Pre–Born-Oppenheimer Dirac-Coulomb-Breit computations for two-body systems

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The 16-component, no-pair Dirac–Coulomb–Breit equation, derived from the Bethe–Salpeter equation, is solved in a variational procedure using Gaussian-type basis functions for the example of positronium, muonium, hydrogen atom, and muonic hydrogen. The α fine-structure-constant dependence of the variational energies, through fitting a function of α^n and $\alpha^n \ln \alpha$ terms, shows excellent agreement with the relevant energy expressions of the (perturbative) nonrelativistic QED framework and thereby establishes a solid reference for the development of a computational relativistic QED approach.

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I. INTRODUCTION

The positronium, $\mathrm{Ps} = \{e^-, e^+\}$, muonium, $\mathrm{Mu} = \{e^-, \mu^+\}$, hydrogen atom, $\mathrm{H} = \{e^-, \mathrm{p}^+\}$, and muonic-hydrogen, $\mu\mathrm{H} = \{\mu^-, \mathrm{p}^+\}$, are the simplest yet some of the most extensively studied bound-state systems. Their simplicity allows for the high-precision evaluation of energy corrections arising from special relativity and interactions from the matter and photon fields [1,2]. The high-precision spectroscopy experiments [3–10], together with the theoretical results (see Refs. [2,11] and references therein), provide a stringent test for the validity of quantum electrodynamics (QED) in the low-energy range and probe physics beyond the Standard Model [12–16]. Ps is a candidate for precision free-fall experiments to test QED and gravity [17], H and μH are the stars of the famous proton-size puzzle [18–20], while Mu has attracted interest in relation with the muon's anomalous magnetic moment [10,21].

For bound-state systems, it is relevant to have a wave equation that can be solved to obtain a good zeroth-order description. So far the nonrelativistic Schrödinger equation has been used as reference, which has an analytic solution for two-body systems. Then relativistic and QED corrections have been derived corresponding to increasing orders of the α fine-structure constant. We call these corrections, for short, nonrelativistic QED (nrQED) corrections. A recent review [11] provides an excellent overview of the extensive literature of higher-order nrQED corrections to positronium energies. Corrections up to α^6 order (in natural units, $\alpha^4 E_\mathrm{h}$ in hartree atomic units) are considered complete, and ongoing work is about α^7-order corrections. Some of the calculations have been carried out not only for equal but arbitrary spin-1/2 fermion masses.

In the present work we do not aim to reproduce the formally derived nrQED expressions but initiate an alternative approach to the two-particle relativistic QED problem based on a zeroth-order wave equation in which special relativity is already accounted for. The theoretical framework for this (computational) relativistic QED program is provided by the Bethe–Salpeter equation [22], derived from field theory [23], and its Salpeter–Sucher exact equal-time form [24,25], which provides us a no-pair, two-particle relativistic wave equation,

$$(H + H_\Delta)\Psi = E\Psi, \tag{1}$$

which has the form of a Schrödinger-like wave equation, for which high-precision numerical solution techniques can be adapted. The Ψ wave function in Eq. (1) depends only on the (spatial) Cartesian coordinates of the particles, H is the positive-energy projected two-electron Hamiltonian with instantaneous (Coulomb or Coulomb–Breit) interaction (I),

$$H = h_1 + h_2 + \Lambda_{++} I \Lambda_{++}, \tag{2}$$

$h_i = c\boldsymbol{\alpha}_i \boldsymbol{p}_i + \beta_i m_i c^2 + U 1^{[4]}$ $(i = 1, 2)$ is the one-particle Dirac Hamiltonian in which U can account for an external static Coulomb field (if there is any), and Λ_{++} projects to the positive-energy (electronic) subspace of the $h_1 + h_2$ noninteracting two-fermion problem. For short, we call H the no-pair Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) Hamiltonian.

Pair corrections, retardation, and radiative corrections are included in the H_Δ term, Eq. (1) [25–27]. Contribution of H_Δ to atomic and molecular energies (QED) can be expected to be small, and hence, it can be treated as perturbation to the no-pair Hamiltonian.

This framework offers a perturbative approach based on a *relativistic* reference, alternative to earlier work using a nonrelativistic reference state. Evaluation of the already-formulated perturbative correction with H_Δ is left for future developments, which appears to be possible along the lines reviewed in Ref. [28]. Although analytic evaluation of the energy and its corrections is not possible in this framework, the numerical results can be converged to high precision, which is demonstrated in the present work.

II. METHODOLOGICAL AND COMPUTATIONAL DETAILS

To compute no-pair, two-particle bound states, let us start with defining overall, center-of-mass, $R^\mu = (T, \boldsymbol{R})$, and

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relative, $r^\mu = (t, \boldsymbol{r})$, covariant space-time coordinates as

$$R^\mu = \frac{m_1}{m_1 + m_2} r_1^\mu + \frac{m_2}{m_1 + m_2} r_2^\mu \tag{3}$$

and

$$r^\mu = r_1^\mu - r_2^\mu. \tag{4}$$

Then, following Salpeter and Bethe [22], the wave function of an isolated system can be factorized as

$$\phi(r_1, r_2) = e^{-iP_\nu R^\nu} \Phi(r^\mu), \tag{5}$$

with the total four-momentum, $P^\nu = (E, \boldsymbol{P})$. By choosing the zero-total-momentum frame, $\boldsymbol{P} = \boldsymbol{0}$, we obtain

$$\phi(r_1, r_2) = e^{-iET} \Phi(r^\mu), \tag{6}$$

where E is the total energy of the system. It is important to note that $\Phi(r^\mu)$, which describes the internal motion, depends on $r^\mu = (t, \boldsymbol{r})$, *i.e.*, not only on the $\boldsymbol{r}$ relative coordinates, but also on the t relative time of the particles. Fourier transformation with respect to this relative time variable yields the relative-energy dependent wave function

$$\tilde{\Phi}(\varepsilon, \boldsymbol{r}) = \int_{-\infty}^{\infty} \frac{dt}{(2\pi)^{1/2}} e^{-i\varepsilon t} \Phi(t, \boldsymbol{r}). \tag{7}$$

In the exact equal-time formalism of Salpeter [24] and Sucher [25], the equal-time ($t = 0$) wave function appears, which depends only on the spatial coordinates,

$$\Psi(\boldsymbol{r}) = \int_{-\infty}^{\infty} d\varepsilon \, \tilde{\Phi}(\varepsilon, \boldsymbol{r}), \tag{8}$$

and the relative-energy dependence of the problem is accounted for in H_Δ in Eq. (1) [25].

To obtain the Hamiltonian for the relative motion, the chain rule for the coordinate transformation, Eqs. (3) and (4), is used, and it is also considered that contribution from terms containing $\boldsymbol{\nabla_R}$ vanishes due to the Eq. (5) choice of the ansatz for an isolated system and our choice of a $\boldsymbol{P} = \boldsymbol{0}$ zero-momentum-frame description, Eq. (6). Hence the spatial momentum operators in this framework can be replaced according to

$$\boldsymbol{p}_1 = -\mathrm{i}\boldsymbol{\nabla}_1 \to \boldsymbol{p} = -\mathrm{i}\boldsymbol{\nabla} \quad \text{and} \quad \boldsymbol{p}_2 = -\mathrm{i}\boldsymbol{\nabla}_2 \to -\boldsymbol{p} = \mathrm{i}\boldsymbol{\nabla}, \tag{9}$$

where $\boldsymbol{\nabla}(= \boldsymbol{\nabla}_r)$ collects the partial derivatives with respect to the $\boldsymbol{r}$ relative displacement vector components. This simple replacement "rule" can be used to construct expressions for the relative motion from the two-particle expressions [29–32]. As a result, the no-pair Dirac–Coulomb–Breit Hamiltonian for the relative motion is obtained as

$$H(1,2) = \Lambda_{++} \begin{pmatrix} V1^{[4]} & -c\boldsymbol{\sigma}_2^{[4]} \cdot \boldsymbol{p} & c\boldsymbol{\sigma}_1^{[4]} \cdot \boldsymbol{p} & B^{[4]} \\ -c\boldsymbol{\sigma}_2^{[4]} \cdot \boldsymbol{p} & V1^{[4]} - 2m_2c^2 1^{[4]} & B^{[4]} & c\boldsymbol{\sigma}_1^{[4]} \cdot \boldsymbol{p} \\ c\boldsymbol{\sigma}_1^{[4]} \cdot \boldsymbol{p} & B^{[4]} & V1^{[4]} - 2m_1c^2 1^{[4]} & -c\boldsymbol{\sigma}_2^{[4]} \cdot \boldsymbol{p} \\ B^{[4]} & c\boldsymbol{\sigma}_1^{[4]} \cdot \boldsymbol{p} & -c\boldsymbol{\sigma}_2^{[4]} \cdot \boldsymbol{p} & V1^{[4]} - 2m_{12}c^2 1^{[4]} \end{pmatrix} \Lambda_{++}, \tag{10}$$

with $m_{12} = m_1 + m_2$, $\boldsymbol{p} = -\mathrm{i}(\frac{\partial}{\partial r_x}, \frac{\partial}{\partial r_y}, \frac{\partial}{\partial r_z})$, $\boldsymbol{\sigma}_1^{[4]} = (\sigma_x \otimes 1^{[2]}, \sigma_y \otimes 1^{[2]}, \sigma_z \otimes 1^{[2]})$, and $\boldsymbol{\sigma}_2^{[4]} = (1^{[2]} \otimes \sigma_x, 1^{[2]} \otimes \sigma_y, 1^{[2]} \otimes \sigma_z)$, where σ_x, σ_y, and σ_z are the 2×2 Pauli matrices. We note that the operator in Eq. (10) contains a $-2m_ic^2$ shift ($i = 1, 2$) to match the nonrelativistic energy scale. Furthermore, the Coulomb interaction,

$$V = \frac{q_1 q_2}{r}, \tag{11}$$

is along the diagonal, whereas the Breit interaction,

$$B^{[4]} = -q_1 q_2 \left[\frac{1}{r} \boldsymbol{\sigma}_1^{[4]} \cdot \boldsymbol{\sigma}_2^{[4]} - \frac{1}{2} \left\{ \left(\boldsymbol{\sigma}_1^{[4]} \cdot \boldsymbol{\nabla} \right) \left(\boldsymbol{\sigma}_2^{[4]} \cdot \boldsymbol{\nabla} \right) r \right\} \right], \tag{12}$$

can be found on the antidiagonal of the Hamiltonian.

The Λ_{++} positive-energy projector in Eq. (10) corresponds to the positive-energy ("electronic") states of the "bare," noninteracting Hamiltonian, i.e., Eq. (10), without Λ_{++} and without the $V1^{[4]}$ and $B^{[4]}$ interaction blocks. Although the Λ_{++} free-particle projector in momentum space has an analytic form [33], we constructed it numerically in coordinate space by computing the eigenstates of the bare, noninteracting Hamiltonian over the space spanned by the basis functions used for the interacting computation. The positive-energy states were identified with the simple energy-cutting approach (which can be checked by the complex scaling procedure) [30].

The no-pair Dirac–Coulomb and Dirac–Coulomb–Breit Hamiltonians are bounded from below (the positive-energy block, which is considered in this work, is decoupled from the rest); hence the $H\Psi = E\Psi$ wave equation can be solved using the variational procedure.

For a single particle, the (four-component) wave function is conveniently partitioned to large (l, first two) and small (s, last two) components. A good basis representation must fulfill a simple symmetry relation, which is necessary to provide a correct matrix representation (Mx) for the $\mathrm{Mx}(p)\mathrm{Mx}(p) = \mathrm{Mx}(p^2)$ identity [34]. The simplest implementation of this relation is provided by the (restricted) kinetic balance (KB) condition [35,36],

$$\varphi^{\mathrm{s}} = \frac{\boldsymbol{\sigma}^{[2]} \cdot \boldsymbol{p}}{2mc} \varphi^{\mathrm{l}}, \tag{13}$$

for the basis function of the φ^{s} small and φ^{l} large components. Two(many)-particle relativistic quantities can be constructed with the block-wise (also called Tracy–Singh) direct product [29–32,37–40], which allows us to retain the large-small block structure, used already to write Eq. (10). The corresponding two-particle function, with highlighting the large (l) and small

TABLE I. Convergence of the no-pair Dirac–Coulomb(–Breit) energies, in E_h, computed in this work. The spatial basis, Eq. (27), used in the relativistic computation was parameterized by (numerical) minimization of the nonrelativistic energy, E_{nr}. The numerical value for the analytic (∞), nonrelativistic energy is shown for reference.

N_b	E_{nr}	E_{DC}	$E_{DC\langle B\rangle}$	$E_{DC\mathcal{B}_2}$	E_{DCB}
Ps ($m_2/m_1 = 1$):					
10	−0.249 999 665 988 4	−0.249 997 227 989	−0.250 016 969 603	−0.250 016 992 755	−0.250 016 992 809
20	−0.249 999 999 919 4	−0.249 997 552 650	−0.250 017 362 124	−0.250 017 403 806	−0.250 017 404 023
30	−0.249 999 999 996 8	−0.249 997 552 766	−0.250 017 362 426	−0.250 017 404 153	−0.250 017 404 371
40	−0.249 999 999 999 6	−0.249 997 552 778	−0.250 017 362 470	−0.250 017 404 205	−0.250 017 404 425
50	−0.249 999 999 999 9	−0.249 997 552 780	−0.250 017 362 477	−0.250 017 404 214	−0.250 017 404 433
∞	−0.250 000 000 000 0				
Mu ($m_2/m_1 = 206.7682830$):					
10	−0.497 592 269 419 4	−0.497 598 739 220	−0.497 599 489 904	−0.497 599 489 917	−0.497 599 489 918
20	−0.497 593 472 285 4	−0.497 600 024 240	−0.497 600 780 916	−0.497 600 780 959	−0.497 600 780 959
30	−0.497 593 472 874 8	−0.497 600 025 977	−0.497 600 782 839	−0.497 600 782 891	−0.497 600 782 891
40	−0.497 593 472 910 8	−0.497 600 026 241	−0.497 600 783 176	−0.497 600 783 235	−0.497 600 783 235
50	−0.497 593 472 915 7	−0.497 600 026 282	−0.497 600 783 233	−0.497 600 783 295	−0.497 600 783 295
∞	−0.497 593 472 917 1				
H ($m_2/m_1 = 1836.15267343$):					
10	−0.499 727 019 644 9	−0.499 733 723 658	−0.499 733 809 460	−0.499 733 809 460	−0.499 733 809 460
20	−0.499 727 839 067 5	−0.499 734 617 695	−0.499 734 704 007	−0.499 734 704 008	−0.499 734 704 008
30	−0.499 727 839 669 3	−0.499 734 619 508	−0.499 734 705 842	−0.499 734 705 843	−0.499 734 705 843
40	−0.499 727 839 706 0	−0.499 734 619 795	−0.499 734 706 138	−0.499 734 706 139	−0.499 734 706 140
50	−0.499 727 839 710 9	−0.499 734 619 840	−0.499 734 706 186	−0.499 734 706 187	−0.499 734 706 187
∞	−0.499 727 839 712 4				
μH ($m_2/m_1 = 8.88024337$):					
10	−92.920 263 579 73	−92.920 730 693 26	−92.923 396 814 39	−92.923 397 816 36	−92.923 397 817 07
20	−92.920 416 825 53	−92.920 890 799 40	−92.923 572 907 75	−92.923 575 558 50	−92.923 575 566 96
30	−92.920 417 297 88	−92.920 891 278 83	−92.923 573 403 13	−92.923 576 058 44	−92.923 576 066 97
40	−92.920 417 310 07	−92.920 891 312 69	−92.923 573 493 64	−92.923 576 164 19	−92.923 576 173 06
50	−92.920 417 311 03	−92.920 891 313 65	−92.923 573 494 58	−92.923 576 165 15	−92.923 576 174 01
∞	−92.920 417 311 31				

(s) component blocks, is

$$\boldsymbol{\varphi} = \begin{pmatrix} \varphi^{ll} \\ \varphi^{ls} \\ \varphi^{sl} \\ \varphi^{ss} \end{pmatrix}. \tag{14}$$

For a variational procedure, we used the simplest two-particle generalization of the one-particle kinetic balance, Eq. (13), and implemented it in the sense of a transformation or metric [29–32,35]:

$$H_{KB} = X^\dagger H X,$$
$$X = \mathrm{diag}\left(1^{[4]}, -\frac{(\boldsymbol{\sigma}_2^{[4]}\cdot\boldsymbol{p})}{2m_2c}, \frac{(\boldsymbol{\sigma}_1^{[4]}\cdot\boldsymbol{p})}{2m_1c}, -\frac{(\boldsymbol{\sigma}_1^{[4]}\cdot\boldsymbol{p})(\boldsymbol{\sigma}_2^{[4]}\cdot\boldsymbol{p})}{4m_1m_2c^2}\right). \tag{15}$$

We also note that the X balance matrix used in this work can be "obtained" from the balance used for the Born–Oppenheimer systems [29–32] through the $\boldsymbol{p}_1 \to \boldsymbol{p}$ and $\boldsymbol{p}_2 \to -\boldsymbol{p}$ replacement, Eq. (9). The fundamental "guiding principle" for our construction of the two-particle balance has been solely to have a correct matrix representation of the $\mathrm{Mx}(p)\mathrm{Mx}(p) = \mathrm{Mx}(p^2)$ identity, since the positive-energy projected Hamiltonian is bounded from below. The transformed DCB Hamiltonian is

$$H_{KB} = X^\dagger H(1,2) X = \begin{pmatrix} D_1^{[4]} & \frac{p^2}{2m_2}1^{[4]} & \frac{p^2}{2m_1}1^{[4]} & B_1^{[4]} \\ \frac{p^2}{2m_2}1^{[4]} & D_2^{[4]} & B_2^{[4]} & \frac{p^4}{8c^2m_1m_2^2}1^{[4]} \\ \frac{p^2}{2m_1}1^{[4]} & B_3^{[4]} & D_3^{[4]} & \frac{p^4}{8c^2m_1^2m_2}1^{[4]} \\ B_4^{[4]} & \frac{p^4}{8c^2m_1m_2^2}1^{[4]} & \frac{p^4}{8c^2m_1^2m_2}1^{[4]} & D_4^{[4]} \end{pmatrix}, \tag{16}$$

with the diagonal blocks

$$D_1^{[4]} = V 1^{[4]} \tag{17}$$

$$D_2^{[4]} = \frac{(\boldsymbol{\sigma}_2\cdot\boldsymbol{p})V1^{[4]}(\boldsymbol{\sigma}_2\cdot\boldsymbol{p})}{4m_2^2c^2} - \frac{\boldsymbol{p}^2}{2m_2}1^{[4]} \tag{18}$$

$$D_3^{[4]} = \frac{(\boldsymbol{\sigma}_1\cdot\boldsymbol{p})V1^{[4]}(\boldsymbol{\sigma}_1\cdot\boldsymbol{p})}{4m_1^2c^2} - \frac{\boldsymbol{p}^2}{2m_1}1^{[4]} \tag{19}$$

$$D_4^{[4]} = \frac{(\boldsymbol{\sigma}_1\cdot\boldsymbol{p})(\boldsymbol{\sigma}_2\cdot\boldsymbol{p})V1^{[4]}(\boldsymbol{\sigma}_1\cdot\boldsymbol{p})(\boldsymbol{\sigma}_2\cdot\boldsymbol{p})}{16m_1^2m_2^2c^4} - \frac{m_{12}\boldsymbol{p}^4}{8m_1^2m_2^2c^2}1^{[4]}, \tag{20}$$

TABLE II. Comparison of variational no-pair results and nrQED corrections. The $F(\alpha) = \varepsilon_0 + \alpha^2\varepsilon_2 + \alpha^3\varepsilon_3 + \alpha^4 \ln(\alpha)\varepsilon'_4 + \alpha^4\varepsilon_4$ function was fitted to the no-pair energies to obtain the coefficients (var-fit). All values correspond to Hartree atomic units. (All coefficients are listed in Table S6 [54].)

	DC			DC⟨B⟩		DCB	
	ε_2	ε_3	ε'_4	ε_2	ε_3	ε_2	ε_3
Ps $= \{e^-, e^+\}$:							
var-fit	0.046 875	−0.128 8	−0.063 4	−0.328 125	0.280 2	−0.328 125	0.189 9
nrQED [a]	0.046 875	−0.128 8	−0.062 5	−0.328 125	0.280 3	−0.328 125	
$\alpha^n(\delta\varepsilon_n)$ [b]	-4.5×10^{-12}	7.2×10^{-12}	2.6×10^{-12}	-2.3×10^{-11}	5.5×10^{-11}	2.3×10^{-11}	
Mu $= \{e^-, \mu^+\}$:							
var-fit	−0.120 227	−0.419 3	−0.967 2	−0.134 526	−0.407 1	−0.134 526	−0.407 2
nrQED [a]	−0.120 227	−0.419 3		−0.134 528		−0.134 528	
$\alpha^n(\delta\varepsilon_n)$ [b]	-4.7×10^{-11}	-1.2×10^{-11}		-1.0×10^{-10}		-1.1×10^{-10}	
H $= \{e^-, p^+\}$:							
var-fit	−0.124 455	−0.423 8	−0.983 7	−0.126 086	−0.422 4	−0.126 086	−0.422 4
nrQED [a]	−0.124 456	−0.423 8		−0.126 087		−0.126 087	
$\alpha^n(\delta\varepsilon_n)$ [b]	-6.1×10^{-11}	-1.0×10^{-11}		-6.8×10^{-11}		-6.8×10^{-11}	
μH $= \{\mu^-, p^+\}$:							
var-fit	−8.437 67	−67.886	−130.550 2	−59.154 212	−18.860 6	−59.154 120	−24.865 6
nrQED [a]	−8.437 70	−67.899		−59.154 516		−59.154 516	
$\alpha^n(\delta\varepsilon_n)$ [b]	-1.7×10^{-9}	-5.4×10^{-9}		-1.6×10^{-8}		-2.1×10^{-8}	

[a]The nrQED expressions and the corresponding literature references [25,27,41,55,58] are collected in the Supplemental Material [54].
[b]$\alpha^n(\delta\varepsilon_n)$, in E_h, with the $\delta\varepsilon_n = E^{(n)} - \varepsilon_n$ difference of the nrQED value and the fitted coefficient. For the ε'_4 term, the deviation corresponds $\alpha^4 \ln\alpha(\delta\varepsilon'_4)$.

and the antidiagonal blocks including the Breit interaction, Eq. (12),

$$B_1^{[4]} = -\frac{B^{[4]}(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p})(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p})}{4c^2 m_1 m_2} \tag{21}$$

$$B_2^{[4]} = -\frac{(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p}_2)B^{[4]}(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p})}{4c^2 m_1 m_2} \tag{22}$$

$$B_3^{[4]} = -\frac{(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p})B^{[4]}(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p})}{4c^2 m_1 m_2} \tag{23}$$

$$B_4^{[4]} = -\frac{(\boldsymbol{\sigma}_2 \cdot \boldsymbol{p})(\boldsymbol{\sigma}_1 \cdot \boldsymbol{p})B^{[4]}}{4c^2 m_1 m_2}. \tag{24}$$

The identity in the X-KB metric is

$$I_{\mathrm{KB}} = X^\dagger X = \mathrm{diag}\left(1^{[4]}, \frac{\boldsymbol{p}^2}{4c^2 m_2^2}1^{[4]}, \frac{\boldsymbol{p}^2}{4c^2 m_1^2}1^{[4]}, \frac{\boldsymbol{p}^4}{16c^4 m_1^2 m_2^2}1^{[4]}\right). \tag{25}$$

Then the 16-component wave function is written as a linear combination of spinor functions,

$$\Psi(\boldsymbol{r}) = \sum_{i=1}^{N_b}\sum_{\chi=1}^{16} c_{i\chi} f_i(\boldsymbol{r})\boldsymbol{d}_\chi, \tag{26}$$

where the $\boldsymbol{d}_\chi$ spinor basis vectors are 16-dimensional unit vectors, $(\boldsymbol{d}_\chi)_\rho = \delta_{\chi\rho}$ $(\chi, \rho = 1, \ldots, 16)$. For the f_i spatial functions, we use spherically symmetric Gaussian functions (S^e, $L = 0$ orbital angular momentum and $p = +1$ even (e) parity),

$$f_i(\boldsymbol{r}) = e^{-\zeta_i r^2}, \tag{27}$$

with $\zeta_i > 0$ (to ensure square integrability). We optimized the ζ_i Gaussian exponents ($i = 1, \ldots, N_b$) by minimization of the nonrelativistic $^1S^e$ ground-state energy to a pE_h($= 10^{-12}\ E_h$) precision range using quadruple precision arithmetic. Convergence of the nonrelativistic and relativistic energies with respect to the basis size is shown in Table I. For selected systems and basis sizes, we continued the optimization of the ζ_i parameters by minimization of the no-pair DC(B) energy, and the computation remained variationally stable, the energy "converged from above." (This variationally stable behavior was absent during minimization of the relevant energy level of the bare DC Hamiltonian.) We also note that there are no triplet contributions to the ground state ($1\ ^1S_0^e$) (p. 419 of Ref. [41]), since even-parity $^3P^e$ states do not exist for a pseudo-one-particle system (in contrast to heliumlike systems [42]).

In addition to variational no-pair DC and DCB computations, we computed the first-order perturbative Breit correction to the nth DC energy (with $n = 1$ in this work) by [31,32]

$$E_{\mathrm{DC}\langle\mathrm{B}\rangle,n} = E_{\mathrm{DC},n} + \langle\Psi_{\mathrm{DC},n}|X^\dagger B X \Psi_{\mathrm{DC},n}\rangle, \tag{28}$$

where B is a 16-dimensional matrix with the $B^{[4]}$ blocks on its antidiagonal. The second-order perturbative Breit correction is computed as

$$E_{\mathrm{DC}\mathcal{B}_2,n} = E_{\mathrm{DC}\langle\mathrm{B}\rangle,n} + \sum_{i\neq n}\frac{|\langle\Psi_{\mathrm{DC},i}|X^\dagger B X \Psi_{\mathrm{DC},n}\rangle|^2}{E_{\mathrm{DC},i} - E_{\mathrm{DC},n}}. \tag{29}$$

The outlined algorithm has been implemented in the QUANTEN computer program, which is used as a molecular physics "platform" for pre-Born–Oppenheimer, nonadiabatic, upper- and lower-bound, perturbative- and variational relativistic de-

TABLE III. Large mass, $m_2 \to \infty$, limit of the $\alpha^3 E_h$-order fitted coefficient of the no-pair DC energy, Eq. (30). ($m_1 = 1$ corresponds to the electron mass.)

	m_2	ε_3
Ps $= \{e^-, e^+\}$	1	−0.128 8
Mu $= \{e^-, \mu^+\}$	206.7682830	−0.419 3
H $= \{e^-, \mathrm{p}^+\}$	1836.15267343	−0.423 8
10H $= \{e^-, 10\mathrm{p}^+\}$	18361.5267343	−0.424 3
$-E^{(3)}_{C_1}(1, m_2)$ Eq. (31)	∞	−0.424 413...

velopments [29–32,42–52]. Throughout this work Hartree atomic units are used, and the speed of light is $c = \alpha^{-1} a_0 E_h/\hbar$ with $\alpha^{-1} = 137.035\,999\,084$ [53].

III. RESULTS AND DISCUSSION

All computed no-pair energies are listed in Table I; their change with the basis size can be used to assess their convergence. Further minimization tests for the no-pair DC(B) energy did not reveal major changes.

For direct comparison of the computed no-pair energies with the current state-of-the-art nrQED values, we have (numerically) determined the α dependence of the no-pair energies. For this reason we repeated the no-pair computations using the $\{\alpha^{-1} \in \alpha_0^{-1} \pm n \mid n \in \{-50, \ldots, 51\}\}$ series of the interaction constant, where α_0 labels the value taken from Ref. [53]. We then fitted the function

$$F(\alpha) = \varepsilon_0 + \alpha^2 \varepsilon_2 + \alpha^3 \varepsilon_3 + \alpha^4 \ln(\alpha) \varepsilon'_4 + \alpha^4 \varepsilon_4 \qquad (30)$$

to the series of the no-pair energies. Inclusion of higher-order, e.g., α^5 and $\alpha^5 \ln \alpha$, terms in Eq. (30) did not make any visible difference at the current numerical precision. A small fitting error was obtained, which had orders of magnitude smaller root-mean-squared deviation than the estimated energy convergence, Table I, and a smooth convergence of the fitted coefficients was observed with respect to the basis set size (see Supplemental Material [54], Tables S2–S5). To obtain consistent results, it was essential to include also the $\alpha^4 \ln \alpha$ term in Eq. (30); a simple α polynomial was insufficient to represent the high-precision no-pair energies (Table I). This feature reveals a nonregular α dependence of the no-pair energy [33], which is different from the known regular behavior of the unprojected DC(B) energy [55] (that is known to be inconsistent with Feynman's propagator [56,57]).

Table II shows the comparison of the α dependence of the no-pair energies (fitted coefficients) and the nrQED corrections that were readily available to us or we could obtain with short calculation (see Supplemental Material [54]). Excellent agreement is observed. The numerical deviation of the perturbative and fitted variational values is on the order of the convergence error of the no-pair energies (Table I). The list of all coefficients fitted according to Eq. (30) is provided in Table S6. Tables S2–S5 can be used to assess the convergence of these values with respect to the basis size (see Supplemental Material [54]).

Regarding the large mass, $m_2 \to \infty$, limit and comparison with the one-electron Dirac energy, it is necessary to consider that the (bare) one-electron Dirac equation is *with*-pair (and correct for one electron). At $\alpha^3 E_h$ order, the one-electron Dirac limit is recovered from our no-pair computations by appending the no-pair energy with the (one) pair correction. For $m_2 \to \infty$, the one-pair Coulomb correction, Eq. (3.9) of Ref. [55] is

$$E^{(3)}_{C_1}(m_1, \infty) = \lim_{m_2 \to \infty} E^{(3)}_{C_1}(m_1, m_2) = \lim_{m_2 \to \infty} \frac{2\mu^3}{3\pi} \left(\frac{2}{m_1^2} - \frac{1}{m_1 m_2} + \frac{2}{m_2^2} \right) = \frac{4 m_1}{3\pi}. \qquad (31)$$

In Table III we can (numerically) observe that the large m_2 limit of the ε_3 coefficient, obtained from fitting $F(\alpha)$ to the no-pair energies, converges to $-E^{(3)}_{C_1}(1, \infty)$ and hence cancels with the pair corrections (the two-pair contribution, Eq. (S12), vanishes) for $m_2 \to \infty$. Thereby, the one-particle Dirac limit is recovered at order $\alpha^3 E_h$. These properties emerge as simple consequence of using a two-particle relativistic wave equation obtained from the full relativistic QED theory. It is also worth noting that the Breit contribution vanishes as $m_2 \to \infty$ (Table S7).

IV. SUMMARY AND CONCLUSION

In this work a computational relativistic quantum electrodynamics approach was put forward based on the exact equal-time Bethe–Salpeter equation. It is demonstrated that a relativistic reference state can be converged to a sub-parts-per-billion relative precision by variational solution of the no-pair Dirac–Coulomb(–Breit) wave equation, including the dominant, instantaneous part of the electromagnetic interaction. The α fine-structure dependence of the computed energies are in excellent agreement with the formal nonrelativistic QED results corresponding to polynomial and logarithmic corrections in α, up to $\alpha^6 \ln \alpha$ order in natural units ($\alpha^4 \ln \alpha E_h$), and reveal a nonregular nature of the α expansion about the nonrelativistic reference. Perturbative retardation, radiative, and pair corrections to the no-pair relativistic states had been formulated long ago [25–27], and their evaluation with the high-precision relativistic reference states computed in this work will be carried out in the future.

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