Analytical solutions of the Schrödinger equation for a hydrogen atom in a uniform electric field

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We consider the Schrödinger equation for the hydrogen atom in a uniform electric field, searching for solutions of this equation in parabolic coordinates in a separable form. With some restrictions on the parameters, we have found the exact analytical expressions for the continuum wave function component and for the most important Stokes multiplier.

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I. INTRODUCTION

The hydrogen atom in a uniform electric field, being the simplest Stark system, has always served as a model for development of various numerical and analytical approaches. This system was studied by Schrödinger [1] in the framework of perturbation theory. It was found that the perturbation series are divergent, indicating serious mathematical difficulties inherent to the problem. These difficulties, in particular, have affected calculations of the ionization rate, the correct expression for which was obtained, after many unsuccessful attempts, only in Refs. [2,3] using the comparison equation method.

The experimental study of photoionization of atomic hydrogen in an electric field [4–6] revealed a number of special features of its cross section, in particular, the resonant structure at negative energies. In theoretical studies, the continuum wave functions of excited states were obtained numerically [7] or in the framework of the semiclassical theory [8–10]. Another approach was based on the concept of resonances. The positions of resonances were determined by various methods, including the perturbation theory [5,11] and the complex variational method [12]. It has been shown that the Stark resonances are uniquely determined by the Borel summing of asymptotic series of perturbation theory [13–15].

Impressive ionization microscopy experiments [16–19] have attracted attention to analysis of a spatial distribution of electron current produced by ionization of atoms in electric field. The numerical calculations of the spatial structure of electronic wave function are based on solution of the coupled channels equations [20,21] and on a wave-packet propagation approach [19]. The theoretical description of microscopic experiments widely uses the semianalytical approach, which is based on the local-frame-transformation theory and on the semiclassical propagation of outgoing waves [22–24].

Modern theoretical results reproduce experiments and still keep improving. However, the theory of the Stark systems cannot be considered as complete. The exact analytical solution of the fundamental Stark problem for atomic hydrogen is still unknown and, therefore, it is impossible to estimate the real accuracy of semiclassical calculations.

A certain progress in overcoming this difficulty has been made [25]. By means of transition into the momentum representation, the problem has been reduced to the study of the triconfluent Heun equation [26]. The detailed analysis of the global asymptotes of solutions of this equation has enabled us to formulate the analytical procedure of calculation of the Stokes multipliers. Also, it was shown that the physical characteristics of the system can be expressed in terms of the Stokes multipliers. However, at negative energies, representation of some of these multipliers in an exact analytical form proved to be impossible and calculations have been carried out with the involvement of semiclassical approach.

In this work, we present the exact analytical solutions of the Stark problem for a hydrogen atom. Such solutions exist if the energy of the atom has some certain values, depending on the strength of the external electric field. The use of these solutions gives opportunities for estimation of accuracy of approximate approaches.

The derivation of the exact solutions is based on the results obtained in our previous work [25]. In Sec. II we briefly describe the basic equations and definitions given in this study. Section III describes the exact solutions and the conditions for their existence. The specific examples of such solutions are given in the appendix. The limiting behavior of the exact wave functions in the asymptotic regions is analyzed in Sec. IV. In the concluding section we apply the exact results to the analysis of the accuracy of the semiclassical approach at calculation of some parameters in our work [25].

II. LAPLACE TRANSFORM AND THE ASYMPTOTIC SOLUTIONS OF A QUARTIC OSCILLATOR

Hydrogen in a uniform electric field is described by the wave function

$$\psi_{E,n_1,m} = \frac{\chi_1(\xi) \,\chi_2(\eta)}{\sqrt{\xi\eta}} e^{im\varphi},\tag{1}$$

where (ξ, η) are parabolic coordinates [1] and the components $\chi_1(\xi)$, $\chi_2(\eta)$ satisfy the coupled reduced biconfluent Heun equations

$$\frac{d^2\chi_1}{d\xi^2} + \left[-\frac{F}{4}\xi + \frac{E}{2} + \frac{\beta_1}{\xi} - \frac{m^2 - 1}{4\xi^2} \right] \chi_1 = 0, \quad (2)$$

$$\frac{d^2\chi_2}{d\eta^2} + \left[\frac{F}{4}\eta + \frac{E}{2} + \frac{\beta_2}{\eta} - \frac{m^2 - 1}{4\eta^2}\right]\chi_2 = 0.$$
(3)

$$\beta_1 + \beta_2 = 1. \tag{4}$$

Here *m* is the integer projection of an angular momentum onto the field direction. *F* is the strength of the field. The parameters β_1 and β_2 are the separation constants.

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For a given energy *E*, Eq. (2) defines the discrete spectrum of parameter β_1 . The parabolic quantum numbers n_1 and n_2 , which correspond to separation constants β_1 and $\beta_2 = 1 - \beta_1$, at negative energies are given by the conventional equations [27]

$$n_1 = n\beta_1 - (|m| + 1)/2, \qquad (5)$$

$$n_2 = n\beta_2 - (|m| + 1)/2, \qquad (6)$$

where the parameter *n* is

$$n = 1/\sqrt{-2E}.\tag{7}$$

In the presence of the external field, the parabolic quantum numbers n_1 and n_2 have noninteger values. For the states with large values of n_1 , the quantum number n_2 is negative.

The eigenvalue problem (2) can be easily solved by a variational method, expanding the solutions on the basis of hydrogen functions. Alternatively, in the physically relevant region $F \ll 1$, the spectrum of the parameter β_1 can be found in frames of the perturbation theory [27].

The solutions of Eq. (3) belong to continuous spectrum and describe the scattering and ionization processes. Analysis of solutions of Eq. (3) is the most complicated and, at the same time, the most physically interesting part of the problem. The existence of exact solutions of this equation is the main focus of our work.

The accurate analysis can be performed in the Laplace representation

$$\chi_2(\eta) = \eta^{(m+1)/2} \int_{\mathcal{L}} e^{a\eta z} e^{\Phi/2} \psi_m(z) \, dz \,, \tag{8}$$

where

$$a = (F/4)^{1/3}, \quad \Phi = z^3/3 - \varepsilon z,$$
 (9)

and the function $\psi_m(z)$ satisfies the equation for the quartic oscillator

$$\frac{d^2\psi_m}{dz^2} + \left[\lambda + mz - \left(\frac{z^2 - \varepsilon}{2}\right)^2\right]\psi_m = 0 \qquad (10)$$

with

$$\varepsilon = \frac{-2E}{(2F)^{2/3}}, \quad \lambda = \frac{2}{(2F)^{1/3}}\beta_2.$$
 (11)

The Laplace transform of Eq. (2) is totaly analogous to that of Eq. (3) and leads to equation for the quartic oscillator with $\lambda = -2\beta_1/(2F)^{1/3}$.

In Refs. [25,28], we have performed a detailed study of asymptotic properties of solutions of the quartic oscillator equation. The asymptotic representation of solutions at $|z| \rightarrow \infty$ is given by the Thomé series [29]

$$\psi_m(z) = C_m(z), \quad D_m(z), \tag{12}$$

where

$$C_m(z) = z^{m-1} e^{-\Phi/2} \sum_n c_n / z^n , \qquad (13)$$

$$D_m(z) = z^{-m-1} e^{\Phi/2} \sum_n d_n / z^n , \qquad (14)$$

and the coefficients c_n and d_n satisfy the recurrence relations

$$nc_n + \lambda c_{n-1} - \varepsilon (n - m - 1)c_{n-2} + (n - m - 1)(n - m - 2)c_{n-3} = 0,$$
(15)

$$nd_n - \lambda d_{n-1} - \varepsilon (n+m-1)d_{n-2} - (n+m-1)(n+m-2)d_{n-3} = 0,$$
(16)

with initial conditions

1

$$c_0 = 1, \quad c_1 = -\lambda, \quad c_2 = \frac{1}{2}(\lambda^2 + \varepsilon - \varepsilon m), \quad (17)$$

$$d_0 = 1, \quad d_1 = \lambda, \quad d_2 = \frac{1}{2}(\lambda^2 + \varepsilon + \varepsilon m).$$
 (18)

The complex plane of the variable z is divided into six domains by the anti-Stokes lines

arg
$$z = i \pi/3 - \pi/6$$
, $i = 1, \dots, 6$, $|z| \to \infty$. (19)

These six domains are labeled by roman numbers from I to VI counterclockwise, starting from the domain around the semiaxis z > 0. The asymptotic representation of a general solution of Eq. (10) in different domains is a linear combination of functions *C* and *D*. The coefficients of this linear combination change their value at the intersection of the Stokes lines. The magnitude of these changes is determined by the Stokes multipliers $T_{m,i}$, specific for *i*th domain (see Refs. [25,28] for details).

In Ref. [30] we have shown that the amplitude of the normalized wave function $\chi_2(\eta)$ near origin $\eta = 0$ and the phase of the function $\chi_2(\eta)$ at $\eta \to \infty$ are determined by the Stokes multiplier $T_{|m|,3}$:

$$\chi_2(\eta \to 0) = \frac{a^{|m|/2}}{|T_{|m|,3}| |m|!} \ \eta^{(1+|m|)/2}, \tag{20}$$

$$\chi_2(\eta \to \infty) = \frac{1}{\sqrt{\pi} a^{3/4} \eta^{1/4}} \cos\left[\frac{2}{3}(a\eta - \varepsilon)^{3/2} + \frac{3\pi m}{2} - \arg T_{|m|,3} + \frac{\pi}{4}\right].$$
 (21)

The Stokes multipliers are revealed in many physical phenomena. In Refs. [25,30] we have shown that the basic physical properties of the Stark system can be expressed in terms of the Stokes multipliers for the quartic oscillator equation. The quantization condition for Eq. (2) is

$$T_{|m|,1}(\beta_1) = 0. (22)$$

The complex Stark resonances are the solutions of equation

$$T_{|m|,3}(\beta_2) = 0. \tag{23}$$

The argument of the multiplier $T_{|m|,3}(\beta_2)$ defines the scattering phase. The absolute value of the Stokes parameter $T_{|m|,3}$ determines the photoionization cross section.

The Stokes multipliers have been found in Refs. [25,28] in an analytical form. The multiplier $T_{m,1}$ for arbitrary energy and the multiplier $T_{m,3}$ at positive energies are expressed through the parameters of asymptotic solutions of recurrences (15) and (16). The multiplier $T_{m,3}$ at negative energies has been found in frame of complex asymptotic analysis. The analytical expressions obtained in Ref. [25] for $T_{m,3}$ at negative energies contain undetermined parameters—the dynamical phase and the dynamical amplitude. These parameters have been calculated in Ref. [25] in semiclassical approximation at the condition

$$\varepsilon \gg 1.$$
 (24)

The exact solutions, which will be described below, provide possibility to check the accuracy of the semiclassical approach.

III. EXACT SOLUTIONS

Analyzing the asymptotic behavior of solutions of Eq. (10), we have found that at some conditions this equation can be solved exactly. Generally, the solution of the recurrence equation (16) is the infinite sequence of coefficients d_n . At the same time, this sequence can be truncated in the case, when the parameter *m* is negative:

$$m = -k - 1, \quad k = 0, 1, 2, \dots$$
 (25)

In this case, when the condition

$$d_{k+1} = 0 \tag{26}$$

is fulfilled, all the subsequent coefficients will vanish automatically, and the truncated asymptotic series (14) becomes an exact solution of the quartic oscillator equation. This exact solution can be recast in the form

$$\psi_m(z) = D_m(z) = e^{\Phi/2} \sum_{n=0}^k d_n z^{k-n}$$
 (27)

The condition (26) is a polynomial equation of |m|th order in λ . Together with Eq. (4) it defines implicitly such a relation between the energy and the field, which ensures the existence of the solution of the Stark problem in an exact analytical form. It can be shown that at low electric fields such solutions exist for negative energies below the Stark resonances. In the limit F = 0, these energies formally coincide with the Coulomb levels

$$E_n = -\frac{1}{2n^2}, \quad n = n_1 + n_2 + |m| + 1,$$
 (28)

with

$$n_1 = 0, 1, 2, \dots,$$
 (29)

but with negative values of the parabolic quantum number n_2 :

$$n_2 = -1, -2, \dots, -|m|.$$
 (30)

To calculate the wave function $\chi_2(\eta)$ in the coordinate representation, we insert expression (27) for the function $\psi_m(z)$ in the integrand of Eq. (8) and we take the integration contour which starts in domain IV at $z \to -\infty$ and ends in the asymptotic region of domain II:

$$\chi_2(\eta) = \eta^{-k/2} \int_{-\infty}^{e^{i\pi/3}\infty} e^{a\eta z} e^{z^3/3-\varepsilon z} \sum_{n=0}^k d_n z^{k-n} dz \,.$$
(31)

The calculation of the integral in Eq. (31) can be performed analytically (see Ref. [31]) and leads to a complex expression for the wave function

$$\chi_2(\eta) = \pi \ \eta^{-k/2} [f_1(\zeta) + i \ f_2(\zeta)], \tag{32}$$

where the variable ζ is

$$\zeta = \varepsilon - a\eta = -\frac{2E + F\eta}{(2F)^{2/3}},\tag{33}$$

and the real functions $f_{1,2}(\zeta)$ are

$$f_1(\zeta) = \sum_{i=0}^k (-1)^i d_{k-i} \operatorname{Bi}^{(i)}(\zeta)$$
(34)

and

$$f_2(\zeta) = \sum_{i=0}^k (-1)^i d_{k-i} \operatorname{Ai}^{(i)}(\zeta).$$
(35)

 $Ai(\zeta)$ and $Bi(\zeta)$ are the Airy functions. The superscripts in parentheses, (*i*), denote the *i*th derivative of functions.

The exact solution $\chi_2(\eta)$, which is given by Eq. (32), is not physical, since it has the singularity at $\eta = 0$. This solution is the combination of two terms,

$$g_{1,2}(\zeta) = \eta^{-k/2} f_{1,2}(\zeta), \tag{36}$$

each of which is also an exact singular solution of Eq. (3). The regular physical solution can be obtained as a linear combination of these two singular solutions,

$$\chi_2(\eta) = \eta^{-k/2} [c_1 f_1(\zeta) + c_2 f_2(\zeta)], \qquad (37)$$

where the coefficients c_1 and c_2 must be chosen from the condition

$$\chi_2(\eta = 0) = 0, \tag{38}$$

which can be satisfied at the choice

$$c_1 = f_2(\varepsilon), \quad c_2 = -f_1(\varepsilon). \tag{39}$$

Finally, the exact physical solution has the form

$$\chi_2(\eta) = \eta^{-k/2} [f_2(\varepsilon) f_1(\zeta) - f_1(\varepsilon) f_2(\zeta)].$$
(40)

IV. THE ASYMPTOTIC BEHAVIOR OF EXACT SOLUTIONS

At small η , the behavior of the exact regular solution (40) is determined by the Taylor series

$$\chi_2(\eta \to 0) = \eta^{-k/2} \sum_n J^{(n)}(\zeta) \Big|_{\zeta = \varepsilon} \frac{(-a\eta)^n}{n!}.$$
 (41)

In this equation, the function $J(\zeta)$ is

$$J(\zeta) = f_2(\varepsilon) f_1(\zeta) - f_1(\varepsilon) f_2(\zeta).$$
(42)

The derivatives $J^{(n)}(\zeta)|_{\zeta=\varepsilon}$ can be calculated as

$$J^{(n)}(\zeta)|_{\zeta=\varepsilon} = \lim_{\zeta \to 0} \tilde{J}_n(\zeta), \tag{43}$$

where

$$\tilde{J}_{n}(\zeta) = f_{2}(\zeta) f_{1}^{(n)}(\zeta) - f_{1}(\zeta) f_{2}^{(n)}(\zeta)$$

= $\eta^{k/2} g_{2}(\zeta) [\eta^{k/2} g_{1}(\zeta)]^{(n)} - \eta^{k/2} g_{1}(\zeta) [\eta^{k/2} g_{2}(\zeta)]^{(n)}$
(44)

[see Eq. (36)]. As it was stated above, the functions $g_i(\zeta)$ are the exact solutions of Eq. (3). Calculating the derivatives $\left[\eta^{k/2}g_i(\zeta)\right]^{(n)}$ sequentially one after the other for n = 1, 2, ...,

and taking into account at small η only the leading term in Eq. (3), we replace at each step the second derivative of functions $g_i(\zeta)$ by

$$\frac{d^2 g_i}{d\eta^2} = \frac{m^2 - 1}{4\eta^2} g_i = \frac{k(k+2)}{4\eta^2} g_i.$$
 (45)

As a result, in the limit of small η we get

$$[\eta^{k/2}g_i(\zeta)]^{(n)} = p_n \eta^{k/2-n}g_i + q_n \eta^{k/2-n+1}g'_i,$$

$$g'_i = \frac{dg_i}{d\zeta}.$$
 (46)

Here the parameters p_n and q_n satisfy the recurrence equations

$$p_{n+1} = \frac{k(k+2)}{4a^2}q_n - \frac{k-2n}{2a}p_n,$$

$$q_{n+1} = p_n - \frac{k-2n+2}{2a}q_n,$$

$$p_0 = 1, \quad q_0 = 0,$$
(47)

which have the simple solution

$$q_n = \frac{k!}{(k+1-n)!(-a)^{n-1}}, \quad p_n = -\frac{k}{2a}q_n, \quad n \ge 1.$$
 (48)

Substituting Eq. (46) into Eq. (44), we get

$$\tilde{J}_n(\zeta) = \eta^{k+1-n} q_n(g_2 g'_1 - g_1 g'_2).$$
(49)

The expression in parentheses, i.e., Wronskian

$$\Omega = g_2 g'_1 - g_1 g'_2, \tag{50}$$

has some constant value, and it is seen from Eq. (49) that k derivatives $J^{(n)}(\zeta)|_{\zeta=\varepsilon}$, n = 1, 2, ..., k, are equal to zero, while

,

$$J^{(k+1)}(\zeta)|_{\zeta=\varepsilon} = q_{k+1}\Omega = \Omega \frac{k!}{(-a)^k}.$$
(51)

The Wronskian Ω can be calculated as [see Eq. (49)]

$$\Omega = \eta^{-k} \tilde{J}_1(\zeta). \tag{52}$$

Here $\tilde{J}_1(\zeta)$, Eq. (44), is

$$\tilde{J}_1(\zeta) = f_2(\zeta) \frac{df_1(\zeta)}{d\zeta} - f_1(\zeta) \frac{df_2(\zeta)}{d\zeta}.$$
(53)

The functions $f_{1,2}(\zeta)$ are given by Eqs. (34) and (35). Then, Eq. (53) reduces to

$$\tilde{J}_{1}(\zeta) = \sum_{i,j=0}^{k} (-1)^{i+j} d_{k-i} d_{k-j} [\operatorname{Ai}^{(i)} \operatorname{Bi}^{(j+1)} - \operatorname{Bi}^{(i)} \operatorname{Ai}^{(j+1)}].$$
(54)

According to the Airy equation,

$$\Psi''(\zeta) = \zeta \Psi,$$

the derivatives of solutions $\Psi(\zeta)$ can be written in the form

$$\Psi^{(i)}(\zeta) = P_i(\zeta)\Psi(\zeta) + Q_i(\zeta)\Psi'(\zeta), \tag{55}$$

where the polynomials $P_i(\zeta)$ and $Q_i(\zeta)$ satisfy the recurrence equations

$$P_{i+1} = P'_i + \zeta Q_i,$$

$$Q_{i+1} = Q'_i + P_i,$$

$$P_0 = 1, \quad Q_0 = 0.$$
(56)

Several first polynomials are

$$P_{1} = 0, \quad Q_{1} = 1,$$

$$P_{2} = \zeta, \quad Q_{2} = 0,$$

$$P_{3} = 1, \quad Q_{3} = \zeta,$$

$$P_{4} = \zeta^{2}, \quad Q_{4} = 2,$$

$$P_{5} = 4\zeta, \quad Q_{5} = \zeta^{2},$$

$$P_{6} = 4 + \zeta^{3}, \quad Q_{6} = 6\zeta.$$
(57)

Applying Eq. (55) to each of the functions $Ai(\zeta)$ and $Bi(\zeta)$, we recast Eq. (54) in the form

$$\tilde{J}_{1}(\zeta) = W \sum_{i,j=0}^{k} (-1)^{i+j} d_{k-i} d_{k-j} [P_{i} Q_{j+1} - Q_{i} P_{j+1}], \quad (58)$$

where W is the Wronskian

$$W = \operatorname{Ai}(\zeta)\operatorname{Bi}'(\zeta) - \operatorname{Bi}(\zeta)\operatorname{Ai}'(\zeta) = \frac{1}{\pi}.$$
 (59)

Now, Eq. (52) reads

$$\Omega = W \eta^{-k} \sum_{i,j=0}^{k} (-1)^{i+j} d_{k-i} d_{k-j} \times [P_i(\zeta) Q_{j+1}(\zeta) - Q_i(\zeta) P_{j+1}(\zeta)].$$
(60)

The Wronskian Ω does not depend on η . Consequently, in this sum of polynomials in $\zeta = \varepsilon - a\eta$, all the terms with powers less than *k* cancel each other. The term with the highest power *k* corresponds to *i*, *j* = *k* and the coefficient before this term is equal to $(-1)^k$. As a result,

$$\Omega = \frac{(a)^k}{\pi} \,. \tag{61}$$

Finally, the derivative $J^{(k+1)}(\zeta)|_{\zeta=\varepsilon}$ reduces to

$$J^{(k+1)}(\zeta)\big|_{\zeta=\varepsilon} = \frac{(-1)^k k!}{\pi},$$
(62)

and, at small η , the behavior of the wave function $\chi_2(\eta)$ is

$$\chi_2(\eta \to 0) = -\frac{a^{k+1}}{\pi(k+1)}\eta^{1+k/2} = -\frac{a^{|m|}}{\pi|m|}\eta^{(1+|m|)/2}.$$
 (63)

Calculation of the asymptotic behavior of the function $\chi_2(\eta)$ at $\eta \to \infty$ is straightforward. The function $\chi_2(\eta)$ is given by Eq. (40) with functions $f_1(\zeta)$ and $f_2(\zeta)$ from Eqs. (34) and (35). Calculating the functions $f_1(\zeta)$ and $f_2(\zeta)$ in the limit $\eta \to \infty$, we take into account only the highest order derivatives in the right-hand side of Eqs. (34) and (35). The asymptotic forms of Airy functions are

Ai
$$(\zeta \to -\infty) = \frac{1}{\sqrt{\pi} |\zeta|^{1/4}} \cos\left[\frac{2}{3} |\zeta|^{3/2} - \frac{\pi}{4}\right],$$
 (64)

$$\operatorname{Bi}(\zeta \to -\infty) = \frac{1}{\sqrt{\pi} |\zeta|^{1/4}} \cos\left[\frac{2}{3} |\zeta|^{3/2} + \frac{\pi}{4}\right]. \quad (65)$$



FIG. 1. The relative error of the semiclassical representation [25] of the Stokes multiplier $T_{2,3}$.

For the function $\chi_2(\eta)$ we get

$$\chi_{2}(\eta \to \infty) = -\frac{R a^{(2|m|-3)/4}}{\sqrt{\pi} \eta^{1/4}} \cos\left[\frac{2}{3}(a\eta - \varepsilon)^{3/2} + \frac{3\pi m}{2} + \varphi + \frac{3\pi}{4}\right],$$
(66)

where

$$\varphi = 2 \arctan\left(\frac{f_1(\varepsilon)}{R + f_2(\varepsilon)}\right), \quad R = \sqrt{f_1^2(\varepsilon) + f_2^2(\varepsilon)}.$$
 (67)

As it was stated in Sec. II, the asymptotic behavior of the wave function $\chi_2(\eta)$ in a general case is given by Eqs. (20) and (21), and it is determined by the Stokes multiplier $T_{|m|,3}$. Comparison of Eqs. (20) and (21) with Eqs. (63) and (66) leads to exact analytical form of the Stokes multiplier $T_{|m|,3}$ in the solvable case:

$$|T_{|m|,3}| = \frac{\pi R}{(|m|-1)!}, \quad \arg T_{|m|,3} = -\frac{\pi}{2} - \varphi.$$
 (68)

V. CONCLUDING REMARKS

In this work we have found some exact solutions for the hydrogen atom in a uniform electric field. These solutions are given by Eq. (40), where the functions $f_{1,2}(\zeta)$, Eqs. (34) and (35), are the finite sums of derivatives of Airy functions. The condition of existence of these solutions is the polynomial equation (26). Analysis of the asymptotic properties of the exact solution made it possible to obtain an exact analytical expression (68) for the Stokes multiplier $T_{|m|,3}$, which is of great importance, since it determines the positions of resonances, the scattering phase, and the photoionization cross section [25,30].

The exact analytical results provide a powerful tool for testing various approximate methods and numerical results. As an example, we have compared the exact values of the Stokes multiplier $T_{|m|,3}$ given by Eq. (68) with the data calculated using the semiclassical representation of the dynamical parameters in the analytical expressions from Ref. [25]. The comparison shows that the semiclassical approach has satisfactory accuracy even for relatively small values of the parameter ε . Figure 1 illustrates this result for the case |m| = 2.

APPENDIX: TWO SPECIFIC EXAMPLES

1. The case m = -1

The parameter k, which is defined by Eq. (25), is equal to zero, and the condition of existence of exact solution, Eq. (26), reads

$$d_1 = 0, \qquad (A1)$$

which leads to

$$\beta_2 = 0 \tag{A2}$$

[see Eqs. (18) and (11)]. At these conditions (i.e., m = -1, $\beta_2 = 0$), the function (40) becomes an exact solution of Eq. (3) at arbitrary values of the energy *E* and the field *F*. In this case, the sums in Eqs. (34) and (35) contain single terms and the function (40) is simplified as

$$\chi_2(\eta) = \operatorname{Ai}(\varepsilon)\operatorname{Bi}(\varepsilon - a\eta) - \operatorname{Bi}(\varepsilon)\operatorname{Ai}(\varepsilon - a\eta).$$
(A3)

Here the reduced energy ε and the force constant *a* are given by Eqs. (11) and (9).

The set of energies, at which the analytical solution (A3) can be applied, is determined by the eigenvalue problem (2) with $\beta_1 = 1 - \beta_2 = 1$. In particular, at $F \ll 1$, this energies are

$$E = -\frac{1}{2(v+1)^2} + \frac{3F}{2}(v+1)^2,$$
 (A4)

$$v = 0, 1, 2, \dots$$
 (A5)

2. The case m = -2

In this case the parameter k is equal to unity and the condition (26) reads

$$d_2 = \frac{1}{2}(\lambda^2 - \varepsilon) = 0. \tag{A6}$$

This equation has two solutions,

$$\lambda = \pm \sqrt{\varepsilon},\tag{A7}$$

and leads to the following coupling between the energy *E* and the parameter β_2 :

$$\beta_2 = \pm \sqrt{-E/2}.\tag{A8}$$

At these conditions, the function (40) becomes an exact solution of Eq. (3). The sums in Eqs. (34) and (35) contain two terms and the function (40) has the form

$$\chi_{2}(\eta) = \eta^{-1/2} \{ [\pm \sqrt{\varepsilon} \operatorname{Ai}(\varepsilon) - \operatorname{Ai}'(\varepsilon)] \\ \times [\pm \sqrt{\varepsilon} \operatorname{Bi}(\varepsilon - a\eta) - \operatorname{Bi}'(\varepsilon - a\eta)] \\ - [\pm \sqrt{\varepsilon} \operatorname{Bi}(\varepsilon) - \operatorname{Bi}'(\varepsilon)] \\ \times [\pm \sqrt{\varepsilon} \operatorname{Ai}(\varepsilon - a\eta) - \operatorname{Ai}'(\varepsilon - a\eta)] \}.$$
(A9)

The set of energies at which the analytical solution (A9) can be applied is determined by the eigenvalue problem (2) with $\beta_1 = 1 - \beta_2 = 1 \pm \sqrt{-E/2}$. In particular, at $F \ll 1$, these energies are

$$E = -\frac{1}{2(\nu+3+n_2)^2} + \frac{3F}{2}(\nu+1)(\nu+2), \quad (A10)$$

$$v = 0, 1, 2, \dots, n_2 = -1, -2.$$
 (A11)

Here n_2 is the parabolic parameter given by Eq. (6).

- [1] E. Schrödinger, Ann. Phys. (Leipzig) 385, 437 (1926).
- [2] S. Y. Slavyanov, Problemy Mat. Fiziki 8, 125 (1970).
- [3] T. Yamabe, A. Tachibana, and H. J. Silverstone, Phys. Rev. A 16, 877 (1977).
- [4] T. Bergeman, C. Harvey, K. B. Butterfield, H. C. Bryant, D. A. Clark, P. A. M. Gram, D. MacArthur, M. Davis, J. B. Donahue, J. Dayton *et al.*, Phys. Rev. Lett. 53, 775 (1984).
- [5] H. Rottke and K. H. Welge, Phys. Rev. A 33, 301 (1986).
- [6] W. L. Glab and M. H. Nayfeh, Phys. Rev. A 31, 530 (1985).
- [7] E. Luc-Koenig and A. Bachelier, J. Phys. B 13, 1743 (1980).
- [8] V. D. Kondratovich and V. N. Ostrovsky, J. Phys. B 17, 1981 (1984).
- [9] D. A. Harmin, Phys. Rev. A 24, 2491 (1981).
- [10] D. A. Harmin, Phys. Rev. A 31, 2984 (1985).
- [11] R. J. Damburg and V. V. Kolosov, J. Phys. B 11, 1921 (1978).
- [12] G. Alvarez, R. J. Damburg, and H. J. Silverstone, Phys. Rev. A 44, 3060 (1991).
- [13] S. Graffi and V. Grecchi, Commun. Math. Phys. 62, 83 (1978).
- [14] I. W. Herbst and B. Simon, Phys. Rev. Lett. 41, 67 (1978).
- [15] S. Graffi, V. Grecchi, and B. Simon, J. Phys. A 12, L193 (1979).
- [16] G. D. Stevens, C.-H. Iu, T. Bergeman, H. J. Metcalf, I. Seipp, K. T. Taylor, and D. Delande, Phys. Rev. A 53, 1349 (1996).
- [17] A. S. Stodolna, A. Rouzée, F. Lépine, S. Cohen, F. Robicheaux, A. Gijsbertsen, J. H. Jungmann, C. Bordas, and M. J. J. Vrakking, Phys. Rev. Lett. **110**, 213001 (2013).

- [18] A. S. Stodolna, F. Lépine, T. Bergeman, F. Robicheaux, A. Gijsbertsen, J. H. Jungmann, C. Bordas, and M. J. J. Vrakking, Phys. Rev. Lett. **113**, 103002 (2014).
- [19] S. Cohen, M. M. Harb, A. Ollagnier, F. Robicheaux, M. J. J. Vrakking, T. Barillot, F. Lépine, and C. Bordas, Phys. Rev. A 94, 013414 (2016).
- [20] L. B. Zhao, I. I. Fabrikant, J. B. Delos, F. Lépine, S. Cohen, and C. Bordas, Phys. Rev. A 85, 053421 (2012).
- [21] L. B. Zhao, I. I. Fabrikant, M. L. Du, and C. Bordas, Phys. Rev. A 86, 053413 (2012).
- [22] D. A. Harmin, Phys. Rev. A 26, 2656 (1982).
- [23] F. Robicheaux and J. Shaw, Phys. Rev. A 56, 278 (1997).
- [24] P. Giannakeas, C. H. Greene, and F. Robicheaux, Phys. Rev. A 94, 013419 (2016).
- [25] V. I. Osherov and V. G. Ushakov, Phys. Rev. A 88, 053414 (2013).
- [26] A. Ronveaux, ed., *Heun's Differential Equations* (Oxford University Press, Oxford, UK, 1995).
- [27] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non*relativistic Theory (Pergamon, Oxford, UK, 1994).
- [28] V. I. Osherov and V. G. Ushakov, J. Phys. A 44, 365202 (2011).
- [29] L. W. Thomé, J. Mathematik 83, 89 (1877).
- [30] V. I. Osherov and V. G. Ushakov, Phys. Rev. A 90, 045401 (2014).
- [31] DLMF, F. W. J. Olver, A. B. Olde Daalhuis, D. W. Lozier, B. I. Schneider, R. F. Boisvert, C. W. Clark, B. R. Miller, and B. V. Saunders, edited by, *NIST Digital Library of Mathematical Functions*, http://dlmf.nist.gov/, Release 1.0.13 (2016).