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Journal Article**Author(s):**

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Publication date:

2011-02-28

Permanent link:

<https://doi.org/10.3929/ethz-a-010783531>

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Originally published in:

Journal of Physics B: Atomic, Molecular and Optical Physics 44(4), <https://doi.org/10.1088/0953-4075/44/4/041001>

Funding acknowledgement:

128274 - Attosecond imaging of chemical dynamics (SNF)

Imaging and Controlling Multielectron Dynamics by Laser-induced Tunnel Ionization

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PACS numbers: 32.80.Rm, 32.80.Qk, 32.80.-t

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Abstract. Using sequential strong-field double ionization in a pump-probe scheme we show through calculations how electronic dynamics can be prepared and imaged. Electronic dynamics arise whenever multiple states of the ion are accessed in the ionization step. The dynamics in the cation influence the rate of the second ionization step and the momentum distribution of the ejected electron, allowing their detailed characterization. We show how the probe step is controlled through spatial propensities of the ionizing orbitals and the energy level structure of the dication. Both the final electronic state of the dication and the spin state of the ejected electron pair can be controlled through the time delay between the two pulses. We discuss how our results will extend to the preparation and measurement of attosecond electron dynamics.

Understanding and controlling the collective dynamics of electrons in molecules and solids is one of the central challenges of modern ultrafast science. Recent efforts have concentrated on the development of methods for the measurement of the electronic dynamics in the valence shell of atoms, molecules and solids [1, 2, 3]. This insight is expected to have important consequences for our understanding of all physical phenomena determined by the interactions between these electrons, ranging from the basic electronic structure of matter to coherent phenomena in large molecules and cooperative phenomena in solids, like superconductivity.

An attractive approach to studying the properties of a complex static system consists in removing it from equilibrium and investigating the induced dynamics. In the case of a multielectron system such a possibility is offered by temporally confined ionization [4]. The temporal confinement makes a broad bandwidth of ionic states accessible. The ensuing dynamics allows the investigation of the properties of the initial wave function and of the interactions of its constituents.

Strong-field ionization (SFI) in the tunneling limit represents an attractive approach to studying and controlling the dynamics of multielectron systems. SFI usually affects multiple electronic shells implying that the ion can be left in different electronic states [5, 6]. The high nonlinearity of the strong-field interaction generates a photoelectron with a very large bandwidth, spanning tens of electron volts under typical experimental conditions. Therefore, strong-field ionization may leave the ion in a partially coherent non-stationary state [5, 7]. Strong-field ionization therefore typically induces collective electron dynamics. In molecules, strong-field ionization also prepares vibrational wave packets whenever the potential surfaces of the neutral and ionic states differ, a phenomenon that has been studied in some detail [8, 9, 10, 11].

In this communication, we show by calculations how an electronic wave packet can be imaged using strong-field ionization and used to control the products of a subsequent ionization step. SFI is known to be highly sensitive to the electronic structure [12, 13, 14] because of its pronounced sensitivity to the shape of the ionizing orbitals. We transfer these concepts from static systems to probing electronic dynamics in atoms and molecules. As an example we use the neon atom, in which strong-field ionization prepares a spin-orbit wave packet [15, 7]. The ground state of the neon cation has two fine-structure components that are separated by 0.1 eV due to spin-orbit interaction. In this case, spin-orbit interaction drives the electronic dynamics in the cation. In virtually all polyatomic molecules, the relaxation of the orbitals upon ionization induces attosecond electronic dynamics driven by electron correlation [16, 17] which may be probed using a second ionization step, in analogy to the case discussed in this article.

As a second aspect, we show how the proposed pump-probe experiment enables a high degree of control over the accessed state of the dication and the ejected electron pair. The dication can be prepared preferentially in either the triplet ground state or in the low-lying singlet states. Through the conservation of total spin, the ionized pair of electrons can therefore be prepared preferentially in the singlet or triplet state. Although we show model calculations for the rare gas atoms only, the underlying principles are directly applicable to all atoms and molecules possessing a fully occupied degenerate highest occupied orbital (e.g. halogen dimers, hydrogen halides, carbon dioxide, allene,

benzene etc.). The ionization of these neutral species prepares a spin-orbit wave packet in the cation that can be imaged through a second ionization step.

We consider the sequential double ionization of a rare gas atom by a pair of intense (10^{14} - 10^{16} W/cm²) femtosecond infrared laser pulses as illustrated in Fig. 1. The atom (Ne, Ar, Kr or Xe) is initially in its ground electronic state 1S_0 of configuration $(...)(ns)^2(np)^6$. The first pulse ionizes the neutral atom almost exclusively from the p orbital aligned along the polarization of the laser pulse because the SFI rate $\Gamma_{\ell,m}$ is highly sensitive to the angular momentum projection quantum number m of the ionizing orbital [18]. As an example, the relative ionization rates of the orbital aligned along the direction of the laser field $m = 0$ to that of the perpendicular orbitals $m = \pm 1$ amounts to $\Gamma_{\ell=1,m=0}/\Gamma_{\ell=1,m=\pm 1} \approx 30$ for a neon atom in a laser field of $5 \cdot 10^{14}$ W/cm². Consequently, SFI prepares the rare gas cation in an electronic state of configuration $(...)(ns)^2(np_0^1 p_{-1}^2 p_{+1}^2)$, i.e. it generates an electron "hole" that is aligned along the laser field [19, 15, 20]. The corresponding wave function density is represented in Fig. 1 for $\Delta t = 0$. However, this electronic configuration does not correspond to an eigenstate of the cation, but rather to a linear combination of its two lowest spin-orbit levels

$$\phi(t=0) = \Phi_{1,0,+1/2} = \sqrt{\frac{2}{3}}\Psi_{3/2,1/2} - \sqrt{\frac{1}{3}}\Psi_{1/2,1/2}. \quad (1)$$

The one-electron wave function of the missing electron has been represented in a space-fixed basis of atomic orbitals with the notation Φ_{ℓ,m,m_s} , where ℓ is the orbital angular momentum quantum number and m and m_s are the orbital and spin angular momentum projection quantum numbers, respectively. This wave function is not an eigenstate of the ion when spin-orbit coupling is taken into account. However, it can be expanded into the multi-electron eigenstates of the ion with the notation Ψ_{J,m_J} , where J is the total angular momentum quantum number and m_J is its projection quantum number.

This non-stationary state evolves in time according to [21]

$$\begin{aligned} \phi(t) &= \sqrt{\frac{2}{3}}e^{-i\omega_{3/2}t}\Psi_{J=3/2,m_J=1/2} - \sqrt{\frac{1}{3}}e^{-i\omega_{1/2}t}\Psi_{J=1/2,m_J=1/2} \\ &= \frac{\sqrt{2}}{3}\left(e^{-i\omega_{3/2}t} - e^{-i\omega_{1/2}t}\right)\Phi_{1,1,-1/2} + \left(\frac{2}{3}e^{-i\omega_{3/2}t} + \frac{1}{3}e^{-i\omega_{1/2}t}\right)\Phi_{1,0,+1/2}, \end{aligned} \quad (2)$$

where $\Delta\omega = \omega_{1/2} - \omega_{3/2}$ is related to the energetic separation ΔE_{SO} of the $^2P_{3/2}$ and $^2P_{1/2}$ states through the relation $\Delta\omega = \Delta E_{SO}/\hbar$. Ionization to $\Phi_{1,0,-1/2}$ results in a similar expression where $\Phi_{1,1,-1/2}$ and $\Phi_{1,0,+1/2}$ are replaced by $\Phi_{1,-1,+1/2}$ and $\Phi_{1,0,-1/2}$, respectively. From these formulae, the population dynamics of the hole in the space-fixed basis can be derived [21]:

$$\begin{aligned} P_{m=0} &= \frac{5}{9} + \frac{4}{9}\cos(\Delta\omega t) \\ P_{|m|=1} &= \frac{4}{9}(1 - \cos(\Delta\omega t)). \end{aligned} \quad (3)$$

Consequently, the population of the hole oscillates between the $m = 0$ and the $|m| = 1$ orbitals with the period $T_{SO} = \hbar/\Delta E_{SO}$ (42.7 fs in Ne⁺). In reality the coefficients of the two spin-orbit states in the coherent superposition differ slightly from those in Eq. (3) because of the energetic separation of the final ionic states which results in slightly different

ionization rates for the two channels. Quantitative calculations have been presented in Ref. [7] which validate our simplified model.

Since strong-field ionization is highly sensitive to the electronic structure of the ionizing orbitals, the wave packet motion will modulate the probability of a second ionization step. Two parameters affect the ionization rate of the evolving wave packet: the geometry of the ionized orbital and the energetic separation from the final states, i.e., the ionization energies of the accessible states of the dication. Ionization from an orbital aligned with the field is favored over ionization from a perpendicular orbital. We calculate ionization rates connecting specific electronic configurations expressed in the space-fixed basis, since simple analytical formulae are available [22]. The electronic wave function of the cation at any time is a linear combination of the two (np^5) configurations

$$\begin{array}{ccc}
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ m = \quad 0 \quad +1 \quad -1 \end{array} & (1) \quad \text{and} \quad & \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ 0 \quad +1 \quad -1 \end{array} & (2)
 \end{array} \quad (4)$$

Removing one of the five electrons leads to an electronic configuration of Ne^{2+} that we resolve in the basis of electronic eigenstates using angular momentum algebra [23]

$$\begin{array}{rcl}
 \begin{array}{c} \text{---} \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & -\sqrt{\frac{1}{3}}^1S_0 + \sqrt{\frac{2}{3}}^1D_2 \\
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & ^3P_J \\
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow + \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow - \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & ^3P_J \\
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow - \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & ^1D_2 \\
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & ^1D_2 \\
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & ^3P_J \\
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow + \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow - \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & ^3P_J \\
 \begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow - \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array} & = & \sqrt{\frac{2}{3}}^1S_0 + \sqrt{\frac{1}{3}}^1D_2 \\
 \text{etc.} & &
 \end{array}$$

The relevant electronic states of Ne^{2+} , i.e. 3P_J , 1D_2 and 1S_0 , and their energetic separations are indicated in Fig. 1. We calculate ionization rates using a kinetic model based on the tunnel ionization rates of the orbitals and their time-dependent occupation amplitude. We calculate the ionization rate of configurations (1) and (2) as a sum of all possible ionization pathways and weight them according to the population of each configuration. The ionization rate of Ne^+ in a coherent superposition state is thus calculated as

$$\Gamma(\Delta t) = \sum_{i=1-5} \sum_{j=1-3} \left(P_{m=0}(\Delta t) |c_{ij}|^2 \Gamma_{ij} + P_{|m|=1}(\Delta t) |c_{ij}|^2 \Gamma_{ij} \right), \quad (5)$$

where the first sum runs over the five valence electrons that can be removed during ionization and the second sum runs over the accessible electronic states of the dication. The c_{ij} are the expansion coefficients of the electronic configuration accessed by tunnel ionization into the set of electronic states given in Eq. (4). Γ_{ij} is the tunnel-ionization rate for removing electron i and accessing the electronic state j of the dication (3P_J , 1D_2 or 1S_0).

We first consider the case of parallel polarizations of pump and probe laser fields. The calculated double ion yield as a function of the delay between the two laser pulses is represented in Fig. 2a. The total double ion yield (full line) is found to peak at delays corresponding to half-integer multiples of the wave packet (spin-orbit) period. A

decomposition of the total yield into the partial yields from the $m = 0$ and $m = \pm 1$ orbitals (dashed and dotted lines, respectively) shows that the modulation is dominated by the contribution from the $m = 0$ orbital. At half-integer multiples of the period, the hole that was created by tunnel ionization in $m = 0$ has moved to the $m = \pm 1$ orbitals according to Eq. (3). Thus, the population of the $m = 0$ orbital has increased from 1 to $1+8/9$. Based on this effect alone, we would expect a modulation of ~ 2 in the ionization yield. The calculation however shows a modulation of the $m = 0$ yield of 6.4 (peak/valley). This is higher than what the population dynamics alone can explain. The higher modulation depth arises because the accessibility of the ionic states also varies in time as the occupation of the orbitals changes. At integer multiples of the delay, the hole is located in the $m = 0$ orbital. Thus, the second ionization step is suppressed, because removing the second electron from the $m = 0$ orbital necessarily leads to the singlet states of the cation that lie more than 3 eV above the triplet ground state. This principle is analogous to Koopman's correlations in single-photon ionization and should be generally observable in strong-field ionization.

Fig. 2b shows the case of perpendicularly polarized pump and probe pulses. The ionization pulse is polarized in the vertical direction (z) and thus still prepares a wave packet as shown in Fig. 1. The probe step preferentially removes an electron from the p_x orbital lying along its polarization direction (x). At integer multiples of the spin-orbit period, ionization from p_x leaves the dication in its 3P_J ground state and is favored by the double occupancy of the orbital. At half-integer multiples of T_{SO} the population of p_x decreases to $3/2$, explaining that the ionization rate decreases. The modulation depth of the ionization rate from p_x is 1.6 (peak/valley), again larger than the ratio $4/3$ expected from the population dynamics. This effect also results from the accessibility of the dication states.

The electronic dynamics triggered by the first ionization step should also be reflected in the momentum distributions of the electron removed in the second ionization step. Having calculated the time-dependent populations of the orbitals, we now predict the momentum distributions of the second electron using a very simple model. It has been shown in Refs. [24, 14] that the continuum electron wave packet in the direction perpendicular to the ionizing laser field is well approximated by the bound momentum space orbital Ψ_b (i.e. the Fourier transform of the spatial orbital) filtered by a Gaussian function that accounts for the suppression of large linear momenta in the tunneling process

$$\Psi_{c,\perp} = \Psi_{b,\perp} \exp\left(-\frac{\sqrt{I_p}}{\sqrt{2}E} p_{\perp}^2\right), \quad (6)$$

where E is the laser electric field amplitude and $p_{\perp}$ is the perpendicular component of the electron momentum.

Using the calculated temporal evolution of the partial ionization rates, we can thus predict the time-dependent shape of the electron momentum distribution as

$$D_{\perp}(\Delta t) = \Gamma_{m=0}(\Delta t) D_{\perp,m=0} + \Gamma_{m=1}(\Delta t) D_{\perp,m=1}, \quad (7)$$

where $D_{\perp,m} = |\Psi_{c,\perp,m}|^2$ is the momentum distribution obtained from ionization of a p_m orbital of Ne^+ . Figure 3 shows the calculated lateral electron momentum distributions for ionization of Ne^+ at time delays nT_{SO} (a) and $[(2n+1)/2]T_{SO}$ (b). The full lines represent

the total distribution and the dashed and dotted lines represent the contributions from the $m = 0$ and $|m| = 1$ orbitals, respectively. As a result of the cylindrical symmetry, the electron momentum distributions have circular symmetry and are fully characterized by a one-dimensional cut through the origin. At integer multiples of the wave packet period (a), the momentum distribution is broad, since $m = 0$ and $m = 1$ orbitals contribute with comparable importance. At half-integer multiples of the delay (b), the distribution becomes narrower as the ionization from the $m = 0$ orbital dominates.

So far, we have shown how electronic dynamics induced by the first ionization step can be probed and imaged using the second step. Every pump-probe experiment also offers an opportunity for quantum control which is particularly interesting in the present case. We have shown how the occupation of orbitals affects the accessible states of the dication. At half-integer multiples of the wave packet period, the 3P_J ground state of the dication is accessible through the preferred ionization from $m = 0$ and is thus the main product of the second ionization step. At integer multiples of the period, the 3P_J states are only accessible through $m = 1$ ionization, whereas the 1D_2 and 1S_0 states are accessible through $m = 0$ ionization - at the cost of a higher ionization energy. This results in a preferred ionization into the singlet states.

The time-dependent yield of Ne^{2+} in triplet or singlet states is represented in Fig. 4. The full line represents the total yield of Ne^{2+} which is identical to that shown in Fig. 2(a). The dashed and dotted lines represent the partial yields of Ne^{2+} in one of the 3P_J or one of the singlet ($^1D_2, ^1S_0$) states, respectively. In addition to the electronic state of the cation, the spin state of the ejected electron pair can also be controlled. Total spin has to be conserved as long as the interaction with the magnetic field of the laser pulses can be neglected. This situation applies for moderate intensities below $10^{17} \text{W}/\text{cm}^2$. Thus, control over the final state of the dication implies control over the spin state of the electron pair. Thus, it is possible to control the entanglement of the electrons ejected in sequential double ionization.

In conclusion, we have shown that sequential strong-field ionization by a pair of ultrashort infrared laser pulses can be used to image electronic dynamics initiated by the first laser pulse. Using the rare gas atoms as an example, we have shown how electronic dynamics influences the ionization rate and momentum distributions of the second ionization step. Spin-orbit dynamics in neon and argon will be readily accessible using 800 nm pulses of less than 10 femtoseconds. In krypton and xenon, the spin-orbit dynamics is faster (6.2 and 3.2 fs, respectively). As pointed out in Ref. [7], this leads to a low degree of coherence after the ionization pulse because the optical cycle period is incommensurate with the electronic dynamics. This limitation can be overcome by using even shorter laser pulses in which a single optical cycle dominates [3] or by synchronizing the optical cycle period to the electronic dynamics that is being prepared. For example, when xenon is tunnel ionized in a laser field of 1900 nm, the half-cycle period matches the internal dynamics of Xe^+ which allows the preparation of a highly coherent state even in a multicycle pulse. A pair of such pulses could then be used to perform the measurements described in this article. Such an experiment would be a highly nonlinear variant of the classical Ramsey fringe experiment.

Looking forward, it appears that strong-field ionization will become an attractive

method to prepare attosecond dynamics. The nonlinearity of the process enforces temporal confinement which results in the formation of the ion in a coherent superposition of multiple electronic states. Therefore, attosecond electronic dynamics can be readily prepared. We have used spin-orbit dynamics to illustrate a general phenomenon: after ionization the cation is usually in a non-stationary state [4]. Electron correlation drives the rearrangement of the electronic structure of the ionized system, providing access to their characterization. The most general method for probing these dynamics will use an isolated attosecond pulse in combination with either photoelectron detection [25] or transient absorption [26].

We thank David Villeneuve, André Staudte and Avner Fleischer for discussions. H.J.W. acknowledges support from the Swiss National Science Foundation under grant PP00P2.128274.

Note added: The method proposed in this article has recently been realized experimentally and extended to molecules [27].

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Figure 1. Illustration of the proposed pump-probe experiment. A neon atom is strong-field ionized using a few-fs infrared laser pulse, preparing Ne⁺ in a coherent superposition of its two lowest fine structure levels. The electron hole subsequently rearranges between the atomic p orbitals, as illustrated through the red contour plots of its density at different time delays. A second delayed infrared laser pulse ionizes Ne⁺ to Ne²⁺. The second ionization step is suppressed at integer multiples of the wave-packet period because ionization accesses the excited singlet states of Ne²⁺.

Figure 2. Calculated ionization rates of Ne^+ at an intensity of 5.10^{15} W/cm^2 as a function of the delay after the first ionization pulse for the case of a probe pulse polarized parallel (a) or perpendicular (b) to the pump pulse. The full lines represent the total ionization rates and the broken lines represent the partial rates coming from individual orbitals. Panel (a) shows partial ionization rates from $m = 0$ (dashed line) and $m = \pm 1$ (dotted line). Panel (b) shows partial rates from all three p orbitals since they are no longer equivalent in this geometry.

Figure 3. Calculated lateral momentum distribution of electrons tunnel ionized by a laser field of intensity 5.10^{15} W/cm^2 from Ne^+ at delays Δt after the pump pulse. At delays corresponding to integer multiples of the spin-orbit period, ionization from $|m| = 1$ significantly contributes to and broadens the total electron distribution as shown in panel (a). At half-integer delays, ionization from $m = 0$ dominates, resulting in a narrower momentum distribution.

Figure 4. Calculated ionization rate of Ne^+ at an intensity of 5.10^{15} W/cm^2 as a function of the delay after the first ionization pulse for parallel polarizations of pump and probe pulses. The full line shows the total ionization rate which is the same as in Fig. 2a. The dashed line represents ionization into the $^3\text{P}_J$ ground state of Ne^{2+} which is accompanied by the formation of an electron pair in a triplet state. The dotted line represents ionization to the $^1\text{D}_2$ or $^1\text{S}_0$ state of Ne^{2+} and the formation of a singlet electron pair.