Inter-shell correlation and time delay measurement in Ar

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Abstract

In a recent Letter [Phys. Rev. Lett. **106**, 143002 (2011)] Klünder *et al* reported their measurement of the time delay difference between electrons photoionized from the $3s^2$ and $3p^6$ shells in argon in the photon energy range from 32 to 42 eV. These measurements, involving two-photon ionization processes, were compared with Wigner time delays obtained from Hartree-Fock calculations. In this Brief Report, we also include the influence of correlation effects which modify strongly photoionization process in Ar near the 3s threshold. We also discuss possible reasons for the observed discrepancy between the measurement and the refined theory.

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The concept of time delay was introduced by Wigner [1] in the context of s-wave quantum scattering. An extension to the total scattering amplitude leads to the concept of angular time delay $\tau_{\ell} = 2d\eta_{\ell}/dE$, where η_{ℓ} is the phase shift in the ℓ th partial wave. One can also define a transmission group delay ϕ' , where ϕ is the phase of the complex transmission amplitude $T(k) = t(k) \exp[i\phi(k)]$ [2]. With some modifications, similar concepts apply to photoionization [3]. As compared to particle scattering, the Wigner time delay should be halved as photoionization does not involve ingoing waves. The group delay of the outgoing electron wave packet can be defined as energy derivative of the phase of the complex photoionization matrix element $D(E) = d(E) \exp[i\delta(E)]$. In general, photoionization may involve several strongly interacting channels. Therefore, δ cannot be reduced to a phase shift η_{ℓ} in some particular ℓ th partial wave. Thus, the photoionization group delay is a more general concept than the Wigner time delay. Nevertheless, in some special cases, the Wigner time delay can be conveniently used to characterize delay in photoemission. One such case is valence shell photoionization of Ne in the XUV range |3, 4|. Here there is no considerable coupling between the $2s \to \epsilon p$ and $2p \to \epsilon s$ or ϵd channels and ϵd is strongly dominant over $\epsilon s.$

However, the case of valence shell photoionization of Ar, considered by Klünder *et al* [5], is very different. The 3s photoionization is radically modified by strong inter-shell correlation with 3p [6]. In result, the photoionization cross-section σ_{3s} goes through a deep "Cooper" minimum at the photon energy $\omega \simeq 40$ eV, which is absent in the independent electron Hartree-Fock (HF) model. It is precisely this photon energy range where the measurement of Klünder *et al* [5] was performed (harmonics 22 to 26 of a 800 nm Ti-sapphire laser). It is for this reason that the relative time delay $\tau_{3s} - \tau_{3p}$ cannot be attributed solely to the difference of the Wigner time delays in the dominant $3s \to \epsilon p$ and $3p \to \epsilon d$ partial waves, as was done by Klünder *et al* [5].

We illustrate these findings in Fig. 1. On the top panel, we plot σ_{3s} calculated in the HF and random-phase (RPA) approximations, the latter taking full account of the inter-shell correlation with 3p. The most recent experimental data are from Möbus *et al* [7]. On the middle panel, we plot the correlation-induced phase shifts of the dipole matrix elements $\delta_{3s} = \arg[D_{3s}(\omega + \epsilon_{3s})]$ and $\delta_{3p} = \arg[D_{3p}(\omega + \epsilon_{3p})]$ from the same RPA calculation. On the bottom panel, we plot the time delay difference $\tau_{3s} - \tau_{3p} = \frac{d}{dE} \left[\eta_{\ell=1}(\omega + \epsilon_{3s}) - \eta_{\ell=2}(\omega + \epsilon_{3p}) \right]$ calculated with elastic scattering phases only (marked HF) and from the full phase of the dipole matrix elements including correlation $\frac{d}{dE} \left[\delta_{3s}(E) - \delta_{3p}(E) \right]$ (marked RPA). Due to a rapid variation of the phase of D_{3s} , especially near the "Cooper" minimum, the RPA correction is substantial.



FIG. 1: Top panel: Photoionization cross-section σ_{3s} calculated in the HF and random-phase (RPA) approximations is compared with experimental data from Möbus *et al* [7]. Middle panel: Correlation-induced phase shifts for the 3s and 3p dipole matrix elements. Bottom panel: Comparison between the measured delay differences $\tau_{3s} - \tau_{3p}$ between the 3s and 3p shells (crosses) with delays obtained by Klünder *et al* [5] using HF (dashed) and RPAE (solid) single-photon ionization phases. Also shown is the delay expected for one-photon ionization with and without correlation (solid and dashed red line) and the laser driven continuum-continuum transition (blue line)

In the experiment of Klünder *et al* [5], the phase information is obtained through an interference between two-photon processes, one with absorption of a harmonic photon and an IR laser photon, the second with absorption of the next harmonic and emission of an IR photon [8]. The interference signal depends on the difference in phase between both two-photon ionization amplitudes [9]. Using the asymptotic form of the continuum matrix elements involved in the two-photon process, the following expression for the amplitude corresponding to two-photon absorption can be derived [11]:

$$M_a^{(2)}(k) \propto \underbrace{e^{i\eta_1(k_a)}}_{(\mathrm{I})} \times \underbrace{\left(\frac{i}{k_a - k}\right)^{iz} \frac{(2k_a)^{\frac{i}{k_a}}}{(2k)^{\frac{i}{k}}} \Gamma(2 + iz)}_{(\mathrm{II})} . \tag{1}$$

Here k and k_a denote the wave numbers of the final and intermediate states respectively,

 $z = 1/k_a - 1/k$ and $\Gamma(z)$ is the complex Gamma function [12]. The first phase term (I) is the phase of the corresponding one-photon ionization which was equated in [5] to the elastic scattering phase obtained from the HF model [10]. We argue presently that it is the full phase of the corresponding dipole matrix element δ_{3s} or δ_{3p} , but not only its elastic scattering part, should be used in Eq. (1). The phase of term (II) can be assigned to the laser-driven transition connecting the intermediate and final states in the presence of the long-range Coulomb potential. On the bottom panel of Fig. 1, the time delay due to the influence of the laser-driven transitions is indicated by the blue line. The black lines in the same figure represent the sum of the two contributions, with (solid) and without (dashed) correlation effects. The experimental points, shown by the crosses, deviate from the black solid line.

We now discuss possible reasons for the discrepancy. Our calculation of the influence of the dressing by the IR laser field is approximate. It only uses the asymptotic form of the continuum wave functions (both in the final and intermediate states), thereby neglecting the effect of the core. This approximation should be tested against theoretical calculations, and especially in a region where correlation effects are important. We also neglect the influence of the two-photon processes where the IR photon is absorbed (or emitted) first [8]. The corresponding matrix elements are usually small, except possibly close to a minimum of the cross section, where the other process, usually dominant, is strongly reduced.

In conclusion, the results shown in Fig. 1 point out to the need for explicit time-dependent calculations, which would account for many-electron correlation and include not only one-photon but also two-photon ionization. Our results also demonstrate the potential of the experimental tools using single attosecond pulses [3] or attosecond pulse trains [5]. These tools now enable one to measure atomic and molecular transitions, more specifically, quantum phases and phase variation, i.e. group delays, which could not be accessed previously.

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