Relativistic Hylleraas configuration-interaction method projected into positive-energy space

M. Bylicki,[*] G. Pestka,[†] and J. Karwowski[‡]

Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Grudziadzka 5, PL-87-100 Toruń, Poland

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A positive-energy-space-projected relativistic Hylleraas configuration-interaction method has been formulated. The projection procedure is based on the complex coordinate rotation method and may be applied independently of the specific form of the trial function.

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I. INTRODUCTION

Relativistic models of atoms are usually derived from the n-electron Dirac-Coulomb (DC) equation

$$\mathbf{H}_{DC}(1,2,\dots,n)\Psi(1,2,\dots,n) = E\Psi(1,2,\dots,n), \quad (1)$$

where

$$\mathbf{H}_{DC}(1,2,\dots,n) = \mathbf{H}_D^0(1,2,\dots,n) + \sum_{i<j}^{n} 1/r_{ij}, \quad (2)$$

$$\mathbf{H}_D^0(1,2,\dots,n) = \sum_{j=1}^{n} \mathbf{h}(j), \quad (3)$$

$\mathbf{h}(j)$, is the one-electron hydrogenic Dirac Hamiltonian and $\mathbf{H}_D^0(1,2,\dots,n)$ is referred to as the n-electron Dirac Hamiltonian. The space of eigenstates of $\mathbf{h}$ may be expressed as

$$\mathcal{H}_1 = \mathcal{Q}_1 \oplus \mathcal{P}_1, \quad (4)$$

where $\mathcal{Q}_1$ is the one-electron positive-energy space (PES) which comprises states of the positive continuum and of the discrete part of the spectrum, and its orthogonal complement, $\mathcal{P}_1 \equiv \mathcal{Q}_1^\perp$, contains states belonging to the negative continuum. The eigenvalue problems of $\mathbf{H}_D^0$ and $\mathbf{H}_{DC}$ are defined in

$$\mathcal{H}_n = \mathcal{H}_1^{\wedge n} = [\mathcal{Q}_1 \oplus \mathcal{P}_1]^{\wedge n}, \quad (5)$$

i.e., in the antisymmetric part of the direct product of the one-electron spaces. It may be split to the n-electron PES, $\mathcal{Q}_n$, and its orthogonal complement $\mathcal{P}_n$,

$$\mathcal{H}_n = \mathcal{Q}_n \oplus \mathcal{P}_n, \quad (6)$$

where $\mathcal{Q}_n = \mathcal{Q}_1^{\wedge n}$ and $\mathcal{P}_n = \mathcal{Q}_n^\perp$. In particular, in a two-electron case

$$\mathcal{P}_2 = \mathcal{Q}_1 \wedge \mathcal{P}_1 \oplus \mathcal{P}_1 \wedge \mathcal{P}_1. \quad (7)$$

The part of the continuum composed of $\mathcal{Q}_1$ and $\mathcal{P}_1$ (in the two electron case $\mathcal{Q}_1 \wedge \mathcal{P}_1$) we refer to as the Brown-Ravenhall (BR) continuum.

The spectrum of $\mathbf{H}_{DC}^0$ is a superposition of the one-electron Dirac spectra and is composed of multiple continua spreading from $-\infty$ to $+\infty$ and discrete energy levels. In particular, the discrete eigenstates may be expressed as the antisymmetrized products of the one-electron Dirac spinors and are orthogonal to the states describing continuum. The electron-electron interaction operator in $\mathbf{H}_{DC}$ couples the discrete and the continuum states. Then, as noticed by Brown and Ravenhall more than one-half of a century ago [1], the DC Hamiltonian does not have square-integrable eigenstates. More precisely, in the DC model the bound states of an n-electron system are represented by Feshbach-type resonances. In terms of the Feshbach theory [2,3] such resonances belong to the closed-channel space which is the same as $\mathcal{Q}_n$ whereas the states of the continuum, into which the resonances decay, belong to the open-channel space, $\mathcal{P}_n$. The appearance of the physically bound states as resonances is an artifact of the DC model. In order to distinguish these eigenstates from the ones describing the physical resonances, we refer to them as pseudoresonances.

There are several ways to deal with the artifacts of the DC equation. In the most common approach the effects of coupling between the discrete states and the BR continuum can be removed up to an adequate accuracy by imposing the relations between the components of the trial functions and the boundary conditions specific for the bound states [4–6]. However, this approach meets serious difficulties in methods which go beyond the one-electron model, in particular when the nuclear charge Z is large and the required accuracy is very high. In these cases the energies of the bound states, due to the interference of the BR continuum, are numerically unstable [7,8]. One of the ways to amend the model is to project the DC Hamiltonian onto the PES [9–11]. The projected Hamiltonian is called Brown-Ravenhall operator. Its spectrum is bounded from below and the discrete eigenvalues are not embedded in a continuum [12–14]. Consequently, all pseudoresonances of the nonprojected DC model become stationary. The resulting model is known as the no-pair approximation. The pseudoresonances may also be separated from the BR continuum using the complex coordinate rotation method (CCR) [15]. In this method the eigenvalue problem of the DC Hamiltonian is solved in the complete (nonprojected) space and the pseudoresonances are treated using techniques specific for autoinizing states. As expected [16], the resulting energies differ from the ones of the no-pair model by a correction to the Coulomb electron-electron interaction proportional to $(Z\alpha)^3$ and equal to the contribution from the virtual pairs [17].

The problems related to the presence of the unphysical BR continuum are particularly sharp when the trial function

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*mirekb@fizyka.umk.pl
†gp@fizyka.umk.pl
‡jka@fizyka.umk.pl

contains geminals. On the other hand, in order to correctly describe the electron correlation cusp, the wave function should explicitly depend on the interelectron distances [18–22]. The relativistic Hylleraas-configuration-interaction (R-Hy-CI) method derived from the minimax principle [23] by Kolakowska and Talman [21,22], gave very encouraging results. However, strong instabilities of the results related to the admixture of the BR continuum states were observed for large Z in the case of large model spaces [8]. The effects of the continuum may either be treated by CCR method or removed by a PES projection. A combination of R-Hy-CI and CCR resulting in the R-CCR-Hy-CI method [15] gave numerically stable and accurate results [17]. A PES-projected R-Hy-CI method is presented in this Brief Report.

The projection procedure is described in the next section. Then, the results obtained for the ground states of He isoelectronic series atoms are presented and compared with the ones in the literature. The final remarks conclude the paper. The Hartree atomic units are used. The fine structure constant has been taken as $\alpha = 1/137.035\ 9895$.

II. PROJECTION PROCEDURE

Usually the PES projection is achieved by a proper construction of the space of the trial functions [24–26]. In this construction, the n-electron basis of the variational model space is formed by antisymmetrized products of Dirac spinors corresponding to the positive-energy solutions of a Dirac equation. Then, the eigenvectors of $\mathbf{H}_D^0$ which belong to $\mathcal{Q}_n$ may be expressed in terms of the one-electron Dirac spinors belonging to $\mathcal{Q}_1$. Thus, in the one-electron model, the PES space of $\mathbf{H}_D^0$ may be constructed in a rather straightforward way. Otherwise, in particular, in R-Hy-CI, when each basis function may contain contributions from both $\mathcal{Q}_n$ and $\mathcal{P}_n$, the procedure described above cannot be applied.

Independently of the form of the trial function, a separation of the eigenvectors of $\mathbf{H}_D^0$ belonging to $\mathcal{Q}_n$ from the ones in $\mathcal{P}_n$ may be facilitated by the CCR method. The CCR eigenspectrum of $\mathbf{H}_D^0$ splits into the complex plane. The discrete eigenvalues do not change under the CCR whereas the eigenvalues associated with the states containing a continuum component, move to the complex plane and, most important, the energies associated with different kinds of continua move to the complex plane in different ways [15]. This behavior of the spectrum is shown in Fig. 1 where the CCR spectrum of a two-electron Dirac Hamiltonian, $\mathbf{H}_D^0$, with $Z = 90$ is displayed. The scattered circles and full points reflect the results of an actual, finite basis set, calculation. Three disjoint areas may be identified as sets of eigenvalues related to all-negative one-electron energies (the leftmost strip), negative+positive one-electron energies, i.e., the BR continuum (the central, diagonal, strip) and all-positive one-electron energies corresponding to the PES. The solid line separates the eigenvalues associated with the spaces $\mathcal{Q}_2$ and $\mathcal{P}_2$. In the limit of a complete basis set all eigenvalues with nonpositive imaginary parts and located to the right of this line correspond to the eigenstates which belong to $\mathcal{Q}_2$. The number of expected positive-energy solutions is determined by the dimension N_Q of $\mathcal{Q}_n$. Due to the incompleteness of the
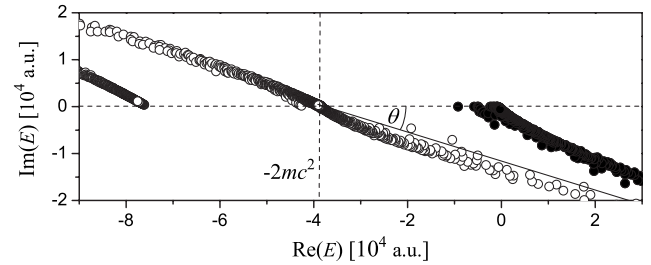

FIG. 1. The spectrum of complex-coordinate-rotated two-electron $\mathbf{H}_D^0$ with $Z = 90$ point nucleus, obtained in a space of 1826 Hylleraas-type functions with the rotation angle $\theta = 0.3$. The full points correspond to the energies of the states assigned to PES and the open circles correspond to the ones assigned to its orthogonal complement. The solid line marks the theoretical border between the PES eigenvalues and those related to the BR continuum.

model space the assignment of some of the eigenvectors to a specific space may be ambiguous. Therefore, in practical calculations we select $M \leq N_Q$ eigenvectors of $\mathbf{H}_D^0$, to represent the $\mathcal{Q}_n$ space. They form an $N \times M$ matrix $\mathbb{Q}$, where N is the dimension of the original model space.

Now we turn to the full DC Hamiltonian (2). First it must be complex-coordinate-rotated by the same rotation angle as $\mathbf{H}_D^0$ in the procedure of the construction of $\mathbb{Q}$. Then its matrix representation $\mathbb{H}_{DC}$ in the original variational basis is built. The matrix representation of the PES-projected DC Hamiltonian, i.e., its M-dimensional representation in $\mathcal{Q}_n$, is given by

$$\mathbb{H}^Q = \mathbb{Q}^T H_{DC} \mathbb{Q}. \tag{8}$$

The last step is the diagonalization of $\mathbb{H}^Q$. Its lowest eigenvalues correspond to the bound-state energies of our system.

III. RESULTS AND DISCUSSION

The ground-state DC energies of heliumlike atoms with infinite-mass point nuclei have been obtained using two different methods: The nonprojected R-CCR-Hy-CI, as described in Ref. [15], and the PES-projected R-Hy-CI, as described in the preceding section. The same basis sets as in Ref. [17], composed of $N = 502$ and $N = 1826$ explicitly correlated Hylleraas-type functions and referred to, respectively, as A and B, have been used. The dimensions of the PES corresponding to bases A and B and, thus, dimensions M of $\mathbb{H}^Q$ are equal to 120 and 422, respectively (in both cases $M = N_Q$). The resulting ground-state energies are collected in Table I.

The relativistic Coulomb correlation energies

$$E_{\text{corr}} = E_{DC} - E_{DF}, \tag{9}$$

where E_{DC} and E_{DF} are, respectively, Dirac-Coulomb and Dirac-Fock energies, are compared with the ones in the literature [24–26] in Fig. 2. If finite nuclei were used then the results have been recalibrated to the point nucleus model as described in Ref. [17]. Two sets of results of Watanabe *et al.* [24] were obtained using either positive-energy projected or nonprojected CI. Plante *et al.* [25] and Cheng *et al.* [26]

TABLE I. Eigenvalues of the DC Hamiltonian corresponding to the ground states of He-like atoms obtained using PES-projected R-Hy-CI in basis B (in 10^{-3} a.u.). The digits which differ from the ones in the eigenvalues of the nonprojected Hamiltonian [17] are boldface.

Z	E	Z	E	Z	E	Z	E	Z	E	Z	E	Z	E
1	−527.75676**66**	21	−430539.**049**	41	−1694049.**22**	61	−3885086.**86**	81	−7204453.**23**	101	−12091148.**1**
2	−2903.8568**7**	22	−473436.**350**	42	−1780445.**02**	62	−4021927.**62**	82	−7406202.**67**	102	−12391809.**9**
3	−7280.699**48**	23	−518411.**874**	43	−1869155.**99**	63	−4161580.**99**	83	−7611825.**53**	103	−12699148.**3**
4	−13658.258**7**	24	−565473.**234**	44	−1960199.**56**	64	−4304082.**60**	84	−7821402.**93**	104	−13013415.**2**
5	−22037.869**9**	25	−614628.**432**	45	−2053593.**73**	65	−4449469.**24**	85	−8035018.**94**	105	−13334881.**5**
6	−32421.01**81**	26	−665885.**871**	46	−2149357.**10**	66	−4597779.**20**	86	−8252762.**30**	106	−13663840.**2**
7	−44809.44**80**	27	−719254.**359**	47	−2247509.**00**	67	−4749052.**22**	87	−8474726.**04**	107	−14000606.**2**
8	−59205.2**017**	28	−774743.**118**	48	−2348069.**48**	68	−4903329.**60**	88	−8701007.**88**	108	−14345519.**4**
9	−75610.6**346**	29	−832361.**792**	49	−2451059.**30**	69	−5060654.**40**	89	−8931710.**52**	109	−14698951.**2**
10	−94028.4**241**	30	−892120.**458**	50	−2556499.**95**	70	−5221070.**83**	90	−9166942.**14**	110	−15061307.**3**
11	−114461.**572**	31	−954029.**632**	51	−2664413.**71**	71	−5384625.**65**	91	−9406817.**02**	111	−15433027.**7**
12	−136913.4**13**	32	−1018100.**28**	52	−2774823.**65**	72	−5551367.**04**	92	−9651454.**72**	112	−15814593.**9**
13	−161387.6**13**	33	−1084343.**83**	53	−2887753.**70**	73	−5721345.**24**	93	−9900982.**36**	113	−16206538.**1**
14	−187888.1**76**	34	−1152772.**18**	54	−3003228.**59**	74	−5894612.**27**	94	−10155533.**8**	114	−16609448.**8**
15	−216419.4**45**	35	−1223397.**72**	55	−3121273.**97**	75	−6071222.**71**	95	−10415251.**4**	115	−17023973.**6**
16	−246986.**108**	36	−1296233.**31**	56	−3241916.**47**	76	−6251233.**23**	96	−10680284.**9**	116	−17450833.**1**
17	−279593.**203**	37	−1371292.**36**	57	−3365183.**66**	77	−6434703.**25**	97	−10950794.**5**	117	−17890843.**0**
18	−314246.**117**	38	−1448588.**75**	58	−3491104.**13**	78	−6621694.**36**	98	−11226950.**2**	118	−18344906.**5**
19	−350950.**597**	39	−1528136.**93**	59	−3619707.**52**	79	−6812271.**16**	99	−11508930.**2**		
20	−389712.**752**	40	−1609951.**90**	60	−3751024.**49**	80	−7006500.**79**	100	−11796928.**3**		

performed their calculations using the no-pair DC Hamiltonian with many body perturbation theory (MBPT) and CI methods, respectively.

The results displayed in Fig. 2 are in agreement with the analyses by Sucher [16] and by Johnson *et al.* [11] as well as
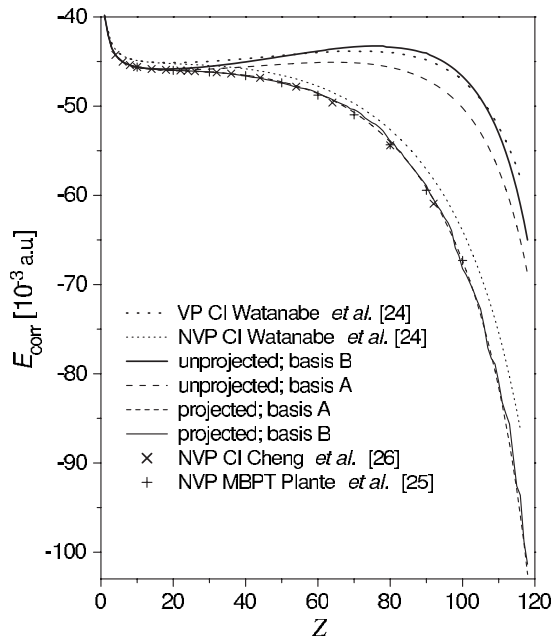
FIG. 2. Relativistic Coulomb correlation energy in the ground states of helium-like atoms.

with the results of our previous work [17] and of Watanabe *et al.* [24]: The energies derived from the methods using a PES-projected Hamiltonian and the energies corresponding to the nonprojected Hamiltonian converge to two different limits. As it was already noticed [17], the difference ΔE_{BR}, corresponding to the energy shift due to the coupling to the BR continuum, is very well approximated by the virtual pair contribution to the electron-electron Coulomb repulsion equal, in the lowest order of MBPT and for the hydrogenic functions, to $\Delta E_{\text{BR}}^0 = (Z\alpha)^3/6\pi$ [27,28]. The ratio
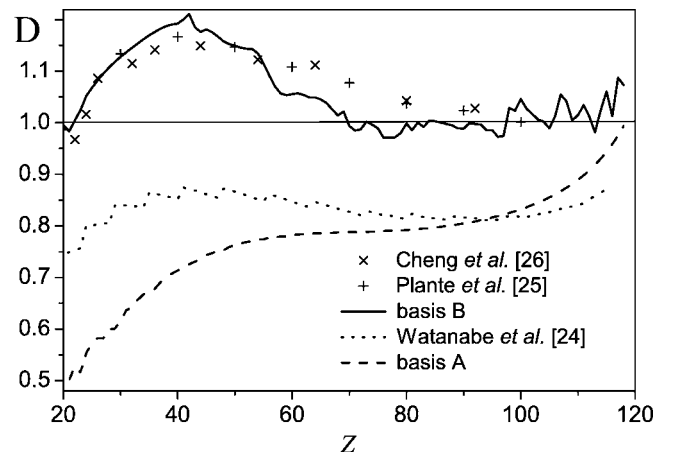
FIG. 3. The ratio D of the difference between nonprojected and PES projected ground-state energies to the hydrogenic MBPT value (10) versus Z.

$$D = \Delta E_{\mathrm{BR}}/\Delta E_{\mathrm{BR}}^0 \tag{10}$$

is shown in Fig. 3. As one can see, the relation $\Delta E_{\mathrm{BR}} \approx \Delta E_{\mathrm{BR}}^0$ has been confirmed by consistent calculations of the DC energies in both PES-projected R-Hy-CI and non-projected R-CCR-Hy-CI approaches. Consequently, being aware of this difference, one can apply either one approach or the other, and then, respectively, either include or not the appropriate contribution as one of the QED corrections.

IV. FINAL REMARKS

The no-pair approach has been implemented within a geminal-based formalism. The PES-projected model space has been constructed by an extraction of the appropriate sub-space from the space spanned by the eigenvectors of the complex-coordinate rotated n-electron Dirac Hamiltonian. The no-pair eigenvalues of the DC Hamiltonian have been approximated by the eigenvalues of its matrix representation in the PES-projected model space. The approach may be applied independently of both the structure of the n-electron basis functions and the form of the interaction operator. In particular, it is also applicable in the case of the Dirac-Coulomb-Breit Hamiltonian.

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