

# Theory and computation of the attosecond dynamics of pairs of electrons excited by high-frequency short light pulses

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By defining and solving from first principles, using the state-specific expansion approach, a time-dependent pump-probe problem with real atomic states, we show computationally that, if time resolution reaches the attosecond regime, strongly correlated electronic “motion” can be probed and can manifest itself in terms of time-dependent mixing of symmetry-adapted configurations. For the system that was chosen in this study, these configurations, the He  $2s2p$ ,  $2p3d$ , and  $3s3p$   $^1P^o$ , whose radials are computed by solving multiconfigurational Hartree-Fock equations, label doubly excited states (DES) of He inside the  $1s\epsilon p$   $^1P^o$  scattering continuum and act as nonstationary states that mix, and simultaneously decay exponentially to  $1s\epsilon p$   $^1P^o$  via the atomic Hamiltonian,  $H_A$ . The herein presented theory and analysis permitted the computation of attosecond snapshots of pairs of electrons in terms of time-dependent probability distributions of the angle between the position vectors of the two electrons. The physical processes were determined by solving ab initio the time-dependent Schrödinger equation, using as initial states either the He  $1s^2$  or the  $1s2s$   $^1S$  discrete states and two femtosecond Gaussian pulses of 86 fs full width at half-maximum, having frequencies in resonance with the energies of the correlated states represented by the  $2s2p$  and  $2p3d$  configurations. We calculated the probability of photoabsorption and of two-photon resonance ionization and of the simultaneous oscillatory mixing of the configurations  $2s2p$ ,  $2p3d$ ,  $3s3p$ , and  $1s\epsilon p$   $^1P^o$ , within the attosecond scale, via the interactions present in  $H_A$ . Among the possible channels for observing the attosecond oscillations of the occupation probabilities of the DES, is the de-excitation path of the transition to the He  $1s3d$   $^1D$  discrete state, which emits at 6680 Å.

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## I. INTRODUCTION

Over the past four decades, the development of picosecond and femtosecond laser pulse technologies and of concomitant time-resolved spectroscopies have made possible the observation of atomic and molecular processes as a function of time. Such dynamical effects are associated with the concepts of energy transfer and of wave packet motion. For example, such spectroscopies provide substantial information about molecular transformations, where the nuclei are treated as classical particles.

Recently, experimental results concerning an as yet untapped frontier of hyperfast processes were reported [1,2]. They refer to the creation and spectroscopic use of high-energy light pulses with duration of the order of atomic units, i.e., in the *attosecond* scale (1 attosec =  $10^{-18}$  sec, 1 a.u. = 24.4 attosec). The researchers of Refs. [1,2] succeeded in registering the emission of an attosecond electron wave packet and in carrying out elements of “time-resolved atomic inner-shell spectroscopy”. Specifically, using the pump-probe technique with extreme ultraviolet (attosecond) and optical (femtosecond) pulses, Drescher *et al.* [1] measured the Auger decay time of hole-excited *Kr* with attosecond resolution.

Also recently, the first *ab initio* theory and computation revealing, at a resolution of attoseconds, aspects of quantum dynamics of correlating electrons inside the atom were published [3]. The electronic structure was analyzed in terms of symmetry-adapted orbital configurations and the time evolution of electronic correlation was computed from first principles, by implementing the state-specific expansion approach (SSEA) [4]. By treating these configurations as nonstationary states interacting among themselves via the time-independent atomic Hamiltonian  $H_A$ , the existence of hyperfast processes of interelectronic energy transfer and of “motion” was demonstrated computationally for a prototypical system, where excitation by two short pulses reaches the energy region of strongly correlated doubly excited states (DESs) of He. It was shown how bound configurations undergo a time-dependent oscillatory mixing while they lose probability to a free electron configuration resulting from the exponential decay of the autoionization process.

The theoretical approach was based on a methodology allowing a reliable and transparent solution of the time-dependent Schrödinger equation (TDSE) from first principles, for a “mechanical” system (atom) that evolves first under the influence of the total Hamiltonian (free atom plus interaction with laser pulses of large frequencies), and then, when the duration of the pulse is over, under its own Hamiltonian.

Specifically, in Ref. [3] we studied the time-dependent interaction of He in its  $1s2s$   $^1S$  metastable state with two laser-generated pulses of trapezoidal or Gaussian shape, with

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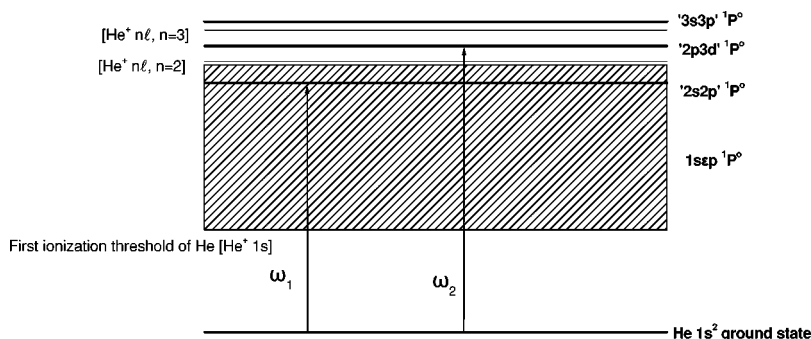


FIG. 1. The system of atom plus laser excitation that was treated in this work via the state-specific expansion approach to the solution of the time-dependent Schrödinger equation. The two frequencies,  $\omega_1$  and  $\omega_2$ , are in resonance with the correlated energies of the two He doubly excited states, “ $2s2p$ ” $^1P^o$  and “ $2p3d$ ” $^1P^o$ .

a full width at half-maximum (FWHM) equal to 86 fs and of frequencies  $\omega_1=1.453$  a.u. and  $\omega_2=1.781$  a.u. The frequencies were chosen so as to match the levels of two DESs of  $^1P^o$  symmetry, separated by about 8.9 eV, which, in the Hartree-Fock approximation of stationary state quantum mechanics, are described by the configurations  $2s2p$  and  $2p3d$ . The use of two, laser pulses, rather than one, exciting simultaneously the two configurations of interest, enhances the probability of the sought after phenomenon. By time resolving the mixing among the main nonstationary configurations induced by  $H_A$ , including the  $1s\epsilon p$   $^1P^o$  scattering continuum, we obtained numerical results and drew a number of related conclusions.

### System examined in this work

Given that no information on this topic existed prior to Ref. [3], opting for a suitable real system to be analyzed in terms of first principles was less than obvious as well as crucial. By “system” we mean a combination of the initial state, the spectrum of states, and the characteristics of the laser pulses. The choice of the He  $1s2s$   $^1S$  state as the initial one [3] had to do with the relative ease—for weak intensities—of one-photon excitation to the He  $2s2p$   $^1P^o$  and with the related clarity of the results, since the dipole coupling between the  $1s2s$   $^1S$  and the  $2s2p$   $^1P^o$  configurations is allowed, while it is forbidden between the  $1s2s$   $^1S$  and the  $2p3d$   $^1P^o$  configurations. We note that the components of angular electron correlation in the “ $1s2s$ ” $^1S$  stationary state are so small that they cannot influence significantly the probability of time-dependent electric dipole excitation of the doubly excited configurations.

The purpose of the work described in this paper is to expand the scope of the calculations and analysis and to provide additional results and discussion on the dynamics that appears to exist at the attosecond scale, using the system of the He  $1s^2$   $^1S$  ground state interacting simultaneously with two laser pulses (Fig. 1). By choosing to start the two-pulse time-dependent excitation from this state, a direct comparison and physical understanding of the excitation using either the metastable He  $1s2s$   $^1S$  state or the ground He  $1s^2$   $^1S$  state as the initial state can be achieved. Furthermore, this system is probably more convenient for experimentalists, since the He atoms can be readily available in large numbers in the ground state. [We stress that the spectroscopic technology and arrangement for the probe (attosecond) part is still a desideratum for such experiments.] On the other hand, even

before the detailed calculation is done, it is understood that in order for excitation from the He  $1s^2$   $S$  state to be of practical significance, the intensity of both pulses has to be much larger than that which we used before for the metastable state. In turn, this implies that, now, the theoretical prediction must account for the effect of two-photon resonance ionization, namely, for the depopulation of the DES by additional photon absorption into the scattering continua lying above. This requirement made the theoretical treatment more complex, and the solution of the TDSE much more demanding as regards computational time. As we shall discuss later on, the new results confirm and expand the previously deduced picture of time-dependent excitation and of the possibility of clocking two-electron “motion” as the symmetry-adapted two-electron bound configurations mix and as the autoionization process evolves.

## II. THEORY

The problem was formulated around the following two questions, the first one being more general.

(1) Is it possible to probe the electronic structure in such a way as to extract from it meaningful information on dynamics that can be resolved within the attosecond regime? If so, what is an observable process that can reflect the concept of “motion” of electrons?

(2) Considering the first question, given the quantum mechanical formalism of stationary states and of corresponding eigenfunctions of  $3N$  coordinates, how are we to probe and reveal the possible connection of electronic structure to atomic dimensions, to hypershort time scales and to electron correlation?

In examining the theoretical and computational implications of the above questions, there are a number of practical issues that have to be considered, regarding computability and observability. For example, given the lack of previous knowledge, the issues of what real system should and could be investigated and which quantum mechanical property should and could be computed reliably had to be examined.

We focused on the concept of electron correlation in strongly correlated DESs inside the continuous spectrum. These can in principle be excited by short pulses from a lower state, be it the ground state (this work) or a metastable excited one [3]. Specifically, following our earlier results and experience on the theory and computation of correlated wave functions, in the theoretical framework used here electron correlation in ground and excited states is analyzed in terms

of the interaction of configurations consisting of self-consistent as well as of variationally optimized orbitals. In this context, strong correlation means heavy mixing of the multiconfigurational Hartree-Fock (MCHF) zero order configurations.

The superposition of configurations is a conceptually simple, yet general, computational methodology for obtaining approximate solutions for bound or quasibound states of the time-independent Schrödinger equation. In addition to that, it has direct physical relevance, especially when the orbitals are state specific, and can reveal the gross features of the interplay between electronic structure and conventional, stationary-state electronic spectroscopy. For example, the coefficients of the configurations constitute a direct index for the semiquantitative understanding of spectra created by electronic transitions, even without a full calculation of the transition moment. In other words, by establishing the overwhelmingly dominant coefficients of the mixing configurations with self-consistent orbitals, in initial and final state wave functions, interpretations as well as a heuristic understanding and predictions of observable quantities on the energy axis can be made. This argument was made three decades ago [5,6], and has since been used successfully in a variety of problems. For example, in the present case, following the state-specific theory of excited states it is a simple matter to recognize the basic electronic structure character of the lowest DES of He of  $1P^o$  symmetry, at 60.1 eV, in terms of two or three configurations, with orbitals obtained by solving the corresponding MCHF equations. Specifically, to a very good approximation the electronic structure of this DES can be reduced to the simple form

$$\begin{aligned} \text{He}|1P^o\rangle = & 0.948\varphi_1(2s2p) - 0.308\varphi_2(2p3d) \\ & - 0.0743\varphi_3(3s3p). \end{aligned} \quad (1)$$

The energy of this wave function is  $-0.6906$  a.u., which is 60.21 eV above the ground state while the experimental one is 60.13 eV [7]. Furthermore, using wave function (1) as the initial state, the frozen core HF  $1s\epsilon p$  as the final state and the golden rule expression, we calculate the autoionization width for this state to be 38 meV, in excellent agreement with experiment ( $38 \pm 4$  meV) [7].

Based on Eq. (1), which shows a heavy mixing between the first two configurations, one may reason that it is very probable that a higher lying DES, represented by a correlated wave function having as its major component the  $\varphi_2(2p3d)$  configuration, should affect, albeit with a smaller probability, the energy-dependent photoabsorption cross-sections of the He ground ( $1s^2$ ) or first metastable ( $1s2s$ )  $1S$  states.

We now turn to a time-dependent picture, the essence of this study. We focus on the two  $1P^o$  resonances, which, in the stationary-state version, have as their major configurational components the  $\varphi_1(2s2p)$  and  $\varphi_2(2p3d)$  wave functions. These functions have the quantum mechanical restriction of antisymmetry and are eigenstates of the operators  $L^2$  and  $S^2$ . However, they are not eigenstates of  $H_A$ . It is the interaction via  $H_A$  that mixes them. The question is whether this mixing, apart from being a computational necessity of stationary state quantum mechanics, is also a computable time-

dependent process with physical meaning, provided one considers a hyperfast time resolution, i.e., a probe in the attosecond scale.

Given Eq. (1), the electric dipole excitation from the He  $1s^2$   $1S$  state has its largest matrix element with  $\varphi_1(2s2p)$ . We call this configuration the “*bright*” one. Note that, regardless of whatever contribution ground-state correlation makes to the dipole matrix element, for state-specific orbitals the overlap  $\langle 1s|2s'\rangle$  ( $2s'$  represents the radial of the doubly excited configuration) is not zero and, therefore, the two-electron excitation has finite probability at the level of the single configurations,  $1s^2$   $1S$  and  $2s2p$   $1P^o$  [5,6]. On the other hand, this matrix element is much smaller than the  $\langle 1s2s|r|2s'2p\rangle$  one, which dominates the excitation from the metastable state [3]. This is basically why we have found that the laser-induced transfer of population to the excited configurations requires much higher (two orders of magnitude—see below) intensities in the case of the ground state examined here.

The electric dipole matrix element of  $1s^2$   $1S$  with the  $\varphi_2(2p3d)$  configuration is rigorously zero for reasons of orbital symmetry, and therefore, even with the addition of correlation corrections to the ground-state wave function, this configuration is essentially inaccessible from the ground state. [If the corresponding correlated wave function is considered in a standard stationary-state quantum mechanics analysis, the DES labeled by  $\varphi_2(2p3d)$  is excited from the He  $1s^2$  or  $1s2s$  states because of the presence of angular-correlation configurations, such as  $2p^2$  and  $3d^2$   $1S$ , which, however, take relatively small coefficients.] We call  $\varphi_2(2p3d)$  the “*dark*” configuration. The  $\varphi_3(3s3p)$  configuration, whose contribution approximates that of the rest of the full space of bound configurations, is named the “*gray*” configuration. They are all embedded in the continuous spectrum of the “*bath*” configurations,  $1s\epsilon p$ , into which they autoionize. The meaning of these names has to do with the basic features of the spectrum of interest, as regards both the pump and the probe stage of the overall process.

In order to treat the case of two-photon resonance ionization, the number of open scattering channels must increase. As we state below, [Eq. (5)], in addition to the  $1s\epsilon p$  channel, we took into account ten open channels above the  $n=2$  and  $n=3$  hydrogenic thresholds.

### III. CALCULATIONS AND RESULTS

#### A. Double resonance absorption

The first set of calculations aimed at producing comparative results for the cases where either the  $|1s2s$   $1S\rangle$  or the  $|1s^2$   $1S\rangle$  stationary states are pumped by two femtosecond laser pulses, of frequencies in resonance with the positions of the two DESs labeled by the  $2s2p$  and  $2p3d$   $1P^o$  configurations. For both cases, the pulses have the same duration, shape and field strength. Specifically, we consider the system “laser pulses plus atomic spectrum” as it evolves, starting from the He  $|1s^2$   $1S\rangle$  or the  $|1s2s$   $1S\rangle$  states at  $t=0$ , and we apply the SSEA in order to solve the TDSE [4]. Since the  $|1s2s$   $1S\rangle$  case was treated in Ref. [3], from which we took a

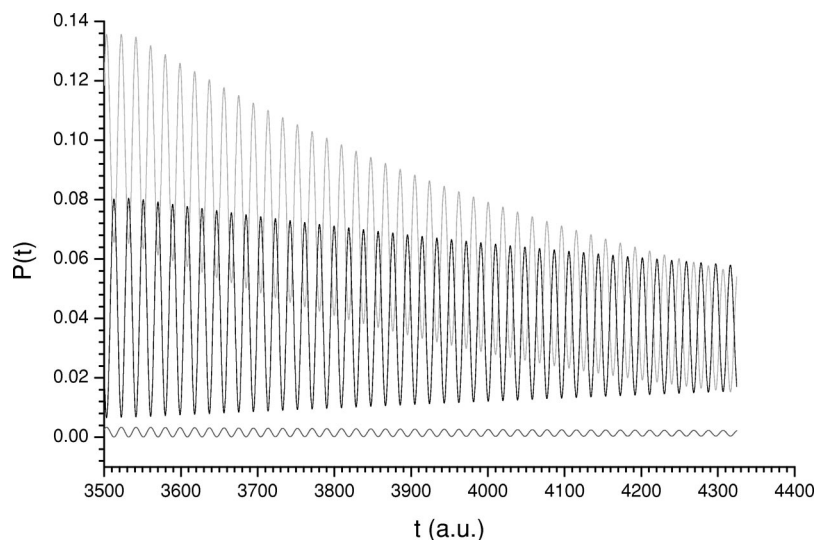


FIG. 2. Time-dependent excitation probability,  $P(t)$ , where the process is initiated from the He  $1s2s^1S$  metastable state. Population transfer to the configurations of wave function (1), takes place through the interaction with the dichromatic laser pulse of Eq. (4) for a Gaussian pulse with full width at half-maximum of 86 fs. The two frequencies,  $\omega_1=1.453$  a.u. and  $\omega_2=1.781$  a.u., are in resonance with the calculated positions of the correlated states labelled by  $2s2p$  and  $2p3d$  configurations. The corresponding field strengths are  $F_1=2.0 \times 10^{-3}$  a.u., and  $F_2=1.4 \times 10^{-3}$  a.u. The light color, black and gray curves correspond to the  $2s2p^1P^o$  (bright),  $2p3d^1P^o$  (dark), and  $3s3p^1P^o$  (gray) configurations respectively.

portion of the results in order to compare with the present ones (Fig. 2), here we discuss the case of the ground state only.

The wave function  $\Psi(t)$  that satisfies the TDSE is written as

$$\Psi(t) = a(t)\varphi_0 + b_1(t)\varphi_1 + b_2(t)\varphi_2 + b_3(t)\varphi_3 + \int d\epsilon c(\epsilon, t)\varphi(\epsilon), \quad (2)$$

where  $\varphi_1, \varphi_2, \varphi_3$ , and  $\varphi(\epsilon)$  stand for the configurations defined above. The energy-normalized scattering functions  $\varphi(\epsilon)$  are obtained numerically in the frozen core plus exchange approximation.  $\varphi_0$  is the  $1s^2^1S$  state, computed as a six-term MCHF wave function [8]:

$$\varphi_0(“1s^2”^1S) = \alpha_1(1s^2) + \alpha_2(2s^2) + \alpha_3(3s^2) + \alpha_4(2p^2) + \alpha_5(3p^2) + \alpha_6(3d^2) \quad (3)$$

with  $\alpha_1=0.995965$ ,  $\alpha_2=-0.06229$ ,  $\alpha_3=-0.007349$ ,  $\alpha_4=0.010282$ ,  $\alpha_5=0.062454$ , and  $\alpha_6=-0.012099$ . The energy of this MCHF wave function is  $E_0=-2.901840$  a.u. (The accurate value of the He  $1s^2^1S$  energy is  $-2.903724$  a.u.)

The total Hamiltonian of the system contains two laser-generated pulses, of frequencies  $\omega_1$  and  $\omega_2$ , having a Gaussian shape with a FWHM equal to 86 fs. The two frequencies correspond to the computed MCHF energy difference between the  $1s^2^1S$  state and the two  $^1P^o$  DESs,  $|“2s2p”\rangle$  and  $|“2p3d”\rangle$ , obtained from the  $3 \times 3$  MCHF calculation. The choice of two laser pulses exciting simultaneously two states far apart enhances the probability of population transfer from the initial state at the beginning of the laser-atom interaction.

Specifically, the form of the Hamiltonian that was used for the solution of the TDSE is

$$H(t) = H_A + V_1(\omega_1, t) + V_2(\omega_2, t), \quad (4a)$$

$$H_A = \text{free-atom Hamiltonian for He}, \quad (4b)$$

$$V_1(\omega_1, t) = zF_1g(t)\sin(\omega_1t), \quad (4c)$$

$$V_2(\omega_2, t) = zF_2g(t)\sin(\omega_2t). \quad (4d)$$

The field strengths  $F_1$  and  $F_2$  are  $4 \times 10^{-2}$  and  $3 \times 10^{-2}$  a.u. respectively.  $g(t)$  represents the Gaussian temporal pulse shape with a FWHM equal to 86 fs.  $\omega_1=2.211$  a.u. = 60.17 eV, i.e., it reaches the energy region of the  $|“2s2p”\rangle^1P^o$  resonance state.  $\omega_2=2.539$  a.u. = 69.09 eV, i.e., it reaches the energy region of the  $|“2p3d”\rangle^1P^o$  energy region. The peak intensity is  $10^{13}$  W/cm<sup>2</sup>.

This order of magnitude for the intensity suggests that we should investigate the possible differences in the fingerprints of attosecond dynamics, between the weak-and strong-field cases. Such differences may be seen in the contributions of higher-order processes to the one-photon absorption by the  $|“2s2p”\rangle^1P^o$  and  $|“2p3d”\rangle^1P^o$  resonance states. As will be shown below, the two-photon resonance ionization at this intensity is not capable of distorting the essential physics of the attosecond dynamics studied here.

In order to compute the whole time-dependent phenomenon we evaluated the interaction matrix elements and solved the TDSE by transforming it to a system of coupled integrodifferential equations with time-dependent coefficients. The initial condition at  $t=0$  was that  $a(0)=1$ . As soon as  $t>0$ , all configurations of Eq. (1) are mixed via the total  $H(t)$ . The propagation of  $\Psi(t)$  in time, i.e., the calculation of the time-dependent coefficients of Eq. (2), was done by the Taylor-series expansion method described in Ref. [4].

The pertinent results are shown in Figs. 2–5. Figure 2 depicts, on logarithmic scale, the probability of populating the three configurations of Eq. (1) after the end of the pulse, when the system is initially in the He  $1s2s^1S$  state. The occupation probabilities for these configurations are clearly different. As the antisymmetric, single-configuration two-electron wave functions interact via the Coulomb force, the occupation probabilities oscillate with a period that is of the order of a few hundred attoseconds. The oscillation continues after the end of the pulse, at which time the occupation probabilities for the two configurations have started approaching each other while decaying exponentially to the free-electron continuum. Thus, the phenomenology of two

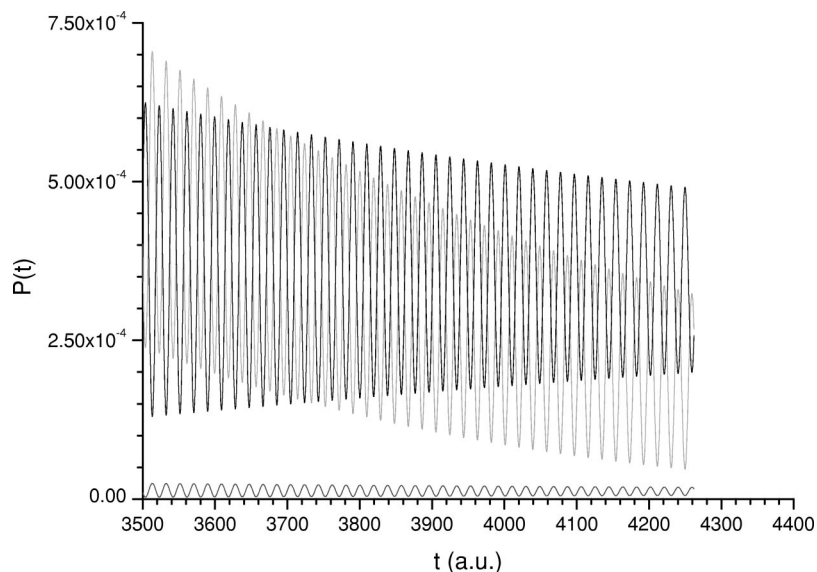
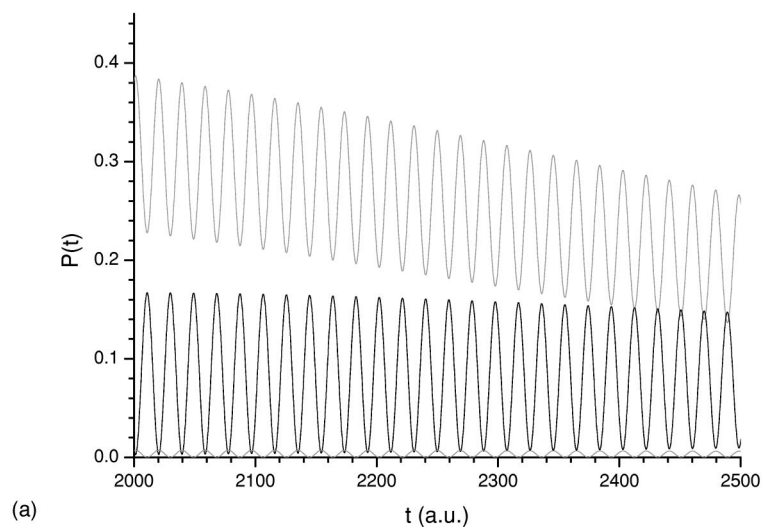
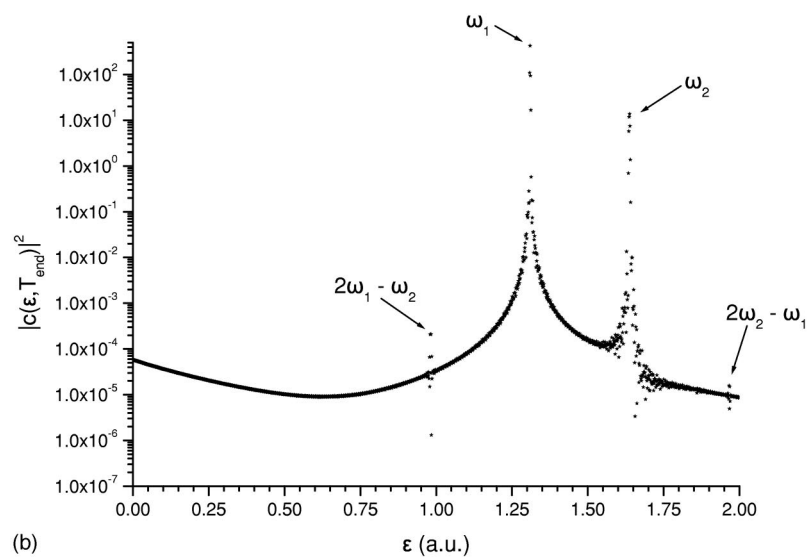


FIG. 3. As in Fig. 2, for the initial state He  $1s^2 \ ^1S$ , and for  $\omega_1=2.211$  a.u. and  $\omega_2=2.539$  a.u.



(a)



(b)

FIG. 4. (a) As in Fig. 3, for  $F_1=4 \times 10^{-2}$  a.u. and  $F_2=3 \times 10^{-2}$  a.u. (b) The probability distribution of the ionized electron, calculated at the end of the laser pulse in terms of the coefficient  $c(\epsilon, t)$  of Eq. (2), as a function of the energy  $\epsilon$ . The laser pulse characteristics are the same as those in (a).

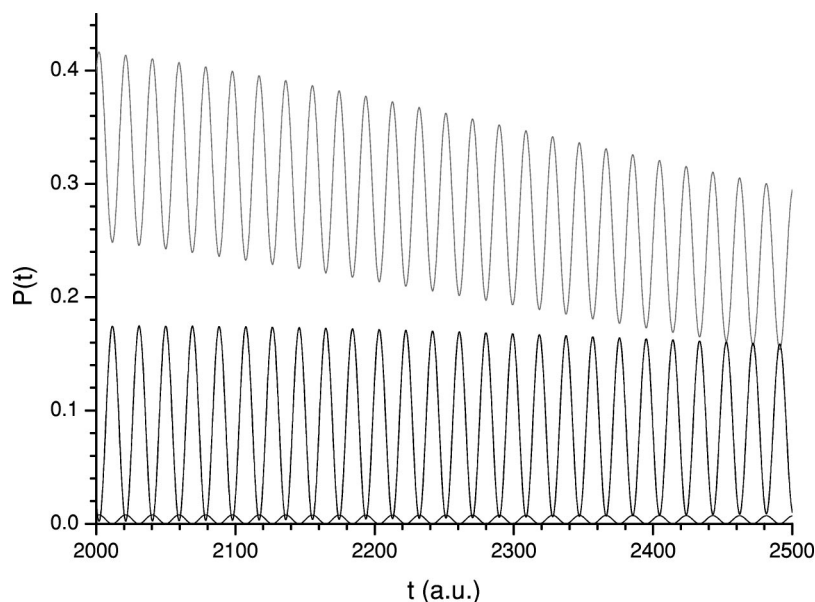


FIG. 5. As in Fig. 4(a), for the extended basis set of Eq. (5), which incorporates the function spaces for the most important multiphoton resonance ionization processes above the  $n=2$  and 3 hydrogenic thresholds.

well-known quantum mechanical features is exhibited here as a result of our time-dependent handling of strongly correlated real systems: The two-level oscillation and the exponential decay into a purely continuous spectrum.

We now compare with the case where the excitation starts from the ground state, for which the results, computed for the same laser intensities, are shown in Fig. 3.

A comparison of Figs. 2 and 3 demonstrates that the probability of excitation of the He  $|1s2s\rangle^1S$  state is approximately three orders of magnitude larger than the one for the He  $1s^2^1S$  state. In addition, the amplitude of the oscillations stemming from the Coulomb interactions is smaller. This characteristic implies that, for intensities of the order of  $10^{11}$  W/cm<sup>2</sup>, as is the case in Figs. 1 and 2, if the He  $1s^2^1S$  state is pumped, the possibility of experimental observation of the oscillations among the three configurations of Eq. (1) is lean. We conclude that, for practical reasons, if excitation starts from the He ground state the laser fields must have higher intensities.

Indeed, Fig. 4(a) shows that for laser field peak intensities of the order of  $5 \times 10^3$  W/cm<sup>2</sup>, the three configurations of Eq. (1) acquire significant population and large amplitude of oscillations. On the other hand, even for the large frequencies used, as intensities increase one must be concerned with “collateral damage”, namely, the contribution of multiphoton processes. Even without expanding the function space beyond that of Eq. (2), their importance is revealed in Fig. 4(b), which depicts the probability distribution of the free electron, calculated at the end of the laser pulse from the coefficient  $c(\varepsilon, t)$  of Eq. (2), as a function of the energy  $\varepsilon$ . The spectrum above the ionization threshold consists of four peaks. Specifically, the two dominant peaks correspond to the absorption of a single photon of frequencies  $\omega_1$  and  $\omega_2$ , respectively. But, in addition, two smaller peaks have emerged that correspond to higher order processes involving more than one photon. The first corresponds to the absorption of two photons with frequency  $\omega_1$  and the emission of one with frequency  $\omega_2$ , while the second one corresponds to the absorption of two photons with frequency  $\omega_2$  and the emission of one with frequency  $\omega_1$ .

### B. Two-photon resonance ionization. A multichannel time-dependent calculation

The conclusion that we draw from the results of Figs. 2 and 3 is that in order to achieve sufficient population of the DESs when the excitation starts from the He  $1s^2^1S$  state, it is necessary for the intensities of laser fields to be of the order of  $10^{13}$  W/cm<sup>2</sup> or higher. However, in such a case multiphoton resonance ionization via the DESs, becomes more probable. In order to examine the impact that this additional processes have on the phenomenon that we are interested in here, we enlarged the computation as follows. The function space which is used for the solution of the TDSE was expanded so as to contain at least the most probable ionization channels above the  $n=2$  and 3 thresholds (Fig. 1). This implies the addition of ten scattering channels, and the solution of the TDSE using

$$\Psi(t) = a(t)\varphi_0 + b_1(t)\varphi_1 + b_2(t)\varphi_2 + b_3(t)\varphi_3 + \int d\varepsilon c(\varepsilon, t)\varphi(\varepsilon) + \sum_{i=1}^{10} \int d\varepsilon d_i(\varepsilon, t)\varphi_i(\varepsilon). \quad (5)$$

The new scattering functions  $\varphi_i(\varepsilon)$  are obtained numerically as frozen core, energy-normalized functions  $n\ell\varepsilon\ell$ , where  $n\ell$  are the He<sup>+</sup> hydrogenic wave functions  $2s$ ,  $2p$ , and  $3d$ . Specifically, the additional ten symmetry-adapted scattering functions represent the following ionization continua:  $2s\varepsilon s^1S$ ,  $2s\varepsilon d^1D$ ,  $2p\varepsilon p^1S$ ,  $2p\varepsilon p^1P$ ,  $2p\varepsilon p^1D$ ,  $2p\varepsilon f^1D$ ,  $3d\varepsilon s^1D$ ,  $3d\varepsilon d^1S$ ,  $3d\varepsilon d^1P$ , and  $3d\varepsilon d^1D$ . These are connected via the electric dipole operator with the  $1P^o$  DES. For the solution of the TDSE, the number of equations is now 4855, i.e., an order of magnitude larger than in the case of one-photon resonance absorption.

Figure 5 shows the population that the three configurations of Eq. (1) acquire, for the same time interval and for the same laser pulse parameters as in Fig. 3. By comparing Figs. 3 and 4(a), we see that the effect of the multiphoton

processes via the DESs on the amplitude and position of the oscillations (with a period of approximately 500 attosec), does not have substantial consequence on the essence of the attosecond dynamics in this system. In retrospect this is reasonable since the field strength is substantially weaker than the internal atomic field and so the energy spectrum and wave functions are only slightly perturbed.

#### IV. TIME-DEPENDENT QUANTUM MECHANICAL GEOMETRIES

The present work is about the quantum mechanical excitation and propagation of correlating electronic nonstationary states, which are taken to be properly symmetrized multi-electron configurations. Contrary to the case of femtosecond spectroscopy of nuclear motion in molecular rearrangements, where the nuclei are treated as classical particles and geometries are conceptualized directly in real space, here any attempt to “visualize” electronic geometries as a function of time must follow quantum mechanical rules. In order to achieve this, we opted for a first-principles calculation of the time dependence of the angle,  $\theta_{12}$ , formed by the position vectors of the two electrons, as the system is being distributed on the attosecond scale over the two main  $^1P^o$  configurations,  $2s2p$  and  $2p3d$ . The calculation was as follows.

In previous work [9,10], the concept of the *shape of atomic states* was defined and computed quantum mechanically in terms of the probability distribution  $\rho(\cos \theta_{12})$  of  $\theta_{12}$ . This quantity is obtainable directly from the state-specific expression of the Coulomb interaction, where the  $R^k$  integrals are replaced by Legendre polynomials  $P_k$ , multiplied by normalization constants and radial overlaps. This connection is based on the observation that the  $N$ -electron energy due to the two-body interaction  $v(r_1, r_2)$  can be written in terms of the diagonal second-order density matrix, in its spinless form,  $\Gamma(r_1, r_2; r_1, r_2)$ , as

$$E = N(N-1)/2 \int v(r_1, r_2) \Gamma(r_1, r_2; r_1, r_2) dr_1 dr_2, \quad (6)$$

while the probability that the position vectors of two electrons form an angle  $\theta_{12}$  can be written as

$$\rho(\cos \theta_{12}) = \int_{\theta_{12}=\text{const}} \Gamma(r_1, r_2; r_1, r_2) dr_1 dr_2. \quad (7)$$

Let  $\Psi$  be a linear combination of  $N$ -electron determinants over a set of orthonormal spin orbitals. If two determinants differ by more than two spin orbitals, their product does not contribute to  $\rho(\cos \theta_{12})$ . Otherwise, their contribution is computed according to the Slater-Condon rules. In general, the calculation of  $\rho(\cos \theta_{12})$  requires the evaluation of the following expression over four orbitals:

$$\int_{\theta_{12}=\text{const}} u_a(r_1) u_b(r_2) u_c^*(r_1) u_d^*(r_2) dr_1 dr_2. \quad (8)$$

Separating radial and angular parts, this is written as

$$\begin{aligned} & \langle R_a | R_c \rangle \langle R_b | R_d \rangle \int_{\theta_{12}=\text{const}} Y_{l_a m_a}(\theta_1, \phi_1) Y_{l_b m_b}(\theta_2, \phi_2) \\ & \times Y_{l_c m_c}^*(\theta_1, \phi_1) Y_{l_d m_d}^*(\theta_2, \phi_2) dr_1 dr_2. \end{aligned} \quad (9)$$

The integral can be expanded in terms of the orthogonal Legendre polynomials  $P_k(\cos \theta_{12})$ . After some straightforward algebra, the coefficients of this expansion, expressed in terms of 3- $j$  symbols, are found to be

$$\begin{aligned} c_k &= \delta_{m_a+m_b, m_c+m_d} \sqrt{(2l_a+1)(2l_b+1)(2l_c+1)(2l_d+1)} \\ & \times (-1)^{m_b+m_c} \frac{2k+1}{2} \begin{pmatrix} l_a & l_c & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_b & l_d & k \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \begin{pmatrix} l_a & l_c & k \\ m_a & -m_c & -m_a+m_c \end{pmatrix} \begin{pmatrix} l_b & l_d & k \\ m_b & -m_d & -m_b+m_d \end{pmatrix}. \end{aligned} \quad (10)$$

Apart from the factor  $(2k+1)/2$ , these coefficients are the same as the ones appearing in the expression of the Coulomb-interaction matrix elements in terms of the  $R^k$  integrals. In this case, the integral over three spherical harmonics appears because of the expansion of the two-body operator  $r_{12}^{-1}$  in terms of the Legendre polynomials. A comparison of the two cases provides a correspondence with practical significance:

$$R^k(a, b; c, d) \Rightarrow \langle R_a | R_c \rangle \langle R_b | R_d \rangle \frac{2k+1}{2} P_k(\cos \theta_{12}). \quad (11)$$

In other words, an expression for the Coulomb interaction, which is normally obtained from an energy computation, can be transformed into an expression for  $\rho(\cos \theta_{12})$  by the above substitution. Therefore,  $\rho(\cos \theta_{12})$  of each state is computable and is directly related to the two-electron interaction energy expression of this state, either in the independent particle approximation or with electron correlation included. We note that when prescription (11) is followed, division of the energy expression by the number of electron pairs  $N(N-1)/2$  is required in order that the normalization condition

$$\int_0^\pi \rho(\cos \theta_{12}) \sin \theta_{12} d\theta_{12} = 1 \quad (12)$$

is satisfied, as it is seen by comparing Eqs. (6) and (7).

By employing the above theory of atomic structure in conjunction with the time-dependent coefficients of the mixing of the  $2s2p$  and  $2p3d$  configurations, it was possible to compute the distribution  $\rho(\cos \theta_{12})$  as a function of time, thereby obtaining for the first time, to our knowledge, an understanding of the geometrical variation of the two electrons as a function of the time-dependent excitation and configurational mixing amplitudes.

The results are shown in Fig. 6 where the values of  $\rho(\cos \theta_{12})$  are plotted for four values of time after the commencement of the excitation. We note that the ground state

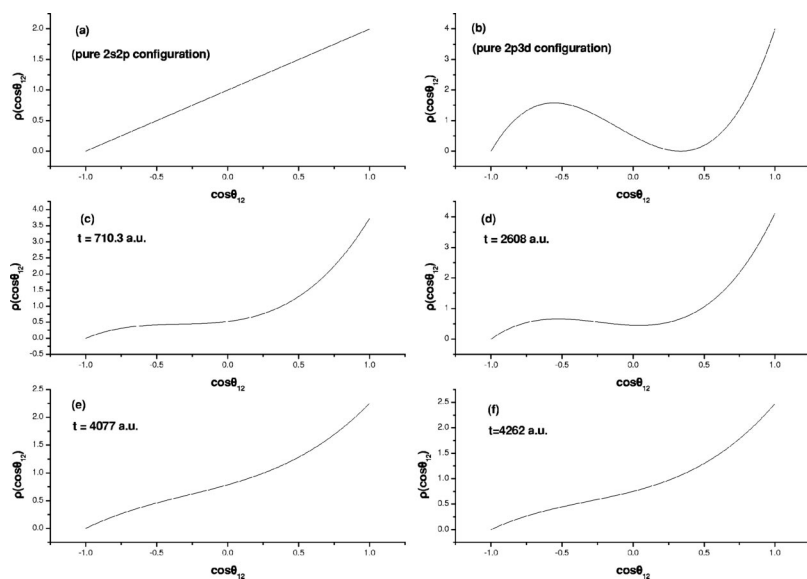


FIG. 6. The probability density  $\rho(\cos \theta_{12})$ , that the position vectors of two electrons form an angle  $\theta_{12}$  as a function of  $\cos(\theta_{12})$ , for the following cases: (a) “Pure”  $2s2p \ ^1P^o$  configuration, where the mixing coefficient  $b_1=1$ . (b) “Pure”  $2p3d \ ^1P^o$  configuration ( $b_2=1$ ). (c) Using the mixing coefficients  $b_1(t)$ ,  $b_2(t)$ , and  $b_3(t)$  for  $t = 710.3$  a.u. (before the peak value of the intensity). (d)  $t=2608$  a.u. (after the peak value of the intensity). (e)  $t=4077$  a.u. (after the end of the two pulses). (f)  $t=4262$  a.u.

$1s^2 \ ^1S$  is spherically symmetric. The angular electronic motion is imprinted in these figures. Given that for the  $\varphi(2s2p)$  wave function  $\rho(\cos \theta_{12})$  has a linear dependence on  $\cos(\theta_{12})$ , the time-dependent mixing of the relevant configurations is imprinted on the depicted variations of  $\rho(\cos \theta_{12})$  as a function of time. We note that since the average radii for these configurations are very close, there is very little variation of the interelectronic radial density  $\rho(r_{12})$ . Of course things would be different if one of the mixing configurations had a Rydberg character.

## V. CONCLUSION

We defined and solved from first principles a problem with real atomic systems concerning the possibility of observing the “motion” of electrons that are correlating inside the atom, at the time scale of attoseconds, in terms of time-dependent occupation probabilities of the main mixing configurations acting as nonstationary states. This correlation leads to an oscillation between the bound configurations, and, since energy conservation allows it, to the emission of an Auger electron. Each such configuration is a quantum mechanical object, satisfying the proper symmetry constraints, from which the time-dependent geometry of the two electrons is extracted via snapshots of the time-dependent probability distribution of the angle between the two electrons (Fig. 6).

Specifically, using the SSEA [4] we solved the TDSE for the following dynamical systems: The  $1s^2 \ ^1S$  ground state or the  $1s2s \ ^1S$  metastable excited state of He were allowed to interact, at  $t=0$ , with two femtosecond laser pulses of frequencies that are in electric-dipole resonance with two strongly correlated doubly excited states in the continuous spectrum of He  $1s\epsilon p \ ^1P^o$ . The system is first driven by the full (time-dependent) Hamiltonian for the duration of the laser Gaussian pulses (86 fs), and then by  $H_A$ . The configurations that are found computationally to label the two DESs, the  $2s2p \ ^1P^o$  and the  $2p3d \ ^1P^o$ , interact between them and with the  $3s3p \ ^1P^o$  and  $1s\epsilon p \ ^1P^o$ , via  $H_A$ . By computationally

achieving attosecond resolution, it was shown that there is observable configurational time-dependent mixing induced by  $H_A$  and that the occupation probabilities of the strongly mixing configurations oscillate and decay to the scattering continuum while tending to the average values represented by the correlated wave function of the corresponding stationary state. The theory and calculations accounted for the main possible processes of two-photon resonance ionization, whereby the doubly excited configurations are ionized to the  $n=2$  and 3 continua. In total, eleven open channels, with scattering states above the  $n=1, 2,$  and 3 He<sup>+</sup> thresholds were included in the computation. It was found that, at the level of the intensity that was used ( $10^{13}$  W/cm<sup>2</sup>), resonance ionization did not alter significantly the essential physics of the attosecond dynamics.

The herein proposed theoretical time-dependent attosecond spectroscopy is based on the interplay between electronic structure and dynamics, as revealed by the character of the stationary correlated wave functions of the DESs. This is a consequence of the connection between the wave function  $|^1P^o\rangle$  of Eq. (1) and the data depicted in Figs. 2–6. Obviously, if another type of wave function were used, say with a different quality or kind of basis sets and a different number of terms, although the stationary state energy might be the same, or approximately the same, the corresponding Figs. 2–5 might not be, even qualitatively. This implies that future possible experiments capable of probing the attosecond dynamics described here, could, in principle, be able to differentiate between different constructions of correlated stationary states represented by superposition of configurations.

As regards channels for the observation of the results of probing, these could involve the continuous as well as the discrete spectrum. For example, given the electronic structure of He, the probe pulses could register the oscillating doubly excited configurations by de-exciting to the He  $1s3d \ ^1D$  state, which emits at 6680 Å. This discrete state connects via the electric dipole operator with the dark configuration,  $2p3d \ ^1P^o$ , but not with the bright one,  $2s2p \ ^1P^o$ .



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