Multiphoton ionization of helium under uv radiation: Role of the harmonics

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(Received 14 September 2006; published 15 December 2006)

We present a quantitative theory with detailed calculations pertaining to multiphoton ionization of helium under moderately strong uv radiation of photon energy 13 eV. Employing both, the nonperturbative solution of the time-dependent Schrödinger equation, as well as perturbation theory, we obtain detailed results for all processes expected to be of quantitative relevance within the range of intensities and pulse durations in this work, which have been chosen so as to match the conditions of a recent experiment on exactly this problem [T. Laarman *et al.*, Phys. Rev. A **72**, 023409 (2005)]. The conclusion, in connection with the experimental data, which our results lead to is that, without the presence of the second harmonic of the fundamental in the radiation, it is impossible to reconcile the reported observations with fundamental features of the processes involved. A more general conclusion seems to be that the presence of these harmonics, even at intensities less than 1% of that of the fundamental, are apt to produce profound side effects that will mask multiphoton processes by the fundamental.

DOI: 10.1103/PhysRevA.74.063410 PACS number(s): 32.80.Rm

I. INTRODUCTION

Relatively strong coherent radiation in the uv and xuv recently available at free-electron laser (FEL) facilities and possibly higher-order harmonic generation (HOHG) sources provide the opportunity to explore multiphoton processes involving more than one electron [1–9]. This will certainly be the case in the xuv with some first experimental results already in print [10–12]. For the time being, intensities around 10^{13} W/cm [2] are available. At such intensities, issues of perturbative versus nonperturbative behavior are known to become relevant in the long-wavelength range, and specifically for the Ti-sapphire laser at ~800 nm, which is the main radiation source for strong field physics. The first issue that needs to be addressed then is the meaning of strong field at shorter wavelengths. Given the existence of experimental results at photon energy 13 eV and intensity around 10^{13} W/cm^2 [4], and some controversy that has surrounded the relevant papers [13–16], it appears desirable to attempt a quantitative analysis, which takes into account the accumulated, over the last 30 years, experience on multiphoton processes.

The strength of a field is often characterized by the so-called Keldysh parameter γ. We find it preferable to measure the strength of an electromagnetic field in terms of the ponderomotive energy U_p, representing the quiver energy of an electron in the field, averaged over one cycle, given by $U_p = I/\omega^2$. Thus the ratio of the U_p to the photon energy is inversely proportional to the third power of the latter. It is well established, theoretically as well as experimentally, that if U_p is considerably smaller than the photon energy ω and the pulse duration longer than, say 10 cycles or so, then multiphoton ionization as described by lowest-order perturbation theory (LOPT) is the dominant mechanism. This means that above-threshold ionization (ATI), to the extent that it is observable, is also described by terms of higher order in perturbation theory (PT) which, however, decrease with increasing order quite rapidly. The fact that they involve a pole in the continuum presents no fundamental formal difficulty, as there are well-established techniques for dealing with them [17,18]. Similarly, harmonic generation, again to the extent that it is observable, appears only in a very limited number of peaks, also decreasing rapidly with increasing order.

As a point of calibration, let us note that for photons of wavelength 1064 nm ($\omega \sim 1.17$ eV) and intensity 10^{13} W/cm^2, $U_p = 1$ eV. Consequently, for the same intensity but photon energy 13 eV, U_p is approximately 0.01 eV, which is three orders of magnitude smaller than the photon energy. It is therefore safe to assume that, even for intensities up to 10^{15} W/cm^2, LOPT is a valid approach to the problem. Since for the radiation of 13 eV, the corresponding cycle is 0.3 fs, a pulse of duration of tens of fs, clearly satisfies the conditions for the validity of LOPT. The pulse duration would have to be less than 3 fs for this condition to be violated.

Under the above conditions, what is needed for the theoretical description of multiphoton processes are, to start with, the generalized cross sections relevant to the order of the processes involved. These cross sections are then employed in the derivation of differential equations governing the evolution of the yields—be it ionization or excitation—as a function of time during the pulse [19]. This shall be referred to here as time dependent perturbation theory (TDPT). For an accurate simulation of experimental yields, a reasonably realistic temporal pulse shape pertaining to the particular experiment should be employed. For wavelengths well into the xuv and even soft x rays, the dipole approximation is perfectly valid for the calculation of the cross sections, even if ATI is involved.

Any source of electromagnetic radiation of intensity sufficient to be employed in multiphoton processes is a classical source describable, for our purposes, by the time-dependent amplitude of the electric field or the associated vector potential, as they appear in Maxwell's equations. This is the well-known semiclassical description of radiation-atom interactions, in which the field is treated classically and the atom quantum mechanically. There is no reason whatsoever to employ a description in terms of the quantized field, as it would add nothing missing from the semiclassical description. If vacuum-field effects, such as spontaneous emission were expected to be of relevance, they can be accounted for by simply including the relevant spontaneous decay rates in the differential equations, which in that case may have to be cast in terms of the density matrix [20]. If on the other hand, one were to insist on describing the field quantum mechanically, then a description in terms of photon number states is inappropriate, if not inconsistent, because no matter how large the number of photons may be, a number state cannot approach a classical field [21]. It is the coherent states that provide a consistent description of a classical field, which bears repeating, is totally unnecessary in our context. It is of course known that, as long as the processes under consideration simply involve energy exchange between the field and the atom, a description in terms of number states will give the same formal result. If, however, issues concerning the phase of the field need be taken into consideration, number states are at best cumbersome and in most cases useless, not to mention the fact that formulating a problem involving a pulse in terms of number states is, at best, inconsistent.

In considering the interaction of short wavelength (shorter than optical) radiation with an atom other than hydrogen, excitation and/or ionization of more than one electron may become significant at intensities lower than those required at infrared or optical wavelengths, although this is not the case for helium and photon energy of 13 eV, within the range of intensities of interest in this paper. In any case, the calculation of reliable multiphoton cross sections, even if one electron is ionized, should be based on a reliable and flexible description of the two-electron atomic system. This can be accomplished through a number of well-developed and tested approaches [22,23]. In this paper, we employ a configuration-interaction (CI) approach, implemented in terms of B splines, that we have found useful and have tested in a number of contexts. In the text, while in the presentation of the formulation we use atomic units, in the discussion of the results and the figures we use SI units.

II. FORMULATION

Although, as explained above, it would be perfectly valid to cast our analysis in terms of TDPT, using cross sections obtained through LOPT, it is more convenient for our purposes here to formulate the basic analysis in terms of the solution of the time-dependent Schrödinger equation (TDSE), digressing occasionally into the use of LOPT, in order to document and interpret our results as elaborately as possible. Since the formalism we employ has been presented elsewhere [22,24], we outline below those equations that are necessary for the reader to follow the flow of the approach and calculation.

Let H_a be the Hamiltonian of the atom and $D(t)$ the interaction with the field, which in the dipole approximation can be written in the form

$$D(t) = -\frac{1}{c}\mathbf{p}\cdot A + \frac{1}{2c^2}\mathbf{A}^2(t),$$

where $\mathbf{p}$ is the momentum operator of the electron (s) and $\mathbf{A}(t)$ is the vector potential of the field from which, in the absence of charges, the electric field is obtained through the relation $\mathbf{E}_f(t) = -c^{-1}\partial\mathbf{A}/\partial t$.

As has been established long ago [25], in the dipole approximation, whether within LOPT or the TDSE, the term $\mathbf{A}^2$ does not contribute to transitions. Specifically, in the expression for a multiphoton ionization or excitation cross section in LOPT, this term can not contribute because the matrix elements appearing in that expression connect mutually orthogonal atomic states, and the term $\mathbf{A}^2$ contains no atomic operator, assuming of course that, as is normally the case, an orthogonal atomic basis is employed. In the TDSE formalism, this term appears as a phase factor, which is simply factored out. Either way, the point is that this term, in the dipole approximation, cannot contribute to the physics of the problem. Recall that, in quantum electrodynamics, this term contributes only to Rayleigh scattering because, in that special case of a two-photon process, the initial and final atomic states are identical and therefore nonorthogonal. In the event a nonorthogonal atomic basis is employed as has been the case in a recent paper [26] related to our problem, obviously, contributions from the term $\mathbf{A}^2$ will appear which, however, cannot account for physical effects.

A. Time-dependent Schrödinger equation formulation

Our objective is to solve the TDSE,

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r}_1,\mathbf{r}_2;t) = [H_a + D(t)]\Psi(\mathbf{r}_1,\mathbf{r}_2;t). \quad (1)$$

The time-dependent interaction $D(t)$ of the helium atom with an external laser pulse in the dipole approximation and velocity gauge can be written as

$$D(t) = -\mathbf{A}(t)\cdot(\mathbf{p}_1 + \mathbf{p}_2), \quad (2)$$

with the vector potential $\mathbf{A}(t)$ here assumed to have the form,

$$\mathbf{A}(t) = \hat{\mathbf{e}}\cdot\sum_i A_i f_i(t)\sin(\omega_i t), \quad (3)$$

where $\mathbf{p}_1, \mathbf{p}_2$ are the momenta of the two electrons and A_i the amplitudes of the harmonics with polarization vector $\hat{\mathbf{e}}$. The pulse-shape envelope is represented as $f_i(t) = \cos^2(\pi t/T)$, where T is the pulse duration. The velocity form of the interaction operator is chosen, because it makes the calculation converge faster in terms of the number of angular momenta included [25]. The reason for assuming in, Eq. (3), $\mathbf{A}(t)$ to consist of more than one pulse, is that radiation from short-wavelength sources appear to contain one or two of the harmonics of the fundamental at non-negligible intensities [4,27].

The time-dependent wave function is now expanded on the basis of eigenfunctions $\Psi^{\Lambda}_{E_i}(\mathbf{r}_1,\mathbf{r}_2)$ of the atomic Hamiltonian H_a,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2;t)=\sum_I U_I(t)\Psi_I(\mathbf{r}_1,\mathbf{r}_2), \tag{4}$$

with the index I to denote the set of quantum numbers $I \equiv (E_i,\Lambda)$. Here the index Λ represents the set of angular quantum numbers (LSM_LM_S) and E_i the eigenenergies. This expansion transforms the TDSE into a set of first-order differential equations for the time-dependent coefficients $U_I(t)$, namely,

$$i\frac{d}{dt}U_I(t)=E_iU_I(t)-\sum_{I'} D_{II'}(t)U_{I'}(t), \tag{5}$$

subject to the initial conditions $|U_I(t=0)|^2=|U_{E_iL}(t=0)|^2=\delta_{E_iE_1}\delta_{L0}$ with E_1 being the energy of the initial state. In the present case where the uv field is linearly polarized, and the helium atom initially in its ground state $(L_1=0,M_1=0)$, we need to consider only the $M=0$ singlet states $(S=0)$. Thus, the quantities $D_{II'}(t)$ represent the matrix elements of $D(t)$ calculated between the states characterized by the quantum numbers E_iL and $E_{i'}(L+1)$.

At the end of the pulse, we obtain the coefficients $U_{E_iL}(t\to\infty)$, from which we can extract information about the ionization yields and the photoelectron energy spectrum (PES) as well as photoelectron angular distributions [22,28,29].

B. Multiphoton cross-section formulation

Within lowest-order perturbation theory, the N-photon transition amplitude from an initial state $|i\rangle$ of energy E_i to a final state $|f\rangle$ is given by an $(N-1)$-fold summation over the whole spectrum of the allowed states [23]

$$M^{(N)}_{if}=\sum_{m_{N-1}}\cdots\sum_{m_1}\frac{\langle i|D|m_1\rangle\cdots\langle m_{N-1}|D|f\rangle}{\omega_{i1}\omega_{i2}\cdots\omega_{i(N-1)}}, \tag{6}$$

where $\omega_{ij}=E_i+j\omega-E_{m_j}$, $j=1,\ldots,N-1$ are the detunings, ω is the field frequency, and D is the atom-field electric dipole operator. When the state $|f\rangle$ belongs to the singly ionized continuum spectrum, the expressions for the N-photon total- and partial-ionization cross sections, are given by

$$\sigma^{(N)}_{if}=\sum_L \sigma^{(N)}_L=2\pi(2\pi\alpha)^N\omega^N\sum_L |M^{(N)}_L(E_f)|^2, \tag{7}$$

with α the fine-structure constant. The expression for the partial-ionization cross sections σ_L into the Lth angular momentum channel is obtained by inspection of the above formula. All multiphoton transition matrix elements are calculated at the final energy E_f. The summation over L is performed over all allowed symmetries and up to $L=N$ for an N-photon ionization process. From the N-photon transition amplitude it is possible to derive expressions for ionization yields induced by an N-photon absorption and given the differential generalized cross sections, photoelectron angular distributions can also be obtained. The relevant expressions as well as calculations for the single and two-photon cross sections in helium, with the present method, may be found in Refs. [30–33]. In the present work we use the ionization cross sections only for the calculation of the ionization yields. By using the well-known relationship between the cross section and ionization rate $W_N=\sigma_N(I/\omega)^N$, with I the peak intensity and ω the photon energy of the radiation field [34], we calculate ionization yields from a pulse having envelope $f(t)$ as follows

$$Y_N(t)=\sigma_N\left(\frac{I}{\omega}\right)^N\tau_N, \tag{8}$$

with the effective time τ_N defined as $\int_{-\infty}^{\infty}f(t)^{2N}dt$.

C. Two-electron helium eigenstates

Though the method has been presented in detail elsewhere and applied to various two-electron systems [22–24,33] we feel that a brief description is necessary for the sake of completeness. The Hamiltonian of the helium atom H_a can be written as

$$H_a=h(\mathbf{r}_1)+h(\mathbf{r}_2)+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}, \tag{9}$$

with $h(\mathbf{r}_i)=-\nabla_i^2/2-2/r_i$ being the single-electron Hamiltonian for the ith electron (here the He^+ Hamiltonian). By expanding the single-electron wave function of He^+ in spherical coordinates $\psi(\mathbf{r})=[P(r)/r]Y_{lm}(\theta,\phi)$, with Y_{lm} the well-known spherical harmonics, we solve the radial Schrödinger equation (SE) $h_l(r)P_{nl}(r)=\epsilon_{nl}P_{nl}(r)$ for each partial wave. The radial Hamiltonian for the lth partial wave of the He^+ is expressed as $h_l(r)=-(1/2)d^2/dr^2+l(l+1)/(2r^2)-2/r$. We expand the radial wave function $P_{nl}(r)=\Sigma_{i_b}c_{i_b}B_{i_b,k_b}(r)$ on a set of B-spline polynomial functions of order k_b, defined in an interval $[0,R]$ [35], and solve the resulting eigenvalue matrix equations for the coefficients c_{i_b,k_b}. In the present case, we force the wave function to be zero at the boundaries by selecting the radial functions $P_{nl}(r)$ to be the one-electron radial solutions of He^+, which by construction vanish at the boundaries of a box of radius R [33,36].

Having produced the He^+ one-electron radial eigenstates $P_{nl}(r)$ for each partial wave $l=0,1,2,\ldots$, we calculate the two-electron eigenstates of helium by solving the time-independent SE,

$$H_a\Psi^{\Lambda}_{E_i}(\mathbf{r}_1,\mathbf{r}_2)=E_i\Psi^{\Lambda}_{E_i}(\mathbf{r}_1,\mathbf{r}_2). \tag{10}$$

By expanding the two-electron eigenstates $\Psi^{\Lambda}_{E_i}(\mathbf{r}_1,\mathbf{r}_2)$ on the eigenstates of the zero-order Hamiltonian $[H_0=h(\mathbf{r}_1)+h(\mathbf{r}_2)]$, we obtain

$$\Psi^{\Lambda}_{E_i}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{nln'l'} C^{(E_i,\Lambda)}_{nll'n'}\Phi^{\Lambda}_{nln'l'}(\mathbf{r}_1,\mathbf{r}_2), \tag{11}$$

with $\Phi^{\Lambda}_{nln'l'}=A_{12}C_{LM_L}C_{SM_S}[P_{nl}(r_1)/r_1][P_{n'l'}(r_2)/r_2]$, where A_{12} is the antisymmetrization operator. Finally, C_{LM_L} and C_{SM_S} contain the appropriate Clebsch-Gordan coefficients to

ensure total angular momentum and spin equal to L and S, respectively. The SE [Eq. (10)] is transformed into a generalized eigenvalue matrix equation, from the diagonalization of which we obtain the CI coefficients $C_{nll'n'}(E_i,\Lambda)$ for each discrete eigenvalue E_i [24,31].

We produce the initial ground state of helium in a box of radius $R=1000$ a.u. in which we have included 20 configuration series of the type $nln'l'$ with l up to 5, n up to 3, and n' up to 800. The number of B-splines basis was 800 and the order 9. This choice of the basis resulted in a value for the ground-state energy equal to 78.8 eV. For the two-electron bound and continuum states of total angular momentum $L=0-6$ we have used single-electron orbitals with similar quantum numbers. The single-electron angular momenta were as high as $l,l'=6$. We have ascertained that the results obtained with the present method compare well with existing theoretical and experimental reports for the eigenenergies and dipole transition amplitudes between helium eigenstates.

III. RESULTS AND DISCUSSION

A. Pulse including the fundamental and the third harmonic frequency

According to the information provided in the experimental paper by Laarman *et al.* [4], the output of the FEL at 13 eV possibly contained also a small percentage (about 0.001) of its third harmonic, at 39 eV. At this photon energy, helium can undergo single-photon ionization which, at lower intensities, is much more probable than any higher-order process. Therefore, despite the relatively small percentage of this harmonic, its contribution must be included in any quantitative analysis of ionization yields, leaving it up to the results to tell us whether it is significant or not.

1. Total ionization yields

At 13 eV, the absorption of two photons is required for the ionization of helium, according to

$$\mathrm{He}(1s^2)+2\omega_1 \rightarrow \mathrm{He}^+(1s)+e^-(1.4\ \mathrm{eV}), \qquad (12)$$

leaving the ion in its ground state $\mathrm{He}^+(1s)$ while releasing an electron of kinetic energy of about 1.4 eV, as depicted in the energy-level diagram in Fig. 1 (P1, solid line). The additional ionization channel due to the third harmonic ω_3 is

$$\mathrm{He}(1s^2)+\omega_3 \rightarrow \mathrm{He}^+(1s)+e^-(14.4\ \mathrm{eV}), \qquad (13)$$

which contributes the second peak in the PES (Fig. 1: P2, solid line). There is, however, an additional contribution to this PES peak due to three-photon absorption from the fundamental, namely,

$$\mathrm{He}(1s^2)+3\omega_1 \rightarrow \mathrm{He}^+(1s)+e^-(14.4\ \mathrm{eV}). \qquad (14)$$

The imprint of these various processes on the ion yield is to be found on its dependence on laser intensity. This intensity dependence, as obtained in our calculation, is presented in Fig. 2, for a pulse as specified in Ref. [4] (dotted line-filled squares), where the intensity of the third harmonic is 0.001 of the fundamental. In this figure the horizontal axis represents the peak intensity of the fundamental. As a point of calibration, we present also the ionization yield that would be expected if only the fundamental were present (Fig. 2: solid line-empty circles). In this latter case, the yield as a function of intensity has a slope of two, i.e., it varies as I^2, over the entire range of intensities considered in the figure. Although the result has been obtained through the solution of the TDSE, it is consistent with LOPT, according to which the yield of N-photon ionization is proportional to the N-photon generalized ionization cross section multiplied by the Nth power of the intensity or—depending on units—the photon flux. The yield is expected to begin departing from this power dependence, tilting towards a smaller exponent, near the point of saturation, defined as the intensity at which the probability of ionization by the respective channel (during the pulse) approaches unity.

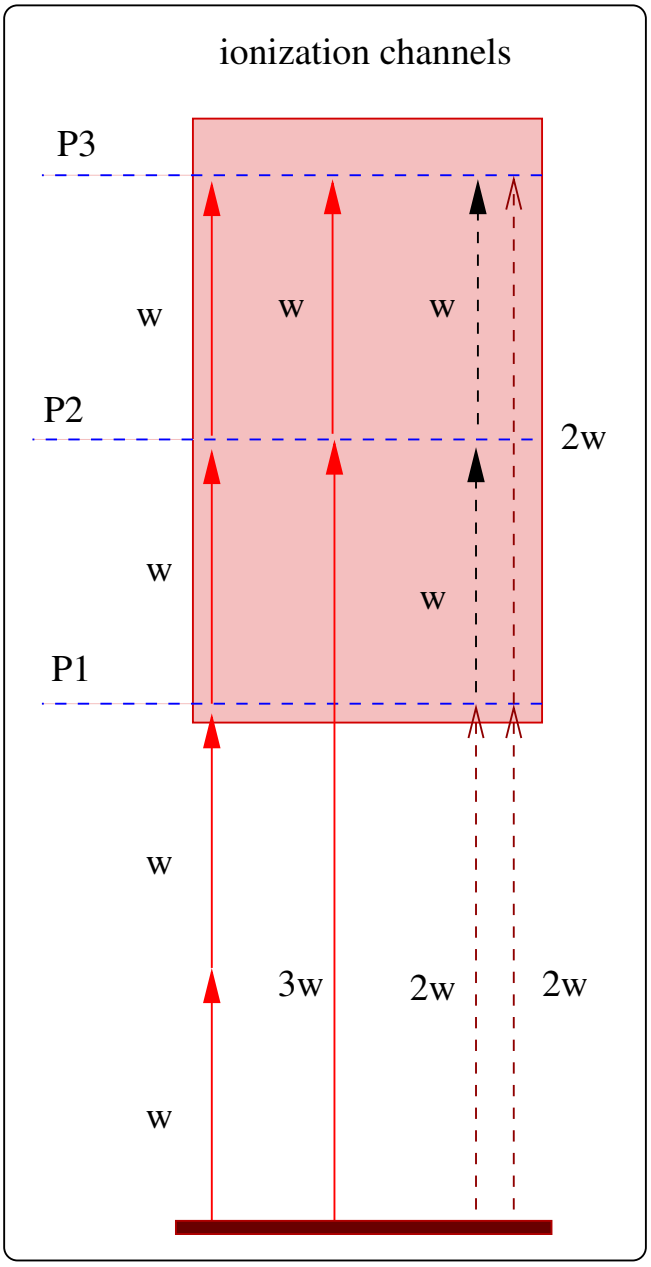

FIG. 1. (Color online) Schematic diagram of the possible ionization channels.

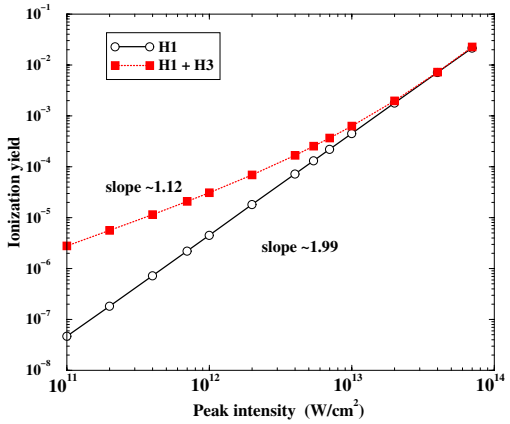

FIG. 2. (Color online) Ionization yields as a function of the peak intensity of the fundamental for a 104 fs pulse duration. In the figure we present the cases where (a) only the fundamental (H1) (solid line-empty circles) and (b) the fundamental and its third harmonic are present (H1+H3) (dotted line-filled squares). The intensity of the third harmonic has been chosen to be 0.001 of the fundamental.

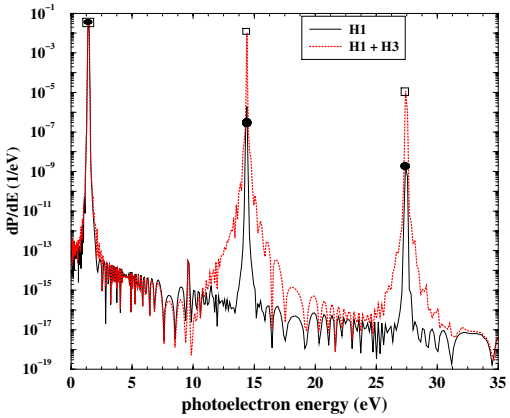

FIG. 3. (Color online) Above-threshold ionization spectrum for the fundamental (H1) (solid line) and the experimental (H1+H3) pulse (dotted line). The filled circles and the empty squares, at peaks P1, P2, and P3, denote the signals due to the fundamental alone and the fundamental and its third harmonic, respectively. The peak intensity of the fundamental is $I_0=5.4\times10^{12}$ W/cm^2 and the pulse duration 104 fs.

Clearly, the result of the calculation exhibits no such tendency, pointing to two-photon ionization within LOPT. The consistency of this result with the experimental conditions can be verified through the examination of the relevant cross sections. As we have already pointed out, the ponderomotive potential is negligible for the range of intensities of the uv field under consideration. Consequently, there is no appreciable shift of the ionization threshold, which means we expect the two-photon process shown in Eq. (12), with the known cross section $\sigma_2(\omega_1)\sim1.75\times10^{-51}$ cm^4 s [32]. For the pulse duration of relevance here, of about 100 fs [4], and the equation $\sigma_2(I_1^{(s)}/\omega_1)^2\tau_2\sim1$ we obtain a saturation intensity of about $I_1^{(s)}\sim2\times10^{14}$ W/cm^2, which is well above the range of intensities in the experiment. Note that for the specific form of the pulse employed in the calculation, we have taken $\tau_1=3/8$ and $\tau_2=35/128$.

Now, the situation changes drastically if the pulse does contain even a small percentage of its third harmonic. In that case, as demonstrated by the dotted line in Fig. 2, at low intensities the yield begins with a slope of about 1.1, merging with the curve of slope 2 at around 3×10^{13} W/cm^2. This is consistent with the expectation that at lower intensities, the yield will be dominated by the single-photon process due to the third harmonic [Eq. (13)]. With rising intensity, the single-photon signal increases linearly with I_3, while the two-photon signal increases as I_1^2, eventually catching up with the single-photon one. Again, we can calculate the respective intensities at which the two contributions are expected to become comparable and the curves to begin merging. Using the known single-photon ionization cross section at 39 eV [37], namely, 3.3×10^{-18}cm^2, in combination with the two-photon ionization cross section cited above, and equating the two contributions, i.e., $\sigma_2(I_1/\omega_1)^2\tau_2\sim\sigma_1(I_3/\omega_3)\tau_1$, we obtain $\sim2\times10^{12}$ W/cm^2 for the fundamental. A word of caution is necessary here as to the connection of this value to Fig. 2. The reason the two curves in Fig. 2 do not merge at this intensity is that the upper curve contains the contributions of both the fundamental and the harmonic, while the above value was obtained by equating the contribution by the fundamental with that of the harmonic alone. Let us, in addition, calculate the intensity of the third harmonic at which the single-photon signal is expected to reach saturation. From $\sigma_1(\omega_3)(I_3/\omega_3)\tau_1\sim1$ we obtain $I_3^{(s)}\sim2\times10^{13}$ W/cm^2, clearly well above the value one might expect in the experiment. Given that both intensities are well below the saturation values, it makes no sense to inquire about the well-known effect of the expansion of the interaction volume, which is of relevance only around and above saturation.

Summarizing the above analysis, we see that on the basis of the intensities cited in the experimental paper, namely, $\sim5.4\times10^{12}$ W/cm^2, neither the fundamental nor its third harmonic could have caused saturation of the ion yield, which implies that the observed slope should have been ~2 if the signal had been dominated by the two-photon process, or ~1 if it had been dominated by the third harmonic. Obviously, it is not only the slope but also the amount of ionization that is dominated by the third harmonic, under the assumed conditions.

2. Photoelectron energy spectra

Given that PES have also been reported in Ref. [4], and in an effort to examine the problem from all angles, we have also calculated and analyzed the PES, including ATI. Our results are shown in Fig. 3. Again, as in Fig. 2, we present results as a function of the peak intensity of the fundamental, corresponding to the presence of the fundamental alone, as well as to the combination of the fundamental plus its third harmonic. The lowest in energy peak (P1) (1.43 eV) in the figure represents the signal due to two-photon absorption and as such cannot be influenced by the presence of the third harmonic. The second peak (P2) (14.43 eV) corresponds to three-photon ATI by the fundamental plus single-photon ion-

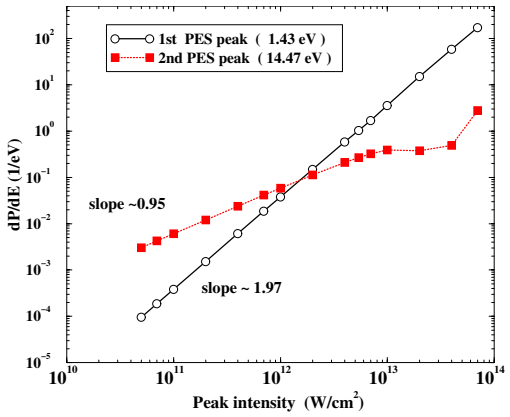

FIG. 4. (Color online) The maximum value of the first (solid line-empty circles) and second (dotted line-filled squares) PES peak (P1, P2) as a function of the peak intensity of the fundamental for 104 fs pulse duration. In the figure the fundamental and its third harmonics are present (H1+H3).

ization by the third harmonic, with the third peak (P3) (27.43 eV) corresponding to four-photon ATI by the fundamental as well as a 1+1 ATI process involving one photon from the third harmonic plus one from the fundamental. As is evident in the figure, peak P1 is indeed not affected by the presence of the third harmonic, while both P2 and P3 are not only affected but in fact dominated by the harmonic. Moreover, in the presence of the harmonic, the signal at P2 is practically equal to that at P1, which underscores the influence of the harmonic. Checking again the consistency of the above with LOPT and using the known cross sections, the two-photon ionization yield is $Y_2 \sim \sigma_2(\omega_1)(I_1/\omega_1)^2\tau_2 \sim 3.3 \times 10^{-4}$, while the single-photon yield is $Y_1 \sim \sigma_1(\omega_3) \times (I_3/\omega_3)\tau_1 \sim 1.7 \times 10^{-4}$, remarkably near Y_2.

We have also examined the dependence of the yield at the PES peaks as a function of the radiation intensity, with the results shown in Fig. 4 for intensities ranging from 5×10^{10} up to 10^{14} W/cm^2, again for a pulse with the features specified in Ref. [4]. The peak heights are found to increase with rising intensity, with the peak (P1) exhibiting a rise with a slope of ~1.97, for the entire range of intensities in the figure. This represents additional (and consistent with all preceding aspects) evidence that saturation has not been approached, and that its behavior is in complete agreement with LOPT predictions. Regarding the second peak (P2), the situation is somewhat different. As already explained, two ionization channels contribute to this peak; single-photon by the third harmonic and three-photon by the fundamental. As a result, at lower intensities, the single-photon channel dominates, leading to a linear intensity dependence, with a slope ~0.95. At an intensity between 1 and 3×10^{13} W/cm^2, where the contributions of the two channels become comparable, the slope exhibits an abrupt decrease, resuming its rise after $\sim 3 \times 10^{13}$ acquiring eventually a slope of 3, in accordance with the LOPT expectation, since at this intensity and beyond, the three-photon process becomes dominant. Clearly, whatever role interference effects due to two contributing channels may have played, it should have been confined in the range of intensities between 1 and 5×10^{13} W/cm^2. However, since the signal in both interfering channels is well below saturation, the interference is also fully accountable via TDPT. But, as long as the radiation contains only the fundamental and its third harmonic, in any case interference could not possibly affect the two-photon channel, as there is nothing to interfere with. As we have shown above, interference between channels could only affect peak P2 and higher ones. Yet, remarkably, in the theoretical modeling of the experimental results (Fig. 9 of Ref. [4] and Fig. 2 of Ref. [26]), a nonmonotonic behavior of the two-photon process has been reported, with this rather peculiar behavior beginning at about 5×10^{12} W/cm^2 which, without any documentation, has been attributed to nonspecific interference effects.

B. Pulse including the fundamental, its second and its third harmonic

Although no mention of the second harmonic has been made in Refs. [4,26], for the sake of completeness, we have explored the possible effect of the second harmonic on all of the features discussed above. Part of the motivation for this addition to our calculations stems from evidence that the second harmonic may also be present in short-wavelength FEL radiation. We assumed that, if present, the second harmonic would be somewhat stronger than the third. Thus if according to the theoretical evidence alluded to in Ref. [4], the third harmonic was about 0.001 of the fundamental, we chose 0.01 for the second harmonic. If present, it would affect the two-photon peak (P1) by contributing a single-photon channel, with cross section $\sigma_1(\omega_2) \sim 6.9 \times 10^{-18}$ cm^2 [37], the first ATI peak (P2) by contributing a two-photon channel (via the combination of one second-harmonic photon with one from the fundamental) and the second ATI peak (P3) by contributing a two-photon channel (with two second-harmonic photons), as well as a three-photon channel involving one second-harmonic photon plus two photons of the fundamental (Fig. 1, dotted lines).

We have thus repeated all calculations by solving the TDSE under the assumption of both harmonics (second and third) being present, at the percentages mentioned above. Needless to point out that all of the above combinations of channels are automatically taken into account in the calculation, which is one of the advantages of using TDSE. The results are presented in Figs. 5 and 7. Not surprisingly, the presence of the second harmonic dominates all features. In Fig. 5, which is the counterpart of Fig. 2, we note that the slope of the signal, including all three channels, is now closer to 1, with the absolute yield more than one order of magnitude larger. That is because the cross section for single-photon ionization by the second harmonic is somewhat larger than that for the third harmonic, and in addition, the intensity assumed for the second harmonic is higher than that of the third. Moreover, the two-photon signal by the fundamental alone will not merge with the total until a much higher intensity than in Fig. 2. In Fig. 6, the counterpart of Fig. 3, all three peaks are affected and dominated by the second harmonic, for an intensity of the fundamental 5.4×10^{12} W/cm^2. Finally, Fig. 7, the counterpart of Fig. 4, con-

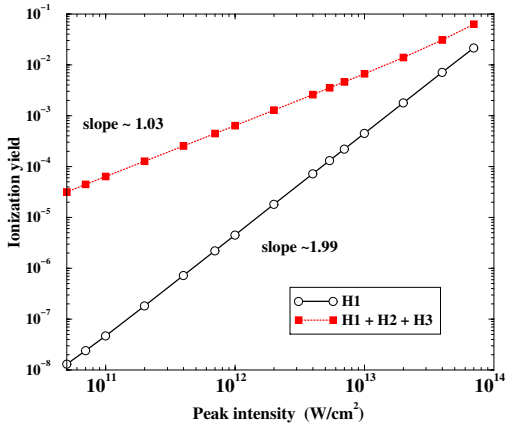

FIG. 5. (Color online) Ionization yields as a function of the peak intensity of the fundamental for a 104 fs pulse duration. In the figure we present the cases where (a) only the fundamental (H1) (solid line-empty circles) and (b) the fundamental, its second and its third harmonics are present (H1+H2+H3) (dotted line-filled squares). The intensity of the second harmonic has been chosen to be 0.01 of the fundamental, while that of the third harmonic has been chosen to be 0.001 of the fundamental.

sistently with the other figures and the expectation on the basis of LOPT, demonstrates that the signal at P1 now dominates throughout the range of intensities, owing again to the dominance of single-photon ionization by the second harmonic.

Having examined the effects expected in the event an admixture of the second harmonic were present, even if not alluded to in the experimental paper, we should point out that in our calculations, it is only in the presence of the second harmonic that we obtained a slope of ~ 1 for the signal at peak P1, which is where the two-photon signal is expected. And that is the slope of the signal in Fig. 6(a) of Ref. [4] interpreted as the two-photon channel, despite the fact that its slope is not compatible with a two-photon process. Could it be that the second harmonic was indeed present?

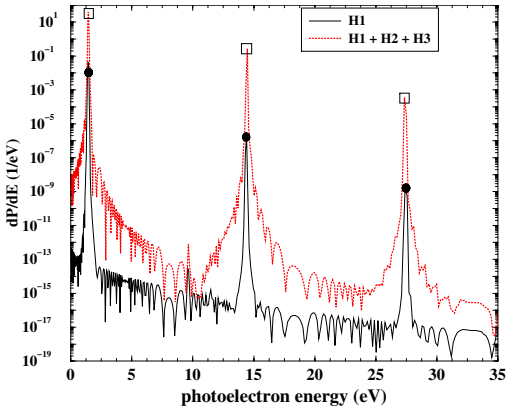

FIG. 6. (Color online) Above-threshold ionization spectrum for the fundamental (H1+H2+H3) pulse. The filled circles and empty squares at peaks P1, P2, and P3, denote the signals due to the fundamental alone (H1) and the field with all the three harmonics (H1+H2+H3), respectively. The peak intensity of the fundamental is $I_0=5.4\times10^{12}$ W/cm^2 and the pulse duration 104 fs.

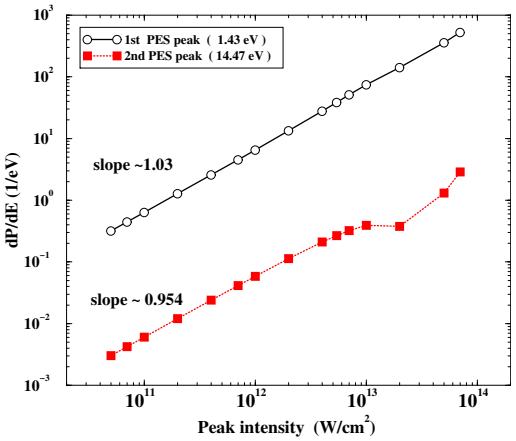

FIG. 7. (Color online) The maximum value of the first (solid line-empty circles) and second (dotted line-filled squares) PES peak (P1, P2) as a function of the peak intensity of the fundamental for a 104 fs pulse duration. In the figure the fundamental, its second and its third harmonics are present (H1+H2+H3).

As pointed out in the subsection above, some interference, albeit undefined, invoked in Ref. [4] in order to rationalize the slope of 1, does not exist as long as only the fundamental and the third harmonic are present. Interference in that channel would, however, be possible in the presence of the second harmonic, which would contribute via single-photon absorption. But given the dominance of the yield by the second harmonic, this interference would not be of relevance until intensities above 10^{14} W/cm^2 were reached (see Fig. 5); well above the intensity 5×10^{12} W/cm^2 at which interference is invoked in Ref. [4]. Thus interference in the signal expected at the position of the two-photon channel cannot justify the slope of 1, even in the presence of the second harmonic.

It may be useful to end this section with an estimated upper bound for the percentage of harmonics that can be tolerated. Actually, this can be read off the curves in Figs. 2 and 5. But first we should note that the answer depends on the intensity of the fundamental. The reason is that the contribution of the fundamental, being a nonlinear process, will eventually overtake those of the harmonics, which represent linear processes. Considering now, as an example, the intensity 10^{12} W/cm^2 for the fundamental, the results of Fig. 2 show that the third harmonic would have to be about two orders of magnitude less, if its contribution were to be, say, 10% of the contribution of the fundamental. Since the results in that figure have been obtained under the assumption of a 10^{-3} admixture of third harmonic, this means that the admixture should be reduced to 10^{-5}. Similarly, from Fig. 5 and the same intensity of the fundamental, we can infer that the second harmonic—whose contribution dominates the signal by more than two orders of magnitude—should be reduced by three orders of magnitude, which means to the percentage 10^{-5}, assuming again that its contribution should be limited to 10%. The results in this paper pertaining to the role of the harmonics transcend the context of the particular experiment and its interpretation. It should be evident that the observation of any nonlinear, which means two-or more-photon process, will inevitably be masked, in most cases, by the lower-order contribution of one or more harmonics, unless of

course the respective admixtures are sufficiently low. Another case in point is two-photon direct double ionization of helium [10], where even a modest ($\sim 1\%$) admixture of the second harmonic would produce much more single-photon double ionization than the two-photon direct channel. It is our understanding that this in fact seems to be the stumbling block in the observation of this process by radiation in FLASH (free electron laser at Hamburg). Whether and how the presence of such harmonics can be reduced to a tolerable level is an issue beyond our expertise.

It might seem that one way to decrease the relative contribution of the harmonics would be to raise the intensity of the fundamental, assuming the percentages of the harmonic admixtures remain the same. If possible, this may indeed circumvent the difficulty in some, but not necessarily all, cases. For a counterexample, the reader is referred to Refs. [10,19,33] pertaining to the direct two-photon double ionization of helium mentioned above. In that case, too high an intensity of the fundamental would lead to an undesirable increase of the sequential process, which would mask the direct two-photon double ionization.

IV. SUMMARY AND CONCLUSION

We have presented an elaborate quantitative theory and calculations for multiphoton ionization of helium under relatively strong uv radiation of photon energy 13 eV. The work was motivated by experimental results [4] obtained at the FEL facility in Hamburg and the debate [13–16] about the interpretation of the results that has appeared in the literature. We took the opportunity to set up a theoretical framework employing the TDSE as well as LOPT, in order to explore the validity of the latter, as it can provide insight and additional input into the interpretation of the observations. Given the relative simplicity of the atom and the expectation that further experiments, at even shorter wavelengths, are likely to produce results, this work will hopefully serve as an assessment of theoretical approaches appropriate for the task. We have also endeavored to connect the theory and interpretation to and profit from the vast experience on multiphoton processes in the optical and near-uv range of wavelengths accumulated over the last thirty-five years or so. The basic process on which the experiment was focused was the two-photon ionization of the atom. As is well known by now, even at the modest intensities employed in the experiment, other processes, such as ATI even if to a limited extent, inevitably play a role. Thus both theory and experiment must take into consideration all of these aspects and sort out their influence, as well as the information they can provide, for the interpretation of the data. And this is something we paid serious attention to in this work. The main conclusion that our results force upon us is that one or more harmonics of the fundamental appear to have played a decisive, even if uninvited, role in the observation. Otherwise, it is virtually impossible to reconcile fundamental features such as the radiation intensity dependence of certain key ionization signals, with equally fundamental demands of the theory. In the absence of a complete characterization of the radiation source, the theory can only point to possible contradictions in the interpretation. In our calculations we have assumed smooth pulse envelopes of duration in accordance with the information in Ref. [4]. It is known, however, that FEL pulses undergo intensity fluctuations, also referred to as spikes [6]. Depending on the time scale of such fluctuations, there are two possibilities. Either the number of spikes is small (say less than ten), in which case one would have to run calculations for a variety of pulses with the same envelope but random spikes, and take the average, or the number of spikes is considerably larger, in which case the field can be viewed as chaotic. A chaotic field is known to enhance an N-photon ionization process by a factor of $N!$, because strictly speaking, N-photon ionization is proportional to the Nth-order intensity correlation function. It is too early in the development of the FEL sources to say which is or will be the case. For the problem at hand, such effects would be of marginal importance, and certainly should not affect fundamental features, such as intensity dependence of the signals and most importantly the relative importance of contributions from the fundamental and its harmonics.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Kavli Institute for Theoretical Physics of the University of California in Santa Barbara (KITP-UCSB). This research was supported in part by the National Science Foundation under Grant No. PHY99-07949.

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