Lowering the Dirac-Fock minimizer by pair correlation

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Abstract

We prove by a simple computation that a suitable coupling to the *positronic* sector lowers the energy of the purely electronic minimizer of the Dirac-Fock functional.

Key words. Dirac-Coulomb operator, Dirac-Fock theory, electron-positron field.

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1 Introduction and motivation

The energy of a quantum system consisting of massive relativistic spin-$1/2$ point particles in an exterior field and interacting via Coulombic (or other) forces may approximately be described by means of *Dirac-Fock theory*: Each particle effectively feels an additional potential created by the rest of the system. Although this theory has *not* yet been rigorously derived from QED it is nevertheless used in practice yielding good agreement with experimental data. Steps in the direction of a rigorous justification are presently undertaken, cf. [1, 2, 3, 4] and references therein.

A state of such a system is approximated in this theory to be quasi-free, generalizing the notion of a Slater determinant. Due to the fact that a quasi-free state is uniquely determined by its corresponding one particle density matrix given by a self-adjoint trace class operator γ on the one particle Hilbert space $\mathfrak{h}$, cf. [2], we can write the Dirac-Fock energy functional $\mathcal{E}_{DF}$ as

$$\mathcal{E}_{DF}(\gamma) = \mathrm{tr}(H_c\gamma) + \mathcal{Q}(\gamma,\gamma) \tag{1.1}$$

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where H_c denotes the Dirac-Coulomb operator, and $\mathcal{Q}$ is the difference of the *direct* and the *exchange* terms well-known from Hartree-Fock theory, cf. [2] and Section 2 below for precise definitions.

As it has been shown in [4, Corollary 3.9] there exists a (not necessarily unique) minimizer γ_0 of the Dirac-Fock functional (1.1) if the minimization procedure is carried out over the space $\mathcal{S}^{(\delta)}$ of one particle density matrices which are, in addition, *diagonal*, i.e., $(1-\Lambda^{(\delta)})\gamma\Lambda^{(\delta)}=0$, and have prescribed charge $\mathrm{tr}\gamma = N \in \mathbb{N}$. Here,

$$\Lambda^{(\delta)} := \chi_{(0,\infty)}(H^{(\delta)})$$

denotes the projection onto the positive spectral part of the Dirac-Fock operator $H^{(\delta)} = H_c + W^{(\delta)}$ where the mean-field potential $W^{(\delta)}$ is given by

$$W^{(\delta)}\psi(x) = (\rho_\delta * V)(x)\,\psi(x) - \int dy\; V(x-y)\,\kappa_\delta(x,y)\,\psi(y), \tag{1.2}$$

(ρ_δ and κ_δ are given below in Section 2, V is the Coulomb potential). Note that $W^{(\delta)}$ is specified by the *electron-positron distribution* δ taken from the set $F=\{0\le\delta,\ \mathrm{tr}(|H_c|^{1/2}|\delta||H_c|^{1/2})<\infty\}$. The space $\Lambda^{(\delta)}\mathfrak{h}$ is thus the set of *one-electron states*.

In the case of *charge one*, this minimizer γ_0 is found to be an orthogonal projection of the form $\gamma_0 = |\psi_0\rangle\langle\psi_0|$, $\psi_0\in\mathrm{Ran}\,\Lambda^{(\delta)}$, which fulfills the Dirac-Fock equations $\Lambda^{(\delta)}H^{(\gamma_0)}\Lambda^{(\delta)}\psi_0=\varepsilon\psi_0$, $\varepsilon\ge 0$ (see [4, Lemma 4.3, Corollary 4.5]). Since $\psi_0\in\mathrm{Ran}\,\Lambda^{(\delta)}$ and $W^{(\gamma_0)}\psi_0=0$, this is equivalent to $\Lambda^{(\delta)}H_c\Lambda^{(\delta)}\psi_0=\varepsilon\psi_0$. But any eigenfunction ψ of $\Lambda^{(\delta)}H_c\Lambda^{(\delta)}$ with positive eigenvalue has its corresponding $\gamma=|\psi\rangle\langle\psi|$ in $S^{(\delta)}$. Hence, γ_0 being a minimizer, ε is the ground state energy of $\Lambda^{(\delta)}H_c\Lambda^{(\delta)}$, i.e., the lowest positive eigenvalue of $\Lambda^{(\delta)}H_c\Lambda^{(\delta)}$.

Moreover, for a system of charge 1, using boundedness of $W^{(\delta)}$ [4, Appendix A.], Theorem 3 (i) in [5] yields

$$\inf_{\gamma\in S^{(\delta)}}\mathcal{E}_{DF}(\gamma) \;=\; \mathcal{E}_{DF}(\gamma_0)=\varepsilon\le\inf\left\{\sigma(H_c)\cap[0,mc^2]\right\}=\inf_{\gamma\in S^{(\delta=0)}}\mathcal{E}_{DF}(\gamma)=\mathcal{E}_{DF}(\gamma_c)$$

where ψ_c is the electronic ground state of H_c, and $\gamma_c=|\psi_c\rangle\langle\psi_c|$. This implies that the "$\sup\inf$"

$$\sup_{\delta\in F}\inf_{\gamma\in S^{(\delta)}}\mathcal{E}_{DF}(\gamma) \tag{1.3}$$

is attained by the pair $(\delta=0,\gamma_c)$ for a system of charge 1: Mittleman in [7] (for the general case of charge N) argued that the right choice of $\Lambda^{(\delta)}$ that determines the one-electron space should be given by the stationary points of the δ-dependent functional $\mathcal{E}_{DF}(\gamma_0)=\mathcal{E}_{DF}(\gamma_0(\delta))$, which motivates to investigate the "$\sup\inf$" problem (1.3).

A further reason to consider this pair $(\delta = 0, \gamma_c)$, is that for a system of change one the mean-field potential is expected to vanish, in which case the minimizer is a pure electronic ground state of the relativistic hydrogen atom.

In the present paper, we show that for $\Lambda^{(\delta=0)} = \chi_{(0,\infty)}(H_c)$ and in the case of *non-vanishing* electron-positron correlations in the one particle density matrix γ, i.e., for *off-diagonal* γ, $(1-\Lambda^{(\delta)})\gamma\Lambda^{(\delta)} \neq 0$, the energy of the Dirac-Fock functional can be *lowered* compared to the energy of the purely electronic minimizer γ_c.

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2 The setting

We prove in this section that we can lower the Dirac-Fock energy $\mathcal{E}_{DF}$ on its purely electronic minimizer by adding an off-diagonal perturbation. In order to give precise definitions of the ingredients we recall the following facts.
The Dirac-Coulomb operator H_c describes the relativistic motion of a *single* massive spin-$1/2$ point particle in an external electrostatic Coulomb field V of an infinitely heavy point-like nucleus,

$$H_c = c\,\alpha \cdot p + mc^2\beta + V,$$

with orbital momentum $p = -i\nabla$, mass $m = 1$, and Coulomb potential $V(x) := -\kappa|x|^{-1}$ coupled by some $\kappa \in \mathbb{R}_+$; furthermore, α and β denote the usual Dirac matrices (we will use their standard representation, cf. appendix A). Our notation hides all the dependencies on possible parameters but the dependence on the speed of light, c, since we are merely interested in the limit of large c. If κ is not too large, $\kappa \in]0, \sqrt{3}/2\,c[$, the operator H_c in the Hilbert space $\mathfrak{h} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^4 =: L^2(\mathbb{R}^3)^4$ is essentially self-adjoint on $C_0^\infty(\mathbb{R}^3 \setminus \{0\})^4$ and self-adjoint on $H^1(\mathbb{R}^3)^4$, the domain of the free Dirac operator $H_c - V$, cf. [8]; set $\kappa = 1$.

Now, for a given electron-positron distribution $\delta \in F$ as above, the Dirac-Fock energy is defined by the functional

$$\mathcal{E}_{DF} : \begin{array}{ccc} \mathcal{S}_{\text{off}}^{(\delta)} & \to & \mathbb{C} \\ \gamma & \mapsto & \operatorname{tr}(H_c\gamma) + \mathcal{Q}(\gamma,\gamma) \end{array}$$

where the space of one particle density matrices $\mathcal{S}_{\text{off}}^{(\delta)}$ of charge one is defined by

$$\mathcal{S}_{\text{off}}^{(\delta)} := \{\gamma \in \mathcal{L}^1(\mathfrak{h}), \gamma^* = \gamma, \operatorname{tr}\gamma = 1 \,|\, H_c\gamma \in \mathcal{L}^1(\mathfrak{h}), -(1-\Lambda^{(\delta)}) \leq \gamma \leq \Lambda^{(\delta)}\},$$

for $\mathcal{L}^1(\mathfrak{h})$ the trace class operators on $\mathfrak{h}$. We set $W_c := W^{(\gamma_c)}$ from (1.2). The functional $\mathcal{Q} : (\mathcal{S}_{\rm off}^{(\delta)})^{\times 2} \to \mathbb{C}$ is defined to be the difference between the *direct* and the *exchange* terms, $\mathcal{D}$ and $\mathcal{E}$ respectively, $\mathcal{Q}(\gamma_1, \gamma_2) := \mathcal{D}(\rho_{\gamma_1}, \rho_{\gamma_2}) - \mathcal{E}(\kappa_{\gamma_1}, \kappa_{\gamma_2})$. The direct term $\mathcal{D}$ is given by

$$\mathcal{D}(\rho_1, \rho_2) := \frac{1}{2} \int_{\mathbb{R}^6} d^3x d^3y \; V(x-y) \; \rho_1^*(x) \, \rho_2(y)$$

for $\rho_j : \mathbb{R}^3 \to \mathbb{C}$, $j = 1, 2$, and the exchange term $\mathcal{E}$ has the form

$$\mathcal{E}(\kappa_1, \kappa_2) := \frac{1}{2} \int_{\mathbb{R}^6} d^3x d^3y \; V(x-y) \; \mathrm{tr}_{\mathbb{C}^4} \left[\kappa_1^*(x, y) \, \kappa_2(x, y)\right]$$

where $\kappa_j : \mathbb{R}^3 \times \mathbb{R}^3 \to M_4$, $j = 1, 2$, and M_4 denotes the set of complex 4×4 matrices. The definition of the integral kernel $\kappa_\gamma : \mathbb{R}^3 \times \mathbb{R}^3 \to M_4$ of $\gamma \in \mathcal{S}_{\rm off}^{(\delta)}$ reads $\kappa_\gamma(x, y) := \sum_{i,j} (e_i, \gamma e_j)_{L^2(\mathbb{R}^3)^4} \;\; e_i(x) \otimes e_j^*(y)$ where $\{e_j\}$ is an orthonormal basis of $\mathfrak{h}$, and e_j^* denotes the row covector of the column vector e_j (in $\mathbb{C}^4$). Furthermore, $\rho_\gamma : \mathbb{R}^3 \to \mathbb{C}$ is just the trace of the diagonal of the integral kernel κ_γ, $\rho_\gamma(x) := \mathrm{tr}_{\mathbb{C}^4} \;\kappa_\gamma(x, x)$. Hence, we have

$$\mathcal{Q}(\gamma_1, \gamma_2) = \frac{1}{2} \, \mathrm{tr} \;\gamma_1 W^{(\gamma_2)}. \tag{2.4}$$

In the following we concentrate on the case $\delta = 0$, as it has been discussed in the introduction. Note that we know from [2, Theorem 4] that $\mathcal{E}_{DF}$ is *nonnegative* on $\mathcal{S}_{\rm off}^{(\delta=0)}$.

3 Lowering the minimizer

After having specified the ingredients of the Dirac-Fock functional $\mathcal{E}_{DF}$ we now turn to the problem described in the introduction.

Let ψ_c be an electronic ground state of the Dirac-Coulomb operator H_c (2-fold degenerate), and $\epsilon \in \mathbb{R}$ a perturbation parameter. We claim that we can find an off-diagonal perturbation, γ_ϵ say, of the electronic Dirac-Coulomb ground state projector $\gamma_c := |\psi_c\rangle\langle\psi_c| \in \mathcal{S}_{\rm off}^{(\delta=0)}$ such that we can *strictly lower* the Dirac-Fock energy of γ_c, i.e.,

$$\mathcal{E}_{DF}(\gamma_c + \gamma_\epsilon) < \mathcal{E}_{DF}(\gamma_c) + \mathcal{O}(\epsilon^2). \tag{3.5}$$

Hence, defining the perturbation γ_ϵ as

$$\gamma_\epsilon := \epsilon^2 \; (|\psi_>\rangle\langle\psi_>| - |\psi_<\rangle\langle\psi_<|) + \epsilon(1-\epsilon^2)^{1/2} \; (|\psi_>\rangle\langle\psi_<| + |\psi_<\rangle\langle\psi_>|),$$

we claim that there exists $\psi_<$ from the negative spectral subspace of H_c and $\psi_>$ in the positive spectral subspace of H_c without the electronic ground state ψ_c,

$$\psi_< \in \chi_{(-\infty,0]}(H_c)\mathfrak{h}, \quad \psi_> \in \chi_{(0,\infty)}(H_c)\mathfrak{h} \cap \{\psi_c\}^\perp \tag{3.6}$$

such that the claim (3.5) is fulfilled. Plugging γ_c and γ_ϵ into (3.5) and taking into account the first order in ϵ only, we find

$$\begin{aligned} \mathcal{E}_{DF}(\gamma_c + \gamma_\epsilon) - \mathcal{E}_{DF}(\gamma_c) &= 2\epsilon \,\mathrm{Re}\; \mathcal{Q}(|\psi_>\rangle\langle\psi_<| + |\psi_<\rangle\langle\psi_>|, \gamma_c) + \mathcal{O}(\epsilon^2) \\ &= 2\epsilon \,\mathrm{Re}\; (\psi_<, W_c\, \psi_>) + \mathcal{O}(\epsilon^2), \end{aligned} \tag{3.7}$$

where $\gamma_c + \gamma_\epsilon \in \mathcal{S}^{(\delta=0)}_{\mathrm{off}}$, $\epsilon \in [0,1]$, and $W_c = X_c - Y_c$ on $L^2(\mathbb{R}^3)^4$, cf. (1.2) and (2.4), with

$$X_c\psi := \left(|\psi_c|^2_{\mathbb{C}^4} * V\right)\, \psi, \quad Y_c\psi := \left((\psi_c, \psi)_{\mathbb{C}^4} * V\right)\, \psi_c. \tag{3.8}$$

Therefore, in order to prove the claim (3.5), it suffices to show that

$$\mathrm{Re}\;\,(\psi_<, W_c\, \psi_>) \neq 0 \tag{3.9}$$

and to choose the sign of ϵ appropriately. That's what we will do next. To this end we introduce the orthogonal projection Λ_c onto the negative spectral part of H_c, $\Lambda_c := \chi_{(-\infty,0]}(H_c)$.

Theorem 3.1 *There exists a $\psi_> \in \chi_{(0,\infty)}(H_c)\mathfrak{h} \cap \{\psi_c\}^\perp$ such that for c sufficiently large,*

$$\Lambda_c W_c \psi_> \neq 0. \tag{3.10}$$

Remark Of course, this now implies (3.9) for the choice $\psi_< := \Lambda_c W_c \psi_>$:

$$\mathrm{Re}\;\,(\psi_<, W_c\, \psi_>) = \|\Lambda_c W_c \psi_>\|^2 \neq 0.$$

In order to prove (3.10) we extract zeroth and first order terms from Λ_c, W_c, and ψ_c for large c. This will eventually lead to a first order term on the rhs of (3.10) plus *remainder terms* of higher order.

Lemma 3.2

$$\Lambda_c = \Lambda^{(0)} + \frac{1}{c}\,\Lambda^{(1)} + \frac{1}{c^2}\,\Lambda^{(c)}, \quad \Lambda^{(0)} = \frac{1}{2}(1-\beta), \quad \Lambda^{(1)} = -\frac{1}{2}\alpha\cdot p, \tag{3.11}$$

and $\Lambda^{(c)}$ is $\mathcal{O}(1)$ on the states appearing in the remainder terms of (3.10).

Proof 3.2 Since $0 \in \mathbb{R}$ lies in the spectral gap $(-c^2, E_c)$ of H_c, with $c^2 > E_c > 0$ the ground state energy of H_c on its positive spectral subspace, we can write Λ_c as (cf. [6], p.359)

$$\Lambda_c = \underset{\delta\to 0,\rho\to\infty}{\mathrm{s}-\lim} \frac{1}{2}\left(\mathbf{1} - U_{\delta,\rho}(H_c)\right), \quad U_{\delta,\rho}(H_c) \;\; := \;\; \frac{1}{\pi}\left[\int_{-\rho}^{-\delta} + \int_{\delta}^{\rho}\right] d\eta \; (H_c - i\eta)^{-1}.$$

In order to extract the potential V at order $1/c^2$ from the resolvent in this principal value like integral we rescale $U_{\delta,\rho}(H_c) = U_{\delta/c^2,\rho/c^2}(H_c/c^2)$ and apply the second resolvent identity:

$$(H_c/c^2 - i\eta)^{-1} = R^{(0)} + \frac{1}{c}\, R^{(1)} + \frac{1}{c^2}\, R^{(c)}, \tag{3.12}$$

where we write down the zeroth and first order here,

$$R^{(0)} := (\beta - i\eta)^{-1}, \quad R^{(1)} := -(\beta - i\eta)^{-1}\alpha\cdot p\,(\beta - i\eta)^{-1},$$

whereas $R^{(c)}$ is treated in appendix B. Note that the application of the resolvent identity is well-defined on the domain of p, $D(p) = H^1(\mathbb{R}^3)$. Defining now for $j = 0, 1, c$,

$$\Lambda^{(j)} := \underset{\delta\to 0,\rho\to\infty}{\mathrm{s}-\lim} \frac{1}{2}\left(\mathbf{1} - \frac{1}{\pi}\left[\int_{-\rho/c^2}^{-\delta/c^2} + \int_{\delta/c^2}^{\rho/c^2}\right] d\eta\; R^{(j)}\right), \tag{3.13}$$

and performing some elementary integration we find $\Lambda^{(0)}$ and $\Lambda^{(1)}$ in (3.11). The estimates involving $\Lambda^{(c)}$ are carried out in appendix B. $\square$

The expansion of a bound state $\psi_c \in \mathfrak{h}_{pp}(H_c)$ is given in [8].

Lemma 3.3 *Let $\psi_c \in \mathfrak{h}_{pp}(H_c)$ with eigenvalue E_c.*

$$\psi_c = \psi_c^{(0,1)} + \frac{1}{c^2}\,\psi^{(c)}, \quad \psi_c^{(0,1)} := \begin{pmatrix} \phi \\ \frac{1}{2c}\sigma\cdot p\,\phi \end{pmatrix}, \qquad \|\psi^{(c)}\|_{H^1(\mathbb{R}^3)^4} = \mathcal{O}(1), \tag{3.14}$$

and $\phi \in \mathfrak{h}_{pp}((-\Delta/2 + V)\mathbf{1}_2)$ with eigenvalue $\lim_{c\to\infty}(E_c - c^2)$.

In the next lemma we extract the low order terms of $W_c = X_c - Y_c$ by computation using the bispinor notation $\psi =: (\psi_+, \psi_-)^T$. The expressions ϕ, $\psi_c^{(0,1)}$, $\psi^{(c)}$ stem from (3.14). The higher order terms are estimated in appendix B.

Lemma 3.4 *The direct part decomposes as*

$$X_c = X^{(0)} + \frac{1}{c^2} X^{(c)}, \quad X^{(0)} = |\phi|^2{}_{\mathbb{C}^2} * V, \tag{3.15}$$

and the exchange part reads

$$\begin{aligned} Y_c\psi &= \left(Y^{(0)}\psi_+ + \frac{1}{c} Y^{(1)}\psi_- + \frac{1}{c^2} Y^{(c)}\psi \right) \psi_c^{(0,1)} + \frac{1}{c^2} Y_c \psi^{(c)} \\ Y^{(0)} &= (\phi, \cdot)_{\mathbb{C}^2} * V, \quad Y^{(1)} = \frac{1}{2}(\sigma \cdot p\, \phi, \cdot)_{\mathbb{C}^2} * V. \end{aligned}$$

The contribution $Y^{(c)}$ is $\mathcal{O}(1)$ on the states appearing in the remainder terms of (3.10).

Now we can prove Theorem 3.1 by assembling the forgoing large c expansions.

Proof 3.1 Denote again by E_c the electronic ground state energy of H_c. Choose $\psi_> := \varphi_c := \psi_{-1/2}$ and $\psi_c := \psi_{1/2}$ the corresponding spinors with quantum numbers $(n, j, m) = (1, 1/2, -1/2)$ and $(1, 1/2, 1/2)$, respectively, $\psi_c, \varphi_c \in \ker(H_c - E_c)$. Note that the condition (3.6) on $\psi_>$ is satisfied since $\psi_{-1/2}$ is L^2 orthogonal to $\psi_{1/2}$ since even $(\psi_{-1/2}, \psi_{1/2})_{\mathbb{C}^4} = 0$. This implies that the exchange energy on this state vanishes $Y_c\varphi_c = 0$, leaving us with the direct term X_c in W_c only. Until the final formula (3.18), we carry out the computation for a general $\mathcal{J}\psi_c$ where $\mathcal{J}$ is a general $SU(2)$ rotation in $\mathfrak{h}$, cf. appendix A.

In order to proof the claim we just assemble the expansions given in Lemma 3.2, 3.3, 3.4. Let us first compute $W_c\mathcal{J}\psi_c$:

$$W_c\mathcal{J}\psi_c = X^{(0)}\mathcal{J}\psi_c^{(0,1)} - (Y^{(0)}A\phi \circ R^{-1})\,\psi_c^{(0,1)} + \frac{1}{c^2}\sum_{j=1}^{5} S_j. \tag{3.16}$$

All the remainder terms S_j, $j = 1, 2, ...$, and S below are defined and estimated in appendix B. We apply now Λ_c on (3.16),

$$\Lambda_c W_c \mathcal{J}\psi_c = \left(\Lambda^{(0)} + \frac{1}{c}\Lambda^{(1)} \right) W_c\mathcal{J}\psi_c + \frac{1}{c^2} S_6,$$

and compute the zeroth order contribution,

$$\Lambda^{(0)}\, W_c\mathcal{J}\psi_c = \frac{1}{2}(1-\beta)\left(X^{(0)}\mathcal{J}\psi_c^{(0,1)} - (Y^{(0)}A\phi \circ R^{-1})\,\psi_c^{(0,1)} \right) + \frac{1}{c^2}\sum_{j=1}^{5} \Lambda^{(0)} S_j.$$

For the action in first order $\Lambda^{(1)}$ we find that

$$\begin{aligned}\frac{1}{c}\Lambda^{(1)}\, W_c\mathcal{J}\psi_c \;&=\; -\,\Lambda^{(0)}\, W_c\mathcal{J}\psi_c\\ &\quad+\frac{1}{2}\left((\phi, A\phi\circ R^{-1})_{\mathbb{C}^2} * p_jV\right)\begin{pmatrix}0\\ \sigma_j\phi\end{pmatrix}-\frac{1}{2}\left(|\phi|^2_{\mathbb{C}^2} * p_jV\right)\begin{pmatrix}0\\ \sigma_jA\phi\circ R^{-1}\end{pmatrix}\\ &\quad+\frac{1}{c^2}\sum_{j=1}^{5}\left(\Lambda^{(0)}+\frac{1}{c}\Lambda^{(1)}\right)S_j+\frac{1}{c^2}\sum_{j=7}^{10}S_j.\end{aligned}$$

Putting it all together we finally arrive at

$$\Lambda_cW_c\mathcal{J}\psi_c \;=\; \frac{i}{2c}\begin{pmatrix}0\\ \xi\end{pmatrix}+\frac{1}{c^2}S, \tag{3.17}$$

where we used the relation $A\,z\cdot\sigma A^* = (Rz)\cdot\sigma$ from appendix A, and ξ is given by

$$\xi := \left((\phi, A\phi\circ R^{-1}))_{\mathbb{C}^2} * (-\nabla V)\cdot\sigma\right)\phi-\left(|\phi|^2{}_{\mathbb{C}^2} * (-\nabla V)\cdot\sigma\right)\,A\phi\circ R^{-1}. \tag{3.18}$$

In order to prove that ξ is *non-zero* we use the fact stated in Lemma 3.3 that for our choice of $\psi_c = \psi_{1/2}$ the wavefunction ϕ in (3.18) is the ground state ψ_0 of the (Pauli) hydrogen atom,

$$\phi(x) = \psi_0(|x|)\,\chi_+, \tag{3.19}$$

where $\chi_+ := (1,0)^T$, and $\chi_- := (0,1)^T$ (we could have chosen χ_- instead of χ_+ in (3.19)). Plugging $A = -i\sigma_2$ into (3.18) (the rotation $\mathcal{J}$ with this A and the corresponding R being a rotation around the 2-axis by the angle π maps $\psi_{1/2}$ onto $\psi_{-1/2}$) and using the fact that ψ_0 has vanishing angular momentum (3.19) we find the lower component ξ_- of $\xi \in L^2(\mathbb{R}^3)^2$ to be

$$\xi_- = \left(|\psi_0|^2 * (-\nabla V)\right)\,\psi_0.$$

But the factor $E := |\psi_0|^2 * (-\nabla V)$ is just the electrostatic Coulomb field generated by the spherically symmetric charge distribution $|\psi_0|^2$. Hence, Newton's theorem implies that E is a central field generated by the *point charge* $Q(|x|)$ centered at the origin composed of all the charge inside the ball $B_{|x|}(0)$ of radius $|x|$ around 0, and $Q(|x|)$ is *strictly positive* due to the nature of ψ_0,

$$E(x) = Q(|x|)\,\frac{x}{|x|},\quad Q(|x|) = \|\psi_0\|^2_{L^2(B_{|x|}(0))} > 0.$$

This concludes the proof of Theorem 3.1. $\square$

A Ingredients for the Dirac equation

A.1 $SU(2)$ rotation in $L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$

We denote by $\mathcal{J} : L^2(\mathbb{R}^3)^4 \to L^2(\mathbb{R}^3)^4$ the $SU(2)$ rotations on $\mathfrak{h} = L^2(\mathbb{R}^3)^4$,

$$\mathcal{J}\psi(x) := e^{-i\varphi nJ}\psi(x) = e^{-i\varphi nS}\psi(R^{-1}(n,\varphi)\,x)$$

for the spin angular momentum $S = -i/4\alpha \wedge \alpha$, the orbital angular momentum $L = x \wedge p$, and the total angular momentum $J = L + S$; $R(\varphi, n)$ denotes the $SO(3)$ rotation by the angle $\varphi \in [0, 4\pi)$ around the axis $n \in \mathbb{R}^3$, $|n|_{\mathbb{R}^3} = 1$. Using the standard representation (A.20) and the bispinor notation $\psi =: (\psi_+, \psi_-)^T$, we can write the action of $\mathcal{J}$ as

$$\mathcal{J}\psi = \begin{pmatrix} A\psi_+ \circ R^{-1} \\ A\psi_- \circ R^{-1} \end{pmatrix},$$

where $A \in SU(2)$ and $R \in SO(3)$ are connected by the above $SU(2)/_{\{\pm\mathbf{1}\}} \simeq SO(3)$ epimorphism stemming from the defining relation $A\,z \cdot \sigma A^* = (Rz) \cdot \sigma$, where again $\sigma = (\sigma_1, \sigma_2, \sigma_3)$, and $z \in \mathbb{C}^3$.

A.2 The standard representation of the Dirac matrices

The standard representation for the Dirac matrices reads as follows.

$$\beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad \alpha_j = \begin{pmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{pmatrix}, \tag{A.20}$$

for $j = 1, 2, 3$, $\alpha = (\alpha_1, \alpha_2, \alpha_3)$, with the Pauli matrices

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

B Estimates on higher order terms

In the following are collected all the higher order terms from the large c expansions used in the proof of Theorem 3.1. By definition, all the S_j are multiplied by the factors $1/c^2$. Hence, given (3.17), it suffices to show that for c sufficiently large,

$$\|S_j\|_{L^2(\mathbb{R}^3)^4} = \mathcal{O}(1).$$

Since in our case at hand the *exchange* energy vanishes, $Y_c\psi_{-1/2} = 0$, we will restrict ourselves to the discussion of the terms involving the *direct* operator X_c only. The estimates involving Y_c are similar.

B.1 Direct remainder terms

In the sequel, all the norms and scalar products *without* index act on $\mathfrak{h} = L^2(\mathbb{R}^3)^4$. A norm $\|\cdot\|_{m,p}$ stands for the norm in the Sobolev space $W^{m,p}(\mathbb{R}^3)$, $m = 0, 1, 2, ...$, $1 \leq p \leq \infty$, and we denote the L^p norms $\|\cdot\|_{0,p}$ simply as $\|\cdot\|_p$. Furthermore, we write L^2 instead of $L^2(\mathbb{R}^3)^4$ and similarly for the other spaces ($H^1 \equiv W^{1,2}$). Finally, let us write φ_c instead of $\psi_{-1/2} = \mathcal{J}\psi_c$.

Lemma B.1 *The following remainder terms are uniformly bounded in c as soon as c is sufficiently large,*

$$\|S_j\| = \mathcal{O}(1), \quad j = 1, 2, 6, 7, 8.$$

The remainder terms stemming from the direct part are given by

$$\begin{aligned}
S_1 &:= W_c\mathcal{J}\psi^{(c)}, \\
S_2 &:= X^{(c)}\mathcal{J}\psi_c^{(0,1)}, \\
S_6 &:= \Lambda^{(c)}\, W_c\mathcal{J}\psi_c, \\
S_7 &:= -\frac{1}{4}\left(|\phi|^2_{\mathbb{C}^2} * p_jV\right)\begin{pmatrix}\sigma_j A(\sigma\cdot p\phi)\circ R^{-1}\\ 0\end{pmatrix}, \\
S_8 &:= -\frac{1}{4}\left(|\phi|^2_{\mathbb{C}^2} * V\right)\begin{pmatrix}\sigma_j A(R^{-1}(p(\sigma\cdot p\phi))\circ R^{-1})_j\\ 0\end{pmatrix}, \\
S &:= \sum_{j=1}^{2}\left(\Lambda^{(0)} + \frac{1}{c}\Lambda^{(1)}\right)S_j + \sum_{j=6}^{8} S_j.
\end{aligned}$$

Proof B.1
We use the decomposition of the Coulomb potential as $V = -1/|x| = V_0 + V_\infty$ with $V_0 := V\chi_B \in L^1 \cap L^{3-\varepsilon}$ and $V_\infty := V\chi_{\mathbb{R}^3\setminus B} \in L^{3+\varepsilon} \cap L^\infty$ where $\epsilon > 0$, χ_A is the characteristic function χ of the subset $A \in \mathbb{R}^3$, and $B := B_R(0)$ denotes the ball of finite radius $R < \infty$ centered at the the origin $0 \in \mathbb{R}^3$.

• S_1
We start with an L^∞ estimate on the direct term $X_c = |\psi_c|^2 * V$ where $\psi_c \in W^{1,2}$. Using Kato's

inequality [6, p.307], $\|\psi/|x|^{1/2}\|^2 \leq \pi/2\,(\psi, |\nabla|\psi)$, we immediately have

$$\|X_c\|_\infty \leq \frac{\pi}{2}\|\psi_c\|\,\|\nabla\psi_c\| < \infty,$$

and hence, due to Lemma 3.3, uniformly in the speed of light c, $\|S_1\| = \|X_c\varphi_c\| \leq \|X_c\|_\infty\|\varphi_c\|$.

• S_2

All the terms in S_2 have the form $((fg) * V)\varphi_c^{(0,1)}$ for $f, g \in W^{1,2}$ and $\varphi_c^{(0,1)} \in L^1 \cap L^\infty$ due to the nature of the ground state wave function $\phi(x) = e^{-1/2\,|x|}$. Using Hölder and Young we have

$$\|((fg) * V)\varphi_c^{(0,1)}\| \leq \|f\|\,\|g\|\,\|V_0\|\,\|\varphi_c^{(0,1)}\|_\infty + \|f\|\,\|g\|\,\|V_\infty\|_\infty\,\|\varphi_c^{(0,1)}\|.$$

Uniformity in c follows again from Lemma 3.3.

• S_6

We use the expansions of Λ_c from (3.11), of X_c from (3.15), and the one of φ_c from (3.14),

$$\begin{aligned} S_6 &= \Lambda^{(c)}X_c\varphi_c = \Lambda^{(c)}X^{(0)}\varphi_c^{(0,1)} + \frac{1}{c^2}\Lambda^{(c)}X^{(0)}\varphi^{(c)} + \frac{1}{c^2}\Lambda^{(c)}X^{(c)}\varphi_c \\ &= \Lambda^{(c)}X^{(0)}\varphi_c^{(0,1)} + \left(\Lambda_c - \Lambda^{(0)} - \frac{1}{c}\Lambda^{(1)}\right)X^{(0)}\varphi^{(c)} + \left(\Lambda_c - \Lambda^{(0)} - \frac{1}{c}\Lambda^{(1)}\right)X^{(c)}\varphi_c, \end{aligned}$$

and write $S_6 =: \sum_{j=1}^{3} S_{6,j}$.

• $S_{6,1}$

Using the definition of $\Lambda^{(c)}$ given in (3.13) we decompose $S_{6,1}$ into the following parts, $S_{6,1} = S_{6,1,1} + S_{6,1,2} + S_{6,1,3}$,

$$\begin{aligned} S_{6,1,1} &:= \frac{1}{2}X^{(0)}\varphi_c^{(0,1)}, \\ S_{6,1,2} &:= \lim_{\delta\to0,\rho\to\infty}\frac{1}{\pi}\left[\int_{-\rho/c^2}^{-\delta/c^2} + \int_{\delta/c^2}^{\rho/c^2}\right] d\eta\; R_1^{(c)}(\eta)X^{(0)}\varphi_c^{(0,1)}, \\ S_{6,1,3} &:= \lim_{\delta\to0,\rho\to\infty}\frac{1}{\pi}\left[\int_{-\rho/c^2}^{-\delta/c^2} + \int_{\delta/c^2}^{\rho/c^2}\right] d\eta\; R_2^{(c)}(\eta)X^{(0)}\varphi_c^{(0,1)}, \end{aligned} \tag{B.21}$$

for the ingredients $R^{(c)} = R_1^{(c)} + R_2^{(c)}$ of $\Lambda^{(c)}$ in (3.12) which are well-defined on the domain of p, $D(p) = W^{1,2}$:

$$\begin{aligned} R_1^{(c)} &:= (\beta - i\eta)^{-1}\alpha\cdot p\left(\frac{1}{c}\alpha\cdot p + \beta - i\eta\right)^{-1}\alpha\cdot p\,(\beta - i\eta)^{-1}, \\ R_2^{(c)} &:= -\left(\frac{1}{c}\alpha\cdot p + \beta + \frac{1}{c^2}V - i\eta\right)^{-1} V\left(\frac{1}{c}\alpha\cdot p + \beta - i\eta\right)^{-1}. \end{aligned}$$

Since $X^{(0)} \in L^\infty$ we can immediately estimate $S_{6,1,1}$ as $\|S_{6,1,1}\| \leq 1/2\,\|X^{(0)}\|_\infty \|\varphi_c^{(0,1)}\|$. In order to estimate $S_{6,1,2}$ we split $\phi_c^{(0,1)}$ into its upper part $\varphi_0 \in W^{2,2}$ and its lower part $\varphi_1 \in W^{1,2}$,

$$\varphi_c^{(0,1)} = \varphi_0 + \frac{1}{c}\varphi_1, \quad \varphi_0 := \begin{pmatrix} \phi \\ 0 \end{pmatrix}, \quad \varphi_1 := \frac{1}{2}\begin{pmatrix} 0 \\ \sigma \cdot p\, \phi \end{pmatrix}.$$

We will treat the action of $R_1^{(c)}$ on φ_0 and on φ_1 differently. This leads us to the further decomposition $S_{6,1,2} =: S_{6,1,2,1} + S_{6,1,2,2}$. Consider first $S_{6,1,2,1}$, i.e., the action on φ_0. In order to act on the domain of the Laplacian $W^{2,2}$ we can write

$$\begin{aligned} R_1^{(c)} &= \left(\frac{1}{c}\alpha \cdot p + \beta - i\eta\right)^{-1} \alpha \cdot p\,(\beta - i\eta)^{-1}\alpha \cdot p\,(\beta - i\eta)^{-1} \\ &= -\frac{1}{1+\eta^2}\left(\frac{1}{c}\alpha \cdot p + \beta - i\eta\right)^{-1} \begin{pmatrix} -\Delta & 0 \\ 0 & -\Delta \end{pmatrix}, \end{aligned}$$

where we used $(\beta - i\eta)^{-1}\alpha \cdot p\,(\beta - i\eta)^{-1} = -1/(1+\eta^2)\,\alpha \cdot p$ and $\alpha \cdot p\,\alpha \cdot p = \mathrm{diag}(-\Delta, -\Delta)$. Now, since $\Delta(X^{(0)}\phi) = (\Delta X^{(0)})\phi + 2(\nabla X^{(0)})(\nabla\phi) + X^{(0)}\Delta\phi$ and $\Delta X^{(0)} = |\phi|^2$, we estimate the integrand of $S_{6,1,2,1}$ as follows,

$$\|R_1^{(c)} X^{(0)}\varphi_0\| \leq \frac{1}{1+\eta^2}\,\left(\|\phi\|_\infty^2 + \|X^{(0)}\|_\infty + \|\nabla X^{(0)}\|_\infty\right)\|\phi\|_{2,2},$$

using $\nabla X^{(0)} \in L^\infty$, and we bounded the resolvent by 1 uniformly in c. $S_{6,1,2,1}$ is now uniformly bounded in c since the integrand decays sufficiently fast in η.
We now turn to the estimate on $S_{6,1,2,2}$, i.e., to the action of $R_1^{(c)}$ on φ_2. To this end, we rewrite $R_1^{(c)}$ by inserting β in order to bound $1/c\,\alpha \cdot p + \beta$ by its resolvent. Using the formula $H(H-z)^{-1} = 1 + z(H-z)^{-1}$ leads to

$$\begin{aligned} R_1^{(c)} &= -\frac{c}{1+\eta^2}\,\alpha \cdot p - \frac{c}{1+\eta^2}\,(\beta - i\eta)^{-1} i\eta\,\left(\frac{1}{c}\alpha \cdot p + \beta - i\eta\right)^{-1}(\beta - i\eta)\,\alpha \cdot p \\ &\quad + \frac{c}{1+\eta^2}\,(\beta - i\eta)^{-1}\beta\,\left(\frac{1}{c}\alpha \cdot p + \beta - i\eta\right)^{-1}(\beta - i\eta)\,\alpha \cdot p. \end{aligned} \tag{B.22}$$

Similarly to $S_{6,1,2,1}$ acting on $1/c\,\varphi_1$ yields the estimate

$$\frac{1}{c}\|R_1^{(c)}\varphi_1\| \leq \frac{2}{(1+\eta^2)}\,\left(\|X^{(0)}\|_\infty + \|\nabla X^{(0)}\|_\infty\right)\|\phi\|_{2,2}$$

where, this time, we used the decay of the resolvents in η to compensate the additional factor η^2 in (B.22). Collecting all the estimates yields a finite bound on $S_{6,1,2}$ which is uniform in c.

In order to come to an end with the desired bound on $S_{6,1}$ it remains to estimate $S_{6,1,3}$ given in (B.21). This time, we estimate the integrand by using the fact that the Coulomb potential V is relatively bounded with respect to the momentum p, i.e., $\|V\psi\| \leq 2\|p\psi\|$ (Hardy's inequality, uncertainty principle).

$$\|R_2^{(c)}\varphi_c^{(0,1)}\| \leq \frac{1}{\sqrt{((1/2)^2+\eta^2)(1+\eta^2)}}\,\|V(p+i)^{-1}\|\,\|(p+i)X^{(0)}\varphi_c^{(0,1)}\|$$

Here, we estimated the resolvents by extracting each time a decaying factor ($1/2$ for the ground state energy of $1/c^2\,H_c$ on the electronic sector), and we introduced $1=(p+i)^{-1}(p+i)$ on $W^{1,2}$ which bounds V. Concluding the estimate on $S_{6,1}$ we have

$$\|R_2^{(c)}\varphi_c^{(0,1)}\| \leq \frac{8}{1+\eta^2}\left(\|X^{(0)}\|_\infty + \|\nabla X^{(0)}\|_\infty\right)\|\varphi_c^{(0,1)}\|_{1,2}.$$

• $S_{6,2}$

Due to the fact that Λ_c is a projection we immediately have $\|S_{6,2,1}\| = \|\Lambda_c X^{(0)}\varphi^{(c)}\| \leq \|X^{(0)}\|_\infty\|\varphi^{(c)}\|_{1,2}$. The same estimate holds for $S_{6,2,2} := \Lambda^{(0)}X^{(0)}\varphi^{(c)}$ and $S_{6,2,3} := \Lambda^{(1)}X^{(0)}\varphi^{(c)}$ due to (3.11) and $X^{(0)} \in W^{1,\infty}$, $\varphi^{(c)} \in W^{1,2}$, cf. above.

• $S_{6,3}$

Since $X^{(c)} \in L^\infty$ we immediately have for $S_{6,3,1} := \Lambda_c X^{(c)}\varphi_c$ and $S_{6,3,2} := \Lambda^{(0)}X^{(c)}\varphi_c$ that $\|S_{6,3,1}\|, \|S_{6,3,2}\| \leq \|X^{(c)}\|_\infty\|\varphi_c\|$ which is again uniform in c. It remains to estimate $S_{6,3,3} := \Lambda^{(1)}X^{(c)}\varphi_c$ which is of the form $((fg)*\nabla V)\varphi_c$ for $f,g \in W^{1,2}$. Using the Sobolev imbedding $W^{1,2}(\mathbb{R}^3) \hookrightarrow (L^2\cap L^6)(\mathbb{R}^3)$ we finally find

$$\|((fg)*\nabla V_0)\varphi_c\| \leq \|f\|_6\|g\|_6\|\varphi_c\|_6\|V_0\|_1, \quad \|((fg)*\nabla V_\infty)\varphi_c\| \leq \|f\|\,\|g\|\,\|\varphi_c\|\,\|V_\infty\|_\infty.$$

• S_7, S_8, S

The estimates of S_7, S_8 are carried out as above, only using the properties of V and its gradient ∇V. The estimates in S correspond to the estimates already performed in $S_{6,2}$ and $S_{6,3}$. $\square$

B.2 Exchange remainder terms

For the sake of completeness we list he exchange remainder terms. The estimates on these terms may be performed following similar lines as for the direct part.

$$
\begin{aligned}
S_3 &:= -\frac{1}{2}(Y^{(1)}A(\sigma\cdot p\phi)\circ R^{-1})\,\psi_c^{(0,1)} \\
S_4 &:= -(Y^{(c)}\mathcal{J}\psi_c^{(0,1)})\,\psi_c^{(0,1)} \\
S_5 &:= -Y_c\psi^{(c)} \\
S_9 &:= \frac{1}{4}\big((\phi, A\phi\circ R^{-1})_{\mathbb{C}^2} * p_j V\big)\begin{pmatrix}\sigma_j(\sigma\cdot p\phi)\\ 0\end{pmatrix} \\
S_{10} &:= \frac{1}{4}\big((\phi, A\phi\circ R^{-1})_{\mathbb{C}^2} * V\big)\begin{pmatrix}\sigma\cdot p(\sigma\cdot p\phi)\\ 0\end{pmatrix} \\
S &:= \sum_{j=3}^{5}\left(\Lambda^{(0)}+\frac{1}{c}\Lambda^{(1)}\right)S_j+\sum_{j=9}^{10}S_j
\end{aligned}
$$

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