Attosecond quantum-beat spectroscopy in helium

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Abstract
The evolution of electron wavepackets determines the course of many physical and chemical phenomena, and attosecond spectroscopy aims to measure and control such dynamics in real time. Here, we investigate radial electron wavepacket motion in helium by using an XUV attosecond pulse train to prepare a coherent superposition of excited states and a delayed femtosecond IR pulse to ionize them. Quantum-beat signals observed in the high resolution photoelectron spectrogram allow us to follow the field-free evolution of the bound electron wavepacket and determine the time-dependent ionization dynamics of the low-lying 2p state.

Keywords: attosecond, femtosecond, wavepacket, quantum beat, photoelectron, helium

Wavepackets form a connection between quantum mechanics and the classical concept of an electron and nuclear motion in atoms and molecules. Due to their importance in physics, chemistry and biology, wavepackets have been studied extensively by both theorists and experimentalists over the past several decades [1, 2]. Most studies of electronic wavepackets have focused on high Rydberg wavepackets composed of closely spaced electronic states which have dynamics timescales of hundreds of femtoseconds or of picoseconds [3–5]. This was mainly because of the lack of short light pulses with enough bandwidth to create and detect fast evolving coherent superpositions of multiple states spanning a wide energy range. With the availability of attosecond pulse trains [6] and single isolated attosecond pulses [7], which can have a bandwidth of nearly a hundred electron volts, it is now possible to create wavepackets composed of excited states [8–13], valence states [14], and even core electronic states [15], and study their dynamics on attosecond timescales.

Due to its simplicity and ease of modeling, the helium atom forms a convenient test bed for the study of electron wavepacket dynamics. Here, we use extreme ultraviolet (XUV) high harmonics in attosecond pulse trains to excite a radial wavepacket of 2p, 7p, 8p, ... states in helium and study its dynamics with attosecond resolution. We use a delayed near-infrared (IR) pulse to photoionize excited states and measure photoelectrons as a function of XUV-IR time delay. We focus on interferences between ionization paths which are related to the quantum beats of the excited electron wavepacket and coupling effects induced by the ionizing IR pulse. Most prior studies have focused on short time evolution [10, 11, 16–18] or study slow beats over long timescales [19, 20], except a recent study of anisotropic emission in quantum-beat spectroscopy [21]. Here we report unique investigations of field-free dynamics spanning hundreds of femtoseconds with attosecond time resolution and high photoelectron energy resolution. We resolve both the slow wavepacket beating between high Rydberg states and the fast 2p–np state beating. From this information we deduce the detailed energy and time dependence of the ionization amplitude of the low-lying 2p state in the wavepacket, which has not been explored in previous studies. This approach yields new insight into the complex ionization dynamics of the XUV excited attosecond wavepacket.
The experimental setup is described in [22]. Briefly, it consists of a Ti:sapphire laser amplifier, which produces 45 fs (full-width at half maximum), 2 mJ energy IR pulses at a central wavelength of 785 nm. The laser beam is divided into two arms. In one arm, the laser pulses are focused into a Xe gas filled waveguide to generate an attosecond pulse train consisting predominantly of 13th and 15th harmonics. After using an aluminum filter to remove residual IR, the high harmonics are focused onto an effusive helium gas jet where they create excited 'np' states of the helium atom, forming a wavepacket which can be written as (in atomic units)

\[ \psi(\mathbf{r}, t) = \sum_n \psi_n(\mathbf{r}) e^{-iE_n t} \]  

where \( l = 1 \) corresponds to p-states and from the energies of the harmonics we know that the sum is over \( n = 2 \) (from HH 13) and \( n = 7, 8 \) (from HH 15), as shown in figure 1 (c).

In the other arm of the setup, an IR pulse is time delayed and after passing through a lens it is recombined with the high harmonic beam to propagate collinearly. The XUV and IR pulses have the same polarization. The IR pulse ionizes excited helium atoms in the focal region at an intensity of \( \sim 5 \times 10^{13} \) W cm\(^{-2}\) and the photoelectrons produced are imaged using a velocity map imaging setup [23]. The XUV-IR time delay is varied over a large range from \(-50 \) fs to 880 fs in 65 as steps, where positive delay corresponds to IR arriving after the XUV pulse. The interferometer was passively stabilized by accounting for and eliminating the sources of vibration and drift. The stability was verified through a long-term observation of the optical fringe pattern generated by interference of IR pulses propagating in the two arms. Time delay over a large range with 65 as resolution is achieved using a digital piezo translator (Queensgate DPT-C), which can repeatably move in 1 nm steps over a range of 16 microns, in conjunction with a stepper motor (CVI Melles-Griot) for longer travel. The photoelectron data is processed by measuring the electron yield in a narrow window along the XUV and IR polarization direction and this yield is plotted as a function of electron energy and time delay to obtain a photoelectron spectrogram.

In the raw photoelectron spectrogram shown in figure 1(a), we clearly observe oscillations in the electron yield as a function of time delay. As we discuss below, the oscillation frequency changes with the electron energy, corresponding to presence of different interference channels. In order to understand the origin of these oscillations we Fourier transform the raw data. The fast Fourier transform (FFT) in figure 1(b) shows clear peaks corresponding to specific quantum-beat signals. We observe two dominant peaks which occur at an oscillation frequency of 3.08 eV and 3.14 eV. An oscillation frequency of 3.16 eV corresponds to \( 2\omega_{IR} \) or half the IR optical cycle period. The peak at 3.08 eV is consistent with a beat occurring due to the interference of photoelectrons from three IR photon ionization of the 2p state
and one IR photon ionization of the 7p state (figure 1 (c)). The peak at 3.14 eV is consistent with interference of $2p + 3\omega_{IR}$ and $8p + 1\omega_{IR}$. The locations of these peaks in energy is also consistent with the energy locations of the 2p, 7p and 8p states. The peaks very close to the 2p–7p and the 2p–8p peaks are Fourier transform artifacts, though the peak near 3.18 eV may arise from 2p–9p interference. Since 2p–7p and 2p–8p interferences have a dominant contribution, we also expect a slow quantum beat of ~65 fs corresponding to the energy gap between 7p and 8p states.

In order to focus on specific channels with greater detail, we remove the noise and the DC value of the electron yield by bandpass filtering with a window around prominent peaks in the FFT shown in figure 1(b). The photoelectron spectrogram resulting from the Fourier bandpass filtering is shown in figure 2(a). Since the data in figure 2(a) are for a time-delay scan of about 1 ps, the features and variations on attosecond timescales are not visible. However, we see clear beats which occur with a period of about 65 fs, that agrees well with the energy difference between 7p and 8p states discussed above. Though this plot shows a scan of a time-delay range that includes the temporal overlap region between the XUV and IR pulses, in the following we focus only on the dynamics in the non-overlap region since we are interested in field-free wavepacket dynamics.

Figure 2(b) shows the same experimental data as in figure 2(a) but zoomed in to show fine features in the range of 50 fs to 120 fs. First, we see fast oscillations in the electron yield as a function of time delay, and these oscillations occur with a period of about 1.3 fs, which is half an IR optical cycle (frequency $2\omega_{IR}$). More interestingly, we see that the oscillatory behavior is not the same at all photoelectron energies. There appears to be a slight variation in oscillation frequency at different energies between 1.1 eV and 1.5 eV. This results in these oscillations going out of phase and coming into phase, as indicated in figure 2(b). Also shown in figure 2(b) are the expected central energies of photoelectrons arising from IR induced ionization of unperturbed XUV excited 2p, 7p and 8p states.

We also performed time-dependent Schrödinger equation (TDSE) simulations to model the wavepacket dynamics observed in our experiments with a single-active-electron model potential [24]. Using XUV and IR parameters similar to those of the experiments, we numerically obtained photoelectron spectrograms [25, 26] that also exhibit fast $2\omega_{IR}$ oscillations along with dephasing and rephasing of beat signals in good agreement with the experimental results. In figure 3(a) we plot the bandpass filtered simulation spectrogram zoomed in to show fine features. In figure 3(b) we plot the Fourier transform of the simulated spectrogram. The peaks corresponding to the quantum beats between 2p–6p, 2p–7p and 2p–8p stand out distinctly. The comparison with experimental figure 1(b) is good except that the peak due to 2p–6p interference is indistinguishable in the experiment, probably due to small differences between simulation and experimental parameters stemming from the uncertainties in exact widths and amplitudes of XUV harmonics, uncertainties in the IR intensity and focal volume averaging effects. In the simulation (figure 3(b)), we observe a secondary peak around 1.2 eV photoelectron energy below the 2p–7p and 2p–8p
peaks, with a minimum in signal levels around 1.25 eV photoelectron energy. This secondary peak feature is also seen in the experimental data (figure 1(b)) at 1.15 eV photoelectron energy.

In order to quantitatively compare the quantum-beat signals in the experiment and simulation, in figure 4(a) we show photoelectron energy lineouts of figure 3(b) taken at the frequency of the 2p–7p and 2p–8p beats along with the corresponding lineouts of the experimental data from figure 1(b). The locations of the main peaks in experimental and simulation lineouts differ by less than about 20 meV, though the main peaks agree well. (b) The 2p ionization amplitude (convolved with spectral amplitudes of light fields) extracted from the experimental data and simulation. Experimental results are also convoluted with our spectrometer resolution. (c) Simulation results for the 2p–7p and 2p–8p beat amplitudes for the case where np and nf states near 7p and 8p are removed, leading to the disappearance of the secondary peaks seen near 1.2 eV in (a).
ionization matrix elements for various excited states composing the wavepacket.

The IR pulse induced ionization of the 2p, 7p, 8p states leads to interferences in the continuum, and various oscillatory components of the time and energy dependent electron yield can be written as

\[ I_{\text{nw}}(\epsilon, \tau) = A_{\text{np}}(\epsilon, \tau)A_{\text{np}}(\epsilon, \tau)\cos(\omega_{\text{np},\text{np}}\tau + \phi_{\text{np},\text{np}}) \]  

(2)

where \( A_{\text{np}}(\epsilon, \tau) \) and \( A_{\text{np}}(\epsilon, \tau) \) are amplitudes of the ionization matrix element (henceforth referred to as ionization amplitudes) from the interfering \( mp \) and \( np \) states, which depend on photoelectron energy \( \epsilon \) and slowly vary with time delay \( \tau \). \( \omega_{\text{np},\text{np}} \) represents the energy difference between the \( mp \) and \( np \) states (in atomic units), \( \tau \) is the time delay between XUV and IR pulses and \( \phi_{\text{np},\text{np}} \) is the phase difference between the ionization matrix elements from the \( mp \) and \( np \) states. The spectral amplitude and phase of the XUV and IR pulses, which could in principle be obtained separately, have been absorbed here into \( A_{\text{np}} \) and \( \phi_{\text{np},\text{np}} \). The lineouts shown in figure 4(a) are thus a measure of the amplitude of two dominant \( I_{\text{nw}}(\epsilon, \tau) \) terms corresponding to products \( A_{2p}A_{7p} \) and \( A_{2p}A_{8p} \). When this information is combined with the amplitude of slow beating between 7p and 8p which gives us \( A_{2p} \), we can extract the individual ionization amplitude for the low-lying 2p state which is not accessible through other methods. It should be noted that, apart from the convolution with the spectral amplitudes of the light fields, the experimental data are also convolved with the resolution of the photoelectron spectrometer. Furthermore, the slow time-delay dependence of the 2p ionization amplitude will be discussed later and is ignored in this analysis. The result of the above exercise for both experimental data and simulation is shown in figure 4(b). The ionization amplitude of 2p also exhibits a double peak structure similar to the Fourier amplitudes, although the amplitude of the secondary lower energy peak in the experimental data is now quite significant compared to the main peak. We discuss the physical origin of the secondary peak below.

During multiphoton above-threshold ionization (ATI) of atoms, new structures and enhancements have been observed in photoelectron peaks [27–29]. These structures have been attributed to field-dressed/ponderomotively shifted states which are resonant with the ground state on the way to the continuum during ionization and are known as Freeman resonances [27]. We believe that the secondary lower energy peak in the ionization amplitude of 2p observed here is due to field-dressed states that are two-photon resonant with the 2p state. From selection rules these states are of \( p \) and \( f \) character. We identify that the \( nf \) and \( np \) states have an almost equal contribution to the secondary peak by removing the \( np \) and \( nf \) states near 7p and 8p in the TDSE simulations. Figure 4(c) shows the results of these simulations for the beats shown in 4(a) with \( np \) and \( nf \) states near 7p and 8p removed. It is clearly seen that the secondary peak near 1.2 eV almost completely disappears, indicating that these states are responsible for the observed secondary peak. In addition, we find that Freeman resonances corresponding to \( n = 6 \) states play a dominant role in creation of this structure in 2p ionization amplitude.

We now focus our attention on studying the time-dependent dynamics of the XUV excited wavepacket. In previous studies [3–5], it has been shown that when high lying Rydberg wavepackets are excited they periodically move close to the core and back. Ionization mainly occurs when the wavepacket is close to the core because the overlap with continuum wavefunctions is larger. This is well known and has been experimentally observed for Rydberg wavepackets [30]. Here, we are interested in the ionization dynamics of the tightly bound portion of the XUV excited wavepacket in a narrow energy window around the low-lying 2p state. We extend the analysis done above where we obtained the energy-dependent ionization amplitude of the 2p state to obtain the time-dependent ionization amplitude corresponding to a narrow energy window around the 2p state. This is done by performing a Fourier transform on the photoelectron spectrum, gating the \( mp–np \) beat peak followed by an inverse Fourier transform to obtain the energy- and delay-dependent products \( A_{2p}(\epsilon, \tau)A_{7p}(\epsilon, \tau) \) and \( A_{2p}(\epsilon, \tau)A_{8p}(\epsilon, \tau) \), from which we obtain \( A_{2p}(\epsilon, \tau) \). Figure 5(a) shows the experimental 2p ionization amplitude as a function of photoelectron energy and time delay. We apply the same procedure to the simulated photoelectron spectrum, and the 2p ionization amplitude obtained is shown in figure 5(b). It should be understood here that the time-dependent 2p ionization amplitude does not refer to a single state but is a measure of the ionization dynamics of the tightly bound portion of the wavepacket with a narrow width around 2p.

The simulation plot, figure 5(b), has a lot more structure than the experimental plot in figure 5(a). This difference is mainly due to the lower energy resolution in the experiment, focal volume averaging effects and the uncertainty in IR intensity and XUV parameters. The overall temporal behavior

![Figure 5](image-url)
of experimental ionization amplitude agrees very well with the TDSE calculation. To see this better, we integrate the data in figure 5 along the photoelectron energy axis and plot them in figure 6(a). The 2p ionization amplitude varies as a function of time delay by nearly a factor of five between maximum and minimum points, which are about 325 fs apart.

The time-dependent ionization amplitude corresponding to an energy window around 2p is intricately tied to the radial motion of the entire wavepacket consisting of 2p, 7p, 8p and higher Rydberg states (whose contributions are not directly apparent in the beat spectrum). At times when the wavepacket is closer to the core, ionization is larger [30]. In figure 6(b), we show the TDSE calculations of the modulus squared radial wavefunction of the XUV excited wavepacket corresponding to delay times of 40 fs and 375 fs. The average radial distances of the wavepacket are also shown. It is apparent from these plots that the wavepacket moves closer to the core at 375 fs, which in turn leads to higher ionization amplitude observed in experiments. This long time scale in the wavepacket motion most likely arises from the presence of other Rydberg states in the excited wavepacket, which do not interfere with the 2p ionization channel in the continuum. It is very interesting that even a low-lying state like 2p shows such a large sensitivity to the radial motion of the wavepacket during ionization. We have thus followed the evolution of a radial wavepacket and measured the effect of radial motion on the ionization probability of wavepacket components around the low-lying 2p state.

In conclusion, we have performed a high resolution attosecond quantum-beat spectroscopy measurement in helium using XUV and IR pulses. The XUV excited wavepacket, predominantly consisting of 2p, 7p and 8p states, was probed by a time delayed IR pulse on a time scale close to a picosecond with attosecond resolution. The photoelectron yield was measured as a function of energy and XUV-IR time delay and beats between the 2p, 7p and 8p states due to interferences between multiple paths to the continuum are clearly observed. Using Fourier analysis, we observed structures in the photoelectron energy dependent ionization amplitude of the 2p state and attributed them to Freeman resonances. Finally, we used a time–frequency analysis technique to extract the time-dependent ionization amplitude of wavepacket components in a narrow window around the low-lying 2p state, which shows a high sensitivity to the radial motion of the wavepacket. Extending these measurements to study electronic wavepackets in molecular systems can yield detailed information about the dynamics of such wavepackets, especially on the interplay between electronic and nuclear degrees of freedom [31].

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References

[1] Gruebele M and Zewail A H 1993 J. Chem. Phys. 98 883–902
[2] Garraway B M and Suominen K A 1995 Rep. Prog. Phys. 58 365
[3] Alber G, Ritsch H and Zoller P 1986 Phys. Rev. A 34 1058–64
[4] Parker J and Stroud C R 1986 Phys. Rev. Lett. 56 716–9
[5] Yeazell J A and Stroud C R Jr 1988 Phys. Rev. Lett. 60 1494–7
[6] Antoine P, L’Huillier A and Lewenstein M 1996 Phys. Rev. Lett. 77 1234–7
[7] Sansone G et al 2006 Science 314 443–6
[8] Johnsson P, Mauritssson J, Remetter T, L’Huillier A and Schafer K J 2007 Phys. Rev. Lett. 99 233001
[9] Choi N N, Jiang T F, Morishita T, Lee M H and Lin C D 2010 Phys. Rev. A 82 013409

Figure 6. (a) Data from figure 5 integrated over photoelectron energies. The experimental and simulated ionization amplitudes for 2p agree very well. (b) Simulation results for the modulus squared radial wavefunction of the XUV excited wavepacket at two different time delays corresponding to low ionization amplitude (40 fs) and high ionization amplitude (375 fs). The average distances $r_{\text{avg}}$ of the radial wavepacket are also shown.
[10] Mauri
tsson J et al 2010 Phys. Rev. Lett. 105 053001
[11] Shivaram N, Timmers H, Tong X M and Sandhu A 2012 Phys. Rev. Lett. 108 193002
[12] Beck A R, Bernhardt B, Warrick E R, Wu M, Chen S, Gaarde M B, Schafer K J, Neumark D M and Leone S R 2014 New J. Phys. 16 113016
[13] Chini M, Wang X, Cheng Y and Chang Z 2014 J. Phys. B: At. Mol. Opt. Phys. 47 124009
[14] Goulielmakis E, Loh Z H, Wirth A, Santra R, Rohringer N, Yakovlev V S, Zherebtsov S, Pfeifer T, Azzeer A M, Kling M F et al 2010 Nature 466 739–43
[15] Neppl S, Ernstorfer R, Bothschafter E M, Cavalieri A L, Menzel D, Barth J V, Krausz F, Kienberger R and Feulner P 2012 Phys. Rev. Lett. 109 087401
[16] Ranitovic P et al 2010 New J. Phys. 12 013008
[17] Kim K T, Ko D H, Park J, Choi N N, Kim C M, Ishikawa K L, Lee J and Nam C H 2012 Phys. Rev. Lett. 108 093001
[18] Shivaram N, Timmers H, Tong X M and Sandhu A 2013 Chem. Phys. 414 139 – 148
[19] Verlet J R R, Stavros V G, Minns R S and Fielding H H 2003 J. Phys. B: At. Mol. Opt. Phys. 36 3683
[20] Geiseler H, Rottke H, Steinmeyer G and Sandner W 2011 Phys. Rev. A 84 033424
[21] Lucchini M, Ludwig A, Zimmermann T, Kasmi L, Herrmann J, Scrinzi A, Landsman A S, Gallmann L and Keller U 2015 Phys. Rev. A 91 063406
[22] Shivaram N, Roberts A, Xu L and Sandhu A 2010 Opt. Lett. 35 3312–4
[23] Eppink A T J B and Parker D H 1997 Rev. Sci. Instrum. 68 3477–84
[24] Tong X M and Lin C D 2005 J. Phys. B: At. Mol. Opt. Phys. 38 2593
[25] Tong X M, Ranitovic P, Cocke C L and Toshima N 2010 Phys. Rev. A 81 021404
[26] Tong X M and Toshima N 2010 Phys. Rev. A 81 063403
[27] Freeman R R, Bucksbaum P H, Milchberg H, Darack S, Schumacher D and Geusic M E 1987 Phys. Rev. Lett. 59 1092–5
[28] Nandor M J, Walker M A, Woerkom L D V and Muller H G 1999 Phys. Rev. A 60 R1771–4
[29] Potvliege R M and Vučič S 2009 J. Phys. B: At. Mol. Opt. Phys. 42 055603
[30] Ten Wolde A, Noordam L, Lagendijk A and van Den Heuvel H V L 1988 Phys. Rev. Lett. 61 2099
[31] Ranitovic P et al 2014 Proc. Natl Acad. Sci. USA 111 912–7