A Pseudo-Relativistic Operator for a Two-Electron Ion

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Abstract

By means of a unitary transformation scheme, the Coulomb-Dirac operator for two electrons in a central potential is transformed into a pseudo-relativistic operator which allows for the decoupling of the electron and positron degrees of freedom to arbitrary order n in the potential strength. In case of $n = 2$, relative boundedness properties and positivity of the resulting operator are shown for subcritical potential strength.

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1 Introduction

Due to the positron degrees of freedom, the one-electron Dirac operator as well as its generalisation to more particles has a spectrum which is unbounded from below. However, in the spectroscopy of static ions, negative energy states play no role. One therefore aims at constructing an operator with positive spectrum, but otherwise with similar properties as the Dirac operator. Such an operator allows for the application of conventional variational principles to determine its ground state and low lying excited states.

The first approach to eliminate the positron degrees of freedom was made by Pauli [1] who invented a systematic procedure to reduce the 4-spinor (one-electron) Dirac equation to a Schrödinger-type equation. The idea of reducing the Dirac operator to a semibounded operator with the same ground-state properties by means of elimination and substitution methods applied to the Dirac equation, or by constructing appropriate Hamiltonians which become exact in the nonrelativistic case, was pursued further (see e.g. [2] and references in [3]).

An alternative approach, to decouple the electron and positron degrees of freedom by means of a unitary transformation scheme applied to the Dirac operator, was put forth by Douglas and Kroll [4]. For a helium atom, they derived explicitly the transformed Coulomb-Dirac operator up to second order in the potential strength. Such a Douglas-Kroll-type operator was used later by Hess and coworkers [5, 6] in atomic structure calculations for multi-electron atoms.

For a single electron with mass m in a central Coulomb field of strength γ the Dirac equation is exactly solvable [7], with ground-state energy given by $m\sqrt{1-\gamma^2}$. This restricts the potential strength to $\gamma \leq 1$. Moreover, this exact reference value can be used to test perturbative approaches. Indeed, the Douglas-Kroll transformation scheme was carried out up to the $n = 5$-th order in the potential strength, and it was shown numerically [6] that the respective ground-state energies calculated for n increasing from 1 to 5 approach the exact value in an alternating way.

In the present work we use a transformation scheme which is based on the perturbation theory of Morse and Feshbach [8], see also [9]. By introducing projectors onto the positive and, respectively, negative spectral subspace of a free electron, unitary transformations are constructed in such a way that the resulting operator is block-diagonal to any given order in the potential strength with respect to these spectral projections. The transformation scheme used by Douglas and Kroll [4] is a special case of the scheme described here, and their resulting operator for $n = 2$ is unitarily equivalent to the operator derived below. However, the present representation of the operator is much simpler and therefore allows not only for a detailed mathematical analysis, but also for its generalisation to the multi-electron case.

The layout of the paper is as follows. In section 2 the transformation scheme is described and in section 3 the operator is explicitly constructed for $n = 2$. Section 4 deals with the form boundedness of the potential terms of this operator relative to the free Dirac operator, and in section 5 the subdominance of the second-order potential terms relative to the first-order terms is demonstrated. The latter property is a necessary requirement for convergence of the perturbation series. Finally, in section 6, positivity of the operator is shown. The work is concluded by an outlook to the N-particle case (section 7). The mathematical proofs will only be outlined; details can be found in [10]. Relativistic units ($\hbar = c = 1$) are used throughout.

2 The Coulomb-Dirac operator and the transformation scheme

The Coulomb-Dirac operator which describes two interacting electrons in a central Coulomb field is given by

$$H \;=\; \sum_{k=1}^{2}(D_0^{(k)} + V^{(k)}) \;+\; P_{++}\, V^{(12)}\, P_{++} \tag{2.1}$$

where $D_0^{(k)} + V^{(k)}$ is the Dirac operator for electron k,

$$D_0^{(k)} \;=\; -i\boldsymbol{\alpha}^{(k)}\nabla_{\mathbf{x}_k} + \beta^{(k)}m, \qquad V^{(k)} \;=\; -\frac{\gamma}{x_k}, \qquad \gamma \;=\; Ze^2 \tag{2.2}$$

where $\boldsymbol{\alpha}^{(k)}$ and $\beta^{(k)}$ are the Dirac matrices for electron k [7], m is the electron mass and $e^2 \approx 1/137$ the fine structure constant. $x_k = |\mathbf{x}_k|$ gives the location of the electron with respect to the nucleus. The nucleus is assumed to have infinite mass, charge number Z and to sit in the origin.

It is an important fact that interacting relativistic electrons cannot adequately be described by an operator where the electron-electron interaction

$$V^{(12)} \;=\; \frac{e^2}{|\mathbf{x}_1 - \mathbf{x}_2|} \tag{2.3}$$

is simply added to the sum of single-particle operators. This is so because, due to the coupling of negative- and positive-energy continuum states by $V^{(12)}$, no stable bound states would exist [11]. Instead, an appropriate operator has to be derived from quantum electrodynamics (QED). The operator (2.1) is due to Sucher who derived it from the Bethe-Salpeter equation of QED by neglecting pair creation and the radiation field [12] (see also [4]). The two-particle operator P_{++} projects onto the positive spectral subspace of $\sum_{k=1}^{2}(D_0^{(k)}+V^{(k)})$ and is defined by the product of the single-electron projectors [9]

$$P_{++} \;=\; P_+^{(1)}P_+^{(2)}, \qquad P_\pm^{(k)} \;=\; \frac{1}{2}\,(1\;\pm\;\frac{1}{\pi}\int_{-\infty}^{\infty} d\eta\;\frac{1}{D_0^{(k)}+V^{(k)}+i\eta}\,), \qquad k=1,2. \quad (2.4)$$

The projectors $P_+^{(k)}$ and $P_-^{(k)}=1-P_+^{(k)}$ (which projects onto the negative spectral subspace) are well-defined because of the existence of a gap in the spectrum of the (single-particle) Dirac operator. For later purpose we define $P_{+-}=P_+^{(1)}P_-^{(2)}$, $P_{--}=P_-^{(1)}P_-^{(2)}$ and $P_{-+}=P_-^{(1)}P_+^{(2)}$.

H acts on the Hilbert space of antisymmetrised two-electron 4-spinors, $\mathcal{H}_2 := \mathcal{A}(H_1(\mathbb{R}^3)\otimes\mathbb{C}^4)^2$ where $H_1(\mathbb{R}^3)$ is the Sobolev space of first order,

$$H_1(\mathbb{R}^3) \;=\; \{\varphi\in L_2(\mathbb{R}^3):\;\int_{\mathbb{R}^3}(1+p^2)\,|\hat{\varphi}(\mathbf{p})|^2\,d\mathbf{p}\;<\infty\}, \quad (2.5)$$

$L_2(\mathbb{R}^3)$ being the space of of square-integrable one-electron functions, $p=|\mathbf{p}|$ and $\hat{\varphi}$ denoting the Fourier transform of φ.

The way to construct the desired operator is most readily displayed in the one-electron case. Let $D_V^{(k)} := D_0^{(k)}+V^{(k)}$. Then one has the decomposition

$$D_V^{(k)} \;=\; P_+^{(k)}\,D_V^{(k)}\,P_+^{(k)} \;+\; P_-^{(k)}\,D_V^{(k)}\,P_-^{(k)} \quad (2.6)$$

because $P_\pm^{(k)}$ commutes with $D_V^{(k)}$. We apply a unitary transformation $U^{(k)}$ to $D_V^{(k)}$ with the property

$$U^{(k)-1}\,D_V^{(k)}\,U^{(k)} \;=\; \Lambda_+^{(k)}\,(U^{(k)-1}D_V^{(k)}U^{(k)})\,\Lambda_+^{(k)} \;+\; \Lambda_-^{(k)}\,(U^{(k)-1}D_V^{(k)}U^{(k)})\,\Lambda_-^{(k)} \quad (2.7)$$

where the operators $\Lambda_\pm^{(k)}$,

$$\Lambda_\pm^{(k)} \;=\; \frac{1}{2}\,(1\;\pm\;\frac{D_0^{(k)}}{E_{p_k}}), \qquad E_{p_k} \;=\; \sqrt{p_k^2+m^2}, \quad (2.8)$$

project onto the positive/negative spectral subspace of the *free* Dirac operator $D_0^{(k)}$ satisfying $D_0^{(k)}(\Lambda_\pm^{(k)}\varphi) = \pm E_{p_k}(\Lambda_\pm^{(k)}\varphi)$, and $\mathbf{p}_k=-i\nabla_{\mathbf{x}_k}$. (2.7) is a consequence of (2.6) if $U^{(k)}$ fulfils $U^{(k)-1}P_+^{(k)}U^{(k)} = \Lambda_+^{(k)}$, but $U^{(k)}$ is not uniquely determined [9] (see also [6]). Once $U^{(k)}$ is found (which in fact is done perturbatively according to the scheme described below), a second transformation $U_0^{(k)}$, introduced by Foldy and Wouthuysen [13] (see also [4]),

$$U_0^{(k)} \;=\; A(p_k)\,(1\;+\;\beta^{(k)}\,\frac{\boldsymbol{\alpha}^{(k)}\mathbf{p}_k}{E_{p_k}+m}), \qquad A(p_k) \;=\; \left(\frac{E_{p_k}+m}{2E_{p_k}}\right)^{\frac{1}{2}} \quad (2.9)$$

with its inverse $U_0^{(k)-1} = (1\;-\;\beta^{(k)}\,\frac{\boldsymbol{\alpha}^{(k)}\mathbf{p}_k}{E_{p_k}+m})\,A(p_k)$, casts $D_V^{(k)}$ into a block-diagonal form such that the electron's positive and negative spectral subspaces are decoupled,

$$M := \;U_0^{(k)}U^{(k)-1}\,D_V^{(k)}\,U^{(k)}U_0^{(k)-1} \;=\; \frac{1}{2}\,(1+\beta^{(k)})\,M\,\frac{1}{2}\,(1+\beta^{(k)}) + \frac{1}{2}\,(1-\beta^{(k)})\,M\,\frac{1}{2}\,(1-\beta^{(k)}), \quad (2.10)$$

since $U_0^{(k)} \Lambda_\pm^{(k)} U_0^{(k)-1} = \frac{1}{2}(1 \pm \beta^{(k)}) = \begin{pmatrix} I & 0 \\ 0 & 0 \end{pmatrix}$ resp. $\begin{pmatrix} 0 & 0 \\ 0 & I \end{pmatrix} \in \mathbb{C}^{4,4}$ for the plus resp. minus sign, with I the unit matrix in $\mathbb{C}^{2,2}$. Note that each of the two operators in (2.10) effectively acts on a 2-spinor space, because for $\binom{u_+}{u_-} \in H_1(\mathbb{R}^3) \otimes \mathbb{C}^4$, one has e.g. $\frac{1}{2}(1+\beta^{(k)})\binom{u_+}{u_-} = \binom{u_+}{0}$. Unitary transformations preserve the spectrum such that we have $\frac{1}{2}(1+\beta^{(k)})\, M \,\frac{1}{2}(1+\beta^{(k)}) \geq 0$ from $P_+^{(k)} D_V^{(k)} P_+^{(k)} \geq 0$. This positive operator is therefore the desired one-particle operator for describing solely the electronic degrees of freedom.

Let us turn to the two-electron case. We follow Douglas and Kroll [4] to work with products of single-particle projectors. We have $P_{++} + P_{+-} + P_{-+} + P_{--} = 1$ as well as $P_{+-}P_{++} = P_{-+}P_{++} = P_{--}P_{++} = 0$ and the decomposition

$$H \;=\; P_{++}\, H\, P_{++} \;+\; P_{+-}\, H\, P_{+-} \;+\; P_{-+}\, H\, P_{-+} \;+\; P_{--}\, H\, P_{--} \tag{2.11}$$

where it is used that single-particle operators acting on electron 1 commute with those acting on electron 2. One should keep in mind that (2.11) differs from the decomposition $H = P_+^{(12)} H P_+^{(12)} + P_-^{(12)} H P_-^{(12)}$ if $P_\pm^{(12)}$ were chosen to project onto the positive/negative spectral subspace of H (*including* the electron-electron interaction). Now we translate the step from (2.6) to (2.7) to the two-particle case, i.e. we search for a unitary transformation U which casts H into an operator that does not couple the positive and negative spectral subspaces of any of the free electrons. This is done by means of a perturbative approach in terms of the coupling constant e^2 which determines the strength of $V^{(12)}$ as well as (enhanced by the nuclear charge number) of the single-particle potentials $V^{(k)}$. We make the ansatz $U = e^{iB},\; B = B_1 + B_2 + ... + B_n$, and require that the transformed Coulomb-Dirac operator has the desired block-diagonal shape to order n in e^2,

$$U^{-1}\, H\, U \;=\; H^{(n)} \;+\; R^{(n+1)} \tag{2.12}$$

$$H^{(n)} \;=\; \Lambda_{++}\,(\sum_{l=0}^{n} H_l)\,\Lambda_{++} \;+\; \Lambda_{+-}\,(\sum_{l=0}^{n} H_l)\,\Lambda_{+-} \;+\; \Lambda_{-+}\,(\sum_{l=0}^{n} H_l)\,\Lambda_{-+} + \;\Lambda_{--}\,(\sum_{l=0}^{n} H_l)\,\Lambda_{--}$$

where H_l is an operator depending on U and containing the potential strength e^2 to l-th order, $l = 0, 1, ..., n$, while $R^{(n+1)}$ is a remainder which still allows for transitions between the positive and negative spectral subspaces of the electrons and which is of $(n+1)$-st order in e^2 relative to the free Dirac operator. The two-particle projectors are defined in terms of products of the single-particle projectors as before (e.g. $\Lambda_{+-} = \Lambda_+^{(1)} \Lambda_-^{(2)}$).

For $U(t) = e^{iBt},\; t \in \mathbb{R}$, we have the operator identity (see e.g. Sobolev [14])

$$U(-t)\, H\, U(t) \;=\; H \;+\; i \int_0^t dt'\; U(-t')\,[H, B]\, U(t')$$

$$\Longrightarrow \qquad U^{-1}\, H\, U \;=\; H \;+\; i[H, B] \;+\; \frac{i^2}{2}\,[\,[H, B], B] \;+ ... \tag{2.13}$$

where $U = U(1)$. The commutator $[H, B] = HB - BH$, and the second line in (2.13) results from iterating the operator identity and subsequently setting $t = 1$. By using $1 = \Lambda_+^{(k)} + \Lambda_-^{(k)}$, any operator A can be decomposed into

$$A \;=\; \text{proj}\;(A) \;+\; \text{off}\;(A), \tag{2.14}$$

$$\text{proj}\;(A) \;=\; \Lambda_{++}\, A\, \Lambda_{++} \;+\; \Lambda_{+-}\, A\, \Lambda_{+-} \;+\; \Lambda_{-+}\, A\, \Lambda_{-+} \;+\; \Lambda_{--}\, A\, \Lambda_{--},$$

where proj(A) does not couple the spectral subspaces while off(A) consists of all 12 off-diagonal terms (such as $\Lambda_{++} A \Lambda_{+-},\; \Lambda_{++} A \Lambda_{-+},\; \Lambda_{++} A \Lambda_{--}, ...$). The operators $B_1, ..., B_n$

defining U are determined in the following way. We decompose the potential in H into diagonal and off-diagonal terms according to (2.14) and consider $B_1, ..., B_n$ as expansion coefficients of B in the potential strength e^2, B_l being of order $(e^2)^l$, $l = 1, ..., n$.

In order to obtain a consistent perturbative expansion we also have to expand $P_+^{(k)}$ in powers of e^2. This is done by inserting the resolvent identity, $(D_0^{(k)} + V^{(k)} + i\eta)^{-1} = (D_0^{(k)} + i\eta)^{-1} - (D_0^{(k)} + i\eta)^{-1} V^{(k)} (D_0^{(k)} + V^{(k)} + i\eta)^{-1}$, repeatedly into the definition (2.4),

$$P_+^{(k)} \;=\; \Lambda_+^{(k)} \;-\; \frac{1}{2\pi}\int_{-\infty}^{\infty} d\eta\, \frac{1}{D_0^{(k)} + i\eta}\, V^{(k)}\, \frac{1}{D_0^{(k)} + V^{(k)} + i\eta} \tag{2.15}$$

$$= \Lambda_+^{(k)} \;-\; \frac{1}{2\pi}\int_{-\infty}^{\infty} d\eta \frac{1}{D_0^{(k)} + i\eta}\, V^{(k)} \left(\frac{1}{D_0^{(k)} + i\eta} \;-\; \frac{1}{D_0^{(k)} + i\eta}\, V^{(k)}\, \frac{1}{D_0^{(k)} + i\eta} \;+ ... \right)$$

$$=: \Lambda_+^{(k)} \;+\; F_0^{(k)} \;+\; F_1^{(k)} \;+ ...$$

This leads to the expansion of the electron-electron interaction term,

$$P_{++}\, V^{(12)}\, P_{++} \;=\; \Lambda_{++}\, V^{(12)}\, \Lambda_{++} \;+\; W_2 \;+\; W_3 \;+ ... \tag{2.16}$$

$$W_2 \;=\; F_0^{(1)} \Lambda_+^{(2)} V^{(12)} \Lambda_{++} \;+\; \Lambda_+^{(1)} F_0^{(2)} V^{(12)} \Lambda_{++} \;+\; \Lambda_{++} V^{(12)} F_0^{(1)} \Lambda_+^{(2)} \;+\; \Lambda_{++} V^{(12)} \Lambda_+^{(1)} F_0^{(2)}$$

with corresponding expressions for the terms W_l of l-th order in e^2, $l > 2$. Then (2.13) is written in the following way

$$U^{-1}\, H\, U \;=\; \sum_{k=1}^{2} D_0^{(k)} \;+\; \mathrm{proj}\,(\sum_{k=1}^{2} V^{(k)}) \;+\; \mathrm{off}\,(\sum_{k=1}^{2} V^{(k)}) \;+\; \Lambda_{++}\, V^{(12)}\, \Lambda_{++}$$

$$+\, W_2 \;+ ... +\; i\,[\sum_{k=1}^{2} D_0^{(k)}, B_1 + ... + B_n] \;+\; i\,[\sum_{k=1}^{2} V^{(k)}, B_1 + ... + B_n] \tag{2.17}$$

$$+\, i\,[\Lambda_{++} V^{(12)} \Lambda_{++}, B_1 + ... + B_n] \;+ ... +\; \frac{i^2}{2}\,[\,[\sum_{k=1}^{2} D_0^{(k)}, B_1 + ... + B_n], B_1 + ... + B_n] \;+ ...$$

where ... symbolise terms of at least third order in e^2. The operator B_1 is determined from the requirement that the linear off-diagonal term in (2.17) is cancelled,

$$\mathrm{off}\,(\sum_{k=1}^{2} V^{(k)}) \;+\; i\,[\sum_{k=1}^{2} D_0^{(k)}, B_1] \;=\; 0 \tag{2.18}$$

and it follows that B_1 is linear in the potential (i.e. in e^2).

We continue by collecting all terms on the r.h.s. of (2.17) which contain the potential to second order (and call them $V_2 := W_2 + i[\sum_{k=1}^{2} V^{(k)}, B_1] + i[\Lambda_{++} V^{(12)} \Lambda_{++}, B_1] + \frac{i^2}{2}\,[\,[\sum_{k=1}^{2} D_0^{(k)}, B_1], B_1]\,)$ and split them into $V_2 = \mathrm{proj}(V_2) + \mathrm{off}(V_2)$. Then B_2 is determined from the condition that the second-order off-diagonal term disappears,

$$\mathrm{off}\,(V_2) \;+\; i\,[\sum_{k=1}^{2} D_0^{(k)}, B_2] \;=\; 0. \tag{2.19}$$

This procedure, continued to order n, determines successively all operators B_l, $l = 1, ..., n$. It can be shown that all B_l are bounded self-adjoint operators on $(L_2(\mathbb{R}^3) \otimes \mathbb{C}^4)^2$, such that the transformation U is well-defined.

3 The transformed pseudo-relativistic second-order operator

For $n=2$, we obtain the transformed operator (to order $(e^2)^3$) in terms of B_1, using (2.18)

$$H^{(2)} \;=\; \mathrm{proj}\,(\sum_{k=1}^{2}(D_0^{(k)}+V^{(k)}) \;+\; i\,[\mathrm{proj}\,(\sum_{k=1}^{2}V^{(k)}),B_1] \;+\; \frac{i}{2}\,[\mathrm{off}\,(\sum_{k=1}^{2}V^{(k)}),B_1]$$
$$+\,i\,[\Lambda_{++}V^{(12)}\Lambda_{++},B_1] \;+\; W_2 \;+\; \Lambda_{++}V^{(12)}\Lambda_{++}). \tag{3.1}$$

Since $\Lambda_\pm^{(k)}$ commutes with $D_0^{(k)}$ one has $\mathrm{off}(\sum_{k=1}^2 D_0^{(k)})=0$, and from $(\Lambda_\pm^{(k)})^2=\Lambda_\pm^{(k)}$ one has $\Lambda_{++}V^{(12)}\Lambda_{++} = \mathrm{proj}(\Lambda_{++}V^{(12)}\Lambda_{++})$.

It remains to determine B_1. From the defining equation (2.18) it is easily seen that one can decompose B_1 into a sum of one-particle operators, $B_1=B_1^{(1)}+B_1^{(2)}$, each obeying $\Lambda_+^{(k)}V^{(k)}\Lambda_-^{(k)}+\Lambda_-^{(k)}V^{(k)}\Lambda_+^{(k)}+i[D_0^{(k)},B_1^{(k)}]=0,\;\; k=1,2$. In order to obtain B_1 explicitly it is convenient to work in Fourier space and to consider $B_1^{(k)}$ as a pseudodifferential operator. It is defined by its symbol $\phi_1^{(k)}$ and acts on $\varphi\in L_2(\mathbb{R}^3)\otimes\mathbb{C}^4$,

$$(B_1^{(k)}\varphi)(\mathbf{x}) \;=\; \frac{1}{(2\pi)^3}\int d\mathbf{p}\int d\mathbf{q}\; e^{i(\mathbf{p}+\mathbf{q})\mathbf{x}}\;\phi_1^{(k)}(\mathbf{q},\mathbf{p})\;\hat{\varphi}(\mathbf{p}) \tag{3.2}$$

where $\hat\varphi$ is the Fourier transform of φ and if not denoted explicitly, the integration is over the whole space $\mathbb{R}^3$. Using the Fourier representation of the Coulomb potential, $1/x=(2\pi^2)^{-1}\int d\mathbf{q}\,e^{i\mathbf{q}\mathbf{x}}/q^2$, and recalling that $D_0^{(k)}$ and $\Lambda_\pm^{(k)}$ are multiplication operators in momentum space, one obtains the (unique) solution

$$\phi_1^{(k)}(\mathbf{q},\mathbf{p}) \;=\; -\,\frac{i\gamma}{\sqrt{2}\pi q^2}\;\frac{1}{E_p+E_{|\mathbf{q}+\mathbf{p}|}}\;(\tilde D_0^{(k)}(\mathbf{q}+\mathbf{p})\;-\;\tilde D_0^{(k)}(\mathbf{p})) \tag{3.3}$$

where $\tilde D_0^{(k)}(\mathbf{p}) \;=\; D_0^{(k)}(\mathbf{p})/E_p \;=\; (\boldsymbol{\alpha}^{(k)}\mathbf{p}+\beta^{(k)}m)/E_p$. There is a close relation between $B_1^{(k)}$ and $F_0^{(k)}$ which helps to simplify the operator $H^{(2)}$. From (2.15) we have the Fourier representation

$$(F_0^{(k)}\varphi)(\mathbf{x}) \;=\; \frac{\gamma}{(2\pi)^{\frac52}}\int_{-\infty}^{\infty}d\eta\;\frac{1}{D_0^{(k)}+i\eta}\int d\mathbf{q}\;e^{i\mathbf{q}\mathbf{x}}\;\frac{1}{2\pi^2q^2}\;\frac{1}{D_0^{(k)}+i\eta}\int d\mathbf{p}\;e^{i\mathbf{p}\mathbf{x}}\;\hat\varphi(\mathbf{p}). \tag{3.4}$$

Using $(D_0^{(k)}+i\eta)^{-1}e^{i\mathbf{s}\mathbf{x}} \;=\; (D_0^{(k)}(\mathbf{s})-i\eta)/(E_s^2+\eta^2)\,e^{i\mathbf{s}\mathbf{x}}$, the theorem of residues can be applied to evaluate the η-integral. Defining the symbol $f_0^{(k)}$ of $F_0^{(k)}$ by means of a (3.2)-type equation, one obtains $f_0^{(k)}(\mathbf{q},\mathbf{p}) \;=\; -i\tilde D_0^{(k)}(\mathbf{q}+\mathbf{p})\phi_1^{(k)}(\mathbf{q},\mathbf{p})$. This leads to the operator relations

$$F_0^{(k)} \;=\; -i\,\tilde D_0^{(k)}B_1^{(k)}, \qquad B_1^{(k)} \;=\; i\,\tilde D_0^{(k)}F_0^{(k)} \;=\; -i\,F_0^{(k)}\tilde D_0^{(k)} \tag{3.5}$$

since $(\tilde D_0^{(k)})^2=1$. With (3.5), B_1 can be eliminated from the second-order terms of $H^{(2)}$.

In the following we restrict $H^{(2)}$ to the positive spectral subspace of the two (free) electrons, $\mathcal{H}_{+,2}:=\Lambda_{++}\,(\mathcal{A}\,(H_1(\mathbb{R}^3)\otimes\mathbb{C}^4)^2)$. Then one obtains for $\psi\in\mathcal{H}_{+,2}$ the identity $\Lambda_{++}\psi=\psi=\Lambda_+^{(1)}\psi=\Lambda_+^{(2)}\psi$ and only the first term of $\mathrm{proj}(A)$ in (2.14) survives. Eliminating B_1 with the help of (3.5) from the two-particle second-order term, the expectation value of $H^{(2)}$ can be reduced to the following expression

$$(\psi,H^{(2)}\,\psi) \;=\; (\psi,\left(\sum_{k=1}^{2}(D_0^{(k)}+V^{(k)}\;+\;\frac{i}{2}\,[\mathrm{off}\,(V^{(k)}),B_1^{(k)}])\;+\;V^{(12)}\;+\;C^{(12)}\right)\psi) \tag{3.6}$$

$$C^{(12)} \;=\; \sum_{k=1}^{2} (V^{(12)} \Lambda_-^{(k)} F_0^{(k)} \;+\; F_0^{(k)} \Lambda_-^{(k)} V^{(12)}).$$

We note that the expectation value of $[\text{proj}(V^{(k)}), B_1^{(k)}]$ can be shown to vanish since $B_1^{(k)}$ induces an off-diagonal coupling of the spectral subspaces. In the analysis below we identify $H^{(2)}$ restricted to $\mathcal{H}_{+,2}$ with the operator given on the r.h.s. of (3.6).

For numerical purposes it is sometimes convenient to construct from $H^{(2)}$ an operator $h^{(2)}$ which acts on $\mathcal{A}\,(H_1(\mathbb{R}^3) \otimes \mathbb{C}^2)^2$ rather than on $\mathcal{H}_{+,2}$. This corresponds to the step from (2.7) to (2.10) in the single-particle case and relies on the fact that any single-particle state φ in the positive spectral subspace $\Lambda_+^{(k)}\,(H_1(\mathbb{R}^3) \otimes \mathbb{C}^4)$ can be expressed by

$$\varphi \;=\; U_0^{(k)-1} \begin{pmatrix} u_+ \\ 0 \end{pmatrix} \;=\; U_0^{(k)-1}\, \frac{1}{2}(1+\beta^{(k)}) \begin{pmatrix} u_+ \\ u_- \end{pmatrix} \tag{3.7}$$

with $u_+, u_- \in H_1(\mathbb{R}^3) \otimes \mathbb{C}^2$ and $U_0^{(k)}$ the Foldy-Wouthuysen transformation from (2.9). In the two-particle case we define for $u \in \mathcal{A}\,(H_1(\mathbb{R}^3) \otimes \mathbb{C}^2)^2$ the operator $h^{(2)}$ by means of

$$(\psi, H^{(2)}\,\psi) \;=\; (u, h^{(2)}\,u) \tag{3.8}$$

$$\begin{pmatrix} h^{(2)} & 0 \\ 0 & 0 \end{pmatrix} \;=\; \frac{1}{2}(1+\beta^{(1)})\,\frac{1}{2}(1+\beta^{(2)})\, U_0^{(1)} U_0^{(2)}\, H^{(2)}\, U_0^{(1)-1} U_0^{(2)-1}\, \frac{1}{2}(1+\beta^{(1)})\,\frac{1}{2}(1+\beta^{(2)})$$

where $h^{(2)}$ is a 4,4 matrix-valued operator. It can be shown that $h^{(2)}$ agrees with the second-order operator derived in [4] (except for an error corrected by Jansen and Hess [15]). The single-particle part of $h^{(2)}$ is termed Jansen-Hess operator and its semiboundedness and spectral properties are derived in [16, 17].

4 The relative form boundedness of the potential

For a mathematical analysis the pseudo-relativistic operator in its representation $H^{(2)}$ is more appropriate than the representation $h^{(2)}$, in particular because the two-particle contribution to $h^{(2)}$ is very involved (its second-order term has up to now been dropped in all atomic structure calculations, while the first-order term has been replaced by the untransformed operator $V^{(12)}$ [6]).

The operator $H^{(2)}$ defined in (3.6) is for brevity written in the following way

$$H^{(2)} \;=\; T \;+\; W, \tag{4.1}$$

$$T \;=\; D_0^{(1)} \;+\; D_0^{(2)}, \qquad W \;=\; \sum_{k=1}^{2} (V^{(k)} \;+\; V_2^{(k)}) \;+\; V^{(12)} \;+\; C^{(12)}$$

with $V_2^{(k)} \;=\; \frac{i}{2}\,[\Lambda_+^{(k)} V^{(k)} \Lambda_-^{(k)} \;+\Lambda_-^{(k)} V^{(k)} \Lambda_+^{(k)}, B_1^{(k)}]$.

In this section we will show the $|T|$-form boundedness of W and determine the potential strength $\gamma = Ze^2$ such that the form bound c is less than one,

$$|(\psi, W\,\psi)| \;\leq\; c\,(\psi, T\psi) \;+\; C\,(\psi,\psi) \tag{4.2}$$

with $\psi \in \mathcal{H}_{+,2}$ and $C \geq 0$ a real number. This proves that $H^{(2)}$ is bounded from below,

$$(\psi, (T+W)\,\psi) \;\geq\; (1-c)\,(\psi, T\psi) \;-\; C\,(\psi,\psi) \;\geq\; -C\,(\psi,\psi) \tag{4.3}$$

since $1-c>0$ and $|T|\geq 0$. Therefore, the symmetric operator $H^{(2)}$ is well-defined in the form sense, and there exists its Friedrichs extension to a self-adjoint operator on $\Lambda_{++}(\mathcal{A}(L_2(\mathbb{R}^3)\otimes\mathbb{C}^4)^2)$.

We recall that for any state ψ in the positive spectral subspace $\mathcal{H}_{+,2}$ one has $(\psi,T\psi)=(\psi,(E_{p_1}+E_{p_2})\psi)$. Since $E_{p_k}=\sqrt{p_k^2+m^2}\geq p_k$ it is therefore sufficient to show that all contributions to W are form bounded relative to p_1+p_2. Moreover, the bounds of an operator are not changed by a unitary transformation, such that the single-particle estimates can be taken from existing work on the Jansen-Hess operator.

For the one-particle operator $D_V^{(k)}$ acting on $\varphi\in\Lambda_+(H_1(\mathbb{R}^3)\otimes\mathbb{C}^4)$ (known by the name Brown-Ravenhall operator), Burenkov and Evans [18] derived the following bound,

$$(\varphi,(D_0^{(k)}-\frac{\gamma}{x_k})\varphi)\;\geq\;(1-\frac{\gamma}{\gamma_{BR}})\,(\varphi,E_{p_k}\varphi) \tag{4.4}$$

with $\gamma_{BR}=\frac{2}{\pi/2+2/\pi}=0.906$. When $D_V^{(k)}$ is estimated by using a two-particle function $\psi\in\mathcal{H}_{+,2}$, we set $\psi(\mathbf{x}_1,\mathbf{x}_2)=:\psi_{x_2}(\mathbf{x}_1)$ and consider $\mathbf{x}_2$ as parameter. Then (4.4) holds for $\varphi:=\psi_{x_2}(\mathbf{x}_1)$ and $k=1$, and subsequent integration over $\mathbf{x}_2$ proves the general result that the estimates of single-particle operators are unchanged if two-particle functions are used. The estimate of the electron-electron interaction follows immediately from (4.4) for $\psi\in\mathcal{H}_{+,2}$,

$$(\psi,V^{(12)}\psi)\;\leq\;\frac{e^2}{\gamma_{BR}}\,(\psi,E_{p_1}\psi)\;=\;\frac{e^2}{2\gamma_{BR}}\,(\psi,(E_{p_1}+E_{p_2})\psi), \tag{4.5}$$

where in the last step the antisymmetry of ψ with respect to particle exchange is used.

Next we estimate the potential $C^{(12)}$. It is sufficient to prove the relative boundedness for the $k=1$ contribution to $C^{(12)}$, $V^{(12)}\Lambda_-^{(1)}F_0^{(1)}+F_0^{(1)}\Lambda_-^{(1)}V^{(12)}=:C_1^{(12)}$. The estimate is performed in momentum space where T is diagonal. $C_1^{(12)}$ is represented by its kernel k_C,

$$(\widehat{C_1^{(12)}\psi})(\mathbf{p}_1,\mathbf{p}_2)\;=\;\int d\mathbf{p}_1'\,d\mathbf{p}_2'\;k_C(\mathbf{p}_1,\mathbf{p}_2;\mathbf{p}_1',\mathbf{p}_2')\;\hat{\psi}(\mathbf{p}_1',\mathbf{p}_2') \tag{4.6}$$

where the integral is over 6-dimensional space $\mathbb{R}^3\times\mathbb{R}^3$. Equivalently, $C_1^{(12)}$ can be defined through its symbol ϕ_C,

$$(C_1^{(12)}\psi)(\mathbf{x}_1,\mathbf{x}_2)\;=\;\frac{1}{(2\pi)^6}\int d\mathbf{p}_1'\,d\mathbf{p}_2'\,d\mathbf{p}_1\,d\mathbf{p}_2\;e^{i(\mathbf{p}_1'+\mathbf{p}_1)\mathbf{x}_1}\;e^{i(\mathbf{p}_2'-\mathbf{p}_2)\mathbf{x}_2} \tag{4.7}$$

$$\cdot\phi_C(\mathbf{p}_1,\mathbf{p}_2;\mathbf{p}_1',\mathbf{p}_2')\;\hat{\psi}(\mathbf{p}_1',\mathbf{p}_2')$$

and k_C is related to the symbol via $k_C(\mathbf{p}_1,\mathbf{p}_2;\mathbf{p}_1',\mathbf{p}_2')=(2\pi)^{-3}\,\phi_C(\mathbf{p}_1-\mathbf{p}_1',\mathbf{p}_2'-\mathbf{p}_2;\mathbf{p}_1',\mathbf{p}_2')$. With the help of (3.5), (3.3) and the Fourier representation of $V^{(12)}$, one obtains

$$\begin{aligned} k_C(\mathbf{p}_1,\mathbf{p}_2;\mathbf{p}_1',\mathbf{p}_2')\;&=\;-\frac{\gamma e^2}{(2\pi)^4}\,\frac{1}{|\mathbf{p}_2-\mathbf{p}_2'|^2}\,\frac{1}{|\mathbf{p}_2-\mathbf{p}_2'+\mathbf{p}_1-\mathbf{p}_1'|^2}\\ &\cdot\left\{\frac{1}{E_{|\mathbf{p}_2-\mathbf{p}_2'+\mathbf{p}_1|}+E_{p_1'}}\,(1-\tilde{D}_0^{(1)}(\mathbf{p}_2-\mathbf{p}_2'+\mathbf{p}_1))\,(1+\tilde{D}_0^{(1)}(\mathbf{p}_1'))\right.\\ &\left.+\frac{1}{E_{p_1}+E_{|\mathbf{p}_2'-\mathbf{p}_2+\mathbf{p}_1'|}}\,(1+\tilde{D}_0^{(1)}(\mathbf{p}_1))\,(1-\tilde{D}_0^{(1)}(\mathbf{p}_2'-\mathbf{p}_2+\mathbf{p}_1'))\right\}. \end{aligned} \tag{4.8}$$

For the estimate of $C_1^{(12)}$, the Lieb and Yau formula is used, which is a consequence of the Schur test for the boundedness of integral operators, and which can be derived from the Schwarz inequality [19] (see also [10, Lemma II.1])

$$|(\psi, C_1^{(12)}\,\psi)| \;=\; |(\hat{\psi}, \widehat{C_1^{(12)}\psi})|$$

$$\leq \int d\mathbf{p}_1\, d\mathbf{p}_2\, d\mathbf{p}_1'\, d\mathbf{p}_2'\; |\hat{\psi}(\mathbf{p}_1,\mathbf{p}_2)|\; |k_C(\mathbf{p}_1,\mathbf{p}_2;\mathbf{p}_1',\mathbf{p}_2')|\; |\hat{\psi}(\mathbf{p}_1',\mathbf{p}_2')|$$

$$\leq \int d\mathbf{p}_1\, d\mathbf{p}_2\; |\hat{\psi}(\mathbf{p}_1,\mathbf{p}_2)|^2 \cdot J_0(\mathbf{p}_1,\mathbf{p}_2) \tag{4.9}$$

$$J_0(\mathbf{p}_1,\mathbf{p}_2) \;=\; \int d\mathbf{p}_1'\, d\mathbf{p}_2'\; |k_C(\mathbf{p}_1,\mathbf{p}_2;\mathbf{p}_1',\mathbf{p}_2')|\; \frac{f(p_1)}{f(p_1')}\, \frac{g(p_2)}{g(p_2')}$$

since the estimate of $|k_C|$ is symmetric with respect to the interchange $(\mathbf{p}_1,\mathbf{p}_2) \leftrightarrow (\mathbf{p}_1',\mathbf{p}_2')$. The functions $f(p) > 0$ and $g(p) > 0$ for $p > 0$ are suitably chosen convergence generating functions. We take $f(p) = p^2$ and $g = 1$ and use spherical coordinates, i.e. $\int_{\mathbb{R}^3} d\mathbf{p} = \int_0^\infty p^2 dp \int_{S^2} d\omega$ with $\int_{S^2} d\omega = 2\pi \int_{-1}^1 d(\cos\vartheta)$. Estimating $\frac{1}{E_p} \leq \frac{1}{p}$ and $|1 \pm \tilde{D}_0| \leq 2$, one can use the formulae

$$\int_{\mathbb{R}^3} \frac{d\mathbf{p}_1'}{p_1'^2}\, \frac{1}{q+p_1'}\, \frac{1}{|\mathbf{q}+\mathbf{p}_1'|^2} \;=\; \frac{2\pi}{q} \int_0^\infty \frac{dp_1'}{p_1'}\, \frac{1}{q+p_1'}\, \ln \frac{q+p_1'}{|q-p_1'|} \;=\; \frac{\pi^3}{2q^2}$$

$$\int_{\mathbb{R}^3} \frac{d\mathbf{q}}{q^2}\, \frac{1}{|\mathbf{q}+\mathbf{p}_1|^2} \;=\; \frac{\pi^3}{p_1} \tag{4.10}$$

to obtain $J_0(\mathbf{p}_1,\mathbf{p}_2) \leq \frac{\gamma e^2 \pi^2}{4}\, p_1$ and therefore

$$|(\psi, C^{(12)}\,\psi)| \;=\; 2\,|(\psi, C_1^{(12)}\psi)| \;\leq\; \gamma e^2\, \frac{\pi^2}{2} \int d\mathbf{p}_1\, d\mathbf{p}_2\; |\hat{\psi}(\mathbf{p}_1,\mathbf{p}_2)|^2\, p_1$$

$$=\; \gamma e^2\, \frac{\pi^2}{4}\, (\psi, (p_1+p_2)\,\psi). \tag{4.11}$$

For an upper estimate of the single-particle potential $V^{(k)} + V_2^{(k)}$ we use that for $\gamma \leq 4/\pi$ the massless ($m = 0$) version of this potential fulfils $V_{m=0}^{(k)} + V_{2,m=0}^{(k)} \leq 0$ [17]. In addition one has the relative form boundedness of $V^{(k)}$ and $V_2^{(k)}$ with respect to the $m = 0$ potentials, $|(\psi, (V^{(k)} - V_{m=0}^{(k)})\,\psi)| \leq \frac{3}{2} m\gamma(\psi,\psi)$ and $|(\psi, (V_2^{(k)} - V_{2,m=0}^{(k)})\psi)| \leq m d_0 \gamma^2 (\psi,\psi)$, respectively [20, 16] with $d_0 = 8 + 12\sqrt{2}$. Then one obtains

$$(\psi, W\,\psi) \;\leq\; (3m\gamma \,+\, 2md_0\gamma^2)\,(\psi,\psi) \;+\; (\frac{e^2}{2\gamma_{BR}} \,+\, \frac{\gamma e^2 \pi^2}{4})\,(\psi, (E_{p_1}+E_{p_2})\,\psi). \tag{4.12}$$

For the lower bound we use $V^{(12)} \geq 0$ and $(\psi, V_2^{(k)}\psi) \geq -md_0\gamma(\psi,\psi)$ since $(\psi, V_{2,m=0}^{(k)}\psi) \geq 0$ [16]. Then with (4.4) and (4.11),

$$(\psi, W\,\psi) \;\geq\; -\frac{\gamma}{\gamma_{BR}}\,(\psi, (E_{p_1}+E_{p_2})\,\psi) \,-\, 2md_0\gamma\,(\psi,\psi) \,-\, \gamma e^2\, \frac{\pi^2}{4}\,(\psi, (E_{p_1}+E_{p_2})\,\psi). \tag{4.13}$$

Combining (4.12) and (4.13) we obtain the final result

$$|(\psi, W\,\psi)| \;\leq\; c\,(\psi, T\,\psi) \;+\; (3m\gamma \,+\, 2md_0\gamma^2)\,(\psi,\psi) \tag{4.14}$$

with $c = \gamma(\frac{1}{\gamma_{BR}} + \frac{e^2\pi^2}{4})$ for $\gamma > e^2/2$, and $c \ll 1$ for $\gamma \leq e^2/2$. When $\gamma < 0.89$ (corresponding to $Z \leq 122$), the form bound c is smaller than one which proves the assertion (4.2).

5 Subdominance of the second-order poptentials

We wish to establish up to which central field strength γ the single-particle as well as two-particle second-order potentials are controlled by the respective first-order potentials, i.e. we want to prove for $\psi \in \mathcal{H}_{+,2}$,

$$|(\psi, V_2^{(k)}\,\psi)| \;\leq\; c_1\,(\psi, (-V^{(k)})\,\psi) \tag{5.1}$$

and

$$|(\psi, C^{(12)}\,\psi)| \;\leq\; c_2\,(\psi, V^{(12)}\,\psi) \tag{5.2}$$

with constants c_1 and c_2 smaller than one. In contrast to the previous section where we relied on $D_0^{(k)}$ being a multiplication operator in momentum space to carry out all estimates in Fourier space, we are now in the situation that $V^{(k)}$ as well as $V^{(12)}$ are diagonal operators in coordinate space. This poses the problem tht the kernels of $V_2^{(k)}$ and $C^{(12)}$ which are known in momentum space have to be transformed to coordinate space. The method of proof will be displayed for the one-particle case (5.1).

From the definition of $V_2^{(k)}$ in (4.1), the explicit expression (3.3) for the symbol of $B_1^{(k)}$ and the Fourier representation of the Coulomb field $V^{(k)}$, one obtains for the kernel $k_V^{(k)}$ of $V_2^{(k)}$,

$$k_V^{(k)}(\mathbf{p},\mathbf{p}') \;=\; \frac{\gamma^2}{16\pi^4}\int d\mathbf{p}''\,\frac{1}{|\mathbf{p}''-\mathbf{p}|^2}\,\frac{1}{|\mathbf{p}''-\mathbf{p}'|^2}\,(1-\tilde{D}_0^{(k)}(\mathbf{p}''))\,(\frac{1}{E_{p''}+E_p}\;+\;\frac{1}{E_{p''}+E_{p'}}) \tag{5.3}$$

where the relation $k_V^{(k)}(\mathbf{p},\mathbf{p}') \;=\; (2\pi)^{-3/2}\,\phi_V^{(k)}(\mathbf{p}-\mathbf{p}',\mathbf{p}')$ between the kernel and the symbol $\phi_V^{(k)}$ of $V_2^{(k)}$ was used. We write for $k=1$

$$(\psi, V_2^{(1)}\,\psi) \;=\; \int d\mathbf{x}_1\,d\mathbf{x}_2\,\overline{\psi(\mathbf{x}_1,\mathbf{x}_2)}\int d\mathbf{x}'\,\check{k}_V^{(1)}(\mathbf{x}_1,\mathbf{x}')\,\psi(\mathbf{x}',\mathbf{x}_2) \tag{5.4}$$

with

$$\check{k}_V^{(1)}(\mathbf{x}_1,\mathbf{x}') \;=\; \frac{1}{(2\pi)^3}\int d\mathbf{p}\,e^{i\mathbf{p}\mathbf{x}_1}\int d\mathbf{p}'\,k_V^{(1)}(\mathbf{p},\mathbf{p}')\,e^{-i\mathbf{p}'\mathbf{x}'}. \tag{5.5}$$

Making use of the Fourier representations

$$\int d\mathbf{q}\,e^{i\mathbf{q}\mathbf{x}}\,\frac{1}{q^2} \;=\; \frac{2\pi^2}{x}, \qquad \int d\mathbf{q}\,e^{i\mathbf{q}\mathbf{x}}\,\frac{1}{q} \;=\; \frac{4\pi}{x^2}, \tag{5.6}$$

(5.5) reduces to a 6-dimensional integral

$$\check{k}_V^{(1)}(\mathbf{x}_1,\mathbf{x}') \;=\; 2\pi^2\,\frac{\gamma^2}{(2\pi)^7}\,\left[\frac{1}{x'}\,I_1(\mathbf{x}_1,\mathbf{x}')\;+\;\frac{1}{x_1}\,I_1(-\mathbf{x}',-\mathbf{x}_1)\right]$$

$$I_1(\mathbf{x}_1,\mathbf{x}') \;=\; \int d\mathbf{p}\,d\mathbf{p}''\,e^{i\mathbf{p}\mathbf{x}_1}\,e^{-i\mathbf{p}''\mathbf{x}'}\,\frac{1}{|\mathbf{p}''-\mathbf{p}|^2}\,(1-\tilde{D}_0^{(1)}(\mathbf{p}''))\,\frac{1}{E_{p''}+E_p}. \tag{5.7}$$

We did not find it possible to evaluate the integral analytically, but instead apply a peaking approximation. We make the substitution $\mathbf{q} = \mathbf{p}'' - \mathbf{p}$ for $\mathbf{p}$ which leads to the factor $\frac{1}{q^2}\,(E_{p''} + E_{|\mathbf{p}''-\mathbf{q}|})^{-1}$. This enhances small values of q and we therefore drop $\mathbf{q}$ in the energy denominator. Additionally we set the mass to zero and use that $\|1-\tilde{D}_0^{(1)}(\mathbf{p}'')\| = 2$ to replace $(1-\tilde{D}_0^{(1)}(\mathbf{p}''))$ by 2. The convergence properties of the integral remain thereby unchanged, but one picks up an additional multiplicative constant C (of order unity) in the estimate of $|\check{k}_V^{(1)}(\mathbf{x}_1, \mathbf{x}')|$. The result is

$$|I_1(\mathbf{x}_1, \mathbf{x}')| \;\le\; C \left(\int d\mathbf{q}\, e^{-i\mathbf{q}\mathbf{x}_1}\, \frac{1}{q^2} \right) \left(\int d\mathbf{p}''\; e^{i\mathbf{p}''(\mathbf{x}_1 - \mathbf{x}')}\, \frac{1}{p''} \right) \;=\; C\, \frac{2\pi^2}{x_1} \cdot \frac{4\pi}{|\mathbf{x}_1 - \mathbf{x}'|^2}. \tag{5.8}$$

Going back to the desired estimate of $V_2^{(1)}$, we apply the Lieb and Yau formula for the one-particle case to (5.4) and obtain

$$\begin{aligned} |(\psi, V_2^{(1)}\, \psi)| \;&\le\; \int d\mathbf{x}_1\, d\mathbf{x}_2\; |\psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \int d\mathbf{x}'\; |\check{k}_V^{(1)}(\mathbf{x}_1, \mathbf{x}')|\; \frac{f(x_1)}{f(x')} \\ &\le\; \int d\mathbf{x}_1\, d\mathbf{x}_2\; |\psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \cdot C\, \frac{\pi\gamma^2}{4}\, \frac{1}{x_1} \end{aligned} \tag{5.9}$$

where $f(x) = x$ and (4.10) was used. The same estimate holds for $V_2^{(2)}$. Hence we get

$$|(\psi, V_2^{(k)}\, \psi)| \;\le\; c_1\, (\psi, (-V^{(k)})\, \psi) \tag{5.10}$$

with $c_1 = C\,\gamma\pi/4$ which is less than one for $\gamma < \frac{4}{\pi C}$. This proves that the total one-particle interaction is negative,

$$(\psi, (V^{(k)} + V_2^{(k)})\, \psi) \;\le\; (1 - c_1)\, (\psi, V^{(k)}\, \psi) \;<\; 0 \tag{5.11}$$

if $c_1 < 1$. We recall that in the massless case, (5.11) holds for $\gamma < 4/\pi$ i.e. $C = 1$. However, the proof for $m = 0$ is done in a very different way, involving the partial wave representation of the operators and their Mellin transforms [16, 17]. This method is not applicable in the $m \neq 0$ case.

In a similar way, the two-particle estimate is obtained,

$$|(\psi, C^{(12)}\, \psi)| \;\le\; \tilde{C}\, \gamma\pi\; (\psi, V^{(12)}\, \psi), \tag{5.12}$$

again with $\tilde{C}$ a constant of order unity. Thus $c_2 = \tilde{C}\gamma\pi$ is smaller than one for $\gamma < \frac{1}{\pi\tilde{C}}$ which for $\tilde{C} = 1$ gives $\gamma < \frac{1}{\pi}$ (corresponding to $Z \le 43$). We note that this rather low estimate for the critical γ is not sharp: We have estimated the factors in the kernel of $C^{(12)}$ of the type $(1 - \tilde{D}_0^{(1)}(\mathbf{q} + \mathbf{p}'))\,(1 + \tilde{D}_0^{(1)}(\mathbf{p}'))$ by 4 while the peaking value ($\mathbf{q} = 0$) would be $(1 - \tilde{D}_0^{(1)}(\mathbf{p}'))\,(1 + \tilde{D}_0^{(1)}(\mathbf{p}')) \;= 0$. Therefore, we conjecture that the value for c_2 is smaller than $\gamma\pi$.

6 Positivity of the pseudo-relativistic operator $H^{(2)}$

The operator which we have selected by means of restriction to the positive spectral subspace $\mathcal{H}_{+,2}$ of the free Dirac operator, $\Lambda_{++} H^{(2)} \Lambda_{++}$, is not from the outset a positive operator. Whereas in the single-particle case one has $P_+^{(k)} D_V^{(k)} P_+^{(k)} \;\ge 0$ and hence also $\Lambda_+^{(k)}\, U^{(k)-1} D_V^{(k)} U^{(k)}\, \Lambda_+^{(k)} \ge 0$ for an exact choice of U (see section 2), the neglect of the interelectronic interaction in the two-particle projectors as well as the perturbative treatment of the unitary transformation U can in principle destroy this property. Therefore we give a proof of positivity by using the explicit representation of $H^{(2)}$.

Again we make use of a single-particle estimate [21]

$$(\psi, (D_0^{(k)} + V^{(k)} + V_2^{(k)})\,\psi) \;\geq\; (1 - \frac{\gamma}{\gamma_{BR}} - d\gamma^2)\,(\psi, E_{p_k}\,\psi) \tag{6.1}$$

where $d = \frac{1}{8}\,(\frac{\pi}{2} - \frac{2}{\pi})^2$. Estimating $V^{(12)} \geq 0$ as before and applying the estimate (4.11) for $C^{(12)}$, one gets

$$(\psi, H^{(2)}\,\psi) \;\geq\; (1 - \frac{\gamma}{\gamma_{BR}} - d\gamma^2)\,(\psi, T\,\psi) \;-\; \gamma e^2\,\frac{\pi^2}{4}\,(\psi, T\,\psi). \tag{6.2}$$

The r.h.s. is positive if $c_0 := 1 - \gamma(\frac{1}{\gamma_{BR}} + e^2\pi^2/4) - d\gamma^2 > 0$ which is the case for $\gamma < 0.825$ $(Z \leq 113)$. We conjecture that this bound for $H^{(2)}$ is not sharp, because for the massless single-particle operator one obtains $(1 - \frac{\gamma}{\gamma_{BR}} + d\gamma^2)\,(\psi, p_k\psi)$ in place of the r.h.s. of (6.1) (this result is again found with the help of Mellin transform techniques [16]). This bound for $m = 0$ leads to positivity of $H^{(2)}$ for $\gamma < 0.986$, which is very close to the limiting value $\gamma = 1$ from the exact one-electron Dirac theory.

7 Concluding remarks

We have established a pseudo-relativistic operator $H^{(2)}$ which describes two electrons in a central Coulomb potential of strength γ. This operator, which includes terms up to second order in the coupling constant e^2, is well-defined for potential strengths $\gamma < 0.89$. Moreover, the terms of $H^{(2)}$ describing interaction potentials of second order in e^2 are shown to be smaller than the corresponding first-order terms for at least $\gamma < 1/\pi$, which assures that the single-particle potential of $H^{(2)}$ is attractive and the two-particle potential repulsive as is the case for the Coulomb-Dirac operator. The spectrum of $H^{(2)}$ is positive for $\gamma < 0.825$.

It is straightforward to derive a pseudo-relativistic operator for the N-electron ion with $N \leq Z$, applying the same transformation scheme. It can be shown that to second order in e^2, potentials affecting more than two electrons simultaneously do not occur. Rather, we get a simple generalisation of $H^{(2)}$, if acting on the positive spectral subspace $\mathcal{H}_{+,N} = \Lambda_{+,N}\,(\mathcal{A}(H_1(\mathbb{R}^3) \otimes \mathbb{C}^4)^N)$ of antisymmetrised N-electron spinors, where $\Lambda_{+,N} = \Lambda_+^{(1)}\Lambda_+^{(2)}\cdots\Lambda_+^{(N)}$ is the product of the free single-particle projectors. The operator is given by

$$\begin{aligned} H_N^{(2)} \;=\; \sum_{k=1}^{N}(D_0^{(k)} + V^{(k)} + V_2^{(k)}) \;+\; \sum_{\substack{n,k=1\\ n<k}}^{N} \Big\{ V^{(nk)} \;+\; V^{(nk)}\,(\Lambda_-^{(n)}F_0^{(n)} \;+\; \Lambda_-^{(k)}F_0^{(k)}) \\ +\; (F_0^{(n)}\Lambda_-^{(n)} \;+\; F_0^{(k)}\Lambda_-^{(k)})\,V^{(nk)} \Big\} \end{aligned} \tag{7.1}$$

where $V^{(nk)}$ is the Coulomb repulsion between electrons n and k. Thus, our earlier estimates can be used when determining the bounds for the N-electron operators. In particular, using the antisymmetry of $\psi_N \in \mathcal{H}_{+,N}$ with respect to interchange of any two electrons, positivity can be established,

$$(\psi_N, H_N^{(2)}\,\psi_N) \;\geq\; c_N\,\sum_{k=1}^{N}(\psi_N, D_0^{(k)}\,\psi_N) \tag{7.2}$$

which is > 0 for $c_N = 1 - \frac{\gamma}{\gamma_{BR}} - d\gamma^2 - \gamma e^2\,\frac{\pi^2}{4}(N-1) > 0$, requiring $\gamma < 0.446$ $(Z \leq 61)$ in the case of a neutral atom, $N = Z$. Again, this estimate is not sharp because we have used the rather crude (in the large-N case) estimate $V^{(nk)} \geq 0$. However, the additional scaling with $(N-1)/2$ of the sum of electron-electron interaction terms, as well as the marginal dominance of $V^{(nk)}$ with respect to $C^{(nk)}$ when Z approaches 43, make clear that the second-order two-particle interaction terms should not be neglected in atomic structure calculations for high-N ions.

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