Inter-shell correlation-induced time delay in atomic photoionization

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(Dated: April 10, 2018)

We predict an observable Wigner time delay in outer atomic shell photoionization near inner shell thresholds. The near-threshold increase of time delay is caused by inter-shell correlation and serves as a sensitive probe of this effect. The time delay increase is present even when the inner and outer shell thresholds are hundreds of electron volts apart. We illustrate this observation by several prototypical examples in noble gas atoms from Ne to Kr. In our study, we employ the random phase approximation with exchange (RPAE) and its relativistic generalization RRPA. We also support our findings by a simplified, yet quite insightful, treatment within the lowest order perturbation theory.

PACS numbers: 32.80.Aa 32.80.Fb 32.80.RM 32.80.Zb 42.50.Hz

I. INTRODUCTION

The effect of inter-shell correlation is an established phenomenon in atomic photoionization. This effect manifests itself particularly clearly in valence subshells of noble gas atoms where it can be accounted for accurately within the random phase approximation with exchange (RPAE) [1] and its relativistic analogue, the relativistic random-phase approximation (RRPA) [2, 3]. Correlation of the outer atomic shell with its inner counterparts is known to be weaker as the corresponding thresholds can be separated by hundreds of electron volts [4]. The discrete spectrum below the inner shell threshold manifests itself by series of auto-ionization resonances in the outer shell photoionization cross-section [5]. However, the outer shell photoionization cross-section can remain relatively flat and unaffected immediately above the inner shell threshold. This is so because the inter-electron Coulomb interaction that drives the inter-shell correlation is weak in atomic shells that are so wide apart.

At the same time, the opening of the inner shell at a sufficiently large photon energy can add a sizable phase shift to the photoionization amplitude of the outer shell even though the modulus of the amplitude is only changed slightly. A rapid change of the phase occurs in a narrow span of several electron volts and the energy derivative of the phase is large. When this derivative is converted to the time delay by the Wigner formula [6]

\[ \tau_W = \frac{\partial \arg f(\epsilon)}{\partial \epsilon} = \text{Im} \frac{f'(\epsilon)}{f(\epsilon)} \]  

it is translated into a measurable quantity of the order of 10 as (1 as = $10^{-18}$ s). This time delay becomes a sensitive probe of inter-shell correlation in a situation where measurement of the total photoionization cross-section of the outer shell brings little evidence of this correlation. We note that modern experiments can detect photoemission time delay with a sub-attosecond precision [7] and attosecond streaking measurements can now be expanded to the soft-x-ray range up to 350 eV [8].

We illustrate this effect by considering several prototypical examples in inner and outer shells of noble gas atoms. We employ the RPAE methodology as described in [9] and its relativistic counterpart RRPA [2, 3]. We intentionally leave out the question of the probe field and associated effect of the laser-Coulomb coupling which modifies the atomic time delay as

\[ \tau_a = \tau_W + \tau_{CLC} \]  

The CLC, known also as continuum-continuum (CC) correction, is hardly changed from atom to atom, and a hydrogenic approximation for this correction can be readily employed [10, 11]. In addition, at such large photoelectron energies, this correction should be vanishingly small.

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So in the following we concentrate solely on the Wigner component of the time-delay $\tau_W$. Atomic units are used throughout the paper unless otherwise specified. One atomic unit of time is equal to 24.2 as and 1 atomic unit of energy is equal to 2 Ry or 27.2 eV.

II. THEORY

A. Random phase approximation

The random phase approximation was first applied to valence shell photoionization in noble gas atoms some forty years ago [12]. Since then, it became a standard technique to account for inter-shell correlation in valence shell photoionization in these atoms (see [1] and references therein). It had been generalized for inner shell photoionization by adopting experimental ionization thresholds and including the lifetime of the inner vacancy due to its Auger decay. These generalizations are collectively termed GRPAE [13]. The RPAE [14] and RRPA [15] had been previously employed to evaluate the Wigner time delay in valence and inner shells of noble gas atoms. Therefore we describe the theory of these methods only briefly.

We adopt the notation of [14] and write the (nonrelativistic) amplitude of photoionization from a bound state $i$ to an ingoing scattering state defined by the photoelectron momentum $k$ as

$$f_{n,l_i}(k) \equiv \langle \psi_{k}^{(-)} | \hat{z} | \phi_i \rangle \propto \sum_{l_{m}=l_{m_1}} e^{ih_k(k)} \int \hat{Y}_{lm}(\hat{k}) \prod_{j} \left( \begin{array}{c} l_i \ 1 \ 0 \\ -m \ 0 \ m \end{array} \right) d_{ik} \right) \propto \langle kl || n_i l_i \rangle \quad (3)$$

We consider the case of linearly polarized incident photons whose polarization direction is taken as the quantization $\hat{z}$ axis. The proportionality constant depends on the normalization of the final-state scattering wave function. The reduced dipole matrix element, stripped of all the angular momentum projections, is defined as

$$(kl||n_ii_i) = \hat{l}_i \left( \begin{array}{c} l \ 1 \ 0 \\ -m \ 0 \ m \end{array} \right) \int r^2 dr R_{kl}(r) R_{n_ii_i}(r) , \quad (4)$$

where we use a shortcut, $\hat{l} = \sqrt{2l+1}$. Equations (3) and (4) employ the length gauge of the electromagnetic interaction. The analogous expressions in the velocity gauge contain the $\nabla_z$ and $\partial/\partial r$ operators, respectively.

We note that for two competing ionization channels $l = l_i \pm 1$, the phase of the amplitude (3) depends on the direction of the photoelectron $\hat{k}$. In what follows, we restrict our calculations to the polarization direction $\hat{k}||\hat{z}$.

We consider the inter-shell correlation which connects the transition in the outer shell $i \rightarrow k$ with the inner shell transition $j \rightarrow p$. The correlation-affected outer shell amplitude is expressed by the same Eq. (3) in which the reduced dipole matrix element $d_{ik}$ is substituted with the solution of the integral equation:

$$D_{ik}(\omega) = d_{ik} + \frac{1}{3} \sum_p \frac{D_{jp} V_{ik,jp}}{\omega + \epsilon_j - \epsilon_p + i\delta} . \quad (5)$$

Here $d_{ik}$ is a dipole matrix element in the absence of correlation given by Eq. (4) and $V_{ik,jp} = 2U_{ik,jp} - U_{ij,kp}$ is the Coulomb matrix containing the direct and exchange parts. The direct Coulomb matrix is expressed as

$$U_{ik,jp} = \hat{R}_{1i}^{(1)} \hat{R}_{1i}^{(1)} \left( \begin{array}{c} l_i \ 1 \ 0 \\ 0 \ 0 \ 0 \end{array} \right) \left( \begin{array}{cc} l_j \ 1 \ 0 \\ 0 \ 0 \ 0 \end{array} \right) \times \frac{R^{(1)}_{ik,jp}}{r_{ik}^{(1)}}, \quad (6)$$

where $R^{(1)}$ is a Slater integral [1]. In the exchange matrix, the electron $kl$ and the hole $n_j$ states are swapped. By definition, both the dipole and Coulomb matrices are real quantities. The fraction $1/3$ in Eq. (5) is the result of the angular momentum projection summation.

The partial photoionization cross-section in RPAE depends on the absolute square of the dipole matrix element (5)

$$\sigma_{ik}(\omega) = \frac{4}{3} \pi^2 a_0^2 \omega |D_{ik}|^2 \quad (7)$$

Here $\alpha$ is the fine structure constant and $a_0$ is the Bohr radius. The analogous expression with a non-correlated matrix element $d_{ik}$ gives the value which we refer to as the Hartree-Fock approximation.

B. Lowest order perturbation theory

Even though Eq. (5) can be solved numerically to a sufficient accuracy, we provide a simplified treatment which is less accurate but much more physically transparent. In the case of a weak inter-shell correlation, which is typically the case between the inner and outer shells, the correlated matrix element of the inner shell photoionization in the rhs of Eq. (5) can be approximated by its uncorrelated value, and the exchange part of the Coulomb interaction can be dropped, hence

$$D_{ik}(\omega) = d_{ik} + \frac{2}{3} \sum_p \frac{d_{ip} U_{ik,jp}}{\omega + \epsilon_j - \epsilon_p + i\delta} \equiv d_{ik} + \Delta d_{ik} . \quad (8)$$

Here $\Delta d_{ik}$ is a dipole matrix element in the absence of correlation.
We further rewrite the correlation induced part of the dipole matrix of the outer shell as
\[
\Delta d_{ik} = \sum_{p=1}^{\infty} \frac{a_p}{\omega + \epsilon_j - \epsilon_p} + \int_{ \Delta < 0 } \frac{a(\epsilon)}{\omega + \epsilon_j - \epsilon + i\delta} \, \, \, d\epsilon,
\]
where we introduce \( a_p \equiv (2/3) a_{jp} U_{ik,jp} \) for brevity of notation. We split the principle value and the singular part of the integral
\[
\int_{ \Delta < 0 } \frac{a(\epsilon)}{\omega + \epsilon_j - \epsilon + i\delta} \, \, \, d\epsilon = P \int_{ 0 }^{ \infty } \frac{a(\epsilon)}{\omega + \epsilon_j - \epsilon} - i\pi a(\epsilon) (\omega_{ik} + \epsilon_j)
\]
where \( \omega_{ik} = \epsilon_k - \epsilon_i \) is the energy of the outer shell transition. Near the inner shell threshold, the principle value integral is logarithmically divergent at the lower limit. However, this divergence is compensated for by the infinite part of the discrete sum. Indeed, because of the continuity of the oscillator strength across the ionization threshold,
\[
\lim_{ \omega \to \infty } \frac{a_p}{\Delta d_{ip}} = a(\epsilon = 0)
\]
and then absorb an infinite part of the sum into the integral:
\[
\Delta d_{ik} = \sum_{h=1}^{N>1} \frac{a_p}{\omega + \epsilon_j - \epsilon_p} + \int_{ \Delta < 0 } \frac{a(\epsilon)}{\omega + \epsilon_j - \epsilon + i\delta} \, \, \, d\epsilon
\]
(9)
The remaining finite sum describes the series of the autoionizing states below the threshold. We omit this region from our consideration and concentrate on the above-threshold ionization. Once the divergence in the principle value integral is removed, it becomes small and can be ignored in comparison with the direct photoionization matrix element because of the weakness of the correlation. With this in mind, we write the dipole matrix element of the outer shell photoionization near the inner shell threshold as
\[
D_{ik} = d_{ik} - i(2/3) \pi d_{jp} U_{ik,jp}
\]
arg\(D_{ik}=\) -arctan \( \frac{2}{3} \pi d_{jp} U_{ik,jp} \)
(10)
where the continuous states in both transitions are bound by the energy conservation \( \epsilon_k - \epsilon_j = \epsilon_p - \epsilon_j \). Eq. (10) gives the lowest order perturbation theory (LOPT) estimate for the correlation induced phase of the ionization amplitude.

### C. Relativistic extensiton

In the relativistic formalism, we consider a one-electron transition from an initial state characterized by the quantum numbers \( njm \) to a final continuum state \( k\bar{m} \).

The relativistic counterpart of Eq. (3) is the electric dipole amplitude which, for a linearly polarized light, is given by Eqs. (7-8) of [16]:
\[
T_{n_j\bar{m}}^{\nu} = \sum_{k\bar{m}} C_{nm-n\bar{m}}^{jm} Y_{m-n\bar{m}}(\hat{k})
\]
(11)
\[
\times(-1)^{2j+1} \left( \begin{array}{ccc} j & 1 & j \\ -m & 0 & m \end{array} \right) \, i^{1-l} i^{\delta_{x}} \langle \hat{\alpha} | Q_{k}^{(1)} | \alpha \rangle
\]

Here and below we use the notation \( \kappa = \mp(j + \frac{1}{2}) \) for \( j = l \pm \frac{1}{2} \), \( \nu \) is the photoelectron spin polarization, the \( C \)'s are the Clebsch-Gordon coefficients and the \( Y \)'s are the spherical harmonics. We will also use an asterisk for the lower \( j \) component of a spin-orbit doublet, \( j = l - \frac{1}{2} \), e.g., \( np_{1/2} \equiv np^* \). The reduced matrix element of the spherical tensor between the initial state \( a = (n\kappa) \) and a final state \( \hat{a} = (\epsilon, k) \) is obtained from a solution of the set of the integral RRPAE equations similar to the RPAE Eq. (5). For the brevity of notation, we absorb the phase factor into the reduced matrix element
\[
D_{lj \rightarrow lj} = i^{1-l} i^{\delta_{x}} \langle \hat{\alpha} | Q_{k}^{(1)} | \alpha \rangle
\]
(12)

In the polarization axis direction \( \hat{k} || \hat{z} \), only the axial, \( Y_{00} \), components of the spherical harmonics in Eq. (11) are non-zero, so only terms with \( m = \nu = \pm 1/2 \) survive. Due to the axial symmetry, then, the final result does not depend on the sign of the spin and the angular momentum projections. The expressions below show the axial components of the relativistic ionization amplitudes for the \( ns, np \) and nd initial states,
\[
T_{nsj/2}^{(1)} = -\frac{1}{3\sqrt{2}} Y_{10} D_{ns_{1/2} \rightarrow ep_{1/2}} - \frac{1}{3} Y_{10} D_{ns_{1/2} \rightarrow ep_{3/2}}
\]
\[
T_{npj/2}^{(1)} = \frac{1}{\sqrt{15}} Y_{20} D_{np_{j/2} \rightarrow ed_{3/2}} + \frac{1}{\sqrt{6}} Y_{00} D_{np_{j/2} \rightarrow es_{1/2}}
\]
\[
T_{npj/2}^{(1)} = \frac{1}{\sqrt{6}} Y_{60} D_{np_{j/2} \rightarrow es_{1/2}} - \frac{1}{5\sqrt{6}} Y_{20} D_{np_{j/2} \rightarrow ed_{3/2}}
\]
(13)
\[
T_{ndj/2}^{(1)} = -\frac{1}{3\sqrt{2}} Y_{10} D_{nd_{j/2} \rightarrow ep_{1/2}} + \frac{1}{3} Y_{10} D_{nd_{j/2} \rightarrow ep_{3/2}}
\]
\[
+ \frac{3}{70} Y_{30} D_{nd_{j/2} \rightarrow ef_{5/2}}
\]
\[
T_{ndj/2}^{(1)} = \frac{1}{\sqrt{15}} Y_{10} D_{nd_{j/2} \rightarrow ep_{3/2}} - \frac{1}{7\sqrt{10}} Y_{30} D_{nd_{j/2} \rightarrow ef_{5/2}}
\]
\[
- \frac{\sqrt{2}}{7} Y_{30} D_{nd_{j/2} \rightarrow ef_{3/2}}
\]

with the spherical harmonics in Eq. (13) are taken in the \( \hat{z} \) direction i.e., \( \theta = 0 \). The complete set of amplitudes for an arbitrary direction, including the off-axial terms is given in [16, 17]. Each amplitude in Eq. (13) is associated
with its own Wigner time delay defined as

\[ \tau_{nlj} = \frac{d\eta_{nlj}}{d\epsilon}, \quad \eta_{nlj} = \tan^{-1} \left[ \frac{\text{Im}T_{nlj}^{(1)}(\hat{k}||\hat{z})}{\text{Re}T_{nlj}^{(1)}(\hat{k}||\hat{z})} \right], \quad \epsilon = k^2/2. \]  

In the case spin-orbit components are not resolved as in light atoms, the average time delay should be evaluated as a weighted average

\[ \bar{\tau}_{nl} = \frac{\sum_j \tau_{nlj}\sigma_{nlj}}{\sum_j \sigma_{nlj}}. \]  

In a weakly relativistic limit, it tends to its non-relativistic counterpart

\[ \tau_{nl} = \frac{\partial \arg f_{nl}(\hat{k}||\hat{z})}{\partial \epsilon}, \]  

where the amplitude \( f_{nl}(\hat{k}) \) is given by Eq. (3). We also note that the photoelectron in each partial wave has its own \( W \)-time delay defined as

\[ \tau_{nlj} = \frac{\partial \arg D_{nlj}^{\rightarrow l_j}}{\partial \epsilon}. \]  

Because individual partial waves are not presently resolved experimentally, it is the time delay (14) that is of our prime interest. It is instructive, nevertheless, to analyze the group delays in various individual photoelectron channels and to see how they combine to form the group delay for a particular relativistic subshell \( nlj \) or, equivalently, \( nl \) and \( nl^* \).

III. RESULTS AND DISCUSSION

A. Neon 2p photoionization near the 1s threshold

To elucidate the role of the inter-shell correlation in the valence shell photoionization of neon, we carry out the two sets of RRPA calculations. In one calculation, we use the complete set of 9 relativistic channels:

\[ 1s_{1/2} \rightarrow \epsilon p_{1/2}, \epsilon p_{3/2}, \]  

\[ 2s_{1/2} \rightarrow \epsilon p_{1/2}, \epsilon p_{3/2}, \]  

\[ 2p^* \equiv 2p_{3/2} \rightarrow \epsilon s_{1/2}, \epsilon d_{3/2}, \]  

\[ 2p \equiv 2p_{3/2} \rightarrow \epsilon s_{1/2}, \epsilon d_{3/2}, \epsilon d_{5/2}. \]

In a truncated 7-channel calculation, the transitions from the \( K \)-shell \( 1s_{1/2} \rightarrow \epsilon p_{1/2}, \epsilon p_{3/2} \) are omitted. In the complete RPAE calculation, we include all four non-relativistic channels: \( 1s \rightarrow \epsilon p, 2s \rightarrow \epsilon p \) and \( 2p \rightarrow \epsilon s, \epsilon d \).

Results of these calculations are displayed in Fig. 1 where we show the partial 2p photoionization cross-section as a function of the excess energy near the 1s threshold. We observe that the truncated RRPA calculation is smooth across the threshold whereas the full calculation is broken by a series of auto-ionizing resonances below the threshold, while above the threshold, the cross-section is a smooth function again, deviating insignificantly from the truncated result by about 10%.

Simultaneously, however, the inter-shell correlation affects the phase of the 2p photoionization amplitude in a very significant way. This phase above the 1s threshold is shown in the top panel of Fig. 2, as a function of the excess energy, with logarithmic energy scale for clarity. Here the complete 9-channel RRPA result varies quite considerably whereas the corresponding 7-channel RRPA phase is essentially flat. The 9-channel RRPA phase variation is also very close to the LOPT prediction. In other words, without coupling with the 1s channels, the phase of the 2p photoionization amplitude is nearly zero and hardly varies with energy; with the coupling, the phase is significant, and varies considerably with energy.

On the middle panel of Fig. 2, the phase is converted to the Wigner time delay using Eq. (14). The \( 2p_{1/2} \) and \( 2p_{3/2} \) components of the time delay are indistinguishable on the scale of the figure. For a better differentiation accuracy in the vicinity of the threshold, the 9-channel RRPA phase is fitted with the exponential-polynomial ansatz

\[ \phi(E, eV) = \exp[-bE](a_0 + a_1E + a_2E^2) \]  

and the time delay at the threshold is expressed as

\[ \tau(E = 0) = -(ba_0 + a_1) \times 2\text{Ry} \times 24.2\text{(as)} \]

For the 2p shell of Ne this expression returns \( \tau_{2p_{1/2}}(E = 0) = 8.37 \text{ as} \) and \( \tau_{2p_{3/2}}(E = 0) = 8.34 \text{ as} \). The time delay in the truncated 7-channel RRPA calculation is virtually

\[ \text{FIG. 1: Photoionization cross-section of the 2p shell of Ne near the 1s threshold as a function of the excess energy, the energy with respect to the 1s threshold. The complete 9-channel and the truncated 7-channel RRPA calculations are shown with the (red) dots and solid line, respectively. The 4-channel RPAE calculation from [15] is shown with filled triangles.} \]
zero on the scale of the figure. Hence, all the observed time delay in the complete RRPA calculation is due to the 1s/2p interchannel correlation. In the bottom panel of Fig. 1, the time delay is shown on the linear photon energy scale. We see that the rise of the time delay near the 1s threshold is rather steep and the naked eye intercept with the threshold may not provide a very accurate estimate.

The threshold group delays in various photoelectron partial waves are tabulated in Table I. The log scale results refer to Eq. (19) while the linear scale results are obtained by the naked eye threshold intercept. Both sets of results are quite close. We note that the s-wave has negative group delay whereas the d-waves have positive time delay. This sign inversion follows from the \((-1)^{l_{\text{max}}}\) rule since \(l_{\text{max}} = 1\) for \(p\to s\) transition and \(l_{\text{max}} = 2\) for \(p\to d\). As the d-waves are strongly dominant due to the Fano propensity rule \([18]\), the net Wigner time delay for the 2p\(_{1/2}\) and 2p\(_{3/2}\) subshells is close to that of the photoelectron group delay in the d partial waves because the corresponding terms are dominant in the subshell photoionization amplitudes \((13)\).

The negative phase, decreasing in magnitude with excess energy, which is converted to a positive time delay as shown in Fig. 2 can be understood from the LOPT equation \((10)\). We see that the sign of the correlation-induced phase depends on the sign of the three matrix elements: the two dipole matrices in the outer \(d_k\) and inner \(d_{jk}\) channels and the Coulomb interaction \(U_{ik,jp}\). In the present case we consider the strongest outer channel 2p → ed and correlate it with the inner channel 1s → cp. The corresponding dipole matrix elements near the 1s threshold are exhibited in Fig. 3. From this figure we observe that \(d_{2p→ed} > 0\) while \(d_{1s→cp} < 0\). The sign of these matrix elements is determined by the angular factor in Eq. \((4)\):

\[
\hat{l}_l \left( l \begin{array}{cc} 1 \\ l \end{array} \right) \equiv \hat{l}_{l_{\text{max}}} \left( -1 \right)^{l_{\text{max}}} \ , \ l_{\text{max}} = \max(l, l_i) \quad (20)
\]

Indeed, the radial integral in Eq. \((4)\), which contains the nodeless orbitals 1s and 2p, is always positive near the threshold. The angular part of the Coulomb matrix is

![Graph](image-url)
given by the product of the angular parts of the dipole matrices of the interacting channels (see Eq. (8) in [14]). Hence the Coulomb interaction matrix $U_{1s\text{c},2p\text{c}}$ is also negative near the threshold. Therefore both the numerator and the denominator in the LOPT expression for the phase (10) are positive and given the minus sign before the ratio the phase itself is negative. While the matrices $d_{2p\text{-red}}$ and $U_{1s\text{c},2p\text{c}}$ are rather flat, the dipole matrix $d_{1s\text{-red}}$ is noticeably decreasing away from the threshold. Hence the LOPT phase is decreasing in magnitude also. The corresponding time delay is positive and diminishes rapidly as the excess energy grows.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{matrix_elements}
\caption{Dipole matrix elements $d_{1s\text{c}}$ and $d_{2p\text{c}}$ for the inner and outer ionization channels in Ne, shown as (red) filled circles and (purple) open squares, respectively. The Coulomb interaction matrix $U_{1s\text{c},2p\text{c}}$ (multiplied by 10) is shown as (blue) asterisks.}
\end{figure}

**B. Argon near the $2p^*$ threshold**

The complete RRPA calculation on argon contains 16 relativistic channels:

\[
\begin{align*}
1s_{1/2} & \rightarrow \epsilon p_{1/2}, \epsilon p_{3/2} \\
2s_{1/2} & \rightarrow \epsilon p_{1/2}, \epsilon p_{3/2} \\
2p^* & \equiv 2p_{1/2} \rightarrow \epsilon s_{1/2}, \epsilon d_{3/2} \\
2p & \equiv 2p_{3/2} \rightarrow \epsilon s_{1/2}, \epsilon d_{3/2}, \epsilon d_{5/2} \\
3s_{1/2} & \rightarrow \epsilon p_{1/2}, \epsilon p_{3/2} \\
3p^* & \equiv 3p_{1/2} \rightarrow \epsilon s_{1/2}, \epsilon d_{3/2} \\
3p & \equiv 3p_{3/2} \rightarrow \epsilon s_{1/2}, \epsilon d_{3/2}, \epsilon d_{5/2}
\end{align*}
\]

In a truncated 14-channel calculation, the $2p^*$ ionization channels are removed. In a further trimmed 11-channel calculation, the $2p$ ionization channels are dropped. In the RPAE calculation, we include 6 non-relativistic channels: $2s \rightarrow \epsilon p, 2p \rightarrow \epsilon s, d, 3s \rightarrow \epsilon p, 3p \rightarrow \epsilon s, d$.

1. **3s photoionization**

Results of these calculations for the 3s cross-section near the $2p^*$ threshold are shown in Fig. 4. In the complete RRPA calculation, a smooth cross-section is interrupted by a series of auto-ionizing resonances below the threshold (not fully resolved in the figure). In a truncated 14-channel calculation, the resonant region is located below the $2p$ threshold. In a further truncated 11-channel RRPA calculation, all the resonances are removed and the cross-section is smooth across the threshold region.

In the top panel of Fig. 5 we show the phase of the 3s photoionization amplitude from the 16-, 14- and 11-channel RRPA calculations and the LOPT value from Eq. (10). The RRPA phases are fitted with the ansatz (18) and differentiated analytically to produce the time delays shown in the middle panel of the figure. The 3s time delay near the $2p$ threshold is negative. The threshold values are -19.7 as, -9.4 as and -1.9 as in the complete and the two truncated RRPA calculations, respectively. Thus by removing the inter-shell correlation of the sub-valence 3s shell with the inner 2p and 2p* shells, the time delay is significantly reduced. To highlight the utility of the analytical interpolation and differentiation, we show the raw numerical data of the 3s time delay in the bottom panel on the linear photon energy scale. The naked eye intercept with the threshold results in a great numerical uncertainty.

The energy variation of the LOPT phase, Eq. (10), near the threshold is very similar to the complete RRPA calculation. To elucidate the sign of the LOPT phase and its energy dependence, we examine the inner and outer transitions along with their Coulomb interaction. The corresponding dipole matrix elements are exhibited in Fig. 6. We see that the signs of the inner and outer dipole matrix elements are now inverted as compared with the case of Ne shown in Fig. 3. The outer dipole matrix element $d_{3s\text{-red}} < 0$ while the inner matrix element $d_{2p\text{-red}} > 0$, as prescribed by the signs of their respective

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{photoionization}
\caption{Photoionization cross-section of the 3s shell of Ar near the $2p^*$ threshold as a function of the excess energy. The complete 16-channel and the truncated 14- and 11-channel RRPA calculations are shown as (red) dots, (blue) asterisks and open squares, respectively.}
\end{figure}
angular factors, Eq. (20). As the Coulomb matrix element is positive in this case, the LOPT phase is positive also and is rapidly decreasing away from the threshold. This behavior produces a large negative time delay at the inner-shell threshold.

FIG. 5: Top: Phase of the 3s photoionization amplitude of Ar near the 2p* threshold from the 16-, 14- and 11-channel RRPA calculations, shown as (red) filled circles, (blue) asterisks and open squares. The analytic fit using Eq. (18) is shown with similarly colored solid lines. The LOPT calculation is displayed as (blue) open circles. Middle: Analytic fit to the phase of the photoionization amplitude, converted to Wigner time delay using Eq. (1). Bottom: Time delay from the 16-channel RRPA calculation shown on a linear photon energy scale.

FIG. 6: Dipole matrix elements \( d_{3s \epsilon p} \) and \( d_{2p \epsilon d} \) for the inner and outer ionization channels of Ar, shown as (red) filled circles and (purple) open squares, respectively. The Coulomb interaction matrix \( U_{3s \epsilon p, 2p \epsilon d} \) (multiplied by 30) is shown as (blue) asterisks.

FIG. 7: Photoionization cross-section of the 3p shell of Ar near the 2p* threshold as a function of excess energy. The complete 16-channel and the truncated 14- and 11-channel RRPA calculations are shown as (red) dots, (blue) asterisks and open circles, respectively.

2. 3p photoionization

The photoionization cross-section of the valence 3p shell near the 2p* threshold is shown in Fig. 7. Unlike the threshold behavior of the 2p cross-section near the 1s threshold in Ne (Fig. 1) and the 3s cross-section near the 2p* threshold in Ar (Fig. 4), the variation of the 3p cross-section above the 2p* threshold is rather small when the number of coupled channels the RRPA calculation changes. This insensitivity of the cross-section to the inter-shell correlation is reflected in the threshold behavior of the time delay which is exhibited in Fig. 8.

The phases in the individual photoelectron partial waves and the net phase of the photoionization amplitude for the 3p_{1/2} subshell of Ar are depicted in the top
FIG. 8: Top: Phase of the various $3p_{1/2}$ photoionization amplitudes of Ar near the $2p^*$ threshold: $3p_{1/2} \rightarrow \epsilon d_{3/2}$ (red) filled circles, $3p_{1/2} \rightarrow \epsilon s_{1/2}$ (blue) asterisks, sum over all final channels - open squares. The analytic fit using Eq. (18) is shown with similarly colored solid lines. Bottom: Analytic fit to the phase of the photoionization amplitudes, converted to the group delay (17) and Wigner time delay (1) as functions of the photoelectron energy. These phases, when converted to the photoelectron group delays (17) and the net Wigner time delay (14) are displayed in the bottom panel of this figure. As in the case of the Ne $2p$ shell, the group delay is negative for the $s$-continuum and positive for the $d$-continuum.

Unlike in the Ne $2p$ shell, where the $d$-waves dominate the Wigner time delay, various continua compensate for each other in the case of Ar $3p_{1/2}$. While the threshold group delay is large and negative for the $es$ continuum, it is small and positive for the $ed$ continuum and small and negative for the net Wigner time delay. The corresponding values of the group and Wigner time delays at the threshold are given in Table II. Reading these values we observe that a small effect of inter-shell correlation on the photoionization cross-section is commensurate with a similarly insignificant effect of the correlation on the Wigner time delay.

TABLE II: Photoelectron group delays (17) and Wigner time delays (14) of the $3s$ and $3p$ shells of Ar at the $2p^*$ threshold from the full 16-channel RRPA calculation. The Dirac-Fock $E_{DF}$ and experimental $E_{exp}$ [19] threshold energies are displayed.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Delay (as)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ar\ 2p^*$ threshold</td>
<td>$E_{DF} = 262\ eV$</td>
</tr>
<tr>
<td>$E_{exp} = 250\ eV$</td>
<td></td>
</tr>
<tr>
<td>$3p_{1/2} \rightarrow \epsilon d_{3/2}$</td>
<td>-20.2 -24.1</td>
</tr>
<tr>
<td>$3p_{1/2} \rightarrow \epsilon s_{1/2}$</td>
<td>-17.8 -21</td>
</tr>
<tr>
<td>$3p_{1/2}$ total</td>
<td>-3.5</td>
</tr>
<tr>
<td>$3p_{3/2} \rightarrow \epsilon d_{3/2}$</td>
<td>-10.0 12.7</td>
</tr>
<tr>
<td>$3p_{3/2} \rightarrow \epsilon s_{1/2}$</td>
<td>-17.8 -21</td>
</tr>
<tr>
<td>$3p_{3/2}$ total</td>
<td>1.7</td>
</tr>
<tr>
<td>$3s_{1/2} \rightarrow \epsilon p_{1/2}$</td>
<td>-18.3 -16.6</td>
</tr>
<tr>
<td>$3s_{1/2} \rightarrow \epsilon p_{3/2}$</td>
<td>-20.3 -14.9</td>
</tr>
<tr>
<td>$3s_{1/2}$ total</td>
<td>-19.7</td>
</tr>
</tbody>
</table>
TABLE III: Photoelectron group delays and Wigner time delays of the 3d and 3d* shells of Kr at the 2p and 2p* thresholds. The Dirac-Fock $E_{DF}$ and experimental $E_{exp}$ [19] threshold energies are shown.

<table>
<thead>
<tr>
<th>Channel</th>
<th>Delay (as)</th>
<th>Energy scale</th>
<th>Log</th>
<th>Lin</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p* threshold</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{DF}$ = 1, 765 eV</td>
<td>2p threshold</td>
<td>$E_{DF}$ = 1, 711 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{exp}$ = 1, 730 eV</td>
<td></td>
<td>$E_{exp}$ = 1, 678 eV</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 3d3/2 → ɛp5/2 | -36.15 -34.28 | 3d3/2 → ɛp5/2 | -33.14 -29.64 |
| 3d3/2 total   | 0.29          | 3d5/2 total   | 17.86          |

| 3d5/2 → ɛp3/2 | -14.5 -13.58 | 3d5/2 → ɛp5/2 | -33.14 -29.64 |
| 3d5/2 → ɛf5/2 | 9.10 8.92    | 3d5/2 → ɛf5/2 | 19.49 17.69   |
| 3d5/2 → ɛf7/2 | 16.18 16.45  | 3d5/2 → ɛf7/2 | 17.77 16.72   |
| 3d5/2 total   | 10.84        | 3d5/2 total   | 9.35          |

The compilation of the threshold time delays in Kr is shown in Table IV where it is seen that shells other than 3d display modest time delays, not exceeding 10 as. The respective threshold time delays in Xe (not shown) are significantly smaller. Even the 3d delays in Xe are only of the order of few attoseconds.

TABLE IV: Wigner time delays of various shells of Kr at several inner-shell thresholds

<table>
<thead>
<tr>
<th>Threshold</th>
<th>Time delay (as)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1s1/2</td>
</tr>
<tr>
<td>$E_{DF}$, eV</td>
<td>14.413</td>
</tr>
<tr>
<td>$E_{exp}$, eV</td>
<td>14,326</td>
</tr>
</tbody>
</table>

Shell

<table>
<thead>
<tr>
<th>Shell</th>
<th>4p3/2</th>
<th>4p1/2</th>
<th>3d5/2</th>
<th>3d3/2</th>
<th>3p3/2</th>
<th>3p1/2</th>
<th>2p3/2</th>
<th>2p1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.02</td>
<td>2.26</td>
<td>6.87</td>
<td>7.04</td>
<td>2.90</td>
<td>3.07</td>
<td>2.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.28</td>
<td>-1.58</td>
<td>10.84</td>
<td>0.29</td>
<td>3.18</td>
<td>-2.40</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.65</td>
<td>5.36</td>
<td>9.35</td>
<td>17.86</td>
<td>0.99</td>
<td>5.35</td>
<td>2.95</td>
<td></td>
</tr>
</tbody>
</table>

C. Krypton

1. 3d shell near the 2p and 2p* thresholds

Photoionization of the 3d shell of Kr near the 2p and 2p* thresholds is remarkable as it displays the largest photoelectron group delays and the net Wigner time delays among all the noble gas atoms from Ne to Xe in the present study. Examples of the photoionization phase and its time derivatives for the 3d3/2 and 3d5/2 subshells of Kr near the 2p* threshold are shown in Fig. 9. The corresponding threshold time delays and their counterparts near the 2p threshold are collected in Table III. We see that some group delays are as large as 30 as and the Wigner time delay of the 3d* shell near the 2p threshold is close to 20 as. This result is quite remarkable as a large atomic time delay is predicted at photon energies in the hard x-ray regime. This delay results entirely from inter-shell correlation and is not caused by the Coulomb drag that affects slow photoelectrons near their ionization threshold [15].
FIG. 9: Upper left: Phase of the various 3d_{3/2} photoionization amplitudes of Kr near the 2p_{1/2} threshold: 3d_{3/2} \to \epsilon p_{1/2} - (red) filled circles, 3d_{3/2} \to \epsilon p_{3/2} - (blue) asterisks, 3d_{3/2} \to \epsilon f_{5/2} - triangles and the 3d_{3/2} amplitude summed over all final channels - open squares. Upper right: Analytic fit using Eq. (18) shown with similarly colored solid lines and open squares for the 3d_{3/2} Wigner time delay. Bottom left: The same as above, but for 3d_{5/2} \to \epsilon p_{3/2} - (red) filled circles, 3d_{5/2} \to \epsilon f_{5/2} - (blue) asterisks, 3d_{5/2} \to \epsilon f_{7/2} - triangles and the summed 3d_{5/2} amplitude - open squares. Bottom right: Analytic fit using Eq. (18) shown with the similarly colored solid lines and open squares for the 3d_{5/2} Wigner time delay.

IV. SUMMARY AND CONCLUSIONS

In this work, we have demonstrated that Wigner time delay of outer atomic shells is affected, sometimes quite strongly, by correlation in the form of interchannel coupling with inner-shell photoionization channels in the vicinity of inner-shell thresholds. The phenomenology of this effect is quite rich. The jumps of the time delay near threshold can be quite small or quite large (as large as 36 as). In addition, the jumps due to interchannel coupling can be positive or negative. In other words, time delays that are so far above thresholds that they would have ordinarily gone to essentially zero, can be reactivated to significant values near the inner-shell thresholds owing to many-body interactions. Threshold time delay chronoscopy [20], thus, can be a significant tool in studying these correlation phenomena.

The results presented here provide a road map for experimental investigation of this phenomenology which can be implemented using recently developed technology. Attosecond streaking measurements can be expanded at present to the soft-x-ray water window [8]. We hope that with a rapid development of this technique, the most significant effects predicted here will be within the experimental reach in the near future.

Acknowledgments

V.K.D. acknowledges the support of NSF under grant No. PHY-1305085. S.T.M. acknowledges the support of the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy under Grant No. DE-FG02-03ER15428. P.C.D. appreciates the support of the grant from the Department of Science and Technology, Government of India.


