_\gamma - 1)\Lambda_\gamma \Lambda_0 \psi \rangle
\]

\[
= \langle \psi, \Lambda_0(1 - \Lambda_\gamma^\perp)(D_\gamma - 1)(1 - \Lambda_\gamma^\perp)\Lambda_0 \psi \rangle
\]

\[
= \langle \psi, \Lambda_0(D_\gamma - 1)\Lambda_0 \psi \rangle - \langle \psi, \Lambda_0\Lambda_\gamma^\perp(D_\gamma - 1)\Lambda_\gamma^\perp \Lambda_0 \psi \rangle
\]

\[
= \langle \psi, \Lambda_0(D_\gamma - 1)\Lambda_0 \psi \rangle
\]

\[
- \langle \psi, (\Lambda_0 - \Lambda_\gamma)([D_\gamma] - 1)(\Lambda_0 - \Lambda_\gamma) \psi \rangle.
\]

First of all, we note that

\[
[D_\gamma] - 1 < 0
\] (55)

which allows us to make the crude estimates

\[
|\left[ D_\gamma \right] - 1| = -\left[ D_\gamma \right] + 1 \leq |D_\gamma| + 1 \leq (1 + \frac{1}{\sqrt{1 - \gamma^2}})|D_\gamma|.
\] (56)

Hence,

\[
|\langle \psi, (\Lambda_0 - \Lambda_\gamma)([D_\gamma] - 1)(\Lambda_0 - \Lambda_\gamma) \psi \rangle| \leq (1 + \frac{1}{\sqrt{1 - \gamma^2}})\|D_\gamma\|^2 \|\Lambda_0 - \Lambda_\gamma\| \psi^2.
\]
Now,
\[
A := \| | D_\gamma | \| \left( \Lambda_0 - \Lambda_\gamma \right) \psi \| = \frac{\gamma}{2\pi} \int_{-\infty}^{+\infty} dv \| | D_\gamma | \| \left( \frac{1}{D_\gamma + \imath v} - \frac{1}{D_0 + \imath v} \right) \psi \|
\]
\[
\leq \frac{\gamma}{2\pi} \int_{-\infty}^{+\infty} dv \| | D_\gamma | \| \left( \frac{1}{D_\gamma + \imath v} \right) \| \left( \frac{1}{D_0 + \imath v} \right) \psi \|
\]
Since \( l \geq 1 \), we have \( \langle \psi, D_\gamma \psi \rangle \geq \frac{1}{\sqrt{2}} \) (see (12)) and
\[
\frac{|D_\gamma|}{D_\gamma^2 + v^2} \leq \frac{\max \{ 1/\sqrt{2}, |v| \} }{\max \{ 1/2, v^2 \} + v^2}.
\]
Using Hardy’s inequality we get
\[
A \leq \frac{\gamma}{2\pi} \int_{-\infty}^{+\infty} dv \sqrt{\max \{ 1/\sqrt{2}, |v| \} } \frac{1}{\max \{ 1/2, v^2 \} + v^2} \| | D_\gamma | \| \left( \frac{1}{D_0 + \imath v} \right) \psi \|^2
\]
\[
\leq \frac{\gamma}{2\pi} \left( \int_{-\infty}^{+\infty} dv \sqrt{\max \{ 1/\sqrt{2}, |v| \} } \frac{1}{\max \{ 1/2, v^2 \} + v^2} \int_{-\infty}^{+\infty} d\mu |\mu|^2 \| \frac{1}{D_0 + \imath \mu} \psi \|^2 \right)^{1/2}
\]
\[
\leq \frac{\gamma \sqrt{6}}{2\pi} \left( \int_{-\infty}^{+\infty} dv \max \{ 1, |v| \} \frac{1}{\max \{ 1/2, v^2 \} + v^2} \int_{-\infty}^{+\infty} d\mu |\mu|^2 \| \frac{1}{D_0 + \imath \mu} \psi \|^2 \right)^{1/2} \leq \frac{\gamma \sqrt{6}}{2\pi} \| \psi \|.
\]
\]
4.3. Inserting the trial density matrix. To finish the proof of the upper bound we will insert the trial density matrix constructed in Appendix 6 (in the correct units \( V_c^* dV_c \)) into the Hartree–Fock functional (without exchange energy)
\[
E_{HF}(d) := \text{tr} \left[ \left( c \alpha \cdot p + c^2 \beta - c^2 - \frac{Z}{|x|} \right) d \right] + D[\rho]
\] (57)
where \( \rho(x) := \text{tr}_{C^4} d(x, x) \). We will need the following auxiliary lemma on the Schrödinger energy.

Lemma 7. For \( \gamma := \frac{Z}{c} < 1 \) and \( d \) as defined in (103)
\[
E_S(Z) \geq \text{tr}[\left( \frac{p^2}{2} - \frac{Z}{|x|} d^5 \right)] + \text{tr}[\left( c \alpha \cdot p + c^2 \beta - c^2 - \frac{Z}{|x|} \right) d^\phi] + D[\rho^>] + O(Z^{47/24})
\] (58)
with
\[
\rho^>(x) := \text{tr}_{C^4} (d^\phi (x, x)).
\]
Proof. We recall, following [34] and [66, Proposition 4],
\[ E_S(Z) = \text{tr}[\frac{\mathbf{p}^2}{2} - \frac{Z}{|\mathbf{x}|}]dS + D[\rho^S] + \mathcal{O}(Z^{47/24}) \]  
(59)
where \( \rho^S(\mathbf{x}) := \text{tr}_{C^2}(dS(\mathbf{x}, \mathbf{x})) = \text{tr}_{C^2}(d^S_>(\mathbf{x}, \mathbf{x})) + \text{tr}_{C^2}(d^<_>(\mathbf{x}, \mathbf{x})) \). We drop the Coulomb interaction between orbitals with small angular momenta and the total density, since it is positive. Furthermore, by [35, Lemma 4.7.], it holds
\[ D(\rho^\varphi) = \mathcal{O}(Z^5/3). \]  
(60)
Note that in the reference the statement is given in terms of the transform \( U_c(A) := \Phi_0(p/c)A\Phi_0(p/c) + \Phi_0(p/c)A\Phi_0(p/c) \) and the density
\[ \rho_{U^\varphi}(\mathbf{x}) := \text{tr}_{C^2}(U_c(d^\varphi)(\mathbf{x}, \mathbf{x})). \]  
(61)
However,
\[ \rho_{U^\varphi} \equiv \rho^\varphi_\Phi. \]  
(62)
Finally, by Frank et al. [35, Lemma 4.6.]
\[ \text{tr}[\frac{Z}{|\mathbf{x}|}d^\varphi_\Phi] - \text{tr}[\frac{Z}{|\mathbf{x}|}d^\varphi] = \mathcal{O}(Z^{23/12}) \]  
(63)
and the observation that
\[ \text{tr}[(c\alpha \cdot \mathbf{p} + c^2\beta - c^2)d^\varphi_\Phi] = \text{tr}[(\sqrt{c^2\mathbf{p}^2 + c^4} - c^2)d^\varphi] \leq \frac{1}{2}\text{tr}[\mathbf{p}^2d^\varphi] \]  
(64)
we conclude the proof. \( \square \)

Trivially, the reduced Hartree–Fock functional \( E_{HF} \) as defined above gives an upper bound on the ground state energy for any density matrix in the electron subspace with finite kinetic energy, i.e.,

**Proposition 1.** Assume \( Z/c < 1 \) and \( d, D_0d \in C^1(L^2(\mathbb{R}^3 : \mathbb{C}^4)), \text{tr}(\lambda_{Z,c}d) \leq Z, \) and \( 0 \leq d \leq 1. \) Then
\[ E_Y(Z) = E_{HF}(\Lambda_{Z,c}d\Lambda_{Z,c}) \]

where
\[ \Lambda_{Z,c} := \mathbb{1}_{(0,\infty)}(c\alpha \cdot \mathbf{p} + c^2\beta - Z/|\mathbf{x}|). \]  
(65)
Combining Lemma 7, Proposition 1, and the positivity of the Coulomb energy we find
\[ E_Y(Z) - E_S(Z) \leq \text{tr}[(c\alpha \cdot \mathbf{p} + c^2\beta - c^2 - Z/|\mathbf{x}|)\Lambda_{Z,c}d^\varphi] - \text{tr}[(\mathbf{p}^2/2 - Z/|\mathbf{x}|)d^S_\varphi] \]  
(66)
\[ + \text{tr}[(c\alpha \cdot \mathbf{p} + c^2\beta - c^2 - Z/|\mathbf{x}|)(\Lambda_{Z,c}d^\varphi_\Phi - d^\varphi_\Phi)] \]  
(67)
\[ + D(\rho^F - \rho^\varphi_\Phi, \rho^F + \rho^\varphi_\Phi) + \mathcal{O}(Z^{47/24}). \]  
(68)
Moreover, we write
\[
D(\rho^F - \rho_\geq, \Phi, \rho^F_\geq + \rho_\geq, \Phi) = D(\rho^F_\geq - \rho_\geq, \Phi, \rho^F_\geq + \rho_\geq, \Phi) + D(\rho^F_\leq, \rho^F_\leq) =: R_2
\]
(69)
with
\[
\rho^F_\leq(x) := \text{tr}_C((\Lambda_{Z,c}d_\leq \Lambda_{Z,c})(x, x)) = \text{tr}_C(d_\leq(x, x))
\]
and
\[
\rho^F_\geq(x) := \text{tr}_C((\Lambda_{Z,c}d_\geq, \Phi \Lambda_{Z,c})(x, x)).
\]
(70)

We will see that the first term on the right side of Inequality (66) yields the Scott correction. In the following we will prove that the error terms \( R_1, R_2, \) and \( R_3 \) are negligible.

**Lemma 8.** As \( Z \to \infty \)
\[
R_1 = \text{tr}[(c\alpha \cdot p + c^2 \beta - c^2 - \frac{Z}{|x|})\Lambda_{Z,c}d_\geq, \Phi] = O(Z^{23/12})
\]
(72)
uniformly in \( \gamma \in [0, 1) \).

**Proof.** By Lemmata 5 and 6 and the scaling behavior of the map \( V_c \) we have
\[
0 \leq \text{tr}[(c\alpha \cdot p + c^2 \beta - c^2 - \frac{Z}{|x|})\Lambda_{Z,c}d_\geq, \Phi] - \text{tr}[(c\alpha \cdot p + c^2 \beta - c^2 - \frac{Z}{|x|})d_\geq, \Phi] \leq \sum_l \frac{C}{l^2} \text{tr}_l[p^2 d_\geq]
\]
(73)
The result follows from Lemma 12 (see Appendix 6).

Likewise we can show that \( R_2 \) is negligible.

**Lemma 9.** As \( Z \to \infty \)
\[
D(\rho^F_\geq - \rho_\geq, \Phi, \rho^F_\geq + \rho_\geq, \Phi) = O(Z^{23/12}).
\]
(74)
uniformly in \( \gamma \in [0, 1) \).

**Proof.** By Newton’s theorem and, in the last step, Lemma 5 and scaling,
\[
D(\rho^F_\geq - \rho_\geq, \Phi, \rho^F_\geq + \rho_\geq, \Phi) \leq \frac{1}{2} \int (\rho^F_\geq(x) + \rho_\geq, \Phi(x)) \text{d}x \int \frac{\rho^F_\leq(x) - \rho_\geq, \Phi(x)}{|x|} \text{d}x
\]
\[
\leq Z \text{tr}[\frac{1}{|x|}((\Lambda_{Z,c}d_\leq, \Phi \Lambda_{Z,c} - d_\geq, \Phi)] \leq \sum_l \frac{C}{l^2} \text{tr}_l[p^2 d_\geq].
\]
(75)
The lemma follows again from Lemma 12.

It remains the error estimate for \( R_3 \).
**Lemma 10.** As $Z \to \infty$

$$D(\rho_{<}^{F}, \rho_{>}^{F} + \rho_{<}^{F}) = \mathcal{O}(Z^{11/6})$$

(76)

*uniformly in $\gamma \in [0, 1]$.*

**Proof.** Again, by Newton’s theorem,

$$D(\rho_{<}^{F}, \rho_{>}^{F} + \rho_{<}^{F}) \leq \frac{1}{2} \int (\rho_{<}^{F}(x) + \rho_{>}^{F}(x)) dx \int \frac{\rho_{<}^{F}(x)}{|x|} dx \leq Z \int \frac{\rho_{<}^{F}(x)}{|x|} dx.$$  (77)

The Coulomb energy of the electrons with low angular momenta can be estimated with help of Lemma 2 and scaling

$$\int \frac{\rho_{<}^{F}(x)}{|x|} dx = \text{tr}[\frac{1}{|x|} d<] = \sum_{l=0}^{L-1} \sum_{j \geq \frac{1}{2}, j \neq l \pm \frac{1}{2}} \sum_{m=-j}^{j} \sum_{n=1}^{K-l} \langle \psi_{j,l,m,n}, \frac{1}{|x|} \psi_{j,l,m,n} \rangle$$

$$\leq \sum_{l=0}^{L-1} \sum_{j \geq \frac{1}{2}, j \neq l \pm \frac{1}{2}} \sum_{m=-j}^{j} \sum_{n=1}^{K-l} \frac{CZ}{(n+l)^2}$$

$$\leq CZ \sum_{l=0}^{L-1} (2l+1) \sum_{n=1}^{K-l} \frac{1}{(n+l)^2} \leq CL^2 K^{-1} Z = \mathcal{O}(Z^{5/6}).$$  (78)

□

5. Finishing the Proof

In the previous section we proved

$$E_{\gamma}(Z) - E_{S}(Z)$$

$$\leq \text{tr}[(c\alpha \cdot p + c^2 \beta - c^2 - \frac{Z}{|x|}) \Lambda_{Z,\gamma} d<] - \text{tr}[(\frac{p^2}{2} - \frac{Z}{|x|}) d<] + \mathcal{O}(Z^{47/24}).$$  (79)

Upon scaling with the map $V_{c^{-1}}$ we have

$$\text{tr}[(c\alpha \cdot p + c^2 \beta - c^2 - \frac{Z}{|x|}) \Lambda_{Z,\gamma} d<] - \text{tr}[(\frac{p^2}{2} - \frac{Z}{|x|}) d<]$$

$$= \frac{Z^2}{\gamma^2} \sum_{l=0}^{L-1} \sum_{j \geq \frac{1}{2}, j \neq l \pm \frac{1}{2}} (2j+1) \sum_{n=1}^{K-l} (\lambda_{\gamma,n,l,j} - \lambda_{\gamma,n,l} - \lambda_{\gamma,n,l,j} - \lambda_{\gamma,n,l}) = Z^2 s_{\gamma}^{D}(\gamma) + R_4 + R_5$$  (80)

with $s_{\gamma}^{D}(\gamma)$ defined in (9) and

$$R_4 := \frac{Z^2}{\gamma^2} \sum_{l=0}^{L-1} \sum_{j \geq \frac{1}{2}, j \neq l \pm \frac{1}{2}} (2j+1) \sum_{n=K-l+1}^{\infty} (\lambda_{\gamma,n,l} - \lambda_{\gamma,n,l,j})$$  (81)
and
\[ R_5 := Z^2 \gamma^{-2} \sum_{l=L}^{\infty} \sum_{j \geq \frac{1}{2}, j = l \pm \frac{1}{2}} (2j + 1) \sum_{n=1}^{\infty} (\lambda_{\gamma,n,l}^S - \lambda_{\gamma,n,l,j}^D). \]  

(82)

By Corollary 1, for every \( \gamma \in [0, 1) \) there exists a constant \( C > 0 \) such that
\[ R_4 \leq C Z^2 \gamma^{-2} \sum_{l=0}^{L-1} \sum_{j \geq \frac{1}{2}, j = l \pm \frac{1}{2}} (2j + 1) \sum_{n=K-l+1}^{\infty} \frac{\gamma^4}{(n+l)^3} \leq C \gamma^2 Z^2 L K^{-2} = \mathcal{O}(Z^{17/12}). \]

(83)

Similarly,
\[ R_5 \leq C \gamma^2 Z^2 \sum_{l=0}^{\infty} \sum_{n=K-l+1}^{\infty} \frac{1}{(n+l)^3} \leq C \gamma^2 Z^2 \sum_{l=0}^{\infty} \sum_{n=1}^{\infty} \frac{1}{(n+l)^3} \leq C \gamma^2 Z^2 L^{-1} = \mathcal{O}(Z^{23/12}). \]

(84)

6. Comparison with (Semi-)Empirical Data and Schwinger’s Prediction

As described in the introduction, quantum electrodynamics is believed to describe particles interacting through electromagnetic forces, including heavy atoms. Unfortunately, the numerical evaluation of such systems seems to be beyond present techniques, not to mention the principal problem that QED is only perturbatively defined rendering the treatment of heavy neutral atoms difficult.

In view of this fact, the comparison with experimental values appears to be the only source of validation of the results. This, however, is not directly possible, since our asymptotic result requires to fix \( \alpha \alpha \). Experimentally, though, \( \alpha \) is a fixed constant of value roughly \( 1/137 \), whereas \( Z \) takes integer values up to 120.

Moreover, the published atomic ground state energies \( E_{\text{NIST}}(Z) \) in the NIST Atomic Spectra Data Base [44] are measured only to a small extent. The majority of the energies for large \( Z \) is extrapolated or computed, i.e., assumptions on underlying approximate mathematically uncontrolled models influence those data. In addition the experimental values obviously also contain other QED effects not contained in the Furry Hamiltonian defined through (3).

Thus it is not obvious that our formula for the ground state energy with \( \gamma \) replaced by \( \alpha \) should give an improved quantitative description of large atoms. Nevertheless, emboldened by Sell’s [74] principle of unreasonable utility of asymptotic expansions and its history of successful application, e.g., Lebowitz and Waisman [45] and Schwinger [62], we offer a graphical comparison of
\[ \frac{E_{\text{NIST}}(Z) - E_{\text{TF}}(Z)}{Z^2} \]
Fig. 1. Comparison of the relativistic Scott function with data taken from the NIST database [44], Dirac–Fock calculations [11] and Schwinger’s original prediction [62]

with the relativistic Scott function

\[ \frac{1}{2} - s^D(\alpha_{\text{physical}} Z) \]

in Fig. 1. Additionally we show the Dirac–Hartree–Fock calculations carried out by Desclaux [11]. Note that the Scott function is not divergent for \( Z \to \frac{1}{\alpha_{\text{physical}}} \) (as was claimed in [56]), but instead approaches the numerical value

\[ \lim_{\gamma \to 1} \left( \frac{1}{2} - s^D(\gamma) \right) \approx -1.91. \]  

(85)

Unlike the Chandrasekhar model [49] and the Brown–Ravenhall model [20,35] which give substantially too low energies and break down for \( \gamma = 2/\pi < 1 \) and \( \gamma = 2/(\pi/2 + 2/\pi) \) respectively, the Furry picture—which for numerical purposes is implemented through the Douglas–Kroll–Hess transform—does not only give stable ground state energies and good numerical values in quantum chemistry (see [58] for an extensive overview), but, as Fig. 1 shows, it also offers a step toward a quantitative correct description of heavy atoms.

We will supplement the data with Schwinger’s prediction [62] of the relativistic Scott correction which was derived from the \( \gamma^4 \) fine structure correction to the non-relativistic eigenvalues implied by the Dirac equation, i.e., the second term of the perturbative expansion of the kinetic energy

\[ \langle \psi, -\frac{p^4}{8} \psi \rangle, \]

the spin-orbit coupling

\[ \langle \psi, \frac{\gamma}{2} S \cdot L \frac{1}{|x|^3} \psi \rangle, \]
and the Darwin term
\[ \langle \psi, \frac{\pi}{2} \gamma \delta(x) \psi \rangle. \]
Together they yield
\[ \delta \lambda_{n,l,j} = \frac{\gamma^4}{-2(n+l)^3} \left( \frac{1}{j + \frac{1}{2}} - \frac{3}{4 n + l} \right) \]
(cf. (14)). Following Schwinger’s computations and using the identity
\[ \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{(m+n)^s} = \sum_{m=1}^{\infty} \frac{1}{m^s} = \zeta(s-1) - \zeta(s), \]
we obtain
\[ s_{\text{Schwinger}}^D := \frac{1}{\gamma^2} \sum_{l=0}^{\infty} \sum_{n=1}^{\infty} \sum_{j \geq \frac{1}{2}, j = l \pm \frac{1}{2}} (2j + 1) \delta \lambda_{n,l,j} \]
\[ = - \sum_{n=1}^{\infty} \frac{\gamma^2}{n^3} (1 - \frac{3}{4n}) - \sum_{l=1}^{\infty} \sum_{n=1}^{\infty} \frac{\gamma^2}{(n+l)^3} (2 - \frac{3}{4} \frac{2l+1}{n+l} \]
\[ = -\zeta(3)\gamma^2 + \frac{3}{4} \zeta(4) \gamma^2 - \frac{5}{4} \sum_{l=1}^{\infty} \sum_{n=1}^{\infty} \frac{\gamma^2}{(n+l)^3} + \frac{3}{4} \sum_{l=1}^{\infty} \sum_{n=1}^{\infty} \frac{\gamma^2}{(n+l)^4} \]
\[ = (-\zeta(3) + \frac{3}{4} \zeta(4) - \frac{5}{4} \zeta(2) + \frac{5}{4} \zeta(3) + \frac{3}{4} \zeta(3) - \frac{3}{4} \zeta(4)) \gamma^2 \]
\[ = \left( \frac{5\pi^2}{24} - \zeta(3) \right) \gamma^2 \sim -0.854 \gamma^2 \]
which resulted from an asymptotic expansion of the eigenvalues for \( \gamma \to 0. \)

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Appendix A: Thomas–Fermi Theory

We collect some well known auxiliary facts of the Thomas–Fermi density. For a more exhaustive overview see Lieb and Simon [48] and Lieb [47]. Consider the minimizer \( \rho_{TF}^Z \) of the Thomas–Fermi functional
\[ E_{TF}(\rho) = \frac{3}{5} (3\pi^2)^{\frac{2}{3}} \int_{\mathbb{R}^3} \rho(x)^{\frac{5}{3}} \, dx - \int_{\mathbb{R}^3} \frac{Z \rho(x)}{|x|} \, dx + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x) \rho(y)}{|x-y|} \, dx \, dy \]
in the set \( \mathcal{I} := \{ \rho \in L^{\frac{5}{3}} | \rho \geq 0, \ D[\rho] < \infty \} \). The infimum
\[ E_{TF}(Z) := \inf E_{TF}(\mathcal{I}) \]
is attained and \( \int \rho = Z \). Moreover

\[
E_{\text{TF}}(Z) = E_{\text{TF}}(1) Z^{7/3}. \tag{88}
\]

The Thomas–Fermi energy of hydrogen has been calculated first by Milne [53] and later by Sommerfeld [73] reducing it to the slope of the Thomas–Fermi potential at zero, i.e., Baker’s constant and has the value

\[
E_{\text{TF}}(1) \sim -0.768745[\text{Ha}]. \tag{89}
\]

**Lemma 11** (Properties of the Thomas–Fermi density). The Thomas–Fermi density \( \rho_{Z}^{\text{TF}} \) and its mean-field potential \( V_{Z} := \rho_{Z}^{\text{TF}} \ast \frac{1}{|\cdot|} \) satisfy

\[
\begin{align*}
(1) & \quad \| V_{Z} \|_{\infty} \leq CZ^{\frac{3}{2}} \text{ for some constant } C > 0, \\
(2) & \quad |p V_{Z}| \leq \frac{CZ^{\frac{3}{2}}}{|x|}, \\
(3) & \quad |p^{2} V_{Z}| = |\rho_{Z}^{\text{TF}}| \leq \frac{CZ^{\frac{3}{2}}}{|x|^{2}}.
\end{align*}
\]

This is easily verified by using the scaling relation of the Thomas–Fermi density \( \rho_{Z}^{\text{TF}}(x) = Z^{2} \rho_{1}^{\text{TF}}(Z^{\frac{3}{2}}x) \) and the Thomas–Fermi equation

\[
\frac{1}{2} \left( \frac{3}{2} \pi \right)^{\frac{3}{2}} (\rho_{Z}^{\text{TF}})^{\frac{3}{2}} = \frac{Z}{|\cdot|} - V_{Z}. \tag{90}
\]

**Appendix B: 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 (see, e.g., [35]).

We denote by \( Y_{l,m} \), the normalized spherical harmonics on the unit sphere \( S^{2} \) (see, e.g., [52], 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

\[
\Omega_{j,l,m}(\omega) := \begin{cases} 
\sqrt{\frac{j+m}{2j}} Y_{l,m-\frac{1}{2}}(\omega) & \text{if } j = l + \frac{1}{2}, \\
\sqrt{\frac{j-m}{2j}} Y_{l,m+\frac{1}{2}}(\omega) & \text{if } j = l - \frac{1}{2}.
\end{cases} \tag{91}
\]

The set of admissible indices is \( \mathcal{I} := \{(j,l,m) \mid j \in \mathbb{N} - 1/2, l = j \pm 1/2, m = -j, \ldots, j \} \). It is known that the functions \( \Omega_{j,l,m} \) form an orthonormal basis of the Hilbert space \( L^{2}(S^{2}; \mathbb{C}^{2}) \). They are joint eigenfunctions of \( J_{2} \), \( L_{2} \), and \( J_{3} \) 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 \( J_{2} \) with eigenvalue \( j(j+1) \) and angular momentum \( L_{2} \) with eigenvalue \( l(l+1) \) is given by

\[
\mathfrak{h}_{j,l,m} = \text{span}\{ x \mapsto |x|^{-1} f(|x|) \Omega_{j,l,m}(\omega_{x}) \mid f \in L^{2}(\mathbb{R}_{+}) \}.
\]
where \( \omega_x := x/|x| \). This leads to the orthogonal decomposition

\[
\mathcal{H} = \bigoplus_{j \in \mathbb{N}_0 + \frac{1}{2}} \bigoplus_{l = j \pm 1/2} \mathcal{H}_{j,l}, \quad \mathcal{H}_{j,l} = \bigoplus_{m = -j}^{j} \mathcal{H}_{j,l,m},
\]  

(92)
of the Hilbert space of two spinors.

Note the identity (see, e.g., Greiner [38])

\[
(\sigma \cdot \omega_x) \Omega_{j,l,m}(\omega_x) = -\Omega_{j,2j-l,m}(\omega_x).
\]  

(93)

Furthermore for fixed \( l \)

\[
\dim_I(\{\Omega_{j,l,m}, (j, l, m) \in \mathcal{I}\}) = 2(2l + 1).
\]  

(94)

In \( \mathcal{H} = L^2(\mathbb{R}^3, \mathbb{C}^4) \) the corresponding decomposition is obtained from the discussion above by noting that in \( L^2(S^2; \mathbb{C}^4) \) eigenfunctions corresponding to the operators \( J^2, J_z \) (now acting on 4-spinors) can be constructed as linear combinations of the 2-spinor eigenfunctions

\[
\Phi^+_{j,l,m} = \begin{pmatrix} i\Omega_{j,l,m} \\ 0 \end{pmatrix}, \quad \Phi^-_{j,l,m} = \begin{pmatrix} 0 \\ -\Omega_{j,2j-l,m} \end{pmatrix},
\]  

(95)
i.e.,

\[
\mathcal{H} = \bigoplus_{j,l} \mathcal{H}_{j,l} := \bigoplus_{(j,l,m) \in \mathcal{I}} \mathcal{H}_{j,l,m}
\]  

(96)

where

\[
\mathcal{H}_{j,l,m} = \{x \rightarrow 1/|x|^2 f(|x|) \Phi^+_{j,l,m}(\omega_x) + 1/|x|^2 g(|x|) \Phi^-_{j,l,m}(\omega_x); f, g \in L^2(\mathbb{R}^3_+)\}.
\]  

(97)

The orthogonal projections onto those spaces are denoted by \( \Pi_{j,l} \) and \( \Pi_{j,l,m} \).

While the Dirac operator is not commuting with the orbital angular momentum \( L \), these subspaces of \( \mathcal{H} \) are still left invariant since

\[
i(\alpha \cdot \omega_x) \Phi^+_{j,l,m}(\omega_x) = -\Phi^-_{j,l,m}(\omega_x)
\]

\[
i(\alpha \cdot \omega_x) \Phi^-_{j,l,m}(\omega_x) = +\Phi^+_{j,l,m}(\omega_x)
\]  

(98)

(Balinsky and Evans [2, p. 32, 2.1.30]).

Appendix C: The Foldy–Wouthuysen Transform

The free Dirac operator can be defined using two unitary transforms, the Fourier transform and the Foldy–Wouthuysen transform [32].
\[ u(p) = a_+(p) \mathbf{1} + a_-(p) \beta \mathbf{\sigma} \cdot \omega \quad (99) \]

using \( p = |p| \), \( \omega = \frac{p}{|p|} \), \( a_\pm = \frac{E(p) \pm 1}{2E(p)} \), \( E(p) = \sqrt{p^2 + 1} \), through the following formula

\[
D_0 := \mathcal{F}^{-1} \left( \begin{array}{ccc} \mathbf{1} & c \mathbf{\sigma} \cdot \mathbf{p} & \mathbf{0} \\ c \mathbf{\sigma} \cdot \mathbf{p} & -1 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} \end{array} \right) \mathcal{F}
\]

\[
= \mathcal{F}^{-1} u(p/c)^{-1} \begin{pmatrix} E(p/c) & 0 & 0 & 0 \\ 0 & E(p/c) & 0 & 0 \\ 0 & 0 & -E(p/c) & 0 \\ 0 & 0 & 0 & -E(p/c) \end{pmatrix} u(p/c) \mathcal{F}. \quad (100)
\]

Since the diagonal operator is self-adjoint with domain \( L^2(\mathbb{R} : \mathbb{C}^4, (1 + p^2) dp) \), \( D_0 \), the free Dirac operator is self-adjoint on \( H^1(\mathbb{R}^3, dp) \).

For the Brown–Ravenhall operator this gives rise to the isometry

\[
\Phi_c : \mathfrak{h} := L^2(\mathbb{R}^3 : \mathbb{C}^2) \to \mathfrak{h}^B \quad (101)
\]

\[
\psi \quad \mapsto (\Phi_0 \psi, \Phi_1 \psi)
\]

where, in Fourier representation, \( \Phi_0(p) = \sqrt{\frac{E(p) + 1}{2E(p)}} \), \( \Phi_1(p) = \sqrt{\frac{E(p) - 1}{2E(p)}} \mathbf{\sigma} \cdot \omega \). In particular, the isometric property is easy to see since the map

\[
a \mapsto (\Phi_0(p)a, \Phi_1(p)a) \quad (102)
\]

for \( a \in \mathbb{C}^2 \) is an isometry from \( \mathbb{C}^2 \) to \( \mathbb{C}^4 \) independent of \( p \).

**Appendix D: The Trial Density Matrix**

In this section we define the density matrix \( d \) which is used to bound the Furry energy from above via the usual min-max principle. The construction is in the spirit of [66, 70], in particular the density matrix will be split into two parts, corresponding to low and high angular momenta respectively, i.e.,

\[
d := d_\phi + d_\phi^* = d_\phi + \Phi_c d_\phi \Phi_c^*
\]

acting on \( L^2(\mathbb{R}^3 : \mathbb{C}^4) \) and its non-relativistic version

\[
d^S := d_\phi^S + d_\phi^* \quad (104)
\]

which is acting on \( L^2(\mathbb{R}^3 : \mathbb{C}^2) \). Low angular momenta correspond to orbits with perihe- lion close to the nucleus, while high angular momenta prohibit orbits in the near vicinity of the nucleus. The separation is at \( L := \sqrt{\frac{1}{Z \pi}} \).

Note that for the construction of the relativistic trial density matrix we lift the high angular momentum part of the non-relativistic density matrix from 2-spinor to 4-spinor space via the Foldy Wouthuysen transform (cf. appendix 6). Consequently \( d \) neither belongs to the positive spectral subspaces of the hydrogenic nor the free Dirac operator. However, by construction, the individual parts \( d_\phi \) and \( d_\phi^* \) do.
D.1. Low angular momenta. Close to the nucleus the electron-electron interaction is dominated by the nuclear interaction. This is reflected by choosing the unmodified eigenfunctions of the Coulomb–Dirac operators for small angular momenta,

\[ d_\prec := \sum_{l=0}^{L-1} d_{\prec,l}, \quad d_{\prec,l} = \sum_{j \geq \frac{1}{2}, j = l \pm \frac{1}{2}} d_{\prec,j,l} \]  

(105)

where

\[ d_{\prec,j,l} = \sum_{m=-j}^{j} \sum_{n=1}^{K-l} \langle \psi_{j,l,m,n} | \psi_{j,l,m,n} \rangle \]  

(106)

with \( K = [CZ^{\frac{1}{2}}] \) and \( \psi_{j,l,m,n} \) being eigenfunctions of the Coulomb–Dirac operator \( c\alpha \cdot \mathbf{p} + c^2 \beta - c^2 - \frac{Z}{|x|} \) corresponding to eigenvalue \( c^2 \lambda_{Z,n,l}^D \) (cf. (12)) and azimuthal quantum number \( m \). The cutoff \( K \) is set on the order of the last occupied shell of the Bohr atom. The Dirac eigenfunctions are explicitly known [78]. Likewise, we define the non-relativistic analogue

\[ dS_{\prec} := \sum_{l=0}^{L-1} d_{\prec,l}, \quad d_{\prec,l} = \sum_{j \geq \frac{1}{2}, j = l \pm \frac{1}{2}} d_{\prec,j,l} \]  

(107)

with

\[ d_{\prec,j,l} = \sum_{m=-j}^{j} \sum_{n=1}^{K-l} \langle \psi_{S,j,l,m,n} | \psi_{S,j,l,m,n} \rangle \]  

(108)

where \( \psi_{S,j,l,m,n} \) denote the eigenfunctions of \( p^2 - \frac{Z}{|x|} \) on \( L^2(\mathbb{R}^3, \mathbb{C}^2) \) with eigenvalues \( \lambda_{Z,n,l}^S \) (see (12)).

D.2. High angular momenta. For large angular momenta, the electrons are moving slowly at far distance from the nucleus. Moreover, the correspondence principle demands a quasi-classical behavior for large quantum numbers. These heuristics suggest that for large angular momenta a semi-classical and non-relativistic description of the electrons in their mean field (if assumed interacting) and a description by the unscreened electrons for small angular momenta suffices to obtain not only the leading contribution to the ground state energy (Thomas–Fermi) but also its first correction (Scott), if the cut between the large and high angular momenta is chosen appropriately. This idea originates in [70] and was guiding the construction of trial density matrices in [33, 34, 66]. We will follow it also here. Of course, the same heuristics additionally suggest that the difference between the Furry and Brown–Ravenhall projections will be small for large angular momenta. That this is indeed the case is the essential technical contribution of this paper which allows to treat the Furry picture. We thus choose

\[ d_\succ := \sum_{l \geq L} d_l, \quad d_l := \sum_{j = l \pm \frac{1}{2}}^{m=j} \sum_{m=-j}^{m=j} w_{n,l} \langle \phi_{n,l} \otimes \Omega_{j,l,m} | \phi_{n,l} \otimes \Omega_{j,l,m} \rangle \]  

(109)

The \( \phi_{n,l} \) are the Macke orbitals as constructed in [66]. We do not need their explicit form here and thus refrain from redefining them here. However, we would like to remark
that—similar to coherent states—they yield a simultaneous localization in position and momentum space with the additional benefit that they are orthonormal. Also, like coherent states, they can be used obtain the semi-classical asymptotics of the sum of eigenvalues which has been carried through in [69] for one-dimensional Schrödinger operators.

The kinetic energy estimate for the density matrix $\rho_{\gamma}$ found in [35] will be useful:

**Lemma 12** ([35], Lemma E.1). Let $L = \left[ Z^{1/12} \right]$. Then for large $Z$,

$$
\sum_{l=L}^{\infty} l^{-2} \text{tr}(p^2 \Phi_\gamma d_{\gamma} \Phi_\gamma^*) = \sum_{l=L}^{\infty} l^{-2} \text{tr}(p^2 d_l) = O(Z^2/L).
$$

(110)

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