

Large-order behavior of the perturbation energies for the hydrogen atom in magnetic field

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Large-order behavior for the perturbation energies of the hydrogen atom in magnetic field is derived. By means of the dispersion relations, the large-order behavior of the series is determined by calculating the lifetime of the quasistationary states in an imaginary magnetic field. This problem is treated by means of the modified multidimensional WKB method. The asymptotic formula for the perturbation energies derived by Avron is generalized to the states with an arbitrary degeneracy. The first order correction to the resulting formula is also found. Thus, the multidimensional WKB method is for the first time explicitly carried out beyond the leading approximation. The analytical results are verified numerically and an excellent agreement between the two is found. The connection between our and conventional semiclassical approximation is also briefly discussed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2168689]

I. INTRODUCTION

The problem of the hydrogen atom in the magnetic field is elementary but difficult and great deal of effort has been devoted to its solution over the years (see, e.g., Refs. 1–21 and references given therein). Except for its own importance, it has been used as a relatively simple problem to answer some more general questions, as for example determination of the large-order behavior of the perturbation energies and related problem of the multidimensional WKB approximation,^{1,3,4} summation of the divergent perturbation series,^{2,7,21} application of the perturbation theory in the degenerate case,⁸ determination of the lower bounds to the eigenvalues^{9,14} and so on.

In this paper, we are interested in the problem of the hydrogen atom in magnetic field mainly from the point of view of the multidimensional WKB approximation and related problem of the asymptotic behavior of the corresponding divergent perturbation series. The multidimensional WKB method is important in many areas of physics ranging from the theory of chemical reactions to cosmology, for review see Ref. 22. Knowledge of the large-order behavior of the divergent perturbation series can be used in the summation of the series^{1,2,21,23} and checking correctness of calculated perturbation energies. The latter application is especially important when treating the degenerate states where the perturbation theory is difficult to apply.

Schrödinger equation for the hydrogen atom in a constant magnetic field $\vec{B}=(0,0,B)$ with fixed nucleus and neglecting the spin effects reads

$$\left[-\frac{\nabla^2}{2} - \frac{1}{r} + \frac{BL_z}{2} + \frac{B^2}{8}(x^2 + y^2) \right] \psi = E\psi, \quad (1)$$

where the atomic units are used. The Hamiltonian commutes with the projection of the angular momentum operator \vec{L} onto the direction of the magnetic field and with the parity operator. In the following, we shall restrict ourselves to the states of the zero projection of the angular momentum onto the z axis and even parity.

The energy E has the following perturbation expansion:

$$E = \sum_{n=0}^{\infty} E_n \left(\frac{B^2}{8} \right)^n. \quad (2)$$

This perturbation series is divergent. The reason is that the energy E is not an analytic function in the vicinity of point $B=0$. This can be understood as follows. We consider analytic continuation of the energy E for complex magnetic fields $E=E(B^2)$. In the upper half of the complex plane we take $B^2=|B^2|e^{i \arg(B^2)}$ and in the lower half of the complex plane we take $B^2=|B^2|e^{-i \arg(B^2)}$, $\arg(B^2) \in (0, \pi)$. For real magnetic fields, Eq. (1) is solved with the boundary condition $\psi(\rho \rightarrow \infty) \rightarrow e^{-(B^2/8)^{1/2} \rho^2}$, where $\rho^2=x^2+y^2$. For complex magnetic fields, Eq. (1) is solved with the analytic continuation of this boundary condition. Now, approaching the value $-|B^2|$ from the upper half of the complex plane leads to the boundary condition $\psi(\rho \rightarrow \infty) \rightarrow e^{-i|B^2/8|^{1/2} \rho^2}$, while approaching this value from the lower half of the complex plane leads to the boundary condition $\psi(\rho \rightarrow \infty) \rightarrow e^{+i|B^2/8|^{1/2} \rho^2}$. These different boundary conditions yield different signs of the imaginary part of the energy $\Im[E(B^2)]$. Therefore, the energy E has for real negative values of B^2 the discontinuity $2i\Im[E(-|B^2|+i\varepsilon)]$, $\varepsilon>0$. Using Cauchy theorem one can show that the perturbation energies E_n are related to the imaginary part of the energy for the imaginary values of the magnetic fields via the dispersion relation^{1,24-26}

$$E_n = \frac{(-1)^{n+1}(2N^2)^n}{\pi} \int_0^{\infty} d\lambda \frac{\Im[E(\lambda)]}{\lambda^{n+1}}, \quad (3)$$

where a new coupling constant λ has been introduced via equation

$$\frac{B^2}{8} = -\frac{\lambda}{2N^2}. \quad (4)$$

Here, $N=1, 2, 3, \dots$ denotes the principal quantum number of the hydrogen atom. The imaginary part of the energy is one-half of the inverse lifetime of the quasistationary states in the potential in Eq. (1) with the imaginary magnetic field B .

It is seen from Eq. (3) that the behavior of the perturbation energies E_n for very large n is given by the lifetime of the quasistationary states for small values of the coupling constant λ . Thus, provided we are able to calculate this lifetime, Eq. (3) enables precise determination of the degree of the divergence of the series (2).

Expression for the imaginary part of the energy can be derived as follows. First, since Eq. (1) has an axial symmetry we introduce the cylindric coordinates $x=\rho \cos \varphi$, $y=\rho \sin \varphi$, $z=z$. Since the states with the zero projection of the angular momentum are independent of the coordinate φ , Eq. (1) reads

$$\left[\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{\partial^2}{\partial z^2} \right] \psi = [V(\rho, z) - 2E] \psi, \quad (5)$$

where

$$V(\rho, z) = -\frac{2}{(\rho^2 + z^2)^{1/2}} - \frac{\lambda}{N^2} \rho^2. \quad (6)$$

Equation (5) is solved with the boundary condition $\psi(\rho \rightarrow \infty) \rightarrow e^{-i\lambda^{1/2} \rho^2/N}$. Further, we multiply Eq. (5) by $\rho \psi^*$. We take complex conjugate of Eq. (5) and multiply it by $\rho \psi$. Then we subtract the two equations and integrate the resulting equation over the whole space, i.e., over z from $-\infty$ to ∞ and over ρ from 0 to ∞ . Finally, we integrate this equation by parts and obtain the time-independent version of the continuity equation for the probability density

$$\Im[E] = \frac{J}{2\langle\psi|\psi\rangle}, \quad (7)$$

where the probability flux J in the ρ direction equals

$$J = -\frac{1}{2i} \int_{-\infty}^{\infty} dz \lim_{\rho \rightarrow \infty} \rho \left[\psi^* \frac{\partial}{\partial \rho} \psi - \psi \frac{\partial}{\partial \rho} \psi^* \right] \quad (8)$$

and the norm of the wave function reads

$$\langle\psi|\psi\rangle = \int_0^{\infty} d\rho \int_{-\infty}^{\infty} dz \rho |\psi|^2. \quad (9)$$

To calculate the imaginary part of the energy from Eq. (7) we proceed as follows.²⁴ Inside the potential well, we approximate the wave function by means of the Rayleigh-Schrödinger perturbation theory (RSPT). Since the dominant contribution to the norm of the wave function describing the quasistationary state comes from the interior of the well we replace the exact wave function in the denominator of Eq. (7) by the perturbation wave function. In the tunneling region and outside the potential well we approximate the wave function by the WKB wave function. Since the dominant contribution to the probability current comes from the tunneling, classically forbidden region we replace the exact wave function in Eq. (8) by the WKB wave function. The same normalization of the RSPT and the WKB wave functions is guaranteed by the asymptotic matching of these functions in the overlap region of their mutual validity.

The main obstacle in carrying out the program described above is the construction of the WKB wave function. The standard formulation of the WKB approximation as applied to Eq. (5) leads to the nonseparable nonlinear partial differential equation that is difficult to solve.

The simplification of the problem used here comes out from the fact that the tunneling of the particle takes place in the neighborhood of the line $z=0$, see Eq. (5). Consequently, we do not need to know the wave function in all space, but only in the neighborhood of this line. The situation is further greatly simplified by the fact that the minimum of the potential is the straight line (compare it with the case of the curved lines^{27,28}). This simplification was for the first time realized in Ref. 29 for the problem of the coupled oscillators and later used in Ref. 1 to derive the imaginary part of the energy in Eq. (5) at the leading approximation. However, it seems that the full content of the simplification was not appreciated so far. Indeed, none from the multidimensional WKB calculations for the straight escape paths performed so far^{1,4,29,30} shows how to extend the calculation beyond the leading approximation.

In this paper we show how the WKB wave function for Eq. (5) and the outgoing probability flux can be obtained to the desired accuracy. Our method is not bound to the problem considered here and with appropriate modifications it can be extended to all problems involving multidimensional tunneling along the straight escape paths.

The paper is organized as follows. In Sec. II the modified multidimensional WKB method is suggested and used to calculate the outgoing probability flux, Eq. (8), with accuracy to the order $\lambda^{1/2}$. In Sec. III the calculation of the perturbation energies in Eq. (2) is described. The perturbation wave function is used to calculate the norm of the wave function (9). In Sec. IV the results of the preceding two sections are put together and inserted into Eq. (3) to get the asymptotics of the perturbation energies. Numerical verification of the derived formula is made and an excellent agreement between the analytical and numerical calculation is found. In the Conclusions the perspectives of further applications of the proposed WKB approximation are briefly outlined. In the Appendix the connection between the suggested and conventional WKB method is discussed.

II. WKB METHOD

There are two facts stressed in the next two paragraphs that simplify the calculations enormously and that were not explicitly realized so far. The first one is the approximation of the wave function in the coordinate z by the wave function of the anharmonic oscillator, Eq. (11). The second one is the scaling in the coordinate ρ , Eq. (15).

A. Approximation of the wave function in the transversal direction

First, in the vicinity of the ρ axis the potential $V(\rho, z)$ given by Eq. (6) can be expanded as

$$V(\rho, z) = V_0(\rho) + V_2(\rho)z^2 + V_4(\rho)z^4 + \dots \quad (10)$$

Then, the wave function of the particle in the direction transversal to tunneling can be written as

$$\psi(\rho, z) = e^{f(\rho) + h(\rho)z^2 + q(\rho)z^4 + \dots} \quad (11)$$

Physically, this says nothing else than close to the minimum of the potential in the direction perpendicular to tunneling we can approximate the exact wave function by the wave function of the harmonic oscillator. This approximation can be further improved by considering anharmonic terms.

Inserting the expansions (10) and (11) into Eq. (5) and comparing the terms of the same order of z we get

$$f'(\rho)^2 + f''(\rho) + \frac{f'(\rho)}{\rho} + 2h(\rho) = -2E - \frac{\lambda}{N^2}\rho^2 - \frac{2}{\rho} \quad (12)$$

at the zeroth order,

$$2f'(\rho)h'(\rho) + h''(\rho) + \frac{h'(\rho)}{\rho} + 4h(\rho)^2 + 12q(\rho) = \frac{1}{\rho^3} \quad (13)$$

at the second order and

$$2f'(\rho)q'(\rho) + h'(\rho)^2 + q''(\rho) + \frac{q'(\rho)}{\rho} + 16h(\rho)q(\rho) = -\frac{3}{4\rho^5} \quad (14)$$

at the fourth order of z . Here, the prime denotes the differentiation with respect to ρ .

B. Approximation of the wave function in the longitudinal direction

Second, in the direction of the tunneling we approximate the wave function as follows. In the classically forbidden region the terms $-2E_0$ and $-(\lambda/N^2)\rho^2$ are of the same order of magnitude.³¹ To make these terms of the same order in λ we make the scaling in the coordinate ρ ,

$$\rho = \lambda^{-1/2}u, \quad (15)$$

and expand the real part of the energy in the series (2). Equations (12)–(14) then read

$$\lambda \left(f'(u)^2 + f''(u) + \frac{f'(u)}{u} \right) + 2h = \frac{1-u^2}{N^2} - \frac{2\lambda^{1/2}}{u} - 2 \sum_{n=1}^{\infty} E_n \left(-\frac{\lambda}{2N^2} \right)^n, \quad (16)$$

$$\lambda \left(2f'(u)h'(u) + h''(u) + \frac{h'(u)}{u} \right) + 4h(u)^2 + 12q(u) = \frac{\lambda^{3/2}}{u^3} \quad (17)$$

and

$$\lambda \left(2f'(u)q'(u) + h'(u)^2 + q''(u) + \frac{q'(u)}{u} \right) + 16h(u)q(u) = -\frac{3\lambda^{5/2}}{4u^5}, \quad (18)$$

where the prime denotes now differentiation with respect to u . To get a clue how to expand the functions $f(u)$, $h(u)$, and $q(u)$ in the powers of $\lambda^{1/2}$ we use the fact that for $u \rightarrow 0$ we must recover the wave function of the hydrogen atom. For example, it reads for the ground state

$$\psi_{1s} = e^{-r} = e^{-\sqrt{\rho^2+z^2}} = e^{-\rho-z^2/(2\rho)-z^4/(8\rho^3)+\dots} = e^{-u/\lambda^{1/2}-\lambda^{1/2}z^2/(2u)-\lambda^{3/2}z^4/(8u^3)+\dots}. \quad (19)$$

Therefore we expand the functions $f(u)$, $h(u)$, and $q(u)$ as follows:

$$f(u) = \frac{f_0(u)}{\lambda^{1/2}} + f_1(u) + f_2(u)\lambda^{1/2} + \dots, \quad (20)$$

$$h(u) = h_0(u)\lambda^{1/2} + h_1(u)\lambda + \dots, \quad (21)$$

and

$$q(u) = q_0(u)\lambda^{3/2} + \dots. \quad (22)$$

C. Equations for the WKB wave function

Comparing the terms of the order λ^0 in Eq. (16), of the order λ in Eq. (17) and of the order $\lambda^{1/2}$ in Eq. (16) we get equations for the functions $f_0(u)$, $h_0(u)$, and $f_1(u)$,

$$f_0'(u) = \frac{\pm\sqrt{1-u^2}}{N}, \quad (23)$$

$$2f_0'(u)h_0'(u) + 4[h_0(u)]^2 = 0 \quad (24)$$

and

$$2f_0'(u)f_1'(u) + f_0''(u) + \frac{1}{u}f_0'(u) + 2h_0(u) = -\frac{2}{u}, \quad (25)$$

respectively. Since we want to calculate the imaginary part of the energy beyond the leading approximation, we have to determine also the functions $q_0(u)$, $h_1(u)$, and $f_2(u)$. Comparing the terms of the order λ^2 in Eq. (18), of the order $\lambda^{3/2}$ in Eq. (17) and of the order λ in Eq. (16) we get equations for the functions $q_0(u)$, $h_1(u)$, and $f_2(u)$,

$$2f_0'(u)q_0'(u) + [h_0'(u)]^2 + 16h_0(u)q_0(u) = 0, \quad (26)$$

$$2f_0'(u)h_1'(u) + 2f_1'(u)h_0'(u) + h_0''(u) + \frac{1}{u}h_0'(u) + 8h_0(u)h_1(u) + 12q_0(u) = \frac{1}{u^3}, \quad (27)$$

and

$$2f_0'(u)f_2'(u) + [f_1'(u)]^2 + f_1''(u) + \frac{1}{u}f_1'(u) + 2h_1(u) = \frac{E_1}{N^2}, \quad (28)$$

respectively. The solution of the above equations is determined uniquely by requirement that for u going to zero, the WKB wave function must match the bound state function. This will be discussed in detail below. Before actual solution of the equations given above, let us show that the proposed approximation to the wave function yields systematic approximation to the outgoing probability flux.

D. Approximation to the outgoing probability flux

To calculate the outgoing probability flux from Eq. (8) we need to know the behavior of the wave function for large ρ . Integration of Eq. (25) yields

$$f_1(u) = -\frac{1}{2} \ln(uf'_0(u)) + F_1(u), \quad (29)$$

where the second term is given as

$$F_1(u) = -\frac{N}{2} \ln \frac{1 + (1 - u^2)^{1/2}}{1 - (1 - u^2)^{1/2}} + \frac{1}{2} \ln(h_0(u)) - A_1. \quad (30)$$

The integration constant A_1 is determined from the requirement of the matching of the WKB and bound state functions. Here, we took the solution of Eq. (23) with the minus sign, see discussion after Eq. (37) below.

Thus, the behavior of the wave function (11) for large ρ is given as

$$\psi(\rho, z) = \frac{\exp\{f_0(\rho)/\lambda^{1/2} + F_1(\rho) + \lambda^{1/2}f_2(\rho) + \dots + h(\rho)z^2 + q(\rho)z^4 + \dots\}}{[\rho f'_0(\rho)]^{1/2}}, \quad (31)$$

where we inserted the expansion (20). Differentiation of the function (31) with respect to ρ yields

$$\frac{\partial \psi(\rho, z)}{\partial \rho} \sim \frac{[f'_0(\rho)]^{1/2}}{[\rho \lambda]^{1/2}} \exp\left\{\frac{f_0(\rho)}{\lambda^{1/2}} + F_1(\rho) + \lambda^{1/2}f_2(\rho) + h(\rho)z^2 + q(\rho)z^4 + \dots\right\}. \quad (32)$$

Differentiation of the terms $F_1(\rho)$, $\lambda^{1/2}f_2(\rho)$ and so on yields the contribution to the probability flux that vanishes for ρ approaching infinity. For large ρ the particle moves in the classically allowed region and $f'_0(\rho)$ is purely imaginary, see Eq. (23). Thus it follows from Eqs. (8), (31), and (32) that the nonvanishing contribution to the probability flux for ρ going to infinity is given as^{29,30}

$$\begin{aligned} J &= \frac{1}{\lambda^{1/2}} \exp\{2\Re[f_0(u \rightarrow \infty)/\lambda^{1/2} + F_1(u \rightarrow \infty) + \lambda^{1/2}f_2(u \rightarrow \infty) + \dots]\} \\ &\times \int_{-\infty}^{\infty} dz \exp\{2z^2\Re[\lambda^{1/2}h_0(u \rightarrow \infty) + \lambda h_1(u \rightarrow \infty)] + 2z^4\Re[\lambda^{3/2}q_0(u \rightarrow \infty)] + \dots\}, \end{aligned} \quad (33)$$

where \Re denotes the real part. Here we inserted the expansions (21) and (22) and made the substitution (15). This can be done since the real parts of the functions $f_i(u)$, $h_i(u)$ and so on, goes to the constants for u going to infinity. Therefore, it does not matter if we calculate it in the variable u or ρ .

The integration over the transversal direction can be performed easily. Expanding the above equation in the powers of $\lambda^{1/2}$ as

$$\begin{aligned} J &= \frac{1}{\lambda^{1/2}} \exp\{2\Re[f_0(u \rightarrow \infty)/\lambda^{1/2} + F_1(u \rightarrow \infty)]\} (1 + 2\lambda^{1/2}\Re[f_2(u \rightarrow \infty)] + \dots) \\ &\times \int_{-\infty}^{\infty} dz \exp\{2z^2\Re[\lambda^{1/2}h_0(u \rightarrow \infty)]\} (1 + 2z^2\lambda\Re[h_1(u \rightarrow \infty)] + 2z^4\lambda^{3/2}\Re[q_0(u \rightarrow \infty)] + \dots) \end{aligned} \quad (34)$$

we are left with the Gaussian integrals. The outgoing probability flux accurate up to the first order of $\lambda^{1/2}$ then reads

$$J = \exp\{2\Re[f_0(u \rightarrow \infty)]/\lambda^{1/2} + F_1(u \rightarrow \infty)\} \frac{\sqrt{\pi}}{\lambda^{3/4}(\Re[-2h_0(u \rightarrow \infty)])^{1/2}} (1 + \lambda^{1/2}R_1 + \lambda R_2 + \dots), \quad (35)$$

where the first correction coefficient R_1 equals

$$R_1 = 2\Re[f_2(u \rightarrow \infty)] + \frac{\Re[h_1(u \rightarrow \infty)]}{\Re[-2h_0(u \rightarrow \infty)]} + \frac{3\Re[q_0(u \rightarrow \infty)]}{2(\Re[-2h_0(u \rightarrow \infty)])^2}. \quad (36)$$

It is clear from the above equations that the suggested approximation of the wave function provides systematic approximation to the outgoing probability flux in the form of the series in powers of $\lambda^{1/2}$. It is well known that the WKB approximation fails in the vicinity of the turning point corresponding here to $u=1$, see Eq. (23). There is a number of papers dealing with the approximation of the wave function in the neighborhood of the turning points, see, e.g., Refs. 32–36. It is clear from the above equations that what we actually need is the behavior of the WKB approximation for u going to infinity. The proper normalization of the WKB wave function is guaranteed by matching it to the bound state function for u going to zero. In this region the WKB wave function is valid as an asymptotic expansion. Therefore, we do not have to care at all about the divergence of the WKB approximation at the turning point, see also Ref. 31.

E. Solution of equations

1. Boundary conditions

As becomes apparent during the calculation it is possible and advantageous to normalize the bound state wave function in such a way that it behaves in the overlap region as

$$\psi_0(\rho \rightarrow \infty, z \rightarrow 0) \sim e^{-\rho/N - z^2/(2N\rho) - z^4/(8N\rho^3) - \dots} \rho^{N-1} \left(1 + \frac{Cz^2}{\rho^2} + \dots \right), \quad (37)$$

where C is a constant depending on the form of the bound state wave function and it will be precisely determined in Sec. III. It is seen from Eq. (19) that for the ground state

$$C_{1s} = 0. \quad (38)$$

The solution of Eqs. (23)–(28) is determined uniquely by the requirement that the WKB wave function has this behavior for small u .

2. Calculation of the first approximation

Since for $u > 1$ the integrand in Eq. (23) is purely imaginary we can stop the integration at the turning point $u=1$. We start the integration at the point $u=0$ and take the minus sign in Eq. (23) to get the first term in the argument of exponential function on the right-hand side of Eq. (37) for small u

$$\Re[f_0(u \rightarrow \infty)] = - \int_0^1 du \frac{\sqrt{1-u^2}}{N} = - \frac{\pi}{4N}. \quad (39)$$

Equation (24) is nonlinear first order differential equation whose solution reads

$$h_0(u) = - \frac{1}{2N \arcsin u}, \quad (40)$$

where the integration constant was set to zero to get the second term in the argument of exponential function on the right-hand side of Eq. (37) for small u . We note that for $u > 1$, the function $\arcsin(u)$ is complex and two-valued with the branch point at $u=1$,

$$\arcsin(u) = \frac{\pi}{2} + i \ln(u \pm \sqrt{u^2 - 1}). \quad (41)$$

These two values correspond to the incoming (+) and outgoing (-) waves. Taking the solution with the minus sign we get

$$\Re[h_0(u \rightarrow \infty)] = h_0(u = 1) = -\frac{1}{N\pi}. \quad (42)$$

For u going to zero the function $f_1(u)$ given by Eq. (29) behaves as

$$f_1(u \rightarrow 0) \rightarrow -\frac{2N+1}{2} \ln 2 + (N-1)\ln(u) - A_1 = -\frac{2N+1}{2} \ln 2 + \frac{N-1}{2} \ln \lambda + (N-1)\ln \rho - A_1, \quad (43)$$

where we substituted for u from Eq. (15). To get the leading power term in Eq. (37) we obviously must set

$$A_1 = -\frac{2N+1}{2} \ln 2 + \frac{N-1}{2} \ln \lambda. \quad (44)$$

Using Eqs. (40) and (41) in Eq. (30) we get

$$\Re[F_1(u \rightarrow \infty)] = -\frac{1}{2} \ln N\pi - A_1 = -\frac{1}{2} \ln N\pi - \frac{N-1}{2} \ln \lambda + \frac{2N+1}{2} \ln 2. \quad (45)$$

Now we are ready to calculate the outgoing probability flux at the leading order of $\lambda^{1/2}$ from Eq. (35). By inserting Eqs. (39), (42), and (45) into Eq. (35) we obtain

$$J = \frac{2^{2N+1}}{\lambda^{N-1/4}(2N)^{1/2}} e^{-\pi/(2N\lambda^{1/2})} (1 + R_1\lambda^{1/2} + \dots). \quad (46)$$

3. Calculation of the second approximation

To calculate the coefficient R_1 we must determine the functions $q_0(u)$, $h_1(u)$, and $f_2(u)$.

Equation (26) is inhomogenous linear differential equation for $q_0(u)$. We first solve the homogenous part and then use the variation of a constant. We obtain the function $q_0(u)$ as

$$q_0(u) = [h_0(u)]^4 Q_0(u), \quad (47)$$

where

$$Q_0(u) = N^3 \frac{2u}{(1-u^2)^{1/2}}. \quad (48)$$

The integration constant was set to zero to get the third term in the argument of the exponential function on the right-hand side of Eq. (37). By virtue of Eqs. (42) and (48) the real part of the function $q_0(u)$ vanishes for u going to infinity

$$\Re[q_0(u \rightarrow \infty)] = \Re[Q_0(u \rightarrow \infty)] = 0. \quad (49)$$

The function $h_1(u)$ is obtained similarly as the function $q_0(u)$,

$$h_1(u) = [h_0(u)]^2 H_1(u), \quad (50)$$

where for the function $H_1(u)$ we obtain using Eqs. (24), (25), (47), (48) and integrating by parts

$$H_1'(u) = -\frac{2}{[f_0'(u)]^3} + \frac{1}{2u^3 f_0'(u) [h_0(u)]^2} + \left(3Q_0(u)h_0(u) + \frac{1}{[f_0'(u)]^2} \right)'. \quad (51)$$

Inserting now the explicit form of the functions $f_0'(u)$ and $h_0(u)$, Eqs. (23) and (40), the integration of the last equation yields

$$H_1(u) = 3Q_0(u)h_0(u) + \frac{1}{[f_0'(u)]^2} + 2N^3 \left[\frac{1}{(1-u^2)^{1/2}} + \frac{(1-u^2)^{1/2}}{2u^2} \arcsin^2(u) + \frac{\arcsin(u)}{u} - \int_0^u \frac{\arcsin^2(t)}{t(1-t^2)^{1/2}} dt \right] - A_2. \quad (52)$$

To determine the integration constant A_2 we note that for u going to zero we get from Eqs. (48), (50), and (52),

$$\lambda h_1(u \rightarrow 0) \rightarrow \frac{\lambda}{(2N)^2 u^2} (5N^3 - 2N^2 - A_2) = \frac{1}{(2N)^2 \rho^2} (5N^3 - 2N^2 - A_2), \quad (53)$$

where we substituted for u from Eq. (15). To get the last term on the right-hand side of Eq. (37), we obviously must set

$$A_2 = 4N^2 \left(\frac{5N-2}{4} - C \right). \quad (54)$$

The real part of the asymptotics of the function $h_1(u)$ is by virtue of Eqs. (42) and (48) given as

$$\Re[h_1(u \rightarrow \infty)] = h_0(u=1) \Re[H_1(u \rightarrow \infty)] = h_0(u=1) \left\{ -A_2 - 2N^3 \Re \left[\int_0^u \frac{\arcsin^2(t)}{t(1-t^2)^{1/2}} dt \right] \right\}. \quad (55)$$

Finally, the integration of Eq. (28) is substantially simplified by the identity

$$\frac{f_1''(u)}{2f_0'(u)} = \left(\frac{f_1'(u)}{2f_0'(u)} \right)' + \frac{f_1'(u)f_0''(u)}{2[f_0'(u)]^2}. \quad (56)$$

We note that this identity substantially simplifies the calculation of the higher orders of the WKB approximation in general. Further, it is useful to separate the part of $f_2(u)$ denoted as $F_2(u)$ that depends on the function $h_0(u)$ and the part denoted as $\phi_2(u)$ that is independent of it,

$$f_2(u) = F_2(u) + \phi_2(u). \quad (57)$$

The function $\phi_2(u)$ is integrated easily without any tricks. The real part of its asymptotics is given as

$$\Re[\phi_2(u \rightarrow \infty)] = -\frac{E_1 \pi}{4N}. \quad (58)$$

For the part $F_2(u)$ we find using Eqs. (24), (25), and (51) and integrating by parts

$$F_2'(u) = -\frac{1}{4u^3 f_0'(u) h_0(u)} + \left(\frac{H_1(u)h_0(u)}{2} - \frac{3Q_0(u)h_0(u)^2}{4} \right)'. \quad (59)$$

The real part of the asymptotics of the function $F_2(u)$ is by virtue of Eqs. (23), (40), and (48) given as

$$\Re[F_2(u \rightarrow \infty)] = h_0(u=1) \frac{H_1(u \rightarrow \infty)}{2} + \lim_{u \rightarrow \infty} \frac{N^2}{4} \left\{ \frac{(1-u^2)^{1/2} \arcsin(u)}{u^2} + \frac{1}{u} - \Re \left[\int_0^u \frac{dt \arcsin(t)}{t(1-t^2)^{1/2}} \right] \right\}. \quad (60)$$

By inserting Eqs. (49), (54), (55), (57), (58), and (60) into Eq. (36) we obtain

$$R_1 = -\frac{E_1 \pi}{2N} + \frac{A_2}{2N\pi} + \frac{N^2}{2\pi} \int_0^1 \frac{\arcsin^2(u) - \pi \arcsin(u)}{u(1-u^2)^{1/2}} du = -\frac{E_1 \pi}{2N} + \frac{2N}{\pi} \left(\frac{5N-2}{4} - C \right) - N^2 \frac{7\zeta(3)}{4\pi}, \quad (61)$$

where $\zeta(z)$ denotes Riemann zeta function. The first order perturbation energy E_1 as well as the constant C will be determined in the next section.

III. PERTURBATION METHOD

To calculate the norm of the wave function in Eq. (9) accurate up to the first order in $\lambda^{1/2}$ it is sufficient to take the wave function of the unperturbed hydrogen atom. For the excited states, the unperturbed wave function is degenerate and we must use the first order perturbation theory to determine the correct linear combination of the unperturbed functions. Since we need to calculate the perturbation energies up to the large order for numerical verification of the analytic formulas we describe the application of the perturbation method to Eq. (1) in greater detail.

The method described here is an extension of the method suggested in Ref. 29 for the coupled oscillators. The alternative way of calculation of the perturbation energies for the problem considered here is described for example in Ref. 10 for the ground state energy and in Refs. 8 and 37 for the excited states.

A. Derivation of difference equations

We transform Eq. (1) into the spherical coordinates, $x=r \sin \theta \cos \varphi$, $y=r \sin \theta \sin \varphi$ and $z=r \cos \theta$, multiply it by r , write the wave function in the form

$$\psi(r, \theta) = e^{-r/n} \sum_{k=0} \varphi_k(r, \theta) \left(\frac{B^2}{8} \right)^k, \quad (62)$$

insert the expansion (2) for the energy and compare the terms of the same order of $(B^2/8)$. Equation (1) then reads

$$\left\{ -\frac{r}{2} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left(\frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} \right) \right] + \frac{r}{N} \frac{\partial}{\partial r} + \frac{1-N}{N} \right\} \varphi_k + r^3 \sin^2 \theta \varphi_{k-1} = r \sum_{l=1}^k E_l \varphi_{k-l}. \quad (63)$$

Further, we expand the perturbation functions φ_k in the form of the double series

$$\varphi_k = \sum_{i=0} \sum_{j=0} g_{i,j}^{(k)} r^i \sin^{2j} \theta, \quad (64)$$

where the upper bounds of the summations will be determined later, insert it into Eq. (63) and compare the terms of the same order of r and $\sin^2 \theta$. As a result we get the difference equations for the coefficients $g_{i,j}^{(k)}$,

$$-\frac{1}{2}g_{i+1,j}^{(k)}[(i+1)(i+2)-2j(j+1)]-2(j+1)^2g_{i+1,j+1}^{(k)}+\frac{i+1-N}{N}g_{i,j}^{(k)}+g_{i-3,j-1}^{(k-1)}=\sum_{l=1}^k E_l g_{i-1,j}^{(k-l)}. \quad (65)$$

These equations can be used for the calculation of the perturbation energies as follows. The calculation for the ground state is not difficult and does not differ from that described in Refs. 2 and 29. In the first order of the perturbation theory we get

$$E_1^{1s} = 2. \quad (66)$$

For the excited states, the situation is a bit more complicated because the unperturbed state is degenerate. We describe calculation of the perturbation energies for the $3s$ - $3d$ state in detail.

B. Solution of equations for the $3s$ - $3d$ state

The unperturbed wave function of the $3s$ - $3d$ state reads

$$\psi_{3s-3d} = s\psi_{3s} + d\psi_{3d}, \quad (67)$$

where s and d denotes the coefficients of the linear combination and the unperturbed wave functions of $3s$ and $3d$ states read

$$\psi_{3s} = e^{-r/3} \left(1 - \frac{2r}{3} + \frac{2r^2}{27} \right) \quad (68)$$

and

$$\psi_{3d} = e^{-r/3} r^2 (1 - 3 \cos^2 \theta), \quad (69)$$

respectively. Thus, we set $g_{0,0}^{(0)}=s$, $g_{1,0}^{(0)}=-2s/3$, $g_{2,0}^{(0)}=(2s/27)-2d$, $g_{2,1}^{(0)}=3d$, and $g_{i,j}^{(0)}=0$ otherwise. We express the third term in Eq. (65), $g_{i,j}^{(k)}$, set $g_{i,k+2}^{(k)}=0$, $g_{3k+3,j}^{(k)}=0$ and solve Eq. (65) with $N=3$ for k starting from 1. For given k we solve Eq. (65) for j descending from $k+1$ to 0 and for i descending from $3k+2$ to 3. For $i=2$ the third term in Eq. (65) vanishes. Therefore, for $i=2$ we solve Eq. (65) for j descending from k to 1 to get equations for the coefficients $g_{2,k-1}^{(k)}$. For $i=2$ and $j=0$ we get the equation for the perturbation energies E_k . Finally, for i descending from 1 to 0 we again express $g_{i,j}^{(k)}$ and solve Eqs. (65) for j descending from $k+1$ to 0. The perturbation coefficients calculated in this way agree with those given in Ref. 8.

For the sake of transparency we illustrate this procedure of solving Eqs. (65) for $i=2$ on the first two orders of the perturbation theory. In the first order, $k=1$, we get for $j=1$,

$$30s + (1620 - 27E_1)d = 0 \quad (70)$$

and for $j=0$

$$(72 - 2E_1/3)s + 18E_1d = 0. \quad (71)$$

From Eq. (70) we get

$$d = \frac{10s}{9(E_1 - 60)}. \quad (72)$$

By inserting this value into Eq. (71) we obtain a quadratic equation for E_1 . Two roots of this equation equal

$$(E_1^{3s-3d})_{1,2} = 99 \pm 9\sqrt{41}. \quad (73)$$

In the second order of the perturbation theory, $k=2$, we get for $j=2$,

$$g_{2,2}^{(1)} = 0, \quad (74)$$

for $j=1$,

$$766\,908s + 15\,549\,570d - (5616s + 167\,670d)E_1 + 1701/2E_1^2d - 405g_{2,0}^{(1)} + (9E_1 - 810)g_{2,1}^{(1)} + 27E_2d = 0 \quad (75)$$

and finally for $j=0$,

$$1\,308\,798s + 1\,296\,4536d - (14\,310s + 29\,160d)E_1 + (57s - 567d)E_1^2 + (9E_1 - 972)g_{2,0}^{(1)} - 648g_{2,1}^{(1)} + (2s/3 - 18d)E_2 = 0. \quad (76)$$

We solve Eq. (75) to get the coefficient $g_{2,1}^{(1)}$ and insert it into Eq. (76) to get E_2 . We note that the values of the coefficients s and $g_{2,0}^{(1)}$ are not given by the perturbation theory. We also note that Eq. (76) for E_2 is linear. It means that after splitting of the degenerate energy level at the first order, there is only one solution for given E_1 for higher order perturbation energies E_2, E_3 , and so on.

Since the coefficient s is not given by the perturbation theory, it can be used to normalize the bound state function to behave as in Eq. (37) for large ρ and small z . The function (67) behaves in this region as

$$\psi_{3s-3d} \sim e^{-\rho/3 - z^2/(6\rho)} \rho^2 \left\{ \frac{2s}{27} + d + \frac{z^2}{\rho^2} \left(\frac{2s}{27} - 2d \right) + \dots \right\}. \quad (77)$$

It is seen that to get required behavior (37) we must set

$$\frac{2s}{27} + d = 1 \quad (78)$$

and that the constant C in Eq. (37) equals

$$C_{3s-3d} = \frac{2s}{27} - 2d. \quad (79)$$

C. Solution of equations for the state 5s-5d-5g

Only slight modifications of the above procedure are necessary for the 5s-5d-5g state. The unperturbed wave function in this case equals

$$\psi_{5s-5d-5g} = s\psi_{5s} + d\psi_{5d} + g\psi_{5g}, \quad (80)$$

where the wave functions of the 5s, 5d, and 5g states read

$$\psi_{5s} = e^{-r/5} \left(1 - \frac{4r}{5} + \frac{4r^2}{25} - \frac{4r^3}{375} + \frac{2r^4}{9375} \right), \quad (81)$$

$$\psi_{5d} = e^{-r/5} r^2 \left(1 - \frac{2r}{15} + \frac{2r^2}{525} \right) (1 - 3 \cos^2 \theta) \quad (82)$$

and

$$\psi_{5g} = e^{-r/5} r^4 \left(1 - 10 \cos^2 \theta + \frac{35}{3} \cos^4 \theta \right), \quad (83)$$

respectively.

In the first order of the perturbation theory we get from Eqs. (65) the following three energies:

$$(E_1^{5s-5d-5g})_{1,2,3} = 550,775 \pm 25\sqrt{481}. \quad (84)$$

Further we get the expression for the coefficients d and g ,

$$d = \frac{2s(7E_1 - 2850)}{(E_1 - 300)(E_1 - 750)} \quad (85)$$

and

$$g = \frac{12s}{7(E_1 - 300)(E_1 - 750)}. \quad (86)$$

To get required behavior (37) we set

$$\frac{2s}{9375} + \frac{2d}{525} + g = 1 \quad (87)$$

and the constant C equals

$$C_{5s-5d-5g} = \frac{4s}{9375} - \frac{2d}{525} - 8g. \quad (88)$$

D. Calculation of the norm of the wave function

The norm of the function (19) is calculated from Eq. (9):

$$\langle \psi_{1s} | \psi_{1s} \rangle = \int_0^\infty dr \int_0^\pi d\theta r^2 \sin \theta |\psi_{1s}|^2 = 1/2, \quad (89)$$

where we made change of the variables $\rho = r \sin \theta$ and $z = r \cos \theta$. Further, the norm of the wave functions (67) and (80) equals

$$\langle \psi_{3s-3d} | \psi_{3s-3d} \rangle = 19\,683d^2 + \frac{27s^2}{2} \quad (90)$$

and

$$\langle \psi_{5s-5d-5g} | \psi_{5s-5d-5g} \rangle = \frac{125s^2}{2} + \frac{390\,625d^2}{7} + 136\,718\,750\,000g^2, \quad (91)$$

respectively.

IV. LARGE-ORDER BEHAVIOR OF THE PERTURBATION SERIES

By inserting Eq. (46) into Eq. (7) and the latter equation into Eq. (3) we obtain the large-order behavior of the perturbation energies,

$$E_n = E_n^{\text{asy}} \left(1 + \frac{R_1 \pi}{2N \left(2n + 2N - \frac{3}{2} \right)} + \dots \right), \quad (92)$$

where the leading term of the large-order behavior reads

TABLE I. Comparison of the numerical and analytical values of the coefficient R_1 . See the text after Eq. (94) for details.

| State | E_1 | R_1 , Eq. (94) | R_1 , Eq. (61) |
|----------|--------------------|-----------------------|-----------------------|
| 1s | 2 | -3.333 724 367 368 66 | -3.333 724 367 368 65 |
| 3s-3d | $99+9\sqrt{41}$ | -82.969 565 723 945 | -82.969 565 723 942 |
| 3s-3d | $99-9\sqrt{41}$ | -47.079 674 497 78 | -47.079 674 497 77 |
| 5s-5d-5g | 550 | -273.083 854 65 | -273.083 854 64 |
| 5s-5d-5g | $775+25\sqrt{481}$ | -417.562 256 273 | -417.562 256 272 |
| 5s-5d-5g | $775-25\sqrt{481}$ | -212.681 342 928 | -212.681 342 920 |

$$E_n^{\text{asy}} = \frac{2^{4N} N^{2N-1}}{\pi^{2N+1/2} \langle \psi | \psi \rangle} (-1)^{n+1} \left(\frac{2^{3/2} N^2}{\pi} \right)^n \Gamma \left(2n + 2N - \frac{1}{2} \right). \quad (93)$$

Here, the norm of the wave function $\langle \psi | \psi \rangle$ is given by Eqs. (89)–(91) for 1s, 3s-3d, and 5s-5d-5g states, respectively. The coefficients s and d in Eq. (90) are given by Eqs. (72) and (78), respectively. The coefficients s , d , and g in Eq. (91) are given by Eqs. (85)–(87), respectively.

The coefficient R_1 in Eq. (92) is given by Eq. (61). The first order perturbation energies in this equation are given by Eqs. (66), (73), and (84) for 1s, 3s-3d, and 5s-5d-5g states, respectively. The constant C in Eq. (61) is given by Eqs. (38), (79), and (88) for 1s, 3s-3d, and 5s-5d-5g states, respectively.

Formula (93) for $N=1$ and $N=3$ was for the first time given in Ref. 1 and for $N=1$ rederived in Refs. 3 and 4. The first correction (61) is given here for the first time. To check its correctness we calculated numerically

$$R_1 = \left(\frac{E_n}{E_n^{\text{asy}}} - 1 \right) \frac{2N \left(2n + 2N - \frac{3}{2} \right)}{\pi}, \quad (94)$$

where E_n are the exact perturbation energies calculated from Eqs. (65) by means of the language MAPLE and E_n^{asy} is the leading term of the large-order behavior given by Eq. (93). For 1s state we calculated first 80 perturbation coefficients in the rational form. Numerical values in Eq. (94) were extrapolated by means of the Thiele-Padé extrapolation from the interval $n=70-80$ to infinity. For 3s-3d and 5s-5d-5g states we calculated first 100 coefficients in 200 digits accuracy for both energies in Eq. (73) and all three energies in Eq. (84). Numerical values were extrapolated from the interval $n=90-100$ to infinity. The extrapolated values are compared with the values given by Eq. (61) in Table I. Agreement between numerical and WKB results is excellent and confirms soundness of both the perturbation and WKB methods suggested in this paper.

V. CONCLUSIONS

In this paper the large-order behavior of the perturbation series for the energy of the hydrogen atom in the magnetic field was derived by means of the modified WKB approximation. The asymptotic formula derived by Avron in Ref. 1 was generalized to describe the states of higher than twofold degeneracies. On the other hand, we restricted ourselves to the states of zero projection of the angular momentum and even parity, while in Ref. 1 this restriction was not done. The first correction to the asymptotic formula was given here for the first time. The analytic results were compared with numerical ones and an excellent agreement between the two was found. The calculation of further terms in the expansions (35) and (92), though straightforward in principle, is very tedious. We note that in this case we must take also the correction to the norm of the wave function.^{24,31,33,34} On the basis of the experience with one-dimensional problems^{33,34} we expect that the series (35) and (92) are only asymptotic, i.e., hold for sufficiently small λ and large n only.

The most immediate further application of the WKB method suggested in this paper is the calculation of the ionization rate of the atoms in the weak electric field. The standard calculation of this rate for the many-electron atoms is based on the calculation for the hydrogen atom.³⁸ The latter is based on the separability of the Schrödinger equation in the parabolic coordinates.^{33,35,36,39} However, the separation of the Schrödinger equation for the motion of the electron in the binding potential and applied electric field holds only in the case of a purely Coulombic binding potential. Arbitrarily small perturbation from the other electrons destroys the separability of Schrödinger equation. Even for the hydrogen atom, the separability is lost once the relativistic effects are considered. Only slight modifications of the procedure described here are necessary to derive the ionization rate of the hydrogen atom in the weak electric field without invoking the separability of the Schrödinger equation.

Finally, we note that the WKB approximation suggested here is not bound to the problem of the calculation of the lifetime of quasistationary states. It is a local approximation of the wave function and it can be used, for example, to describe motion of the bound electron in the intense laser field or to estimate forward scattering amplitude for the elastic scattering of the electrons on the atoms.

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APPENDIX

In this Appendix we discuss the relation between the WKB method suggested in Sec. II and the usual semiclassical approximation.

Let us consider the Schrödinger equation where we included the reduced Planck constant \hbar ,

$$\hbar^2 \left[\frac{\partial^2}{\partial \rho^2} + \frac{\partial^2}{\partial z^2} \right] \psi = [V(\rho, z) - E] \psi, \quad (\text{A1})$$

and let us assume that the potential behaves in the vicinity of ρ axis as in Eq. (10). Then we can write the wave function of the particle in the vicinity of ρ axis in the form of Eq. (11). In general case there is no parameter λ associated with the external field driving the particle out of the potential well. Nevertheless, by the scaling

$$z = \hbar \eta \quad (\text{A2})$$

the WKB approximation, very similar to that suggested for Eq. (5), can be obtained. Physically, the scaling (A2) implies that while the longitudinal motion is treated semiclassically, the transversal motion is treated in fully quantum manner. Proceeding then in accordance with the considerations leading to Eq. (35), it can be shown that the expansion of Eq. (A1) in the powers of η and \hbar provides systematic approximations to the probability flux in the ρ direction in form of the series in the reduced Planck constant \hbar .

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