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Short-pulse photoexcitation process in the hydrogen atom

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A short-pulse photoexcitation of $1s \rightarrow 2s, 2p$ transitions in the hydrogen atom is studied with perturbation theory and the finite-element method giving an almost exact solution of the time-dependent Schrodinger equation.

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I. INTRODUCTION

During recent years, atomic physics development has been characterized by major interest in the processes induced by short photopulses [1–9]. Attosecond pulse durations and field amplitudes of the atomic scale are considered. In this regard, the development of adequate theoretical approaches is of interest. To date their number is essentially lower than the number of methods for stationary problems. Let us note the following works. In [8,9], the time-dependent Schrödinger equation for an atom in an external field was reduced, using some simplifying assumptions including an interaction weakness, to equations for two (or small number) one-electron functions. The effective numerical solution scheme was constructed for the gained set of nonstationary equations. Basically, the time-dependent close-coupling method can also be used, however this approach has been applied so far to study only stationary photoprocesses [10–12].

The Feynman path integrals can also be used for the study of dynamic processes. Methods based on the path-integral technique have many advantages, including flexibility and physical obviousness. Such methods have been considered and developed in a number of works. The opportunity for their use was detailed in [13,14] in connection with a study of photoionization process dynamics. In our works [15–17], various path-integral estimate schemes for a solution of scattering problems were considered.

A natural step for the development of new methods is their testing. It is desirable that the test problem keep the basic features of a real one and can also be solved precisely enough. The process of excitation and ionization of the hydrogen atom by the short photopulse is of major interested in this respect.

This problem was considered in [18–20]. In [18], the probabilities of ionization and excitation of the hydrogen atomic levels $n=2,3,4$ from the ground state by electrical pulses of the Gaussian and rectangular shapes were determined. It was considered pulse durations characteristic for adiabatic (long) and nonadiabatic (short) conditions. Probabilities were obtained from a numerical solution of the time-dependent Schröodinger equation and were compared with analytical evaluation within the limits of the adiabatic theory. The reasons for the discrepancies in the previous works [21,22] have been revealed. However, it may be pointed out that the pulse amplitudes in [18] were small enough ($|E_z| \leqslant 0.06$ a.u.) for a perturbation's theory validity and hence results can be gained without a numerical solution of the Schrödinger equation.

The major area of interest in the physics of ultrashort processes is the case of strong fields where the perturbation theory is inapplicable.

In [19,20], a problem of hydrogen atom ionization by ultrashort pulses was considered for both conditions of weak and strong fields. It was done for a case of very short pulses ($\tau \ll 1$ a.u.), when the short pulse approximation [first Magnus approximation] (FMA) is applicable.

In the present work, we consider excitation of a hydrogen atom by a field corresponding to both a condition of perturbation theory validity and its invalidity ($|E_z| \sim 1$ a.u.) for the pulse durations, from small up to large in an atomic scale ($\tau \sim 1$ a.u.). A corresponding problem for the time-dependent Schrödinger equation was solved by a finite-element method realized in the problem-solving environment of Comsol Multiphysics (Femlab).

The gained results are used for subsequent testing of the calculation scheme based on the Feynman path integrals and, besides, they can have independent interest.

II. GENERAL CONSIDERATION

Let us consider some known general provisions of the theory. The reason is that a nonstationary case needs some comments.

Two forms of representation of a transition probability can be used in a system. In a density-matrix formalism, the transition probability from a state $\rho_i(t')$ into a state $\rho_f(t)$ can be written as

$$w_{i,f}(t,t') = \mathrm{tr}[\rho_f(t) \cdot \hat{T}(t,t') \cdot \rho_i(t') \cdot \hat{T}(t',t)]. \tag{1}$$

In the wave-function formalism, the transition probability of a system from a state $\psi_i(t')$ into a state $\psi_f(t)$ can be expressed with the probability amplitude

$$w_{i,f}(t,t') = |A_{i,f}(t,t')|^2, \tag{2}$$

which should be defined as

$$A_{i,f}(t,t') = \langle \psi_f(t) | \hat{T}(t,t') \cdot \psi_i(t') \rangle. \tag{3}$$

Here

$$\hat{T}(t,t') = \hat{U}(t,t') - \hat{U}_a(t,t')$$

is a transition operator. $\hat{U}(t,t')$ is an evolution operator for the full Hamiltonian of a system

$$\hat{H}(t)=\hat{H}_a+\hat{W}(t),$$

where $\hat{H}_a$ is the Hamiltonian of an atom and $\hat{W}(t)$ is an interaction of an atom with a photopulse. We use a dipole approximation for this interaction,

$$\hat{W}(t)=-\vec{E}(t)\cdot\hat{\vec{D}}, \tag{4}$$

where $\vec{E}(t)$ is an electric field tension and $\hat{\vec{D}}$ is an operator of the dipole moment of an atom. $\hat{U}_a(t,t')$ is an evolution operator for an atomic Hamiltonian.

Let us take a time reference point $t=0$ within an interval of pulse duration τ. Initial and final time moments are chosen out of the requirements

$$t'\ll-\tau, \quad \tau\ll t. \tag{5}$$

Under these requirements, it is possible to suppose, that the transition probability (1) does not depend on the initial and final time moments and to introduce a transition probability per unit time (a transition velocity), as

$$\omega_{i,f}=\frac{w_{i,f}}{\tau}. \tag{6}$$

Let us make some notes.

First, it is necessary to say that the treatment considered above is conventional for the stationary processes [23–26]. For the nonstationary processes, the probability dynamics (1) and (2), when requirements (5) are not fulfilled, can also be of interest. In connection with the development of the ultrashort pulses technique, there is a possibility of observation of the processes dynamics, using the pump-probe method [5,6], for example.

Secondly, the transition probability per unit time is sometimes defined through a derivative of probability (1) on time [23,25],

$$\omega_{i,f}=\frac{d}{dt}w_{i,f}(t,t'). \tag{7}$$

The derivative is taken at time moment $t=0$. At small intensity of light when a perturbation theory is applicable, such a definition differs from Eq. (6) a little. However, at greater intensities a probability (1) time dependence can have a complex appearance and the value of Eq. (7) becomes indefinite. So a definition of a transition velocity on the basis of a time derivative is invalid. It can be illustrated by the results presented below of the calculation for hydrogen (Figs. 1 and 2). At the same time, definition (6) [following Eq. (5)] is quite adequate to the problem when the outcome of the collision (instead of its process) is registered.

Two definitions of cross sections are used for photoprocesses, which, generally speaking, do not coincide. One of them corresponds to a conventional definition of a cross section for collision of any particles [23,24],

$$\sigma_{i,f}=\frac{\omega_{i,f}}{J},$$

where J is the colliding particles flux density. An other definition is given in energy terms [25,26],

$$\sigma_{i,f}=\frac{\Delta E_{i,f}\cdot\omega_{i,f}}{P}, \tag{8}$$

where $\Delta E_{i,f}\cdot\omega_{i,f}$ is an energy transfer velocity at collision ($\Delta E_{i,f}=E_f-E_i$), and P is photons energy flux

For an excitation by pulse it is necessary to take some effective value of a flux density, for example medial or maximum for pulse.

We use the energy definition (8) as the photon energy flux can be easily expressed through a field while connection of particle flux with a field is more complex. For the electromagnetic pulse $\vec{E}=\vec{E}_0f(\vec{\nu}\vec{r}-ct)$ spread in a direction of a unit vector $\vec{\nu}$, Poynting's vector looks like

$$\vec{P}=\frac{c}{4\pi}E^2\vec{\nu}.$$

For transitions between the groups of states i,f, it is used an averaging over an initial group and summation over a final one,

$$\rho_i=\frac{1}{g(i)}\sum_{\alpha\in i}\rho_\alpha, \quad \rho_f=\sum_{\beta\in f}\rho_\beta, \tag{9}$$

where $g(i)$ is the statistical weight of an initial group of states.

Further we neglect relativistic effects, including interaction with a spin subsystem. In this case, a density matrix factorizes on the orbital and spin density matrixes $\rho=\rho L\rho S$. In the case of the hydrogen atom, we need not consider an antisymmetrization of states, taking into account Pauli's principle.

For the one-electron system, in the absence of spin polarization, the spin density matrix (medial on a spin projection) is taken in the form

$$\rho S_i=\frac{1}{2}\hat{I},$$

where $\hat{I}$ is the unit matrix [24]. A summary spin density matrix looks like

$$\rho S_f=\hat{I}.$$

By virtue of neglecting interaction with a spin subsystem, a trace for spin variables

$$\mathrm{tr}(\rho S_f\rho S_i)=1$$

can be explicitly separated in the formula (1).

III. THE PROBLEM STATEMENT

The process of photoexcitation of transitions $1s\rightarrow2s,2p$ in the hydrogen atom has been considered, i.e., a photoabsorption resulting in an atom transition between the specified states

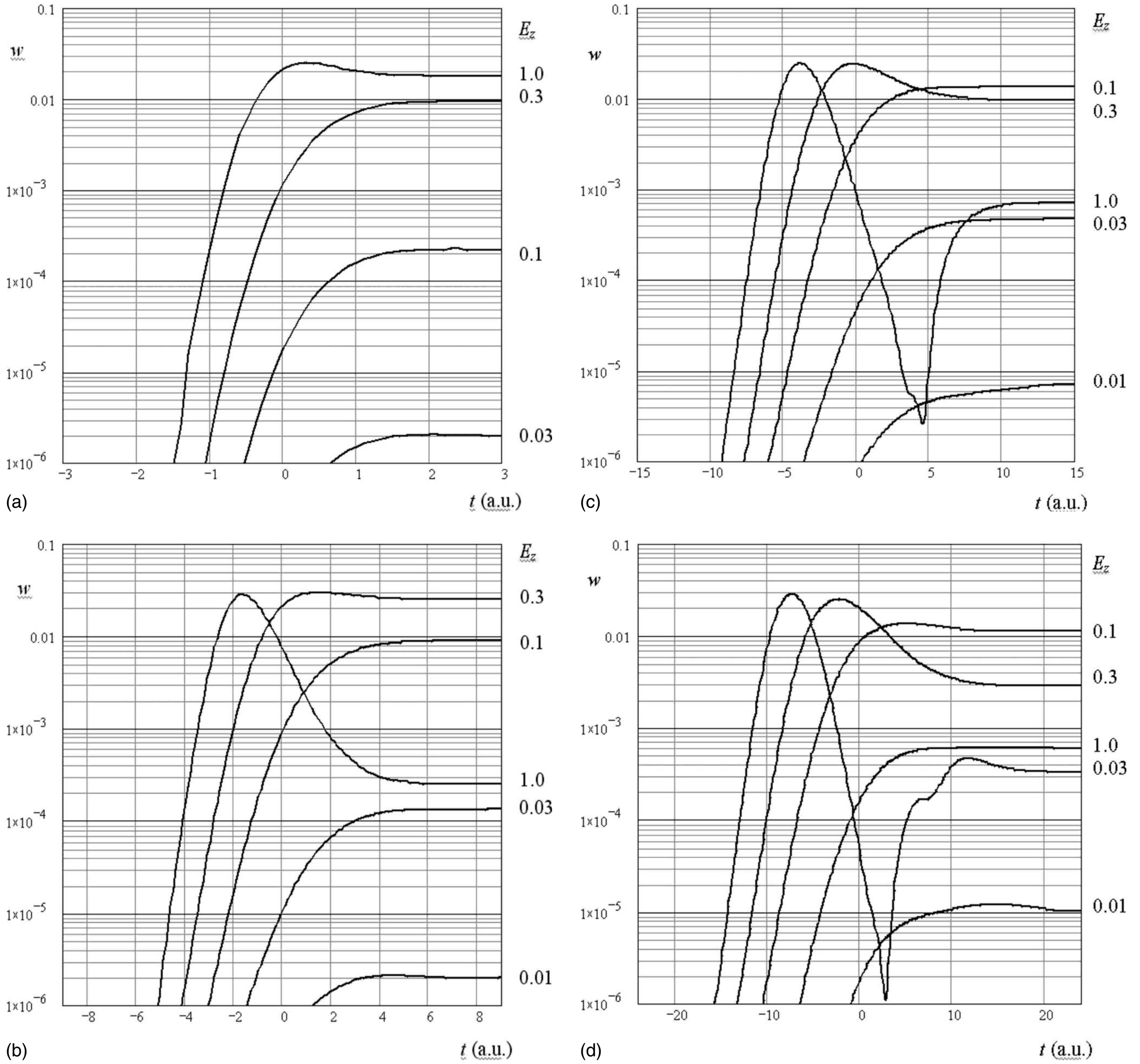

FIG. 1. Transition $1s \rightarrow 2s$. Probabilities w as time dependences. Field amplitudes $E_z = 0.01, 0.03, 0.1, 0.3, 1.0$ (a.u.). Field durations (a.u.): (a) $\tau = 1$, (b) $\tau = 3$, (c) $\tau = 5$, and (d) $\tau = 8$.

$$H + \hbar\nu \rightarrow H^*.$$

Evaluations of a probability and cross section of this process depending on two main parameters of the pulse—its duration and amplitude—have been made.

Photopulse durations have been chosen within an interval $0.1 < \tau < 10$ enveloping the inverse frequency of atomic transition $\tau = \hbar / \Delta E_{i,f} \approx 2.67$. Perturbation theory predicts a cross-section maximum on this domain for optically allowed transition $1s \rightarrow 2p$. All magnitudes, including cross sections and times, are presented in atomic units (1 a.u. of time = 24.2 as). As of now only the upper durations of the chosen domain are accessible in experiment. However, the rapid progress in the area of ultrashort pulses is a good indication that coverage of the entire domain will soon be possible.

The pulse of the Gaussian shape with an electric field linearly polarized along an axis z,

$$E_z \exp\left[-\left(\frac{t}{\tau}\right)^2\right], \tag{10}$$

where τ is its duration, has been chosen. The field magnitudes have been chosen within an interval $0.01 \leqslant E_z \leqslant 1$.

IV. PERTURBATION THEORY EVALUATION

At small photopulse amplitude it is natural to use nonstationary perturbation theory for calculations. According to this theory [24], the first-order transition probability amplitude $i \rightarrow f$ (3) looks like

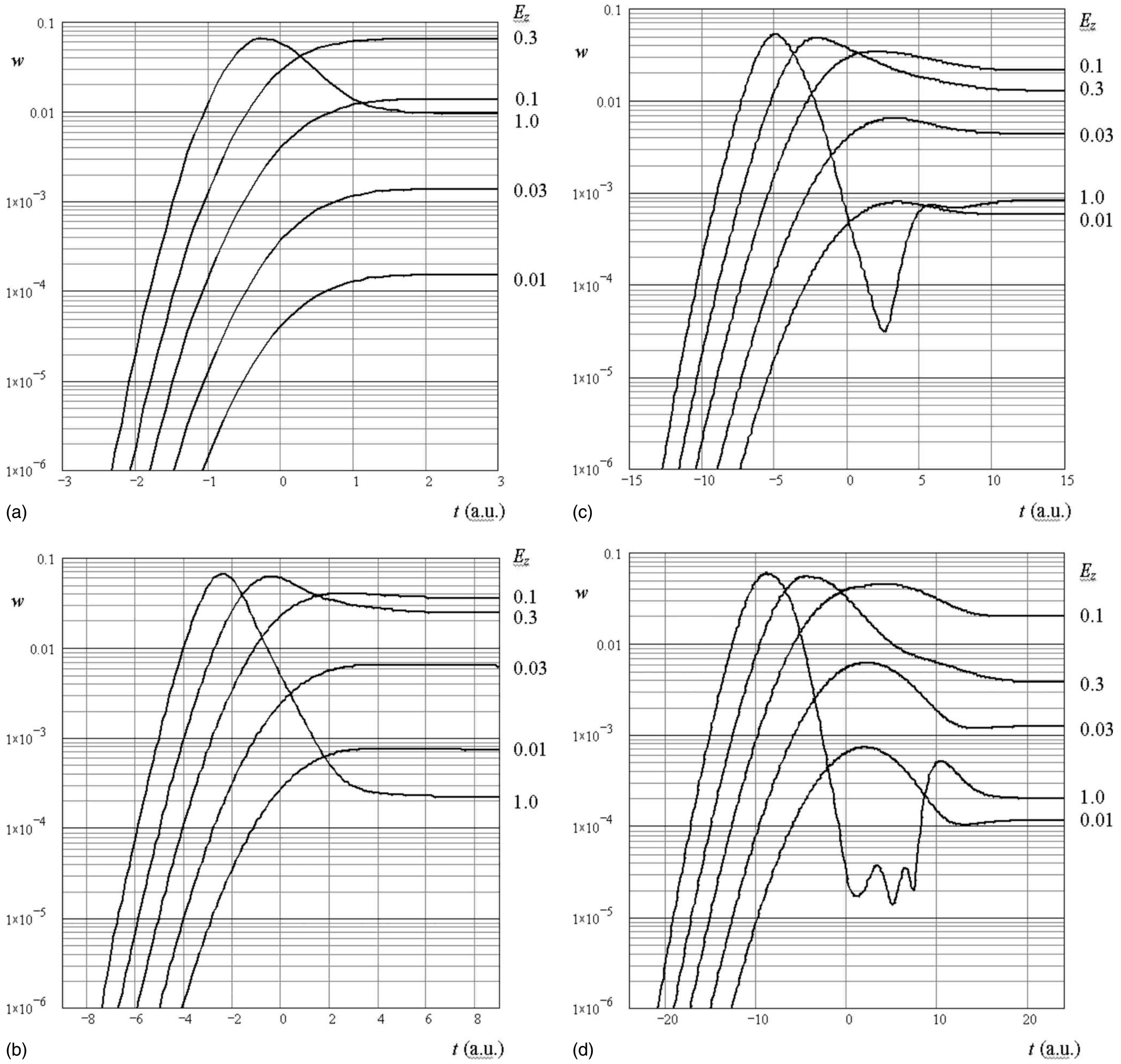

FIG. 2. Transition $1s \rightarrow 2p$. Probabilities w as time dependences. Field amplitudes $E_z = 0.01, 0.03, 0.1, 0.3, 1.0$ (a.u.). Field durations (a.u.): (a) $\tau = 1$, (b) $\tau = 3$, (c) $\tau = 5$, and (d) $\tau = 8$.

$$A_{i,f}(t,t') = -\frac{i}{\hbar}\int_{t'}^{t} \langle \psi_f(s)|\hat{W}(s)|\psi_i(s)\rangle ds.$$

Thus, the transition probability amplitude between the stationary atomic states can be represented in the form of a product of a transition dipole matrix element and photopulse Fourier transform

$$A_{i,f} = \frac{i}{\hbar}\langle \psi_f|\hat{\vec{D}}|\psi_i\rangle \int_{-\infty}^{\infty} \vec{E}(s)\exp\left(\frac{i}{\hbar}\Delta E_{i,f}s\right)ds.$$

For a photopulse of the shape (10), this gives the following expression for a transition probability:

$$w_{i,f} = \frac{\pi}{\hbar^2}|\langle \psi_f|\hat{D}_z|\psi_i\rangle|^2 E_z^2 \tau^2 \exp\left[-\frac{1}{2}\left(\frac{1}{\hbar}\Delta E_{i,f}\tau\right)^2\right].$$

It is convenient to represent a transition probability in the following form:

$$w_{i,f} = \pi\left(\frac{eE_z}{\Delta E_{i,f}}\right)^2 L_{i,f}F(x^2),$$

where

$$x = \frac{1}{\hbar}\Delta E_{i,f}\tau, \qquad F(x) = x\exp\left(-\frac{1}{2}x\right),$$

and

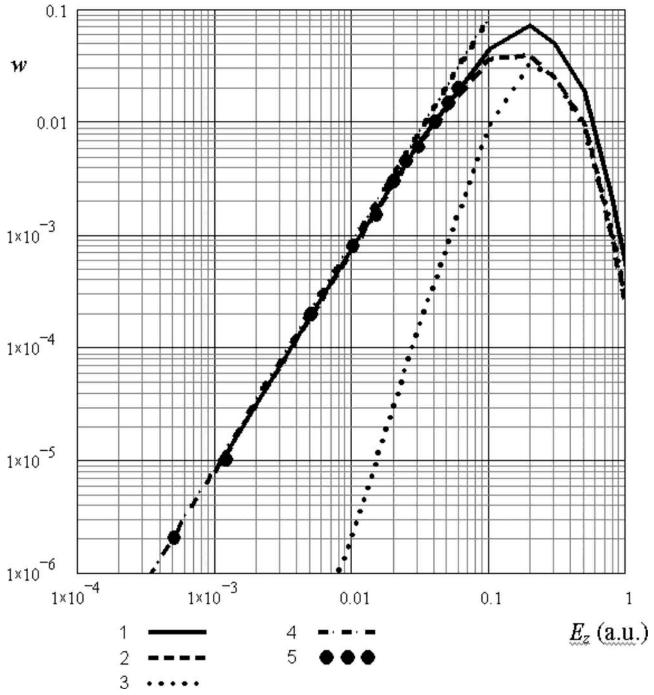

FIG. 3. Probabilities w as functions of field amplitude. Field duration $\tau=3$ (a.u.). Line 1, $2s+2p$, FEM (finite-element method); line 2, $2p$, FEM; line 3, $2s$, FEM; line 4, $2p$, perturbation theory; line 5, $2s+2p$ [18].

$$L_{i,f}=|\langle\psi_f|z|\psi_i\rangle|^2$$

is the so-called line force. With provision for the levels degeneracy according to Eq. (9), a line force is

$$L_{i,f}=\frac{1}{g(i)}\sum_{\alpha\in i}\sum_{\beta\in f}|\langle\psi_\beta|z|\psi_\alpha\rangle|^2. \tag{11}$$

According to Eqs. (6) and (8), the cross section as a function of photopulse duration can be represented in the following form:

$$\sigma_{i,f}(x)=4\pi^2\frac{e^2}{\hbar c}L_{i,f}x^{-1}F(x^2).$$

The explicit evaluation of Eq. (11) for the optically allowed transition $1s\rightarrow 2p$ in the hydrogen atom gives the following value of a line force: $L_{1s,2p}=2^{15}\cdot 3^{-10}\cong 0.555$. A line force for the optically forbidden transition $1s\rightarrow 2s$ is equal to zero.

V. FINITE-ELEMENT METHOD COMPUTATION

For the hydrogen atom it is possible to solve a problem for the time-dependent Schrödinger equation by the finite-element method using the problem-solving environment of Comsol Multiphysics (Femlab). It allows computation of probabilities and cross sections for any pulse amplitudes.

Results are represented in Figs. 1–5.

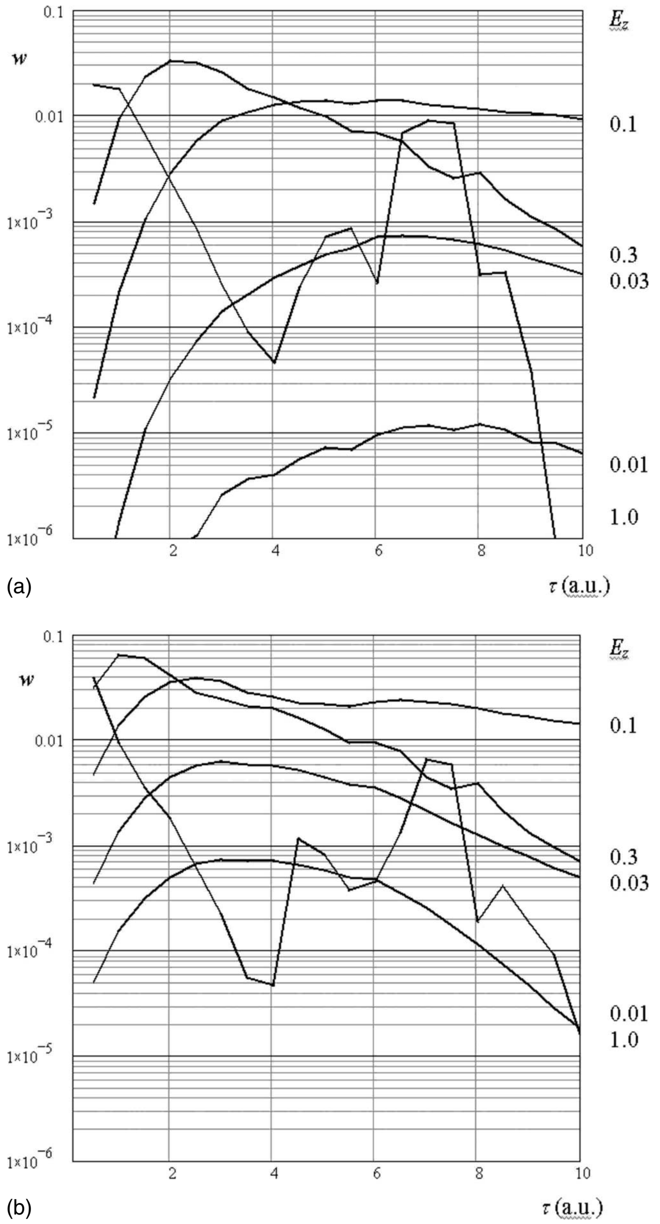

FIG. 4. Probabilities w as functions of field duration. Field amplitudes $E_z=0.01, 0.03, 0.1, 0.3, 1.0$ (a.u.). Transitions (a) $1s\rightarrow 2s$ and (b) $1s\rightarrow 2p$.

Figures 1 and 2 show a transition probability time dependency (2) for various pulse parameters (duration and amplitude). It is seen that with increasing pulse amplitude, a transition probability becomes a complex and nonmonotonic function of time. At the center of excitation ($t=0$), the probability derivative on time can have any values including negative ones. It specifies an inapplicability of definition of a transition probability per unit time by a derivative (7) as was noted in Sec. II. At the same time, in a limit of large times (in comparison with a pulse duration) the probability goes out on a constant value, which corresponds to the probability of detection of a system in a corresponding state as a result of the considered process. This value is used in definition of a transition probability per unit time in the formula (6). Corresponding cross sections were calculated by the formula (8).

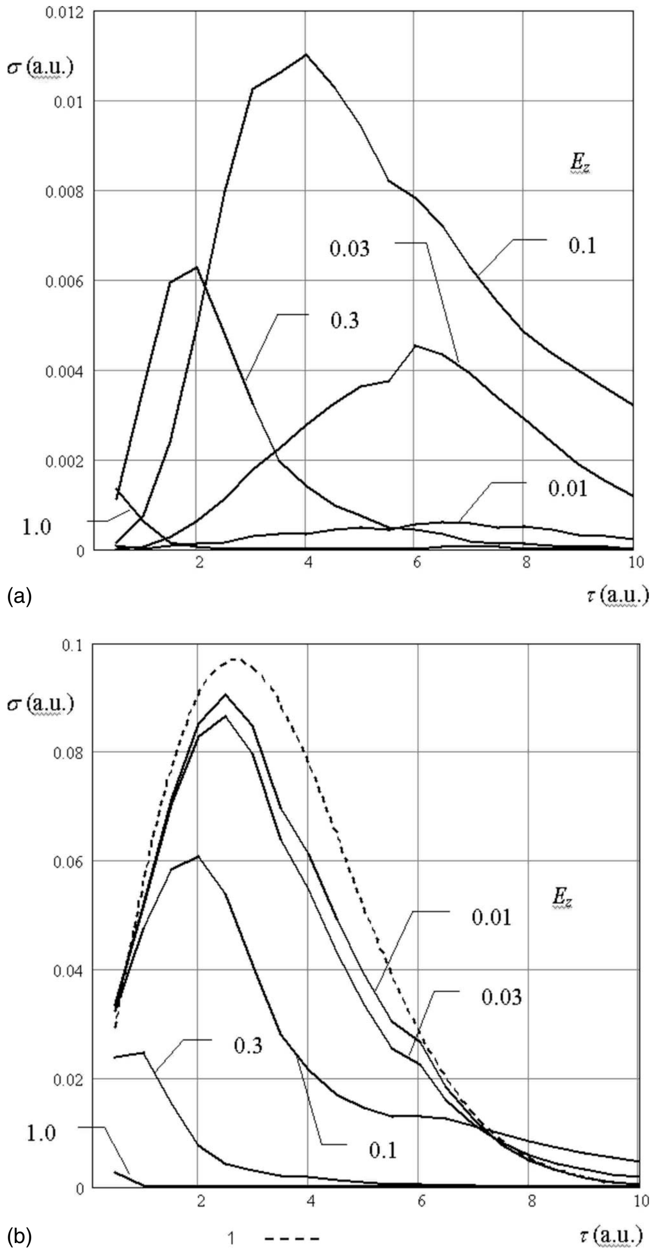

FIG. 5. Cross sections σ (a.u.) as functions of field duration. Field amplitudes E_z=0.01,0.03,0.1,0.3,1.0 (a.u.). Line 1, perturbation theory. Transitions (a) $1s \rightarrow 2s$ and (b) $1s \rightarrow 2p$.

Figure 3 shows a transition probability dependency on pulse amplitude for pulse duration τ=3, which is close to an inverse transition frequency. Results are shown separately for transitions $1s \rightarrow 2s,2p$ and for their total $n=1 \rightarrow n=2$. For the transition $1s \rightarrow 2p$, the result of the perturbation theory calculation is shown for comparison. Also the results of [18] for total transition $n=1 \rightarrow n=2$ are shown.

The nonlinear effect in a transition probability dependency on pulse amplitude is well seen from the present results. For the weak pulses, the results of a finite-element method practically coincide with the results of a perturbation theory. At amplitude enhancing, a violation of the transition $1s \rightarrow 2s$ suppression begins and at greater amplitudes contributions of both transitions $1s \rightarrow 2s,2p$ to the total transition become comparable.

At high enough pulse amplitudes, their increase leads to a probability decrease. It can be interpreted as a redistribution of total excitation and ionization in favor of higher states (mostly ionization).

Figure 4 shows a transition probability dependency on pulse duration, and Fig. 5 shows a transition of cross-section dependency on pulse duration at its various amplitudes. For the excitation cross sections of transition $1s \rightarrow 2p$, perturbation theory results are shown for comparison.

With a pulse duration increase, the probability falls to zero. It corresponds to an adiabatic principle [24] according to which the stationary field does not induce transitions in a system. Let us note that a pulse tends to a stationary electric field at its duration increase.

With the pulse duration decrease, the probability also falls to zero. It can probably be interpreted as system inertia.

VI. CONCLUSION

The obtained results have shown that even for the simple case of a hydrogen atom, the process of its excitation by short intensive pulses is rather complex. At high pulse amplitudes, the excitation probability dynamics has complex and nonmonotonic form. A transition probability and the cross-section dependencies on pulse duration have a structure. The often used definition of a transition velocity on the basis of the time derivative is invalid.

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[1] M. Hentschel, R. Kienberger, Ch. Spielmann, G. A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, and F. Krausz, Nature (London) **414**, 509 (2001).
[2] R. Kienberger, E. Goulielmakis, M. Uiberacker, A. Baltuska, V. Yakovlev, F. Bammer, A. Scrinzi, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, M. Drescher, and F. Krausz, Nature (London) **427**, 817 (2004).
[3] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, V. Yakovlev, A. Scrinzi, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, and F. Krausz, Nature (London) **419**, 803 (2002).
[4] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, Th. Westerwalbesloh, U. Kleineberg, U. Heinzmann, and F. Krausz, J. Electron Spectrosc. Relat. Phenom. **137-140**, 259 (2004).
[5] O. Smirnova, V. S. Yakovlev, and A. Scrinzi, Phys. Rev. Lett. **91**, 253001 (2003).
[6] M. Wickenhauser, J. Burgdorfer, F. Krausz, and M. Drescher, Phys. Rev. Lett. **94**, 023002 (2005).
[7] Z. X. Zhao and C. D. Lin, Phys. Rev. A **71**, 060702(E) (2005).
[8] A. K. Kazansky and N. M. Kabachnik, Phys. Rev. A **72**,

052714 (2005).

[9] A. K. Kazansky and N. M. Kabachnik, J. Phys. B **39**, L53 (2006).

[10] M. S. Pindzola and F. Robicheaux, Phys. Rev. A **57**, 318 (1998).

[11] M. S. Pindzola and D. R. Schultz, Phys. Rev. A **53**, 1525 (1996).

[12] M. S. Pindzola and F. Robicheaux, Phys. Rev. A **54**, 2142 (1996).

[13] D. B. Miloševic, G. G. Paulus, and W. Becker, Phys. Rev. A **71**, 061404(R) (2005).

[14] P. Salières, B. Carré, L. Le Déroff, F. Grasbon, G. G. Paulus, H. Walther, R. Kopold, W. Becker, D. B. Miloševic, A. Sanpera, and M. Lewenstein, Science **292**, 902 (2001).

[15] V. V. Smirnov and A. A. Mityureva, J. Phys. B **29**, 2865 (1996).

[16] A. A. Mityureva and V. V. Smirnov, Opt. Spectrosc. **101**, 344 (2006).

[17] V. V. Smirnov, Phys. Rev. A **76**, 052706 (2007).

[18] D. Dimitrovski, T. P. Grozdanov, E. A. Solov'ev, and J. S. Briggs, J. Phys. B **36**, 1351 (2003).

[19] D. Dimitrovski, E. A. Solov'ev, and J. S. Briggs, Phys. Rev. Lett. **93**, 083003 (2004).

[20] D. Dimitrovski, E. A. Solov'ev, and J. S. Briggs, Phys. Rev. A **72**, 043411 (2005).

[21] S. Geltman, J. Phys. B **33**, 4769 (2000).

[22] A. Scrinzi, Phys. Rev. A **61**, 041402(R) (2000).

[23] Marvin L. Goldberger and Kenneth M. Watson, *Collision Theory* (Krieger, Huntington, NY, 1975).

[24] L. D. Landau and E. M. Lifschitz, *Quantum mechanics: Nonrelativistic theory* (Nauka, Moscow, 1989), Vol. 3.

[25] Rodney Loudon, *The Quantum Theory of Light* (Clarendon, Oxford, 1973).

[26] I. I. Sobelman, *Introduction to the Theory of Atomic Spectrum* (Nauka, Moscow, 1977).