SIMPLIFIED DIRAC–COULOMB EQUATIONS

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A description of N-electron systems on the level of Dirac–Coulomb (DC) equation in many cases is either unfeasible or unnecessary. In this work, the N-particle DC equation has been simplified. The simplified DC Hamiltonians, defined on a reduced N-electron Dirac spinor space, are correct to the order of α^2. Simplified DC equations retain linearity and do not introduce any inverse operators and singularities. The solutions of the corresponding eigenvalue problem are correct to α^2, but they also contain terms of higher order. In the case of one-particle, the simplified DC Hamiltonian is equal to the exact Dirac one. As an example, the simplified eigenvalue problems have been solved for the case of two noninteracting electrons. The energies are more accurate than the ones derived from the Pauli approximation (due to the higher order terms). The method may be easily extended to obtain Hamiltonians correct to an arbitrary order in α.

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1. Introduction

The description of some part of the chemical systems needs to be done within the relativistic framework. This is being done from two opposite directions. One of them starts from the non-relativistic approach, then it is extended by the appropriate relativistic corrections, which due to the convergence problems and the appearance in some of them nonintegrable singularities, may be used in the limited way. These features limit essentially the accuracy of such approaches. This sort of quantum mechanical treatment belongs to the general group of one- and two-component approaches [1–11].

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This group contains also more accurate methods in which the dependence on the small components of Dirac bispinor is eliminated by bringing the equations to the nonlinear form.

From the other side when the group of two component approaches fail, the fully relativistic Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) equations need to be used [8–10]. These equations also posses their own unwanted features and limitations [12, 13] which sometimes make them problematic in use. As we show here, it is possible to reduce the original many electron DC equation to the simplified one which is correct up to α^2 of all relativistic corrections, where the awkward properties of the original equation are minimized and the simple linear structure is retained with no singularities and inverse operators involved.

The resulted reduced DC equation may be solved within one-electron approximation framework in which the N-electron wave functions are constructed from products of one-electron bispinors. And what is more adequate to the case, it may also be solved beyond the one-electron model, where explicit many electron functions are used, like *e.g.* explicitly correlated functions. Such approaches which are not based on the one-electron approximation were applied to the DC equation in a very limited way [14–19]. The present formulation of reduced DC Hamiltonians aims in the application of such approaches in very accurate relativistic calculations of several electron systems. Let us notice that the Direct Perturbation Theory [20, 21], in principle, does not need to employ the one-electron model [22] and may as well be applied to simplified Hamiltonians.

The energy spectrum of a one-electron Dirac Hamiltonian can be divided into two parts: the positive one and the negative one. The positive spectrum, present also in the Schrödinger model, is composed of the positive continuum extending above 0 energy threshold, and the discrete energy levels located below this continuum. The negative part, extending below $-2mc^2$, is composed of the negative continuum. In the case of an N-electron system, additionally to the N-electron positive spectrum, composed of N one-electron positive spectra, the spectrum of the Hamiltonian contains also $2^N - 1$ superpositions of the one-electron positive and negative spectra. These $2^N - 1$ spectra can be collected in N groups associated with N thresholds $-2mc^2, -4mc^2, \ldots, -2Nmc^2$. Each of these thresholds is associated with a term in the N-electron DC Hamiltonian proportional, respectively, to α^2, $\alpha^4, \ldots, \alpha^{2N}$ [23–25]. Their presence obstructs, in an essential way, calculations which are not based on the one-electron model [12, 13]. As we noticed earlier, the main objective of this work is to construct a relativistic Hamiltonian correct to α^2 with a spectrum free of all negative-energy continua except the one associated with the α^2 terms in the Hamiltonian. One of the most important features of the approximate Hamil-

tonian is its linear and nonsingular character. It is expected that applications of this Hamiltonian in numerical calculations would lead to a reduction of their complexity, for example, by dimension reduction of respective eigenvalue problem and restriction of the continuum dissolution problem [26] to the one Brown–Ravenhall continuum. The applications may also lead to new computational algorithms.

2. Dirac–Coulomb Hamiltonian

Two noninteracting electrons may be described by the two-particle Dirac Hamiltonian

$$\hat{H}_{[2]} = \hat{H}_{[1]} \otimes \hat{I}_{[1]} + \hat{I}_{[1]} \otimes \hat{H}_{[1]} \equiv \hat{H}_{[2]}(1) + \hat{H}_{[2]}(2) = \hat{H}_{[2]}(1,2) \qquad (1)$$

composed of two one-electron Dirac Hamiltonians $\hat{H}_{[1]}$. Subscripts in square brackets $[N]$ refer to the N-particle spinor space on which an operator is defined. In the expression, a specific particle is identified by the position of the one-particle operator in the pertinent Kronecker product. Then, $\hat{H}_{[2]}(1) \equiv \hat{H}_{[1]} \otimes \hat{I}_{[1]} \equiv \hat{H}_{[1]}(1) \otimes \hat{I}_{[1]}(2)$. Therefore, for simplicity, the indices identifying particles will be in most cases omitted.

The Hamiltonian $\hat{H}_{[1]}$ and the unit operator $\hat{I}_{[1]}$ are defined on the one-electron Dirac space $\mathcal{H}_{[1]}$. It is convenient to express the elements of $\mathcal{H}_{[1]}$ as

$$\Psi_{[1]} = \begin{bmatrix} \Phi_{\mathrm{l}} \\ \Phi_{\mathrm{s}} \end{bmatrix},$$

where Φ_{l} and Φ_{s} are two-component Pauli spinors traditionally referred to, respectively, as *large* and *small* components of the wave function [27, 28]. In the case of electrons or, in general, spin 1/2 identical fermions, Hamiltonian (1) is defined on a space

$$\mathcal{H}^{\mathrm{A}}_{[2]} = \left[\mathcal{H}_{[1]} \otimes \mathcal{H}_{[1]}\right]^{\mathrm{A}}, \qquad (2)$$

where the superscript A stands for the antisymmetric part of the product.

In the standard Dirac–Pauli representation,

$$\hat{H}_{[1]} = \begin{bmatrix} v(1)\,\hat{I}_{(1)} & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}} \\ c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}} & \left[v(1) - 2mc^2\right]\,\hat{I}_{(1)} \end{bmatrix}, \qquad (3)$$

where subscripts in the round brackets (N) refer to the number of particles described by the two-component Pauli spinors. The operators $\hat{I}_{(1)}$ and $\boldsymbol{\sigma}$ are defined on the two-dimensional one-particle Pauli space, the external potential is described by a scalar function v and $\hat{\boldsymbol{p}}$ is the one-particle momentum operator. The remaining symbols have their traditional meaning.

In order to describe a realistic physical system, it is necessary to include an interaction between electrons. Since a Lorentz-invariant interaction potential cannot be expressed in a finite form, we have to use approximate model potentials. The most commonly used is either the non-relativistic repulsive Coulomb potential $g(1,2)$ or accurate to α^2 Breit potential. For our aims, it is sufficient to assume that the interaction potential is described by a scalar function of coordinates of two particles. The function $g(1,2)$ has to be invariant with respect to the transposition of the particles. A generalization of the formalism to account for the Breit terms is rather straightforward. For simplicity, we assume that there is no external vector potential and, consequently, the total potential for two electrons or spin 1/2 identical fermions is simply given by

$$\hat{V}_{[2]} = V(1,2)\,\hat{I}_{[2]}\,,$$

where $V(1,2) = v(1) + v(2) + g(1,2)$ is a scalar function.

After including the interaction, the two-electron Hamiltonian (1) may be expressed as

$$\hat{H}^{\mathrm{DC}}_{[2]} \;=\; \hat{H}^{0}_{[1]} \otimes \hat{I}_{[1]} + \hat{I}_{[1]} \otimes \hat{H}^{0}_{[1]} + \hat{V}_{[2]}\,, \tag{4}$$

where $\hat{H}^0$ is the free-particle Dirac Hamiltonian

$$\hat{H}^{0}_{[1]} \;=\; \begin{bmatrix} \hat{0} & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}} \\ c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}} & -2mc^2\,\hat{I}_{(1)} \end{bmatrix}. \tag{5}$$

The Hamiltonian $\hat{H}^{\mathrm{DC}}_{[2]}$ is referred to as the Dirac–Coulomb (DC) Hamiltonian. In (5) and hereafter, symbol $\hat{0}$ denotes a zero operator.

After executing the Kronecker product, the DC Hamiltonian may be expressed in the form of (*cf.* [14, 15, 27, 28])

$$\hat{H}^{\mathrm{DC}}_{[2]} = \begin{bmatrix} V\,\hat{I}_{(2)} & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 & \hat{0} \\ c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 & \left(V-2mc^2\right)\,\hat{I}_{(2)} & \hat{0} & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 \\ c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 & \hat{0} & \left(V-2mc^2\right)\,\hat{I}_{(2)} & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 \\ \hat{0} & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 & \left(V-4mc^2\right)\,\hat{I}_{(2)} \end{bmatrix}, \tag{6}$$

where operators

$$\begin{aligned} \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 \;&\equiv\; \boldsymbol{\sigma}\hat{\boldsymbol{p}} \otimes \hat{I}_{(1)}\,, \\ \boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 \;&\equiv\; \hat{I}_{(1)} \otimes \boldsymbol{\sigma}\hat{\boldsymbol{p}} \end{aligned}$$

are defined on the four-dimensional two-particle Pauli space.

The DC Hamiltonian may also be rewritten as

$$\hat{H}^{\mathrm{DC}}_{[2]} \;=\; \begin{bmatrix} V\,\hat{I}_{(2)} & c\,\hat{T}_{\{2\}} & \hat{0} \\ c\,\hat{T}^{\dagger}_{\{2\}} & \left(V-2mc^2\right)\,\hat{I}_{\{2\}} & c\,\hat{T}'^{\dagger}_{\{2\}} \\ \hat{0} & c\,\hat{T}'_{\{2\}} & \left(V-4mc^2\right)\,\hat{I}_{(2)} \end{bmatrix}, \tag{7}$$

where

$$\begin{aligned} \hat{T}_{\{2\}} &\stackrel{\mathrm{def}}{=} [\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2, \quad \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1]\,, \\ \hat{T}'_{\{2\}} &\stackrel{\mathrm{def}}{=} [\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1\,, \quad \boldsymbol{\sigma}\hat{\boldsymbol{p}}_2] \end{aligned} \tag{8}$$

are rectangular 4×8 matrices, and

$$\hat{I}_{\{2\}} \;\stackrel{\mathrm{def}}{=}\; \hat{I}_{(2)} \oplus \hat{I}_{(2)}\,. \tag{9}$$

The eigenfunctions of the DC Hamiltonians (7) and (6) may be expressed as

$$\Psi_{[2]} \;=\; \begin{bmatrix} \Phi_{\mathrm{ll}} \\ \Phi_{\{\mathrm{ls}\}} \\ \Phi_{\mathrm{ss}} \end{bmatrix} \;\equiv\; \begin{bmatrix} \Phi_{\mathrm{ll}} \\ \Phi_{\mathrm{ls}} \\ \Phi_{\mathrm{sl}} \\ \Phi_{\mathrm{ss}} \end{bmatrix}, \tag{10}$$

where

$$\Phi_{\{\mathrm{ls}\}} \;=\; \begin{bmatrix} \Phi_{\mathrm{ls}} \\ \Phi_{\mathrm{sl}} \end{bmatrix}, \tag{11}$$

and subscripts in braces [Eqs. (7)–(11)] mean that the domain of the operator is spanned by $\Phi_{\{\mathrm{ls}\}}$.

The antisymmetry of the spinor wave function (10) is equivalent to the following set of conditions:

$$\begin{aligned} \Phi_{\mathrm{ll}} \;&\equiv\; \Phi_{\mathrm{ll}}(\mathbf{x}_1, \mathbf{x}_2) = -\Phi_{\mathrm{ll}}(\mathbf{x}_2, \mathbf{x}_1)\,, \\ \Phi_{\mathrm{ss}} \;&\equiv\; \Phi_{\mathrm{ss}}(\mathbf{x}_1, \mathbf{x}_2) = -\Phi_{\mathrm{ss}}(\mathbf{x}_2, \mathbf{x}_1) \end{aligned} \tag{12}$$

and

$$\Phi_{\mathrm{sl}}(\mathbf{x}_1, \mathbf{x}_2) \;=\; -\Phi_{\mathrm{ls}}(\mathbf{x}_2, \mathbf{x}_1)\,, \tag{13}$$

where $\mathbf{x}_1, \mathbf{x}_2$ denote the position and the Pauli-spin coordinates of the electrons [24, 25]. In the representation used in this paper, each component Φ_{xy} may be expressed as a Kronecker product of two Pauli spinors, *i.e.* it is a four-component spinor. Consequently, $\Psi_{[2]}$ is a $4 \times 4 = 16$ component spinor.

In a general N-particle case, the DC Hamiltonian may be written as a $4^N \times 4^N$ matrix $\hat{H}^{\mathrm{DC}}_{[N]}$ consisting of components

$$\left[\hat{H}^{\mathrm{DC}}_{[N]}\right]_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} = \hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} \left[V - 2N_{\mathrm{s}}\, mc^2\right] + c \sum_{i=1}^{N} \hat{\delta}^{i}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i\right) , \tag{14}$$

where indices $\bar{\boldsymbol{u}}, \bar{\boldsymbol{v}}$ stand for N-element strings of indices l and s, $N_{\mathrm{s}} \equiv N_{\mathrm{s}}(\bar{\boldsymbol{u}})$ is equal to the number of small components in the string $\bar{\boldsymbol{u}}$

$$\hat{\delta}^{i}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} = \begin{cases} \hat{I}_{(N)}\,, & \text{if } \bar{\boldsymbol{u}} \text{ and } \bar{\boldsymbol{v}} \text{ differ in the } i^{\mathrm{th}} \text{ component only}\,, \\ \hat{0}\,, & \text{otherwise}\,, \end{cases}$$

and symbol $\hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}}$ has its standard meaning, *i.e.*

$$\hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} = \begin{cases} \hat{I}_{(N)}\,, & \text{if } \bar{\boldsymbol{u}} = \bar{\boldsymbol{v}}\,, \\ \hat{0}\,, & \text{if } \bar{\boldsymbol{u}} \neq \bar{\boldsymbol{v}}\,. \end{cases}$$

Hamiltonian (14) acts in a space of 4^N-component antisymmetric functions $\Psi_{[N]}$. Similarly as in Eq. (10), a function $\Psi_{[N]}$ may be decomposed to 2^N Pauli components $\Phi_{\bar{\boldsymbol{u}}}$ indexed by strings $\bar{\boldsymbol{u}}$. Every Pauli component $\Phi_{\bar{\boldsymbol{u}}}$ belongs to a 2^N-dimensional Pauli spinor space spanned by the N-fold Kronecker products of one-particle two-component Pauli spinors. For a given Hamiltonian (14), we can write its eigenvalue equation as a set of 2^N equations

$$\sum_{i=1}^{N} c\, \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i\right) \Phi_{\bar{\boldsymbol{u}}_i} + \left[V - E - 2N_{\mathrm{s}}\, mc^2\right] \hat{I}_{(N)}\, \Phi_{\bar{\boldsymbol{u}}} = 0\,, \tag{15}$$

where $\bar{\boldsymbol{u}}_i$ is the string which differs from $\bar{\boldsymbol{u}}$ in its i^{th} component. A detailed description of the structure of the DC Hamiltonian is given in Ref. [23].

3. Partition of the Dirac–Coulomb Hamiltonian

A partition of the Dirac Hamiltonian to parts proportional to powers of fine structure constant α has been explored during the last three decades by several authors. The most important effect of these studies was the formulation of the formally correct relativistic perturbation theory, often referred to as the Direct Perturbation Theory [20, 21]. The Dirac eigenvalue equation

$$\hat{H}_{[1]}\, \Psi_{[1]} \;=\; E\, \Psi_{[1]} \tag{16}$$

after performing the transformation

$$\left(\hat{C}_{[1]} \hat{H}_{[1]} \hat{C}_{[1]}\right) \left(\hat{C}^{-1}_{[1]} \Psi_{[1]}\right) \;=\; E\, \hat{C}^{2}_{[1]} \;\left(\hat{C}^{-1}_{[1]} \Psi_{[1]}\right) , \tag{17}$$

with

$$\hat{C}_{[1]} \;=\; \begin{bmatrix} \hat{I}_{(1)} & \hat{0} \\ \hat{0} & \alpha\,\hat{I}_{(1)} \end{bmatrix}$$

becomes

$$\left(\hat{H}^{\mathrm{L}}_{[1]} + \alpha^2 \hat{R}^{1}_{[1]}\right) \tilde{\Psi}_{[1]} \;=\; E\,\left(\hat{G}^{0}_{[1]} + \alpha^2 \hat{G}^{1}_{[1]}\right) \tilde{\Psi}_{[1]}\,, \tag{18}$$

where $\tilde{\Psi}_{[1]} \;=\; \hat{C}^{-1}_{[1]} \Psi_{[1]}$,

$$\hat{H}^{\mathrm{L}}_{[1]} \;=\; \begin{bmatrix} v\hat{I}_{(1)} & \boldsymbol{\sigma}\hat{\boldsymbol{p}} \\ \boldsymbol{\sigma}\hat{\boldsymbol{p}} & -2m\hat{I}_{(1)} \end{bmatrix}\,, \qquad \hat{R}^{1}_{[1]} \;=\; \begin{bmatrix} \hat{0} & \hat{0} \\ \hat{0} & v\hat{I}_{(1)} \end{bmatrix}\,,$$

and

$$\hat{G}^{0}_{[1]} \;=\; \mathrm{diag}\left[\hat{I}_{(1)},\, \hat{0}\right]\,, \qquad \hat{G}^{1}_{[1]} \;=\; \mathrm{diag}\left[\hat{0},\, \hat{I}_{(1)}\right]\,.$$

In the non-relativistic limit ($\alpha = 0$), equation (18) transforms into Lévy-Leblond (LL) equation [29]

$$\hat{H}^{\mathrm{L}}_{[1]}\, \tilde{\Psi}_{[1]} \;=\; E\, \hat{G}^{0}_{[1]}\, \tilde{\Psi}_{[1]}\,, \tag{19}$$

with semimetric $\hat{G}^{0}_{[1]}$. By the elimination of two small components of the four-component spinor $\tilde{\Psi}_{[1]}$, we can easily transform equation (19) into the Schrödinger equation.

Transformation (17) plays only an auxiliary role in the derivation and shows the magnitude of the relativistic correction. The same partition of the Dirac equation may be obtained without this transformation [20]. The resulting formalism has been used to perturbative solving of several one- and two-particle Dirac eigenvalue problems with α^2 being the perturbation parameter [20].

A similar partitioning technique may be applied to the eigenvalue problem of a many-particle DC Hamiltonian. In the case of a two-particle Hamiltonian (4), the analog of transformation (17) is given by the matrix

$$\hat{C}_{[2]} = \begin{bmatrix} \hat{I}_{(1)} & \hat{0} \\ \hat{0} & \alpha\,\hat{I}_{(1)} \end{bmatrix} \otimes \begin{bmatrix} \hat{I}_{(1)} & \hat{0} \\ \hat{0} & \alpha\,\hat{I}_{(1)} \end{bmatrix} \equiv \begin{bmatrix} \hat{I}_{(2)} & \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & \alpha\,\hat{I}_{(2)} & \hat{0} & \hat{0} \\ \hat{0} & \hat{0} & \alpha\,\hat{I}_{(2)} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} & \alpha^2\,\hat{I}_{(2)} \end{bmatrix}\,.$$

The resulting partition of the DC equation reads [22]

$$\left(\hat{H}^{\mathrm{L}}_{[2]} + \alpha^2 \hat{R}^{1}_{[2]} + \alpha^4 \hat{R}^{2}_{[2]}\right) \tilde{\Psi}_{[2]} \;=\; E\,\left(\hat{G}^{0}_{[2]} + \alpha^2 \hat{G}^{1}_{[2]} + \alpha^4 \hat{G}^{2}_{[2]}\right) \tilde{\Psi}_{[2]}\,, \tag{20}$$

where

$$\hat{H}^{\mathrm{L}}_{[2]} = \begin{bmatrix} V\,\hat{I}_{(2)} & \boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 & \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 & \hat{0} \\ \boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 & -2m\,\hat{I}_{(2)} & \hat{0} & \hat{0} \\ \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 & \hat{0} & -2m\,\hat{I}_{(2)} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} & \hat{0} \end{bmatrix},$$

$$\hat{R}^1_{[2]} = \begin{bmatrix} \hat{0} & \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & V\,\hat{I}_{(2)} & \hat{0} & \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 \\ \hat{0} & \hat{0} & V\,\hat{I}_{(2)} & \boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 \\ \hat{0} & \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1 & \boldsymbol{\sigma}\hat{\boldsymbol{p}}_2 & -4m\,\hat{I}_{(2)} \end{bmatrix}, \qquad \hat{R}^2_{[2]} = \begin{bmatrix} \hat{0} & \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} & V\hat{I}_{(2)} \end{bmatrix},$$

and

$$\begin{aligned} \hat{G}^0_{[2]} &= \mathrm{diag}\left[\hat{I}_{(2)},\ \hat{0},\ \hat{0},\ \hat{0}\right], \\ \hat{G}^1_{[2]} &= \mathrm{diag}\left[\hat{0},\ \hat{I}_{(2)},\ \hat{I}_{(2)},\ \hat{0}\right], \\ \hat{G}^2_{[2]} &= \mathrm{diag}\left[\hat{0},\ \hat{0},\ \hat{0},\ \hat{I}_{(2)}\right]. \end{aligned}$$

Depending on the required accuracy of the results, one can set in equation (20) $\alpha = 0$, neglect terms proportional to α^4 or include all terms. In the first case, equation (20) reduces to the two-particle LL equation, corresponding to the Schrödinger equation. The neglected terms are proportional to $\alpha^2 \simeq 5 \times 10^{-5}$. In the second case, terms $\hat{R}^2_{[2]}$ proportional to $\alpha^4 \simeq 3 \times 10^{-9}$ are neglected. In this context, it is worthwhile to note that the Breit interaction is correct up to α^2 only.

An analogous partitioning of the eigenvalue equation may be performed in a general N-particle case. The matrix

$$\hat{C}_{[N]} = \begin{bmatrix} \hat{I}_{(1)} & \hat{0} \\ \hat{0} & \alpha\,\hat{I}_{(1)} \end{bmatrix}^{\otimes N} \equiv \left[\alpha^{N_{\mathrm{s}}}\,\hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}}\right]$$

transforms equation (15) into

$$\left(\hat{H}^{\mathrm{L}}_{[N]} + \sum_{k=1}^{N} \alpha^{2k}\,\hat{R}^k_{[N]}\right)\tilde{\Psi}_{[N]} = E\left(\sum_{k=0}^{N} \alpha^{2k}\,\hat{G}^k_{[N]}\right)\tilde{\Psi}_{[N]}, \tag{21}$$

where elements of the matrix operators $\hat{R}^k_{[N]}$ are equal to

$$\begin{aligned} \left[\hat{R}^k_{[N]}\right]_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} &= \hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}}\left[\delta_{k,N_{\mathrm{s}}}\,V - \delta_{k+1,N_{\mathrm{s}}}\,2(k+1)\,m\right] \\ &\quad + \delta_{2k+1,N_{\mathrm{ss}}} \sum_{i=1}^{N} \hat{\delta}^i_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}}\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i), \end{aligned} \tag{22}$$

with $\hat{R}^0_{[N]} \equiv \hat{H}^{\rm L}_{[N]}$ being the N-particle LL Hamiltonian, and the elements of $\hat{G}^k_{[N]}$ equal to

$$\left[\hat{G}^k_{[N]}\right]_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} \;=\; \delta_{k,N_{\rm s}}\hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}}\,. \tag{23}$$

The symbol $N_{\rm ss} \equiv N_{\rm ss}(\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}) = N_{\rm s}(\bar{\boldsymbol{u}}) + N_{\rm s}(\bar{\boldsymbol{v}})$ in equation (22) denotes the number of small components in both strings: $\bar{\boldsymbol{u}}$ and $\bar{\boldsymbol{v}}$. In the non-relativistic limit of $\alpha = 0$, equation (21) reduces to the N-particle LL equation

$$\hat{H}^{\rm L}_{[N]}\,\tilde{\Psi}_{[N]} \;=\; E\,\hat{G}^0_{[N]}\,\tilde{\Psi}_{[N]}\,.$$

4. Hamiltonians accurate to α^2

The two-particle Hamiltonian accurate to α^2 may be obtained by neglecting the α^4 correction in equation (20). The same results may be obtained by dropping out V in the third row of the two-particle Hamiltonian (7) and by assuming the semimetric

$$\hat{Q}_{[2]} = \mathrm{diag}\left[\hat{I}_{(2)},\;\; \hat{I}_{(2)},\;\; \hat{I}_{(2)},\;\; \hat{0}\right]\,.$$

The resulting eigenvalue equation reads

$$\hat{H}^Q_{[2]}\,\Psi_{[2]} \;=\; E\,\hat{Q}_{[2]}\,\Psi_{[2]}\,, \tag{24}$$

where

$$\hat{H}^Q_{[2]} = \begin{bmatrix} V\,\hat{I}_{(2)} & c\,\hat{T}_{\{2\}} & \hat{0} \\ c\,\hat{T}^\dagger_{\{2\}} & -2mc^2\,\hat{I}_{\{2\}} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} \end{bmatrix} + \begin{bmatrix} \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & V\,\hat{I}_{\{2\}} & c\,\hat{T}'^\dagger_{\{2\}} \\ \hat{0} & c\,\hat{T}'_{\{2\}} & -4mc^2\,\hat{I}_{(2)} \end{bmatrix} \tag{25}$$

due to equation (20) consists of the LL Hamiltonian and the α^2 correction. The third row of (24) gives

$$c\,\hat{T}_{\{2\}}\,\Phi_{\{\rm ls\}} - 4mc^2\Phi_{\rm ss} = 0\,. \tag{26}$$

The last relation allows for the elimination of $\Phi_{\rm ss}$ from (24). The resulting equation may be expressed as

$$\begin{bmatrix} V\,\hat{I}_{(2)} & c\,\hat{T}_{\{2\}} \\ c\,\hat{T}^\dagger_{\{2\}} & (V-2mc^2)\,\hat{I}_{\{2\}} + \frac{1}{2m}\hat{K}_{\{2\}} \end{bmatrix} \begin{bmatrix} \Phi_{\rm ll} \\ \Phi_{\{\rm ls\}} \end{bmatrix} \;=\; E \begin{bmatrix} \Phi_{\rm ll} \\ \Phi_{\{\rm ls\}} \end{bmatrix}, \tag{27}$$

where

$$\hat{K}_{\{2\}} \;\stackrel{\rm def}{=}\; \frac{1}{2}\,\hat{T}^\dagger_{\{2\}}\hat{T}_{\{2\}} \;=\; \frac{1}{2}\begin{bmatrix} \hat{\boldsymbol{p}}_1^2 & (\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1)\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2) \\ (\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2)\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1) & \hat{\boldsymbol{p}}_2^2 \end{bmatrix}, \tag{28}$$

$\hat{\boldsymbol{p}}_1^2 = \hat{\boldsymbol{p}}^2 \otimes \hat{I}_{(1)}$ and $\hat{\boldsymbol{p}}_2^2 = \hat{I}_{(1)} \otimes \hat{\boldsymbol{p}}^2$.

Equations (24) and (27) have been derived without assuming antisymmetry of the two-particle wave function $\Psi_{[2]}$ [*cf.* equation (10)]. If $\Psi_{[2]}$ is antisymmetric then, according to (12), $\Phi_{\rm ss} = \hat{A}_{(2)}\Phi_{\rm ss}$, where $\hat{A}_{(2)}$ is the two-particle idempotent antisymmetrizer. Consequently, equation (26) becomes

$$c\,\hat{A}_{(2)}\hat{T}_{\{2\}}\,\Phi_{\{\rm ls\}} - 4mc^2\Phi_{\rm ss} = 0\,, \tag{29}$$

and in equation (27), $\hat{K}_{\{2\}}$ has to be replaced by

$$\hat{K}'^{\rm A}_{\{2\}} \stackrel{\rm def}{=} \frac{1}{2}\begin{bmatrix} (\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1)\,\hat{A}_{(2)}\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1) & (\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1)\,\hat{A}_{(2)}\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2) \\ (\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2)\,\hat{A}_{(2)}\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1) & (\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2)\,\hat{A}_{(2)}\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2) \end{bmatrix}.$$

It is easy to see that $\hat{K}'^{\rm A}_{\{2\}}$ and

$$\hat{K}^{\rm A}_{\{2\}} \;=\; \begin{bmatrix} {}^{\rm A}\hat{\boldsymbol{p}}_1^2 & \hat{0} \\ \hat{0} & {}^{\rm A}\hat{\boldsymbol{p}}_2^2 \end{bmatrix}, \tag{30}$$

where

$${}^{\rm A}\hat{\boldsymbol{p}}_i^2 \stackrel{\rm def}{=} (\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,\hat{A}_{(2)}\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,,$$

when acting on $\Phi_{\{\rm ls\}}$ corresponding to an antisymmetric wave function [equation (13)], give the same result. Consequently, in the space of antisymmetric wave functions, $\hat{K}'^{\rm A}_{\{2\}} = \hat{K}^{\rm A}_{\{2\}}$.

The N-particle DC equation accurate to α^2 is of the same form as in the two-particle case (24), *i.e.*

$$\hat{H}^Q_{[N]}\,\Psi_{[N]} \;=\; E\,\hat{Q}_{[N]}\,\Psi_{[N]}\,, \tag{31}$$

with semimetric given by

$$\hat{Q}_{[N]} = \hat{G}^0_{[N]} + \hat{G}^1_{[N]} = \mathrm{diag}\left[\underbrace{\hat{I}_{(N)},\ \hat{I}_{(N)},\ldots,\hat{I}_{(N)}}_{N+1},\underbrace{\hat{0},\hat{0},\ldots,\hat{0}}_{2^N-(N+1)}\right].$$

The Hamiltonian $\hat{H}^Q_{[N]}$ consists of elements

$$\begin{aligned}\left[\hat{H}^Q_{[N]}\right]_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} \;=\; & V\,\delta_{0,N_{\rm s}}\hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} + \left(V - 2mc^2\right)\delta_{1,N_{\rm s}}\hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} - 4mc^2\delta_{2,N_{\rm s}}\hat{\delta}_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}} \\ & + c\sum_{i=1}^{N}\left(\delta_{1,N_{\rm ss}} + \delta_{3,N_{\rm ss}}\right)\hat{\delta}^i_{\bar{\boldsymbol{u}},\bar{\boldsymbol{v}}}\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,.\end{aligned}$$

Equation (31) may be rewritten in a more explicit form as

$$(V-E)\,\Phi_{\bar{\boldsymbol{u}}^0} + c\sum_{i=1}^{N}(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,\Phi_{\bar{\boldsymbol{u}}_i^0} = 0\,, \tag{32}$$

$$\left(V-E-2mc^2\right)\Phi_{\bar{\boldsymbol{u}}_i^0} + c\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,\Phi_{\bar{\boldsymbol{u}}^0} + c\sum_{\substack{j=1\\(j\neq i)}}^{N}\left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right)\Phi_{\bar{\boldsymbol{u}}_{i,j}^0} = 0\,, \tag{33}$$

$$-4mc^2\,\Phi_{\bar{\boldsymbol{u}}_{i,j}^0} + c\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,\Phi_{\bar{\boldsymbol{u}}_j^0} + c\left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right)\Phi_{\bar{\boldsymbol{u}}_i^0} = 0\,, \tag{34}$$

where $1 \le i,j \le N$ and $i \neq j$. The string $\bar{\boldsymbol{u}}^0$ is defined by the condition $N_{\mathrm{s}}(\bar{\boldsymbol{u}}^0) = 0$ and $\bar{\boldsymbol{u}}_{i,j}$ is the string which differs from $\bar{\boldsymbol{u}}$ in its i^{th} and j^{th} components, if $i \neq j$, and $\bar{\boldsymbol{u}}_{i,j} = \bar{\boldsymbol{u}}$, if $i = j$. Equation (34) yields

$$\Phi_{\bar{\boldsymbol{u}}_{i,j}^0} \;=\; \frac{1}{4mc}\left[(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,\Phi_{\bar{\boldsymbol{u}}_j^0} + \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right)\Phi_{\bar{\boldsymbol{u}}_i^0}\right]. \tag{35}$$

By substituting it to equation (33), we obtain

$$\left(V-E-2mc^2\right)\Phi_{\bar{\boldsymbol{u}}_i^0} + c\,(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,\Phi_{\bar{\boldsymbol{u}}^0} + \frac{1}{4m}\sum_{\substack{j=1\\(j\neq i)}}^{N}\left[\hat{\boldsymbol{p}}_j^2\Phi_{\bar{\boldsymbol{u}}_i^0} + \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right)(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\,\Phi_{\bar{\boldsymbol{u}}_j^0}\right] = 0\,. \tag{36}$$

Finally, combining equations (32) and (36), we get the N-particle equation accurate to α^2

$$\begin{bmatrix} V\,\hat{I}_{(N)} & c\,\hat{T}_{\{N\}} \\ c\,\hat{T}_{\{N\}}^{\dagger} & (V-2mc^2)\,\hat{I}_{\{N\}} + \frac{1}{2m}\hat{K}_{\{N\}} \end{bmatrix} \begin{bmatrix} \Phi_{\bar{\boldsymbol{u}}^0} \\ \Phi_{\{\mathrm{ls};N\}} \end{bmatrix} \;=\; E \begin{bmatrix} \Phi_{\bar{\boldsymbol{u}}^0} \\ \Phi_{\{\mathrm{ls};N\}} \end{bmatrix}, \tag{37}$$

where

$$\hat{T}_{\{N\}} \;\stackrel{\mathrm{def}}{=}\; \left[\boldsymbol{\sigma}\hat{\boldsymbol{p}}_N,\, \boldsymbol{\sigma}\hat{\boldsymbol{p}}_{N-1}, \ldots, \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1\right],$$

and

$$\left[\hat{K}_{\{N\}}\right]_{\bar{\boldsymbol{v}},\bar{\boldsymbol{w}}} \;\stackrel{\mathrm{def}}{=}\; \frac{1}{2}\sum_{\substack{i,j=1\\(i\neq j)}}^{N}\left(\hat{\delta}_{\bar{\boldsymbol{v}},\bar{\boldsymbol{u}}_i^0}\hat{\delta}_{\bar{\boldsymbol{w}},\bar{\boldsymbol{u}}_i^0}\hat{\boldsymbol{p}}_j^2 + \hat{\delta}_{\bar{\boldsymbol{v}},\bar{\boldsymbol{u}}_i^0}\hat{\delta}_{\bar{\boldsymbol{w}},\bar{\boldsymbol{u}}_j^0}\left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right)(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)\right), \tag{38}$$

where $\bar{\boldsymbol{v}}, \bar{\boldsymbol{w}} \in \{\bar{\boldsymbol{u}};\; N_{\mathrm{s}}(\bar{\boldsymbol{u}}) = 1\}$.

As in the two-particle case, in the space of antisymmetric functions, $\hat{K}_{\{N\}}$ appearing in $\hat{H}^Q_{[N]}$ may be replaced by a simpler equivalent operator. If $\Psi_{[N]}$ is antisymmetric, then $\Phi_{\bar{\boldsymbol{u}}^0}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ is antisymmetric in all N variables and

$$\Phi_{\{\mathrm{ls};N\}} \;=\; \begin{bmatrix} \Phi_{\bar{\boldsymbol{u}}_N^0} \\ \Phi_{\bar{\boldsymbol{u}}_{N-1}^0} \\ \vdots \\ \Phi_{\bar{\boldsymbol{u}}_1^0} \end{bmatrix}$$

consists of N-electrons Pauli spinors, where each spinor $\Phi_{\bar{\boldsymbol{u}}_i^0}$ is antisymmetric in $(N-1)$ variables $(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{i-1}, \mathbf{x}_{i+1}, \ldots, \mathbf{x}_N)$. Moreover, the components $\Phi_{\bar{\boldsymbol{u}}_i^0}$ are linked by the relation [24, 25]

$$\Phi_{\bar{\boldsymbol{u}}_i^0}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = -\Phi_{\bar{\boldsymbol{u}}_j^0}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N)\,.$$

In general, all components $\Phi_{\bar{\boldsymbol{u}}}$ of an antisymmetric N-particle wave function $\Psi_{[N]}$ are antisymmetric in variables $\mathbf{x}_{i_\mathrm{l}}$ corresponding to the large component indices i_l in the string $\bar{\boldsymbol{u}}$ and antisymmetric in variables $\mathbf{x}_{i_\mathrm{s}}$ corresponding to the small component indices i_s. Let $\hat{A}_{\bar{\boldsymbol{u}}}$ be the projection operator on the subspace of functions antisymmetric in the large component indices and, separately, antisymmetric in the small component indices. Now, for $\Phi_{\bar{\boldsymbol{u}}_{i,j}^0} = \hat{A}_{\bar{\boldsymbol{u}}_{i,j}^0} \Phi_{\bar{\boldsymbol{u}}_{i,j}^0}$, equation (35) becomes

$$\Phi_{\bar{\boldsymbol{u}}_{i,j}^0} \;=\; \frac{1}{4mc} \hat{A}_{\bar{\boldsymbol{u}}_{i,j}^0} \left[\left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i\right) \Phi_{\bar{\boldsymbol{u}}_j^0} + \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right) \Phi_{\bar{\boldsymbol{u}}_i^0} \right] . \tag{39}$$

Similarly, equation (36) reads

$$\begin{aligned} &\left(V - E - 2mc^2\right) \Phi_{\bar{\boldsymbol{u}}_i^0} + c\left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i\right) \Phi_{\bar{\boldsymbol{u}}^0} \\ &+ \frac{1}{4m} \sum_{\substack{j=1 \\ (j\neq i)}}^{N} \left[\left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right) \hat{A}_{\bar{\boldsymbol{u}}_{i,j}^0} \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right) \Phi_{\bar{\boldsymbol{u}}_i^0} + \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right) \hat{A}_{\bar{\boldsymbol{u}}_{i,j}^0} \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i\right) \Phi_{\bar{\boldsymbol{u}}_j^0} \right] = 0\,. \end{aligned} \tag{40}$$

Further simplification of equation (40) gives

$$\left(V - E - 2mc^2\right) \Phi_{\bar{\boldsymbol{u}}_i^0} + c\left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i\right) \Phi_{\bar{\boldsymbol{u}}^0} + \frac{1}{2m} \left(\sum_{\substack{j=1 \\ (j\neq i)}}^{N} {}^{\mathrm{A}}\hat{\boldsymbol{p}}^2_{j,(i)} \right) \Phi_{\bar{\boldsymbol{u}}_i^0} \;=\; 0\,, \tag{41}$$

where

$${}^{\mathrm{A}}\hat{\boldsymbol{p}}^2_{j,(i)} \;\stackrel{\mathrm{def}}{=}\; \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right) \hat{A}_{\bar{\boldsymbol{u}}_{i,j}^0} \left(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_j\right) .$$

Finally, equations (39) and (41) lead to an equation analogous to (37) with operator $\hat{K}_{\{N\}}$ replaced by

$$\left[\hat{K}^{\mathrm{A}}_{\{N\}}\right]_{\bar{\boldsymbol{v}},\bar{\boldsymbol{w}}} \;\stackrel{\mathrm{def}}{=}\; \sum_{i=1}^{N} \hat{\delta}_{\bar{\boldsymbol{v}},\bar{\boldsymbol{u}}_i^0} \hat{\delta}_{\bar{\boldsymbol{w}},\bar{\boldsymbol{u}}_i^0} \sum_{\substack{j=1 \\ (j\neq i)}}^{N} {}^{\mathrm{A}}\hat{\boldsymbol{p}}^2_{j,(i)}\,. \tag{42}$$

5. Further simplifications

A further simplification of equation (37) may be obtained by replacement of ${}^{\mathrm{A}}\hat{\boldsymbol{p}}^2_{j,(i)}$ in (42) by the ordinary momentum operators $\hat{\boldsymbol{p}}^2_j$. The components of the simplified operator $\hat{K}^{\mathrm{A}}_{\{N\}}$, denoted $\hat{K}^{\mathrm{d}}_{\{N\}}$, read

$$\left[\hat{K}^{\mathrm{d}}_{\{N\}}\right]_{\bar{\boldsymbol{v}},\bar{\boldsymbol{w}}} \stackrel{\mathrm{def}}{=} \sum_{i=1}^{N} \hat{\delta}_{\bar{\boldsymbol{v}},\bar{\boldsymbol{u}}^0_i}\hat{\delta}_{\bar{\boldsymbol{w}},\bar{\boldsymbol{u}}^0_i} \sum_{\substack{j=1\\(j\neq i)}}^{N} \hat{\boldsymbol{p}}^2_j \,. \tag{43}$$

As we shall see in Section 7, this replacement leads to an error of the order of α^6. In order to understand the procedure leading with this simplification, let us now consider the case of two noninteracting particles, *i.e.* equation (27) with $V = v(1) + v(2)$. In this case, each subsystem (each particle) is described separately by the Hamiltonians $\hat{H}_{[2]}(1)$ and $\hat{H}_{[2]}(2)$ [*cf.* (1)]. Neglecting in $\hat{H}_{[2]}(i)$ $(i = 1, 2)$ terms proportional to α^4, we get the simplified Hamiltonians

$$\hat{H}^{Q}_{[2]}(i) = \begin{bmatrix} v(i)\,\hat{I}_{(2)} & c\hat{T}_{\{2\}}(i) & \hat{0} \\ c\hat{T}^{\dagger}_{\{2\}}(i) & -2mc^2\,\hat{I}_{\{2\}} & \hat{0} \\ \hat{0} & \hat{0} & \hat{0} \end{bmatrix} + \begin{bmatrix} \hat{0} & \hat{0} & \hat{0} \\ \hat{0} & v(i)\hat{I}_{\{2\}} & c\hat{T}'^{\dagger}_{\{2\}}(i) \\ \hat{0} & c\hat{T}'_{\{2\}}(i) & -4mc^2\,\hat{I}_{(2)} \end{bmatrix}, \tag{44}$$

where

$$\begin{aligned} \hat{T}_{\{2\}}(1) &= \left[\hat{0}, \quad \boldsymbol{\sigma}\hat{\boldsymbol{p}}_1\right], & \hat{T}'_{\{2\}}(1) &= \left[\boldsymbol{\sigma}\hat{\boldsymbol{p}}_1, \quad \hat{0}\right], \\ \hat{T}_{\{2\}}(2) &= \left[\boldsymbol{\sigma}\hat{\boldsymbol{p}}_2, \quad \hat{0}\right], & \hat{T}'_{\{2\}}(2) &= \left[\hat{0}, \quad \boldsymbol{\sigma}\hat{\boldsymbol{p}}_2\right]. \end{aligned}$$

In consequence, we obtain two equations

$$\hat{H}^{Q}_{[2]}(i)\,\Psi_{[2]}(i) = E_i\,\hat{Q}_{[2]}\,\Psi_{[2]}(i)\,, \qquad i = 1, 2\,, \tag{45}$$

equivalent to equation (24), where the wave function

$$\Psi_{[2]}(i) = \begin{bmatrix} \Phi_{\mathrm{ll}}(\mathbf{x}_i) \\ \Phi_{\{\mathrm{ls}\}}(\mathbf{x}_i) \\ \Phi_{\mathrm{ss}}(\mathbf{x}_i) \end{bmatrix}$$

depends on the one-particle coordinates, $\mathbf{x}_i$, only. By elimination of the small–small components $\Phi_{\mathrm{ss}}(\mathbf{x}_i)$ from equations (45), and by adding the resulting one-particle Hamiltonians to obtain the two-particle one, we get an equation analogous to (27), in which $\hat{K}_{\{2\}}$ has been replaced by

$$\hat{K}^{\mathrm{d}}_{\{2\}} = \begin{bmatrix} \hat{\boldsymbol{p}}^2_1 & \hat{0} \\ \hat{0} & \hat{\boldsymbol{p}}^2_2 \end{bmatrix}. \tag{46}$$

We have to stress that this equation cannot be derived directly from (4), but only by separate simplifying of the one-particle equations.

6. A physical interpretation of the simplified DC Hamiltonian

In order to better understand the meaning of the reduction of the DC Hamiltonian (4) to its simplified form (25), let us consider the part of the Hamiltonian (1) describing the first particle, *i.e.* $\hat{H}_{[2]}(1)$. It can be expressed in the form of

$$\hat{H}_{[2]}(1) \;=\; \hat{H}_{[1]} \otimes \begin{pmatrix} \hat{I}_{(1)} & \hat{0} \\ \hat{0} & \hat{0} \end{pmatrix} + \hat{H}_{[1]} \otimes \begin{pmatrix} \hat{0} & \hat{0} \\ \hat{0} & \hat{I}_{(1)} \end{pmatrix} .$$

On the other hand, the simplified Hamiltonian (44) can be written as

$$\hat{H}^{Q}_{[2]}(1) \;=\; \hat{H}_{[1]} \otimes \begin{pmatrix} \hat{I}_{(1)} & \hat{0} \\ \hat{0} & \hat{0} \end{pmatrix} + {}^{\mathrm{C}}\hat{H}^{\mathrm{L}}_{[1]} \otimes \begin{pmatrix} \hat{0} & \hat{0} \\ \hat{0} & \hat{I}_{(1)} \end{pmatrix} ,$$

where

$${}^{\mathrm{C}}\hat{H}^{\mathrm{L}}_{[1]} \;\equiv\; \hat{C}^{-1}_{[1]}\hat{H}^{\mathrm{L}}_{[1]}\hat{C}^{-1}_{[1]} \;=\; \begin{bmatrix} v_{(1)}\,\hat{I}_{(1)} & c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}} \\ c\,\boldsymbol{\sigma}\hat{\boldsymbol{p}} & -2mc^2\,\hat{I}_{(1)} \end{bmatrix} \tag{47}$$

is the LL Hamiltonian, equivalent to $\hat{H}^{\mathrm{L}}_{[1]}$ appearing in equation (19). As one can see, the first term in $\hat{H}^{Q}_{[2]}(1)$ gives a complete (relativistic) contribution due to the first particle to the part of the wave function in which appears the large component of the second particle, and the second term gives a simplified (non-relativistic) contribution due to the first particle to the part of the wave function in which appears the small component of the second particle. An analogous interpretation is valid for the part $\hat{H}^{Q}_{[2]}(2)$ describing the second particle.

7. An example: two free particles

Plain waves

If $V \equiv 0$, then the Hamiltonian commutes with $(\boldsymbol{\sigma}\hat{\boldsymbol{p}}_i)$ and we can look for the plane wave solutions: either

$$\Psi_{[2]} \;=\; e^{\frac{i}{\hbar}(\boldsymbol{p}_1\boldsymbol{r}_1+\boldsymbol{p}_2\boldsymbol{r}_2)}\,(\Theta_{\mathrm{ll}},\ \Theta_{\mathrm{ls}},\ \Theta_{\mathrm{sl}},\ \Theta_{\mathrm{ss}})^{\mathrm{T}} \tag{48}$$

[for Hamiltonians (6), (7), (25)], or

$$\Psi_{[2]} \;=\; e^{\frac{i}{\hbar}(\boldsymbol{p}_1\boldsymbol{r}_1+\boldsymbol{p}_2\boldsymbol{r}_2)}\,(\Theta_{\mathrm{ll}},\ \Theta_{\mathrm{ls}},\ \Theta_{\mathrm{sl}})^{\mathrm{T}} \;, \tag{49}$$

[for Hamiltonians of the type presented in equation (27)], where Θ_{ll}, Θ_{ls}, Θ_{sl}, Θ_{ss} are two particle Pauli spinors and T denotes transposition. The eigenvalue problems for the DC Hamiltonian (6) and for the simplified Hamiltonian (25) [equivalent to equation (27) with the operator (28)], reduce to

$$\begin{aligned}
\left(w_{\mathrm{ll}}w_{\mathrm{ss}} - 4p_1^2p_2^2\right)\Theta_{\mathrm{ll}} &= 0\,,\\
w_{\mathrm{ss}}\Theta_{\mathrm{ss}} &= 2\left(\boldsymbol{\sigma p}_1\right)\left(\boldsymbol{\sigma p}_2\right)\Theta_{\mathrm{ll}}\,,\\
\left(E+2mc^2\right)\Theta_{\mathrm{ls}} &= c\left[\left(\boldsymbol{\sigma p}_2\right)\Theta_{\mathrm{ll}} + \left(\boldsymbol{\sigma p}_1\right)\Theta_{\mathrm{ss}}\right]\,,\\
\left(E+2mc^2\right)\Theta_{\mathrm{sl}} &= c\left[\left(\boldsymbol{\sigma p}_1\right)\Theta_{\mathrm{ll}} + \left(\boldsymbol{\sigma p}_2\right)\Theta_{\mathrm{ss}}\right]\,,
\end{aligned} \tag{50}$$

where

$$\begin{aligned}
w_{\mathrm{ll}} &= c^{-2}E\left(E+2mc^2\right) - \left(p_1^2+p_2^2\right)\,,\\
w_{\mathrm{ss}} &= c^{-2}\left(E+2mc^2\right)\left(e+4mc^2\right) - \left(p_1^2+p_2^2\right)\,,
\end{aligned}$$

with $e = E$ in the case of the DC Hamiltonian (6), and $e = 0$ for the simplified Hamiltonian (25). The requirement of $\Theta_{\mathrm{ll}} \neq 0$ reduces equation (50) to

$$\left(w_{\mathrm{ll}}w_{\mathrm{ss}} - 4p_1^2p_2^2\right) = 0\,, \tag{51}$$

which for $e = E$ gives four eigenvalues

$$E = \pm\sqrt{p_1^2+m^2c^4} \pm \sqrt{p_2^2+m^2c^4} - 2mc^2\,. \tag{52}$$

Four solutions (52) can be associated with three continua resulting from the superposition of the one-particle positive (+ sign) and negative (− sign) continua: the first one, $E \approx 0$, is associated with two one-particle positive continua (++ sign), the next continuum, $E \approx -2mc^2$, is associated with positive and negative one-particle continua (+− and −+), and the last one, $E \approx -4mc^2$, with the negative continua (−−). (The approximate relations for E are valid for small p_1 and p_2.) For $e = 0$, equation (51) is the third-order algebraic equation and its solutions may be expressed using the Cardan formulae. Because of their complexity, we restrict the discussion to a qualitative analysis. As one should expect, the solutions are close to three highest eigenvalues given by equation (52): one is close to the positive root (++ positive continuum), and the two remaining ones are close to $E \approx -2mc^2$ (+− and −+ first negative continuum).

Very similar roots to those of equation (27) with operator (28) are obtained by solving this equation with operator (46). In this case, equation (27) reduces to three algebraic equations

$$\left[c^2p_2^2\left(E+2mc^2-\frac{p_1^2}{2m}\right)^{-1} + c^2p_1^2\left(E+2mc^2-\frac{p_2^2}{2m}\right)^{-1} - E\right]\Theta_{\mathrm{ll}} = 0\,, \tag{53}$$

$$\begin{aligned}
\Theta_{\mathrm{ls}} &= c\left(E+2mc^2-\frac{p_1^2}{2m}\right)^{-1}\left(\boldsymbol{\sigma p}_2\right)\Theta_{\mathrm{ll}},\\
\Theta_{\mathrm{sl}} &= c\left(E+2mc^2-\frac{p_2^2}{2m}\right)^{-1}\left(\boldsymbol{\sigma p}_1\right)\Theta_{\mathrm{ll}}\,.
\end{aligned}$$

If $\Theta_{\rm ll} \neq 0$, equation (53) leads to

$$c^2 p_2^2 \left(E + 2mc^2 - \frac{p_2^2}{2m} \right) + c^2 p_1^2 \left(E + 2mc^2 - \frac{p_1^2}{2m} \right) - E \left(E + 2mc^2 - \frac{p_1^2}{2m} \right) \left(E + 2mc^2 - \frac{p_2^2}{2m} \right) = 0 \,.$$

The same dispersion relations for the considered equations can be easily obtained for the antisymmetrized functions (48) and (49).

In the case of the N-particle DC Hamiltonian (14), we get 2^N roots belonging to $(N+1)$ continua: $E \approx 0, -2mc^2, -4mc^2, \ldots, -2Nmc^2$. For the simplified Hamiltonians [equation (37)], we get only $(N+1)$ roots belonging to two continua: $E \approx 0$ and $E \approx -2mc^2$. The dispersion relation for the positive energy and momenta $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ for the Pauli energy $E_{\rm P}$, DC energy $E_{\rm DC}$, and energies derived from the simplified Hamiltonians (28) and (46) (respectively, $E_{\rm A}$ and $E_{\rm d}$) are given by the following equations:

$$\begin{aligned}
E_{\rm P} &= \frac{p_1^2 + p_2^2}{2m} - \frac{p_1^4 + p_2^4}{8m^3}\alpha^2 \,, \\
E_{\rm DC} &= E_{\rm P} + \frac{p_1^6 + p_2^6}{16m^5}\alpha^4 - \frac{p_1^8 + p_2^8}{128m^7}\alpha^6 + \mathcal{O}\left(\alpha^8\right) \,, \\
E_{\rm A} &= E_{\rm DC} + \frac{p_1^2 p_2^2 \left(p_1^2 + p_2^2\right)}{32m^5}\alpha^4 - \frac{p_1^2 p_2^2 \left(7p_1^4 + 10p_1^2 p_2^2 + 7p_2^4\right)}{256m^7}\alpha^6 + \mathcal{O}\left(\alpha^8\right) \,, \\
E_{\rm d} &= E_{\rm DC} + \frac{p_1^2 p_2^2 \left(p_1^2 + p_2^2\right)}{32m^5}\alpha^4 - \frac{3p_1^2 p_2^2 \left(p_1^2 + p_2^2\right)^2}{128m^7}\alpha^6 + \mathcal{O}\left(\alpha^8\right) \,.
\end{aligned}$$

As one can easily check,

$$E_{\rm P} \overset{\alpha^4}{<} E_{\rm DC} \overset{\alpha^4}{<} E_{\rm A} \overset{\alpha^6}{<} E_{\rm d} \,,$$

where in each inequality, the magnitude of terms by which the corresponding energies differ is indicated. Besides, $|E_{\rm P} - E_{\rm DC}| > |E_{\rm d} - E_{\rm DC}|$ and $E_{\rm A} - E_{\rm d} = \mathcal{O}(\alpha^6)$.

8. Conclusions

Though the eigenvalue problems of the simplified Hamiltonians is difficult to solve analytically even for two noninteracting electrons, they may be easily applicable and very useful for numerical solutions of the eigenvalue equations for many-electrons systems, *e.g.* in atomic, molecular and solid state physics. One of the advantages of the simplified equations is the $(N+1) \times 2^N$ component structure of the corresponding wave functions,

compared to $2^N \times 2^N$ component structure of the DC wave functions. However, the spinor structure of obtained reduced DC equations is significantly reduced, the new equations retain linear structure of the original DC equation and still posses intrinsic relativistic character. In contrast to the DC Hamiltonian which has $(N+1)$ bands of eigenvalues associated with energy thresholds $E = 0, -2mc^2, \ldots, -2N\,mc^2$, the simplified Hamiltonians have only two bands of eigenvalues with thresholds $E = 0$ and $E = -2mc^2$. The positive energy band, containing the bound states, is of the primary interest in majority of studies. The simplification of the DC equation has been performed on the level of the N-particle equation and it is valid for an arbitrary potential V describing interactions between particles. Therefore, the simplified equations posses an appealing feature of treating all interactions in a uniform way. It is worthwhile to note that the same reduction procedure can be performed in the case of Dirac–Coulomb–Breit Hamiltonian, which includes all relativistic effects of interacting electrons up to α^2 order. The non-separability of the simplified equations for noninteracting systems is not crucial in practice but disappointing. A search for another, separable form of the simplified Hamiltonian is certainly an interesting challenge.

The formalism presented in this paper can easily be extended to higher orders in α. However, already the α^4 accuracy, in majority of cases, carries corrections which are less significant then the QED effects. In the case of the α^4-accurate Hamiltonians, the $2^N \times 2^N$-dimensional spinor structure is reduced to $\left[1 + \binom{N}{1} + \binom{N}{2}\right] \times 2^N$ structure. Moreover, the addition of the α^4 correction adds only one more continuum ($\approx -4mc^2$) to the spectrum. In general, it seems to be more pragmatic to treat α^4 terms by means of the direct perturbation method.

At the end, let us mention that on every level of simplification of the DC equation, the form of wave function is suitable for using non-separable basis as for example explicitly correlated functions [15–19, 22]. This is particularly useful when approaches based on non-relativistic equation fail and the electron correlation plays significant role in the system. Also quasi-relativistic methods based on the Fouldy–Wouthuysen transformation [6, 30] may be applied to solving the simplified N-electron eigenvalue problem on every level of approximation.

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