

Ionization Branching Ratio Control with a Resonance Attosecond Clock

Luca Argenti* and Eva Lindroth†

Atomic Physics, Fysikum, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden
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We investigate the possibility to monitor the dynamics of autoionizing states in real-time and control the yields of different ionization channels in helium by simulating extreme ultraviolet (XUV) pump IR-probe experiments focused on the $N = 2$ threshold. The XUV pulse creates a coherent superposition of doubly excited states which is found to decay by ejecting electrons in bursts. Prominent interference fringes in the photoelectron angular distribution of the $2s$ and $2p$ ionization channels are observed, along with significant out-of-phase quantum beats in the yields of the corresponding parent ions.

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The evolution of valence electron wave packets in atoms, molecules and solids takes place on a time scale ranging from tens of attoseconds to few femtoseconds [1]. For example, the sudden removal of an electron in CO_2 [2] and N_2 molecules [3] initiates multielectron dynamics that unfolds on the attosecond time scale, a localized vacancy propagates across the full length of a molecule as large as a tetrapeptide [4] within just ~ 1 fs, and a photoelectron escapes through the surface of solid tungsten [5] in 150 as or less. Recent advances in the generation of ultrashort pulses [6–8] provide the tools necessary for a time-resolved pump-probe investigation of such dynamics and bear the promise of its control.

Most of the reactive processes promoted by high electronic excitation, like resonant multiphoton atomic ionization [9], ultrafast electron transfer [10], and molecular dissociative photoionization [11–13], involve the formation of metastable, multiply excited states as a crucial intermediate step. These metastable states differ from bound excited states in that they can decay on a time scale that is comparable to the characteristic time evolution of the electronic wave packet itself. Their dynamics is an essential ingredient of the rearrangement of correlated multielectron wave functions [14–16], and is thus of particular relevance for their eventual control. In the present Letter, we simulate a realistic extreme ultraviolet (XUV) pump IR-probe experiment focused on the $N = 2$ ionization threshold of helium, the prototype of a multielectron system and the simplest neutral atom in which autoionizing states arise. We show that the coherent superposition of doubly excited states (DES) created by the XUV pulse ejects electrons in bursts rather than continuously, and we demonstrate that it is possible to exploit this dynamics to effectively control the branching ratios of the different ionization channels.

In our simulations, the time-dependent external field comprises an XUV-pump pulse followed by an intense IR-probe pulse, both with a Gaussian envelope. The XUV-pump pulse is 385 as long (full width at half maximum of the intensity), with the energy peaked at 60.69 eV, and an intensity of 2×10^{13} W/cm². The probe is a

Ti:sapphire 800 nm (1.55 eV) pulse, 3.77 fs long (fwhm), with an intensity of 10^{12} W/cm². The XUV pulse populates a coherent superposition, $|\psi_P\rangle$, of $^1P^o$ DES below the $N = 2$ threshold, mainly those belonging to the principal sp_n^+ series [17]:

$$|\psi_P\rangle \sim \sum_n |sp_n^+\rangle c_n e^{-iZ_n t/\hbar}, \quad (1)$$

where $Z_n = E_n - i\Gamma_n/2$ is the complex energy of the sp_n^+ resonance, with position E_n and width Γ_n . The localized part of each term in this series is approximately represented by a symmetric linear combination of sp configurations, $sp_n^+ \propto 2snp + 2pns$ [17]. As a consequence, the localized part of $|\Psi_P\rangle$ is characterized by a symmetric breathing of p and s orbitals coupled to the $2s$ and $2p$ parent ions, respectively: With the present pulse parameters, the two lowest DES in the sp^+ series, sp_2^+ and sp_3^+ , which lie ~ 5.04 eV and ~ 1.69 eV below the $N = 2$ threshold, with lifetimes of ~ 17.6 fs and ~ 80.3 fs, respectively, are by far the most populated ones. For several tens of femtoseconds, these two states dominate the dynamics of the metastable wave packet.

For the present simulation, the time-dependent Schrödinger equation is integrated numerically with an exponential propagator

$$\psi(t + dt) = \exp[-iH(t + dt/2)dt/\hbar]\psi(t), \quad (2)$$

where $H(t)$ is the atomic Hamiltonian in velocity gauge. The wave function ψ is expanded in a multichannel close coupling B -spline basis with total angular momentum up to $L = 6$ and the right-hand side of Eq. (2) is evaluated with the Arnoldi algorithm. Each subspace with definite angular momentum L comprises the $1s\phi_L$, $2s\phi_L$, $2p\phi_{L+1}$, and $2p\phi_{L-1}$ (for $L > 0$) close-coupling channels, where the notation $nl\phi_l$ indicates that one electron is frozen in the nl He⁺ orbital, while the other electron has the orbital angular momentum l . In the S symmetry, the basis also includes the Hartree-Fock $1s_{\text{HF}}^2$ configuration for a better representation of the ground state. The radial part of the atomic orbitals is expanded in a B -spline basis of order 10, with an asymptotic spacing between consecutive nodes of 0.5 Bohr

radii, up to a given maximum radius R . To compute the yield of the excited ions, a box with $R \sim 400$ Bohr radii was found to be sufficient, while for the partial differential photoelectron angular distributions (PDPAD) a larger box, $R \sim 800$ Bohr radii, was used. In order to prevent reflections at the box boundaries, a channel-specific absorbing potential V is included in the Hamiltonian

$$V = c \sum_{\alpha} V_{\alpha}, \quad V_{\alpha} = P_{\alpha} (r - R_0)^2 \theta(r - R_0) P_{\alpha}, \quad (3)$$

where the sum runs over all channels, P_{α} is the projector onto the close-coupling channel α , $\theta(x)$ is the Heaviside step function, and c is a complex coefficient chosen as $c = -(1 + 5i)10^{-4}$. The radius beyond which the potential is active, R_0 , is set to ~ 100 Bohr radii from the box boundary. The absorbing potential V allows one to record the annihilation rate in each channel and to reconstruct the yields of all the parent ions. The photoelectron distribution in a channel, identified by a parent ion $\alpha = 1s, 2s, 2p$, is obtained by projecting the propagating wave function $\Psi(t)$ onto the helium scattering states which satisfy incoming boundary conditions in all open channels but α [18]:

$$P_{\alpha}(E, \hat{\Omega}) = \sum_{m\sigma\sigma'} |\langle \psi_{\alpha, m, \sigma; E, \hat{\Omega}, \sigma'}^{-} | \Psi(t) \rangle|^2. \quad (4)$$

In Eq. (4), E and $\hat{\Omega}$ denote the photoelectron energy and propagation direction, and the sum runs over the projection m of the angular momentum of the electron in the parent ion, its spin σ , and the spin of the photoelectron σ' . The scattering states are computed with the B -spline K -matrix method, a well-established configuration interaction technique for the single ionization continuum [19].

In Fig. 1(d) we show the electron density up to 700 Bohr radii at $t = 14.51$ fs after the pump pulse. It consists of distinct wave fronts, spreading out with virtually constant speed, separated by time intervals which correspond closely to the beating period between the sp_2^+ and the sp_3^+ resonances [20]. In other words, the metastable wave packet decays by ejecting electrons in isolated bursts. This peculiar ‘‘cresting’’ behavior [21] can be understood in terms of interference between the long range part of the wave functions describing the decaying sp_2^+ and sp_3^+ states. A more mechanistic interpretation, however, is possible. The Auger decay of DES is known to be triggered by electronic correlation; one of the electrons transfers part of its excitation energy to the other, which in turn is ejected into the continuum. Pisharody and Jones provided a spectacular and extreme example of this mechanism [22]; they showed that the decay of some autoionizing states of helium, where both electrons are highly excited, takes place through a single violent $e-e$ collision. A similar picture applies also when only one of the two electrons is highly excited [23]. In this case, the autoionization is found to take place at the encounter of the external electron satellite with the excited core. In the present case, though, neither of the two electrons is highly excited. In fact, the

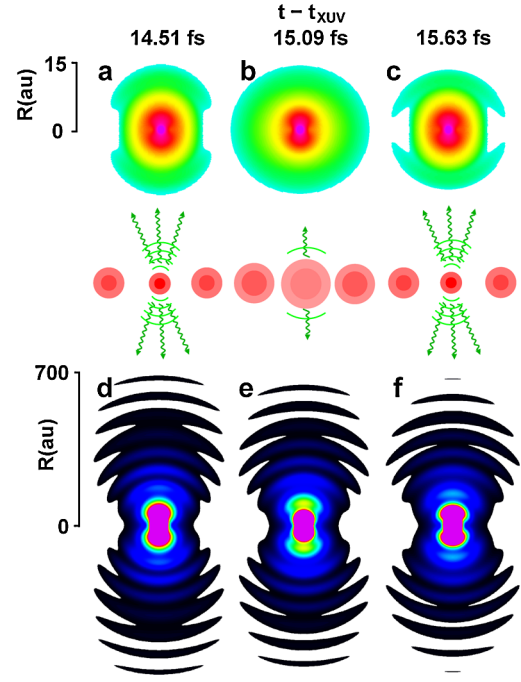


FIG. 1 (color online). Charge density after the XUV-pump pulse, at small (top row) and large (bottom row) radii. At each breathing cycle, the metastable wave packet, formed by a coherent superposition of doubly excited states, ejects a burst of electrons. The peak of the free electron density originating close to the nucleus results in a wave front which propagates outward at almost constant speed, up to very large distances.

metastable wave packet has the smallest excitation possible, it lacks a clear semiclassical analogue, and the two electrons are constantly in close interaction. To investigate whether the collisional point of view still retains any validity, we traced the position of 15 consecutive wave fronts in the time interval from 10 to 30 fs after the pump pulse, and extrapolated their evolution backwards in time to the moments at which they were created in the vicinity of the nucleus. The panels in the first and last columns in Fig. 1 correspond to two selected consecutive times at which a wave front originates close to the nucleus, 14.51 fs and 15.63 fs, while the central column corresponds to a time halfway between these two. In the upper row of Fig. 1 we show the electron density within 15 Bohr radii from the nucleus, which demonstrates its breathing motion. At $t = 14.51$ fs (a) the central part of the wave packet is at the peak of its contraction. At $t = 15.09$ fs (b) it reaches its maximal expansion. Finally, at $t = 15.63$ fs (c), it is contracted again. The instants at which the wave fronts are born in the vicinity of the nucleus therefore correspond closely to the stages of maximum contraction of the localized part of the metastable wave packet. This evidence supports the idea that the collisional description of the autoionization dynamics of the DES of helium is indeed applicable down to the least excited ones. In the present case, though, it is not the encounter between otherwise well-separated electrons [22,23] that triggers the decay, but

rather the squeezing of two electrons in constant close interaction.

The XUV pulse has another major effect: it causes the sudden ejection of electrons in the $1s$ as well as in the $2s$ and $2p$ channels. With the present choice of laser parameters, the proportion between the direct ionization in the $1s$ channel, the population of DES and the direct ionization in the $N = 2$ channels is roughly 10:1:0.01. In Figs. 2(a) and 2(d) we show the photoelectron angular distributions in the $2s$ and $2p$ channels, respectively, immediately following the XUV pulse, as functions of both the electron energy (y axis) and the cosine of the angle between the electron propagation direction and the polarization of the laser (x axis). In the $2s$ channel, one recognizes the characteristic p distribution, proportional to $\cos^2\theta$ (the amplitude is odd), while in the $2p$ channel the angular distribution results from a combination of s and d waves (the amplitude is even).

At the intensity considered, the IR-probe pulse has little effect on the ground state. It has a profound effect, however, on the DES. The population of the $^1P^o$ DES is partly redistributed among other DES with several different symmetries, and partly promoted to the continuum, mainly to the $N = 2$ channels. With an intensity of 10^{12} W/cm², the interaction of the system with the IR-probe pulse is a typical multiphoton process, where up to four IR photons are absorbed. As a consequence, the yield of the $2s$ and the $2p$ parent ions increases roughly by a factor of 2, corresponding to $\sim 1\%$ of the population of the DES. With more intense probe laser pulses, the yield of the excited He⁺ ions can be substantially increased. IR laser pulses with a peak

intensity of 10^{13} W/cm² are routinely produced and preliminary calculations indicate that, at this intensity, the yield of $N = 2$ parent ions increases by more than 1 order of magnitude. The indirect multichannel ionization of DES is interesting because, by tracking the ionization yields in separate channels, one can follow the sharing of both the final energy and angular momentum between the two electrons, and hence the real-time evolution of electron-electron correlation in coherently excited states. In Fig. 3, the increase in the yields of the $2s$ and $2p$ He⁺ parent ions after the IR pulse as functions of the time delay between the two pulses is reported. Both ion yields are modulated by substantial quantum beats [24]. A similar phenomenon, due to the coherent superposition of bound states rather than resonances, was predicted in the ionization of C⁺ [25] and has already been observed in helium, close to the $N = 1$ ionization threshold [26]. In the latter case, the authors demonstrated that it is possible to control both the timing and the probability of ionization. In the present case, on the other hand, we show that this holds also for the branching ratio between different ionization channels. The ion yields track the sp^+ breathing mode. When fitted with the function

$$A \sin(\omega t + \phi) + c_0 + c_1 t + c_2 t^2,$$

the two curves in Fig. 3 give the same $\omega = 0.121(3)$ a.u., which is readily recognized as the energy difference between the two lowest sp^+ resonances, $\Delta E = 0.123$ a.u.. It is interesting to note that the two oscillations are out of phase by as much as 60° , corresponding to a time delay of ~ 200 as; hence, the $2s$ and $2p$ channels sample different stages of the breathing motion of the metastable wave packet. Moreover, the population of the sp_2^+ resonance immediately after the pump pulse is larger than that of the sp_3^+ resonance. Since the sp_2^+ lifetime is the shortest, there is a moment at which the decay rates of the two resonances become comparable. At this point the beating between the two resonances is maximal. These features suggest the possibility to control the branching ratio of the two ionization-excitation channels and, in turn, to alter the course of reactions where metastable electronic states play a dominant role.

There are several ways to detect these quantum beats. First, the radiative lifetimes of the $2s$ and the $2p$ He⁺ states differ by several orders of magnitude (~ 1.9 ms [27] and $\sim 10^{-10}$ s [28] respectively), therefore their yields can be disentangled by looking at their fluorescence decay with ($2s + 2p$) or without ($2p$ alone) the presence of an external quenching electric field. Second, since the photoelectron angular distribution in the $2s$ and $2p$ differ, asynchronous beats should be visible in the signal of electrons collected along different directions, e.g., along the polarization axis and in the plane orthogonal to it. The photoelectrons in the $N = 1$ and $N = 2$ channels should give rise to two well-separated signals already in a velocity map imaging spectrometer [29], because of their very different energies. If

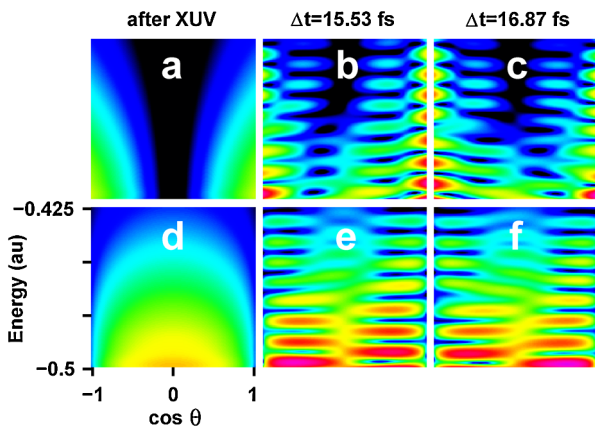


FIG. 2 (color online). Partial differential photoelectron spectra in the $2s$ (top row) and $2p$ (bottom row) ionization channels after the XUV-pump pulse (a),(d) and after the IR pulse with two different time delays Δt between pump and probe pulses separated by half the IR period: 15.53 fs (b),(e), and 16.87 fs (cf.). x axis: cosine of the photoelectron ejection angle with respect to the laser polarization; y axis: photoelectron energy in atomic units. The interplay between the direct ionization by the XUV and the multiphoton ionization of the DES due to the IR-probe results in prominent interference fringes, with a characteristic energy spacing $\Delta\epsilon = 2\pi\hbar/\Delta t$.

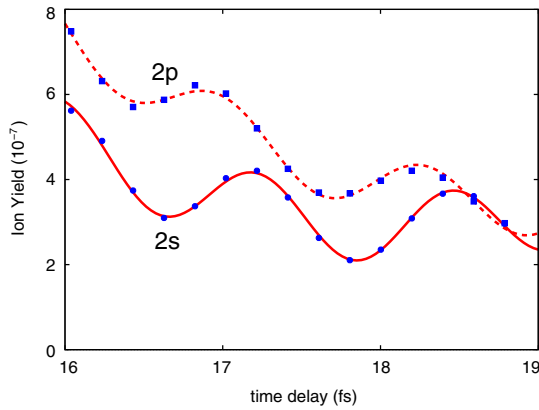


FIG. 3 (color online). Increase in the yields of the 2s and 2p He⁺ excited parent ions, due to the IR probe stage, as functions of the time delay between the pump and probe pulses. Both yields are modulated by large quantum beats, due to the interplay between sp_2^+ and $sp_3^+ {}^1P^o$ DES, which are out of phase by as much as 60°. The continuous curves are obtained by fitting the computed points with a sine function plus a quadratic background.

necessary, the latter could be detected in coincidence with their excited parent-ion counterpart by using a reaction microscope [30].

In Fig. 2(e) we show the 2p PDPAD after an IR pulse delayed from the probe by 15.53 fs. The probe pulse ionizes the DES generating a short series of peaks above the $N = 2$ threshold which interfere with the direct-ionization amplitude. In the lapse between the two pulses, the latter accumulates a phase which is linear in both the energy and the time delay:

$$\varphi_{\text{direct}}(E, t) = \varphi_{\text{direct}}(E, t_0) + E(t - t_0)/\hbar. \quad (5)$$

As a consequence, prominent interference fringes, with characteristic energy spacing $\Delta E \sim 2\pi/(t - t_0)$, emerge. The sp_2^+ and $sp_3^+ {}^1P^o$ resonances are separated from the $N = 2$ ionization threshold by roughly the energy of three and one IR photons, respectively. Since the absorption of an odd number of photons by a ${}^1P^o$ state results in an even parity state, the 2p multiphoton ionization amplitude, created by the IR pulse, should have odd parity just above the threshold and change to even parity for photoelectron energies around 1.4 eV. Indeed, the interference pattern between multiphoton and direct-ionization amplitudes [Fig. 2(e)] is asymmetric with respect to $\cos\theta$ close to the threshold, and symmetric above $E = -0.45$ a.u.. At each increase of the time-delay by half an IR cycle, the relative phase between direct and indirect multiphoton amplitudes changes by π close to the threshold, while it remains the same one photon energy above. Indeed, approximately, Fig. 2(e) is the mirror image of Fig. 2(f). Similar considerations apply for the 2s PDPAD in Figs. 2(b) and 2(c). By measuring the PDPADs at different time delays [26] it is possible to recover the ionization amplitude of the DES. With additional information on the phase

introduced by the IR field in the ionization amplitude of each DES, possibly obtained from simulations, even the original metastable wave packet could in principle be reconstructed.

In conclusion, we have presented evidence that quantum beating between doubly excited states can be monitored experimentally, and that it can be exploited with the available attosecond pump-probe techniques in order to steer the course of atomic photoionization.

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*argenti@physto.se

†lindroth@physto.se

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