 Ionization branching ratio control with a resonance attosecond clock

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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 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 timescale ranging from tens of attoseconds to few femtoseconds [1]. For example, the sudden removal of an electron in CO2 [2] and N2 molecules [3] initiates multielectron dynamics that unfolds on the attosecond timescale, a localized vacancy propagates across the full length of a molecule as large as a tetrapeptide [4] within just \( \sim 1 \) fs, and a photoelectron escapes through the surface of solid tungsten [5] in 150 as or less. Recent advances in the generation of ultra-short 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 timescale 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 wavefunctions [14–16], and is thus of particular relevance for their eventual control. In the present letter, we simulate a realistic 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 \( 2 \times 10^{13} \text{W/cm}^2 \). The probe is a Ti:Sapphire 800 nm (1.55 eV) pulse, 3.77 fs long (fwhm), with an intensity of \( 10^{12} \text{W/cm}^2 \). The XUV pulse populates 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 wavefront which propagates outward at almost constant speed, up to very large distances.

\[
|\psi_P\rangle \sim \sum_n |sp_n^+\rangle c_n e^{-iZ_n t/\hbar} \tag{1}
\]

where \( Z_n = E_n - i\Gamma_n /2 \) is the complex energy of the

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$sp^+_2$ resonance, with position $E_m$ and width $\Gamma_n$. The localized part of each term in this series is approximately represented by a symmetric linear combination of $sp$ configurations, $sp^+_2 \propto 2snp + 2pns$ [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 $sp^+_3$ series, $sp^+_2$ and $sp^+_3$, which lie $\sim 5.04$ eV and $\sim 1.69$ eV below the $N = 2$ threshold, with lifetimes of $\sim 17.6$ fs and $\sim 80.3$ 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
\begin{equation}
\psi(t + dt) = \exp[-iH(t + dt/2)dt/\hbar] \psi(t),
\end{equation}
where $H(t)$ is the atomic Hamiltonian in velocity gauge. The wavefunction $\psi$ is expanded in a multi-channel 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 $2p\phi_{L-1}$ 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 $1s^2$ He 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 $R \approx 400$ Bohr radii was found to be sufficient, while for the partial differential photoelectron angular distributions (PDPAD) a larger box, $R \approx 800$ Bohr radii, was used. In order to prevent reflections at the box boundaries, a channel-specific absorbing potential $V$ is included in the Hamiltonian:
\begin{equation}
V = c \sum_\alpha V_\alpha, \quad V_\alpha = P_\alpha \left(r - R_0\right)^2 \theta(r - R_0)P_\alpha,
\end{equation}
where the sum runs over all channels, $P_\alpha$ is the projector onto the close-coupling channel $\alpha$, $\theta(x)$ 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 $\sim 100$ 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 $\alpha$ [18]:
\begin{equation}
P_\alpha(E, \hat{\Omega}) = \sum_{m\sigma\sigma'} \left|\langle \psi^-(m, \sigma; E, \hat{\Omega}, \sigma') | \Psi(t) \rangle \right|^2.
\end{equation}
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 $\sigma$, and the spin of the photoelectron $\sigma'$. 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 we show the electron density up to 700 Bohr radii at $t = 14.51$ fs after the pump pulse. It consists of distinct wavefronts, 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. In other words, the metastable wave packet decays by ejecting electrons in isolated bursts. This peculiar “cresting” behavior [20] 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 [21]: 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 [22]. 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 metastable wave packet has the smallest excitation possible, it lacks a clear semi-classical analogue, and the two electrons are constantly in close interaction. To investigate whether the collisional point of view still retain any validity, we traced the position of 15 consecutive wavefronts in the time interval from 10 fs 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 wavefront 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 wavefronts 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
FIG. 2: 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 $\Delta t$ between pump and probe pulses separated by half the IR period: 15.53 fs (b,e), and 16.87 fs (c,f). 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 $\Delta \epsilon = 2\pi \hbar / \Delta t$.

otherwise well-separated electrons $\text{21, 22}$ 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 Fig. 2a and Fig. 2d, 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 $^1\text{Po}$ 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/cm$^2$, 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 two, 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/cm$^2$ are routinely produced and preliminary calculations indicate that, at this intensity, the yield of $N=2$ parent ions increases by more than one 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 $\text{23}$. A similar phenomenon, due to the coherent superposition of bound states rather than resonances, was predicted in the ionization of C$^+$ $\text{24}$ and has already been observed in helium, close to the N=1 ionization threshold $\text{25}$. 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

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

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$^\circ$, corresponding to a time delay of $\sim 200$ as; hence, the 2s and 2p channels sample different stages of the breathing motion of the metastable wave packet. Moreover, the population of the $sp^+$ resonance immediately after the pump pulse is larger than that of
the $sp^+_1$ resonance. Since the $sp^+_1$ 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 ($\sim 1.9 \text{ ms}$ and $\sim 10^{-10} \text{ ms}$ 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, because of their very different energies. If necessary, the latter could be detected in coincidence with their excited parent-ion counterpart by using a reaction microscope.

In Fig. 2e we show the 2p PDPAD after an IR pulse delayed from the probe by 15 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:

$$\varphi_{\text{direct}}(E, t) = \varphi_{\text{direct}}(E, t_0) + E(t - t_0)/\hbar.$$  \hspace{1cm} (5)

As a consequence, prominent interference fringes, with characteristic energy spacing $\Delta E \sim 2\pi/(t - t_0)$, emerge. The $sp^+_1$ and $sp^+_3 \text{1po}$ 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 1po 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. 2e) is asymmetric with respect to $\cos \theta$ close to the threshold, and symmetric above $E = -0.45 \text{ a.u.}$ At each increase of the time-delay by half an IR cycle, the relative phase between direct and indirect multiphoton amplitudes changes by $\pi$ close to the threshold, while it remains the same photon energy above. Indeed, approximately, Fig. 2e is the mirror image of Fig. 2f. Similar considerations apply for the 2s PDPAD in Figs. 2a-c. By measuring the PDPADs at different time delays, 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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