Two-body neutral Coulomb system in a magnetic field at rest: From hydrogen atom to positronium

J. C. del Valle* and A. V. Turbiner†
Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, A. Postal 70-543 C. P. 04510, Ciudad de México, México

A. M. Escobar Ruiz‡
Departamento de Fisica, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, C.P. 09340 Ciudad de México, México

(Received 12 January 2021; accepted 23 February 2021; published 16 March 2021)

A simple locally accurate uniform approximation for the nodeless wave function is constructed for a *neutral* system of two Coulomb charges of different masses $(-q, m_1)$ and (q, m_2) at rest in a constant uniform magnetic field for the states of positive and negative parity, $(1s_0)$ and $(2p_0)$, respectively. It is shown that by keeping the mass and charge of one of the bodies fixed, all systems with different second-body masses are related. This allows one to consider the second body as infinitely massive and to take such a system as basic. Three physical systems are considered in detail: the hydrogen atom with (in)finitely massive proton (deuteron, triton) and the positronium atom $(-e, e)$. We derive the Riccati-Bloch and generalized Bloch equations, which describe the domains of small and large distances, respectively. Based on the interpolation of the small- and large-distance behavior of the logarithm of the wave function, a compact ten-parametric function is proposed. Taken as a variational trial function, it provides accuracy of not less than six significant digits (SDs) ($\lesssim 10^{-6}$ in relative deviation) for the total energy in the whole domain of considered magnetic fields $[0\,,\ 10^4]$ a.u. and not less than three SDs for the quadrupole moment Q_{zz}. To get reference points, the Lagrange mesh method with 16 K mesh points was used to get from ten to six SDs in energy from small to large magnetic fields. Based on the Riccati-Bloch equation, the first 100 perturbative coefficients for the energy, in the form of rational numbers, are calculated and, using the Padé-Borel resummation procedure, the energy is found with not less than ten SDs at magnetic fields $\leqslant 1$ a.u.

DOI: 10.1103/PhysRevA.103.032820

I. INTRODUCTION

A hydrogen atom in a constant uniform magnetic field was one of the first problems studied in quantum mechanics. It is stable at any magnetic-field strength. Its importance is related to the fact that it arises in various domains of physics, in particular, in semiconductor physics [1] and in astrophysics (e.g., the physics of strong surface magnetic fields of magnetic white dwarfs and neutron stars). In the former case, the excitons occur as hydrogenlike quasiatoms with a small effective mass and a large dielectric constant. In the latter case, the atmosphere of white dwarfs and neutron stars can contain hydrogen atoms subject to a strong magnetic field. Magnetic fields in nature occur from a few gauss (e.g., the Earth, Jupiter magnetic fields) up to about 10^{16} gauss, corresponding to a surface magnetic field in a few explored magnetars. Hence, they range in 16 orders of magnitude! A hydrogen atom is the simplest Coulomb system in the sequence of one-electron hydrogenic atomic-molecular ions, both traditional and exotic, which may exist in a strong magnetic field [2]. All of that explains the enormous amount of articles published on the subject.

A description of the problem with weak magnetic fields may be found in any textbook on quantum mechanics (see, e.g., Landau and Lifshitz [3]). Early attempts to explore the problem are summarized in the remarkable review paper by Garstang [4]. In the overwhelming majority of considerations, the proton is assumed explicitly to be infinitely heavy, which implies that the atom is at rest, although the hydrogen atom, since it is a neutral two-body Coulomb system, can be at rest even for the case of finite proton mass—the case of zero pseudomomentum [5]. Many years ago it was shown that the problems when the proton is infinitely massive and finitely massive but both at rest are connected via nontrivial scaling relation [6]. It is well known that in the finite mass case, the center-of-mass motion is not separated unlike in the field-free case: it is replaced by the pseudoseparation. This does not lead to complexification in the case of zero pseudomomentum. In general, the specific coupling between the relative and the c.m. motion leads to the prediction of a giant-dipole moment [7].

By increasing the magnetic field, the electronic density evolves from a spherical-symmetrical distribution at weak fields to a cigarlike one (elongated in the field direction) at atomic and larger fields, where the energy grows linearly with field strength. It was a challenge for many years to give a unified description of the evolution in the framework of the same approach with a sufficiently high, uniform in field strength accuracy. This would imply an approximate solution of the problem. It is worth mentioning three approaches,

*delvalle@correo.nucleares.unam.mx
†turbiner@nucleares.unam.mx
‡admau@xanum.uam.mx

which treated the challenge: (i) power series expansion—the method of moments [8], (ii) a numerical approach—the Lagrange mesh method (LMM) [9], and (iii) the variational method with (a) multiconfigurational trial functions [10] and (b) with simple, few-parametric, single-configurational, physically adequate trial functions [11–18]. As a result, in all three approaches, the ground-state energy (and the energies of a few excited states) were found with reasonably high (or excessively high) accuracy. Surprisingly, the quadrupole moment, which is one of the principal consequences of the presence of the magnetic field for the hydrogen atom and which defines the van der Waals-type constant for the repulsion at large distances of two H-atoms in a H_2 molecule, was studied quantitatively in a reliable way only recently [19]. The situation with finite-mass effects [5,7,20], relativistic and QED corrections is far from being complete, see, e.g., Ref. [21]. In general, the finite nuclear mass effects do not change four to five significant digits (SDs), and following Salpeter *et al.* [22] estimates the leading relativistic and QED effects leave three to four SDs unchanged in the ground-state energy.

It should be mentioned that the neutral system can move across magnetic field, see, e.g., Ref. [23] and references therein. The two-dimensional case, where the neutral atom moves on a plane subject to a magnetic field perpendicular to it, has been analyzed in detail (see Ref. [24] and references therein). In particular, a simple physically adequate trial function with the property of being a uniform local approximation of the exact eigenfunction in any point of coordinate space was constructed for the lowest states and *any* constant uniform magnetic field. Remarkably, when the system possesses azimuthal symmetry, the hidden $sl(2)$ algebra occurs and there exists an infinite number of exact analytic eigenfunctions. These eigenfunctions occur for specific values of the magnetic field only. The existence of exact eigenfunctions for the three-dimensional two-body neutral Coulomb system is still an interesting open problem. It should be noted that, usually, studies in a magnetic field are characterized by a high degree of technicality. To get reliable numerical results, two (or more) independent calculations have to be carried out.

The aim of this paper is twofold: (i) using perturbation theory and semiclassical consideration to construct a compact function as a uniform local approximation of the exact (unknown) eigenfunction in the whole range of magnetic fields and (ii) to study finite mass effects for the neutral atom at rest. The main emphasis will be given to the ground state—the state of lowest energy. It will be revisited and then the high accuracy estimates of the quadrupole moment for the hydrogen atom will be provided.

The paper consists of two large parts. The first part is about the infinite (proton) mass case where the Riccati-Bloch and generalized Bloch (GB) equations are derived, the perturbation theory in powers of the magnetic field strength is constructed for both equations, and the approximate expression (the approximant) for the ground-state eigenfunction of positive parity and for another one of negative parity is introduced. In the second part, the case of the two-body neutral Coulomb system of finite masses is studied. The hydrogen atom (p, e) and positronium (e^+, e^-) are considered.

Atomic units will be used through out the paper; the energy will be measured in Rydbergs.

II. INFINITE MASS CASE

The Hamiltonian

$$\hat{H}^{(\infty)} = \frac{1}{2\,m_e}\Big(\hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}\Big)^2 - \frac{e^2}{r}\,, \quad r = \sqrt{x^2+y^2+z^2}\,, \tag{2.1}$$

describes a hydrogen atom in the presence of a constant uniform magnetic field $\mathbf{B} = \gamma\,\hat{\mathbf{z}}$, directed along the z axis, in the static approximation, when the mass of the proton is infinite, $m_p = \infty$ and c is the speed of light. Here m_e and $(-e)$ are the mass and charge of the electron, respectively, $\hat{\mathbf{p}}$ is its momentum, r is its distance from the origin. The infinitely heavy proton of charge $e > 0$ is situated at the origin. In symmetric gauge,

$$\mathbf{A} = \tfrac{1}{2}\mathbf{B}\times\mathbf{r}\,, \tag{2.2}$$

the Hamiltonian (2.1) takes the form

$$\hat{H}^{(\infty)} = -\frac{\hbar^2}{2m_e}\Delta + \frac{|e|\gamma}{2m_e c}\hat{L}_z + V\,, \quad \Delta = \partial_x^2+\partial_y^2+\partial_z^2\,, \tag{2.3}$$

where the potential

$$V = -\frac{e^2}{r} + \frac{e^2\gamma^2}{8m_e c^2}\,\rho^2\,, \quad \rho = \sqrt{x^2+y^2}\,, \tag{2.4}$$

depends on two variables ρ and r, and $\hat{L}_z$ is the projection of the angular momentum operator in the direction of the magnetic field,

$$\hat{L}_z = -i\hbar\,(x\,\partial_y - y\,\partial_x)\,, \tag{2.5}$$

which is conserved, $[\hat{H}^{(\infty)}, \hat{L}_z] = 0$. The parity operator $\hat{\Pi}\Psi(x,y,z) = \Psi(x,y,-z)$ also commutes with $\hat{H}^{(\infty)}$. The Schrödinger equation associated to (2.3) is

$$\hat{H}^{(\infty)}\psi = E^{(\infty)}\psi\,, \quad E^{(\infty)} = E^{(\infty)}(\gamma, e, m_e)\,, \tag{2.6}$$

with boundary conditions imposed in such a way that the wave function is normalizable,

$$\int |\psi|^2\, d\,\mathbf{r} < \infty\,. \tag{2.7}$$

The dependence of the potential (2.4) on the variables ρ, r hints (for discussion, see Ref. [25]) that it might be convenient to write the Schrödinger Eq. (2.6) in the nonorthogonal system of coordinates (ρ, r, φ), see Fig. 1 and make a search for subfamily of eigenfunctions with (ρ, r) dependence alone. In these coordinates, we get

$$-\frac{\hbar^2}{2m_e}\Big[\partial_\rho^2 + \frac{2\rho}{r}\partial_{\rho r} + \partial_r^2 + \frac{1}{\rho}\partial_\rho + \frac{2}{r}\partial_r + \frac{1}{\rho^2}\partial_\varphi^2\Big]\psi - \frac{i|e|\hbar\gamma}{2m_e c}\partial_\varphi\psi + \Big[-\frac{e^2}{r} + \frac{\gamma^2 e^2}{8m_e c^2}\rho^2\Big]\psi = E^{(\infty)}\,\psi\,. \tag{2.8}$$

Needless to say, this equation is nonsolvable for $\gamma \neq 0$: the energy $E^{(\infty)}$ and wave function ψ cannot be written in terms

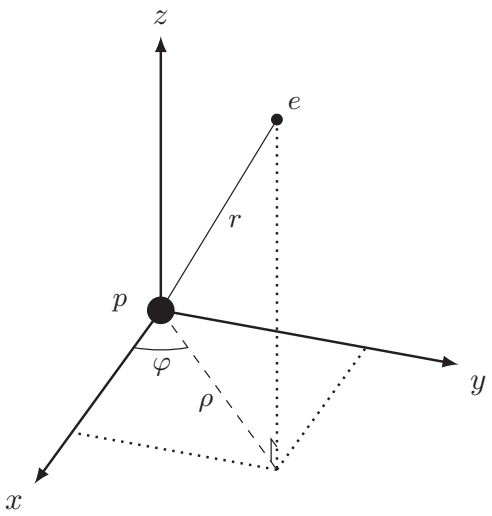

FIG. 1. Coordinates (ρ, r, φ) at half-space $z \geqslant 0$. The infinitely heavy proton is located at the origin.

of known elementary and transcendental functions, they can *only* be found approximately.[1]

Due to cylindrical symmetry, any state is characterized by two quantum numbers: the magnetic quantum number m ($\hbar m$ the eigenvalue of the operator $\hat{L}_z$) and the parity $\nu = \pm$ with respect to a reflection $z \to -z$. It suggests representing a wave function in the form

$$\psi(\rho, r, \varphi) = \rho^{|m|}\, z^p\, \Psi(\rho, r)\, e^{im\varphi}\,, \qquad m = 0, \pm 1, \pm 2, \ldots\,, \quad p = 0, 1\,, \tag{2.9}$$

for the states with magnetic quantum number m and of positive/negative parity $\nu = +/-$, hence, $p = 0, 1$ and $\nu = (-1)^p$, respectively, here $z = \sqrt{r^2 - \rho^2}$, see Fig. 1. The problem is reduced to find the function $\Psi(\rho, r)$, which satisfies the (gauge-rotated) Schrödinger equation

$$-\frac{\hbar^2}{2m_e}\left[\partial_\rho^2 + \frac{2\rho}{r}\partial_{\rho r} + \partial_r^2 + \frac{2|m|+1}{\rho}\partial_\rho + \frac{2(|m|+p+1)}{r}\partial_r\right]\Psi + \left[-\frac{e^2}{r} + \frac{\gamma^2 e^2}{8m_e c^2}\rho^2\right]\Psi = \mathcal{E}^{(\infty)}_{m,p}(\gamma^2, e^2, m_e)\,\Psi\,, \tag{2.10}$$

where

$$\mathcal{E}^{(\infty)}_{m,p} = E^{(\infty)}_{m,p} - \frac{|e|\hbar\gamma\, m}{2m_e c}\,,$$

and the magnetic quantum number m plays a role of parameter. From Eq. (2.10), one can explicitly see that $\mathcal{E}^{(\infty)}_{m,p}$, which is equal to the energy with the linear Zeeman term subtracted, should be even function with respect to the magnetic quantum number m,

$$\mathcal{E}^{(\infty)}_{m,p} = \mathcal{E}^{(\infty)}_{-m,p}\,, \tag{2.11}$$

for both positive and negative parity states, hence, $\mathcal{E}^{(\infty)}_{m,p}$ depends on m^2, therefore,

$$E^{(\infty)}_{m,p} = E^{(\infty)}_{-m,p} + \frac{|e|\hbar\gamma\, m}{m_e c}\,. \tag{2.12}$$

In one-dimensional quantum mechanics, this phenomenon was called the *energy reflection symmetry* [26].

The spectra of the Schrödinger Eq. (2.10) consists of the infinite families characterized by different magnetic quantum numbers m, each family splits into two subfamilies of different parities. For fixed m and ν, the energy levels form an infinitely sheeted Riemann surface in the space of magnetic field γ with square-root branch points, hence, there are quasicrossings at real $\gamma \geqslant 0$ and two-level crossings at complex γ's with vanishing discriminant (the Landau-Zener phenomenon, see, e.g., Ref. [3]). Levels with different m's and/or different ν's can intersect without forming square-root branch points (true crossings). Interestingly, at large γ the zone structure occurs, see, e.g., Ref. [4]. In particular, the lowest energy states with nonpositive $m = 0, -1, -2, \ldots$ and of positive parity $(1s_0, 2p_{-1}, 3d_{-2}, \ldots)$ form the zeroth (lowest) Landau zone, while in the case of negative parity $(2p_0, 3d_{-1}, 4f_{-2}, \ldots)$ the first Landau zone occurs. Inside of these zones, for sufficiently large γ the energy levels can be ordered following the decrease of m, these levels never have quasicrossings. Higher Landau zones can be obtained through analytic continuation in γ from the first two. Levels with $m = 0$ define the lower edges of zones.

A. Riccati equation: Ground state

For any magnetic field γ the global ground state is nondegenerate and is characterized by the quantum numbers $m = 0$ and $\nu = +(p = 0)$. It depends on two variables (ρ, r) only. At $\gamma = 0$, it corresponds to $1s_0$ state of the hydrogen atom. At large γ, this state defines the lower edge of the lowest (zero) Landau zone. From now on, we write the ground wave function and its energy, dropping labels corresponding to quantum numbers, presenting them as Ψ and $\mathcal{E}^{(\infty)}$, respectively. Sometimes, this state is denoted as $1s_0$ even for $\gamma \neq 0$. Following (2.10), the equation that determines Ψ and $\mathcal{E}$ reads

$$-\frac{\hbar^2}{2m_e}\left[\partial_\rho^2 + \frac{2\rho}{r}\partial_{\rho r} + \partial_r^2 + \frac{1}{\rho}\partial_\rho + \frac{2}{r}\partial_r\right]\Psi + \left[-\frac{e^2}{r} + \frac{\gamma^2 e^2}{8m_e c^2}\rho^2\right]\Psi = \mathcal{E}^{(\infty)}\,\Psi\,. \tag{2.13}$$

If $\Psi(\rho, r)$ is written in exponential representation,

$$\Psi(\rho, r) = e^{-\Phi(\rho, r)}\,, \tag{2.14}$$

the *phase* $\Phi(\rho, r)$ satisfies a nonlinear partial differential equation of second order,

$$\partial_\rho^2\Phi + \frac{2\rho}{r}\partial_{\rho r}\Phi + \partial_r^2\Phi + \frac{1}{\rho}\partial_\rho\Phi + \frac{2}{r}\partial_r\Phi - (\partial_\rho\Phi)^2 - \frac{2\rho}{r}(\partial_\rho\Phi)(\partial_r\Phi) - (\partial_r\Phi)^2 = \frac{2m_e}{\hbar^2}\left[\mathcal{E}^{(\infty)} + \frac{e^2}{r} - \frac{\gamma^2 e^2}{8m_e c^2}\rho^2\right], \tag{2.15}$$

[1] It should be emphasized that the title *Exact solution for a hydrogen atom in a magnetic field of arbitrary strength* of Ref. [8] is misleading.

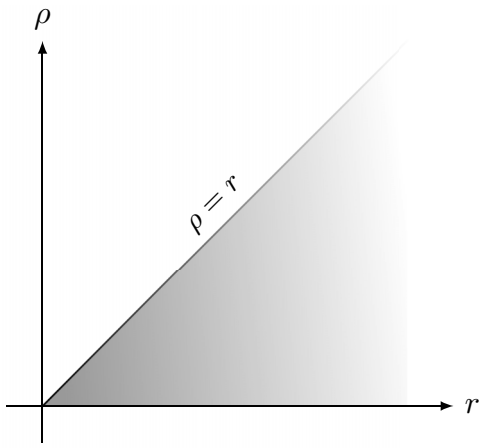

FIG. 2. Domain (shaded in gray) for Eq. (2.15) in (ρ, r) variables.

where $E^{(\infty)} = \mathcal{E}^{(\infty)}$, see (2.11). This equation is defined in the domain $0 \leqslant \rho \leqslant r$ and $0 \leqslant r < \infty$, see Fig. 2. At $\gamma = 0$, this equation can be solved exactly: The solution corresponds to the lowest Coulomb orbital:

$$\Phi_0 \;=\; \alpha r\,,\;\; \mathcal{E}_0^{(\infty)} \;=\; -\frac{\hbar^2}{2m_e}\alpha^2\,,\;\; \alpha \;=\; \frac{m_e\, e^2}{\hbar^2}\,. \qquad (2.16)$$

Note that (2.15) can be regarded as a generalization to two dimensions of the well-known one-dimensional Riccati equation. We will call it *the (two-dimensional) Riccati equation*. Equation (2.15) is the key equation of the present paper.

In Sec. III, we will rewrite the fundamental nonlinear Eq. (2.15) in two forms, introducing two sets of dimensionless variables but with the same effective dimensionless magnetic field λ instead of the original magnetic field $|\mathbf{B}| = \gamma$. One equation is suitable to develop perturbation theory in powers of λ and study the domain of small distances. Another equation can be used to study the domain of large distances and develop semiclassical expansion. This information is important to design our ground-state trial function.

III. FROM RICCATI EQUATION TO RICCATI-BLOCH AND TO GENERALIZED BLOCH EQUATIONS

A. Riccati-Bloch equation

Let us introduce the dimensionless variables

$$s \;=\; \frac{\rho}{a_0}\,,\quad t \;=\; \frac{r}{a_0}\,, \qquad (3.1)$$

where

$$a_0 = \frac{\hbar^2}{m_e\, e^2} \;\simeq\; 5.29\times 10^{-9}\text{cm} \qquad (3.2)$$

is the Bohr radius. In new variables (3.1), the Riccati Eq. (2.15) appears without explicit dependence on parameters c, e, $\hbar$, and m_e,

$$\begin{aligned}\partial_s^2\Phi + \frac{2s}{t}\partial_{st}\Phi + \partial_t^2\Phi \;+\frac{1}{s}\partial_s\Phi + \frac{2}{t}\partial_t\Phi\\ -(\partial_s\Phi)^2 \;-\;\frac{2s}{t}(\partial_s\Phi)(\partial_t\Phi) - (\partial_t\Phi)^2\\ = \varepsilon + \frac{2}{t} \;-\; \frac{\lambda^2 s^2}{4}\,,\end{aligned} \qquad (3.3)$$

where

$$\varepsilon \;=\; \frac{\mathcal{E}^{(\infty)}}{\mathcal{E}_0^{(\infty)}}\,,\quad \mathcal{E}_0^{(\infty)} \;=\; \frac{m_e\, e^4}{2\hbar^2} \qquad (3.4)$$

and

$$\lambda \;=\; \frac{\gamma}{\gamma_0}\,,\quad \gamma_0 \;=\; \frac{c|e|^3 m_e^2}{\hbar^3}\,. \qquad (3.5)$$

Note that $\mathcal{E}_0^{(\infty)}$ is the Rydberg constant—the unit of energy, while γ_0 is the atomic unit of magnetic field (the magnetic field generated by the electron on the Bohr orbit), respectively,

$$\mathcal{E}_0^{(\infty)} \;\approx\; 2.18\times 10^{-18}\text{J} \;=\; 13.6\,\text{eV}\,, \qquad (3.6)$$

$$\gamma_0 \;\approx\; 2.35\times 10^5\,\text{T} \;=\; 2.35\times 10^9\,\text{G}\,. \qquad (3.7)$$

Expressions (3.6) and (3.7) suggest that λ is the magnetic field measured in atomic units γ_0 (a.u.),[2] which occur instead of γ, while ε plays the role of energy measured in rydbergs (Ry).

Equation (3.3) is nothing but the dimensionless version of the Riccati equation, we call it the *Riccati-Bloch (RB) equation* as in Ref. [27] for the case of radial anharmonic oscillators. It is evident that both equations coincide when we set parameters $\hbar = 1$, $m_e = 1$, and $(-e) = 1$. The Riccati-Bloch equation governs the dynamics via the phase Φ in the (s,t)-space. At zero magnetic field $\lambda = 0$, the exact solution of (3.3) reads

$$\Phi_0 \;=\; t\,,\;\; \varepsilon_0 \;=\; -1\,,$$

see (2.16). At $\lambda \to \infty$, the leading behavior of the phase is given by

$$\Phi = \frac{\lambda}{4}s^2 + \ldots$$

and corresponds to the Landau orbital; it is consistent with $\varepsilon = \lambda$.

B. Generalized Bloch equation

Let us introduce in (2.15) a different dimensionless variable u instead of s, keeping t unchanged,

$$u = \frac{\rho}{\rho_0}\,,\quad v = \frac{r}{a_0} = t, \qquad (3.8)$$

where

$$\rho_0 \;=\; \frac{m_e\, c\,|e|}{\hbar\,\gamma} \;=\; \frac{l_\gamma^2}{a_0}, \qquad (3.9)$$

cf. (3.1); $l_\gamma = \sqrt{\frac{\hbar c}{|e|\gamma}}$ is the magnetic length. Note that ρ_0 has explicit dependence on γ, unlike the Bohr radius a_0, being singular at $\gamma = 0$, in turn, the variable v coincides with t, see (3.1) and (3.8). Introducing (3.8) into the Riccati equation (2.15), we obtain a two-dimensional nonlinear equation, we will call it the Generalized Bloch (GB) equation,

$$\begin{aligned}\lambda^2\,\partial_u^2\Phi + \frac{2u}{v}\partial_{uv}\Phi + \partial_v^2\Phi + \frac{\lambda^2}{u}\partial_u\Phi + \frac{2}{v}\partial_v\Phi\\ -\lambda^2(\partial_u\Phi)^2 - \frac{2u}{v}(\partial_u\Phi)(\partial_v\Phi) \;-(\partial_v\Phi)^2\\ = \varepsilon + \frac{2}{v} \;-\; \frac{u^2}{4}\,,\end{aligned} \qquad (3.10)$$

[2]Sometimes, a.u. is defined with $\gamma_0 = 2.3505\times 10^5$ T.

cf. Refs. [27–29], where the potential on the right-hand side does not have any explicit dependence on the parameters of the problem including the magnetic field. The definitions of ε and λ are given in (3.4) and (3.5), respectively. Just as it occurred for the Riccati-Bloch equation, all variables and quantities involved in (3.10) are dimensionless. The GB Eq. (3.10) governs the dynamics via the phase Φ in the (u, v) space. Let us note that variables u and s are related via a remarkably easy relation,

$$u \;=\; \lambda\, s\,, \tag{3.11}$$

which allows us to connect RB and GB equations, see (3.1), (3.5), and (3.8). This relation is $\hbar$ independent: it holds for *any* value of $\hbar$. The variable u looks similar to the classical coordinate introduced in Ref. [28], see also Ref. [27].

IV. PERTURBATION THEORY AND ASYMPTOTIC ANALYSIS

In this section, we will obtain the basic building blocks to construct the ground-state trial function. First, from the Riccati-Bloch equation we will determine the perturbative expansion of the energy ε (3.4) in powers of λ^2 (3.5). Second, we will derive from the Riccati-Bloch and GB equations the exact asymptotic behavior of the phase Φ in (2.14) at small and large distances, respectively. An interpolation of all this information between two limits will lead to our trial ground-state function. The connection between the RB and GB equations will be explained as well.

A. Weak magnetic field expansion from the Riccati-Bloch equation

One of the ways to study the RB Eq. (3.3) in weak magnetic field regime is to develop perturbation theory (PT) in powers of λ^2,

$$\Phi(s,t;\lambda^2) \;=\; \sum_{n=0}^{\infty} \lambda^{2n} \Phi_n(s,t), \quad \varepsilon(\lambda^2) \;=\; \sum_{n=0}^{\infty} \lambda^{2n} \varepsilon_n\,, \tag{4.1}$$

where the zero-order approximation

$$\Phi_0(s,t) \;=\; t, \quad \varepsilon_0 \;=\; -1\,, \tag{4.2}$$

see (2.16), corresponds to the phase and energy of the $1s_0$ ground state of the hydrogen atom at $\gamma = 0$, respectively. It must be emphasized that if $c = 1$, $m_e = 1$, and $e = -1$, the coupling constant is equal to $\lambda = \gamma\hbar^3$ and the PT for energy ε in powers of γ coincides (!) with semiclassical expansion in powers of $\hbar^3$. Corrections ε_n are numbers. This statement is not valid for the perturbation expansion of phase Φ: the nth correction depends explicitly on the Planck constant, $\Phi_n = \Phi_n(\rho\hbar^{-2}, r\hbar^{-2})$.

The nth-order corrections Φ_n and ε_n at $n \geqslant 1$ are determined by a linear partial differential equation,

$$\begin{aligned} &\partial_{ss}\Phi_n + \frac{2s}{t}\partial_{st}\Phi_n + \partial_{tt}\Phi_n \\ &\quad + \left(\frac{1}{s} - \frac{2s}{t}\right)\partial_s\Phi_n \;+ \left(\frac{2}{t} - 1\right)\partial_t\Phi_n \\ &\quad = \varepsilon_n \;-\; Q_n\,, \end{aligned} \tag{4.3}$$

where, on the right-hand side,

$$Q_1 \;=\; \frac{s^2}{4}$$

plays the role of perturbation and at $n > 1$,

$$\begin{aligned} Q_n \;=\; -\sum_{k=1}^{n-1} \Big[&\partial_s\Phi_k\partial_s\Phi_{n-k} + \partial_t\Phi_k\partial_t\Phi_{n-k} \\ &+ \frac{s}{t}(\partial_s\Phi_k\partial_t\Phi_{n-k} + \partial_t\Phi_k\partial_s\Phi_{n-k})\Big] \end{aligned}$$

is defined by the previous corrections as well as the energy correction:

$$\varepsilon_n = \frac{\int Q_n e^{-2\Phi_0} dV}{\int e^{-2\Phi_0} dV}\,.$$

Eventually, the scheme leads to iterative procedure. The first-order correction is

$$\Phi_1(s,t) \;=\; \tfrac{1}{24}s^2 t + \tfrac{1}{16}s^2 + \tfrac{1}{24}t^2, \quad \varepsilon_1 \;=\; \tfrac{1}{2}\,. \tag{4.4}$$

In general, the nth correction Φ_n has the form of a polynomial in variables (s,t) of the following structure:

$$\begin{aligned} &\Phi_n(s,t) = \sum_{j=0}^{n-1}\sum_{k=j}^{n} \left(a_{j,k}^{(n)} t + \; b_{j,k}^{(n)}\right) (s^2)^{(n-k)}\,(t^2)^{(k-j)}, \\ &\quad a_{0,n}^{(n)} = 0\,. \end{aligned} \tag{4.5}$$

By substituting (4.5) in Eq. (4.3), we arrive at the system of recurrence equations. Energy corrections ε_n are found following the consistency of the procedure and related to lowest order coefficients of Φ_n. Interestingly, for any $n > 1$, the relation

$$\varepsilon_n \;=\; 4\, b_{n-1,n-1}^{(n)} + \; 6\, b_{n-1,n}^{(n)} \tag{4.6}$$

holds. It is clear that for any integer n the coefficients $a_{j,k}^{(n)}$ and $b_{j,k}^{(n)}$ are rational numbers. Hence, the energy correction ε_n is also a rational number. Several corrections can be easily computed in this framework as a consequence of the polynomial nature of Φ_n in (s,t) variables. The coefficients a and b in (4.5) are determined by solving recurrence relations by algebraic means. The construction of perturbation theory is ultimately an algebraic procedure. A finite number of terms in expansions (4.1) can be calculated explicitly. In Appendix A, the first three corrections in the expansion of the phase Φ for $n = 2, 3, 4$ are presented. In turn, the expansion of ε in powers of λ is easily computed up to 100th order in the form of rational numbers using MATHEMATICA 12, see Tables VI and VII. Following the Dyson instability argument [30], in (s,t)-space (3.1) both series (4.1) should be divergent. Using multidimensional semiclassical analysis, the asymptotic behavior of ε_n at large order was found [31,32] in the form of $1/n$ expansion

$$\begin{aligned} &\varepsilon_n = 64\,\frac{(-1)^{n+1}}{\pi^{\frac{5}{2}+2n}}\,\Gamma\left(2n+\frac{3}{2}\right)\left(1 \;-\; \frac{A}{n} + \; O\left(\frac{1}{n^2}\right)\right), \\ &\quad n \to \infty\,, \end{aligned} \tag{4.7}$$

with $A > 0$. Thus, it has the index of divergence equal to 2: $\varepsilon_n \sim (n!)^2$. The $1/n$ expansion demonstrates a convergence, for example, at $n = 70\,100$; the leading contribution in (4.7)

agrees with exact $\varepsilon_{70\,100}$ in about two SDs (depending on rounding),[3] see Table VII. The next-to-leading term in (4.7) with $A = 2.61$ improves the agreement to four to five SDs. In spite of the fact that PT for ε is Borel summable, one of the best known summation procedures for an asymptotic series—the Padé-Borel procedure, see, e.g., Ref. [33]—does not provide accurate results for large $\gamma \gtrsim 10$ a.u. even taking into account the first hundred terms ε_{1-100}, although, at small $\gamma \lesssim 1$ a.u., it leads to accurate results providing 11 decimal digits (d.d.) correct (or more), see below Table II for $\gamma = 1$ a.u. as the example.

Following Eq. (4.6), the coefficients $b^{(n)}_{n-1,n-1}$ and $b^{(n)}_{n-1,n}$ grow factorially a large n. It is worth mentioning that the perturbative approach used to solve the Riccati-Bloch equation is nothing but an application of the so-called nonlinearization procedure [15] (sometimes referred to for the ground-state case as the logarithmic perturbation theory). The general description can be found in Ref. [34].

1. Behavior of phase Φ at small distances

The structure of the Taylor series of the phase Φ at small s and t can be obtained from the polynomial form of the correction Φ_n, see (4.5). Collecting the same degrees in s and t coming from different corrections Φ_n, their formal sums result in expansion

$$\Phi(s,t;\lambda^2) = t + \sigma_1(\lambda^2)\, s^2 + \sigma_2(\lambda^2)\, t^2 + \sigma_3(\lambda^2)\, s^2 t + \ldots, \quad (s,t) \to 0\,, \tag{4.8}$$

where the first functions σ_1, σ_2, and σ_3 are given by

$$\sigma_1(\lambda^2) = \sum_{n=1}^{\infty} b^{(n)}_{n-1,n-1}\lambda^{2n}\,, \quad \sigma_2(\lambda^2) = \sum_{n=1}^{\infty} b^{(n)}_{n-1,n}\lambda^{2n}\,,$$
$$\sigma_3(\lambda^2) = \sum_{n=1}^{\infty} a^{(n)}_{n,n-1}\lambda^{2n}\,. \tag{4.9}$$

From Eq. (4.6), it is clear that

$$\varepsilon(\lambda^2) = -1 + 4\,\sigma_1(\lambda^2) + 6\,\sigma_2(\lambda^2). \tag{4.10}$$

From Taylor series (4.8), once variables ρ and r are restored, one can immediately conclude that the presence of a magnetic field does not break the *cusp condition* for the exact ground-state function:

$$C \equiv -\frac{\langle\psi \mid \delta(\vec{r})\frac{\partial}{\partial r} \mid \psi\rangle}{\langle\psi \mid \delta(\vec{r}) \mid \psi\rangle} = \frac{1}{a_0}\,. \tag{4.11}$$

In atomic physics, the parameter C is known as the *cusp parameter*. For nonexactly solvable Coulomb systems which consist of electrons and (infinitely massive) positive charged nuclei, this parameter is used to *measure* the local quality of the approximate wave function near the Coulomb singularities. This parameter has a meaning of residue at the Coulomb singularity. The easiest way to find the cusp parameter in an approximate trial function is to calculate the coefficient (the slope) standing in front of the linear in r term at small r behavior of the phase.

[3]It contradicts the statement in Ref. [32] about the agreement in nine SDs.

B. The weak magnetic field expansion from the generalized Bloch equation

One of the ways to solve the GB equation (3.10) is to develop PT in powers of λ^2,

$$\Phi(u,v;\lambda^2) = \sum_{n=0}^{\infty}\lambda^{2n}\phi_n(u,v) \quad , \quad \varepsilon(\lambda^2) = \sum_{n=0}^{\infty}\lambda^{2n}\varepsilon_n\,, \tag{4.12}$$

where the expansion for ε coincides with one presented in (4.1). The zero-order approximation $\phi_0(u,v)$ is determined by the nonlinear partial differential equation of the second order,

$$\frac{2u}{v}\partial_{uv}\phi_0 + \partial_v^2\phi_0 + \frac{2}{v}\partial_v\phi_0 - \frac{2u}{v}(\partial_u\phi_0)(\partial_v\phi_0) - (\partial_v\phi_0)^2 = \varepsilon_0 + \frac{2}{v} - \frac{u^2}{4}\,, \tag{4.13}$$

at $\varepsilon_0 = -1$. Surprisingly, it can be solved explicitly in closed analytic form,

$$\phi_0(u,v) = A_0^{(0)}(u)\,v + B_0^{(0)}(u)\,, \tag{4.14}$$

where

$$A_0^{(0)}(u) = \sqrt{1+\frac{u^2}{12}},$$
$$B_0^{(0)}(u) = \frac{1}{2}\ln\left(1+\frac{u^2}{12}\right) + \ln\left(1+\sqrt{1+\frac{u^2}{12}}\right).$$

It is convenient to introduce a new variable,

$$w = \sqrt{1+\frac{u^2}{12}} \geqslant 1\,, \tag{4.15}$$

that allows us to represent the zero-order approximation ϕ_0 in compact form,

$$\phi_0(u,v) = w\,v + \ln[w\,(1+w)]\,. \tag{4.16}$$

The $\phi_0(u,v)$ plays a role of classical action, although the classical trajectory is unknown. Evidently, the function $\Psi_0 = e^{-\phi_0(u,v)}$ is square integrable; it can be taken as variational trial function to study $(1s_0)$ state, see below. The correction $\phi_n(u,v)$, $n = 1, 2, \ldots$ obeys a linear partial differential equation,

$$\frac{2u}{v}\partial_{u,v}\phi_n + \partial_v^2\phi_n + \frac{2}{v}\partial_v\phi_n - \frac{2u}{v}(\partial_u\phi_0\,\partial_v\phi_n + \partial_u\phi_n\,\partial_v\phi_0) - 2(\partial_v\phi_n\,\partial_v\phi_0) = \varepsilon_n - q_n, \tag{4.17}$$

where

$$q_n = \partial_u^2\phi_{n-1} + \left(\frac{1}{u} - \partial_u\phi_0\right)\partial_u\phi_{n-1} - \sum_{k=1}^{n-1}\left\{\partial_u\phi_{n-k-1}\partial_u\phi_k + \frac{2u}{v}\partial_u\phi_{n-k-1}\partial_v\phi_k + \partial_v\phi_{n-k-1}\partial_v\phi_k\right\}. \tag{4.18}$$

It can be shown that the correction $\phi_n(u, v)$ is a polynomial in v of degree $(2n+1)$ with u-dependent coefficients:

$$\phi_n(u, v) = \sum_{k=0}^{n}\left\{A_k^{(n)}(u)\, v + B_k^{(n)}(u)\right\}v^{2(n-k)}. \tag{4.19}$$

Functions $A_k^{(n)}(u)$ and $B_k^{(n)}(u)$ are determined by solving (ordinary) linear differential equations of the first degree. In particular,

$$-\phi_1(u, v) = A_0^{(1)}(u)\, v^3 + B_0^{(1)}(u)\, v^2 + A_1^{(1)}(u)\, v + B_1^{(1)}(u), \tag{4.20}$$

where the coefficients can be written conveniently in variable w (4.15) as follows:

$$\begin{aligned}
A_0^{(1)} &= \frac{(w-1)(w+1)}{120\, w^3}, \\
B_0^{(1)} &= \frac{6w^3 - w^2 - 9w - 6}{120\,(w+1)\, w^4}, \\
A_1^{(1)} &= \frac{(w-1)(30w^4 + 52w^3 + 54w^2 + 42w + 15)}{120\,(w+1)\, w^5}, \\
B_1^{(1)} &= \frac{(w-1)(9w^6 + 18w^5 + 38w^4 + 46w^3 + 42w^2 + 30w + 10)}{80\,(w+1)\, w^6}.
\end{aligned}$$

Several next-order corrections $\phi_2, \phi_3, \ldots$ can also be calculated explicitly; for all of them, the coefficients A and B appear usually as rational functions in w.

In the next subsection, some properties of functions $A_k^{(n)}(u)$ and $B_k^{(n)}(u)$ related with their asymptotic behavior at large u and v are presented.

1. Asymptotic behavior of Φ for large distances

Using the perturbation theory corrections obtained from the GB equation (3.10), asymptotic expansions can be calculated along particular directions in the plane (s, t). Let us consider the line

$$s = \alpha\, t, \tag{4.21}$$

where $\alpha \in (0, 1]$ is a parameter. One can see that along this line (by keeping the value of α fixed), the dominant asymptotic behavior of the nth correction to the phase, see (4.12),

$$\phi_n(u, v)|_{v=t} = \phi_n(\lambda s, t)|_{s=\alpha t}, \tag{4.22}$$

where the relation (3.11) is taken into account, at large t comes from the term $A_0^{(n)}(\lambda(\alpha t))t^{2n+1}$ in (4.19), leading to

$$\phi_n(\lambda\, s, t)_{s=\alpha t} \sim \frac{\mathcal{A}_n}{(\alpha\lambda)^{2n-1}}\, t^2 + O\big(t^0\big), \quad t \to \infty, \quad n = 0, 1, 2, \ldots, \tag{4.23}$$

where in the dominant term the coefficients $\mathcal{A}_n$ for the first three corrections $n = 0, 1, 2$ are

$$\mathcal{A}_0 = \frac{1}{2\sqrt{3}}, \quad \mathcal{A}_1 = -\frac{1}{20\sqrt{3}}, \quad \mathcal{A}_2 = -\frac{23}{2800\sqrt{3}}.$$

Finally, from (4.23), one can find the behavior of $\Phi(\lambda\, s, t)|_{s=\alpha t}$,

$$\Phi(\lambda\, s, t)_{s=\alpha t} = \lambda\alpha\left(\sum_{n=0}^{\infty}\mathcal{A}_n\alpha^{-2n}\right)t^2 + 2\ln(t) + \ldots, \quad t \to \infty, \tag{4.24}$$

where the logarithmic term comes from the $B_0^{(0)}(u)$, see (4.14). To determine the sum in (4.24), we can define the generating function

$$\mathcal{A}(\alpha) = \alpha\sum_{n=0}^{\infty}\mathcal{A}_n\alpha^{-2n}, \tag{4.25}$$

which satisfies the Riccati equation,

$$(1-\alpha^2)\,(\mathcal{A}')^2 + 4\,\mathcal{A}^2 - \tfrac{1}{4}\,\alpha^2 = 0, \quad \mathcal{A}(1) = \tfrac{1}{4}. \tag{4.26}$$

This equation can be solved in closed analytic form:

$$\mathcal{A}(\alpha) = \tfrac{1}{4}\,\alpha^2. \tag{4.27}$$

Hence, the behavior of the phase (4.22) at $t \to \infty$ results in

$$\Phi(\lambda\, s, t)|_{s=\alpha t} = \tfrac{1}{4}\,\alpha^2\,\lambda\, t^2 + 2\ln(t) + O(t^0), \quad t \to \infty. \tag{4.28}$$

Some other limits in different directions can be also studied. For example, if s is fixed, $s = s_0$, the asymptotic behavior at large t is of the form

$$\Phi(s_0, t) = C_0(s_0, \lambda)\, t + C_1(s_0, \lambda)\ln t + O(t^0), \quad t \to \infty. \tag{4.29}$$

where constants C_1 and C_2 are unknown generally.

C. Connection between Riccati-Bloch and generalized Bloch equations

We have constructed two different representations for the phase Φ (2.14) of the ground-state wave function. From the RB equation, we obtain

$$\Phi(s,t;\lambda^2) \;=\; \sum_{n=0}^{\infty} \lambda^{2n} \Phi_n(s,t)\,, \quad s \;=\; \frac{\rho}{a_0}\,, \quad t \;=\; \frac{r}{a_0}\,, \tag{4.30}$$

while from the GB equation

$$\Phi(u,v;\lambda^2) \;=\; \sum_{n=0}^{\infty} \lambda^{2n} \phi_n(u,v)\,, \quad u \;=\; \frac{\rho}{\rho_0}\,, \quad v \;=\; \frac{r}{a_0}\,, \tag{4.31}$$

where a_0 and ρ_0 are defined in (3.2) and (3.9), respectively.

It is clear that there must exist a connection between corrections $\Phi_n(s,t)$ and $\phi_n(u,v)$. To establish it, we use the polynomial representation of corrections (4.5) in (4.30)

$$\Phi \;=\; \sum_{n=0}^{\infty} \lambda^{2n} \sum_{j=0}^{n} \sum_{k=j}^{n} \left(a_{j,k}^{(n)}\, t \;+\; b_{j,k}^{(n)}\right) s^{2(n-k)} t^{2(k-j)}\,, \tag{4.32}$$

then change the order of summation and use the relation (3.11) between variables s and u. As the result, we arrive at

$$\Phi \;=\; \sum_{n=0}^{\infty} \lambda^{2n} \sum_{k=0}^{n} \sum_{j=n}^{\infty} \left(a_{k,n}^{(j)}\, v \;+\; b_{k,n}^{(j)}\right) u^{2(j-n)} v^{2(n-k)}\,. \tag{4.33}$$

Comparing (4.31) and (4.33), one can conclude that

$$\phi_n(u,v) \;=\; \sum_{k=0}^{n} \sum_{j=n}^{\infty} \left(a_{k,n}^{(j)}\, v \;+\; b_{k,n}^{(j)}\right) u^{2(j-n)} v^{2(n-k)}\,. \tag{4.34}$$

Eventually, after simple manipulations, Eq. (4.34) can be written as follows:

$$\phi_n(u,v) \;=\; \sum_{k=0}^{n} v^{2(n-k)} \sum_{j=0}^{\infty} \left(a_{k,n}^{(n+j)}\, v \;+\; b_{k,n}^{(n+j)}\right) u^{2j}\,. \tag{4.35}$$

Making a comparison (4.19) and (4.35), we see explicitly that

$$A_k^{(n)}(u) \;=\; \sum_{j=0}^{\infty} a_{k,n}^{(n+j)} u^{2j} \tag{4.36}$$

and

$$B_k^{(n)}(u) \;=\; \sum_{j=0}^{\infty} b_{k,n}^{(n+j)} u^{2j}\,. \tag{4.37}$$

Therefore, the meaning of the connection between the expansion of phase in GB and Riccati-Bloch equations is the following: the coefficient functions $A_k^{(n)}(u)$ and $B_k^{(n)}(u)$ are nothing but the generating functions of the coefficients $a_{k,n}^{(n+j)}$ and $b_{k,n}^{(n+j)}$, respectively. A similar connection exists for anharmonic oscillators [15,27].

V. THE APPROXIMANT

A. Approximant of the ground state

The analytical information for the phase (2.14), obtained from the Riccati-Bloch and GB equations, Taylor expansion at small distances and asymptotic series for large distances, will now be used to design the *approximant*: an approximation of the exact (unknown) ground-state wave function ($1s_0$), denoted by $\Psi^{(t)}$, in the form of interpolations of different expansions. To do so, we follow the prescription proposed in Refs. [15,34], further developed and applied in Refs. [27,35,36], where the approximant was successfully constructed for a 1D anharmonic oscillator and double-well potential, for the D-dimensional radial polynomial anharmonic oscillator, and some other potentials.

We assume the exponential representation (2.14) for the approximant in coordinates (ρ, r),

$$\Psi^{(t)}(\rho,r) \;=\; e^{-\Phi_t(\rho,r)}\,, \tag{5.1}$$

and focus on the construction of $\Phi_t(\rho,r)$. According to the prescription, the approximate phase has to interpolate the expansions at small and large distances, see (4.8), (4.28), and (4.29). In addition, the zero-order approximation ϕ_0 in the GB equation, see (4.14), should be reproduced for particular values of parameters as well as the first terms in weak magnetic field expansions. Following the reflection symmetry ($\rho \to -\rho$), which holds in RB and GB equations, Φ_t has to be a function of ρ^2. One of the simplest interpolations, which accomplishes the prescription given above, is of the form

$$\begin{aligned}\Phi_t(\rho,r) \;=\; & \frac{\alpha_0 \;+\; \alpha_1\, r \;+\; \alpha_2\, r^2 \;+\; \alpha_3\, \gamma\, \rho^2 + \alpha_4\, \gamma\, \rho^2\, r}{\sqrt{1 + \beta_0 w + \beta_1\, r + \beta_2\, r^2 + \beta_3\, \rho^2}} \\ & +\; q \ln(1 + \beta_0 w + \beta_1\, r + \beta_2\, r^2 + \beta_3\, \rho^2)\,,\end{aligned} \tag{5.2}$$

where $\{\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \beta_0, \beta_1, \beta_2, \beta_3; q\}$ are ten free parameters that later will be fixed in variational calculation, $w = \sqrt{1 + \frac{\gamma^2 \rho^2}{12}}$, see (4.15). We call it the *phase approximant*. Making straightforward preliminary minimizations, we found that for all studied magnetic fields up to 10 000 a.u. the parameter β_0 is extremely small and parameter q is invariably close to 1.[4] Thus, without losing much in accuracy in variational energy, we put $\beta_0 = 0$ and $q = 1$ from the very beginning in trial function (5.3), see below, which becomes eight-parametric in the minimization procedure. Interestingly, the deviation of q from 1 and β_0 from 0 influences far distant d.d. in energy, although it significantly improves the cusp parameter $C^{(t)}$ (4.11) making it closer to the exact value $C^{(\text{exact})} = 1$. Releasing those parameters makes the minimization procedure much more complicated and slow. It will be checked for two magnetic fields, 1 a.u. and 10 000 a.u. only.

The logarithmic term (5.2) is included to mimic the appearance of logarithmic terms in the exact wave function treated in the GB equation at $\lambda \to 0$, see (4.14). It will generate a prefactor in the approximate wave function, which ultimately

[4] In detailed minimization, it was found that at large magnetic fields $\gamma > 100$ a.u., the parameter q jumps sharply down to zero, while the variational energies at $q = 1$ and $q = 0$ are very close. The present authors have no explanation for this phenomenon.

is given by

$$\Psi^{(t)}_{1s_0}(\rho, r) = \frac{1}{(1+\beta_0 w+\beta_1 r+\beta_2 r^2+\beta_3 \rho^2)^q} \exp\left(-\frac{\alpha_0+\alpha_1 r+\alpha_2 r^2+\alpha_3 \gamma \rho^2+\alpha_4 \gamma \rho^2 r}{\sqrt{1+\beta_0 w+\beta_1 r+\beta_2 r^2+\beta_3 \rho^2}}\right). \tag{5.3}$$

This is the key expression for the trial function which is going to be used throughout this paper. We have labeled the approximant (5.3) with $(1s_0)$, using the standard notation for the ground state of hydrogen atoms in the absence of magnetic field. Calculations are made mainly with an eight-parametric trial function (5.3) with $\beta_0 = 0$ and $q = 1$. The ten-parametric trial function (5.3) with both β_0, q as variational parameters is used for two magnetic fields $\gamma = 1$ and 10^4 a.u. only to estimate the maximal accuracy which can be reached with it, see discussion above.

Note that the reduced and modified versions of the trial function (5.3) [and the trial phase (5.2)] appeared in previous investigations:

(i) If $\beta_0 = \beta_1 = \beta_2 = \beta_3 = 0$, thus, the prefactor is reduced to one, if $\alpha_0 = \alpha_2 = \alpha_4 = 0$, this function becomes the product of the ground-state Coulomb orbital and the ground-state Landau orbital, see Ref. [15]; if $\alpha_0 = \alpha_1 = \alpha_4 = 0$, the function becomes one which was originally proposed by Yafet *et al.* [11].

(ii) If $\beta_1 = \beta_2 = \beta_3 = 0$ and $\alpha_0 = 0$ [14], in spite of giving wrong asymptotic behavior at large distances, this function provided sufficiently high accuracy at small magnetic fields which then deteriorated with magnetic field increase: At $\gamma =$ 100 a.u. it reproduces in the ground-state energy three SDs only.

(iii) For $\beta_1 = \beta_2 = \beta_3 = 0$, there were other attempts to modify the numerator in the first term in (5.2), see, e.g., Refs. [16,17], to keep functionally correct asymptotic behavior at large distances and adding as many as possible free parameters; none of these attempts allowed us to get accurate results for energy beyond two to three SDs for magnetic fields larger than 10 a.u.

(iv) In 2007, one of the present authors (A.V.T., see Ref. [18]) demonstrated that even keeping the prefactor in (5.3) *equal to one*, $q = 0$ [thus, no logarithmic term in (5.2)] and taking $\alpha_0 = \beta_1 = 0$ in the exponent (thus, having in total six free parameters) allows for $\gamma = 10\,000$ a.u. to obtain the variational energy 9972.05 a.u., which differs from the exact value in the fifth SD; recently, another of the present authors (J.C.dV., see Ref. [37]) carrying out more accurate minimization procedures was able to improve the above result up to 9971.95 a.u. and then performed variational studies in the whole domain $\gamma \in [0, 10\,000]$ a.u., reaching the accuracy of three to four SDs (which was even higher for weak magnetic fields).

(v) It is worth noting that if $\beta_1 = \beta_2 = 0$, $\alpha_0 = \alpha_2 = \alpha_3 = 0$, and $q = 1$, then for $\alpha_1 = 1$ and $\gamma\,\alpha_4 = \beta_3 = \frac{1}{12\,\rho_0^2}$ the nonlogarithmic term in (5.2) coincides to the nonlogarithmic term of zero-order approximation $A_0^{(0)}(u)\,v$ (4.14) to GB equation while the logarithmic terms in $B_0^{(0)}(u)$ coincide with logarithmic term in (5.2) at $\beta_0 = 1$. Hence, the trial function (5.3) is reduced to

$$\Psi_0 = \frac{1}{\left(1+\sqrt{1+\frac{\gamma^2\rho^2}{12}}+\frac{\gamma^2\rho^2}{12}\right)} e^{-r\sqrt{1+\frac{\gamma^2\rho^2}{12}}}, \tag{5.4}$$

which contains no free parameters. This function leads to very accurate energies at $\gamma \leqslant 1$ a.u., see below, Table II, but fails for larger γ. Surprisingly, if the prefactor in (5.4) is dropped by putting $q = 0$ in (5.2) and (5.3), then the amazingly simple, parameter-free function

$$\Psi_1 = e^{-r\sqrt{1+\frac{\gamma^2\rho^2}{12}}} \tag{5.5}$$

leads to reasonably accurate energies for $\gamma \geqslant 10$ a.u. [16]. For both formulas (5.4) and (5.5), the value of the cusp parameter is exact, being equal to 1 for all γ.

As was indicated before, the variational method allows us to fix the values of the free parameters of the approximant (5.3) by minimizing variational energy $E_{\rm var}$: The parameter-dependent, expectation value of the Hamiltonian (2.3) over trial function (5.3) is calculated, which is then minimized. The variational principle guarantees that the variational energy gives an upper bound of the exact energy, $E_{\rm var} \geqslant E_{\rm exact}$. However, it is still an open question how close the variational energy is to the exact one. Hence, the quality of the variational results should be checked by making a comparison with reliable established data obtained independently. Such data are supplied by the LMM [9], which is proved to be among the most reliable numerical methods, where convergence can be easily established.

1. Lagrange mesh method: Results

In this section, we will consider the hydrogen atom in a constant magnetic field in the LMM, for a review see Ref. [9], which is an alternative to the variational method to establish benchmark results.

It has been known for quite some time that LMM is a highly accurate method leading to benchmark results and also simple to implement in order to solve the Schrödinger equation, see Ref. [19]. Using the formulation of the method in spherical coordinates (r, θ, ϕ) presented in Ref. [19], Sec. 2.5, we calculated the ground state energy and its quadrupole moment for magnetic fields in the range $\gamma \in [0.01, 10\,000]$ a.u. Since the Schrödinger equation for the ground state is essentially two-dimensional: ϕ dependence is absent, the mesh is realized on the plane parametrized by r and $u = \cos\theta$. We implemented the LMM in MATHEMATICA 12. For the whole range of studied magnetic fields the mesh was kept unchanged and consisted of $N_r = 80$ radial functions and $N_u = 200$ angular ones. Hence, the approximate ground state function is represented by the expansion in terms of $80 \times 200 = 16\,000$

TABLE I. Energies $E^{(\infty)}$ (2.6) and $E^{(m_p)}$ (6.18) in Ry and quadrupole moment $Q_{zz}^{(\infty)}$ in (a.u.)^2 for the ground state $1s_0$ of the static hydrogen atom in magnetic field $\gamma \in [0.01, 10000]$ in a.u. found in variational method with eight-parametric trial function (5.3) ($q = 1, \beta_0 = 0$) and comparison with results of other calculations (rounded), confirmed and established in LMM.

γ (a.u.)	$E^{(\infty)}$	$E^{(m_p)}$	$-Q_{zz}^{(\infty)}$
0	−1.000 000 000 000	−0.999 455 679 426	0.000 000
0.01	−0.999 950 005 51	−0.999 405 603 19	0.000 248
	−0.999 950 005 52 [a,c]		0.000 249 [c]
0.1	−0.995 052 960 5	−0.994 500 663 9	0.023 270
	−0.995 052 960 8 [a,c]		0.023 2712 [c]
0.5	−0.894 421 065	−0.893 731 173	0.256 143
	−0.894 421 075 [a,c]		0.256 156 21 [c]
1.0	−0.662 337 66	−0.661 393 27	0.417 618
	−0.662 337 70	−0.661 393 31	0.417 635 (*)
	−0.662 337 79 [a,b]		0.417 654 [b]
2.0	−0.044 426 7	−0.042 924 9	0.511 354
	−0.044 427 8 [a,c]		0.511 432 [c]
γ_c	0.000 001	0.001 540	0.513 561
	0.000 000 [c]		0.513 537 [c]
5.0	2.239 209	2.242 422	0.506 493
	2.239 202 [a,c]		0.506 331 [c]
10.0	6.504 427	6.510 476	0.445 22
	6.504 405 [a,b]		0.445 09 [b]
100.0	92.420 7	92.476 6	0.217 5
	92.420 4 [a,b]		0.216 8 [b]
500.0	487.487 31	487.762	0.125 1
	487.485 95		0.123 87 (†)
	487.485 82 [a,c]		0.123 87 [c]
1 000.0	984.678	985.226	0.099 4
	984.675 153 504 [a]		
	984.675 153 511 [c]		0.098 160 [c]
	984.675 153 507 [d]		0.098 160 [d]
10 000.0	9 971.74	9 977.22	0.049 3 ($q = 1, \beta_0 = 0$)
	9 971.72	9 977.18	0.049 1 ($q = 0, \beta_0 = 0$)
	9 971.718 490	9 977.173	0.048 5 (**)
	9 971.72 [c]		0.047 9 [c]
	9 971.718 316 [e]		

*Equation (5.3), ten parameters, $q = 0.994509$, $\beta_0 = 0.0000000036$, see Table II.
†Equation (5.3), ten parameters, $q = -0.130\,064$, $\beta_0 = 0.003\,583$.
**Equation (5.3), ten parameters, $q = -0.089408$, $\beta_0 = 0.000029$.
$\gamma_c = 2.065\,211\,858$.
[a]Power series: method of moments [8].
[b]Lagrange mesh [19].
[c]Lagrange mesh (present paper, 16 K mesh points).
[d]Lagrange mesh (present paper, 80×240 mesh points),
[e]Basis of Splines [38].

functions. With this enormous mesh we are able to reproduce and confirm the results obtained for all magnetic fields studied in previous LMM calculation [19]: 1, 10, 100 and 1 000 a.u. and furthermore improve them, see Table I. It is shown in Table I the maximal number of figures obtained by other methods which are in agreement with the LMM results. It ranges from 11 figures for $\gamma = 0.01$ a.u. up to six figures for 10 000 a.u. From the point of physics, such accuracies are excessive since finite mass contribution changes usually the fourth figure, see a discussion in Sec. VI.

In general, for $\gamma \lesssim 1\,000$ a.u. the LMM allows to reach the accuracy in energy of 10 figures (or more) giving benchmark results except for the outstanding results by Stubbins *et al.* [10] which are checked and confirmed with high accuracy, see, e.g., Table II. The maximum accuracy in energy—19 figures—is reached for magnetic fields $\gamma \lesssim 1$ a.u., see, e.g., Table II as for $\gamma = 1$ a.u. However, for large magnetic fields $\gamma \gtrsim 1\,000$ a.u., the accuracy begins to reduce dramatically. For example, at $\gamma = 10\,000$ a.u. it reaches only six figures. The results for energy and quadrupole moments are shown in Table I. It must be emphasized that for quadrupole moments, the LMM—the present calculation and one performed in Ref. [19]—leads to benchmark results.

To check the local accuracy of the solution for the eigenfunction of the Schrödinger equation obtained in the LMM, one can calculate the cusp parameter C (4.11). As a result, the calculated cusp parameter C deviates from the exact value,

TABLE II. The ground-state energy $E^{(\infty)}$ in Ry for the static hydrogen atom at magnetic field $\gamma = 1$ a.u. obtained by different methods. The results are ranked by accuracy. Rounding up to digits relevant for comparison performed, excessive digits not confirmed by the most accurate calculations not shown. Digits beyond the 12th decimal having no chance to be verified experimentally at present times (see text) shown by italics. Mass effects change fourth d.d., see Table I. Result by present paper marked by bold.

Reference	$E^{(\infty)}$	Method
[11] Yafet *et al.*, 1956	−0.523	Variational
[15] Turbiner, 1984	−0.61	Variational
[12] Larsen, 1968	−0.661	Variational
[40] Praddaude, 1972	−0.662 33	Power series
[17] Potekhin and Turbiner, 2001	−0.662 332	Variational
Present paper, see (5.3)	**−0.662 337 66**	**Variational** (eight parameters) [a]
Present paper, see (5.3)	**−0.662 337 70**	**Variational** (ten parameters)
[38] Wang and Hsue, 1995	−0.662 337 785	B splines
Present paper	**−0.662 337 793 46**	**Padé-Borel** (100 coeffs)
[8] Kravchenko *et al.*, 1996	−0.662 337 793 466	Method of moments
[19] Baye *et al.*, 2008	−0.662 337 793 466 *315 9*	Lagrange mesh
Present paper	**−0.662 337 793 466** *316 071 2*	**Lagrange mesh, 16 K mesh points**
[10] Stubbins *et al.*, 2004	−0.662 337 793 466 *316 6*	Variational (multiconfiguration)

[a] $q = 1$, $\beta_0 = 0$.

$C^{(\text{exact})} = 1$, in the sixth d.d. in the whole range of magnetic fields considered.

2. Variational results

For simplicity, we set $c = \hbar = e = m_e = 1$ in numerical computations, see (3.4). To calculate the expectation value of the Hamiltonian over the trial function (5.3) and minimize it with respect to free parameters to get the optimal variational energy, we need to perform the numerical integration and then minimization. The computer code was written in FORTRAN 77 with use of the integration routine D01FCF from NAG-LIB employing the minimization routine MINUIT from CERN-LIB. Resulting variational parameters versus magnetic field are presented in Appendix B, Fig. 4. Variational energies are shown in Table I for different magnetic fields in the range $\gamma \in [0.01, 10\,000]$ a.u.

Our variational calculations with trial function (5.3) are compared with accurate results known in the past, in particular, with those obtained in the LMM [9] in Ref. [19], which are extended and improved in the present paper, see Sec. G.1. Special attention was paid to the *critical magnetic field* γ_c, for which the ground-state energy (2.6) vanishes:

$$E^{(\infty)}(\gamma_c) \;=\; 0\,.$$

The value of γ_c, obtained in the LMM results in

$$\gamma_c^{(\text{LMM})} \;=\; 2.065\,211\,858\,\text{a.u.}\,, \tag{5.6}$$

with $E^{(\infty)}_{\text{LMM}}(\gamma_c) \;\sim\; 10^{-10}$ Ry while with variational trial function (5.3) with eight parameters it gives $E^{(\infty)}_{\text{var}}(\gamma_c) \sim 10^{-6}$ Ry, see Table I. Note that for the magnetic field γ_c, the Hamiltonian (2.3) has the normalizable zero mode. Surprisingly, for this magnetic field the value of the quadrupole moment $(-Q_{zz})$ appears to be close to its maximal value.[5]

[5]In LMM, the maximum of the quadrupole moment is reached at $\gamma = 2.96869$ a.u.: $\max(-Q_{zz}) = 0.52452$ (a.u.)^2.

For $\gamma = 10,000$ a.u., see Table I, the LMM allows us to reach six figures in energy *only*, even taking a 16 K mesh points basis, while in the calculation by Wang-Hsue [38], based on the use of splines, ten figures were reached. Taking the eight-parametric function (5.3) with $(q = 1, \beta_0 = 0)$, the energy differs from the established value in the sixth figure in two units while, taking $(q = 0, \beta_0 = 0)$, the six figures in energy are reproduced exactly. The ten-parametric function (5.3), where the parameters (q, c) are released, allows us to reproduce seven figures with difference in two units in the eighth figure in comparison with results obtained in Ref. [38].

In general, the relative deviation of the variational energy from the exact one is small in the whole domain of considered magnetic fields:

$$\left|\frac{E^{(\infty)}_{\text{var}} - E^{(\infty)}_{\text{exact}}}{E^{(\infty)}_{\text{exact}}}\right| \lesssim 10^{-6} \quad , \quad \gamma \in [0.01, 10\,000]\,. \tag{5.7}$$

Due to Hasegawa and Howard [39], see also Ref. [32], the ground state energy at large γ behaves like

$$E^{(\infty)} \;=\; \gamma \;-\; \ln^2\gamma + O(\ln\gamma)\,. \tag{5.8}$$

Here the second term defines the asymptotic behavior at large γ of the binding energy, $E^{(\infty)}_{\text{binding}} = \gamma - E^{(\infty)}$. It can immediately be seen that the asymptotic expansion (5.8) is slow convergent: Even at $\gamma = 10^4$ a.u., the binding energy is equal to ∼28.25 Ry, see Table I, it differs from $\ln^2\gamma = 16$ Ry in ∼50% . This magnetic field is close to the Schwinger limit $\gamma_{\text{Schwing}} \sim 2 \times 10^4$ a.u., which limits the domain of applicability of nonrelativistic quantum mechanics. It implies that the expansion (5.8) does not seem relevant to study the nonrelativistic domain $\gamma \lesssim \gamma_{\text{Schwing}}$.

In Table II, different estimates of the ground-state energy are presented following the order of reached accuracy for $\gamma = 1$ a.u. So far, the most accurate energy is found in Ref. [10] via multiconfigurational trial function; in the LMM we are able to confirm 19 d.d., while our eight-parametric compact trial function (5.3) at $(q = 1, \beta_0 = 0)$ gives six d.d. correctly with a difference in the seventh d.d. in one unit. The ten-parametric

TABLE III. Nuclear cusp parameter $C^{(t)}$ (5.10) for the ground state $(1s_0)$ for different magnetic fields calculated with eight-parametric approximant (5.3) with $(q = 1, \beta_0 = 0)$.

γ (a.u.)	$C^{(t)}$	γ (a.u.)	$C^{(t)}$
0.01	1.000 002	5.0	0.997
0.1	0.999 97	10.0	1.002
0.5	0.999 7	100.0	1.065
1.0	0.999 30	500.0	1.159
1.0	0.999 34 [a]	500.0	0.977 767 [a]
2.0	0.996 5	1 000.0	1.23
γ_c	0.996 7	10 000.0	1.7 (5.3), $(q = 1, \beta_0 = 0)$
		10 000.0	1.104 (5.3), $(q = 0, \beta_0 = 0)$
		10 000.0	0.939 [a]

[a]Variational method: (5.3) with ten parameters.

compact trial function (5.3) with released parameters (q, β_0) gives seven d.d. correctly with a difference in the eighth d.d. in nine units.

As for the binding energy $E^{(\infty)}_{\text{binding}} = \gamma - E^{(\infty)}$, it follows from Table I that the variational calculations with the eight-parametric trial function provide not less than six SDs in the domain $\gamma \leqslant 100$ a.u.. This accuracy drops to five and four SDs at $\gamma \approx 100$ a.u. and $\gamma \approx 10\,000$ a.u., respectively. Similar accuracies are inherited by the energy gap.

It is well-known that the hydrogen atom acquires a quadrupole moment in magnetic field $\gamma > 0$, see, e.g., Ref. [17]. Due to the azimuthal symmetry of the system, the quadrupole moment tensor is diagonal and is characterized by a single independent element only, i.e.,

$$Q_{zz} = \langle r^2 \rangle - 3 \langle z^2 \rangle \ . \tag{5.9}$$

Confident results for Q_{zz} were established for the first time by Baye *et al.* in Ref. [19]; see also Ref. [17], they are improved in the present recalculation in the LMM in three to eight SDs, depending on the magnetic field strength, see Table I. Expectation value Q_{zz} (5.9), found with compact variational trial function (5.3) with parameters from Appendix B, agrees with the LMM result with high accuracy for all studied magnetic fields.

Local deviation of the approximant from the exact wave function can be estimated by studying the vicinity near the Coulomb singularity—located at the origin, $r = 0$—it can be *measured* via the cusp parameter (4.11). A straightforward calculation shows that the cusp parameter $C^{(t)}$ derived from the approximant (5.3) is given,

$$C^{(t)} \ = \ \alpha_1 \kappa \ + \ \kappa^2 \Big(q - \frac{\alpha_0 \kappa}{2} \Big) \beta_1 \ , \quad \kappa = (1 + \beta_0)^{-1/2} \ , \tag{5.10}$$

which is the coefficient in front of the linear in r term in the expansion of (5.3) at small distances.[6] Results are presented in Table III where it can be seen that $C^{(t)}$, calculated with eight optimal parameters and $(q = 1, \beta_0 = 0)$ as the entry, satisfies the cusp condition accurately with error $\lesssim 1\%$ for $\gamma \lesssim 10$ a.u., then it begins to grow, reaching $\sim$16% at 500 a.u.

[6]Since β_0 is always small being $\lesssim 10^{-3}$, one can place $\kappa = 1$.

Note that in spite of such a large deviation of $C^{(t)}$ from $C^{(\text{exact})} = 1$, the variational energy obtained is highly accurate. It implies that the vicinity around Coulomb singularity gives a very small contribution to the energy integrals. As for larger magnetic fields $\gamma \gtrsim 500$ a.u., the deviation continues to grow and at $\gamma = 10\,000$ a.u. the deviation reaches 70%. The situation changes dramatically when the trial function (5.3) becomes ten-parametric, upon releasing the parameters (q, β_0). Although the energy improves in one to two far distant digits, see Table I, the cusp parameter gets smaller than 1, it deviates from the exact value $C = 1$ in 3-4-5 d.d. for $\gamma \leqslant 1000$ a.u., then it starts to grow and reaches its maximal deviation at $\gamma = 10\,000$ a.u. being $\sim$6%. It reflects the sensitivity of the cusp parameter to values of parameters (q, β_0), see (5.10). Note that the cusp parameter calculated in the LMM provides the value of C with not less than six d.d. in the whole range of studied magnetic fields $\gamma \leqslant 10\,000$ a.u.

The above-presented formalism developed for the ground state of positive parity $(1s_0)$ can be easily generalized for the family of excited states with $m = 0$ and $\nu = +$. At $\gamma = 0$, the excited states with $\ell = m = 0$ and $\nu = +$ are the S states of the hydrogen atom, $(n\, s_0)$ states with principal quantum number $n = 2, 3, 4, \ldots$, and radial quantum number $n_r = n - 1$. Its spectra is of the form

$$\Psi_{(n\, s_0)} \ = \ P_{n-1}(r) e^{-\frac{r}{n}} \ , \ E_{(n\, s_0)} \ = \ -\frac{1}{2n^2} \ ,$$

where $P_{n-1}(r)$ is the Laguerre polynomial of degree $(n-1)$. Taking the exponential representation of the wave function,

$$\Psi_{(m=0,+)} \ = \ P(\rho, r)\, e^{-\Phi(\rho, r)} \ , \tag{5.11}$$

cf. (2.9) and (2.14), and making substitution to (2.13), we arrive at a generalized Riccati equation, see, e.g., Ref. [15], which later can be transformed into the generalized RB equation and/or the GB equation. Similar analysis of these equations to the one made for the ground state $(1\, s_0)$ can be performed. It leads for $\gamma \neq 0$ to the conclusion that an excited state at $m = 0$ and $\nu = +$ can be studied using the trial function (5.11) in the form of a polynomial in (r, ρ) variables multiplied by the approximant (5.3), see discussion in the Conclusion. It can be done elsewhere.

B. Lowest energy state of negative parity

The lowest energy state of negative parity is described by quantum numbers $m = 0$ and $\nu = -$. For a hydrogen atom (at $\gamma = 0$), it is a $(2p_0)$ excited state. Sometimes it is called the ground state of negative parity. Its eigenfunction can be written as the product of factor z and nodeless function $\Psi^{(-)}(\rho, r)$, see (2.9). The Schrödinger equation that determines $\Psi^{(-)}$ and $\mathcal{E}^{(\infty)}$ reads, see (2.10) at $m = 0, \ p = 1$,

$$-\frac{\hbar^2}{2m_e} \Big[\partial^2_\rho \ + \ \frac{2\rho}{r} \partial_{\rho r} \ + \ \partial^2_r \ + \ \frac{1}{\rho} \partial_\rho \ + \ \frac{4}{r} \partial_r \Big] \Psi + \Big[-\frac{e^2}{r} \ + \ \frac{\gamma^2 e^2}{8 m_e c^2} \rho^2 \Big] \Psi^{(-)} \ = \ \mathcal{E}^{(\infty)}\, \Psi^{(-)} \ , \tag{5.12}$$

cf. (2.13). Taking $\Psi^{(-)}(\rho, r)$ in exponential form,

$$\Psi^{(-)}(\rho, r) \ = \ e^{-\Phi^{(-)}(\rho, r)} \ ,$$

one can see that phase $\Phi^{(-)}(\rho, r)$ satisfies a nonlinear partial differential equation of second order,

$$\partial_\rho^2\Phi + \frac{2\rho}{r}\partial_{\rho r}\Phi + \partial_r^2\Phi + \frac{1}{\rho}\partial_\rho\Phi + \frac{4}{r}\partial_r\Phi - (\partial_\rho\Phi)^2 - \frac{2\rho}{r}(\partial_\rho\Phi)(\partial_r\Phi) - (\partial_r\Phi)^2 = \frac{2m_e}{\hbar^2}\left[\mathcal{E}^{(\infty)} + \frac{e^2}{r} - \frac{\gamma^2 e^2}{8m_e c^2}\rho^2\right], \tag{5.13}$$

cf. (2.15), where for simplicity we dropped the superindex $^{(-)}$. We continue to call it the Riccati equation. By introducing new variables (s, t), see (3.1) and (3.2), the equation (5.13) is transformed into the Riccati-Bloch Eq. (3.3) (with term $\frac{2}{t}\partial_t\Phi$ replaced by $\frac{4}{t}\partial_t\Phi$) for the energy $\varepsilon = \frac{\mathcal{E}^{(\infty)}}{\mathcal{E}_0^{(\infty)}}$, cf. (3.4) and magnetic field λ, see (3.5). It is easy to see that the perturbation theory in powers of λ^2 (4.1) remains algebraic, its zero order correction

$$\Phi_0(s, t) = \tfrac{t}{2}, \quad \varepsilon_0 = -\tfrac{1}{4}, \tag{5.14}$$

cf. (4.2), corresponds to the $(2p_0)$ state of the hydrogen atom, the structure of the nth correction remains the same as for the ground state, see (4.5), and the expansion of ε in powers of λ coincides with the semiclassical expansion in powers of $\hbar^3$. Any finite number of corrections to energy and phase can easily be calculated as was done for the ground state of positive parity, see Appendix A.

By introducing new variables (u, v), see (3.8) and (3.9), Eq. (5.13) is transformed into the GB equation (3.10) (with term $\frac{2}{v}\partial_v\Phi$ replaced by $\frac{4}{v}\partial_v\Phi$) for the same energy ε and magnetic field λ. Surprisingly, at $\lambda = 0$ this equation can be solved exactly in the same form

$$\phi_0^{(-)}(u, v) = A_0^{(0,-)}(u)\, v + B_0^{(0,-)}(u), \tag{5.15}$$

as in (4.14), but with $\varepsilon_0 = -\frac{1}{4}$, see (5.14), where

$$A_0^{(0,-)}(u) = \sqrt{\frac{1}{4} + \frac{u^2}{12}},$$

$$B_0^{(0,-)}(u) = \frac{1}{2}\ln\left(\frac{1}{4} + \frac{u^2}{12}\right) + 2\ln\left(\frac{1}{4} + \frac{1}{2}\sqrt{\frac{1}{4} + \frac{u^2}{12}}\right).$$

In a new variable,

$$w_- = \sqrt{\frac{1}{4} + \frac{u^2}{12}}, \tag{5.16}$$

cf. (4.15), the zero-order approximation is in the form

$$\phi_0^{(-)}(u, v) = w_- v + \ln w_- + 2\ln\left(\frac{1}{4} + \frac{w_-}{2}\right). \tag{5.17}$$

Similar to the ground state, the $\phi_0^{(-)}(u, v)$ plays a role of classical action, although the classical trajectory seems unknown. Evidently, the function $\Psi_0 = z e^{-\phi_0^{(-)}(u,v)}$ is square integrable; it can be taken as a variational trial function to study the $(2p_0)$ state in a way similar to what was done for the ground state, cf. (5.4).

TABLE IV. Excited $(2p_0)$ state (ground state of negative parity): energies $E^{(\infty)}$ and $E^{(m_p)}$ in Ry and quadrupole moment $Q_{zz}^{(\infty)}$ in $(\text{a.u.})^2$ for hydrogen atom in magnetic field for $\gamma \in [0.01, 10000]$ in variational method with eight-parametric trial function (5.19) with $(q = 1, \beta_0 = 0)$, comparison with calculations [8,38] (rounded) made.

γ (a.u)	$E^{(\infty)}$	$E^{(m_p)}$	$-Q_{zz}^{(\infty)}$
0	−0.250 000 000 00	−0.249 863 919 86	24.000
0.01	−0.249 700 831 66	−0.249 564 266 90	23.990
	−0.249 700 83 [a]		
	−0.249 700 831 67 [b]		
0.1	−0.224 820 1	−0.224 649 6	23.064
	−0.224 820 15 [a,b]		
γ_c	0.000 001	0.000 374	18.781
0.5	0.050 480 0	0.050 892 4	18.260
	0.050 479 3 [b]		
1.0	0.479 989	0.480 701	15.585
	0.479 987 [a,b]		
2.0	1.404 583	1.405 877	13.177
	1.404 578 [b]		
5.0	4.304 78	4.307 77	10.663
	4.304 76 [b]		
10.0	9.234 73	9.240 49	9.267 7
	9.234 70 [a,b]		
100.0	99.072 95	99.127 89	6.865 7
	99.072 801		6.830 912 (†)
	99.072 774		6.824 619 (‡)
	99.072 76 [a,b]		
500.0	499.025 2	499.298 1	6.301 2
	499.025 0 [a]		
1 000.0	999.015 2	999.560 4	6.194 9
	999.015 0 [a,b]		
10 000.0	9 999.003	10004.450	6.093 2

[a]Basis of splines [38].
[b]Power series: method of moments [8]. $\gamma_c = 0.436\,663\,244$ found in LMM with 16 K points (see text), $E^{(\infty)} \sim 10^{-10}$.
†Eq. (5.19), eight parameters, $q = 0$, $\beta_0 = 0$.
‡Eq. (5.19), ten parameters, $q = -0.078\,589$, $\beta_0 = 0.000\,46$.

Similar consideration, which led to the approximant (5.2), can be repeated and we eventually arrive at

$$\Phi_t^{(-)}(\rho, r) = \frac{\alpha_0 + \alpha_1 r + \alpha_2 r^2 + \alpha_3 \gamma \rho^2 + \alpha_4 \gamma \rho^2 r}{\sqrt{1 + \beta_0 w_- + \beta_1 r + \beta_2 r^2 + \beta_3 \rho^2}} + q\ln(1 + \beta_0 w_- + \beta_1 r + \beta_2 r^2 + \beta_3 \rho^2), \tag{5.18}$$

where $\{\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \beta_0, \beta_1, \beta_2, \beta_3; q\}$ are ten free parameters that later will be fixed in variational calculation, $w_- = \sqrt{\frac{1}{4} + \frac{\gamma^2\rho^2}{12}}$, see (5.16). We call it the *phase approximant* for the ground state of negative parity. Based on (5.18), one can build the ten-parametric trial function:

$$\Psi_{2p_0} = z\, e^{-\Phi_t^{(-)}}. \tag{5.19}$$

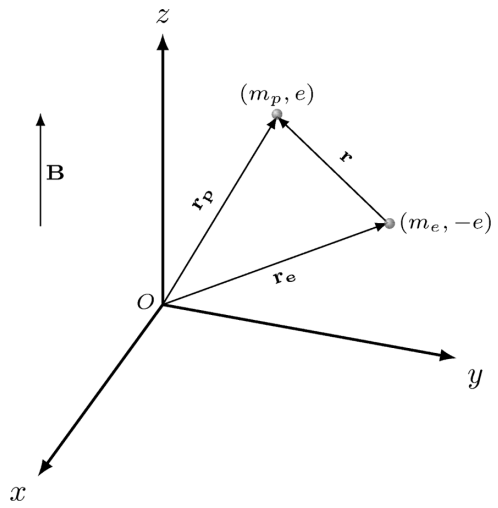

FIG. 3. The three-dimensional two-body neutral system.

The results of variational calculations are presented in Table IV and compared with results by Refs. [38][7] and [8]. For all studied magnetic fields, the variational results based on the eight-parametric variational function (5.19) with ($q = 1, \beta_0 = 0$) reproduce five to six SDs (or more) in the energy $E^{(\infty)}$ of a static hydrogen atom.[8] Resulting variational parameters are presented in Appendix C, Fig. 5. Needless to say, by taking ten-parametric variational function (5.19) with released parameters (q, β_0) allows us to increase accuracy similar to what happened for the ground state $(1s_0)$.

Binding energy $(\gamma - E^{(\infty)})$ grows at a very slow pace with a magnetic field increase from 0.25 Ry at $\gamma = 0$ reaching $\sim$1 Ry at 10^4 a.u. Note that the critical magnetic field found in LMM, when $E^{(\infty)}(\gamma_c = 0) = 0$, hence the Schrödinger operator in (5.12) has the zero mode, drops dramatically to $\gamma_c = 0.436\,663\,244$ in comparison with the ground state $(1s_0)$, see (5.6).

VI. FINITE MASS CASE

We now investigate the effects which occur when finite mass (m_p) of the proton is taken into account. In this case, the Hamiltonian which describes the system is of the form

$$\hat{H} \;=\; \frac{1}{2\,m_p}\Big(\hat{\mathbf{p}}_p - \frac{e}{c}\mathbf{A}_p\Big)^2 \;+\; \frac{1}{2\,m_e}\Big(\hat{\mathbf{p}}_e + \frac{e}{c}\mathbf{A}_e\Big)^2 \;-\; \frac{e^2}{r}\,, \tag{6.1}$$

where

$$\hat{\mathbf{p}}_{p,e} = \big(\hat{p}_{x_{p,e}}, \hat{p}_{y_{p,e}}, \hat{p}_{z_{p,e}}\big)\,, \quad \mathbf{r}_{p,e} \;=\; (x_{p,e}, y_{p,e}, z_{p,e}) \tag{6.2}$$

are the momentum operator and vector position of the proton and electron, respectively. Here $r \;=\; |\mathbf{r}_p - \mathbf{r}_e|$ is the relative distance between the charges. Now, the configuration space is six-dimensional. For the geometrical setting of the system, see Fig. 3.

Just like in the infinite mass case, the *symmetric gauge,*

$$\mathbf{A}_{p,e} \;=\; \tfrac{1}{2}\mathbf{B}\times\mathbf{r}_{p,e}\,, \tag{6.3}$$

is assumed for both vector potentials.

A. Integrals of motion

The total pseudomomentum [5],

$$\hat{\mathbf{K}} \;=\; \hat{\mathbf{p}}_p \;+\; \hat{\mathbf{p}}_e \;+\; \frac{e}{c}(\mathbf{A}_p - \mathbf{A}_e)\,, \tag{6.4}$$

is an integral of motion:

$$[\hat{\mathbf{K}}, \hat{H}] \;= 0\,. \tag{6.5}$$

Explicitly, the Cartesian components of $\hat{\mathbf{K}}$ are given by

$$\begin{aligned}
\hat{K}_x \;&=\; \hat{p}_{x_p} \;+\; \hat{p}_{x_e} \;+\frac{e\,\gamma}{2c}(y_e - y_p)\,,\\
\hat{K}_y \;&=\; \hat{p}_{y_p} \;+\; \hat{p}_{y_e} \;+\frac{e\,\gamma}{2c}(x_p - x_e)\,,\\
\hat{K}_z \;&=\; \hat{p}_{z_p} \;+\; \hat{p}_{z_e}\,,
\end{aligned} \tag{6.6}$$

and obey the following commutation relations:

$$[\hat{K}_x, \hat{K}_y] \;=\; [\hat{K}_x, \hat{K}_z] \;=\; [\hat{K}_y, \hat{K}_z] \;= 0. \tag{6.7}$$

Thus, they span three-dimensional Abelian Lie algebra. The z component of the total angular momentum

$$\hat{L}_z \;=\; (\mathbf{r}_p\times\hat{\mathbf{p}}_p)_z \;+\; (\mathbf{r}_e\times\hat{\mathbf{p}}_e)_z$$

is also conserved, $[\hat{L}_z, \hat{H}] = 0$. Hence, the total number of integrals is five $\{\hat{H}, \hat{K}_x, \hat{K}_y, \hat{K}_z, \hat{L}_z\}$; the system is not (completely) integrable: the sixth integral is missing and five known integrals do not form commutative algebra. It can be checked that the components of $\hat{\mathbf{K}}$ and $\hat{L}_z$ do not commute:

$$[\hat{K}_x, \hat{L}_z] \;=\; -i\hbar\,\hat{K}_y\,, \quad [\hat{K}_y, \hat{L}_z] \;=\; i\hbar\,\hat{K}_x\,, \quad [\hat{K}_z, \hat{L}_z] \;=\; 0\,. \tag{6.8}$$

The second-order Casimir operator of the subalgebra $\{\hat{\mathbf{K}}, \hat{L}_z\}$ is given by

$$\hat{C} \;=\; \hat{K}_x^2 \;+\; \hat{K}_y^2\,. \tag{6.9}$$

Indeed, for the case of a single particle in a constant magnetic field, the Casimir operator of the algebra of the corresponding integrals of motions is nothing but the Hamiltonian.

B. Pseudo-separation of the center of mass variables

In the presence of a magnetic field, the center-of-mass motion cannot be separated out, in this case the so-called *pseudoseparation* occurs. Pseudoseparation of variables as introduced in Ref. [5] is achieved via three steps:

(i) We introduce the center-of-mass vectorial variables

$$\begin{aligned}
&\mathbf{R} \;=\; \mu_p\,\mathbf{r}_p \;+\; \mu_e\,\mathbf{r}_e\,, \quad \mathbf{r} \;=\; \mathbf{r}_p \;-\mathbf{r}_e\,,\\
&\hat{\mathbf{P}} \;=\; \hat{\mathbf{p}}_p \;+\; \hat{\mathbf{p}}_e\,, \quad \hat{\mathbf{p}} \;=\; \mu_e\,\hat{\mathbf{p}}_p \;-\; \mu_p\,\hat{\mathbf{p}}_e\,,\\
&M \;=\; m_p \;+\; m_e\,, \quad \mu \;=\; \frac{m_p\,m_e}{M}\,, \quad \mu_{p,e} \;=\; \frac{m_{p,e}}{M}\,,
\end{aligned} \tag{6.10}$$

[7] In Ref. [38], the binding energies contrary to what was named the energies were presented.

[8] It is worth noting that the results for energies by Wang-Hsue [38] and Kravchenko *et al.* [8] presented in Table IV were recalculated and confirmed in LMM with 16 K mesh points (it is not printed in the table).

where $\hat{\mathbf{P}}$ and $\hat{\mathbf{p}}$ are the canonical conjugate momenta of $\mathbf{R}$ and $\mathbf{r}$, respectively, μ is the reduced mass of the system. In the variables (6.10), the Hamiltonian (6.1) takes the form

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e}{2Mc}(\mathbf{B}\times\mathbf{r})\cdot\hat{\mathbf{P}} - \frac{e}{2\mu c}\cdot(\mathbf{B}\times\mathbf{R})\cdot\hat{\mathbf{p}} - \frac{e(\mu_e-\mu_p)}{2\mu c}(\mathbf{B}\times\mathbf{r})\cdot\hat{\mathbf{p}} + \frac{e^2}{8\mu c^2}(\mathbf{B}\times\mathbf{R})^2 + \frac{e^2(\mu_e-\mu_p)}{4\mu c^2}(\mathbf{B}\times\mathbf{R})\cdot(\mathbf{B}\times\mathbf{r}) + \frac{e^2}{8c^2}\left(\frac{\mu_e^2}{m_p}+\frac{\mu_p^2}{m_e}\right)(\mathbf{B}\times\mathbf{r})^2 - \frac{e^2}{r}. \tag{6.11}$$

(ii) Also, in the coordinates (6.10), the conserved pseudomomentum (6.4) takes the form

$$\hat{\mathbf{K}} = \hat{\mathbf{P}} + \frac{e}{2c}\mathbf{B}\times\mathbf{r}\,, \tag{6.12}$$

see (6.10). Substituting (6.12) into the Hamiltonian (6.11), we obtain

$$\hat{H} = \frac{\left(\hat{\mathbf{K}}-\frac{e}{2c}\mathbf{B}\times\mathbf{r}\right)^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} - \frac{e}{2Mc}(\mathbf{B}\times\mathbf{r})\cdot\left(\hat{\mathbf{K}}-\frac{e}{2c}\mathbf{B}\times\mathbf{r}\right) - \frac{e}{2\mu c}\cdot(\mathbf{B}\times\mathbf{R})\cdot\hat{\mathbf{p}} - \frac{e(\mu_e-\mu_p)}{2\mu c}(\mathbf{B}\times\mathbf{r})\cdot\hat{\mathbf{p}} + \frac{e^2}{8\mu c^2}(\mathbf{B}\times\mathbf{R})^2 + \frac{e^2(\mu_e-\mu_p)}{4\mu c^2}(\mathbf{B}\times\mathbf{R})\cdot(\mathbf{B}\times\mathbf{r}) + \frac{e^2}{8c^2}\left(\frac{\mu_e^2}{m_p}+\frac{\mu_p^2}{m_e}\right)(\mathbf{B}\times\mathbf{r})^2 - \frac{e^2}{r}\,. \tag{6.13}$$

(iii) Since (6.13) describes a neutral system, which can move across a magnetic field, it is natural to look for a unitary-equivalent Hamiltonian $\hat{\mathcal{H}}$ such that $[\hat{\mathcal{H}}, \hat{\mathbf{P}}] = 0$, for which center-of-mass momentum $\hat{\mathbf{P}}$ is conserved, being the integral of motion. To this end, the operator (6.13) is transformed via the gauge rotation

$$\hat{\mathcal{H}} \equiv U^{-1}\hat{H}\,U\,, \tag{6.14}$$

with the gauge factor

$$U = \exp\left(\frac{i}{\hbar}\left[\mathbf{P} - \frac{e}{2c}(\mathbf{B}\times\mathbf{r})\right]\cdot\mathbf{R}\right). \tag{6.15}$$

Here $\mathbf{P}$ denotes the eigenvalue of the total (cms) momentum operator $\hat{\mathbf{P}}$. The action of the gauge rotation[9] to $\hat{\mathbf{K}}$ and $\hat{\mathbf{p}}$ reads

$$U^{-1}\hat{\mathbf{K}}\,U = \mathbf{P}\,, \quad U^{-1}\hat{\mathbf{p}}\,U = \hat{\mathbf{p}} + \frac{e}{2c}(\mathbf{B}\times\mathbf{R})\,, \tag{6.16}$$

whereas $\mathbf{R}$ and $\mathbf{r}$ remain unaffected. Eventually, the gauge rotated Hamiltonian (6.14) takes the form

$$\hat{\mathcal{H}} = \frac{1}{2M}\left(\mathbf{P}-\frac{e}{c}\mathbf{B}\times\mathbf{r}\right)^2 + \frac{1}{2\mu}\left(\hat{\mathbf{p}}-\frac{e_{\rm eff}}{2c}\mathbf{B}\times\mathbf{r}\right)^2 - \frac{e^2}{r}\,. \tag{6.17}$$

Here

$$e_{\rm eff} = e\,(\mu_e - \mu_p)$$

is an effective charge; it vanishes for the case of equal masses (like for positronium) and becomes $-e$ for $m_p = \infty$. It can be checked that the first and third terms in (6.17) are gauge invariant.

[9]It is worth mentioning that the operator $\hat{L}_z$ is gauge invariant with respect to U, i.e. $U^{-1}\hat{L}_z\,U = \hat{L}_z$.

C. Case P = 0: Atom at rest

At zero momentum $\mathbf{P} = \mathbf{0}$ (atom at rest), the Schrödinger equation for the Hamiltonian (6.17) takes the form

$$\hat{\mathcal{H}}_0\,\psi(\mathbf{r}) \equiv \left[\frac{1}{2\mu}\hat{\mathbf{p}}^2 - \frac{e_{\rm eff}}{2\mu c}(\mathbf{B}\times\mathbf{r})\cdot\hat{\mathbf{p}} - \frac{e^2}{r} + \frac{e^2}{8\mu c^2}(\mathbf{B}\times\mathbf{r})^2\right]\psi(\mathbf{r}) = E^{(m_p)}\,\psi(\mathbf{r}), \tag{6.18}$$

with energy denoted $E^{(m_p)} = E^{(m_p)}(\gamma, e, \mu)$. In the coordinates $\{\rho, r, \varphi\}$, see Fig. 1, the eigenvalue problem (6.18) reads

$$-\left[\frac{\hbar^2}{2\mu}\left(\partial_\rho^2 + \frac{2\rho}{r}\partial_{\rho,r}^2 + \partial_r^2 + \frac{1}{\rho}\partial_\rho + \frac{2}{r}\partial_r\right) - \frac{\hat{\ell}_z^2}{2\mu\rho^2} + \frac{e_{\rm eff}\,\gamma}{2\mu c}\hat{\ell}_z + \frac{e^2}{r} - \frac{\gamma^2 e^2}{8\mu c^2}\rho^2\right]\psi = E^{(m_p)}\,\psi\,, \tag{6.19}$$

cf. (2.8), with $\hat{\ell}_z \equiv (\mathbf{r}\times\hat{\mathbf{p}})_z = -i\hbar\,\partial_\varphi$ being the z component of the relative angular momentum. It is evident that the operator $\hat{\ell}_z$ is an integral, $[\hat{\ell}_z, \hat{\mathcal{H}}_0] = 0$. The Hamiltonian $\hat{\mathcal{H}}_0$ is z-reflection invariant, $\hat{\mathcal{H}}_0(-z) = \hat{\mathcal{H}}_0(z)$, hence, the eigenfunctions are characterized by parity, $\psi(-z) = \pm\psi(z)$. In the variables $(\rho,\ r,\ \varphi)$, the eigenfunctions have a factorized form

$$\psi(\rho, r, \varphi) = \rho^{|m|}\,z^p\,\chi(\rho, r)\,e^{im\varphi}\,, \quad m = 0, \pm1, \pm2, \ldots,$$
$$p = 0, 1\,,\ z = \sqrt{r^2-\rho^2}\,, \tag{6.20}$$

similar to (2.9), where m is the magnetic quantum number corresponding to the relative motion and p is parity. Substituting (6.20) into (6.19), we arrive at the two-dimensional

Schrödinger equation

$$-\left[\frac{\hbar^2}{2\,\mu}\left(\partial_\rho^2 + \frac{2\,\rho}{r}\partial^2_{\rho,r} + \partial_r^2 + \frac{2|m|+1}{\rho}\partial_\rho + \frac{2(|m|+p+1)}{r}\partial_r\right) + \frac{e^2}{r} - \frac{\gamma^2\,e^2}{8\,\mu\,c^2}\,\rho^2\right]\chi^{(m)}(\rho,r) = \mathcal{E}^{(m_p)}_{m,p}\,\chi^{(m)}(\rho,r)\,, \tag{6.21}$$

with eigenvalue

$$\mathcal{E}^{(m_p)}_{m,p} = E^{(m_p)}_{m,p} + \frac{e_{\rm eff}\,\hbar\,\gamma}{2\,\mu\,c}\,m\,,$$

cf. (2.10); they coincide if the replacement

$$m_e \to \mu\,, \quad e \to (-e_{\rm eff})\,, \quad \mathcal{E}^{(\infty)}_{m,p} \to \mathcal{E}^{(m_p)}_{m,p}$$

is made in (2.10); the wave functions are related:

$$\Psi^{(\infty)}\left(\frac{\mu}{m_e}\mathbf{r}\,;\,\frac{m_e^2}{\mu^2}\gamma, e, m_e\right) = \Psi^{(m_p)}(\mathbf{r}\,;\,\gamma, e, \mu)\,. \tag{6.22}$$

It should be mentioned that the definition of the Rydberg constant and the atomic unit for the magnetic field is changed as well:

$$\varepsilon = \frac{\mathcal{E}^{(m_p)}}{\mathcal{E}_0(\mu)}\,, \quad \mathcal{E}_0(\mu) = \frac{\mu\,e^4}{2\hbar^2}\,, \tag{6.23}$$

cf. (3.4), and

$$\lambda = \frac{\gamma}{\gamma_0(\mu)}\,, \quad \gamma_0(\mu) = \frac{c|e|^3\mu^2}{\hbar^3}\,, \tag{6.24}$$

cf. (3.5).
As for the ground-state energy, $m = 0$,

$$\mathcal{E}^{(m_p)}_{0,p} = E^{(m_p)}_{0,p}\,, \tag{6.25}$$

while in general,

$$\mathcal{E}^{(m_p)}_{m,p} = \mathcal{E}^{(m_p)}_{-m,p}\,, \tag{6.26}$$

cf. (2.11).

We consider two special cases. One of them is when in (6.18) the proton mass $m_p \to \infty$ while the electron mass m_e is kept finite and another one when both masses are equal. In the former case $\mu \to m_e$, $e_{\rm eff} \to -e$. The Hamiltonian (6.17) takes the form

$$\hat{\mathcal{H}} \equiv \frac{1}{2\,m_e}\left(\hat{\mathbf{p}} + \frac{e}{2\,c}\mathbf{B}\times\mathbf{r}\right)^2 - \frac{e^2}{r}\,, \tag{6.27}$$

where dependence on $\mathbf{P}$ disappears, it coincides with (2.1). In general, the limit $m_p \to \infty$ corresponds to the atomic system where one mass is much heavier than the other (for instance, as in the hydrogen atom). We call this case *atomic*. The latter case corresponds to positronium Ps, when $m_p = m_e$ and $e_{\rm eff} = 0$. The linear Zeeman effect is absent in this case, the Schrödinger equation is of the form (6.21) with μ replaced by $m_e/2$ and

$$\mathcal{E}^{(m_e)}_{m,p} = E^{(m_e)}_{m,p}\,.$$

D. Scaling relations

In general, for nonmoving neutral systems, one can relate the atomic case $m_p \to \infty$ with the finite-mass case of the system at rest $\mathbf{P} = 0$. To do that, we have to make a scale transformation $r \to \frac{\mu}{m_e}\,r$ and $\gamma \to \frac{m_e}{\mu}\,\gamma$. Then the following remarkable scaling relation between the corresponding ground state energies (2.6) and (6.25), respectively, emerges [6]:

$$\frac{\mu}{m_e}\,E^{(\infty)}_{0,0}\left(\frac{m_e^2}{\mu^2}\,\gamma,\, e,\, m_e\right) = E^{(m_p)}_{0,0}(\gamma,\, e,\, \mu)\,, \tag{6.28}$$

where for the case of the hydrogen atom, taking $m_p/m_e = 1836.152673$ (from NIST data), the mass ratio takes the value

$$\frac{m_e}{\mu} \approx 1.000\,545\,. \tag{6.29}$$

Note that the critical magnetic field (5.6) effectively decreases,

$$\gamma_0^{(m_p)} = \frac{\mu^2}{m_e^2}\,\gamma_0\,, \tag{6.30}$$

while for the case of positronium it becomes

$$\gamma_0^{(m_e)} = \frac{\gamma_0}{4}\,.$$

It is evident that the relation (6.28) holds for excited states

$$\frac{\mu}{m_e}\,\mathcal{E}^{(\infty)}_{m,p}\left(\frac{m_e^2}{\mu^2}\,\gamma,\, e,\, m_e\right) = \mathcal{E}^{(m_p)}_{m,p}(\gamma,\, e,\, \mu) \tag{6.31}$$

and also for quadrupole momenta

$$\frac{m_e^2}{\mu^2}\,Q^{(\infty)}_{zz}\left(\frac{m_e^2}{\mu^2}\gamma, e, m_e\right) = Q^{(m_p)}_{zz}(\gamma, e, \mu)\,. \tag{6.32}$$

E. Energy

Since Eq. (6.21) coincides with (2.10) once μ is identified with m_e, both the LMM and the variational method with the eight-parametric approximant (5.3) at ($q = 1$, $\beta_0 = 0$) with parameters presented in Appendix B and with the eight-parametric approximant (5.19) at ($q = 1$, $\beta_0 = 0$) with parameters presented in Appendix C can be applied. In Table I, the ground-state energies for the hydrogen atom with finite proton mass are presented for different magnetic fields; all printed digits correspond to the situation when the results obtained in both methods coincide. In a similar way, in Table IV the variational energies for the $(2p_0)$ excited state for the hydrogen atom with finite proton mass are presented for magnetic fields ranging from 0 to 10^4 a.u.

Making comparison of the energies for infinite and finite mass cases in both tables, one can see that, in general, for a fixed magnetic field the finite mass effects increase the ground-state energy and the energy of the $(2p_0)$ excited state by changing the fourth SD (and subsequent ones) independently on the magnetic field, they are of the order of $(m_e/m_p)\,\gamma$. This result is checked separately via the scaling relation (6.28).

Positronium atom Ps is a much less studied Coulomb system than the hydrogen atom, see, e.g., Refs. [41,42]. In Table V, the results of independent calculations of the

TABLE V. Energy $E^{(\mathrm{Ps})}$ in Ry and quadrupole moment $Q_{zz}^{(\mathrm{Ps})}$ in (a.u.)^2 of the ground state of positronium Ps in magnetic field calculated in variational method with eight-parametric trial function (5.3) with $(q = 1, \beta_0 = 0)$ for $\gamma \in [0.01, 10\,000]$ (first lines) and in LMM with 16 000 basic functions marked by [a]. Comparison with available results presented.

γ	$E^{(m_e)}$	$-Q_{zz}^{(m_e)}$	γ	$E^{(m_e)}$	$-Q_{zz}^{(m_e)}$
0.01	−0.499 600 701 76	0.015 805 4	5.0	7.784 63	1.478
	−0.499 600 701 77 [a]	0.015 806 8 [a]		7.784 60 [a]	1.477 [a]
	−0.499 6 [b]				
0.1	−0.464 605 37	0.812 36	10.0	17.199 03	1.188
	−0.464 605 38 [a]	0.812 32 [a]		17.198 97 [a]	1.186 [a]
	−0.464 6 [b]			17.2 [b]	
0.5	−0.022 213 4	2.045 6	100.0	194.148 9	0.539
	−0.022 213 9 [a]	2.045 7 [a]		194.148 3[a]	0.535 [a]
				194.14 [b]	
				194.177 4 [c]	
γ_c	0.000 001	2.054 24	500.0	990.698	0.319
	0.000 000 [a]	2.054 15 [a]		990.695 [a]	0.314 [a]
1.0	0.719 204	2.073 0	1 000	1 988.801	0.258
	0.719 202 [a]	2.072 7 [a]		1 988.796 [a]	0.253[a]
	0.7192 [b]				
2.0	2.380 622	1.870 7	10 000.0	19 980.5	0.13
	2.380 615 [a]	1.870 4 [a]		19 980.6 [a]	0.11 [a]

$\gamma_c = 0.516\,302\,965$.
[a]LMM (present calculation).
[b]Reference [41].
[c]Reference [42].

ground-state energy performed in the variational method with the eight-parametric approximant (5.3) at $(q = 1, \beta_0 = 0)$ with parameters taken from Appendix B— and in LMM with 16 000 basic functions for different magnetic fields are presented. The obtained energies in both methods coincide systematically in ten SDs for weak magnetic fields and up to six SDs for strong magnetic fields, being far superior than previous results. Quadrupole moment versus magnetic field is calculated in two independent methods, see Table V. There is a good coincidence for all studied magnetic fields. The validity of the scaling relations for energy and quadrupole moments was checked in a separate calculation for different masses m_p and magnetic fields.

VII. CONCLUSIONS

A simple uniform locally accurate approximation for the ground-state nodeless function is constructed for a *neutral* system of two Coulomb charges of different masses at rest in a constant uniform magnetic field of positive and negative parities, $(1s_0)$ and $(2p_0)$ states, respectively. It is shown that by keeping the mass and charge of one body fixed, all systems with different second-body masses are related. This allows us to consider the second body as infinitely massive and to take such a system as basic, which simplifies consideration. Three physical systems are considered: the hydrogen atom with (in)-finitely massive proton (deuteron, triton) and positronium.

Concretely, a ten-parameter approximation for the ground-state functions of different parities for the hydrogen atom with an infinitely massive proton (the so-called one-center case) in a constant uniform magnetic field in the interval $\gamma \in [0\,,\ 10^4]$ a.u. is proposed. If taken as a variational trial function, it allows us to calculate with accuracy of not less than six SDs ($\leqslant 10^{-6}$ in relative deviation) in the whole domain of the considered magnetic fields the total energy and not less than three SDs for the quadrupole moment Q_{zz}. Such accuracies are reached for the quadrupole moment. As for the energy at small magnetic fields $\gamma \leqslant 1$ a.u., the relative deviation ranges from $\sim 10^{-11}$ at $\gamma = 0.01$ a.u. to $\sim 10^{-8}$ for $\gamma = 1$ a.u. with the increase of a magnetic field. Benchmark results used for comparison are established using the LMM with 16 K mesh points. For both ground states of positive/negative parities, the critical magnetic fields $\gamma_c^{(1s_0)} = 2.065211858$ a.u. and $\gamma_c^{(2p_0)} = 0.436\,663\,244$, where the Schrödinger operator has the zero mode, are calculated. The presented approximation remains the same functionally for an *arbitrary* two-body neutral system, it depends effectively on the reduced mass of the system only. This allows us to study the effects of finite proton (deuteron, triton) mass in hydrogen atoms as well as in the positronium—the system of an electron and positron. It manifests an approximate solution of the problem of two Coulomb charges of opposite signs in a constant uniform magnetic field for the two lowest energy states of different parities.

Remarkably, for $c = e = m_e = 1$, the perturbation series for energy appears in powers of $\gamma\hbar^3$ with constant coefficients. This implies that the PT in powers of a magnetic field coincides with semiclassical expansion in powers of $\hbar^3$. A fundamental result of the present study, based on the exploration of the RB/GB equations in PT in powers of γ, is the

TABLE VI. Ground state $1s_0$: First ten perturbative coefficients ε_n written in the form of ratios for the perturbation series for ε calculated in the nonlinearization procedure, see (4.1). These dimensionless coefficients are universal; they do not depend on the concrete two-body system at hand.

n	$(-1)^{n+1}\varepsilon_n$
0	1
1	1/2
2	53/96
3	5581/2304
4	21577397/1105920
5	31283298283/132710400
6	13867513160861/3538944000
7	5337333446078164463/62426972160000
8	995860667291594211123017/419509252915200000
9	866294634238659755927420474 23/1057163317346304000000
10	61278735446135517930916471030330 33/17760343731417907200000000

semiclassical expansion of the ground-state energy in powers of $\hbar^3$ for a true two-dimensional problem.

Due tothe algebraic nature of the PT for the RB equation, the first 100 corrections to the ground-state energy all are rational numbers in atomic units, $c = e = m_e = \hbar = 1$, and the exponential phase (in the form of polynomials in variables ρ, r with rational coefficients) are calculated. The use of a Padé-Borel resummation technique for energy leads to highly accurate results (not less than 11 SDs) at small values of $\gamma \leqslant 1$ a.u. but fails for larger magnetic fields. Similar results can be obtained for the ground state of negative parity.

The key element of the procedure is a construction for exponential phase $\Phi(\rho,\ r)$ (the logarithm of the wave function) as a simultaneous interpolation between (i) the asymptotic series in the weak $\gamma \ll 1$ and strong $\gamma \gg 1$ magnetic field regimes and (ii) the semiclassical and perturbation expansions at large and small distances, respectively. The dimensionless RB (II.16) and GB (II.26) equations for $\Phi(\rho,\ r)$ help us construct the analytic interpolation in the form of a ten-parametric trial wave function, the *approximant* $\Psi^{(t)}$, (II.66) and (II.82) for the states of positive and negative parity, respectively.

For both the $(1s_0)$ and $(2p_0)$ states, the phase approximant Φ_t has a similar functional form

$$\Phi_t(\rho, r) \ = \ \frac{\alpha_0 + \alpha_1\, r + \alpha_3\, r^2 + a_3\, \gamma\, \rho^2 + \alpha_4\, \gamma\, \rho^2\, r}{\sqrt{1 + \beta_0\, w_\pm + \beta_1\, r + \beta_2\, r^2 + \beta_3\, \rho^2}} + q \ln(1 + \beta_0\, w_\pm + \beta_1\, r + \beta_2\, r^2 + \beta_3\, \rho^2)\ , \tag{6.33}$$

with the only difference in w: $w_+ = \sqrt{1 + \frac{\gamma^2\,\rho^2}{12}}$ for the $(1s_0)$ state and $w_- = \sqrt{\frac{1}{4} + \frac{\gamma^2\,\rho^2}{12}}$ for the $(2p_0)$ state. It can be shown that for an arbitrary state with quantum number m and parity p, the phase approximant Φ_t (6.33) remains of the same functional form but with different w,

$$w_{m,p} = \sqrt{\frac{1}{(|m| + p + 1)^2} + \frac{\gamma^2\,\rho^2}{12}}\ ,$$

while the prefactors, which define nodal surfaces, can be quite complicated and nontrivial. Note that the leading term in the semiclassical expansion (which is an analog of the classical action in the one-dimensional case) has a surprisingly simple, closed analytic form:

$$\phi_0(u, v) \ = w_{m,p}\, v \ + \ \ln w_{m,p} \ + \ (|m| + p + 1) \times \ln\left(\frac{1}{(|m| + p + 1)} \ + \ w_{m,p}\right). \tag{6.34}$$

Excluding β_0 and q, all other variational parameters in Φ_t (6.33) are positive (except α_0, which grows as $\gamma \to 0$) and exhibit a monotonous growth as a function of the magnetic field γ. The parameter β_0 is extremely small for all studied magnetic fields; it influences far distant digits in the energy and can be set equal to zero without losing much accuracy. The parameter q has a pretty surprising behavior: it is close to 1 for $\gamma \lesssim 10$ a.u., then it sharply changes to almost zero for larger magnetic fields. In spite of this fact, the optimal eight-parametric function at $q = 1,\ \beta_0 = 0$ provides a relative deviation from the exact numerical solution of order $\lesssim 10^{-5}$ in the whole domain $\gamma \in [0.01,\ 10^4]$ a.u.

In general, variational results with the ten-parametric trial function agree with the ones based on the LMM with 16 K mesh points with high accuracy for all studied magnetic fields. The comparison with other calculations was made in Tables I and II for the $1s_0$ state. As for the ground state $2p_0$ of negative parity, the results are presented in Table IV.

As for the less studied problem of the positronium atom Ps, the trial function $\Phi_t(\rho, r)$ with only eight variational parameters ($q = 1,\ \beta_0 = 0$) provides a ground-state energy that agrees systematically with the accurate numerical result in ten SDs for small γ and up to six SDs at large γ in the whole domain $\gamma \in [0.01,\ 10^4]$ a.u. In this case, the critical magnetic field $\gamma_c = 0.436663$ a.u. turned out to be almost five times smaller than the one for the hydrogen atom. And, not surprisingly, an excellent agreement between the results obtained variationally with use of the approximant and the LMM occurs. This reflects the high quality of the trial function used.

TABLE VII. Ground state ($1s_0$): Exact PT coefficients $\varepsilon_{n=10k}$, $k = 1, 2, ..., 10$ of the series expansion for ε calculated in nonlinearization procedure, see (4.1). The results marked by $\varepsilon_{10k}^{(\mathrm{asymp})}$ obtained in the $1/n$-expansion (4.7) at leading order. Coefficients rounded to four SDs. These dimensionless coefficients are universal; they do not depend on the concrete two-body system considered.

k	$-\varepsilon_{10k}$	$-\varepsilon_{10k}^{(\mathrm{asymp})}$	n	$-\varepsilon_{10k}$	$-\varepsilon_{10k}^{(\mathrm{asymp})}$
1	3.450×10^{9}	4.623×10^{9}	6	5.655×10^{140}	5.911×10^{140}
2	2.160×10^{29}	2.478×10^{29}	7	1.410×10^{173}	1.464×10^{173}
3	3.215×10^{53}	3.518×10^{53}	8	6.046×10^{206}	6.250×10^{206}
4	3.720×10^{80}	3.978×10^{80}	9	3.127×10^{241}	3.220×10^{241}
5	6.263×10^{109}	6.606×10^{109}	10	1.479×10^{277}	1.519×10^{277}

All two-body neutral systems we studied are at rest, they are not moving, $\mathbf{P} = \mathbf{0}$. Dynamics is defined by relative coordinates, see (6.18). The effects of cms motion will be studied elsewhere.

ACKNOWLEDGMENTS

The authors thank J.C. Lopez Vieyra and H. Olivares Pilón for their interest in the work and useful discussions. J.C.dV. thanks E. Dominguez-Rosas for assistance with the MATHEMATICA package. J.C.dV. is supported by CONACyT Ph.D. Grant No. 570617 (Mexico). This work is partially supported by CONACyT Grant No.A1-S-17364 and DGAPA Grant No. IN113819 (Mexico).

APPENDIX A: GROUND STATE $1s_0$: PT CORRECTIONS

We present here the explicit forms the first perturbative corrections Φ_n, $n = 2, 3, 4$ in the expansion (4.1) in addition to Φ_1, see (4.4),

$$\begin{aligned}-\Phi_2(s,t) = {}& \tfrac{1}{1152}s^4t + \tfrac{1}{1440}s^2t^3 + \tfrac{11}{4608}s^4 \\ & + \tfrac{13}{1440}s^2t^2 + \tfrac{1}{2880}t^4 + \tfrac{193}{5760}s^2t + \tfrac{1}{120}t^3 \\ & + \tfrac{193}{3840}s^2 + \tfrac{337}{5760}t^2, \end{aligned} \tag{A1}$$

$$\begin{aligned}\Phi_3(s,t) = {}& \tfrac{1}{27648}s^6t + \tfrac{1}{11520}s^4t^3 + \tfrac{1}{60480}s^2t^5 \\ & + \tfrac{7}{55296}s^6 + \tfrac{163}{138240}s^4t^2 + \tfrac{131}{241920}s^2t^4 \\ & + \tfrac{1}{181440}t^6 + \tfrac{61}{11520}s^4t + \tfrac{8063}{1209600}s^2t^3 \\ & + \tfrac{53}{201600}t^5 + \tfrac{803}{92160}s^4 + \tfrac{33311}{806400}s^2t^2 \\ & + \tfrac{2927}{604800}t^4 + \tfrac{90877}{691200}s^2t + \tfrac{2027}{43200}t^3 \\ & + \tfrac{90877}{460800}s^2 + \tfrac{188173}{691200}t^2, \end{aligned} \tag{A2}$$

$$\begin{aligned}-\Phi_4(s,t) = {}& \tfrac{5}{2654208}s^8t + \tfrac{1}{110592}s^6t^3 + \tfrac{163}{29030400}s^4t^5 \\ & + \tfrac{1}{2419200}s^2t^7 + \tfrac{163}{21233664}s^8 + \tfrac{293}{2211840}s^6t^2 \\ & + \tfrac{9833}{58060800}s^4t^4 + \tfrac{727}{29030400}s^2t^6 + \tfrac{1}{9676800}t^8 \\ & + \tfrac{8819}{13271040}s^6t + \tfrac{1663979}{812851200}s^4t^3 \\ & + \tfrac{24733}{40642560}s^2t^5 + \tfrac{167}{20321280}t^7 \\ & + \tfrac{10577}{8847360}s^6 + \tfrac{13945163}{1083801600}s^4t^2 \\ & + \tfrac{22721}{2822400}s^2t^4 + \tfrac{5989}{22579200}t^6 \\ & + \tfrac{27927329}{650280960}s^4t + \tfrac{29335139}{451584000}s^2t^3 \\ & + \tfrac{4828099}{1016064000}t^5 + \tfrac{816005783}{13005619200}s^4 \\ & + \tfrac{1349713153}{4064256000}s^2t^2 + \tfrac{146213807}{2709504000}t^4 \\ & + \tfrac{16222576613}{16257024000}s^2t + \tfrac{141801871}{338688000}t^3 \\ & + \tfrac{16222576613}{10838016000}s^2 + \tfrac{36642046037}{16257024000}t^2. \end{aligned} \tag{A3}$$

In addition, in Tables VI and VII the higher order energy corrections ε_n are shown.

APPENDIX B: OPTIMAL VARIATIONAL PARAMETERS OF (5.3) FOR ($1s_0$) STATE

Plots of the optimal variational parameters for the eight-parametric approximant (5.3) at ($q = 1, \beta_0 = 0$) are shown below in Fig. 4 for the $1s_0$ state.

APPENDIX C: OPTIMAL VARIATIONAL PARAMETERS OF (5.19) FOR ($2p_0$) STATE

In Fig. 5 we display for the $1p_0$ state plots of the optimal variational parameters for the eight-parametric approximant (5.19) at ($q = 1, \beta_0 = 0$) as a function of $\ln(1 + \gamma^2)$.

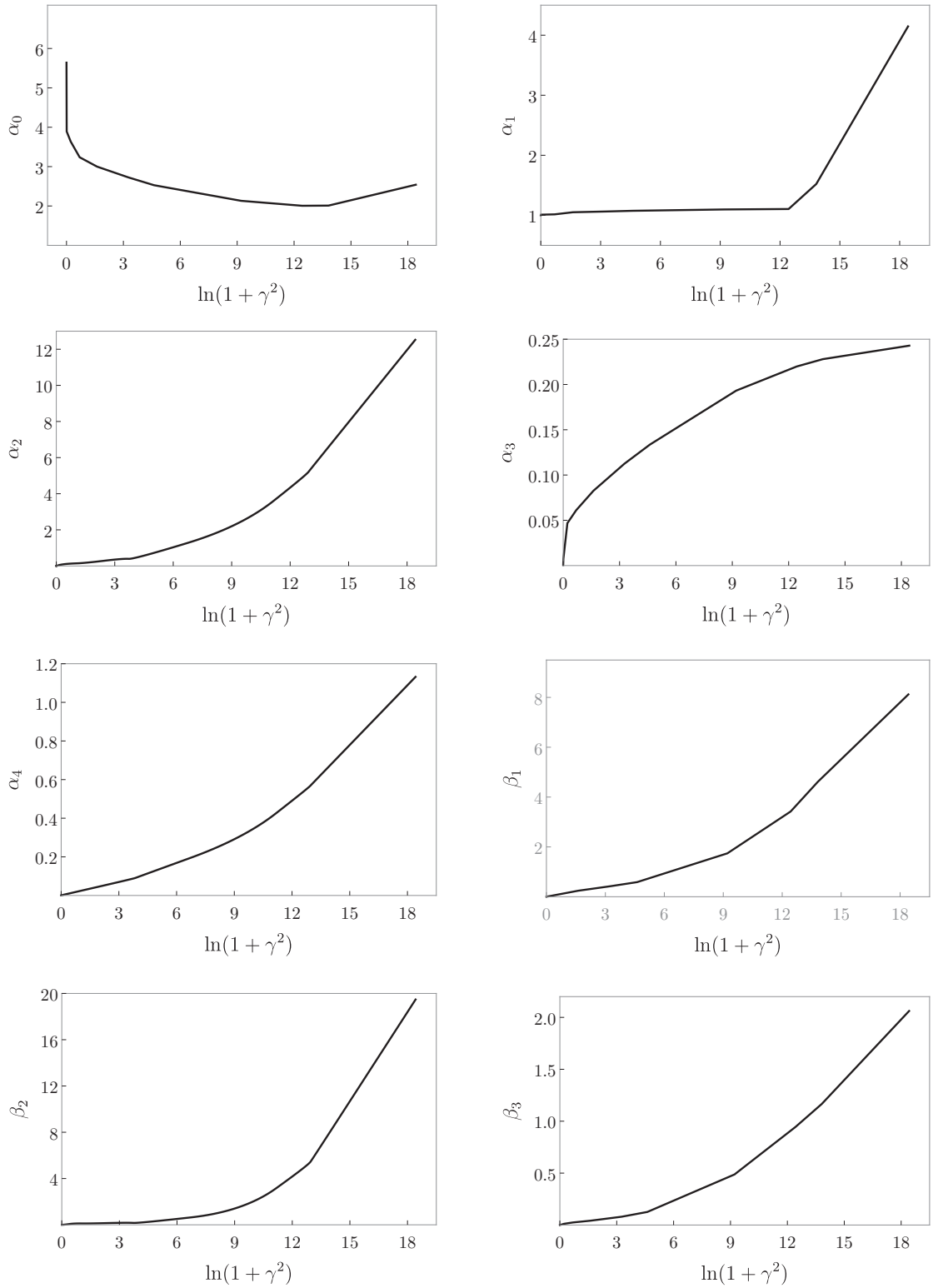

FIG. 4. Optimal variational parameters $\{\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \beta_1, \beta_2, \beta_3\}$ of the eight-parametric approximant (5.3) at $q = 1, \beta_0 = 0$ as functions of $\ln(1+\gamma^2)$.

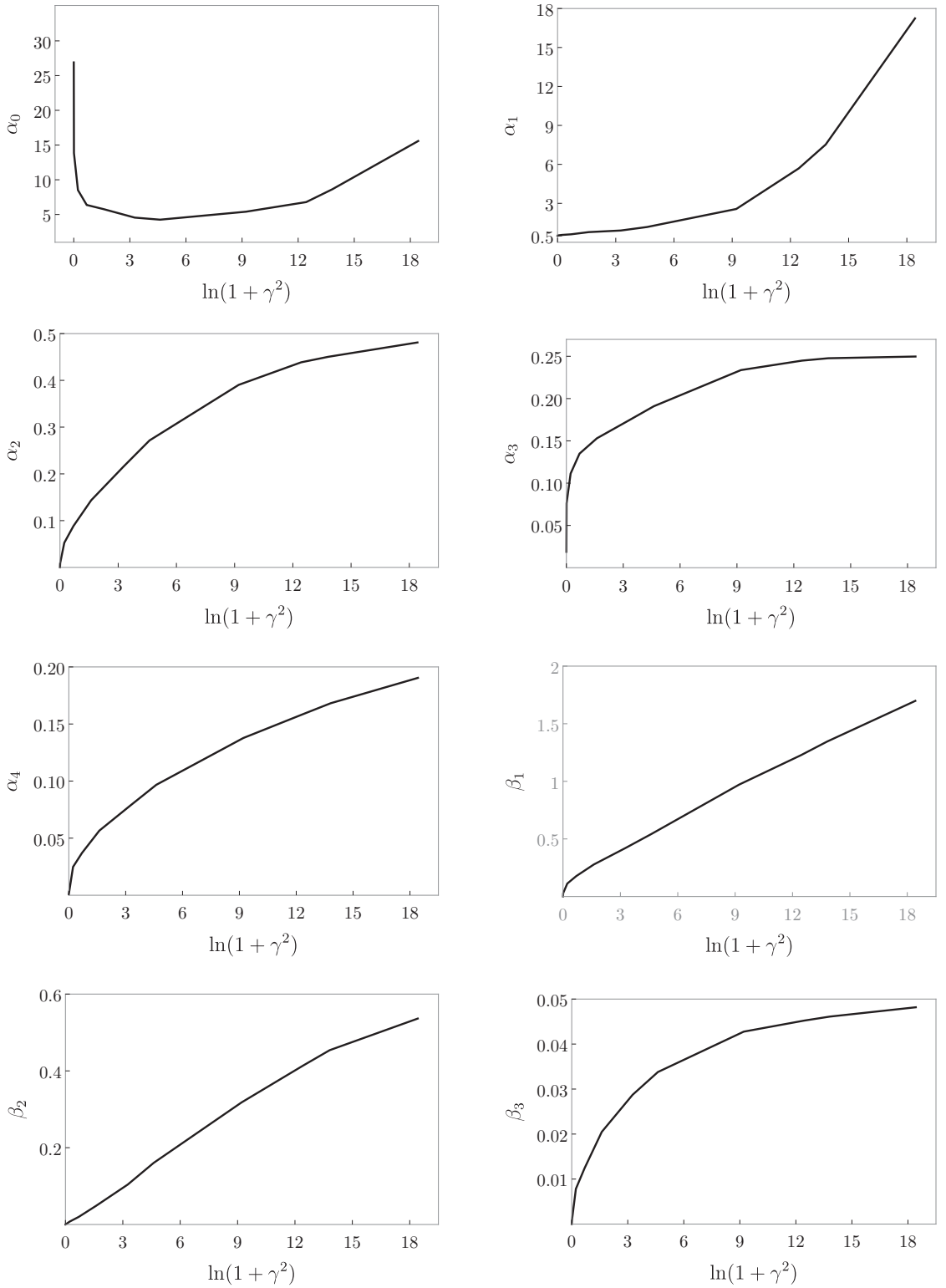

FIG. 5. Optimal variational parameters $\{\alpha_0, \alpha_1, \alpha_2, \alpha_3, \alpha_4, \beta_1, \beta_2, \beta_3\}$ of the eight-parametric approximant (5.19) with ($q = 1$, $\beta_0 = 0$) as functions of $\ln(1+\gamma^2)$, cf. Fig. 4.

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