Photoionization of helium atoms irradiated with intense vacuum ultraviolet free-electron laser light. Part II. Theoretical modeling of multi-photon and single-photon processes

A. R. B. de Castro,[1,2,3] T. Laarmann,[3,*] J. Schulz,[3,†] H. Wabnitz,[3,‡] and T. Möller[3,§]

[1]*LNLS, P.O. Box 6192, CEP 13084-971 Campinas SP, Brazil*
[2]*IFGW UNICAMP, CEP 13083-970 Campinas SP, Brazil*
[3]*HASYLAB at DESY, D-22603 Hamburg, Germany*

We consider the problem of a helium atom under the radiation field of the DESY vacuum ultraviolet (VUV) free electron laser (FEL) (Phase I, $\hbar \cong 13$ eV). We find by solving numerically the time-dependent Schrödinger equation, that there is a large probability for resonant two-photon excitation from the ground state into a low kinetic energy state just above the first He ionization threshold. From this it is possible to go into another quasi-free state higher up, by resonant absorption of an additional photon. There is no double ionization of He. These results are in general agreement with the He photoelectron and time-of-flight (TOF) spectra recorded on March 2002, in the last week of the DESY VUV FEL Phase I operation. A detailed report on the experiments is given in a companion paper.

PACS number(s): 42.50.Hz, 33.60.Cv, 32.80.Rm

I. INTRODUCTION

The interaction of strong VUV pulses with matter brings about novel and unexpected results [1], which we can in a very rough fashion ascribe to the fact that for these shorter wavelengths, the radiation frequency and the electronic characteristic frequencies are of the same order of magnitude. Concepts like field ionization and ponderomotive force become less relevant. The theoretical description of such non-linear interactions between many-electron atoms and strong radiation fields is, of course, very complicated. It must take into account not only the detailed quantum properties of the "isolated" many-electron atom (or molecule, or cluster…) but also the frequency, polarization, photon density, peak intensity, time duration, and pulse shape of the photon field, with perhaps several field modes present. Steady state descriptions of the problem and perturbation approaches become somewhat questionable, and it would seem to be safer to go back to the fundamental equation of motion including the fully quantized field and solve it numerically in a limited but "representative" set of basis states. Here, "representative" means a basis set including all the states which the experimental results, plus considerations of symmetry and energy-momentum conservation, suggest that might be accessed.

Within this context, our efforts would first be directed into setting up a full quantum mechanical Hamiltonian:

$$H = H_{\text{atom}} + H_{\text{radiation}} + H_{\text{inter}}$$

$$H_{\text{inter}} = \sum_{\text{all electrons } j} [(-e/mc)\mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p}_j$$

$$+ (e^2/2mc^2)\mathbf{A}(\mathbf{r}_j) \cdot \mathbf{A}(\mathbf{r}_j)]$$

$$\mathbf{A}(\mathbf{r}) = c(2\pi\hbar/\omega V)^{1/2}\boldsymbol{\epsilon}(a \exp(i\mathbf{k}_{\text{rad}} \cdot \mathbf{r}) + a^+ \exp(-i\mathbf{k}_{\text{rad}} \cdot \mathbf{r})) \tag{1}$$

where the symbols have the usual meaning, explicitly defined after [Eq. (8)]. We use here the "Schrödinger picture" in which the operators are independent of time; all time variation of the problem is vested on the quantum state, without any restrictions on how the radiation fields might depend on time.

A fully quantized radiation field is used because although the number $\mathcal{N}$ of photons in the single-mode laser field is huge, the number of photons exchanged with matter (i.e., with the helium atoms) is in this case very small.

Next, one would seek to solve Schrödinger's equation for the time-dependent system state $|\psi(t)\rangle$.

In this article, we have two main purposes: (1) Develop a first principles explanation for the position of the observed peaks in our He photoelectron spectra, valid for arbitrarily strong field intensities; (2) testing a simplified method for the description of more complex atoms under irradiation with soft X-ray FEL pulses.

Multiphoton ionization has frequently been described in nonperturbation laser-atom interaction theories in terms of just the $\mathbf{A} \cdot \mathbf{p}$ term, as *a sequential process*. We found, in the course of this work, that for He, the $\mathbf{A} \cdot \mathbf{A}$ terms become dominant at very high field, and promote two-photon ionization as *instantaneous processes*. These are qualitatively different from the *sequential processes* mentioned above, and from multiphoton processes described by high-order perturbation theory using $\mathbf{A} \cdot \mathbf{p}$ as well.

*Present address: Max-Born-Institute, Max Born Str. 2a, D-12489 Berlin, Germany.

†Present address: MAX-lab, Box 118, 22100 Lund, Sweden.

‡Present address: Centre d'études de Saclay, 91191 Gif-sur-Yvette, France.

§Present address: Technische Universität Berlin, D-10623 Berlin, Germany.

In trying to solve the time-dependent Schrödinger equation numerically one might set up a grid in real-space, assign initial values to all points of the grid and compute their time evolution. This is a detailed method that requires large computer resources. We have chosen a more economical, albeit less detailed, *spectral* method, where one selects a basis set of space-dependent functions and computes just the time evolution of the *projections* of the system state $|\psi(t)\rangle$ on such basis functions. The procedure allows for the description of relevant processes with a basis of modest size if the laser photon energy is not resonant with relevant atomic bound states. In addition, as the number of basis states is increased, the *spectral and grid* methods are expected to converge to the same result.

In Sec. II we describe the method to be used here. Section III is devoted to the specification of the approximate helium eigen-states used in this calculation. Sections IV–VI discuss mathematical details: How the time-dependent problem is set up, basis states, solution of the coupled differential equations. Our results are given in Sec. VII. Finally, Sec. VIII lists conclusions and limitations of the technique.

II. THE METHOD USED HERE

One wants to solve the Schrödinger equation $i\hbar \ \partial/\partial t|\psi(t)\rangle = H|\psi(t)\rangle$ numerically, under the initial condition $|\psi(0)\rangle = |ground\ state\rangle$, meaning a ground state for the atom and a time-dependent single-mode radiation field whose power density is a prescribed function of time. H is the Hamiltonian describing the radiation field, the atomic system and their mutual interaction.

The time evolution of the coupled atom-radiation field will promote absorption of photons; atomic excited states, including unbound ("quasi-free") states will be populated at the expenses of the energy stored in the radiation field.

One can express the system state $|\psi(t)\rangle$ as a suitable time-dependent linear combination of (time-independent) eigen-states of the atom and radiation field, and transform the Schrödinger equation into a set of coupled first-order ordinary differential equations.

The basic approximation made in this approach is to truncate the infinite set of coupled differential equations. This truncation can be guided by energy and momentum conservation: The most relevant atomic states in the calculation are those that allow quasi-resonant transitions.

A second approximation is needed, which is conceptually rather disturbing but in practice unavoidable. We know no exact eigen-states of many-electron isolated atoms. However, approximate eigen-functions that reproduce the observed spectra to 8 or 9 digits are available.

In this same vein, Parker, Glass, Moore, Smith, Taylor, and Burke [2] advocate the use of several very different theoretical approaches in order to ascertain the quality and reliability of the calculations.

The problem now is seen to involve three steps: First, obtaining suitable descriptions of the many-electron atomic eigen-states; second, computing matrix elements of the full Hamiltonian; third, solving a coupled set of first-order ordinary differential equations. It used to be the case that the

numerical solution of the coupled first-order ordinary differential equations posed a major problem. Given recent advances in software [3] and the continuous improvement in CPU speed, this is no longer true.

III. HELIUM STATES

The Hamiltonian for a helium atom, in dimensionless form, is

$$H_{\text{helium}} = -\tfrac{1}{2}(\nabla_1{}^2 + \nabla_2{}^2) - 2/r_1 - 2/r_2 + 1/r_{12} \qquad (2)$$

where distances are in units of Bohr radius $r_0 = \hbar^2/me^2$ and energies are in units of $e^2/r_0 = 2$ Rydberg.

H_{helium} commutes with the total orbital angular momentum J^2 and its z component J_z and also with the total spin S^2 and its z component S_z, so the eigenstates of the two-electron system can be chosen as simultaneous eigenstates of these five operators. The eigenstates must be odd under interchange of (spatial and spin) coordinates, which means the eigenstates have the two possible forms

singlet helium: $|\Psi_{\text{singl}}\rangle = |\text{orbital even}\rangle|\text{spin singlet } (S = 0)\rangle$

triplet helium: $|\Psi_{\text{tripl}}\rangle = |\text{orbital odd}\rangle|\text{spin triplet } (S = 1)\rangle$.

$$(3)$$

Since the interaction with the radiation field, in the case of interest, is independent of spin, and since the ground state is singlet, all excited states of interest to us are also singlet and we can ignore spin completely.

The orbital states for this three-body problem are known only approximately, but a high degree of precision has been attained. We will use the bound states proposed by Hylleraas [4] and more recently reconsidered by Thakkar and Smith [5]. Thakkar and Smith have further improved on the variational technique, and have paid careful attention to the so-called *cusp conditions* arising from consideration of the singularities in the Hamiltonian. For the ground state wave function used in this work, the *cusp conditions* depart from the values expected for an exact wave function by less than 0.05% and 2%, respectively, see Ref. [5].

The orbital part of the helium states is of the following form:

$$|\Psi(L=0)\rangle = (1 + P_{12}) \left(\sum_m C_m{}^{1sns} \exp(-a_m r_1) \right.$$

$$\times \exp(-b_m r_2)\exp(-c_m r_{12}) \Big)$$

$$|\Psi(L=1)\rangle = (1 + P_{12}) \Big(z_1 \sum_m C_m{}^{1s2p} \exp(-a'_m r_1)$$

$$\times \exp(-b'_m r_2)\exp(-c'_m r_{12}) \Big) \qquad (4)$$

where P_{12} is the permutation operator: $P_{12}f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1)$.

The exponents have been the subject of extensive optimization searches, and the currently accepted technology is to use pseudo random numbers covering a prismatic volume (paralelotope) in space $a_m\ b_m\ c_m$, $m = 1, 2 \ldots N_{\text{sys}}$,
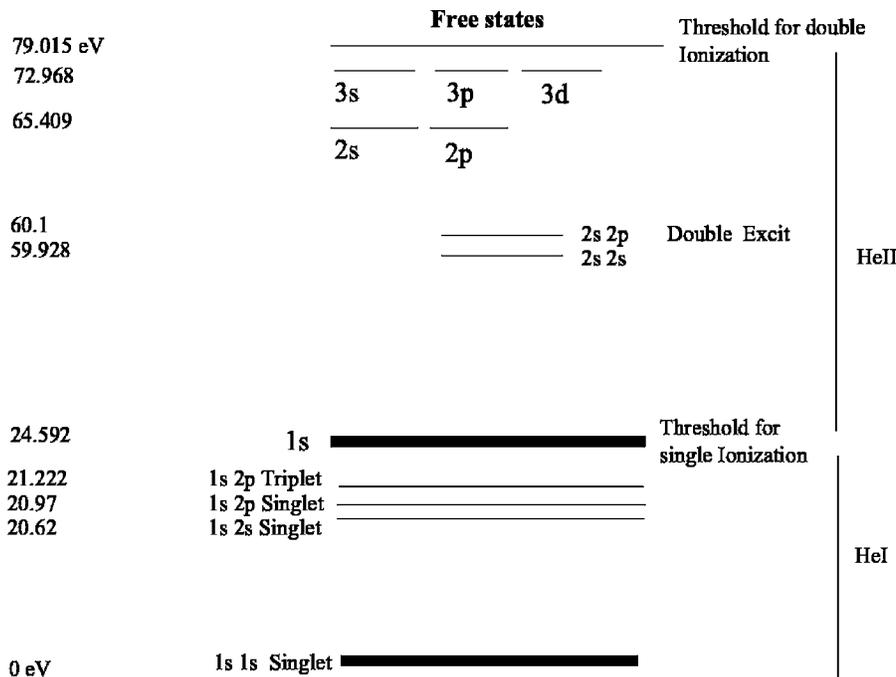
FIG. 1. Energy levels of helium atom.

$$a_m = A_1 + (A_2 - A_1)\text{Fractional Part}[m(m+1)\sqrt{2}]$$

$$b_m = B_1 + (B_2 - B_1)\text{Fractional Part}[m(m+1)\sqrt{3}]$$

$$c_m = G_1 + (G_2 - G_1)\text{Fractional Part}[m(m+1)\sqrt{5}] \quad (5)$$

where N_{sys} is usually in the range of 20–160. The optimum choice of the "paralelotope parameters" $A_1 \ldots G_2$ depends on the dimension N_{sys} of the space, and has been given in the literature [5] for a few low energy states.

All integrals needed for the matrix elements can be computed analytically. A number of relevant eigen-states of H_{helium} was obtained by standard diagonalization procedures [6] with the help of symbolic processing [7]. A detailed description of the calculations is available [8].

We will also have to deal with the state of HeII where one electron is bound in the $Z=2$ nuclear Coulomb potential but the other is quasi-free. In order to avoid subtleties related to Dirac delta function normalization of unbound states, we consider Coulomb states for the quasi-free electron in a wave-packet well localized in k space (see Ref. [8] for a discussion of these states):

$$|1s(Z=2), \text{free } \mathbf{k}_e\rangle = (1 + P_{12})(\psi_{1s(Z=2)}(\mathbf{r}_2)$$

$$\ldots \left\{ (\Delta^3 k_e)^{-1/2}(2\pi)^{-3/2} \int_{\Delta^3 k_e} d^3 u \zeta(\mathbf{r}_1, \mathbf{u}) \right\}$$

$$\zeta(\mathbf{r}, \mathbf{k}) = \Sigma_{lm} C_{kl}[(2ikr)^l/(2l+1)!]\exp(-ikr)Y_{lm}(\theta\phi)$$

$$\times Y^*_{lm}(\mathbf{k})_1 F_1(1 + l + iZ_1/k; 2l+2; 2ikr)$$

$$C_{kl} = \{4/k[1 - \exp(-2\pi/k)]\}^{-1}(l!)\Pi^l_{s=1}(1 + 1/k^2 s^2)^{1/2}$$

$$\xi(\mathbf{r}) = N_0 \exp(-2r)Y_{00} \quad N_0 = 8(2r_B^3)^{-1/2}$$

$$\psi_{1s(Z=2)}(\mathbf{r}) = \xi(\mathbf{r}) \quad (6)$$

where r, k are dimensionless variables (measured in units of r_0 and r_0^{-1}, respectively) and $n! \equiv \text{factorial }(n)$.

The wave function in Eq. (6) is an exact eigen-state of an unbound electron in the Coulomb field of a point like charge $Z_1 e$. It reduces to a plane wave $\exp(-i\mathbf{k} \cdot \mathbf{r})$ if the term iZ_1/k in the first argument of the confluent hypergeometric function $_1F_1$ is neglected. Further properties of the Coulomb wave functions are discussed, for instance, in Refs. [9,10]. It is, however, not an exact eigen-function of He$^+$, as can be appreciated in a simple physical way: If the unbound electron is far from the He$^+$ ion, it sees a point like charge with $Z_1 = 1$, but if it is very close to the ion, it sees a bare He^{++} nuclear charge with $Z_1 = 2$.

The hydrogen-like atomic function $\psi_{1s(Z=2)}(\mathbf{r}_2)$ and the wave packet are each normalized to unity on integration over all space.

Figure 1 shows the singlet-helium energy levels. Overlaps between these approximate eigen-states are given in Table II.

IV. BASIS OF STATES FOR THE TIME-DEPENDENT CALCULATION

Here we want to take advantage of the "interaction representation" [11] in order to deal with the Hamiltonian of Eq. (1) [repeated as Eq. (7) in Sec. V below] because H_{helium} commutes with $H_{\text{radiation}}$. Then, the basis set must be the direct product of eigenstates of H_{helium} and $H_{\text{radiation}}$ separately.

We consider only four radiation field states, denoted by the number of photons in the (single) mode of the FEL:

$$|\mathcal{N}\rangle \quad |\mathcal{N}-1\rangle \quad |\mathcal{N}-2\rangle \quad |\mathcal{N}-3\rangle$$

and five atomic states $|\text{at}_n\rangle$:

$$|1s1s\rangle \quad |1s2s\rangle \quad |1s2p\rangle \quad |1s(Z=2),\mathbf{k}_{e1}\rangle \quad |1s(Z=2),\mathbf{k}_{e2}\rangle$$

where $\mathbf{k}_{e1}$ $\mathbf{k}_{e2}$ the electron wave-vectors for kinetic energy of 1.4 and 14.4 eV, respectively.

Here, the first three atomic states are bound HeI states, and the last two are HeII states with a quasi-free electron. Notice that the 4 photon states are orthonormal, but the atomic states are not. Our basis, then, is the direct product of these two subspaces and has 20 states. However, the states $|\mathcal{N}-m\rangle|1s1s\rangle$, $m=1,2,3$ are always empty, because it is unphysical to destroy photons leaving the He atom in the ground state.

V. THE TIME-DEPENDENT PROBLEM

The helium atom plus VUV FEL radiation field is described by

$$H = H_0 + H_1$$

$$H_0 = H_{\text{helium}} + H_{\text{radiation}}$$

$$H_1 = (e/mc)[\mathbf{A}(\mathbf{r}_1)\cdot\mathbf{p}_1 + \mathbf{A}(\mathbf{r}_2)\cdot\mathbf{p}_2] + (e^2/2mc^2)$$
$$\times[\mathbf{A}(\mathbf{r}_1)\cdot\mathbf{A}(\mathbf{r}_1) + \mathbf{A}(\mathbf{r}_2)\cdot\mathbf{A}(\mathbf{r}_2)] \tag{7}$$

where the vector potential operator is

$$\mathbf{A}(\mathbf{r}) = c(2\pi\hbar/\omega V)^{1/2}\boldsymbol{\epsilon}[a\exp(i\mathbf{k}_{\text{rad}}\cdot\mathbf{r}) + a^+\exp(-i\mathbf{k}_{\text{rad}}\cdot\mathbf{r})] \tag{8}$$

and the wave-vector $\mathbf{k}_{\text{rad}}$ of the radiation field should be distinguished from the wave-vector $\mathbf{k}_e$ of the quasi-free electron. a^+ a are photon creation and destruction operators; V is the volume of a relevant region of space, ω is the photon frequency, and $\boldsymbol{\epsilon}$ the photon polarization.

In our experiment a free jet of He atoms is crossed by the focused photon beam, and the resulting photoelectrons are collected by an electron time-of-flight spectrometer placed along the direction $\boldsymbol{\epsilon}$ of the radiation electric field. We choose axes so that the radiation field propagates in the $\mathbf{x}$ direction linearly polarized in the $\mathbf{z}$ direction ($\boldsymbol{\epsilon}=\mathbf{z}$). The photoelectron analyzer/detector is placed along the z axis, collects electrons over a solid angle θ_M about the z axis and has an energy resolution described by δk_e. The "extent" of the wave-packet describing a photoelectron of wave vector k_e is, therefore, set equal to $\Delta^3 k_e = \pi\theta_M^2 k_e^2 \delta k_e$.

In order to simplify the equations one goes over to the interaction representation [11] as usual, by defining

$$|t\rangle_{\text{int}} = \exp\{iH_0 t/\hbar\}|t\rangle_{\text{Schro}} \tag{9}$$

which casts the equation in the form

$$i\hbar\partial/\partial t|t\rangle_{\text{int}} = \exp\{iH_0 t/\hbar\}H_1\exp\{-iH_0 t/\hbar\}|t\rangle_{\text{int}} \tag{10}$$

Now take a complete set $\{|n\rangle\}$ of basis states independent of time and write

$$|t\rangle_{\text{int}} = \Sigma_n C_n(t)|n\rangle \tag{11}$$

where $C_n(t)$ are unknown time-dependent coefficients to be determined by solving a coupled set of first-order linear dif-

ferential equations. This system can be written in terms of a dimensionless variable $\tau = t/\tau_0$ using atomic time units $\tau_0 = hr_0/e^2$. The dimensionless time dependent problem becomes

$$i\partial/\partial\tau(\Sigma_m C_m(\tau)\langle n|m\rangle) = \Sigma_{m'}\exp(i\varpi_{nm'}\tau)\langle n|H'_1|m'\rangle C_{m'}(\tau)$$

$$\varpi_{nm} = \{\hbar\omega(\mathcal{N}_n - \mathcal{N}_m) + E_{\text{electr }n} - E_{\text{electr }m}\}/(2\text{ Rydberg}) \tag{12}$$

In the interaction term we can make some simplifications. We use states as described in Secs. III and IV. Now, since the number of photons absorbed in the processes of interest is negligible compared to the total number of photons $\mathcal{N}$ in the FEL field, we find that all terms are functions of just the photon volumetric density $\mathcal{N}/V = I/\hbar\omega c$, where I is the peak power density at the sample. If we neglect the reaction of the atomic system on the radiation field (which is justified since $\mathcal{N} \approx 10^{12}$ while the number of absorbed photons is <4), the power density I is a prescribed function of time (laser pulse shape). The matrix element of the interaction becomes, in dimensionless form,

$$\langle\text{at}_n|\langle\mathcal{N}|H'_1|\mathcal{N}'\rangle|\text{at}_m\rangle$$
$$= \sum_{j=1,2}\left\{[2\pi Ie^2\hbar^2/m^2\omega^2 cr_0^2]^{1/2}/(2\text{ Rydberg})\ldots\right.$$

$$\{\langle\text{at}_n|\exp(i\mathbf{k}\cdot\boldsymbol{\rho}_j)\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_{\rho j}|\text{at}_m\rangle\delta_{\mathcal{N},\mathcal{N}'+1}$$

$$+ \langle\text{at}_n|\exp(-i\mathbf{k}\cdot\boldsymbol{\rho}_j)\boldsymbol{\epsilon}\cdot\boldsymbol{\nabla}_{\rho j}|\text{at}_m\rangle\delta_{\mathcal{N},\mathcal{N}'-1}\}$$

$$+ [\pi Ie^2/m\omega^2 c]/(2\text{ Rydberg})\ldots$$

$$\{\langle\text{at}_n|\exp(2i\mathbf{k}\cdot\boldsymbol{\rho}_j)|\text{at}_m\rangle\delta_{\mathcal{N},\mathcal{N}'+2} + 2\langle\text{at}_n||\text{at}_m\rangle\delta_{\mathcal{N},\mathcal{N}'}$$

$$\left. + \langle\text{at}_n|\exp(-2i\mathbf{k}\cdot\boldsymbol{\rho}_j)|\text{at}_m\rangle\delta_{\mathcal{N},\mathcal{N}'-2}\}\right\} \tag{13}$$

with $\mathbf{k}=\mathbf{k}r_0$ being also dimensionless. If the power density I is given in units of W/cm^2, the numerical value of the coefficient $\{[2\pi Ie^2\hbar^2/m^2\omega^2 cr_0^2]^{1/2}/(2\text{ Rydberg})\}$ of the $\mathbf{A}\cdot\mathbf{p}$ term is just $(5.580\ 10^{-9}\ \sqrt{I})$, while the value of the coefficient $\{[\pi Ie^2/m\omega^2 c]/(2\text{ Rydberg})\}$ of the $\mathbf{A}\cdot\mathbf{A}$ terms is $(1.558\ 10^{-17}\ I)$.

Ideally, we would like to choose the complete basis set $\{|n\rangle\}$ such that $(H_{\text{atom}} + H_{\text{radiation}})|n\rangle = E_n|n\rangle$. In practice, for all atoms except Hydrogen, only approximations to the atomic eigenstates are available because of correlation and these are in general not automatically orthogonal as expected for exact eigenstates (corresponding to different eigenvalues) of observables. This is not a very serious difficulty, but we must then consider a complete basis of nonorthogonal states, where $\langle n|m\rangle \equiv O_{nm}$ is the nondiagonal overlap matrix. This matrix is positive-definite, its inverse is guaranteed to exist and we reduce our set of equations to

$$i\partial/\partial\tau C_k(\tau) = \Sigma_{m'n}\exp(i\varpi_{nm'}\tau)O^{-1}_{kn}\langle n|H'_1|m'\rangle C_{m'}(\tau) \tag{14}$$

In the ideal case of an orthonormal basis set, O^{-1}_{kn} reduces to the identity matrix.

TABLE I. Parameters of the DESY VUV-FEL light source used in this calculation.

Quantity	Value	Unit
Photon energy	13	eV
Photon frequency ω	1.975×10^{16}	s^{-1}
Pulse length	100	fs
Focussing mirror reflectivity	0.2	
Pulse energy (at the sample)	1.7	μJ
Photon beam waist diameter (at the sample)	0.002	cm
Power density I_M at the beam waist (at the sample)	5.4×10^{12}	W/cm^2
Number $\mathcal{N}$ of photons in the pulse (at the sample)	0.82×10^{12}	

The probability amplitude for finding the system in state $\langle n|$ is $\mathrm{ampl}(n) = \langle n|t\rangle_{\mathrm{int}} = \Sigma_m C_m(t)\langle n|m\rangle$, while the norm of the state at time t is $\mathrm{norm} = \langle t|_{\mathrm{int}}|t\rangle_{\mathrm{int}} = \Sigma_{mn} C^*_n(t)C_m(t)\langle n|m\rangle$. This norm is always preserved because the time-evolution of the exact solution of the Schrödinger equation is generated by application of a unitary operator.

It is adequate to make the dipolar approximation $\exp(\pm i\mathbf{k}.\boldsymbol{\rho}_j) \approx 1$ since the wave function typical spatial extent is $r_0 \approx a_B = 0.53$ Å, while for the VUV FEL radiation field in our experiments, $k \approx 2\pi/(950$ Å$)$. Then we see that matrix elements connecting states that differ by 1 photon involve $\langle \mathrm{atom}_n|\boldsymbol{\epsilon}.\boldsymbol{\nabla}_{\rho j}|\mathrm{atom}_m\rangle$ while matrix elements connecting states that differ by 2 photons involve the overlaps $\langle \mathrm{atom}_n||\mathrm{atom}_m\rangle$. We have neglected some diagonal elements that can in principle be assigned to the H_0 part of the complete Hamiltonian, and whose only effect is to make a small shift in the whole "unperturbed" spectrum of H_0.

The matrix elements of the interaction H'_1 depend on the parameters of the laser source. These are given in Table I. Final values for the matrix elements are given in Table III, and calculation details are given in Ref. [8].

VI. SOLUTION OF THE COUPLED TIME-DEPENDENT EQUATIONS

The temporal profile of the DESY VUV FEL output varies from pulse to pulse and was not known in detail during our experiments.

The probability amplitudes $C_k(\tau)$ in Eq. (14) were computed by assuming a simple square pulse time dependence for the FEL power density

$$I(\tau) = I_0 \quad \mathrm{if} \quad \tau_1 \geqslant \tau \geqslant 0$$

$$I(\tau) = 0 \quad \mathrm{if} \quad 0 \geqslant \tau \ \mathrm{or} \ \tau \geqslant \tau_1 \quad \tau_1 = 100 \ \mathrm{fs} \quad (15)$$

Although we assumed a square envelope for the FEL pulse, it is very easy to take into account other shapes, for instance, a Gaussian, or even a sequence of "pulselets" with random amplitudes and widths, subject to fixed total energy and time duration.

The FORTRAN code RADAU5 of Wanner and Hairer [3] was used, which implements a Runge-Kutta implicit method (Radau IIA of order 5 with step control, particularly efficient for systems of *stiff* differential equations). It was modified to accept general complex matrix elements, overlaps, and inverse overlaps. It was compiled/linked with Cygwin.

In all computer runs, the He $1s1s$ orbital state plus photon field with $\mathcal{N}$ photons is initially populated with probability 1, while all other orbital and photon states are empty. Then the system is allowed to evolve in time during the FEL pulse duration τ_1 [12].

VII. RESULTS AND DISCUSSION

Figure 2 shows the transition probability as a function of peak power density for the resonant processes (i) $|1s1s\rangle \rightarrow |1s(Z=2)\mathbf{k}_1\rangle$, and (ii) $|1s1s\rangle \rightarrow |1s(Z=2)\mathbf{k}_1\rangle \rightarrow |1s(Z=2)\mathbf{k}_2\rangle$. The transition probability is, in these two cases equal to the number of ions created per laser pulse. The ionization rate ξ_{ion} is given by

$$\xi_{\mathrm{ion}} = \mathcal{W}\mathcal{R}_{\mathrm{laser}}N_{\mathrm{atoms}} \quad (16)$$

where $\mathcal{W}$ is the transition probability, $\mathcal{R}_{\mathrm{laser}}$ is the laser pulse rate, and N_{atoms} is the number of atoms in the interaction region.

We can very easily establish the origin of each transition by setting equal to zero selected matrix elements in the FORTRAN code for solution of the differential equations. We find, for instance, that the transition from the ground state $1s1s$ (two bound electrons) into the He$^+ + \mathbf{k}_1$ (one electron bound to a $Z=2$ nucleus plus a quasi-free electron $\mathbf{k}_1$ where $\hbar^2 k_1^2/2m = 1.4$ eV) is induced by the $\mathbf{A} \cdot \mathbf{A}$ interaction term, as expected. This two-photon transition probability grows initially with a slope close to 2, then presents marked non-monotonic behavior which becomes more complicated as the field intensity increases.

The transition from the previously mentioned excited state into the He$^+ + \mathbf{k}_2$ (where $\hbar^2 k_2^2/2m = 14.4$ eV) is induced by the $\mathbf{p} \cdot \mathbf{A}$ term of the interaction. In all, this is a three-photon transition. It starts off very small, but then picks up strength and competes for the population of the state He$^+ + \mathbf{k}_1$. The occupation of the He$^+ + \mathbf{k}_2$ state depends on a three-photon sequential process; at low field intensity we find that the slopes of the two processes are in the ratio 2/3 as expected.

Figure 3 shows the dependence on FEL pulse length for the two-photon transition probability into the state He$^+ + \mathbf{k}_1$,

TABLE II. Overlap integrals. [a]

1) "Raw" overlap integrals (Non-normalized)	
$\langle 1s1s \vert 1s1s \rangle_{\mathrm{Raw}}$	0.688 958
$\langle 1s2s \vert 1s2s \rangle_{\mathrm{Raw}}$	0.734 223
$\langle 1s2p \vert 1s2p \rangle_{\mathrm{Raw}}$	19.2702
$\langle 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \rangle_{\mathrm{Raw}}$	2.000 14 (KE=1.4 eV)
$\langle 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \rangle_{\mathrm{Raw}}$	2.000 22 (KE=14.4 eV)
$\langle 1s1s \vert 1s2s \rangle_{\mathrm{Raw}}$	0.393 341
$\langle 1s1s \vert 1s2p \rangle_{\mathrm{Raw}}$	zero from symmetry
$\langle 1s2s \vert 1s2p \rangle_{\mathrm{Raw}}$	zero from symmetry
$\langle 1s1s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \rangle_{\mathrm{Raw}}$	−0.014 113 5
$\langle 1s1s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \rangle_{\mathrm{Raw}}$	−0.018 493 1
$\langle 1s2s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \rangle_{\mathrm{Raw}}$	−0.015 926 4
$\langle 1s2s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \rangle_{\mathrm{Raw}}$	−0.012 575 6
$\langle 1s2p \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \rangle_{\mathrm{Raw}}$	0.000 158 585 − 0.047 439 4i
$\langle 1s2p \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \rangle_{\mathrm{Raw}}$	0.001 159 85 − 0.017 305 9i

[a] $N1s1s=30$ $K1s1s=21$
  $N1s2s=30$ $K1s2s=15$
  $N1s2p=30$ $K1s2p=14$
  $\theta_M=0.2$ rad
  $\delta k=0.085\ 73$ ($\Delta KE=0.1$ eV)

2) Normalized overlap integrals	
all diagonal elements	1.0
$\langle 1s1s \vert 1s2s \rangle$	0.553 043
$\langle 1s1s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \rangle$	−0.012 022 9
$\langle 1s1s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \rangle$	−0.015 753 4
$\langle 1s2s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \rangle$	−0.013 142 4
$\langle 1s2s \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \rangle$	−0.010 377 1
$\langle 1s2p \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e1} \rangle$	0.000 025 544 − 0.007 641 28i
$\langle 1s2p \vert 1s(Z=2),\ \mathrm{free}\ \mathbf{k}_{e2} \rangle$	0.000 186 818 − 0.002 787 48i
all other elements zero	

at maximum field intensity. For a FEL pulse with length 100 fs the probability for this transition is high.

This is also related to the fact that the overlap of the corresponding wave functions is large. Physically, we can draw the following picture. There is a large spatial overlap between the HeI two-electron bound state $1s1s$, and a "mixed" excited state where one electron is tightly bound to the $Z=2$ nucleus and the second electron is in a slow quasi-free state that "hangs around" the nucleus for a long time.

Figure 3 also shows the time dependence on FEL pulse length for the three-photon transition probability into the state $\mathrm{He}^+ + \mathbf{k}_2$ and shows how the competition between these two states sets in as a function of irradiation time (FEL pulse length).

At larger field intensities (not shown here) the time dependence becomes very complicated. This is what one expects. We are modeling a closed system with 20 accessible states, the norm of which (sum of occupation probabilities) is kept constant. Now, even for a two-level system it is known that no steady state is reached, rather, one observes a periodic behavior with a Rabi frequency which grows with the strength of the periodic perturbation applied to the system.

At some even higher value of the interaction coefficients, this model predicts a quasi-chaotic behavior of the occupation probabilities.

We have, in addition, computed the probability for occupation of the $\mathrm{He}^+ + \mathbf{k}_2$ state due to a one-photon transition induced by the $\mathbf{A} \cdot \mathbf{p}$ interaction term. This transition is resonant for the third harmonic component (contamination) of the FEL output. The third harmonic (@39 eV) will be present in the spontaneous emission. The SASE process active in the FEL will enhance the fundamental, but still some third harmonic contamination might be present with maximum intensity <0.1% of the intensity in the fundamental [13].

The dependence of this occupation probability on FEL pulse length is shown as a dot line in Fig. 3, and it is comparable to the more interesting nonlinear three-photon process also shown in the same figure. It is recalled, in connection with the nonlinear behavior displayed in Fig. 3, that *linear* behavior for one-photon transitions is expected only in the perturbation regime where the Fermi golden rule is applicable [21]. It requires low field intensities, very long exposure times and existence of a continuum of accessible

TABLE III. Matrix elements.

1)"Raw" matrix elements (non-normalized)	
$\langle 1s2p|P_z|1s1s\rangle_{\mathrm{Raw}}$	1.336 29
$\langle 1s2p|z|1s1s\rangle_{\mathrm{Raw}}$	0.960 73
$\langle 1s2p|P_z|1s2s\rangle_{\mathrm{Raw}}$	8.907 89
$\int d\Omega_{\mathbf{k}1}\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s(Z{=}2)\mathbf{k}_1\rangle_{\mathrm{Raw}}$	0.021 545 8+0.071 641 1i
$\langle 1s(Z{=}2)\mathbf{k}_1|P_z|1s1s\rangle_{\mathrm{Raw}}$	0.025 803 9i
$\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s1s\rangle_{\mathrm{Raw}}$	0.046 192 0i
$\langle 1s(Z{=}2)\mathbf{k}_1|P_z|1s2s\rangle_{\mathrm{Raw}}$	0.013 020 1i
$\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s2s\rangle_{\mathrm{Raw}}$	0.023 669 3i
$\langle 1s(Z{=}2)\mathbf{k}_1|P_z|1s2p\rangle_{\mathrm{Raw}}$	0.207 941
$\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s2p\rangle_{\mathrm{Raw}}$	0.018 730 3
2) Normalized matrix elements	
$\langle 1s2p|P_z|1s1s\rangle$	0.366 747
$\langle 1s2p|P_z|1s2s\rangle$	2.368 20
$\int d\Omega_{\mathbf{k}1}\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s(Z{=}2)\mathbf{k}_1\rangle$	0.010 771 9+0.035 817 3i
$\langle 1s(Z{=}2)\mathbf{k}_1|P_z|1s1s\rangle$	0.021 981 6i
$\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s1s\rangle$	0.039 348 8i
$\langle 1s(Z{=}2)\mathbf{k}_1|P_z|1s2s\rangle$	0.010 744 0i
$\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s2s\rangle$	0.019 531 4i
$\langle 1s(Z{=}2)\mathbf{k}_1|P_z|1s2p\rangle$	0.033 494 0
$\langle 1s(Z{=}2)\mathbf{k}_2|P_z|1s2p\rangle$	0.003 016 9

states, conditions none of which are satisfied in the present context.

We should like to comment on the "*a priori*" possibility for the transition from He$^+$+$\mathbf{k}_1$ into He$^+$+$\mathbf{k}_2$. Transitions driven by a radiation field between two one-electron free states are strictly forbidden. However, here we have not two one-electron free states, but two two-electron "mixed" states with part plane wave, part $1s$ hydrogenic character, and for such states the $\mathbf{A}\cdot\mathbf{p}$ matrix element is nonzero. For similar reasons, it is anticipated that two-photon transitions to states of even larger k_3 would also be possible, although probabilities have not yet been estimated.
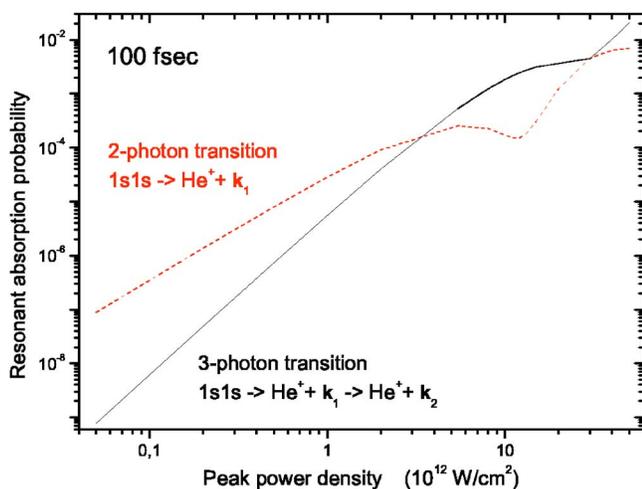

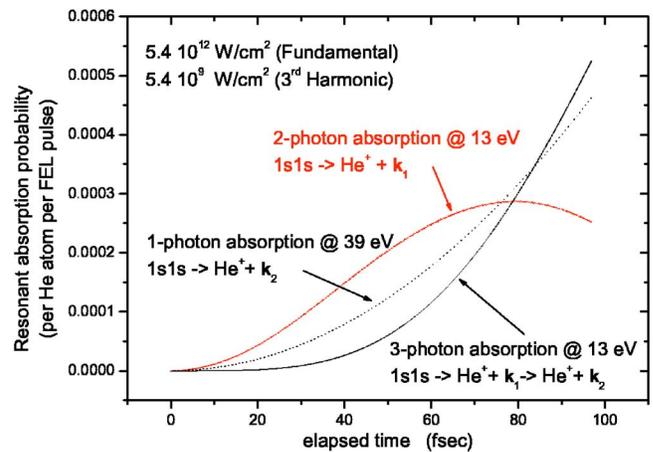FIG. 2. (Color online) Peak power density dependence of the resonant transitions.

FIG. 3. (Color online) Dependence on FEL pulse duration, of the probability for resonant two-photon absorption from the ground state $|1s1s\rangle$ of HeI into a low kinetic energy state $|1s(Z{=}2)$, free $\mathbf{k}_{e1}\rangle$ of HeII. Also, dependence on FEL pulse duration, of the probability for resonant three-photon absorption from the ground state $|1s1s\rangle$ of HeI into a higher kinetic energy state $|1s(Z{=}2)$, free $\mathbf{k}_{e2}\rangle$, using $|1s(Z{=}2)$, free $\mathbf{k}_{e1}\rangle$ as intermediate state. Here the peak power density on the sample is 5.4$>$10^{12} W/cm^2. Finally, we show as a dot curve the probability for resonant one-photon absorption of third harmonic contamination in the FEL output, whose intensity is estimated as being less than 5.4$>$10^9 W/cm^2 (0.1% of the intensity in the fundamental). This would also populate the state $|1s\ (Z{=}2)$, free $\mathbf{k}_{e2}\rangle$ via a direct one-photon transition from the ground state $|1s1s\rangle$.

We can compare our theoretical result for two-photon absorption with the theoretical data of Scrinzi and Piraux [14], a calculation for helium multi-photon ionization made with a much larger basis set and following a different approach, where the $\mathbf{A}\cdot\mathbf{A}$ term of the interaction between radiation field and atom is omitted. We set the laser parameters in our calculation equal to theirs: Peak power density $I=3$ 10^{14} W/cm^2; envelope function for the vector potential $\mathbf{A}$ given by $h(t)=\cos^2(\pi t/T)$ if $-T/2<t<T/2$ and zero otherwise, with total pulse duration $T=156$ atomic units of time (we actually used an envelope $\{1-\cos^2(\pi t/T)\}$ and integrated from $t=0$ to $t=T$). After renormalization to take due account of different solid angles of electron detection, we get for our two-photon ionization rate a value about five times higher than Scrinzi and Piraux. We believe most of the contribution to the two-photon absorption rate comes exactly from the $\mathbf{A}\cdot\mathbf{A}$ term.

We now comment briefly on a few other methods.

Cormier and Lambropoulos [15] solve the time-dependent Schrödinger equation by expanding the time-dependent wave function in a suitable complete basis (B-splines, rather than eigen-functions of the unperturbed Hamiltonian). Since the number of photons in the laser mode of interest is huge, the depletion due to atomic absorption is negligible and it is believed that the field might be treated semiclassically. Yet, the interaction with the atom involves absorption of a very small number of photons and the question as to whether to treat the process semiclassically becomes less clear cut.

Those authors also point out that their treatment in terms of B-splines was suitable only for one-electron atoms. In a

later article, Saenz and Lambropoulos [16] address the many-photon ionization of helium using the *B*-spline basis, but this is only a low-order perturbation calculation, expected to be valid only at relatively low field intensities.

Duchateau, Cormier, and Gayet [17] demonstrated another perturbation approach in the spirit of the first Born approximation. It requires the electric field $\mathbf{F}(t)$ to have a longitudinal character with $\int \mathbf{F}(t)dt > 0$, a condition not met by the DESY FEL pulses during our experiments. This paper also uses the direct solution of the time-dependent Schrödinger equation as the standard against which to judge the quality of the perturbation calculation and finds that the error in the perturbation calculation becomes larger as the field intensity is increased. In a related publication, Rodriguez, Cormier and Gayet [18] further develop the approach in order to discuss subsidiary peaks in the photoelectron spectra. The discussion applies to one-electron atoms under perturbation conditions. The subsidiary peaks are found to be about three orders of magnitude less intense than the main peaks, and would not be detectable in our experiments [22].

Parker, Glass, Moore, Smith, Taylor, and Burke [2], in a very interesting letter, apply time-dependent and time-independent nonperturbation methods to describe the multiphoton ionization of helium. They point out that these two methods are complementary, the former being more readily amenable to the description of the response to short pulses, while the latter yields a more complete spectral description for the same expenditure of computer time.

Lambrecht, Dimou, and Faisal [19] modify the exact Schrödinger equation for a one-electron atom in the presence of arbitrarily intense radiation fields, to make it go into a simpler equation of Floquet type. A periodic time-dependent Coulomb potential appears, which can be developed in a Fourier series with harmonics of the fundamental frequency ω of the radiation field. Basically, this method eliminates time of the problem, it remains a space dependent equation to be solved. The radiation field is assumed to be stationary (because otherwise the Fourier development of the displaced Coulomb potential $1/|\mathbf{r} - \boldsymbol{\alpha}(t)|$ would have components other than just the harmonics $n\omega$, n integer). In addition, it seems to be strictly a one-eletron method.

Bauer, Plucinski, Piraux, Potvliege, Gajda, and Krzywinski [20] have discussed the ionization of hydrogen by intense vacuum-ultraviolet radiation having in mind precisely the Phase I operation of the DESY FEL. They express the hydrogen time-dependent wave function in a Sturmian basis and treat the radiation field semiclassically. The time-dependent Schrödinger equation is solved numerically using an elegant algorithm of high order implicit Runge-Kutta type which could be vectorized, allowing parallel processing. A large number of bound states is used, but no quasi-free states, rather, the ionization probability is derived indirectly. It was pointed out that our method is closely related to theirs, but we explicitly include free states in our calculation. This allowed us to keep track at all times of the total probability to find the He electron in some state, which must, of course, be equal to 1. This condition is met within a tolerance of 10^{-6} in our calculation.

Conceptually, there are two limitations to the method described in our paper.

The first is that the infinite basis of states is truncated. It was mentioned that there are excellent physical arguments to help in the choice of the truncation.

The second is that the many-electron states available are all approximate. We find that the overlap matrix depends, for instance, on the dimension of the Hylleraas space, although the energy eigenvalues are always correct to better than 7 digits (the accuracy of the numerical solution of the time-dependent equations).

Other than good correspondence to the measured energy eigenvalues, we have very few other criteria on which to judge the wave functions used to compute the matrix elements of the interaction. One such criterion might be a comparison between the two quantities $\langle \text{final} | p_z | \text{initial} \rangle$ and $m(E_{\text{final}} - E_{\text{initial}}) \langle \text{final} | z | \text{initial} \rangle / i\hbar$ involving different matrix elements which can each be computed independently. These two quantities would be identical for *exact* helium eigenfunctions with $S=0$ (and a variety of other atomic Hamiltonians with no spin-orbit coupling) [21]. For the Hylleraas wave functions used here, we find that the former evaluates to 1.33 while the latter to 0.74. Hence, only order-of-magnitude agreement is reached. This indicates the limitations of the atomic wave functions used, but says nothing about the proposed method of direct numerical solution of the Schrödinger equation in a limited basis set, except that the quality of results is not expected to be better than the quality of the atomic inputs. We feel, as a matter of fact, that a careful comparison between the measured intensity of the photoelectron lines and the prediction of this model is a more stringent check on the correctness of the wave functions. We found, for instance, significant difference between the values of the matrix elements calculated using simple plane waves (not reported here), and those calculated using the Coulomb states.

VIII. CONCLUSIONS

We have discussed a model for the nonlinear photoionization of helium which is in general agreement with the basic experimental facts described in detail elsewhere [22]: Observation of photoelectrons with kinetic energy $\hbar^2 k_1^2 / 2m = 2\hbar\omega - E_{\text{single ionization}}$ and also at $\hbar^2 k_2^2 / 2m = 3\hbar\omega - E_{\text{single ionization}}$, and absence of double ionization. The intensity dependence of these two processes is rather complicated at the highest intensities probed in the calculation.

The model does not have adjustable parameters, but the normalization of the unbound states $\mathbf{k}_1 \mathbf{k}_2$ influences the values of the overlaps and of the matrix elements of the interaction terms $\mathbf{A} \cdot \mathbf{p}$ and $\mathbf{A} \cdot \mathbf{A}$. Here we invoked arguments of energy and angular resolution of the photoelectron detector in order to choose the normalization parameters. In addition, it considers a fully quantized radiation field with arbitrary time dependence, and the complete interaction between radiation and matter. We used, in the evaluation of some matrix elements, the electric dipole approximation $\exp(i\mathbf{k}_{\text{rad}} \cdot \mathbf{r}) = 1$, but this is in no way an essential element of the method.

As obvious enhancements of the technique, one might consider including in the calculation more photon modes, in order to describe spontaneous radiative decay of the excited

states, for instance. This is, however, expected to be a small effect because the matrix element of $\mathbf{p} \cdot \mathbf{A}$ for such transitions will be about six orders of magnitude smaller than the ones listed in Table III, on account of the scarce population of these photon modes as compared with the FEL. A more interesting endeavor would be to include more photon modes within the spectral width of the FEL. Better techniques of symbolic processing of these overlaps and interaction matrix elements would help.

[1] H. Wabnitz, L. Bittner, A. R. B. de Castro, R. Döhrmann, P. Gürtler, T. Laarmann, W. Laasch, J. Schulz, A. Swiderski, K. von Haeften, T. Möller, B. Faatz, A. Fateev, J. Feldhaus, C. Gerth, U. Hahn, E. Saldin, E. Schneidmiller, K. Tiedke, R. Treusch, and M. Yurkov, Nature (London) **420**, 482 (2002).

[2] J. S. Parker, D. H. Glass, L. R. Moore, E. S. Smith, K. T. Taylor, and P. G. Burke, J. Phys. B **33**, L239 (2000).

[3] E. Hairer and G. Wanner, *Solving Ordinary Differential Equations II: Stiff and Differential-Algebraic Problems* (Springer Verlag, Heidelberg, 1996).

[4] E. A. Hylleraas, Z. Phys. **54**, 347 (1929).

[5] A. J. Thakkar and V. H. Smith, Phys. Rev. A **15**, 1 (1977); **15**, 16 (1977).

[6] J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon, Oxford, 1965).

[7] S. Wolfram, *The Mathematica Book*, 4th ed. (Cambridge University Press, Cambridge, MA, 1999).

[8] A. R. B. de Castro and T. Möller, LNLS Tech Memo (Nov. 2002). Details of the helium calculations are described in file *HeliumPaper10Appendix.doc* All files can be obtained by email, contact sau@lnls.br.

[9] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, sec. 36 (Pergamon, London, 1977).

[10] J. Schwinger, *Quantum Mechanics* (Springer, Heidelberg, 2001).

[11] J. J. Sakurai, *Advanced Quantum Mechanics*, Sec. 4-2 (Addison-Wesley, New York, 1967).

[12] The data shown here were generated by C:/Cygwin/Home/Administrator/RRadau5/helium7.f for the FEL fundamental, C:/Cygwin/Home/Administrator/RRadau5/helium3H.f for the FEL third harmonic.

[13] E. Saldin, M. Yurkov, and E. Schneidmiller (private communication).

[14] A. Scrinzi and B. Piraux, Phys. Rev. A **58**, 1310 (1998).

[15] E. Cormier and P. Lambropoulos, J. Phys. B **30**, 77 (1997).

[16] A. Saenz and P. Lambropoulos, J. Phys. B **32**, 5629 (1999).

[17] G. Duchateau, E. Cormier, and R. Gayet, Phys. Rev. A **66**, 023412 (2002).

[18] V. D. Rodriguez, E. Cormier, and R. Gayet, Phys. Rev. A **69** 053402 (2004).

[19] U. Lambrecht, L. Dimou, and F. H. M. Faisal, Phys. Rev. A **57**, 2832 (1998).

[20] J. Bauer, L. Plucinski, B. Piraux, R. Potvliege, M. Gajda, and J. Krzywinski, J. Phys. B **34**, 2245 (2001).

[21] A. Messiah, *Quantum Mechanics II* (North Holland, Amsterdam, 1966), Chap. XVII Sec. 4 and Chap. XXI Sec. 31.

[22] T. Laarmann, A. R. B. de Castro, P. Gürtler, W. Laasch, J. Schulz, H. Wabnitz, and T. Möller, preceding paper, Phys. Rev. A **72**, 023409 (2005).