Photoionization of a hydrogen atom in a uniform electric field as visualization of the Stokes phenomenon

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To describe the photoionization of a hydrogen atom in a static electric field, we considerably rely on the properties of a global asymptotic of the Stark wave functions in momentum representation. The accurate analytical photoionization cross section is found in terms of the Stokes multipliers for the quartic oscillator.

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Photoionization of an atom in a static electric field is one of the direct manifestations of the Stark effect. Therefore, the study of this process still proceeds, despite the significant understanding already reached [1–13]. Particularly, considerable efforts have focused in recent years on the theoretical and experimental study of the spatial distribution of Stark electrons [14–17]. The recently developed photoionization microscopy technique has been successfully applied for studying the dynamics of Rydberg states and for direct visualization of the Stark wave functions [18,19].

The traditional approach in calculations of the photoionization cross section is based on the first-order perturbation theory and the dipole approximation. The complicated part of the direct application of the theory is the calculation of the continuum wave function of the final electronic state of an atom in an electric field. The numerical calculations of the ionization cross section include direct integration of the Schrödinger equation for the Stark wave function [1–3] or the complex coordinate method for calculation of Stark resonances [4,5]. The main difficulties in direct calculations are associated with the resonance structure of the Stark wave functions. Calculations by numerical integration in the complex coordinate space are very reliable, but there still remains the problem of convergence of the series over resonances and, also, the problem of the background term. Analytical approaches are based on classical or semiclassical WKB techniques in coordinate representation [7–10]. They include matching of semiclassical waves in the barrier region and meet difficulties already at the description of an isolated resonance. Therefore, attempts to obtain accurate analytical results for the cross section of photoionization of an atom in an electric field are fully justified.

The accurate analytical calculations of the principal Stark system were not available until recently as they require the knowledge about the behavior of solutions of the reduced biconfluent Heun equations. Some of the necessary results were finally obtained in [20] by transformation of the Stark equations into momentum representation. That opens the way for analytical description by applying the global asymptotes of solutions of a quartic oscillator equation. In this Brief Report, we propose to implement this idea and to represent the Stark photoionization as the Stokes phenomenon.

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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 [21] and the components $\chi_1(\xi)$, $\chi_2(\eta)$ satisfy the coupled reduced biconfluent Heun equations,

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

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

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

and physical boundary conditions. Equation (2) defines the discrete spectrum of β_1, which is labeled by the parabolic quantum number n_1. The solutions of Eq. (3) belong to the continuous spectrum of energy E.

The Stark photoionization cross section in dipole approximation is

$$\sigma(E) = \frac{4\pi^2 q^2\omega}{c}\sum_{m,n_1}\sigma_{E,n_1,m}, \tag{5}$$

where c is the speed of light, q is the charge of electron, and ω is the frequency of light. The partial cross sections $\sigma_{E,n_1,m}$ are

$$\sigma_{E,n_1,m} = |\langle\psi_0|\mathbf{r}\cdot\mathbf{e}|\psi_{E,n_1,m}\rangle|^2, \tag{6}$$

where $\mathbf{e}$ is the unit vector of light polarization, and ψ_0 is the normalized wave function of the initial electronic state of the atom. The wave function $\psi_{E,n_1,m}$ of the final electronic state is normalized to $\delta_{m\,m'}\delta_{n_1n_1'}\delta(E-E')$.

Following the strategy of Kondratovich and Ostrovsky [9], we assume that the matrix elements in Eq. (6) converge at relatively small distances, where one can neglect the influence of the external field, and the wave functions $\chi_1(\xi)$ and $\chi_2(\eta)$ coincide with the Coulomb functions

$$\chi_1(\xi) = A_1\, f(m,\nu,\beta_1,\xi), \tag{7}$$

$$\chi_2(\eta) = A_2\, f(m,\nu,\beta_2,\eta), \tag{8}$$

where

$$f(m,\nu,\beta,\zeta) = e^{-\zeta/2\nu}\,\zeta^{(|m|+1)/2} \times F\left(\frac{|m|+1}{2} - \nu\beta,\, |m|+1,\, \zeta/\nu\right), \tag{9}$$

$F(a,b,z)$ is the confluent hypergeometric function, and A_1 and A_2 are the normalization constants. The parameter ν is $\nu = 1/\sqrt{-2E}$.

Using expressions (7) and (8) for functions $\chi_1(\xi)$ and $\chi_2(\eta)$, we obtain the partial cross section

$$\sigma_{m,n_1,E} = A_1^2 A_2^2 |I_{m,n_1,E}|^2, \tag{10}$$

where the reduced matrix element $I_{m,n_1,E}$,

$$I_{m,n_1,E} = \int \psi_0^* \mathbf{r}\cdot\mathbf{e}\, \frac{f(m,\nu,\beta_1,\xi)\, f(m,\nu,\beta_2,\eta)}{\sqrt{\xi\eta}} e^{im\varphi} dV, \tag{11}$$

can be calculated analytically.

Calculation of the normalization constant A_2 for the continuum wave function $\chi_2(\eta)$ is the most complicated and the most significant part of the problem. The accurate calculations can be performed in the Laplace representation

$$\chi_2(\eta) = W_2\, \eta^{(m+1)/2} \int_{\mathcal{L}} e^{zx}\, \Phi_2(z)\, dz. \tag{12}$$

Here, W_2 is the normalization constant, $x = (F/4)^{1/3}\eta$, $\Phi_2(z) = e^{\Phi/2}\psi_m(z)$, $\Phi = z^3/3 + tz$, and the function $\psi_m(z)$ satisfies the equation for the quartic oscillator,

$$\frac{d^2\psi_m}{dz^2} + \left[\lambda + m\,z - \left(\frac{z^2+t}{2}\right)^2\right]\psi_m = 0, \tag{13}$$

with

$$t = \frac{2E}{(2F)^{2/3}}, \quad \lambda = \frac{2}{(2F)^{1/3}}\beta_2. \tag{14}$$

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

As will be shown below, the normalization constant A_2 is determined by the asymptotic behavior of the function $\psi_m(z)$ at $|z| \to \infty$. The asymptotic representation of solutions of the quartic oscillator equation at $|z| \to \infty$ is given by the Thomé series [22]

$$\psi_m(z) = C_m(z),\ D_m(z), \tag{15}$$

where

$$C_m(z) = z^{m-1} e^{-\Phi/2} \sum c_n/z^n, \tag{16}$$

$$D_m(z) = z^{-m-1} e^{\Phi/2} \sum d_n/z^n. \tag{17}$$

The coefficients c_n and d_n satisfy the recurrence relations (see [20,23] for details)

$$nc_n + \lambda c_{n-1} + t(n-m-1)c_{n-2} + (n-m-1)(n-m-2)c_{n-3} = 0, \tag{18}$$

$$nd_n - \lambda d_{n-1} + t(n+m-1)d_{n-2} - (n+m-1)(n+m-2)d_{n-3} = 0, \tag{19}$$

with initial conditions

$$c_0 = 1, \quad c_1 = -\lambda, \quad c_2 = \tfrac{1}{2}(\lambda^2 - t + t\,m), \tag{20}$$

$$d_0 = 1, \quad d_1 = \lambda, \quad d_2 = \tfrac{1}{2}(\lambda^2 - t - t\,m). \tag{21}$$

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

$$\arg z = \pi k/3 - \pi/6, \quad k = 1,\ldots,6, \quad |z| \to \infty. \tag{22}$$

These six domains are labeled by roman numbers from I to VI counterclockwise, starting from the domain around the semiaxis $z > 0$. The function C_m is exponentially small (recessive) in comparison with the function D_m in domains I, III, and V. The function D_m is recessive in domains II, IV, and VI, where the function C_m is dominant.

At $|z| \to \infty$, the asymptotic representation of a general solution of Eq. (13) in different domains is

$$\text{Domain I:} \quad \psi_m = s_1 D_m(z) + (s_1 T_{m,1}\,\Theta_1 + r_1)\, C_m(z), \tag{23}$$

$$\text{Domain II:} \quad \psi_m = s_2 C_m(z) + (s_2 T_{m,2}\,\Theta_2 + r_2)\, D_m(z), \tag{24}$$

$$\text{Domain III:} \quad \psi_m = s_3 D_m(z) + (s_3 T_{m,3}\,\Theta_3 + r_3)\, C_m(z), \tag{25}$$

$$\text{Domain IV:} \quad \psi_m = s_4 C_m(z) + (s_4 T_{m,4}\,\Theta_4 + r_4)\, D_m(z), \tag{26}$$

$$\text{Domain V:} \quad \psi_m = s_5 D_m(z) + (s_5 T^*_{m,3}\,\tilde{\Theta}_5 + r_5)\, C_m(z), \tag{27}$$

$$\text{Domain VI:} \quad \psi_m = s_6 C_m(z) + (s_6 T^*_{m,2}\,\tilde{\Theta}_6 + r_6)\, D_m(z). \tag{28}$$

Here, the step functions Θ_k and $\tilde{\Theta}_k = 1 - \Theta_k$ are defined in domains k ($k = \mathrm{I}\ldots\mathrm{VI}$). The function Θ_k is changed from 0 to 1 when the Stokes line is crossed in the positive direction. The constant coefficients s_k and r_k satisfy the condition that the asymptotic expansions in the adjacent domains coincide on the anti-Stokes line between these domains. Parameter $T_{m,k}$ is the Stokes multiplier for domain k. The Stokes multipliers for domains VI and V are complex conjugate to those of domains II and III.

The coefficients c_n and d_n obey the following relation:

$$d_n(-m) = (-1)^n\, c_n(m). \tag{29}$$

The symmetry of coefficients c_n and d_n leads to the following symmetry of asymptotic solutions $C_m(z)$ and $D_m(z)$:

$$\begin{aligned} C_{-m}(ze^{\pm i\pi}) &= -e^{\mp i\pi m} D_m(z), \\ D_{-m}(ze^{\pm i\pi}) &= -e^{\pm i\pi m} C_m(z). \end{aligned} \tag{30}$$

This symmetry is the consequence of the symmetry of Eq. (13), which conserves its shape at variable change

$$z = -z, \quad m \to -m. \tag{31}$$

As a result, together with the solution $\psi_m(z)$, the function $\psi_{-m}(-z)$ is also a solution of Eq. (13) and we find the following symmetry properties of the Stokes multipliers:

$$T_{m,1} = e^{2i\pi m} T_{-m,4}, \quad T_{m,2} = -e^{2i\pi m} T^*_{-m,3}. \tag{32}$$

In [20], 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 complex

Stark resonances are the solutions of equation

$$T_{|m|,3}(\beta_2) = 0. \tag{33}$$

The argument of the multiplier $T_{|m|,3}(\beta_2)$ defines the scattering phase. The quantization condition for Eq. (2) is

$$T_{|m|,1}(\beta_1) = 0. \tag{34}$$

The Stokes multipliers have been found in [20,23] 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 (18) and (19). The multiplier $T_{m,3}$ at negative energies has been found in the frame of complex asymptotic analysis.

Below we show that the Stark photoionization is also directly related to the Stokes phenomenon.

To calculate the function $\chi_2(\eta)$, we choose in Eq. (12) the integration contour $\mathcal{L}$ which goes parallel to the imaginary axis in the right half-plane of complex variable z. Taking into account the asymptotic behavior of functions $\psi_m(z)$ at $|z| \to \infty$, we can show that at such choice of integration contour, the Laplace transform (12) exists for any $m < 1$. For that reason, below we take

$$m \leqslant 0. \tag{35}$$

To satisfy the physical boundary condition for the function $\chi_2(\eta)$ at $\eta \to 0$, the function $\psi_m(z)$ must be taken recessive in domain I. In this case, in the limit $\eta \to 0$, the integration contour $\mathcal{L}$ can be displaced into the asymptotic region $|z| \to \infty$ to make the integrand in Eq. (12) as small as possible. The function $\psi_m(z)$ in the asymptotic region is described by the leading term of the asymptotic expansion $C_m(z)$, and we find

$$\chi_2(\eta \to 0) = W_2\, \eta^{(m+1)/2} \int_{\mathcal{L}} e^{zx} z^{m-1} dz \tag{36}$$

$$= W_2 \left(\frac{4}{F}\right)^{m/3} \frac{2i\pi}{\Gamma(1-m)}\, \eta^{(1-m)/2}. \tag{37}$$

At $\eta \to \infty$, the main contribution to the integral in Eq. (12) originates from two saddle points located in the asymptotic region of the imaginary axis. In the vicinity of the imaginary axis (along the anti-Stokes lines), the asymptotic form of the function $\Phi_2(z)$ is

$$\Phi_2(z) = \begin{cases} e^{\Phi/2}(C_m + T_{m,2}D_m) \approx z^{m-1} + T_{m,2}e^{\Phi} z^{-m-1}, & \mathrm{Im}(z) \to +\infty, \\ e^{\Phi/2}(C_m + T^*_{m,2}D_m) \approx z^{m-1} + T^*_{m,2}e^{\Phi} z^{-m-1}, & \mathrm{Im}(z) \to -\infty. \end{cases} \tag{38}$$

The saddle points correspond to terms $T_{m,2}e^{\Phi}z^{-m-1}$ and $T^*_{m,2}e^{\Phi}z^{-m-1}$ in this asymptotic expansion. Calculating contributions of the saddle points, we find the asymptotic form of solution at $\eta \to \infty$,

$$\chi_2(\eta \to \infty) = \frac{B\, W_2 |T_{m,2}|}{\eta^{1/4}} \cos\left[\frac{1}{3F}(F\eta + 2E)^{3/2} - \pi\frac{m+1}{2} + \arg T_{m,2} - \frac{\pi}{4}\right] \tag{39}$$

$$= \frac{B\, W_2 |T_{|m|,3}|}{\eta^{1/4}} \cos\left[\frac{1}{3F}(F\eta + 2E)^{3/2} + \frac{3\pi m}{2} - \arg T_{|m|,3} + \frac{\pi}{4}\right], \tag{40}$$

with $B = 2i\sqrt{\pi}\,(4/F)^{m/6+1/4}$.

The normalization coefficients for functions $\chi_1(\xi)$ and $\chi_2(\eta)$ are determined by conditions

$$\int_0^\infty \frac{\chi_1^*(\xi)\, \chi_1(\xi)}{\xi}\, d\xi = \frac{1}{\pi}, \tag{41}$$

and

$$\int_0^\infty \chi^*_{2,E}(\eta)\, \chi_{2,E'}(\eta)\, d\eta = 2\delta(E - E') \tag{42}$$

(cf. [9]). The asymptotic form (40) of solution $\chi_2(\eta)$ and normalization condition (42) lead to

$$W_2 = -\frac{i}{2\pi\, |T_{|m|,3}|} \left(\frac{F}{4}\right)^{m/6}. \tag{43}$$

As a result, we get

$$\chi_2(\eta \to 0) = \frac{1}{|T_{|m|,3}|\, |m|!} \left(\frac{4}{F}\right)^{m/6} \eta^{(1+|m|)/2}. \tag{44}$$

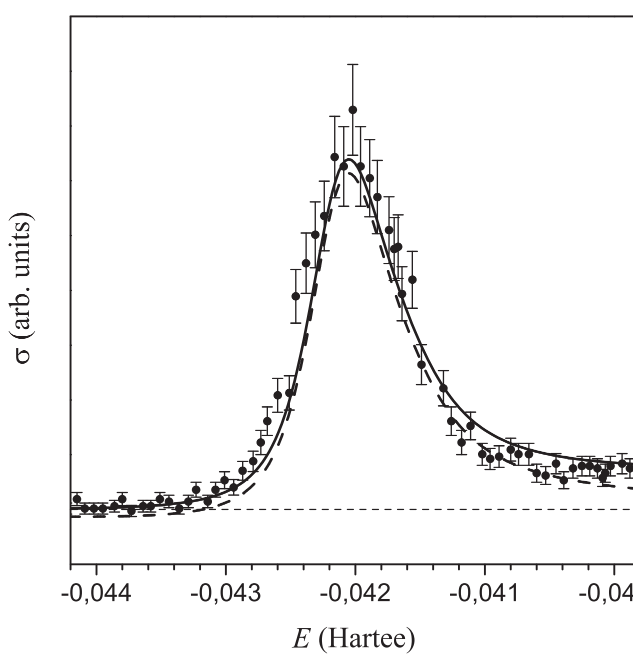

FIG. 1. The (0,3,0) resonance in the photoionization cross section of hydrogen in the field of 2.61 MV/cm. The solid curve is calculated via Eq. (45). The dashed curve presents the Fano profile from work [5]. Theoretical data are convoluted with the experimental line-shape function. Points are the experimental data taken from Fig. 3 in [11].

A comparison of Eq. (8) with Eq. (44) results in the following expression for the normalization constant A_2:

$$A_2 = \frac{1}{|T_{|m|,3}|\,|m|!}\left(\frac{4}{F}\right)^{m/6}. \qquad (45)$$

As it was already mentioned, zeros of the Stokes multiplier $T_{|m|,3}$ determine the positions and widths of the Stark resonances. The resonance behavior of the Stokes multiplier $T_{|m|,3}$ at negative energies directly reveals itself in the behavior of the normalization constant A_2 and, consequently, in the resonance structure of ionization cross section.

Figure 1 illustrates the result of application of Eq. (45) to calculation of the photoionization cross section of the ground-state hydrogen near the $(n_1,n_2,m) = (0,3,0)$ resonance, which has been observed in the intense static electric field of 2.61 MV/cm in the experiment [11]. This resonance is located almost on the top of the Stark potential barrier and reveals an elevation of the base line on the high-energy side. This elevation is the direct consequence of the transition from tunneling to the over-barrier photoionization dynamic and, also, it reflects the qualitatively different behavior of the Stokes multiplier $T_{|m|,3}$ at λ below and above the barrier between the wells of the quartic oscillator potential.

Figure 1 presents our theoretical results (solid curve) and the Fano profile from [5] (dashed curve). To compare the calculated cross sections with the experimental data, both our data and the Fano profile have been convoluted with the instrumental line-shape function [8,11]. The vertical scale of the experimental points has been adjusted for best match with the solid curve. The small difference between solid and dashed curves is due to the background term, which was neglected in [5].

It should be noted that the values of normalization constant A_1 and of the reduced matrix element $I_{m,n_1,E}$ do not change inside the width of the resonance shown in Fig. 1. The shape of this resonance is totaly described by the behavior of the Stokes multiplier $T_{|m|,3}$ in Eq. (45). In this sense, the Stark photoionization is the direct physical visualization of the Stokes phenomenon.

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