J Math Chem (2012) 50:510–533
DOI 10.1007/s10910-011-9823-6

ORIGINAL PAPER

Geminals in Dirac–Coulomb Hamiltonian eigenvalue problem

Grzegorz Pestka · Mirosław Bylicki ·
Jacek Karwowski

Received: 24 March 2011 / Accepted: 16 April 2011 / Published online: 6 May 2011

Abstract The applicability of the Dirac–Coulomb model in computational analysis of the properties of many-electron systems has been, since many years, a subject of dispute and controversy. The most common and numerically safe approach, based on the restriction of the variational space to the many-electron spinors spanning a subspace of the positive-energy part of the complete Hilbert space has been challenged by alternative models in which carefully selected both positive and negative energy functions are taken into account. However, these constructions are not possible when one goes beyond the one-electron model, e.g. when geminal-containing trial functions are used. Then the problem becomes particularly difficult and subtle. In this report several aspects specific for the geminal-based variational approach to the Dirac–Coulomb eigenvalue problem are discussed.

Keywords Dirac–Coulomb model · Hylleraas-CI · Complex coordinate rotation · Kinetic balance · Brown–Ravenhall disease

1 Introduction

The one-electron Schrödinger Hamiltonians describing systems of chemical interest are bounded from below. Many-electron generalizations are well defined, unique and free of internal contradictions. Therefore, the mathematical aspects of theoretical studies of many-electron systems based on the Schrödinger model are relatively simple and well understood. The algebraic representation of the many-electron Schrödinger equation, controlled by the Hylleraas–Undheim–McDonald [1,2] theorem, gives results which converge to the correct ones as the basis set approaches completeness.

G. Pestka (✉) · M. Bylicki · J. Karwowski
Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Grudziądzka 5, 87-100 Toruń, Poland
e-mail: gp@fizyka.umk.pl

In principle, the trial functions do not have to be restricted by any constrain other than square integrability. In particular, there are no conceptual difficulties related to the use of explicitly-correlated, geminal-containing functions.

The story is entirely different if we are going to apply a relativistic model based on the Dirac equation. Already one-electron relativistic quantum models are logically inconsistent and contain intrinsic contradictions. As we know, the Dirac Hamiltonian is unbounded form below. In principle, this implies that it cannot describe a physically stable system: unboundedness from below means that the ground state does not exist. In order to save his equation, Dirac introduced the infinite number of non-observable electrons which occupy the negative-energy continuum and prevent the positive energy particles to move to the negative energy states. The model is evidently self-contradictory: the equation is basically one-electron however it cannot give any reasonable solution unless it comprises an infinite number of electrons which have no effect on the observable properties of the only observable, positive-energy electron, except keeping it away from the negative-energy continuum. A very strong feature of this model, due to which the equation not only survived but also brought the Nobel Prize to Dirac, is its ability to describe the creation and annihilation of the electron-positron pairs. And, though very shortly after the Dirac equation was introduced, Pauli and Weiskopf demonstrated that the energy of a quantized field is always positive [3], the Dirac model survived and its development created a basis for what is frequently called *relativistic quantum chemistry*. More to say, there is no practical alternative to the relativistic quantum models of many-electron systems. The formulations based on the quantum electrodynamics, though free of all contradictions mentioned above, are too complicated to be applied to systems containing more than two or three electrons.

Many-electron generalizations of the Dirac equation result in so called *Dirac–Coulomb* (DC) model. A hybrid approach based on a Hamiltonian in which the one-electron terms are equal to the Dirac Hamiltonians for electrons moving in the external field generated by fixed nuclei and the two-electron interaction terms are equal to the non-relativistic Coulomb operators. This formulation is evidently non-covariant. Also after the interaction operator is supplemented by retardation and magnetic corrections, the covariance is limited to the terms proportional to α^2, where α is the fine-structure constant.

The eigenvalue problem of the Dirac–Coulomb Hamiltonian, additionally to being unbounded from below, suffers from another mathematical inconvenience: the discrete and continuous spectra of its one-electron part overlap and the corresponding wavefunctions are coupled by the interaction term. In effect, the spectrum of DC Hamiltonian does not contain bound states. All its solutions either belong to continuum or are autoionizing. This awkward property of the DC eigenvalue problem, discovered by Brown and Ravenhall [4], is referred to as the Brown–Ravenhall disease and the continuum which spreads over the entire energy range (from $-\infty$ to $+\infty$) is known as the Brown–Ravenhall (BR) continuum.

In the two-electron case an artificial construction similar to the one used in the Dirac equation would not work.[1] This feature of the model results in serious interpretative

---

[1] Let us note that such a construction is not effective also in the case of one-electron Klein–Gordon equation which describes bosons and also has unbounded from below spectrum.

problems. Most common escape is to project the Hamiltonian or, at least, its part describing the interaction between electrons, to the positive energy subspace of the complete Hilbert space. In practical terms this means that the many-electron basis in the variational space is constructed as a Kronecker product of the one electron Dirac spinors corresponding to the positive-energy state solutions of a Dirac equation. In such a space the algebraic representation of the DC Hamiltonian corresponds to an operator bounded from below and free from the Brown–Ravenhall disease.

The projection method offers a conceptually simple solution but it carries several drawbacks. First—the projected variational space can never approach completeness. Second—the results of the projection depend upon the choice of the one-electron Dirac Hamiltonian. Third—the approach is easily applicable only if we use the one-electron model. In particular, it cannot be applied in a standard way in the case of geminal-containing trial functions [5].

The non-projected DC equation is essentially different from the projected one. The non-projected equation may be solved using methods specific for the treatment of autoionizing states, in particular the complex coordinate rotation (CCR) method [6–8], using carefully selected basis functions which do not contain contributions from the BR continuum [9,10] or imposing strict conditions on the relations between variational spaces spanned by different components of the two-electron Dirac spinors [11–14].

This paper is concerned with using CCR approach to solving the DC Hamiltonian eigenvalue problem in a basis of explicitly-correlated configurations, i.e. with a relativistic generalization of the Hylleraas-CI (Hy-CI) method. In particular, it is demonstrated how due to CCR, one can identify these solutions of the DC equation which correspond to the physically bound states and how the separation of the discrete representations of the BR continuum states from the ones corresponding to the bound states is essential for the numerical stability of the solutions.

Hartree atomic units are used in this paper though the mass m is usually written explicitly. The velocity of light is taken as $c = 137.035\,9895$.

2 Many-electron Dirac model

The Dirac equation

$$\mathsf{H}_{\mathrm{D}}(\mathbf{r})\,\boldsymbol{\Psi}_{\mathrm{D}}(\mathbf{r},t) = i\,\frac{\partial}{\partial t}\boldsymbol{\Psi}_{\mathrm{D}}(\mathbf{r},t) \tag{1}$$

where

$$\mathsf{H}_{\mathrm{D}}(\mathbf{r}) = \begin{bmatrix} (\mathsf{V}+mc^2)\,\mathsf{I}_2, & c\left[\boldsymbol{\sigma}\cdot(\mathbf{p}-\mathbf{A})\right] \\ c\left[\boldsymbol{\sigma}\cdot(\mathbf{p}-\mathbf{A})\right], & (\mathsf{V}-mc^2)\,\mathsf{I}_2 \end{bmatrix}, \tag{2}$$

$$\boldsymbol{\Psi}_{\mathrm{D}}(\mathbf{r},t) = \begin{bmatrix} \boldsymbol{\psi}_{\mathrm{D}}^{\mathrm{l}}(\mathbf{r},t) \\ \boldsymbol{\psi}_{\mathrm{D}}^{\mathrm{s}}(\mathbf{r},t) \end{bmatrix}, \tag{3}$$

$\boldsymbol{\psi}_{\mathrm{D}}^{\mathrm{l}}$, $\boldsymbol{\psi}_{\mathrm{D}}^{\mathrm{s}}$ are two-component spinors, respectively the large and the small components of the Dirac wavefunction, $\boldsymbol{\sigma}$ are Pauli spin matrices, I_2 is a 2×2 unit matrix and the other symbols have their standard meaning, is a covariant one-particle equation describing a relativistic spin $1/2$ particle. In particular, it describes an electron. For simplicity we assume hereafter that in the external potential $\mathbf{A} = 0$. For an isolated system, i.e. if the Dirac Hamiltonian is time-independent, one can derive from the Dirac equation the Hamiltonian eigenvalue problem

$$\mathsf{H}_{\mathrm{D}}(\mathbf{r})\, \Psi(\mathbf{r}) = E_{\mathrm{D}}\, \Psi(\mathbf{r}), \tag{4}$$

where E_{D} is the energy and $\Psi(\mathbf{r})$ is the time-independent wavefunction of a stationary state. The spectrum of the Dirac Hamiltonian consists of three parts: the positive and the negative continua, Σ^+ and Σ^- respectively, and the discrete energy levels.[2] The continua are separated by a $2mc^2$ energy gap in which the discrete energy levels, corresponding to the bound states, are located. The negative continuum is not accessible to the electron occupying positive energy states due to a weird assumption that all Σ^- states are occupied by electrons which are physically not observable except for blocking electronic transitions to Σ^-.

2.1 General formulation

In order to compare the results of the Dirac model with the non-relativistic ones, described by the Schrödinger equation, it is convenient to shift the energy scale by subtracting the rest energy of the electron. Thus, we define

$$E = E_{\mathrm{D}} - mc^2 \tag{5}$$

and

$$\mathsf{H}(\mathbf{r}) = \mathsf{H}_{\mathrm{D}}(\mathbf{r}) + mc^2. \tag{6}$$

Then, Eq. (4) becomes

$$\mathsf{H}(\mathbf{r})\, \Psi(\mathbf{r}) = E\, \Psi(\mathbf{r}), \tag{7}$$

or more explicitly

$$\begin{bmatrix} (\mathsf{V} - E)\, \mathsf{I}_2, & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}), & (\mathsf{V} - E - 2mc^2)\, \mathsf{I}_2 \end{bmatrix} \begin{bmatrix} \psi^{\mathrm{l}} \\ \psi^{\mathrm{s}} \end{bmatrix} = 0. \tag{8}$$

---

[2] This is strictly correct for a specific class of external potentials (e.g. for the Coulomb potential). For some potentials also autoionizing states (resonances), appear.

In the non-relativistic limit $c \to \infty$ Eq. (8) transforms to the Lévy–Leblond (LL) equation:

$$\begin{bmatrix} (\mathsf{V} - E)\,\mathsf{I}_2, & (\boldsymbol{\sigma} \cdot \mathbf{p}) \\ (\boldsymbol{\sigma} \cdot \mathbf{p}), & -2m\,\mathsf{I}_2 \end{bmatrix} \begin{bmatrix} \psi^{\mathrm{l}} \\ \tilde{\psi}^{\mathrm{s}} \end{bmatrix} = 0, \tag{9}$$

where

$$\tilde{\psi}^{\mathrm{s}} = \lim_{c \to \infty} c\,\psi^{\mathrm{s}}.$$

The second pair of Eq. (9) may be rewritten as

$$\tilde{\psi}^{\mathrm{s}} = \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p})\,\psi^{\mathrm{l}}. \tag{10}$$

The elimination of $\tilde{\psi}^{\mathrm{s}}$ from the first pair of (9) gives:

$$\left[\frac{(\boldsymbol{\sigma} \cdot \mathbf{p})^2}{2m} + (\mathsf{V} - E)\,\mathsf{I}_2 \right] \psi^{\mathrm{l}} = 0. \tag{11}$$

Since $(\boldsymbol{\sigma} \cdot \mathbf{p})^2 = \mathbf{p}^2\,\mathsf{I}_2$, we get two identical Schrödinger equations.[3] Their solution ψ^{l} corresponds to two spinorbitals with spins α and β:

$$\psi^{\mathrm{l}}_{\alpha} = \psi \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \text{and} \quad \psi^{\mathrm{l}}_{\beta} = \psi \begin{bmatrix} 0 \\ 1 \end{bmatrix}. \tag{12}$$

A generalization of the Dirac model to many particles is hampered by very serious formal and conceptual problems [15]. First, each particle has its own time. Therefore, in order to construct a Hamiltonian eigenvalue problem, one has to assume that we have the same time variable for all particles. For this reason the n-particle formulation, even if the particles do not interact, cannot be covariant. Then, let us assume that we have a system of n non-interacting electrons moving in an external potential[4]

$$\mathsf{V}_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \sum_{j=1}^{n} \mathsf{V}(\mathbf{r}_j) \tag{13}$$

with a common time t. Consequently, the n-particle counterpart of Eq. (7) may be written as

$$\mathsf{H}_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)\,\Psi^{(n)}_{\{q\}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = E^{(n)}_{\{q\}}\,\Psi^{(n)}_{\{q\}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n), \tag{14}$$

---

[3] If we considered an external magnetic field, i.e. if we allowed for $\mathbf{A} \neq 0$, Eq. (11) would contain the Pauli term and two components of the nonrelativistic wavefunction would be different.

[4] In Eqs. (1)–(12) and hereafter we have dropped out the indices referring to the number of electrons or characterizing the quantum state, wherever it does not lead to a misunderstanding or confusion.

where $\{q\} = \{q_1, q_2, \ldots, q_n\}$ is a set of quantum numbers and q_j, $j = 1, 2, \ldots, n$ stands collectively for the set of quantum numbers describing the one-electron state,

$$\mathsf{H}_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \bigoplus_{j=1}^{n} \mathsf{H}(\mathbf{r}_j), \tag{15}$$

$$E^{(n)}_{\{q\}} = \sum_{j=1}^{n} E^{(1)}_{q_j} \tag{16}$$

and

$$\Psi^{(n)}_{\{q\}}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = \bigotimes_{j=1}^{n} \Psi_{q_j}(\mathbf{r}_j). \tag{17}$$

Let us note that the n-electron Hamiltonian is an operator represented by $4^n \times 4^n$ matrix and the wavefunction has 4^n components.

For simplicity we shall limit our further discussion to the case of $n = 2$. Thus, the two-electron Dirac equation may be written as

$$\left[\mathsf{H}(\mathbf{r}_1) \oplus \mathsf{H}(\mathbf{r}_2)\right]\left[\Psi_{q_1}(\mathbf{r}_1) \otimes \Psi_{q_2}(\mathbf{r}_2)\right] = E^{(2)}_{q_1,q_2}\left[\Psi_{q_1}(\mathbf{r}_1) \otimes \Psi_{q_2}(\mathbf{r}_2)\right] \tag{18}$$

where

$$E^{(2)}_{q_1,q_2} = E^{(1)}_{q_1} + E^{(1)}_{q_2}. \tag{19}$$

As it was already mentioned, the spectrum of the one-electron Dirac Hamiltonian consists of the discrete part $\mathcal{D}^{(1)}$ covering $E^{(1)}_q \in (0, -2mc^2)$ and two continua Σ^+ with $E^{(1)} > 0$ and Σ^- with $E^{(1)} < -2mc^2$. The structure of the two-electron spectrum resulting from different combinations of the one-electron states is shown in Table 1 and in Fig. 1. As one can see, apart of the positive and negative energy continua analogous to the ones in the one-electron case and the continua associated with the ionization of one of the electrons, we have the Brown–Ravenhall (BR) continuum spreading over the entire energy range. All discrete states of the two-electron Hamiltonian are degenerate with the states of this continuum. Let us note however, that if the electrons do not interact, we can separate the two-electron eigenvalue problem to two independent one-electron problems and eliminate the influence of the BR continuum on *numerical* solutions of the two-electron problem.

2.2 Variational approach

Similarly as in the Schrödinger case, the aim of the variational procedure is the identification of the stationary points of the Rayleigh quotient

$$K[\Phi] = \frac{\langle \Phi | \mathsf{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \tag{20}$$

Table 1 Structure of spectrum of two-electron Dirac Hamiltonian

One-electron states	Two-electron states		
$E^{(1)}_{q1}, E^{(1)}_{q2}$	$E^{(2)}_{q1,q2}$	Range	Description
$\mathcal{D}^{(1)}, \mathcal{D}^{(1)}$	$\mathcal{D}^{(2)}$	$E^{(1)}_{q1} + E^{(1)}_{q2} \in (-4mc^2, 0)$	Discrete
Σ^+, Σ^+	Σ^{++}	$(0, +\infty)$	Positive continuum
Σ^-, Σ^-	Σ^{--}	$(-\infty, -4mc^2)$	Negative continuum
Σ^+, Σ^-	Σ^{+-}	$(-\infty, +\infty)$	Brown–Ravenhall continuum
$\mathcal{D}^{(1)}, \Sigma^+$	Σ^+_{d}	$(E^{(1)}_{q1}, +\infty)$	Positive-energy ionization
$\Sigma^-, \mathcal{D}^{(1)}$	Σ^-_{d}	$(-\infty, E^{(1)}_{q2})$	Negative-energy ionization

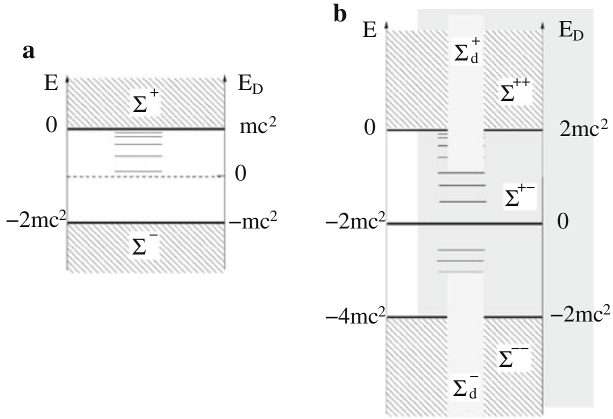

Fig. 1 Spectrum of the Dirac Hamiltonian for one electron (**a**) and for two non-interacting electrons (**b**). In the one-electron case there are two continua: Σ^+ and Σ^- corresponding, respectively, to the positive- and to the negative-energy states. In the two-electron case the states with both electrons occupying the same one-electron continuum generate either upper or the lower continuum, Σ^{++} and Σ^{--} respectively. The Brown–Ravenhall continuum, Σ^{+-}, spreads from $-\infty$ to $+\infty$ and comprises two-electron states with one electron in Σ^+ and the other one in Σ^-. If one electron occupies a discrete state and the other one Σ^+ / Σ^- we get the two electron continuum Σ^+_d / Σ^-_d associated with the one-electron ionization

in a properly selected space $\mathcal{H}\{\Phi\}$ of the trial functions Φ. A basis set expansion of the components of the trial function

$$\Phi^{\mathrm{l}} = \sum_{k=1}^{N_{\mathrm{l}}} C^{\mathrm{l}}_k \, \phi^{\mathrm{l}}, \quad \Phi^{\mathrm{s}} = \sum_{k=1}^{N_{\mathrm{s}}} C^{\mathrm{s}}_k \, \phi^{\mathrm{s}} \tag{21}$$

leads to the algebraic approximation to the Dirac equation. But, while in the Schrödinger model Φ is a one-component function fulfilling the appropriate constrains (square integrability, boundary conditions, etc.) and we have one variational space, in the Dirac and Lévy–Leblond models the variational space is split to two mutually orthogonal variational subspaces, $\mathcal{H}^{\mathrm{l}} = \mathcal{H}\{\Phi^{\mathrm{l}}\}$ and $\mathcal{H}^{\mathrm{s}} = \mathcal{H}\{\Phi^{\mathrm{s}}\}$, in which, respectively, large and small components of the trial functions are expanded. The dimensions of the subspaces are denoted N_l and N_s, respectively, and $N = N_\mathrm{l} + N_\mathrm{s}$.

As a consequence, the variational approach to solving both Dirac and Lévy–Leblond equation is qualitatively different from the one used to solve the Schrödinger equation and, contrary to a common belief, the main difference stems from the multi-component structure of the wavefunction rather than from the unboundedness from below of the Dirac Hamiltonian. It appears that the structures of the variational space in the Dirac and in the Lévy–Leblond cases are very similar [16,17]. As a straightforward consequence of Eqs. (9)–(11), the variational spectrum of the LL equation is bounded from below if the components of the trial function fulfill the *kinetic balance condition*:

$$\Phi^{\mathrm{s}} \sim (\boldsymbol{\sigma} \cdot \mathbf{p})\, \Phi^{\mathrm{l}}. \tag{22}$$

As one can show [18,19], a more general and more flexible relation between the variational spaces

$$(\boldsymbol{\sigma} \cdot \boldsymbol{p})\mathcal{H}^{\mathrm{l}} \subset \mathcal{H}^{\mathrm{s}} \tag{23}$$

is sufficient to the fulfillment of the Hylleraas–Undheim–McDonald bound conditions for the variational eigenvalues.

The same applies to the Dirac equation. Retaining the correct relations between the components of the wavefunctions appears to be sufficient for the stability of the variational procedure applied to the large component [18,19]. If

$$\bigcup_{\nu=1}^{N_\mathrm{l}} \left[\left(1 - \frac{\mathsf{V} - \tilde{E}_\nu}{2mc^2} \right)^{-1} (\boldsymbol{\sigma} \cdot \mathbf{p})\, \mathcal{H}^{\mathrm{l}} \right] \subset \mathcal{H}^{\mathrm{s}}, \tag{24}$$

where $\tilde{E}_\nu$ is the variational energy, then the Hylleraas–Undheim–McDonald bound conditions are fulfilled for the Dirac eigenvalues as long as

$$\frac{\mathsf{V} - \tilde{E}_\nu}{2mc^2} < 1. \tag{25}$$

The last condition is always fulfilled for the negative defined external potentials (in particular for the Coulomb potential). This also explains why in the numerical Dirac–Fock procedures, where large-small component relations are always exactly fulfilled, no sign of the variational collapse was ever observed [20,21].

Equation (24) implies that in order to get a numerically stable approach one has to sufficiently expand the variational space of the small components. This observation has been structured to a theorem known as the *minimax principle* [22,23]:

$$E = \min_{\{\mathrm{l}\}} \left[\max_{\{\mathrm{s}\}} \frac{\langle \Phi | \mathsf{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right]. \tag{26}$$

In fact, it may be considered as a recipe for reaching the stationary point in the energy hypersurface in the space of variational parameters [24].

In the algebraic approximation to the Dirac equation the variation of $K[\Phi]$ leads to a $N \times N$ matrix eigenvalue problem:

$$\begin{pmatrix} \boldsymbol{H}^{\mathrm{ll}} - E\boldsymbol{S}^{\mathrm{ll}} & c\,\boldsymbol{H}^{\mathrm{ls}} \\ c\,\boldsymbol{H}^{\mathrm{sl}} & \boldsymbol{H}^{\mathrm{ss}} - E\boldsymbol{S}^{\mathrm{ss}} \end{pmatrix} \begin{pmatrix} \boldsymbol{C}^{\mathrm{l}} \\ \boldsymbol{C}^{\mathrm{s}} \end{pmatrix} = 0, \tag{27}$$

where $\boldsymbol{H}^{\mathrm{ab}}$, $\mathrm{ab} = \mathrm{l}, \mathrm{s}$, are matrix representations of the appropriate blocks of the operator in Eq. (8), $\mathbf{S}$ is the overlap matrix and the subscripts refer to the large- and small-component space. The LL equation is represented as $N_{\mathrm{l}} \times N_{\mathrm{l}}$ matrix eigenvalue equation:

$$\left(\boldsymbol{H} - E\boldsymbol{S}^{\mathrm{ll}}\right)\boldsymbol{C}^{\mathrm{l}} = 0, \tag{28}$$

where

$$\boldsymbol{H} = \boldsymbol{H}^{\mathrm{ll}} + \frac{1}{2m}\boldsymbol{H}^{\mathrm{ls}}\left(\boldsymbol{S}^{\mathrm{ss}}\right)^{-1}\boldsymbol{H}^{\mathrm{sl}}. \tag{29}$$

Using condition (24) within the algebraic approximation is impractical. Therefore it is usually replaced by its approximate form (23). In more precise calculations it may be replaced by a more restrictive *asymptotic balance condition* [19]

$$\left[(\boldsymbol{\sigma}\cdot\mathbf{p})\ \mathcal{H}^{\mathrm{l}}\right] \cup \left[r\,(\boldsymbol{\sigma}\cdot\mathbf{p})\ \mathcal{H}^{\mathrm{l}}\right] \subset \mathcal{H}^{\mathrm{s}}. \tag{30}$$

valid for the Coulomb external potentials.

3 Dirac–Coulomb model

If the Dirac electrons, as described by Eqs. (14)–(17), are assumed to interact by the non-relativistic Coulomb potential, we get the *Dirac–Coulomb (DC) model*. This is a rather weird hybrid composed of a relativistic one-electron part and a non relativistic two-electron term. Its eigenvalue problem has been a subject of controversy for more than half a century, since Brown and Ravenhall noticed in 1951 that the eigenvalues corresponding to the bound-state solutions embedded in the BR continuum are coupled to this continuum by the electron-electron interaction [4]. As a consequence, all eigenvalues of the DC Hamiltonian corresponding to the physically bound states (including, for example, the ground state of helium atom) are autoionizing. This means, that the DC Hamiltonian does not have normalizable eigenfunctions. Removing the BR continuum by a projection implies that the model space is incomplete and the results depend on the way the projection is performed. On the other hand, the presence of the BR continuum results in a shift of the energy levels corresponding to the bound states. For these reasons some researchers consider using the DC Hamiltonian as physically unjustified. Nevertheless, most of computational methods of the relativistic quantum chemistry has been derived from the DC equation [25].

For two electrons the DC Hamiltonian may be written as

$$\mathsf{H}_{\mathrm{DC}}(\mathbf{r_1},\mathbf{r_2}) = \mathsf{H}(\mathbf{r_1}) \oplus \mathsf{H}(\mathbf{r_2}) + \frac{1}{r_{12}}\,\mathsf{I}_{16} \tag{31}$$

$$= \begin{bmatrix} \mathsf{V}\,\mathsf{I}_4 & c\,(\boldsymbol{\sigma}_2\cdot\mathbf{p}_2) & c\,(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1) & \mathbf{0} \\ c\,(\boldsymbol{\sigma}_2\cdot\mathbf{p}_2) & (\mathsf{V}-2mc^2)\,\mathsf{I}_4 & \mathbf{0} & c\,(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1) \\ c\,(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1) & \mathbf{0} & (\mathsf{V}-2mc^2)\,\mathsf{I}_4 & c\,(\boldsymbol{\sigma}_2\cdot\mathbf{p}_2) \\ \mathbf{0} & c\,(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1) & c\,(\boldsymbol{\sigma}_2\cdot\mathbf{p}_2) & (\mathsf{V}-4mc^2)\,\mathsf{I}_4 \end{bmatrix}$$

where $\boldsymbol{\sigma}_1 = \boldsymbol{\sigma} \otimes \mathsf{I}_2,\ \boldsymbol{\sigma}_2 = \mathsf{I}_2 \otimes \boldsymbol{\sigma}$ are 4×4 matrices, I_{16} is a 16×16 unit matrix and

$$\mathsf{V} \equiv \mathsf{V}(\mathbf{r_1},\mathbf{r_2}) = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \tag{32}$$

The corresponding DC equation reads

$$\mathsf{H}_{\mathrm{DC}}(\mathbf{r_1},\mathbf{r_2})\ \Psi(\mathbf{r_1},\mathbf{r_2}) = E\,\Psi(\mathbf{r_1},\mathbf{r_2}). \tag{33}$$

The 16-component wavefunction is composed of four-component quantities:

$$\Psi(\boldsymbol{r_1},\boldsymbol{r_2}) = \begin{bmatrix} \psi^{\mathrm{ll}}(\boldsymbol{r}_1,\boldsymbol{r}_2) \\ \psi^{\mathrm{ls}}(\boldsymbol{r}_1,\boldsymbol{r}_2) \\ \psi^{\mathrm{sl}}(\boldsymbol{r}_1,\boldsymbol{r}_2) \\ \psi^{\mathrm{ss}}(\boldsymbol{r}_1,\boldsymbol{r}_2) \end{bmatrix}, \tag{34}$$

where the superscripts refer to one-electron *large* or *small* contributions. The antisymmetry condition $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$ implies:

$$\begin{aligned} \psi^{\mathrm{ll}}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= -\psi^{\mathrm{ll}}(\boldsymbol{r}_2,\boldsymbol{r}_1), \\ \psi^{\mathrm{ls}}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= -\psi^{\mathrm{sl}}(\boldsymbol{r}_2,\boldsymbol{r}_1), \\ \psi^{\mathrm{ss}}(\boldsymbol{r}_1,\boldsymbol{r}_2) &= -\psi^{\mathrm{ss}}(\boldsymbol{r}_2,\boldsymbol{r}_1) \end{aligned} \tag{35}$$

In the non-relativistic limit Eq. (33) transforms to the two-electron LL equation:

$$\begin{aligned} (\boldsymbol{\sigma}_2\cdot\boldsymbol{p}_2)\,\psi^{\mathrm{ls}} + (\boldsymbol{\sigma}_1\cdot\boldsymbol{p}_1)\,\psi^{\mathrm{sl}} &= (E-V)\,\psi^{\mathrm{ll}}, \\ (\boldsymbol{\sigma}_2\cdot\boldsymbol{p}_2)\,\psi^{\mathrm{ll}} &= 2m\,\psi^{\mathrm{ls}}, \\ (\boldsymbol{\sigma}_1\cdot\boldsymbol{p}_1)\,\psi^{\mathrm{ll}} &= 2m\,\psi^{\mathrm{sl}}. \end{aligned} \tag{36}$$

The elimination of ψ^{ls} and ψ^{sl} gives the two-electron Schrödinger equation. The one-electron kinetic balance condition (23) has to be replaced by

$$\begin{bmatrix} (\boldsymbol{\sigma}_2\cdot\boldsymbol{p}_2) \\ (\boldsymbol{\sigma}_1\cdot\boldsymbol{p}_1) \end{bmatrix} \mathcal{H}^{\mathrm{ll}} \subset \mathcal{H}^{[ls]}, \tag{37}$$

where

$$\mathcal{H}^{[ls]} = \mathsf{A}\left(\mathcal{H}^{ls} \oplus \mathcal{H}^{sl}\right) \tag{38}$$

and A is the antisymmetrization operator. The two-electron DC equation implies [13, 26]

$$\left\{\begin{bmatrix} (\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) \\ (\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) \end{bmatrix} \mathcal{H}^{\mathrm{ll}} \cup \begin{bmatrix} (\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1) \\ (\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2) \end{bmatrix} \mathcal{H}^{\mathrm{ss}}\right\} \subset \mathcal{H}^{[ls]}, \tag{39}$$

and

$$\left[(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p}_1)\,,\ (\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2)\right] \mathcal{H}^{[ls]} \subset \mathcal{H}^{\mathrm{ss}}. \tag{40}$$

As one can see, conditions (37)–(40) couple the variational spaces in a rather complicated way.

In the non-relativistic, Schrödinger, model the singularity of the electron interaction potential results in a cusp of the wavefunction at $r_{12} = 0$ [27,28]. The cusp condition for the ground state of helium-like atoms described by the Schrödinger equation is very simple:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2)|_{r_{12}\to 0} \sim 1 + \tfrac{1}{2} r_{12}. \tag{41}$$

In the case of the DC equation the wavefunction is singular at $r_{12} \to 0$. This singularity is very weak and, as one should expect, independent of Z. As one can show [29,30], for helium-like atoms

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \sim a\, r_{12}^{q} + b\, r_{12}^{q+1}, \quad \text{if } r_{12} \to 0, \tag{42}$$

where a, b are state-dependent constants and

$$q = \sqrt{1 - \alpha^2/4} - 1 \approx -1.3 \times 10^{-5}. \tag{43}$$

The representation of both cusp and singularity by expansions in the orbital space is rather difficult (it requires long expansions containing functions with very large exponents). Therefore using variational functions which explicitly depend on r_{12}, initiated by Hylleraas [31], always attracted attention despite computational complexity of the resulting algorithms.

Usually, in variational calculations the DC Hamiltonian eigenvalue problem is replaced by an eigenvalue problem of its matrix representative in a properly constructed **model space**. In the two-electron case the model space is split to three subspaces:

- $\mathcal{H}^{\mathrm{ll}}$—In the one-electron picture both electrons occupy the positive-energy space (PES). In the non-relativistic limit it is the model space of the Lévy–Leblond equation.

- $\mathcal{H}^{[\mathrm{ls}]}$—In the one-electron picture one electron occupies PES and the other one the negative energy space. This subspace describes the Brown–Ravenhall continuum spreading from $-\infty$ to $+\infty$.
- $\mathcal{H}^{\mathrm{ss}}$—Both electrons occupy the negative-energy space. This subspace corresponds to the negative continuum of the DC Hamiltonian, spreading from $-4mc^2$ to $-\infty$.

Each of these subspaces is spanned by a separate basis set of the primitive functions. The basis sets have to be related by two-electron generalizations of the kinetic balance condition. The two-electron wavefunctions are obtained as a result of the diagonalization of the Hamiltonian matrix. Thus, each wavefunction contains contributions from all subspaces of the model space. The eigenvalues of the Hamiltonian matrix form a finite and discrete set. Some of them represent either the bound or the autoionizing states, but the majority correspond to the three continua of the DC Hamiltonian. An example of the algebraic representation of the spectrum of the DC Hamiltonian in a basis selected to describe the ground state of helium-like atoms is shown in Fig. 2. If the basis set was chosen in a random way, the eigenvalues would be distributed in a random way over a broad range of energies. However, due to a careful selection of the basis functions the eigenvalues are concentrated in three well separated areas corresponding to $\mathcal{H}^{\mathrm{ll}}$ (around $E = 0$), $\mathcal{H}^{[ls]}$ (around $E = -2mc^2$) and $\mathcal{H}^{\mathrm{ss}}$ (around $E = -4mc^2$) and referred to hereafter as bundle 1, 2 and 3 respectively. The lowest edge of the upper bundle corresponds to the ground states. The eigenvalues of bundle 1 are all located above the ground states. Thus, increasing the dimension of $\mathcal{H}^{\mathrm{ll}}$ would result in pushing the ground states down. For the same reason increasing the dimension of $\mathcal{H}^{\mathrm{ss}}$ (all eigenvalues are below $-4mc^2$) would result in pushing the ground states up. The influence of bundle 2 is more complicated. It represents the BR continuum and with increasing the dimension of $\mathcal{H}^{[ls]}$, as well as with increasing Z, some of its eigenvalues may move above the ground state. As long as all eigenvalues of bundle 2 are below bundle 1, increasing the dimension of the corresponding variational space would push up the ground states (and all the states represented by bundle 1). However, the crossings (actually, very narrow avoided crossings) between the eigenvalues of the two bundles result in numerical instabilities. This is illustrated in the right panel of Fig. 2 and in Fig. 3.

4 Relativistic Hylleraas-CI

The electron correlation effects in relativistic calculations based on the algebraic approximation of the DC equation derived from the Rayleigh–Ritz variational principle may be described using configuration interaction (CI), multiconfiguration Dirac–Fock (MCDF), and Hylleraas CI (Hy-CI). Let us assume that we have a set of properly constructed primitive spinors χ_j, $j = 1, 2, \ldots, q$. The one-electron spinors φ_p, $p = 1, 2, \ldots, K$ (corresponding to the atomic orbitals of the non-relativistic theory) are linear combinations of the primitive spinors:

$$\varphi_p = \sum_{j=1}^{q} c_{jp}\,\chi_j. \tag{44}$$

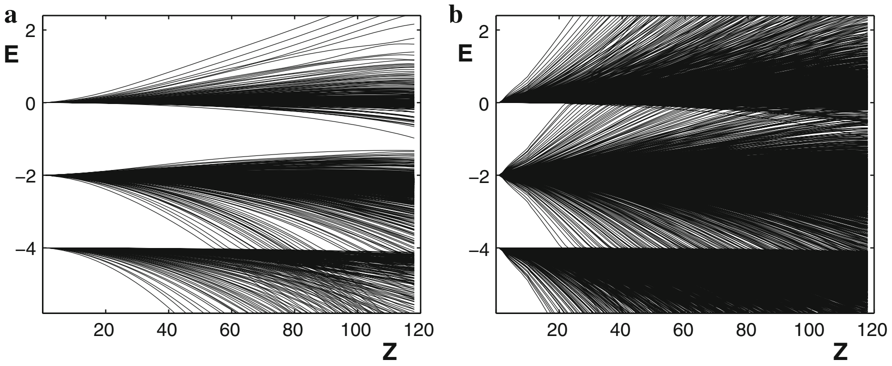

Fig. 2 Eigenvalues of the DC Hamiltonian matrix for helium like atoms, in mc^2 units, versus Z in a basis of 502 (*left panel*) and 1826 (*right panel*) of Hylleraas-type configuration state functions. The bundles of lines correspond (starting from the *top*) to $\mathcal{H}^{\rm ll}$, $\mathcal{H}^{\rm [ls]}$ and $\mathcal{H}^{\rm ss}$. The *numbers* of lines in the bundles are equal to the dimensions of the subspaces of the model space. The lower edge of the upper bundle corresponds to the ground states. It is seen that in the large basis, for $Z > 20$, the energy levels belonging to the BR continuum cross the ground state

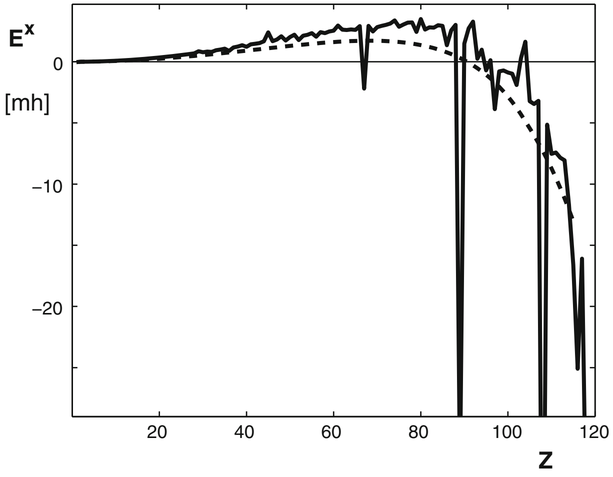

Fig. 3 Relativity-correlation cross-term energy of the ground states of He-like atoms in two basis sets represented in Fig. 1. The *broken line* corresponds to the small Hy-CI basis and the *solid line* to the large one

The n-electron configuration state functions are antisymmetrized and angular-momentum-adapted products of the one-electron spinors. The total variational wavefunctions Φ in the three methods under consideration are defined in the way explained in Table 2. The superscript (t) refers to a preselected set of the configuration state functions and $B_{\rm t}$ is the set of indices numbering these functions. The coefficients C_i or C_{ti} are always optimized. The coefficients c_{jp} are optimized in MCDF but predetermined (usually in an independent variational procedure) and fixed in CI and in Hy-CI.

Table 2 Methods of description the electron correlation effects

Method	Wavefunction	Spinors
CI	$\Phi_{\mathrm{CI}}^{(\mathrm{t})} = \sum_{i\in B_t} C_i \phi_i^{(\mathrm{t})}\ (\{\varphi\})$,	Fixed spinors $\{\varphi_p\}_{p=1}^{K}$,
Hy-CI	$\Phi_{\mathrm{HyCI}} \ = \sum_t r_{12}^t \sum_{i\in B_t} C_{ti} \phi_i^{(\mathrm{t})}\ (\{\varphi\})$	Fixed spinors $\{\varphi_p\}_{p=1}^{K}$,
MCDF	$\Phi_{\mathrm{MCDF}}^{(\mathrm{t})} = \sum_i C_i \phi_i^{(\mathrm{t})}\ (\{\varphi\})$	Spinors $\{\varphi_p\}_{p=1}^{K}$ optimized

In the nonrelativistic model the electron correlation energy is defined as [32]

$$E_{\mathrm{nr}}^{\mathrm{corr}} = E_{\mathrm{Schr}} - E_{\mathrm{HF}}, \tag{45}$$

where the subscripts denote, respectively, 'non-relativistic', 'Schrödinger' and 'Hartree–Fock'. In a similar way is defined the relativistic correlation energy:

$$E_{\mathrm{rel}}^{\mathrm{corr}} = E_{\mathrm{DC}} - E_{\mathrm{DF}}, \tag{46}$$

where E_{DC} and E_{DF} stand, respectively, for the energy derived from the Dirac–Coulomb and from the Dirac–Fock models. In this work we take the extrapolated values of the Schrödinger energies of the ground states of helium-like atoms calculated by Midtdal and Aashamar [33], exact to 10 significant figures. The Hartree–Fock and the Dirac–Fock energies, calculated using package GRASP developed by the Oxford group [34], are also exact to the same accuracy. The DC energies, obtained using different methods, are the only components of Eqs. (45) and (46) which may be not exact numerically. The quantities we consider to be the most convenient when comparing different approaches to solving the DC equation are the relativity-correlation cross-term energies [35]

$$E^{\mathrm{x}} = E_{\mathrm{rel}}^{\mathrm{corr}} - E_{\mathrm{nr}}^{\mathrm{corr}}. \tag{47}$$

Their values plotted in Fig. 3 behave in a regular way in a small basis set but show very strong instabilities, particularly at high Z, in the large basis. A similar observation by Indelicato was concerned with the behavior of MCDF at high Z when the length of the expansion was increasing [36]. As it was already mentioned, the standard approach to the problem is a projection of the DC equation to the PES. However, as it was 20 years ago stated by Brown [37] and recently confirmed numerically by Watanabe et al. [9,10] and by the present authors [5–8], the projection is not necessary if the computational procedure is performed in a consistent way.

4.1 The formalism of the relativistic Hy-CI method

The relativistic Hy-CI method is based on the same ideas as its nonrelativistic counterpart [13]. However, the spinor structure of the relativistic wavefunction and its specific behavior in the singular points of the Hamiltonian introduce some technical complications absent in the nonrelativistic formulation [38,39].

The basis functions (two-electron configuration state functions) may be expressed in the form

$$\Phi_{\Gamma;\Lambda}^{[r],JM\Pi}(\mathbf{r}_1,\mathbf{r}_2)=f_s^{[r]}(r_{12})R_\Gamma(r_1,r_2)\Omega_\Lambda^{JM\Pi}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2), \tag{48}$$

where $\hat{\mathbf{r}}_a=\mathbf{r}_a/r_a$, $a=1,2$, are the angular parts of the electron coordinate $\mathbf{r}_a$, R_Γ is the radial function, $f_s^{[r]}(r_{12})$ is a correlation factor, $\Omega_\Lambda^{JM\Pi}$ is the two-electron angular and spinor function, $\Lambda=\{j_1,\pi_1,j_2,\pi_2\}$ is a collective index for the parity $\pi_a=\pm1$ and the total angular momentum $j_a=l_a+\pi_a/2$, $a=1,2$ (l_a is the orbital angular momentum quantum number) of the one-electron spinors, J, M and Π are, respectively, the total angular momentum and parity quantum numbers. The radial functions with the correct asymptotic behavior at the origin and in the infinity are

$$R_\Gamma(r_1,r_2)=r_1^{\gamma_1+p_1}r_2^{\gamma_2+p_2}\,e^{-\beta_1r_1+\beta_2r_2}, \tag{49}$$

where p_a are integers,

$$\gamma_a=\sqrt{(j_a+1/2)^2-(Z\alpha)^2}-(j_a+1/2), \tag{50}$$

$\beta_a>0$, $a=1,2$, and

$$\Gamma\equiv\{\gamma_1,\gamma_2,p_1,p_2,\beta_1,\beta_2\} \tag{51}$$

is a collective symbol for the set of parameters describing the radial function. We also have

$$R_{\Gamma'}R_{\Gamma''}=R_{\Gamma'''}, \tag{52}$$

with

$$\Gamma'''=\{\gamma_a'+\gamma_a'',p_1'+p_1'',p_2'+p_2'',\beta_1'+\beta_1'',\beta_2'+\beta_2''\}. \tag{53}$$

The two-electron spin-angular functions are defined as

$$\Omega_\Lambda^{JM\Pi}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\epsilon\sqrt{2J+1}\sum_{m_1,m_2}\begin{pmatrix}j_1 & j_2 & J\\ m_1 & m_2 & -M\end{pmatrix}\phi_\Lambda^{m_1m_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2), \tag{54}$$

where $\epsilon=(-1)^{j_1-j_2+M}$,

$$\phi_\Lambda^{m_1m_2}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)=\varphi_{j_1,m_1}^{\pi_1}(\hat{\mathbf{r}}_1)\otimes\varphi_{j_2,m_2}^{\pi_2}(\hat{\mathbf{r}}_2), \tag{55}$$

and $\varphi_{j_a,m_a}^{\pi_a}$ are the one-electron spin-angular functions.

The two-electron kinetic balance conditions (39) and (40), generate new correlation factors:

$$\left[(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1)f_s^{[r]}(r_{12})\right]\quad\text{and}\quad\left[(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1)(\boldsymbol{\sigma}_2\cdot\mathbf{p}_2)f_s^{[r]}(r_{12})\right]$$

in, respectively, Φ^{ls} and Φ^{ss} [38,39]. Additionally, the relations between components of the two electron wavefunction resulting from the DC equation lead to similar correlation factors in Φ^{ll} and, consequently, an infinite chain of products of $(\boldsymbol{\sigma}\cdot\mathbf{p})$ acting on $f_s^{[r]}(r_{12})$ is generated. The simplest form of the basic correlation factor is

$$f_s^{[0]}(r_{12}) = r_{12}^s, \tag{56}$$

where s is chosen to satisfy the cusp condition. The higher-order correlation factors generated by the two-electron kinetic balance conditions are

$$\begin{aligned} f_s^{[1]}(r_{12})_1 &= i\left[(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1)f_s^{[0]}(r_{12})\right](\boldsymbol{\sigma}_1\cdot\hat{\mathbf{r}}_1),\\ f_s^{[1]}(r_{12})_2 &= i\left[(\boldsymbol{\sigma}_2\cdot\mathbf{p}_2)f_s^{[0]}(r_{12})\right](\boldsymbol{\sigma}_2\cdot\hat{\mathbf{r}}_2),\\ f_s^{[2]}(r_{12}) &= \left[(\boldsymbol{\sigma}_1\cdot\mathbf{p}_1)(\boldsymbol{\sigma}_2\cdot\mathbf{p}_2)f_s^{[0]}(r_{12})\right](\boldsymbol{\sigma}_1\cdot\hat{\mathbf{r}}_1)(\boldsymbol{\sigma}_2\cdot\hat{\mathbf{r}}_2), \end{aligned} \tag{57}$$

where index r in $f_s^{[r]}(r_{12})$ is equal to the number of $(\boldsymbol{\sigma}\cdot\mathbf{p})$ operators acting on $f_s^{[0]}(r_{12})$. As we see, the two-electron kinetic balance condition requires different two-electron basis sets in the subspaces of the Hy-CI model space.

Matrix elements appearing in the relativistic Hy-CI method may be expressed in terms of the primitive two-electron integrals: $\langle B|f(r_{12})\hat{\tau}|K\rangle$, where B and K stand for the non-correlated configuration state functions and

$$\hat{\tau} = \mathbf{1},\ (\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2),\ \left(\boldsymbol{\sigma}_a\cdot\hat{\boldsymbol{r}}_a\right),\ \left(\boldsymbol{\sigma}_a\cdot\hat{\boldsymbol{r}}_b\right),\ \left[\left(\boldsymbol{\sigma}_1\cdot\hat{\boldsymbol{r}}_1\right)\left(\boldsymbol{\sigma}_2\cdot\hat{\boldsymbol{r}}_2\right)\right], \tag{58}$$

$$f(r_{12}) = \begin{cases} r_{12}^s, & s > -1 \in \boldsymbol{R},\\ r_{12}^q, & q = -1, 0, 1, 2, \ldots,\\ \ln(r_{12}). \end{cases} \tag{59}$$

Details may be found in [38,39].

4.2 Complex coordinate rotation approach to the relativistic Hy-CI

As it was already mentioned, the electron interaction operator couples the discrete and the BR continuum states of the two-electron Dirac Hamiltonian. Therefore, all states of the DC Hamiltonian either belong to one of the continua or are resonances. The projection of the DC equation to the subspace of the positive energy states [40,41] removes this coupling and leads to an equation in which the physically bound states are described by the bound-state solutions. The projection method appears to be applicable also in the case of the Hy-CI [7,8]. However, it is tempting to investigate the properties of solutions of non-projected DC equation. In calculations based on the one-electron model with the relations between the components of the one-electron wavefunctions exactly fulfilled, the projection is not necessary because, by the construction, we can get many-electron wavefunctions corresponding to the bound states [25,42]. Also if the basis set is carefully selected and the algebraic representations of the positive-energy states are sufficiently well separated from the ones of the BR continuum (cf. Figs. 2, 3), one can get a correct description of the bound states without using a projection procedure [9–13]. A very efficient approach, which may also be applied if the energies of the positive-energy states and of the ones representing the BR continuum overlap, is the complex coordinate rotation (also known as the complex scaling) method [6–8].

The CCR method, originally developed to describe the autoionizing states in the Schrödinger model [43,44], has later been applied to study the spectral properties of the Dirac Hamiltonian [45–47]. Very recently the present authors applied this method to solving the DC equation [5–8].

The basic theorem of the method says that the complex rotation of coordinates in the Hamiltonian

$$\mathbf{r} \rightarrow \mathbf{r}e^{i\Theta}, \tag{60}$$

does not change the bound state energies while the continua move to the complex plane. After the rotation the Hamiltonian as well as its matrix representative, are non-Hermitian and the eigenvalues z are complex. The energies are equal to

$$E = \mathrm{Re}(z). \tag{61}$$

The imaginary parts are related to the widths Γ of the energy levels as

$$\Gamma = -2\,\mathrm{Im}(z). \tag{62}$$

The spectrum of the two-electron Dirac Hamiltonian displayed in Fig. 1, after the rotation by the angle Θ, is shown in Fig. 4. As one can see, the discrete energies are here separated from the continua and each continuum occupies a well defined area in the complex plane.

One of the most important benefits of introducing CCR method to solving the DC eigenvalue problem in the algebraic approximation is a simple way for identifying the eigenvalues corresponding to the physically bound states. The procedure is obvious if the interaction term is neglected: The real eigenvalues of the Hamiltonian matrix correspond to the bound states. If the interaction is taken into account all eigenvalues are complex. However, the Θ dependence of the eigenvalues corresponding to the states which are physically bound (more precisely, to the ones which in the DC model are resonances) is different from the behavior of the continua. The resonances (i.e. also the eigenvalues corresponding to the bound states) are, in the complex plane, isolated from the continuum, remain close to the real axis and, in a range of Θ, are Θ-independent, while the continuum eigenvalues depend on Θ in a regular way.

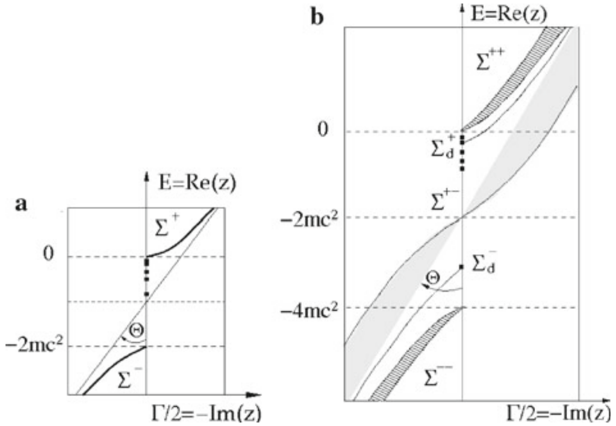

Fig. 4 The same as in Fig 1 but after complex coordinate rotation by the angle Θ. The continua are represented by *lines* and strips extending towards the imaginary axis. The *dots* in the real axis represent the bound-state energies

The effects of removing the degeneracy between the bound-state and the continuum eigenvalues can be seen in Figs. 5 and 6. In Fig. 5 the stabilizing effect of CCR is illustrated. In the lower panel

$$\delta = \frac{100}{|E_0 - E_{\mathrm{a}}|} \tag{63}$$

where E_0 is the eigenvalue corresponding to the ground state energy and E_{a} is the eigenvalue nearest to E_0 in the original (not rotated DC Hamiltonian) is plotted versus Z. In the upper panel the relativity-correlation cross-term energies are displayed. In the curve corresponding to the non-rotated Hamiltonian a strong correlation between near degeneracies in its spectrum (shown in the lower panel) and the spikes in the energy is visible. After the rotation the energy curve is smooth. In Fig. 6 the distance from the ground state eigenvalue to the remaining eigenvalues in the Hy-CI spectra before (left panel) and after (right panel) CCR rotation are plotted versus Z. Before the rotation the distance is defined as

$$\Delta_0 = \frac{E - E_0}{Z^2} \tag{64}$$

and after the rotation as

$$\Delta = \frac{E - E_0}{Z^2}\sqrt{1 + \left[\frac{\Gamma - \Gamma_0}{2(E - E_0)}\right]^2}, \tag{65}$$

where the subscript 0 refers to the ground state. The randomly distributed dots in the left panel, describing the effect of the *continuum dissolution* [48,49], disappear after the rotation.

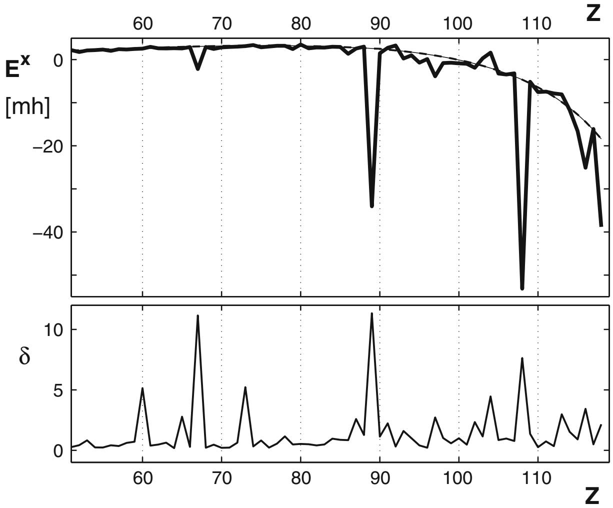

Fig. 5 *Upper panel* Relativity-correlation cross-term energies calculated without (*thick solid line*) and with (*broken line*) complex coordinate rotation. *Lower panel* The values of δ, as defined in Eq. (63)

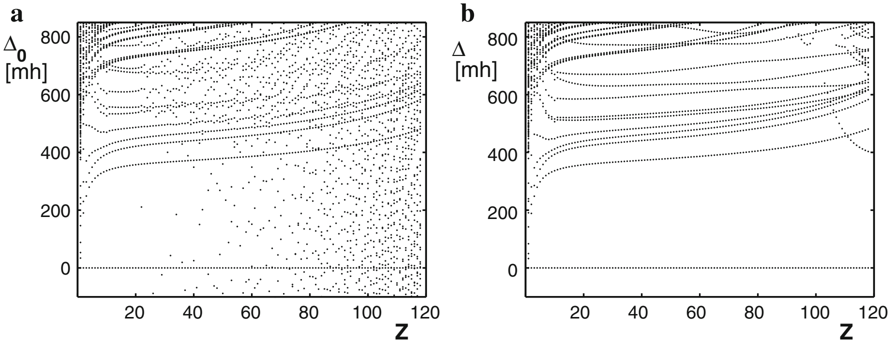

Fig. 6 Hy-CI spectrum of helium-like atoms relative to the ground states without (*left panel*) and with (*right panel*) complex coordinate rotation. The locations of the energy levels are defined in Eqs. (64) and (65)

The influence of the BR continuum on the discrete part of the spectrum, absent in the PES-projected methods, is always present in the non-projected approaches. The difference between the PES-projected and complex coordinate rotated (but unprojected) energies is equal to the virtual pair contribution to the Coulomb electron-electron repulsion energy [8] which, up to the first order is equal to [50,51]

$$\Delta E_{\mathrm{BR}}^{0} = \frac{(Z\alpha)^3}{6\pi}. \tag{66}$$

One should expect that the projected and non-projected results should differ, approximately, by $\Delta E_{\mathrm{BR}}^{0}$. The agreement appears to be surprisingly good. A comparison of the results derived from the projected and non-projected approaches is shown in

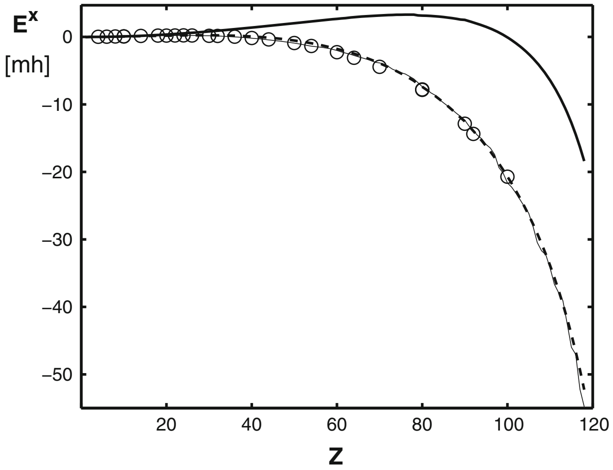

Fig. 7 Relativity-correlation cross-term energies in 1826-function Hy-CI basis CCR non-projected (*thick solid line*), CCR PES-projected (*thin solid line*), CCR non-projected shifted by $\Delta E^0_{\rm BR}$ (*broken line*) and PES-projected CI [52] and MBPT [53] (*circle*)

Fig. 7. In large variational spaces, when the results are expected to be numerically exact, the non-projected CCR Hy-CI [6] results differ from the PES projected CCR Hy-CI [5], the PES projected CI [52], and the PES projected many-body perturbation theory (MBPT) [53] ones by nearly exactly $\Delta E^0_{\rm BR}$.

The relativity-correlation cross-term energies derived from Hy-CI calculations in a basis of 502 configuration state functions without PES projection and without CCR, represented by the broken line in Fig. 3, are also affected by the BR continuum. The difference $D_{\rm BR}$ between the complex coordinate rotated and non-rotated energies in the 502-function Hy-CI basis is shown in the left panel of Fig. 8. The difference ranges from several microhartree for small Z to nearly 1 milihartree for very large Z. The ratio $R_{\rm BR} = D_{\rm BR}/\Delta E^0_{\rm BR}$, for $Z \geq 10$ is shown in the right panel of Fig. 8. As one can see, it may reach as much as 50% of $\Delta E^0_{\rm BR}$ correction. Thus, this effect, though small, is not negligible in accurate calculations. In this context one may quote Johnson et al. [54]: "*It should be noted that errors in* $E_{\rm Dirac}$ *from incorrect treatments of electron-positron and positron-positron terms can be very subtle and* $E_{\rm Dirac}$ *may look perfectly normal (…) when negative-energy basis functions are also included. Nevertheless, it is very difficult, if not impossible, to identify and correct the intrinsic errors in* $E_{\rm Dirac}$ *(…)*". Clearly, the CCR approach allows for such an identification and correction.[5]

Another effect which may influence the DC energies is the singularity of the relativistic wavefunction caused by the singularity of $1/r_{12}$ operators (42). In Table 3 the differences between the ground state energies obtained using the trial functions in the 502-function Hy-CI basis with the exact and with the integer powers of r_{12} are collected. The difference affects at most the 10th significant figure in the total energy.

---

[5] It seems that the CI results of Watanabe et al. [9,10], due to a very careful selection of the basis set, are also free from these errors.

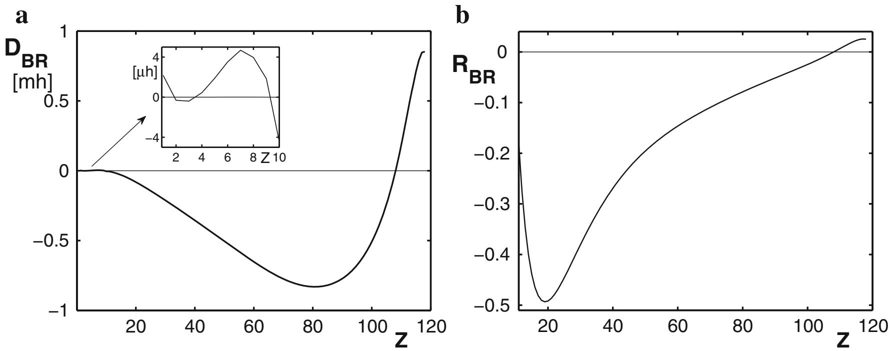

Fig. 8 *Left panel* The difference D_{BR} between the complex coordinate rotated and non-rotated energies in the 502-function Hy-CI basis. *Right panel* The ratio $R_{\mathrm{BR}} = D_{\mathrm{BR}}/\Delta E^0_{\mathrm{BR}}$

Table 3 The differences D between the energies obtained using the trial functions with the exact and the integer powers of r_{12} and the relative value of this difference

Z	D (μhartree)	$(D/E) \times 10^{10}$
10	0.02	1.9
20	0.05	1.4
30	0.08	0.9
40	0.09	0.6
50	0.18	0.7
60	0.19	0.5
70	0.66	1.2
80	2.10	3.0

In a larger Hy-CI basis this difference should be even smaller. Therefore this effect is negligible and using integer powers of r_{12} is justified.

5 Conclusions

The relativistic Hy-CI without PES projection may be applied to solving the DC equation and its accuracy may be controlled when using the CCR approach. Otherwise, the stability of the results strongly depends on the quality of the basis set (the degree to which the correct relations between the components of the trial function are fulfilled) and deteriorates when the basis set increases.

One of the artifacts of the DC model, which is removed by the PES projection but not by the CCR, is the appearance of the bound states as resonances. This disturbing effect is of the order $(Z\alpha)^3$ [7,8], thus it is smaller than the threshold of validity of the DC model.

Acknowledgments This paper was presented at the workshop 'Mathematical Methods for ab initio Quantum Chemistry', Nice, October 2007. JK and GP thank Patrick Cassam-Chennai for his hospitality. Illuminating discussions with Ingvar Lindgren and Hiroshi Tatewaki are gratefully acknowledged by JK.

References

1. E.A. Hylleraas, B. Undheim, Numerische Berechnung der 2S-Terme von Ortho- und Par-Helium. Z. Phys. A **65**, 759–772 (1930)
2. J.K.L. McDonald, Successive approximations by the Rayleigh–Ritz variation method. Phys. Rev. **43**, 830–833 (1933)
3. W. Pauli, V. Weisskopf, Über die Quantisierung der skalaren relativistischen Wellengleichung. Helv. Phys. Acta **7**, 709–731 (1934)
4. G.E. Brown, D.G. Ravenhall, On the interaction of two electrons. Proc. R. Soc. A **208**, 552–559 (1951)
5. M. Bylicki, G. Pestka, J. Karwowski, Relativistic Hylleraas configuration-interaction method projected into positive-energy space. Phys. Rev. A **77**, 044501-1–044501-4 (2008)
6. G. Pestka, M. Bylicki, J. Karwowski, Application of the complex coordinate rotation to the relativistic Hylleraas-CI method: a case study. J. Phys. B: At. Mol. Opt. Phys. **39**, 2979–2987 (2006)
7. G. Pestka, M. Bylicki, J. Karwowski, Complex coordinate rotation and relativistic Hylleraas-CI: helium isoelectronic series. J. Phys. B: At. Mol. Opt. Phys. **40**, 2249–2259 (2007)
8. G. Pestka, M. Bylicki, J. Karwowski, in *Frontiers in Quantum Systems in Chemistry and Physics*, ed. by S. Wilson, P.J. Grout, J. Maruani, G. Delgado-Barrio, P. Piecuch Dirac–Coulomb Equation: Playing with Artifacts (Springer, New York, 2008), pp. 215–238
9. Y. Watanabe, H. Nakano, H. Tatewaki, Effect of removing the no-virtual-pair approximation on the correlation energy of the He isoelectronic sequence. J. Chem. Phys. **126**, 174105-1–174105-8 (2007)
10. Y. Watanabe, H. Nakano, H. Tatewaki, Effect of removing the no-virtual-pair approximation on the correlation energy of the He isoelectronic sequence. II. Point nuclear charge model. J. Chem. Phys. **132**, 124105-1–124105-7 (2010)
11. A. Kolakowska, J.D. Talman, K. Aashamar, Minimax variational approach to the relativistic two-electron problem. Phys. Rev. A **53**, 168–177 (1996)
12. A. Kolakowska, Explicitly correlated trial functions in relativistic variational calculations. J. Phys. B: At. Mol. Opt. Phys. **30**, 2773–2779 (1997)
13. G. Pestka, J. Karwowski, in *Explicitly Correlated Wave Functions in Chemistry and Physics: Theory and Application*, ed. by J. Rychlewski Hylleraas-CI Approach to Dirac–Coulomb Equation (Kluwer, Dordrecht, 2003), pp. 331–346
14. G. Pestka, H. Tatewaki, J. Karwowski, Relativistic correlation energies of heliumlike atoms. Phys. Rev. A **70**, 024501-1–024501-3 (2004)
15. M. Nooijen, Explorations of many-body relativistic wave equations within a one-dimensional model. Can. J. Chem. **87**, 212546087 (2009)
16. J. Karwowski, G. Pestka, M. Stanke, in *Quantum Systems in Chemistry and Physics, Vol. 1: Basic Problems and Model Systems*, ed. by A. Hernandez Laguna, J. Maruani, R. McWeeny, S. Wilson Variational Principle in the Dirac Theory: Theorems, Examples and Counterexamples (Kluwer, London, 2000), pp. 177–193
17. M. Stanke, J. Karwowski, in *New Trends in Quantum Systems in Chemistry and Physics, Vol. 1*, ed. by J. Maruani, C. Minot, R. McWeeny, Y.G. Smeyers, S. Wilson Variational Principle in the Dirac Theory: Spurious Solutions, Unexpected Extrema and Other Traps (Kluwer, Lancaster, 2001), pp. 175–190
18. J. Dolbeault, M.J. Esteban, E. Séré, M. Vanbreugel, Minimization methods for the one-particle Dirac equation. Phys. Rev. Lett. **85**, 4020–4023 (2000)
19. G. Pestka, Upper bounds to the eigenvalues of the Dirac Hamiltonian. Phys. Scripta **69**, 203–207 (2004)
20. I.P. Grant, H.M. Quiney, Rayleigh-Ritz approximation of the Dirac operator in atomic and molecular physics. Phys. Rev. A **62**, 022508-1–022508-14 (2000)
21. F.A. Parpia, I.P. Grant, Accurate Dirac–Coulomb energies for the ground states of helium-like ions. J. Phys. B: At. Mol. Phys. **23**, 211–217 (1990)
22. J.D. Talman, Minimax principle for the Dirac equation. Phys. Rev. Lett. **57**, 1091–1094 (1986)
23. S.N. Datta, G. Deviah, The minimax technique in relativistic Hartree–Fock calculations. Pramana **30**, 387–405 (1988)
24. W. Kutzelnigg, Relativistic one-electron Hamiltonians 'for electrons only' and the variational treatment of the Dirac equation. Chem. Phys. **225**, 203–222 (1997)
25. I.P. Grant, *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation. Springer Series on Atomic, Optical, & Plasma Physics* (Springer, New York, 2007)
26. G. Pestka, J. Karwowski, Dirac–Coulomb Hamiltonian in N-electron model spaces. Collect. Czech. Chem. Commun. **68**, 275–294 (2003)

27. T. Kato, On the eigenfunctions of many-particle systems in quantum mechanics. Commun. Pure Appl. Math. **10**, 151–177 (1957)
28. W. Kutzelnigg, in *Explicitly Correlated Wave Functions in Chemistry and Physics: Theory and Application*, ed. by J. Rychlewski Theory of Electron Correlation (Kluwer, Dordrecht, 2003), pp. 3–90
29. W. Kutzelnigg, in *Aspects of Many Body Effects in Molecules and Extended Systems, Lecture Notes in Chemistry, Vol. 50*, ed. by D. Mukherjee, Generalization of Kato's Cusp Condition to the Relativistic Case (Springer, Berlin, 1989), p. 353
30. W. Kutzelnigg, J.D. Morgan, III., Rates of convergence of the partialwave expansions of atomic correlation energies. J. Chem. Phys. **96**, 4484–4508 (1992); Erratum **97**, 8821 (1992)
31. E.A. Hylleraas, Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium. Z. Phys. A **54**, 347–366 (1929)
32. P.-O. Löwdin, Correlation problem in many-electron quantum mechanics. Adv. Chem. Phys. **2**, 207 (1959)
33. J. Midtdal, K. Aashamar, Perturbation theory expansions through 20th order of mass polarization correction, relativistic effects and Lamb shift of the two-electron system $(1s)^2\ {}^1S$. Phys. Norv. **2**, 99–109 (1967)
34. K.G. Dyall, I.P. Grant, C.T. Johnson, F.A. Parpia, E.P. Plummer, GRASP: A general-purpose relativistic atomic structure program. Comput. Phys. Commun. **55**, 425–456 (1989)
35. J. Karwowski, J. Styszyński, Ground state energies of closed-shell atoms. Int. J. Quantum Chem. **28**, 27–37 (1985)
36. P. Indelicato, Projection operators in multiconfiguration Dirac–Fock calculations: application to the ground state of heliumlike ions. Phys. Rev. A **51**, 1132–1145 (1995)
37. G.E. Brown, The relativistic atomic many-body problem. Phys. Scripta **36**, 71–76 (1987)
38. G. Pestka, Variational solution of the Dirac–Coulomb equation using explicitly correlated wavefunctions. Matrix elements and radial integrals. J. Phys. A: Math. Gen. **31**, 6243–6252 (1998)
39. G. Pestka, J. Karwowski, in *Recent Advances in Computational Chemistry: Molecular Integrals Over Slater Orbitals*, ed. by T. Ozdogan, M.B. Ruiz Two-electron One-center Integrals in Relativistic Hy-CI Method (Transworld Research Network, Trivandrum, 2008), pp. 213–232
40. D.R. Plante, W.R. Johnson, J. Sapirstein, Relativistic all-order many-body calculations of the $n = 1$ and $n = 2$ states of heliumlike ions. Phys. Rev. A **49**, 3519–3530 (1994)
41. K.T. Cheng, M.H. Chen, W.R. Johnson, J. Sapirstein, Relativistic configuration-interaction calculations for the ground state and $n = 2$ singlet states of helium-like ions. Phys. Rev. A **50**, 247–255 (1994)
42. I.P. Grant, H.M. Quiney, Application of relativistic theories and quantum electrodynamics to chemical problems. Int. J. Quantum Chem. **80**, 283–297 (2000)
43. J. Aguilar, J.M. Combes, A class of analytic perturbations for one-body Schrödinger Hamiltonians. Commun. Math. Phys. **22**, 269–279 (1971)
44. W.P. Reinhardt, Complex coordinates in the theory of atomic and molecular structure and dynamics. Ann. Rev. Chem. **33**, 223–255 (1982)
45. R.A. Weder, Spectral Properties of the Dirac Hamiltonian. Ann. Soc. Sci. Bruxelles T **87**, 341–355 (1973)
46. P. Seba, The Complex Scaling method for Dirac resonances. Lett. Math. Phys. **16**, 51–59 (1988)
47. A.D. Alhaidari, Relativistic extension of complex scaling method. Phys. Rev. A **75**, 042707-1–042707-11 (2007)
48. J. Sucher, Foundations of the relativistic theory of many-electron bound states. Int. J. Quantum Chem. **25**, 3–21 (1984)
49. J. Sucher, Continuum dissolution and the relativistic many-body problem: a solvable model. Phys. Rev. Lett. **55**, 1033–1035 (1985)
50. S.A. Blundell, P.J. Mohr, W.R. Johnson, J. Sapirstein, Evaluation of two-photon exchange graphs for highly charged helium-like ions. Phys. Rev A **48**, 2615–2626 (1993)
51. I. Lindgren, H. Persson, S. Salomonson, L. Labzowsky, Full QED calculations of two-photon exchange for helium-like systems: analysis in the Coulomb and Feynman gauges. Phys. Rev. A **51**, 1167–1195 (1995)
52. K.T. Cheng, M.H. Chen, W.R. Johnson, J. Sapirstein, Relativistic configuration-interaction calculations for the ground state and $n = 2$ singlet states of helium-like ions. Phys. Rev. A **50**, 247–255 (1994)

53. D.R. Plante, W.R. Johnson, J. Sapirstein, Relativistic all-order many-body calculations of the $n = 1$ and $n = 2$ states of heliumlike ions. Phys. Rev. A **49**, 3519–3530 (1994)
54. W.R. Johnson, K.T. Cheng, M.H. Chen, in *Relativistic Electronic Structure Theory: Part 2. Applications; Theoretical and Computational Chemistry, Vol. 14, Chap. 3*, ed. by P. Schwerdtfeger Accurate Relativistic Calculations Including QED Contributions for Few-electron Systems (Elsevier, Amsterdam, 2004), pp. 120–187