Calculation of the relativistic Bethe logarithm in the two-center problem

Vladimir I. Korobov
Bogolyubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia

L. Hilico and J.-Ph. Karr
Laboratoire Kastler Brossel, UPMC-Paris 6, ENS, CNRS Case 74, 4 place Jussieu, 75005 Paris, France
(Received 16 April 2013; published 17 June 2013)

We present a variational approach to evaluate relativistic corrections of order α^2 to the Bethe logarithm for the ground electronic state of the Coulomb two-center problem. That allows us to estimate the radiative contribution at $m\alpha^7$ order in molecular-like three-body systems such as hydrogen molecular ions H_2^+ and HD^+ or antiprotonic helium atoms. While we get ten significant digits for the nonrelativistic Bethe logarithm, calculation of the relativistic corrections is much more involved, especially for small values of bond length R. We were able to achieve a level of three to four significant digits starting from $R = 0.2$ bohr, which will allow us to reach 10^{-10} relative uncertainty on transition frequencies.

DOI: 10.1103/PhysRevA.87.062506 PACS number(s): 31.15.A−, 31.30.jf, 31.15.xt

I. INTRODUCTION

Considerable effort is currently devoted to high-precision laser spectroscopy of three-body molecular (or molecule-like) systems such as HD^+ [1,2], H_2^+ [3], and antiprotonic helium [4]. These experiments aim at improving the present accuracy of the electron-to-proton and -antiproton mass ratios, for which the uncertainty of spectroscopic data, as well as of theoretical calculations of transition frequencies, should reach a level of about 0.1 ppb. Systematic evaluation of leading QED corrections up to the $m\alpha^6$ order has improved the theoretical precision in hydrogen molecular ions [5] and antiprotonic helium [6] to 0.3–0.4 and 1 ppb, respectively. The main source of theoretical uncertainty is the $m\alpha^7$-order one-loop self-energy correction [7], which so far has been evaluated only in hydrogenlike systems. Considering the aimed-for accuracy, it is enough to calculate the relativistic Bethe logarithm with three to four significant digits, and thus it may be obtained in the framework of the adiabatic approximation, i.e., for an electron in the field of two fixed nuclei.

For hydrogenlike ions, the one-loop self-energy contribution to the binding energy of an electron is traditionally expressed as follows [8]:

$$\Delta E_{1-\mathrm{loop}} = \frac{m_e\alpha}{\pi}\frac{(Z\alpha)^4}{n^3}\left(\{A_{41}(n)\ln[(Z\alpha)^{-2}] + A_{40}(n)\right\} + (Z\alpha)A_{50}(n) + (Z\alpha)^2\{A_{62}(n)\ln^2[(Z\alpha)^{-2}] + A_{61}(n)\ln[(Z\alpha)^{-2}] + A_{60}(n)\} + \cdots). \quad (1)$$

It is known that among $m\alpha^5$-order terms, the Bethe logarithm (which appears in the low-energy part of the nonlogarithmic contribution A_{40}) is the most difficult quantity for numerical evaluation. Similarly, at the $m\alpha^7$ order the low-energy part of A_{60} contains the relativistic Bethe logarithm [9–12], which gives rise to even more severe difficulties. In the present work, we describe a numerical method which allows us to obtain these quantities with very good accuracy for a two-center system.

This paper is organized as follows. In Sec. II, we briefly outline the origin of Bethe logarithm contributions in a nonrelativistic quantum electrodynamics (NRQED) approach [13,14] and give their precise definition. In Sec. III, the asymptotic behavior of the integrands is derived. In Sec. IV the numerical method is described in detail, and finally, the nonrelativistic and relativistic Bethe logarithms are calculated for the hydrogen atom, hydrogen molecular ions, and antiprotonic helium.

II. BETHE LOGARITHM: DEFINITIONS

In this section natural relativistic units ($\hbar = c = m = 1$) are used, while starting from Sec. III we switch over to the atomic units, which are more suitable for numerical calculations.

As a starting point, we take the nonrelativistic Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + V, \quad V = -\frac{Z_1\alpha}{r_1} - \frac{Z_2\alpha}{r_2}, \quad (2)$$

where r_1 and r_2 are the distances from the electron to nuclei 1 and 2, respectively. The case of $Z_1 = Z_2 = 1$ corresponds to the hydrogen molecular ions, and $Z_1 = 2$, $Z_2 = -1$ corresponds to the antiprotonic helium atom.

A. The NRQED one-loop self-energy at $m\alpha^5$ order (low photon energy)

The leading-order NRQED interaction with the magnetic field is determined by

$$H_I^{(0)} = -\frac{e}{m}\,\mathbf{p}\cdot\mathbf{A} - \frac{e}{2m}\,\boldsymbol{\sigma}\cdot\mathbf{B}.$$

The first term in this expression is the "dipole" interaction, while the second one is called Fermi's interaction.

It may be shown [15] that the NRQED diagram in Fig. 1 with the Fermi-type interactions on one or both sides of the transverse photon line gives vanishing contributions. Thus the low-energy contribution, which stems from the NRQED diagram in Fig. 1 with two dipole vertices, may be expressed as

$$E_{L-ret} = \frac{\alpha^3}{4\pi^2 m^2}\int_{|\mathbf{k}|<\Lambda}\frac{d^3k}{k}\left(\delta^{ij} - \frac{k^i k^j}{k^2}\right) \times\left\langle e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{p}\left(\frac{1}{E_0 - H - k}\right)\mathbf{p}e^{-i\mathbf{k}\cdot\mathbf{r}}\right\rangle - \delta m\langle\psi_0|\psi_0\rangle, \quad (3)$$

FIG. 1. The NRQED diagram for the leading-order one-loop self-energy contribution.

where δm is a "mass-renormalization" term. Here and throughout this paper it is assumed that in $\langle\cdots\rangle$ on the left- and right-hand sides of the brackets stands ψ_0, a stationary Schrödinger eigenstate of the Hamiltonian operator of Eq. (2), if not otherwise stated.

To get the leading $m\alpha^5$-order contribution, one neglects retardation, replacing the exponential factors in (3) by unity, which leads to the nonrelativistic dipole approximation

$$E_{L0} = \frac{2\alpha^3}{3\pi m^2}\int_0^\Lambda k\,dk\,\left\langle \mathbf{p}\left(\frac{1}{E_0-H-k}\right)\mathbf{p}\right\rangle - \delta m\,\langle\psi_0|\psi_0\rangle$$
$$= \frac{2\alpha^3}{3\pi m^2}\int_0^\Lambda k\,dk\;P_{nd}(k) - \delta m\,\langle\psi_0|\psi_0\rangle\,, \tag{4}$$

with

$$P_{nd}(k) = \langle \mathbf{p}\,(E_0-H-k)^{-1}\,\mathbf{p}\rangle. \tag{5}$$

The integral in (4) contains a linearly divergent term which corresponds to the electron's mass renormalization, as was shown by Bethe in 1947 [16]. It also contains a logarithmic term, where the dependence on the cutoff parameter Λ is canceled by the logarithmic contribution from the high-energy part [17]. After these two terms are dropped, the remaining nonlogarithmic contribution at order $m\alpha^5$ may be written ($E_h = m\alpha^2$ is the Hartree energy)

$$\mathcal{N}(n;R) = \int_0^{E_h} k\,dk\left\langle \mathbf{p}\left(\frac{1}{E_0-H-k}+\frac{1}{k}\right)\mathbf{p}\right\rangle$$
$$+\int_{E_h}^\infty \frac{dk}{k}\left\langle \mathbf{p}\frac{(E_0-H)^2}{E_0-H-k}\mathbf{p}\right\rangle, \tag{6}$$

and it determines the numerator of the Bethe logarithm, while the denominator is expressed by

$$\mathcal{D}(n;R) = \tfrac{1}{2}\langle(\nabla^2 V)\rangle, \tag{7}$$

where V is a two-center potential from Eq. (2). The Bethe logarithm itself is defined as the ratio

$$\beta_{nr}(n;R) = \frac{\mathcal{N}}{\mathcal{D}}\,. \tag{8}$$

Here n denotes a set of state quantum numbers.

B. One-loop self-energy contributions at $m\alpha^7$ order

Here, for convenience of reading, we keep the notation of [12] wherever possible. There are three types of relativistic corrections to the leading-order expression (4) which give a contribution at order $m\alpha^7$.

(1) Relativistic corrections due to the Breit-Pauli interaction (Fig. 2)

$$E_{L1} = \frac{2\alpha^3}{3\pi m^2}\int_0^\Lambda k\,dk\;\delta_{H_B}\left\langle \mathbf{p}\left(\frac{1}{E_0-H-k}\right)\mathbf{p}\right\rangle$$
$$= \frac{2\alpha^3}{3\pi m^2}\int_0^\Lambda k\,dk\;P^{(1)}_{rc}(k), \tag{9}$$

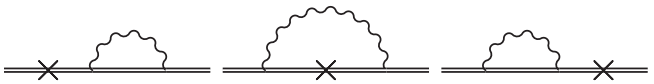

FIG. 2. NRQED diagrams for relativistic corrections to the electron line, which contribute to self-energy at order $m\alpha^7$.

where

$$P^{(1)}_{rc}(k) = \delta_{H_B}\left\langle \mathbf{p}\left(\frac{1}{E_0-H-k}\right)\mathbf{p}\right\rangle$$
$$\equiv 2\langle H_B Q(E_0-H)^{-1}Q\mathbf{p}(E_0-H-k)^{-1}\mathbf{p}\rangle$$
$$+\langle \mathbf{p}(E_0-H-k)^{-1}(H_B-\langle H_B\rangle)$$
$$\times(E_0-H-k)^{-1}\mathbf{p}\rangle. \tag{10}$$

Here Q is a projection operator: $Q = I - |\psi_0\rangle\langle\psi_0|$. Equation (10) represents the third-order term in the Rayleigh-Schrödinger perturbation theory. The relativistic Breit-Pauli Hamiltonian for the two-center problem is expressed

$$H_B = -\frac{\mathbf{p}^4}{8m^3} + \frac{1}{8m^2}\left[4\pi(Z_1\alpha)\delta(\mathbf{r}_1) + 4\pi(Z_2\alpha)\delta(\mathbf{r}_2)\right],$$

where the spin interaction is neglected.

For reasons which will be discussed later, it is convenient to split $P^{(1)}_{rc}$ into two parts:

$$P^{(1a)}_{rc}(k) = \langle \mathbf{p}(E_0-H-k)^{-1}(H_B-\langle H_B\rangle)(E_0-H-k)^{-1}\mathbf{p}\rangle, \tag{11a}$$

$$P^{(1b)}_{rc}(k) = 2\langle H_B Q(E_0-H)^{-1}Q\mathbf{p}(E_0-H-k)^{-1}\mathbf{p}\rangle. \tag{11b}$$

(2) The second type is modification of vertex interactions in the self-energy diagram.

The next-order NRQED interactions ($\sim\alpha^2 H_I^{(0)}$) with a magnetic field are determined by [14,18]

$$H_I^{(2)} = \frac{e}{2m^3}\,p^2\,\mathbf{p}\cdot\mathbf{A} + \frac{e^2}{4m^2}\,\sigma^{ij}(\nabla^j V)A^i,$$

thus modifying vertex functions as shown in the diagrams in Fig. 3; one gets

$$E_{L3} = \frac{4\alpha^3}{3\pi m^2}\int_0^\Lambda k\,dk\left\langle \delta\mathbf{J}\left(\frac{1}{E_0-H-k}\right)\mathbf{p}\right\rangle$$
$$= \frac{4\alpha^3}{3\pi m^2}\int_0^\Lambda k\,dk\;P^{(2)}_{rc}(k), \tag{12}$$

where $\delta J^i = -p^2 p^i - \frac{1}{2}\sigma^{ij}\nabla^j V$, and

$$P^{(2)}_{rc}(k) = \left\langle\left(-p^2p^i - \tfrac{1}{2}\sigma^{ij}\nabla^j V\right)(E_0-H-k)^{-1}p^i\right\rangle. \tag{13}$$

(3) It remains to consider the effect of retardation [see Eq. (3)]. We obtain the nonrelativistic quadrupole contribution, which results from the Taylor series expansion of

FIG. 3. The NRQED diagrams for the self-energy with modified vertex interactions at order $m\alpha^7$.

$$e^{i(\mathbf{k}\cdot\mathbf{r})} = 1 + i(\mathbf{k}\cdot\mathbf{r}) - (\mathbf{k}\cdot\mathbf{r})^2/2 + \cdots,$$

$$E_{L2} = \frac{2\alpha^3}{3\pi m^2}\int_0^\Lambda k\,dk\; P_{nq}(k), \tag{14}$$

$$\begin{aligned} P_{nq}(k) = {} & \frac{3k^2}{8\pi}\int_S d\Omega_{\mathbf{n}}(\delta^{ij} - n^i n^j) \\ & \times \{\langle p^i(\mathbf{n}\cdot\mathbf{r})(E_0 - H - k)^{-1}(\mathbf{n}\cdot\mathbf{r})p^i\rangle \\ & - \langle p^i(\mathbf{n}\cdot\mathbf{r})^2(E_0 - H - k)^{-1}p^i\rangle\}, \end{aligned} \tag{15}$$

where $\mathbf{k} = k\mathbf{n}$.

Similar to the nonrelativistic Bethe logarithm considered above, the relativistic Bethe logarithm corresponds to the finite part of integrals (9), (12), and (14); i.e., divergent terms in Λ must be subtracted [12]. It is thus essential to study the asymptotic behavior of the integrands in the $k \to \infty$ limit.

III. ASYMPTOTIC BEHAVIOR OF THE INTEGRANDS AT $k \to \infty$

Our approach to obtain asymptotic expansions stems from ideas first formulated by Schwartz [19]. The first step is to note that in expression (4) the integrand's form is that of a second-order perturbation correction. It may be calculated via the first-order perturbation wave function ψ_1, which can be obtained by solving the differential equation

$$(E_0 - H - k)\psi_1 = \nabla\psi_0, \tag{16}$$

and then one calculates the integrand by evaluating

$$P_{nd}(k) = \langle\psi_0|\nabla|\psi_1\rangle\ . \tag{17}$$

A. Nonrelativistic Bethe logarithm

The first-order nonrelativistic perturbation wave function for $k \to \infty$ to a good extent may be approximated (see [19,20]) by

$$\begin{aligned} \psi_1(\mathbf{r}) \approx {} & \frac{1}{k}\left[\frac{Z_1\mathbf{r}_1}{r_1} + \frac{Z_2\mathbf{r}_2}{r_2}\right]\psi_0(r) \\ & - \frac{1}{k^2}\left\{\frac{Z_1\mathbf{r}_1}{r_1^3}[1 - e^{-\mu r_1}(1+\mu r_1)]\right. \\ & \left. + \frac{Z_2\mathbf{r}_2}{r_2^3}[1 - e^{-\mu r_2}(1+\mu r_2)]\right\}\psi_0(r), \end{aligned} \tag{18}$$

where $\mu = \sqrt{2k}$. This function has a proper smooth behavior at the Coulomb centers and tends to zero when $r_1 \to 0$ (or $r_2 \to 0$).

By substituting (18) into the expression $\frac{1}{k}\langle\nabla^2\rangle - \frac{1}{k}\langle\psi_0|[H,\nabla]|\psi_1\rangle$ (see, for details, [19,20]) one gets for the nonrelativistic dipole term

$$\begin{aligned} P_{nd}(k) = {} & \frac{1}{k}\langle\nabla^2\rangle + \frac{1}{2k^2}\left\langle(\nabla^2 V)\right\rangle \\ & - \frac{1}{k^3}\left\{\left[Z_1^2\sqrt{2k} - Z_1^3\ln k\right]4\pi\langle\delta(\mathbf{r}_1)\rangle\right. \\ & \left. + \left[Z_2^2\sqrt{2k} - Z_2^3\ln k\right]4\pi\langle\delta(\mathbf{r}_2)\rangle\right\} + \cdots, \end{aligned} \tag{19}$$

in which all terms (including the last one in $\ln k/k^3$) provide correct analytical expressions for the expansion coefficients. For higher-order terms in $1/k$ we use the same expansion with unknown coefficients Q_{1n}^{nd}, Q_{2n}^{nd}, and Q_{3n}^{nd} taken in the same form as for the hydrogen atom

$$\sum_{m=1}^{M}\frac{Q_{1m}^{nd}\sqrt{k} + Q_{2m}^{nd}\ln k + Q_{3m}^{nd}}{k^{m+3}}, \tag{20}$$

which is in the latter case known analytically [21] (see also [9]). These coefficients will be obtained by fitting a numerically calculated $P_{nd}(k)$ by expression (20) at some interval of $k \approx [20, 10^4]$.

B. Relativistic Bethe logarithm

Substituting again the wave function ψ_1 from (18) into the matrix elements which appear in the integrands $P_i(k)$ in Eqs. (15), (11a), (11b), and (13), one gets

$$\begin{aligned} P_{nq}(k) = {} & -\frac{1}{2}\langle\nabla^2\rangle - \frac{1}{k}\left\{\frac{\langle\nabla^4\rangle}{5} + 2\pi[Z_1\langle\delta(\mathbf{r}_1)\rangle + Z_2\langle\delta(\mathbf{r}_2)\rangle]\right\} \\ & + \frac{2Z_1^2(\sqrt{2k} - Z_1\ln k)}{k^2}4\pi\langle\delta(\mathbf{r}_1)\rangle \\ & + \frac{2Z_2^2(\sqrt{2k} - Z_2\ln k)}{k^2}4\pi\langle\delta(\mathbf{r}_2)\rangle + \cdots \\ = {} & F_{nq} + \frac{A_{nq}}{k} + \frac{B_{nq}}{k^{3/2}} + \frac{C_{nq}\ln k}{k^2} + \frac{D_{nq}}{k^2} + \cdots, \end{aligned} \tag{21a}$$

$$\begin{aligned} P_{rc}^{(1a)}(k) = {} & -\frac{Z_1^2\sqrt{2k}}{4k^2}4\pi\langle\delta(\mathbf{r}_1)\rangle - \frac{Z_2^2\sqrt{2k}}{4k^2}4\pi\langle\delta(\mathbf{r}_2)\rangle + \cdots \\ = {} & \frac{B_{rc}^{(1a)}}{k^{3/2}} + \frac{D_{rc}^{(1a)}}{k^2} + \cdots, \end{aligned} \tag{21b}$$

$$\begin{aligned} P_{rc}^{(1b)}(k) = {} & \frac{2}{k}\langle(H_B - \langle H_B\rangle)(E_0 - H)^{-1}\nabla^2\rangle \\ & + \frac{Z_1^2(2\sqrt{2k} + Z_1\ln k)}{4k^2}4\pi\langle\delta(\mathbf{r}_1)\rangle \\ & + \frac{Z_2^2(2\sqrt{2k} + Z_2\ln k)}{4k^2}4\pi\langle\delta(\mathbf{r}_2)\rangle + \cdots \\ = {} & \frac{A_{rc}^{(1b)}}{k} + \frac{B_{rc}^{(1b)}}{k^{3/2}} + \frac{C_{rc}^{(1b)}\ln k}{k^2} + \frac{D_{rc}^{(1b)}}{k^2} + \cdots, \end{aligned} \tag{21c}$$

$$\begin{aligned} P_{rc}^{(2)}(k) = {} & \frac{\langle p^4\rangle}{k} + \frac{Z_1^2(-\sqrt{8k} + Z_1\ln k)}{k^2}4\pi\langle\delta(\mathbf{r}_1)\rangle \\ & + \frac{Z_2^2(-\sqrt{8k} + Z_2\ln k)}{k^2}4\pi\ \langle\delta(\mathbf{r}_2)\rangle + \cdots \\ = {} & \frac{A_{rc}^{(2)}}{k} + \frac{B_{rc}^{(2)}}{k^{3/2}} + \frac{C_{rc}^{(2)}\ln k}{k^2} + \frac{D_{rc}^{(2)}}{k^2} + \cdots. \end{aligned} \tag{21d}$$

For higher-order terms, in the case of P_{nq}, $P_{rc}^{(1a)}$, and $P_{rc}^{(2)}$ the form of the asymptotic expansion is found to be similar to the nonrelativistic Bethe logarithm [Eq. (20)], for example,

$$\begin{aligned} & P_{rc}^{(1a)}(k) - \frac{B_{rc}^{(1a)}}{k^{3/2}} - \frac{D_{rc}^{(1a)}}{k^2} \\ & = \sum_{m=1}^{M}\frac{Q_{1m}^{(1a)}\sqrt{k} + Q_{2m}^{(1a)}\ln k + Q_{3m}^{(1a)}}{k^{m+2}}, \end{aligned} \tag{22}$$

with equivalent expressions for $P_{nq}(k)$ and $P^{(2)}_{rc}(k)$. The $P^{(1b)}_{rc}$ term has an essentially different asymptotic behavior:

$$P^{(1b)}_{rc}(k) - \frac{A^{(1b)}_{rc}}{k} - \frac{B^{(1b)}_{rc}}{k^{3/2}} - \frac{C^{(1b)}_{rc}\ln k}{k^2} - \frac{D^{(1b)}_{rc}}{k^2} = \frac{1}{k^2}\sum_{m=1}^{M}\sum_{n=0}^{m}\frac{S^{(1b)}_{mn}\ln^n k}{k^{m/2}}. \tag{23}$$

This is one of the reasons why the $P^{(1)}_{rc}$ term has been separated into two contributions.

In actual calculations coefficients of the asymptotic expansion A, B, C, and F are calculated from expectation values of the operators appearing in the Eqs. (21a)–(21d), while the unknown coefficients D, Q, and S are obtained by fitting of the numerically evaluated integrand using Eqs. (22) and (23).

C. Final expression of the relativistic Bethe logarithm

In view of the asymptotic expansion obtained in the previous paragraph, the relativistic Bethe logarithm, which is given by the finite part of integrals (9)–(14), can be written as follows:

$$\mathcal{L} = \beta^{(a)}_1 + \beta^{(b)}_1 + \beta_2 + \beta_3\,, \tag{24a}$$

$$\beta^{(a)}_1 = \frac{2}{3}\int_0^{E_h} k\,dk\left[P^{(1a)}_{rc}(k) - \frac{B^{(1a)}_{rc}}{k^{3/2}}\right] + \frac{2}{3}\int_{E_h}^{\infty} k\,dk\left[P^{(1a)}_{rc}(k) - \frac{B^{(1a)}_{rc}}{k^{3/2}} - \frac{D^{(1a)}_{rc}}{k^2}\right], \tag{24b}$$

$$\beta^{(b)}_1 = \frac{2}{3}\int_0^{E_h} k\,dk\left[P^{(1b)}_{rc}(k) - \frac{A^{(1b)}_{rc}}{k} - \frac{B^{(1b)}_{rc}}{k^{3/2}}\right] + \frac{2}{3}\int_{E_h}^{\infty} k\,dk\left[P^{(1b)}_{rc}(k) - \frac{A^{(1b)}_{rc}}{k} - \frac{B^{(1b)}_{rc}}{k^{3/2}} - \frac{C^{(1b)}_{rc}\ln k}{k^2} - \frac{D^{(1b)}_{rc}}{k^2}\right], \tag{24c}$$

$$\beta_2 = \frac{4}{3}\int_0^{E_h} k\,dk\left[P_{nq}(k) - F_{nq} - \frac{A_{nq}}{k} - \frac{B_{nq}}{k^{3/2}}\right] + \frac{4}{3}\int_{E_h}^{\infty} k\,dk\left[P_{nq}(k) - F_{nq} - \frac{A_{nq}}{k} - \frac{B_{nq}}{k^{3/2}} - \frac{C_{nq}\ln k}{k^2} - \frac{D_{nq}}{k^2}\right], \tag{24d}$$

$$\beta_3 = \frac{2}{3}\int_0^{E_h} k\,dk\left[P^{(2)}_{rc}(k) - \frac{A^{(2)}_{rc}}{k} - \frac{B^{(2)}_{rc}}{k^{3/2}}\right] + \frac{2}{3}\int_{E_h}^{\infty} k\,dk\left[P^{(2)}_{rc}(k) - \frac{A^{(2)}_{rc}}{k} - \frac{B^{(2)}_{rc}}{k^{3/2}} - \frac{C^{(2)}_{rc}\ln k}{k^2} - \frac{D^{(2)}_{rc}}{k^2}\right]. \tag{24e}$$

Here the terms which are subtracted from the first line of each equation appear in the expansions due to a formal Taylor series expansion in powers of $(Z\alpha)^2$ of the QED one-loop self-energy correction, which is expressed as [8]

$$\Delta E = -i\frac{e^2}{(2\pi)^4}\int\frac{d^4k}{k^2+i\epsilon}\langle\overline{\psi}^D_0(\mathbf{r})|e^{i\mathbf{kr}}\gamma_\mu S_F(\mathbf{r},\mathbf{r}',E_0-k^0) \times\gamma^\mu e^{-i\mathbf{kr}'}|\psi^D_0(\mathbf{r}')\rangle - \delta m\langle\overline{\psi}^D_0|\psi^D_0\rangle, \tag{25}$$

where $S_F(\mathbf{r},\mathbf{r}',E)$ is the Dirac-Coulomb propagator and ψ^D_0 is the Dirac wave function. These extra terms do not appear in asymptotic expansion of the integrand in Eq. 25 and should be withdrawn.

Thus our definition coincides with that of [12] (see prescriptions after Eq. (3.16) in that reference).

IV. NUMERICAL SCHEME

Here we present a numerical scheme to evaluate the Bethe logarithm (8) and its relativistic corrections (24) for the two-center Coulomb problem.

A. Variational expansion

A variational expansion for the electronic wave function is taken in the form ($Z_1 \neq Z_2$) [22]

$$\Psi_m(\mathbf{r}) = e^{im\varphi}r^{|m|}\sum_{i=1}^{\infty}C_i e^{-\alpha_i r_1-\beta_i r_2}, \tag{26}$$

where r is a distance from the electron to the z axis and

$$r = \frac{1}{2R}\sqrt{2r_1^2r_2^2+2r_1^2R^2+2r_2^2R^2-r_1^4-r_2^4-R^4}.$$

For $Z_1 = Z_2$ the variational wave function should be symmetrized

$$\Psi(\mathbf{r_1},\mathbf{r_2}) = e^{im\varphi}r^{|m|}\sum_{i=1}^{\infty}C_i(e^{-\alpha_i r_1-\beta_i r_2} \pm e^{-\beta_i r_1-\alpha_i r_2}), \tag{27}$$

where a plus is used to get a *gerade* electronic state and a minus is for an *ungerade* state. Parameters α_i and β_i are generated in a quasirandom manner [23],

$$\alpha_i = \left\lfloor\tfrac{1}{2}i(i+1)\sqrt{p_\alpha}\right\rfloor(A_2-A_1)+A_1. \tag{28}$$

Here $\lfloor x\rfloor$ designates the fractional part of x, p_α is a prime number, and $[A_1,A_2]$ is a real variational interval, which has to be optimized. Parameters β_i are obtained in a similar way. Details may be found elsewhere [22,24].

All the integrands in Eqs. (5), (15), (11a), (11b), and (13) have the form of a second-order perturbation expression; i.e., they involve an operator $(E_0-H-k)^{-1}$. We thus diagonalize the matrix of the Hamiltonian for intermediate states to get a set of (pseudo)state wave functions ψ_m and energies E_m. A similar approach was used to compute the nonrelativistic Bethe logarithm for the three-body Coulomb problem in [20].

The basis for intermediate states is constructed as follows.

(1) We use a regular basis set (with regular values of the exponents α,β), similar to that used for the initial state.

(2) We build a special basis set with exponentially growing parameters for r_1:

$$A^{(0)}_1 = A_1,\quad A^{(0)}_2 = A_2,\qquad A^{(n)}_1 = \tau^n A_1,\quad A^{(n)}_2 = \tau^n A_2, \tag{29}$$

where $\tau = A_2/A_1$. Typically, $[A_1,A_2] = [2.5,4.5]$, and $n_{max} = 5-7$, which corresponds to the photon energy interval $k\in[0,10^4]$.

(3) We add a similar basis set for r_2. Note that this last step may be omitted in the case $Z_1 = Z_2$, where the basis is symmetrized.

B. Nonrelativistic Bethe logarithm

After expansion on the basis for the intermediate state, the expression of the integrand becomes

$$P_{nd}(k) = \sum_m \frac{\langle\psi_0|\nabla|\psi_m\rangle^2}{E_0 - E_m - k}, \tag{30}$$

so the integral appearing in the low-energy part of the numerator is

$$\int_0^\Lambda k dk P_{nd}(k) = \sum_m \langle\psi_0|\nabla|\psi_m\rangle^2 \times \left[\Lambda - (E_0 - E_m)\ln\left|\frac{E_0 - E_m}{E_0 - E_m - \Lambda}\right|\right]. \tag{31}$$

It remains to calculate the matrix elements of the impulse operator. Its standard components are

$$\nabla_0^{(1)} = \nabla_z, \quad \nabla_{\pm1}^{(1)} = \mp\frac{1}{\sqrt{2}}(\nabla_x \pm i\nabla_y). \tag{32}$$

Assuming, from now on, that ψ_0 is a σ state, action on ψ_0 of the impulse operator may be expressed as follows:

$$\begin{aligned}\nabla_0^{(1)}\psi_0 &= \left[\left(z + \frac{R}{2}\right)\frac{1}{r_1}\partial_{r_1} + \left(z - \frac{R}{2}\right)\frac{1}{r_2}\partial_{r_2}\right]\psi_0,\\ \nabla_{\pm1}^{(1)}\psi_0 &= re^{\pm i\varphi}\left(\frac{1}{r_1}\partial_{r_1} + \frac{1}{r_2}\partial_{r_2}\right)\psi_0.\end{aligned} \tag{33}$$

Here $z = (r_1^2 - r_2^2)/(2R)$. Using these relations, the calculation of the matrix elements is straightforward [22,24].

C. Relativistic corrections to the Bethe logarithm

We devote one paragraph to each term of Eq. (24), giving additional details which are necessary for their numerical evaluation. Note that the terms $\beta_1^{(a)}$ and $\beta_1^{(b)}$ are treated numerically in an independent way, which is a further reason for separating these two contributions.

(1) For $\beta_1^{(a)}$, the integrand can be written as

$$P_{rc}^{(1a)}(k) = \langle\psi_1|(H_B - \langle H_B\rangle)|\psi_1\rangle. \tag{34}$$

To evaluate $\langle\psi_1|\mathbf{p}^4|\psi_1\rangle$, it is convenient to use the following identity [see Eq. (16)]:

$$\mathbf{p}^2\psi_1 = 2[(E_0 - V - k)\psi_1 - \nabla\psi_0]. \tag{35}$$

Then

$$\begin{aligned}\langle\psi_1|\mathbf{p}^4|\psi_1\rangle &= 4\langle\psi_1|(E_0 - V - k)^2|\psi_1\rangle\\ &\quad - 4\langle\psi_1|(E_0 - V - k)|\psi_0\rangle + \langle\nabla^2\rangle,\end{aligned} \tag{36}$$

and, for arbitrary k, $\psi_1(k)$ may be expressed as

$$\psi_1(k) = \sum_m \frac{|\psi_m\rangle\langle\psi_m|\nabla|\psi_0\rangle}{E_0 - E_m - k}. \tag{37}$$

(2) In order to get $P_{rc}^{(1b)}(k)$ we first solve the equation

$$(E_0 - H)\psi_B = (H_B - \langle H_B\rangle)\psi_0. \tag{38}$$

It can be shown that ψ_B behaves at small r_1 (or r_2) as

$$\begin{aligned}\psi_B(r_1,r_2) &= \left(\frac{Z_1}{4r_1} - \frac{Z_1^2}{2}\ln r_1\right)\psi_0(r_1,r_2)\\ &\quad + \left(\frac{Z_2}{4r_2} - \frac{Z_2^2}{2}\ln r_2\right)\psi_0(r_1,r_2) + \tilde{\psi}_B(r_1,r_2),\end{aligned} \tag{39}$$

where $\tilde{\psi}_B(r_1,r_2)$ is a regular function. Then the equation for $\tilde{\psi}_B(r_1,r_2)$ may be written

$$\begin{aligned}&(E_0 - H)\,\tilde{\psi}_B\\ &= (H_B - \langle H_B\rangle)\psi_0\\ &\quad + \left[H, \left(\frac{Z_1}{4r_1} + \frac{Z_2}{4r_2} - \frac{Z_1^2}{2}\ln r_1 - \frac{Z_2^2}{2}\ln r_2\right)\right]\psi_0.\end{aligned} \tag{40}$$

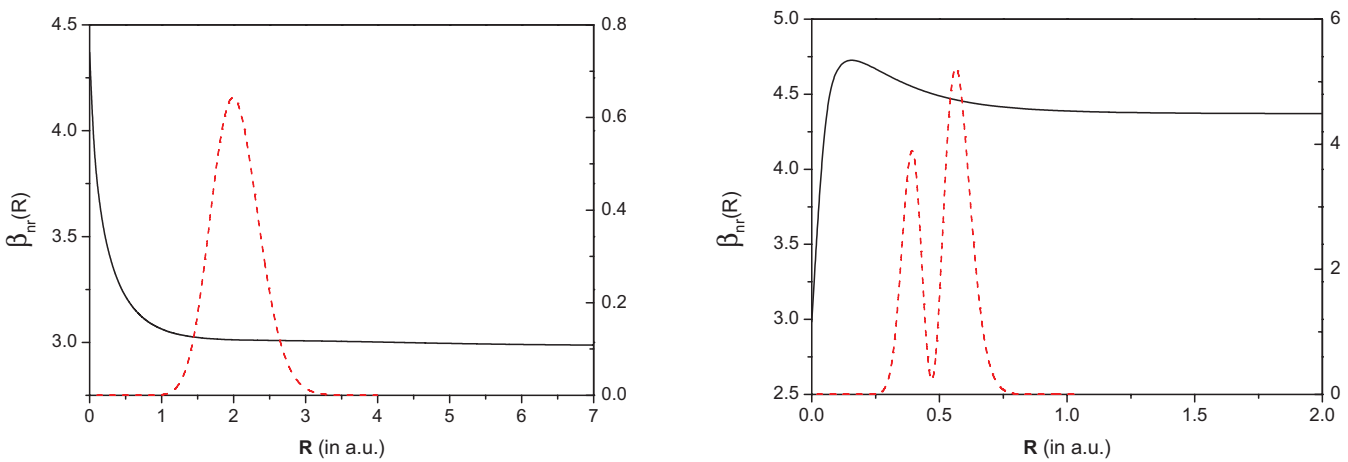

FIG. 4. (Color online) The nonrelativistic Bethe logarithm for the ground $(1s\sigma)$ electronic state for (left) $Z_1 = Z_2 = 1$ and (right) $Z_1 = 2$, $Z_2 = -1$. Dashed lines show the vibrational wave functions for the ground state in (left) the H_2^+ ion and (right) the (36,34) state in $^4He^+\bar{p}$.

Thus, substituting $\psi_B(r_1,r_2)$ from Eq. (39) into Eq. (11b), one gets

$$P_{rc}^{(1b)}(k) = 2\left\langle\left(\frac{Z_1}{4r_1}+\frac{Z_2}{4r_2}-\frac{Z_1^2}{2}\ln r_1-\frac{Z_2^2}{2}\ln r_2\right)\times Q\mathbf{p}(E_0-H-k)^{-1}\mathbf{p}\right\rangle + 2\langle\tilde{\psi}_B|\,Q\mathbf{p}(E_0-H-k)^{-1}\mathbf{p}|\,\psi_0\rangle. \quad (41)$$

The derivation of matrix elements involving logarithms may be found in the Appendix.

(3) For the evaluation of $P_{nq}(k)$, Eq. (15) must be transformed to separate contributions from operators of different ranks. Denoting $A_s = (E_0 - H - k)^{-1}$,

$$P_{nq}(k) = \frac{3}{8\pi}\int d\Omega_{\mathbf{n}}(\delta^{ij}-n^in^j)n^ln^m \times \int k^3dk\{\langle p^ir^l\,A_s\,r^mp^j\rangle - \langle p^ir^lr^m\,A_s\,p^j\rangle\}, \quad (42)$$

and one obtains

$$\frac{3}{8\pi}\int d\Omega_{\mathbf{n}}(\delta^{ij}-n^in^j)n^ln^m\int k^3dk\langle p^ir^l\,A_s\,r^mp^j\rangle = \int k^3dk\left\{\frac{3}{10}\langle[S_{ij}^{(2)}]^\dagger A_s\,S_{ij}^{(2)}\rangle-\frac{1}{4}\langle[\mathbf{p}\times\mathbf{r}]A_s[\mathbf{r}\times\mathbf{p}]\rangle\right\} = \int k^3dk\left\{\frac{9}{20}\langle[S_{\mu}^{(2)}]^\dagger A_s\,S_{\mu}^{(2)}\rangle-\frac{1}{4}\langle[\mathbf{p}\times\mathbf{r}]A_s[\mathbf{r}\times\mathbf{p}]\rangle\right\}, \quad (43)$$

TABLE I. Relativistic Bethe logarithm for the ground $(1s\sigma_g)$ electronic state for $Z_1 = Z_2 = 1$.

R	$\beta_1^{(a)}$	$\beta_1^{(b)}$	β_2	β_3	$\mathcal{L}$	$\mathcal{L}/N(R)$
0.2	199.124	−362.792	−718.74	500.9	−381.5	−37.9097
0.3	71.425	−155.864	−408.41	244.09	−248.76	−30.8595
0.4	26.866	−73.891	−293.55	153.814	−186.76	−28.3923
0.5	8.5247	−36.4368	−232.469	111.218	−149.163	−27.2764
0.6	0.3419	−17.8754	−192.985	86.9905	−123.529	−26.7053
0.7	−3.4173	−8.19603	−164.670	71.3995	−104.884	−26.3920
0.8	−5.1044	−2.99381	−143.164	60.5041	−90.7581	−26.2137
0.9	−5.7669	−0.16341	−126.255	52.4484	−79.7371	−26.1091
1.0	−5.94144	1.36042	−112.653	46.2540	−70.9802	−26.0581
1.1	−5.85242	2.14699	−101.528	41.3527	−63.8807	−26.0336
1.2	−5.64166	2.50981	−92.3095	37.3908	−58.0506	−26.0285
1.3	−5.37875	2.62712	−84.5938	34.1346	−53.2109	−26.0386
1.4	−5.10067	2.60269	−78.0750	31.4227	−49.1503	−26.0581
1.5	−4.82677	2.49792	−72.5270	29.1400	−45.7159	−26.0850
1.6	−4.56684	2.34961	−67.7744	27.2013	−42.7903	−26.1177
1.7	−4.32531	2.17994	−63.6799	25.5425	−40.2828	−26.1549
1.8	−4.10371	2.00222	−60.1351	24.1145	−38.1221	−26.1956
1.9	−3.90197	1.82441	−57.0531	22.8786	−36.2520	−26.2391
2.0	−3.71921	1.65108	−54.3637	21.8045	−34.6274	−26.2848
2.1	−3.55413	1.48479	−52.0099	20.8676	−33.2117	−26.3322
2.2	−3.40532	1.32679	−49.9446	20.0480	−31.9752	−26.3810
2.3	−3.27133	1.17755	−48.1290	19.3294	−30.8933	−26.4307
2.4	−3.15078	1.03708	−46.5306	18.6985	−29.9458	−26.4811
2.5	−3.04237	0.90509	−45.1223	18.1441	−29.1155	−26.5318
2.6	−2.94493	0.78117	−43.8811	17.6566	−28.3883	−26.5826
2.7	−2.85740	0.66481	−42.7875	17.2283	−27.7518	−26.6332
2.8	−2.77881	0.55550	−41.8248	16.8522	−27.1958	−26.6834
2.9	−2.70829	0.45272	−40.9786	16.5527	−26.6814	−26.7031
3.0	−2.64510	0.35594	−40.2365	16.2347	−26.2909	−26.7820
3.2	−2.53796	0.17881	−39.0229	15.7664	−25.6156	−26.8768
3.4	−2.45271	0.02095	−38.1126	15.4188	−25.1256	−26.9664
3.6	−2.38557	−0.12013	−37.4498	15.1695	−24.7860	−27.0497
3.8	−2.33346	−0.24634	−36.9899	15.0008	−24.5689	−27.1259
4.0	−2.29385	−0.35913	−36.6963	14.8980	−24.4513	−27.1942
4.2	−2.26461	−0.45961	−36.5387	14.8490	−24.4139	−27.2541
4.4	−2.24395	−0.54861	−36.4913	14.8435	−24.4404	−27.3054
4.6	−2.23034	−0.62682	−36.5320	14.8726	−24.5165	−27.3482
4.8	−2.22246	−0.69487	−36.6417	14.9288	−24.6303	−27.3826
5.0	−2.21917	−0.75336	−36.8039	15.0053	−24.7712	−27.4091

$$\frac{3}{8\pi}\int d\Omega_{\mathbf{n}}(\delta^{ij}-n^i n^j)n^l n^m \int k^3 dk\langle p^i r^l r^m\, A_s\, p^j\rangle$$
$$=\int k^3 dk\left\{\frac{2}{5}\langle p^i\, r^2 A_s\, p^i\rangle-\frac{1}{5}\langle(\mathbf{pr})r^j\, A_s\, p^j\rangle\right\}. \quad (44)$$

Here the quadrupole operator is defined as

$$S^{(2)}_{ij}=\tfrac{1}{2}\big[r_i p_j+r_j p_i-\tfrac{2}{3}\delta_{ij}(\mathbf{r}\cdot\mathbf{p})\big], \quad (45)$$

and its standard components are

$$S^{(2)}_0=S^{(2)}_{zz}=\frac{1}{3}(2zp_z-xp_x-yp_y),$$
$$S^{(2)}_{\pm1}=\mp\sqrt{\frac{2}{3}}\big(S^{(2)}_{xz}\pm iS^{(2)}_{yz}\big)$$
$$=\mp\frac{1}{\sqrt{6}}[xp_z+zp_x\pm i(yp_z+zp_y)], \quad (46)$$
$$S^{(2)}_{\pm2}=\frac{1}{\sqrt{6}}\big(S^{(2)}_{xx}-S^{(2)}_{yy}\pm 2iS^{(2)}_{xy}\big)$$
$$=\frac{1}{\sqrt{6}}[xp_x-yp_y\pm i(xp_y+yp_x)].$$

Matrix elements can be computed from the relations (valid for a σ state)

$$S^{(2)}_0=\frac{1}{3}(2zp_z+r_+p_-+r_-p_+)$$
$$=-\frac{i}{3}\left\{2z\left[\left(z+\frac{R}{2}\right)\frac{1}{r_1}\partial_{r_1}+\left(z-\frac{R}{2}\right)\frac{1}{r_2}\partial_{r_2}\right]\right.$$
$$\left.-r^2\left(\frac{1}{r_1}\partial_{r_1}+\frac{1}{r_2}\partial_{r_2}\right)\right\},$$
$$S^{(2)}_{\pm1}=\frac{1}{\sqrt{3}}(r_\pm p_z+zp_\pm)$$
$$=\pm\frac{i}{\sqrt{6}}re^{\pm i\varphi}\left[\left(2z+\frac{R}{2}\right)\frac{1}{r_1}\partial_{r_1}+\left(2z-\frac{R}{2}\right)\frac{1}{r_2}\partial_{r_2}\right],$$
$$S^{(2)}_{\pm2}=\frac{2}{\sqrt{6}}r_\pm p_\pm=-\frac{i}{\sqrt{6}}r^2e^{\pm i2\phi}\left(\frac{1}{r_1}\partial_{r_1}+\frac{1}{r_2}\partial_{r_2}\right). \quad (47)$$

Here $r_\pm$ and $p_\pm$ are standard components of vector operators $\mathbf{r}$ and $\mathbf{p}$, respectively.

Finally, the matrix elements of the $[\mathbf{r}\times\mathbf{p}]$ operator can be obtained from

$$[\mathbf{r}\times\mathbf{p}]_{\pm1}=\frac{ire^{\pm i\phi}}{\sqrt{2}}\frac{R}{2}\left(\frac{1}{r_1}\partial_{r_1}-\frac{1}{r_2}\partial_{r_2}\right). \quad (48)$$

(4) In the expression of $P^{(2)}_{rc}(k)$ in Eq. (13), the two terms can be respectively written as

$$-2\langle(E_0-V)p^i(E_0-H-k)^{-1}p^i\rangle \quad (49)$$

and

$$\frac{1}{2}\left\langle\left(Z_1\frac{[\boldsymbol{\sigma}\times\mathbf{r}_1]^i}{r_1^3}+Z_2\frac{[\boldsymbol{\sigma}\times\mathbf{r}_2]^i}{r_2^3}\right)(E_0-H-k)^{-1}p^i\right\rangle. \quad (50)$$

We now show that the second term does not contribute here. Since the right-hand transition does not change spin, then on the left-hand side we may keep only those terms which contain σ_z:

$$\mp\frac{i}{2}\left\langle\sigma_z\frac{re^{\pm i\varphi}}{\sqrt{2}}\left(\frac{Z_1}{r_1^3}+\frac{Z_2}{r_2^3}\right)(E_0-H-k)^{-1}p^i\right\rangle. \quad (51)$$

This contribution results in fine splitting of the main line, which is spin dependent, and thus will not be considered here.

V. RESULTS

A. Nonrelativistic Bethe logarithm

First, we perform calculations of the nonrelativistic Bethe logarithm for the two-center Coulomb problem for two cases: $Z_1=Z_2=1$ and $Z_1=2$, $Z_2=-1$. Results are plotted in Fig. 4. The numerical data for $\beta_{nr}(R)$ is as accurate as ten significant digits and has been obtained for a large range of internuclear bond lengths $R=0-7$ a.u. with a step of 0.05 a.u. For the hydrogen molecular ion our results are in a good agreement with previous calculations [25]. The complete tables are too lengthy to be reported here and may be found in the Supplemental Material [26].

B. Relativistic corrections to the Bethe logarithm

The numerical scheme has been tested on the ground state of the hydrogen atom. Our results are

$$\beta_1(1s)=-3.26821319,\quad \beta_2(1s)=-40.647026693.$$
$$\beta_3(1s)=16.655330436.$$

They are in perfect agreement with those of [12].

TABLE II. Relativistic Bethe logarithm for the ground $(1s\sigma)$ electronic state for $Z_1=2$ and $Z_2=-1$.

R	β_1	β_2	β_3	$\mathcal{L}$	$\mathcal{L}/N(R)$
0.20	29.65	−584.1	62.514	−491.9	−34.59
0.25	17.558	−799.9	159.373	−622.9	−36.755
0.30	1.741	−998.9	236.611	−760.5	−38.079
0.35	−15.627	−1191.9	305.525	−902.0	−38.857
0.40	−33.158	−1382.7	369.822	−1046.0	−39.361
0.45	−49.903	−1566.8	430.590	−1186.1	−39.589
0.50	−65.195	−1743.3	487.854	−1320.6	−39.685
0.55	−78.929	−1909.9	541.306	−1447.5	−39.709
0.60	−91.000	−2064.5	590.636	−1564.8	−39.684
0.65	−101.172	−2207.3	635.664	−1672.8	−39.655
0.70	−109.370	−2335.7	676.345	−1768.7	−39.578
0.75	−116.075	−2451.0	712.787	−1854.2	−39.498
0.80	−121.547	−2553.7	745.209	−1930.0	−39.418
0.85	−125.908	−2645.8	773.901	−1997.8	−39.363
0.90	−127.846	−2727.0	799.189	−2055.6	−39.280
0.95	−130.235	−2797.5	821.408	−2106.3	−39.205
1.00	−131.770	−2860.8	840.902	−2151.6	−39.159
1.10	−133.766	−2963.8	872.905	−2224.6	−39.062
1.20	−134.563	−3041.6	897.365	−2278.7	−38.962
1.30	−134.679	−3101.3	916.090	−2319.8	−38.882
1.40	−134.430	−3147.1	930.468	−2351.0	−38.818
1.50	−134.006	−3182.5	941.556	−2374.9	−38.766
1.60	−133.517	−3209.9	950.148	−2393.2	−38.725
1.70	−133.025	−3231.3	956.847	−2407.4	−38.692
1.80	−132.561	−3248.2	962.102	−2418.6	−38.666
1.90	−132.140	−3261.4	966.255	−2427.2	−38.644
2.00	−131.766	−3272.0	969.562	−2434.2	−38.627

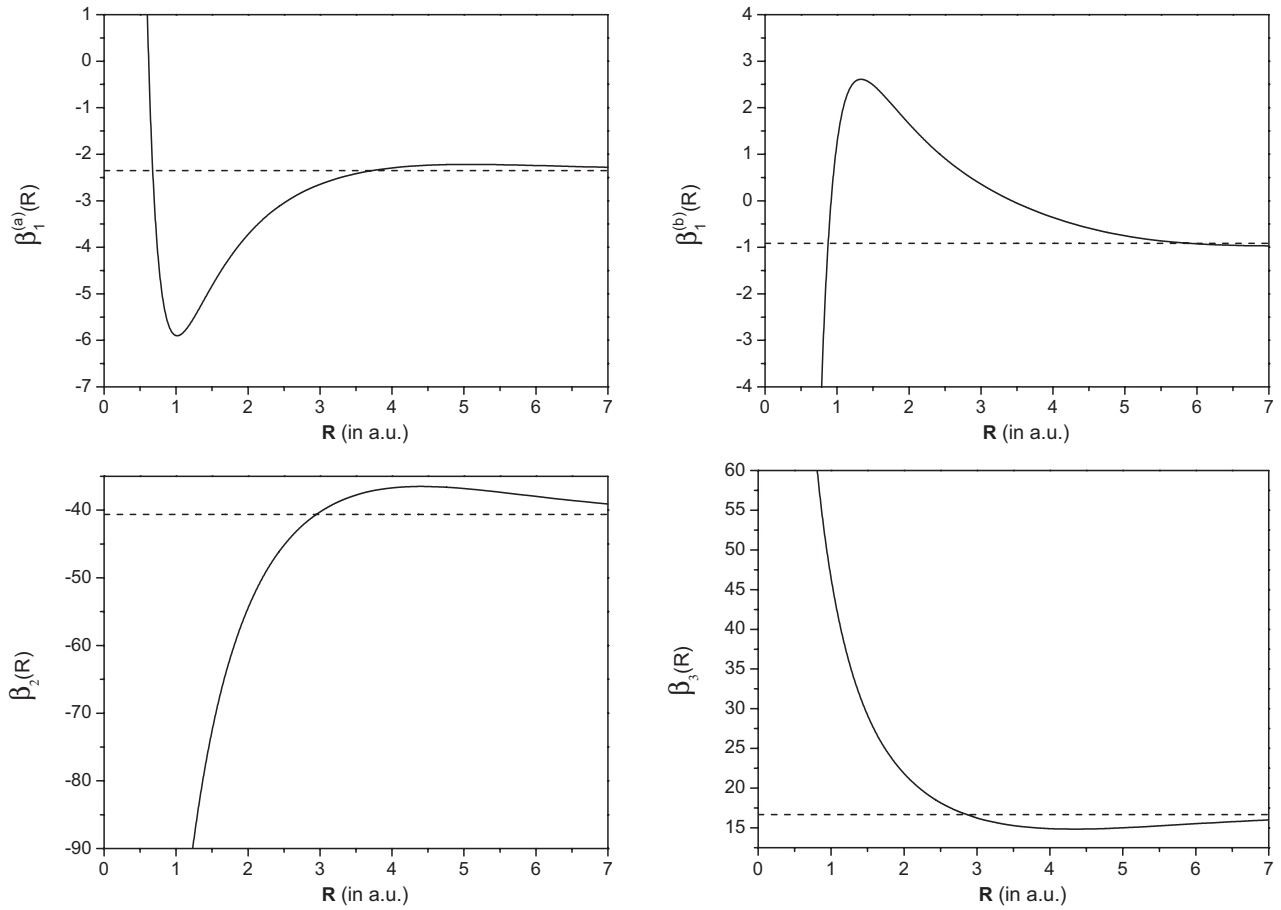

FIG. 5. The four contributions to the relativistic Bethe logarithm for the ground $(1s\sigma_g)$ electronic state for $Z_1 = Z_2 = 1$. Dashed lines show their respective values for the $1s$ state of a hydrogen atom [12].

The main results of this work are presented in Tables I and II. Particular behavior of different components of the relativistic Bethe logarithm $\mathcal{L}$, namely, $\beta_1^{(a)}$, $\beta_1^{(b)}$, β_2, β_3, for the case of a hydrogen molecular ion are shown in Fig. 5. In Figs. 6 and 7 our final results for the low-energy contribution $\mathcal{L}(R)$ are plotted.

The numerical calculations have been performed in multiple-precision arithmetic with 64 decimal digits. Special care has been required for the nonrelativistic quadrupole contribution at small R, in this case a 96-decimal-digit arithmetic has been used. In the worst case of $R = 0.2$ for the antiprotonic helium we found that at least two digits

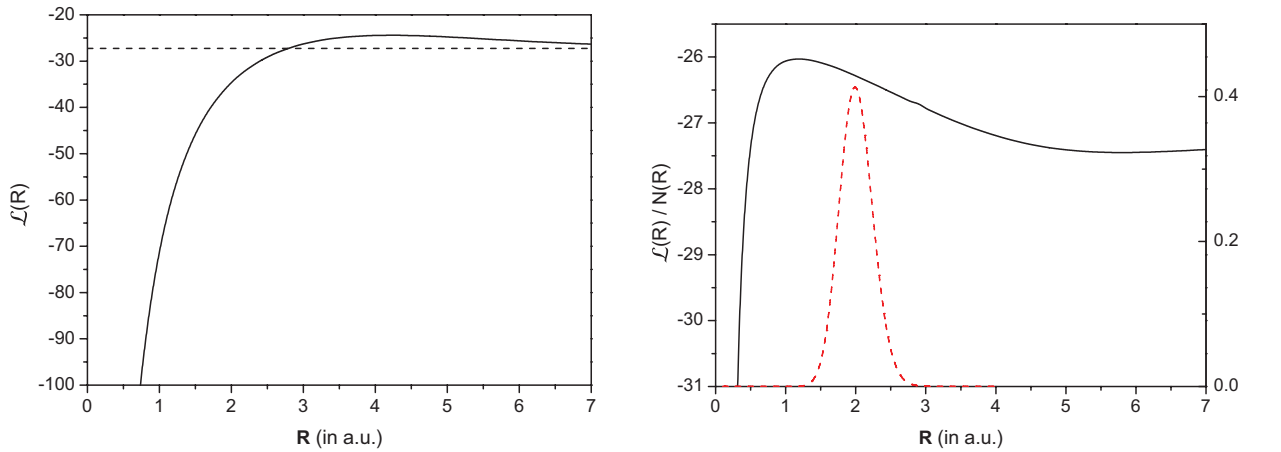

FIG. 6. (Color online) (left) The relativistic Bethe logarithm for the ground $(1s\sigma_g)$ electronic state for $Z_1 = Z_2 = 1$. The dashed line is $\mathcal{L}(1s)$ for the $1s$ state of a hydrogen atom [12]. (right) The same data, but normalized by the δ function distribution: $N(R) = \pi[Z_1^3\delta(\mathbf{r}_1) + Z_2^3\delta(\mathbf{r}_2)]$. The dashed line is the vibrational wave function for the ground state of H_2^+.

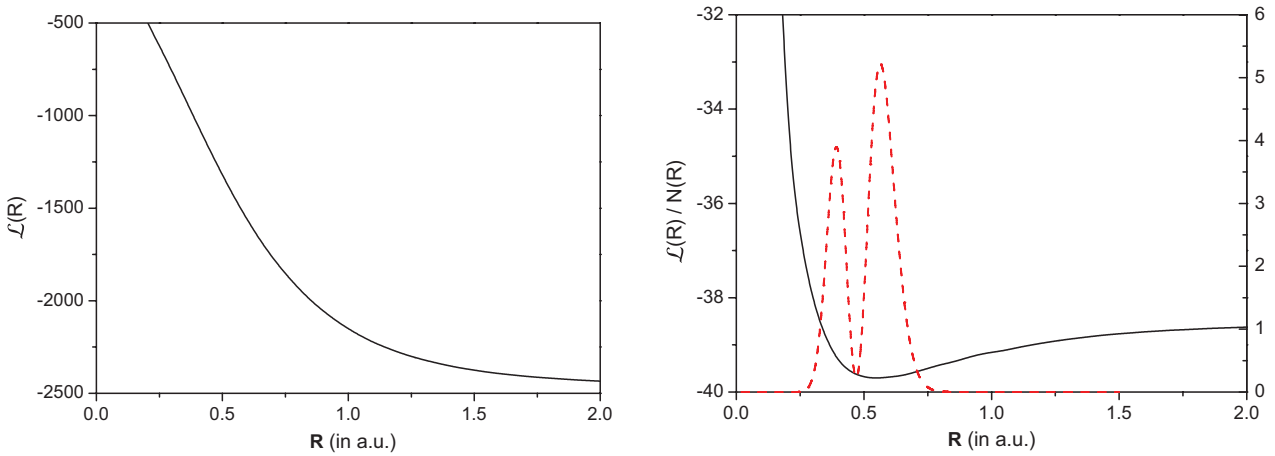

FIG. 7. (Color online) (left) The relativistic Bethe logarithm for the ground $(1s\sigma)$ electronic state for $Z_1 = 2$ and $Z_2 = -1$. (right) The same data, but normalized by the δ function distribution: $N(R) = \pi[Z_1^3\delta(\mathbf{r}_1) + Z_2^3\delta(\mathbf{r}_2)]$. The dashed line is the vibrational wave function for the (36,34) state of $^4\mathrm{He}^+\bar{p}$.

are converged. For large R, convergence becomes much improved and we estimate our data to be accurate upto 4 to 6 significant digits. The reason for numerical complications at small bond lengths is the rapid growth of the coefficients of asymptotic expansions, Eqs. (21), when R goes to zero. Similar behavior may be observed in the nonrelativistic case for $P_{nd}(k)$.

In the last columns of Tables I and II we found it useful to normalize the low-energy contribution $\mathcal{L}(R)$ by the following distribution:

$$N(R) = \pi\big[Z_1^3\delta(\mathbf{r}_1) + Z_2^3\delta(\mathbf{r}_2)\big]. \tag{52}$$

This δ function distribution appears in front of the leading $\ln^2(Z\alpha)^{-2}$ term at this order [see Eqs. (21)–(21d)]. It is worth noting that in the region where the wave function is essentially nonzero the quantity $\mathcal{L}/N(R)$ is about constant: $\mathcal{L}/N(R) \approx 26.3$ for $Z_1 = Z_2 = 1$ and $\mathcal{L}/N(R) \approx 39.7$ for $Z_1 = 2$, $Z_2 = -1$. That may help in a qualitative estimate within two- to three-digit accuracy of the one-loop self-energy contribution to the transition frequencies of not only hydrogen molecular ions but also the neutral hydrogen molecule H_2.

In conclusion, we have computed the low-energy part of the $m\alpha^7$-order self-energy correction for the two-center problem, with a numerical accuracy that exceeds three significant digits, in the whole range of internuclear distances $R \in [0.2,7]$. Calculation of the high-energy part is under consideration now. A complete result then should be averaged over vibrational wave functions to get proper correction for rovibrational transition frequencies at $m\alpha^7$ order. Taking into account as well the vacuum polarization and two-loop electron self-energy contributions at this order, we expect that a relative precision for transition frequencies will be at a level of 10^{-10} or better both for hydrogen molecular ions and for antiprotonic helium.

ACKNOWLEDGMENTS

The authors are in debt to Krzysztof Pachucki for helpful discussions. V.I.K. acknowledges support from the Russian Foundation for Basic Research under Grant No. 12-02-00417-a. This work was supported by École Normale Supérieure, which is gratefully acknowledged.

APPENDIX: TWO-CENTER MATRIX ELEMENTS INVOLVING $\ln r_1$ or $\ln r_2$

In this Appendix we want to consider an analytical evaluation of the two-center integrals of type [22], which contain either $\ln r_1$ or $\ln r_2$ as a multiplier. We start from the basic integral

$$\Gamma_{\ln r_1,00}(\alpha,\beta) = \int dr_1 dr_2 \big[\ln r_1\, e^{-\alpha r_1 - \beta r_2}\big]. \tag{A1}$$

Using the identities

$$\int_R^\infty dr\ \ln r\, e^{-\gamma r} = \frac{1}{\gamma}[E_1(R\gamma) + \ln R\, e^{-\gamma R}]$$

and

$$\int_0^R dr\ \ln r\, e^{-\gamma r} = -\frac{1}{\gamma}[E_1(R\gamma) + \ln\gamma + \ln R\, e^{-\gamma R} + \gamma_E],$$

one may get

$$\int_R^\infty dr_1\ \ln r_1\, e^{-\alpha r_1} \int_{r_1-R}^{r_1+R} dr_2\, e^{-\beta r_2} = \frac{1}{\beta}\int_R^\infty dr_1\big[\ln r_1\, e^{-\alpha r_1}\big(e^{-\beta(r_1-R)} - e^{-\beta(r_1+R)}\big)\big]$$
$$= \frac{e^{\beta R} - e^{-\beta R}}{\beta} \times \frac{E_1(R(\alpha+\beta)) + \ln R e^{-(\alpha+\beta)R}}{\alpha+\beta} \tag{A2a}$$

and

$$\int_0^R dr_1\ \ln r_1\, e^{-\alpha r_1} \int_{R-r_1}^{R+r_1} dr_2\, e^{-\beta r_2} = \frac{1}{\beta}\int_0^R dr_1\Big[\ln r_1\, e^{-\alpha r_1}\big(e^{-\beta(R-r_1)} - e^{-\beta(R+r_1)}\big)\Big]$$
$$= \frac{e^{-\beta R}}{\beta}\left[\int_0^R dr_1\ \ln r_1\, e^{-(\alpha-\beta)r_1} - \int_0^R dr_1\ \ln r_1\, e^{-(\alpha+\beta)r_1}\right]$$
$$= \frac{e^{-\beta R}}{\beta} \times \left[\frac{E_1(R(\alpha+\beta)) + \ln(\alpha+\beta) + \ln R\, e^{-(\alpha+\beta)R} + \gamma_E}{\alpha+\beta}\right.$$
$$\left. - \frac{E_1(R(\alpha-\beta)) + \ln(\alpha-\beta) + \ln R e^{-(\alpha-\beta)R} + \gamma_E}{\alpha-\beta}\right]. \tag{A2b}$$

Summing up the two contributions, we obtain the final expression

$$\Gamma_{\ln r_1,00}(\alpha,\beta) = -\frac{4\pi}{R}\,\frac{e^{-\beta R}\,\gamma_E + e^{-\alpha R}\ln R}{\alpha^2-\beta^2} + \frac{2\pi}{R\beta}\,\frac{e^{\beta R}\,E_1(R(\alpha+\beta)) + e^{-\beta R}\ln(\alpha+\beta)}{\alpha+\beta}$$
$$- \frac{2\pi}{R\beta}\,\frac{e^{-\beta R}[E_1(R(\alpha-\beta)) + \ln(\alpha-\beta)]}{\alpha-\beta}. \tag{A3}$$

To generate other integrals one may use

$$\Gamma_{\ln r_1,kl}(\alpha,\beta) = \left(-\frac{\partial}{\partial\alpha}\right)^k \left(-\frac{\partial}{\partial\beta}\right)^l \Gamma_{\ln r_1,00}(\alpha,\beta). \tag{A4}$$

[1] J. C. J. Koelemeij, B. Roth, A. Wicht, I. Ernsting, and S. Schiller, Phys. Rev. Lett. **98**, 173002 (2007); U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, and S. Schiller, *ibid.* **108**, 183003 (2012); J. Shen, A. Borodin, M. Hansen, and S. Schiller, Phys. Rev. A **85**, 032519 (2012).

[2] J. C. J. Koelemeij, D. W. E. Noom, D. de Jong, M. A. Haddad, and W. Ubachs, Appl. Phys. B **107**, 1075 (2012).

[3] J.-Ph. Karr, A. Douillet, and L. Hilico, Appl. Phys. B **107**, 1043 (2012).

[4] M. Hori, A. Sótér, D. Barna, A. Dax, R. Hayano, S. Friedreich, B. Juhász, Th. Pask, E. Widmann, D. Horváth, L. Venturelli, and N. Zurlo, Nature (London) **475**, 484 (2011).

[5] V. I. Korobov, Phys. Rev. A **77**, 022509 (2008).

[6] V. I. Korobov, Phys. Rev. A **77**, 042506 (2008).

[7] M. I. Eides, H. Grotch, and V. A. Shelyuto, *Theory of Light Hydrogenic Bound States*, Springer Tracks in Modern Physics Vol. 222 (Springer, Berlin, 2007).

[8] J. R. Sapirstein and D. R. Yennie, in *Quantum Electrodynamics*, edited by T. Kinoshita (World Scientific, Singapore, 1990).

[9] K. Pachucki, Phys. Rev. A **46**, 648 (1992); Ann. Phys. (NY) **226**, 1 (1993).

[10] U. D. Jentschura, E.-O. Le Bigot, P. J. Mohr, P. Indelicato, and G. Soff, Phys. Rev. Lett. **90**, 163001 (2003).

[11] A. Czarnecki, U. D. Jentschura, and K. Pachucki, Phys. Rev. Lett. **95**, 180404 (2005).

[12] U. D. Jentschura, A. Czarnecki, and K. Pachucki, Phys. Rev. A **72**, 062102 (2005).

[13] W. E. Caswell and J. P. Lepage, Phys. Lett. B **167**, 437 (1986).

[14] T. Kinoshita and M. Nio, Phys. Rev. D **53**, 4909 (1996).

[15] K. Pachucki, J. Phys. B **31**, 3547 (1998).

[16] H. A. Bethe, Phys. Rev. **72**, 339 (1947).

[17] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).

[18] V. I. Korobov, L. Hilico, and J.-Ph. Karr, Phys. Rev. A **79**, 012501 (2009).

[19] C. Schwartz, Phys. Rev. **123**, 1700 (1961).

[20] V. I. Korobov, Phys. Rev. A **85**, 042514 (2012).

[21] M. Gavrila and A. Costescu, Phys. Rev. A **2**, 1752 (1970).

[22] Ts. Tsogbayar and V. I. Korobov, J. Chem. Phys. **125**, 024308 (2006).

[23] V. I. Korobov, Phys. Rev. A **61**, 064503 (2000).

[24] V. I. Korobov and Ts. Tsogbayar, J. Phys. B **80**, 2661 (2007).

[25] R. Bukowski, B. Jeziorski, R. Moszyński, and W. Kołos, Int. J. Quantum Chem. **42**, 287 (1992).

[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevA.87.062506 for complete tables of the numerical data.