Dynamics of multiphoton ionization in a femtosecond laser pulse

E. A. Volkova, A. M. Popov, and O. B. Popovicheva

Scientific-Research Institute of Nuclear Physics
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A one-dimensional model of multiphoton ionization of atoms in a laser field is investigated by numerically solving the time-dependent Schrödinger equation for a quantum system in an electromagnetic wave field. The temporal dynamics of the photoelectron spectrum is analyzed for various intensities of the laser radiation. The photoionization of a quantum system by a laser pulse of finite duration is considered.

1. INTRODUCTION

The availability of powerful lasers makes possible the experimental and theoretical investigation of the atomic processes of multiphoton ionization.[1] At low intensities of the laser radiation, atoms are ionized by absorbing the minimum number of photons needed for their ionization. This process is well described by standard perturbation theory. At higher laser intensities the absorption of a number of additional photons has been observed experimentally,[2-4] and the energy spectrum consists of peaks separated from each other by the amount of energy in a photon. The amplitudes of the peaks depend on the field intensity, and there are circumstances[3,4] under which the less energetic peaks appear inhibited by comparison with the more energetic ones. This phenomenon of above-threshold ionization cannot be explained by standard theories, and a number of authors have attempted to model it (see the review in Ref. 1).

In low-frequency strong fields the atomic ionization has a tunneling nature. In Ref. 5 one can find the general expression for the probability of transition from the discrete states of atomic electrons to the continuum, described in various limiting cases as either a multiquantum photoeffect or tunnel ionization of the atom in the radiation field.

Advances in the generation of supershort laser pulses makes possible the study of atomic photoionization by pulses of femtosecond durations.[6] Such pulses are characterized by record high laser intensities, which may have a considerable effect on the dynamics of the photoionization process and on the time evolution of the energy spectrum of photoelectrons. Moreover, the use of femtosecond laser pulses allows an *ab initio* comparison of the experimental results with numerical calculations based on the time dependent Schrödinger equation for an atom in the field of an electromagnetic wave.

The phenomenon of above-threshold atomic ionization was investigated[7] by this approach for lasers with pulse durations on the order of ten wave periods. The photoelectron spectra were calculated by expanding the wave function in eigenfunctions of the unperturbed Hamiltonian. In Ref. 8 the rate of ionization of the hydrogen atom was calculated by numerically integrating the time-dependent Schrödinger equation in low-intensity laser fields.

In the present work, by numerically integrating the one-dimensional time-dependent Schrödinger equation for an atom in the field of an electromagnetic wave, we shall provide a consistent space-time picture of the atomic ionization by a femtosecond laser pulse for a broad range of field intensities. The results thus obtained will be compared with those obtained from analytic calculations.

2. THEORETICAL MODEL

We consider an atom with only one valence electron, and describe its interaction with the electromagnetic field of a wave in the dipole approximation. The evolution of the atomic system is governed by the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t}=-\frac{\hbar^2}{2m}\nabla^2\psi+U(\mathbf{r})\psi+V(\mathbf{r},t)\psi, \tag{1}$$

in which $U(\mathbf{r})$ is the potential energy of interaction between the electron and the rest of the atom,

$$V=-(\mathbf{dE})$$

is the operator describing the interaction between the electron and the electric field $\mathbf{E}(t)$ of the electromagnetic wave, and $\mathbf{d}$ is the dipole moment of the system.

Unless otherwise explicitly specified, the electric field will be considered harmonic

$$\mathbf{E}(t)=\mathbf{E}_0\cos\omega t.$$

We assume that initially the system is in the ground state, the wave function of which is an eigenfunction of the unperturbed Hamiltonian

$$H_0=-\frac{\hbar^2}{2m}\nabla^2+U,$$

i.e.,

$$\psi(\mathbf{r},t=0)=\varphi_1(\mathbf{r}). \tag{2}$$

The basic idea of Ref. 5 is to view the photoionization process as a transition from the initial state φ_1 to a state in the continuum, described by the wave function of a free electron in the field of an electromagnetic wave:

$$\psi_{\mathbf{p}}(\mathbf{r},t)=\exp\left[\frac{i}{\hbar}\left(\mathbf{P}(t)\mathbf{r}-\int\frac{\mathbf{P}^2(t')}{2m}\,dt'\right)\right], \tag{3}$$

where

$$\mathbf{P}(t)=\mathbf{p}-\frac{\mathbf{eE}_0}{\omega}\sin\omega t,$$

with $\mathbf{p}$ the initial electron momentum, the transition being induced by the perturbation V.

The nature of the photoionization process depends on the adiabatic parameter

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$$\gamma = \frac{\omega (mI)^{1/2}}{eE_0},$$

where I is the ionization potential. For $\gamma \ll 1$ the transition between a state of the discrete spectrum and continuum is a form of tunnel ionization; in the opposite case ($\gamma \gg 1$) it is a multiquantum photoeffect.

Another important parameter of the theory can be obtained by expanding (3) in a power series:

$$\psi_p(\mathbf{r}, t) = \sum_n J_n \left(\frac{e\mathbf{E}_0\mathbf{P}(t)}{m\hbar\omega^2} \right) \times \exp\left\{ \frac{i}{\hbar} \left[\mathbf{Pr} - \left(\frac{p^2}{2m} + \frac{e^2\mathbf{E}_0^2}{4m\omega^2} + n\hbar\omega \right) t \right] \right\}. \quad (4)$$

The quantity

$$N = \frac{e\mathbf{E}_0\mathbf{P}}{m\hbar\omega^2} \approx \max\left[\frac{(\varepsilon_e \varepsilon)^{1/2}}{\hbar\omega}, \frac{\varepsilon_e}{\hbar\omega} \right].$$

in which

$$\varepsilon = p^2/2m, \text{ and } \varepsilon_e = e^2E_0^2/4m\omega^2$$

are the kinetic and vibrational energy of the electron in the field of the wave, respectively, will be called the multiquantum parameter. This parameter determines the probability of absorption of various numbers of quanta. As we shall see below, the above-threshold effect is observed in sufficiently strong fields when $N \geqslant 1$.

3. NUMERICAL CALCULATIONS

Following Ref. 7, in numerically solving the problem (1), (2), we shall restrict ourselves to a one-dimensional model of the photoionization process. The atomic potential will be chosen in the form of a one-sided rectangular well

$$V(x) = \begin{cases} \infty, & x<0, \\ -V_0, & 0 \leqslant x \leqslant d, \\ 0, & x>d. \end{cases} \quad (5)$$

In numerical calculations, we took $V_0 = 7$ eV and $d = 5$ Å. In such a well there are two energy levels, at $\varepsilon_1 = -5.87$ eV and $\varepsilon_2 = -2.61$ eV, respectively. The quantum energy of the field is chosen to be $\hbar\omega = 2.5$ eV. Consequently, the ionization of the "atom" requires the absorption of at least three quanta if the "atom" is in the ground state, or of two, if it is in the excited state.

In Fig. 1 we show the quantity $|\varphi_1(x)|^2$ and the momentum distribution $|\tilde{\varphi}_1(k)|^2$ for the ground state. As it can be seen, the width of this distribution is ≈ 10 eV. Consequently, the absorption of quanta will appear in the electron energy spectrum as peaks separated by a quantity $\hbar\omega$, on the background of the unperturbed state $|\tilde{\varphi}_1(k)|^2$.

The Schrödinger equation (1) with the initial condition (2) was solved by the method of finite differences for $x \in (0.170$ Å) with a cubic approximation for the ψ function on the element. The integration time step was 1/60 of the period T of the laser field. For $\hbar\omega = 2.5$ eV, time

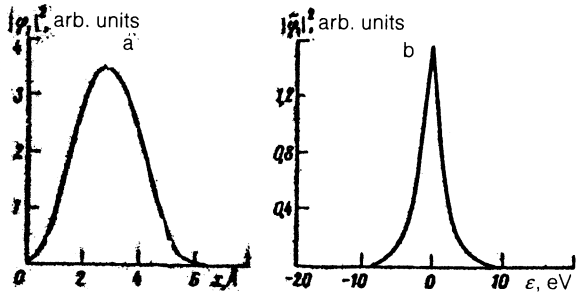

FIG. 1. Space (a) and momentum (b) densities of probability distributions for the ground state of the "atom."

$\Delta t = 0.0276$ fsec. More details concerning the solution of the problem (1), (2) are given in the Appendix.

We now discuss the results obtained from this model of photoionization of the "atom" by the electromagnetic radiation.

In the k-representation, the spectrum of electron states is defined by

$$|\tilde{\psi}_k(t)|^2 = \left| \int \psi(x, t) \exp\left(-ikx + i\frac{k^2}{2m} t \right) dx \right|^2. \quad (6)$$

Since in free space the momentum operator commutes with the Hamiltonian, the momentum distribution also represents the energy spectrum, for which $\varepsilon = \hbar^2 k^2/2m$.

In Fig. 2 we show the electron spectra in the process of interaction with the electromagnetic wave at time $t = 4T$ and for intensities between $3 \cdot 10^{12}$ and $3 \cdot 10^{14}$ W/cm^2. These curves allow us to follow the transition from the regime of the photoelectric effect (Fig. 2, a, b) when the adiabatic parameter satisfies $\gamma \gg 1$, to the tunnel ionization regime when $\gamma \ll 1$ holds. As an intermediate case we have the above-threshold ionization regime (Fig. 2, c, d), when there are a large number of peaks in the electron spectrum, separated by a quantity $\hbar\omega$. As the intensity is further increased (which can be realized by reducing the frequency of the radiation), the peaks merge forming a complex spectrum corresponding to tunnel ionization in a variable field (see Fig. 2, e).

Let us examine the photoionization process in the more interesting case of above-threshold ionization ($Q = 10^{14}$ W/cm^2).

In Fig. 3 we show the distribution of the probability density $|\psi(x,t)|^2$ to find the electron at various points in space and at various times from the switching on of the laser radiation. The arrow indicates the extension of the potential well. In this case, the ionization of the "atom" occurs with a probability close to unity in a time on the order of five periods of the laser field. During this time, the quantity $|\psi(x,t)|^2$ spreads out over a distance ≈ 150 Å.

It is important to note that outside the "atom" the distribution $|\psi|^2$ can be represented by a superposition of distinct wave packets traveling away from the potential well, equal in number to the laser field periods. The reason for this is that the electron leaves the well preferentially when the direction of the electric field coincides with the direction of the x axis. Such a representation of the process is typical for tunnel ionization, when the transition from discrete to continuous spectrum occurs so rapidly that the field of the electromagnetic wave appears to be practically stationary.

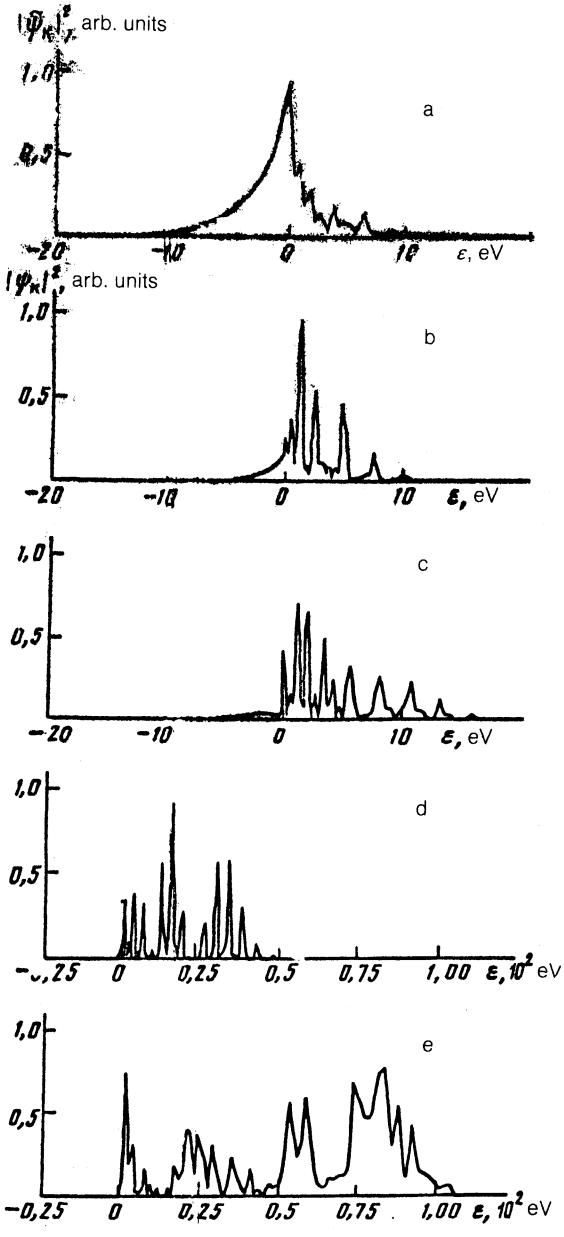

FIG. 2. Spectra of the electron states at $t = 4T$ for various wave field intensities in W/cm^2: a—3.10^{12}; b—10^{13}; c—3.10^{13}; d—10^{14}; e—3.10^{14}.

In this case, the adiabatic parameter is

$$\gamma = \omega(mI)^{1/2}/eE \approx 1,$$

i.e., the photoionization process has the characteristics both of the tunnel effect and of the photoeffect. That this is indeed the case can be seen by inspecting the spectra of the electron states at various times, shown in Fig. 4. These are characterized by a large number of sharp equally spaced peaks, which are typical for above-threshold ionization. The peak with zero energy corresponds to the bound state of the electron in the well, and the distance between peaks is approximately equal to $\hbar\omega$. Interestingly, such a spectral structure is formed in the time of one or two periods of the laser field, because as the duration of the interaction increases, the peaks sharpen. This is easily understood: the longer the electromagnetic wave acts upon the electron, the more it appears to be monochromatic.

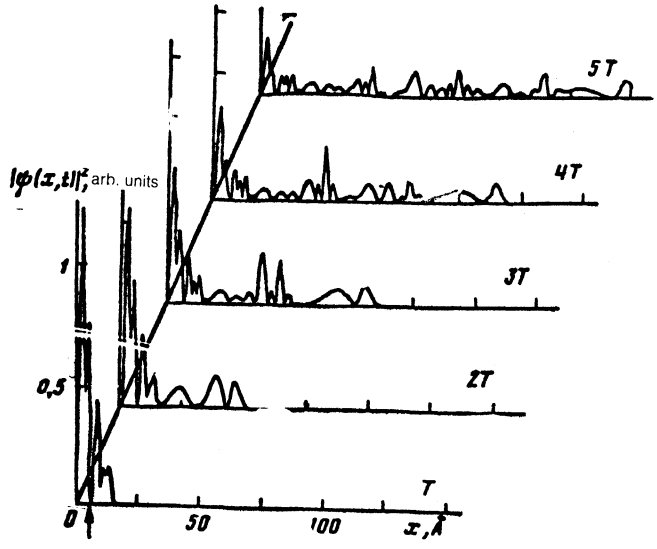

FIG. 3. Density of probability distribution to find an electron at various points at different times in the field of a laser of intensity $Q = 10^{14}$ W/cm^2, with $\hbar\omega = 2.5$ eV.

Let us also note that, during the action of the laser field, the relative amplitude of the various spectrum peaks varies: the height of the peaks at low energies gradually decreases, while the probability to find an electron in the high energy region of the spectrum increases. It follows then that the electron continues to absorb energy even after the atom undergoes photoionization (e.g., as the result of an induced retardation effect). The average energy of the photoelectron can be estimated from the spectrum or from the velocity of the wave packet to be of the order of 15–20 eV; i.e., the electron absorbs above threshold 5–10 photons from the laser field. This value is in agreement with the value of the multiphoton parameter N, which determines the number of absorbed photons in analytic theories.

A detailed examination of the dynamics of the energy spectrum in photoionization, however, leads to a more com-

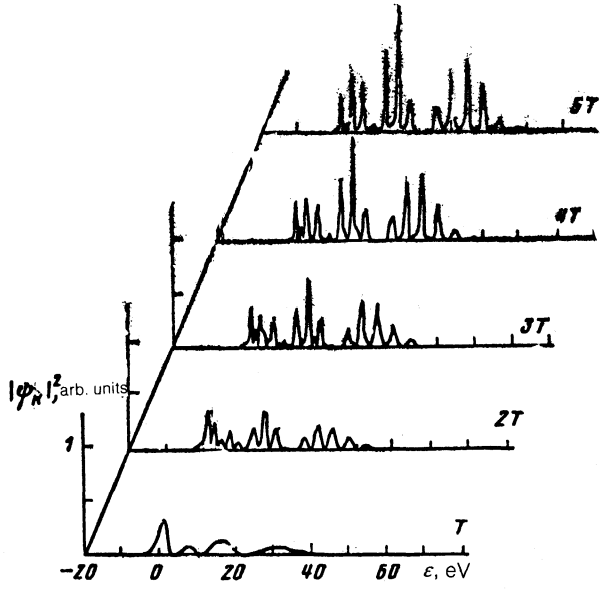

FIG. 4. Spectra of electron states at $t = T$, $2T$, $3T$, $4T$, and $5T$.

plicated picture of the process. In Fig. 5 we give the spectra of the photoelectron states at various phases of the electromagnetic wave. It can be seen that the energy interval between neighboring peaks oscillates in time and equals $\hbar\omega$ only twice during a period, i.e., from

$$\omega t = 0,\ \pi$$

(see also Ref. 7). This effect can be explained by the existence of an oscillation energy of the free electron in the field of the electromagnetic wave. Indeed, it follows from (3) that the energy of an electron with momentum

$$p_n = \hbar k_n$$

is

$$\varepsilon_n(t) = \frac{1}{2m}\left(\hbar k_n - \frac{eE_0}{\omega}\sin\omega t\right)^2. \qquad (7)$$

Hence, the separation between neighboring maxima in the spectrum is

$$\Delta\varepsilon(t) = \varepsilon_n - \varepsilon_{n-1} = \hbar\omega - (p_n - p_{n-1})\frac{eE_0}{m\omega}\sin\omega t, \qquad (8)$$

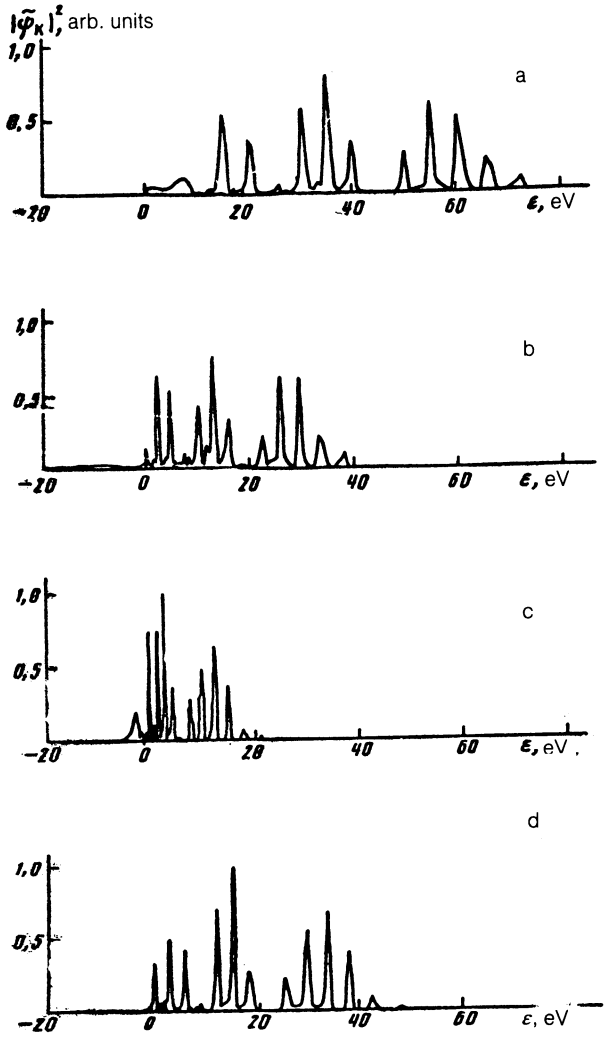

FIG. 5. Spectra of electron states at various phases of the field period: $\omega t = 0$ (a), $\pi/2$ (b), π (c), $3\pi/2$ (d). Radiation intensity $Q = 10^{14}$ W/cm^2.

which confirms the numerically calculated results. As seen from (8), the movement of peaks in the spectrum of electron states is significant only in sufficiently strong fields, when the oscillation energy of the electron is comparable with the photon energy: $\varepsilon_e \geqslant \hbar\omega$. Precisely such fields are required for the above-threshold ionization to occur.

In addition to the peaks separated by $\hbar\omega$, one can also notice in the spectrum of photoelectrons some "extra" peaks in Fig. 2 c. The appearance of these peaks is related to the photoionization of the "atom" from the excited state of -2.61 eV, induced by the strong radiation field. The dynamics of the population densities of the ground, W_1, and excited, W_2, states for $Q = 3.10^{13}$ W/cm^2 is shown in Fig. 6. These population densities are defined as

$$W_i(t) = \left|\int \psi(x,t)\varphi_i(x)\exp\left(\frac{i}{\hbar}\varepsilon_i t\right)dx\right|^2 \qquad (9)$$

in which $\varphi_i(x)$ and ε_i are the wave function and energy of the ith stationary state ($i = 1,2$). The calculations have shown that these populations oscillate with the Rabi frequency

$$\Omega = \left[\frac{|d_{21}E_0|^2}{4\hbar^2} + \left(\frac{\Delta\omega}{2}\right)^2\right]^{1/2}, \qquad (10)$$

where d_{21} is the matrix element of the dipole moment operator, and

$$\Delta\omega = \omega - \frac{\varepsilon_2 - \varepsilon_1}{\hbar}$$

is the deviation from resonance. Although the average population of the excited state is smaller than the population of the ground state, its ionization requires the absorption of only two photons, which leads to the appearance of additional peaks in the spectrum. Experimentally, such intermediate resonances in the above-threshold atomic ionization appear as a fine structure of the spectrum.[9]

In contrast with the predictions emerging from calculations, the dynamic mixing of peaks in above-threshold ionizations, which should spread out the resonance structure of the photoelectron spectra in sufficiently strong fields, has not been observed experimentally. As mentioned before,[1] an agreement between calculations and experimental data must take into account the change in the energy distribution of electrons which occurs when they move towards the detec-

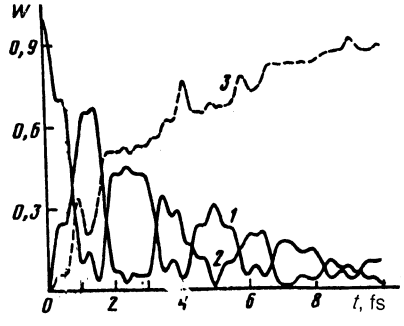

FIG. 6. Population dynamics of the ground (1) and excited (2) states during a laser pulse of intensity $Q = 3\cdot10^{13}$ W/cm^2.

tor, through the spatially inhomogeneous field of the focusing laser, and/or the variation of the intensity of the electric field of the wave during the laser pulse. In femtosecond pulses, during which the displacement of the electrons is significantly smaller than the size of the focusing region (≈ 10–$100\,\mu$m,) the investigation of above-threshold ionization necessitates a more realistic profile of the laser pulse.

We assume that the generating pulse has a Gaussian form:

$$Q(t)=Q_0 \exp[-(t-t_0)^2/\tau^2],$$

where 2τ is the length of the pulse, and Q_0 its maximum intensity, reached at a time t_0.

The main results obtained in calculations assuming a 10 fs pulse duration and a peak intensity of 3.10^{13} W/cm^2 (see Fig. 7) are the following. After the pulse has passed, the photoionization probability is ≈ 0.8, and the probability of finding the electron on the excited level is practically zero. The effective photoionization of the "atom" occurs only for radiation intensities close to their maximum, whereas transitions between the discrete levels occur also in weaker fields. The de-excitation of the "atom" in the "tail" of the pulse is due to the fact that, at this stage, the induced emission of photons dominates their absorption.

To conclude, let us examine the evolution of the photoelectron spectrum during a realistic pulse. In establishing a connection between the experimental data and the theoretical modeling it is most essential that when the electromagnetic field is turned on smoothly, i.e., when $\omega\tau \gg 1$ holds (a condition which is fulfilled even in the considered case of ultrashort pulses) there appears a gradual "switching on" of the oscillatory motion of the electron and that the stationary spectrum with peaks separated by $\hbar\omega$ is established (see Fig. 8). The "switching on" effect of the oscillation energy can be understood in classical terms. The equation of motion of a free electron in the field of an electromagnetic wave is

$$m\dot{v}=eE(t)\cos\omega t. \qquad (12)$$

Setting

$$E(t)=E_0 \exp\left(-\frac{1}{2}\frac{t^2}{\tau^2}\right),$$

and assuming $\omega\tau \gg 1$ (i.e., that the wave field is switched on adiabatically) we find that

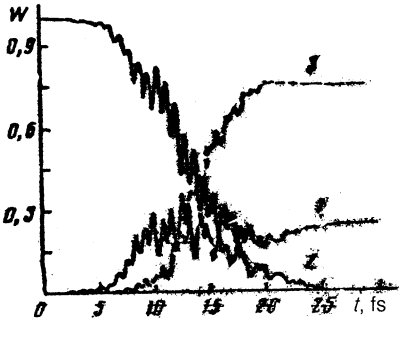

FIG. 7. Time dependence of the probability of finding the electron in the ground (1), excited (2), and continuum (3) states during a laser pulse of 10 fs with a peak intensity of 3.10^{13} W/cm^2. (The maximum radiation intensity is reached at $t = 12$ fs.)

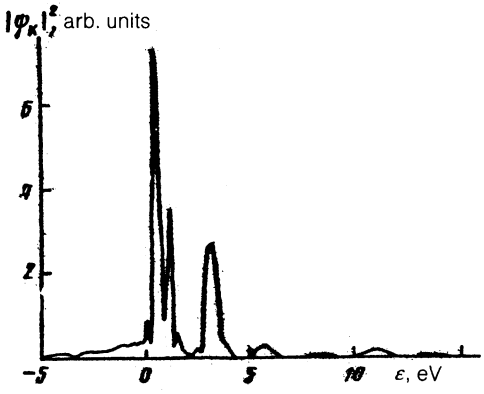

FIG. 8. Spectrum of the electron state at the end of a laser pulse of 10 fs and a peak intensity of 3.10^{13} W/cm^2.

$$v(t\to\infty)=\frac{eE_0}{m}\int_0 \exp\left(-\frac{1}{2}\frac{t^2}{\tau^2}\right)\cos\omega t\,dt$$

$$\approx\frac{eE_0}{m}\exp\left(-\frac{\omega^2\tau^2}{2}\right)\to 0.$$

When the field is switched on instantaneously, the photoelectron spectrum is determined by the phase of the oscillation velocity at the end of the pulse.

A comparative examination of the Figs. 3 and 7 shows that in the case of a realistic pulse the peaks corresponding to the absorption of several photons dominate, which shows that the photoeffect with the absorption of a minimum possible number of photons in the front and back of the pulse is the dominant mechanism.

APPENDIX

In the numerical solution of the equation (1) we used the method of splitting up the physical processer each step. Thus, the equation during the step

$$\Delta t = t^{k+1} - t^k$$

is replaced by a coupled system of equations, the first of which describes the motion of electrons in free space, and the second the change of phase of the wave function of the electron in the potential field:

$$i\hbar\frac{\partial\psi^{FM}}{\partial t}=-\frac{\hbar^2}{2m}\frac{\partial^2\psi^{FM}}{\partial x^2}, \qquad \psi^{FM}(x,t^k)=\psi(x,t^k),$$

$$i\hbar\frac{\partial\psi^{FS}}{\partial t}=(U(x)+V(x,t))\psi^{FS}, \qquad \psi^{FS}(x,t^k)=\psi^{FM}(x,t^{k+1}).$$

$$\psi(x,t^{k+1})=\psi^{FS}(x,t^{k+1}). \qquad (13)$$

The equation for ψ^{FS} is an ordinary differential equation with respect to time. For potentials of the type used in this work

$$V(x,t) = -exE_0\cos\omega t,$$

the integration can be done analytically:

$$\psi(x,t^{k+1})=\psi(x,t^k)\exp\left\{-\frac{i}{\hbar}[exE_0(\sin\omega t^{k+1}-\sin\omega t^k)+U(x)]\Delta t\right\},$$

where

$\psi(x,t) \equiv \psi^{FS}(x,t)$.

If the amplitude E_0 depends on time, its change during the step Δt is neglected, and we set

$E_0 = E_0(t^k)$.

The equation for ψ^{FM} is solved by the method of finite elements. The finite element approximation refers only to the spatial variable. The difficulty in solving this problem consists in the fact that the function $\psi(x,t)$ is rapidly oscillating in space, so that a satisfactory solution requires a considerable numerical effort.

Numerical calculations using various approximating polynomials showed that the best is the cubic approximation of the function $\psi^{FM}(x,t)$ (from now on the superscript FM will be dropped) on the element. By using the method of finite elements, one obtains the discrete form of the Schrödinger equation:

$$i\hbar M \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} D\Psi, \tag{14}$$

where

$\Psi(t) = \{\psi(x_1,t),...,\psi(x_N,t)\}$

is the vector of nodal solutions, N the number of nodes in the spatial mesh, M is the analog of the weight matrix, and D is the evolution matrix.[10]

For the integration with respect to time of the equation (14) we used the Crank–Nicolson difference scheme:

$$i\hbar M \frac{\Psi^{k+1} - \Psi^k}{\Delta t} = -\frac{\hbar^2}{2m} D \frac{\Psi^{k+1} + \Psi^k}{2}. \tag{15}$$

[1] N. V. Delone and M. V. Fedorov, Usp. Fiz. Nauk **158**, 215 (1989) [Sov. Phys. Usp. **32**, 500 (1989)].
[2] P. Agostini *et al.*, Phys. Rev. Lett. **42**, 1127 (1979).
[3] P. Kruit *et al.*, Phys. Rev. A **28**, 248 (1983).
[4] L. A. Lompre *et al.*, J. Opt. Soc. Am. B **2**, 1906 (1985).
[5] L. V. Keldysh, Zh. Eksp. Teor. Fiz. **47**, 1945 (1964) [Sov. Phys. JETP **20**, 1307 (1965)].
[6] H. G. Muller *et al.*, Phys. Rev. Lett. **60**, 565 (1988).
[7] J. Javainen, J. H. Eberly, and Q. Su, Phys. Rev. A **38**, 3430 (1988).
[8] K. C. Kulander, Phys. Rev. Lett. **35**, 445 (1987).
[9] R. R. Freeman *et al.*, Phys. Rev. Lett. **59**, 1092 (1987).
[10] J. Tinsley Oden and J. N. Reddy, *An Introduction to the Mathematical Theory of Finite Elements*, Wiley, N. Y. 1976.

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