Time delay in valence shell photoionization of noble gas atoms

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We use the non-relativistic random phase approximation with exchange to perform calculations of valence shell photoionization of Ne, Ar, Kr and Xe from their respective thresholds to photon energy of 200 eV. The energy derivative of the complex phase of the photoionization matrix elements is converted to the photoelectron group delay that can be measured in attosecond streaking or two-photon transitions interference experiments. Comparison with reported time delay measurements in Ne and Ar at a few selected photon energies is made. Systematic mapping of time delay across a wide range of photon energies in several atomic targets allows to highlight important aspects of fundamental atomic physics that can be probed by attosecond time delay measurements.

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I. INTRODUCTION

Time delay in atomic photoionization has become an active and rapidly expanding field of research after pioneering experiments on attosecond streaking [1] and reconstruction of attosecond bursts by interference of two-photon transitions [2]. Both techniques use the XUV pump and IR probe pulses to ionize the target atom and to obtain timing information on the photoemission process. In attosecond streaking, the varying time delay between the pump and probe pulses is mapped onto the photoelectron kinetic energy. The whole valence band is projected onto a photoelectron kinetic energy map (the so-called spectrogram) which is then modeled, in the strong field or Coulomb-Volkov approximations, with the photoionization time delay being treated as a fitting parameter. This measurement revealed a relative time delay of $21\pm 5$ as between photoemission from the $2p$ and $2s$ shells in Ne at 106 eV photon energy. The positive sign of the relative time delay indicates that emission of the photoelectron from the $2p$ shell is seemingly delayed relative to that from the $2s$ shell. This result was interpreted in terms of the Wigner time delay (or photoelectron group delay, both terms will be used interchangeably in the present contents) which is defined as the energy derivative of the complex phase of the photoionization matrix element [1, 3]. More details on the Wigner time delay theory can be found in the review article by de Carvalho and Nussenzveig [4].

In the two-photon interferometric technique, the varying time delay between the pump and probe pulses is mapped onto the two-photon sidebands (SB) which exhibit an oscillating pattern of peaks and troughs. The phase of these oscillations depends on the sum of time delays in the XUV photon absorption (atomic photoionization) and subsequent IR photon absorption (continuum-continuum transition). The latter is modeled using the lowest order perturbation theory and asymptotic forms of the continuum wave functions thus allowing to obtain the former from an experimental measurement [5]. By reconstructing the oscillations of the SB 22 to 26 of the titanium:sapphire laser at 800 nm, Klünder et al. [2] reported the relative time delay between the photoelectron emission from the $3s$ and $3p$ shells of Ar in the photon energy range of 34 to 40 eV. Whether the $3p$ electron was delayed relative to the $3s$ one or vice versa was found to depend on the photon energy. This measurement was repeated later by Guénot et al. [6] and the sign of the relative time delay was reversed with the $3s$ photoelectron being delayed relative to the $3p$ one near the top end of the photon energy scale.

This repeated measurement was prompted by observation that the photon energy of 40 eV fell very close to the Cooper’s minimum of the $3s$ shell. Photoionization process in this region is driven very strongly by the many-electron correlation between the $3s$ and $3p$ shells [7]. Such a process cannot be theoretically described using an independent electron model like the Hartree-Fock (HF) theory. So the interpretation of the two-photon interferometric measurement Klünder et al. [2] based on this theory should be re-evaluated. A more adequate model that accounts for inter-shell correlation in noble gas atoms is the random phase approximation with exchange (RPAE or, shorter, RPA, both acronyms are used interchangeably) [8]. However, even after including the RPA corrections, the agreement between theory and experiment did not improve [6].

Theoretical interpretation of the attosecond streaking measurement of Schulz et al. [1] is also not straightforward. The group delay difference between the $2p$ and $2s$ shells in Ne calculated in the HF approximation is only 6.2 as [3]. With the added RPA correction of 2.2 as, it accounts for less that a half of the experimental value of $21\pm 5$ as. A more accurate modeling that accounted both the XUV and IR fields returned a similar value of $10.2 \pm 1.3$ as [9]. This prompted several authors to question the accuracy of attosecond streaking measurements [10, 11, 12]. This question is still being debated.

For the purpose of the present paper, we presume that the time delay in the Wigner’s sense, i.e. the photoelec-

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tron group delay, can be measured experimentally. To
support such measurements and to provide them with a
“road map” of consistent theoretical data, we embark
on the systematic studies of the time delay in a series
of noble gas atoms from Ne to Xe across a wide range of
photon energies. We demonstrate that such a systematic
study allows to highlight important aspects of fundamen-
tal atomic physics that can be revealed by attosecond
time delay measurements.

The paper is organized as follows. In Sec. II we in-
troduce our computational models for the independent
electron descriptions and that with account for the inter-
shell correlations. In Sec. III we present our numerical
results for outer valence ns and np shells in Ne and Ar
and ns, np, (n − 1)d shells in Kr and Xe. We conclude in
Sec. IV by revealing the systematic trends in time delay
of noble gases driven by the peculiarities of the elastic
scattering phases and many-electron correlations.

II. THEORETICAL MODEL

1. Independent electron HF model

We adopt the photoionization formalism as outlined
in the monograph [13]. We evaluate the one-photon
dipole matrix element \( \langle \psi_k^-|\hat{\varepsilon}|\phi_i^+\rangle \) of the transition from
a bound state \( i \) to an incoming continuous wave with
the given photoelectron momentum \( k \). The magnitude
of the momentum is restricted by the energy conserva-
tion \( E \equiv k^2/\hbar^2 = \omega + \varepsilon_i \), where \( \omega \) is the photon
energy. The atomic units are used throughout the paper
with \( e = m = \hbar = 1 \) and the atomic unit of time equal to
24 as. We split the radial and angular dependence in the
initial state \( \phi_i^+(r) = Y_{l_m}(\hat{r})R_{n_{l_i}}(r) \) and use the partial
wave expansion in the final state

\[
\psi_k^-(r) \propto \sum_{lm} \int e^{-i\delta(E)Y_{lm}(\hat{k})Y_{lm}(\hat{r})R_{kl}(r)} ,
\]

where the proportionality constant depends on the con-
tinuum normalization. We align the quantization axis \( z \)
with the polarization axis of light and write the dipole
operator in the length gauge as \( \hat{\varepsilon} = \int r^2 dr \langle kl|d|n_{l_i}\rangle \)

\[
\langle kl|d|n_{l_i}\rangle \propto \sum_{m_i = \pm 1} \sum_{l_i = \pm 1} \frac{e^{i\delta(E)l_i}}{l_i}Y_{lm}(\hat{k})
\]

\[
\times \left( \begin{array}{ccc} l & 1 & l_i \\ m & 0 & m_i \end{array} \right) \langle kl||d||n_{l_i}\rangle
\]

Here the reduced dipole matrix element, stripped of all
the angular momentum projections, is defined as

\[
\langle kl||d||n_{l_i}\rangle = \tilde{l}_i \left( \begin{array}{ccc} l & 1 & l_i \\ 0 & 0 & 0 \end{array} \right) \int r^2 dr \langle kl|d|n_{l_i}\rangle \ ,
\]

where \( \tilde{l} = \sqrt{2l+1} \). The partial photoionization cross
section for the transition from an occupied state \( n_{l_i} \)
to the photoelectron continuum state \( kl \) is calculated as

\[
\sigma_{n_{l_i}\rightarrow kl} = \frac{4\pi^2\alpha_0^2\omega}{|\langle kl||d||n_{l_i}\rangle|^2} .
\]

Here \( \alpha \) the fine structure constant and \( a_0 \) the Bohr radius.

The basis of occupied atomic states \( |n_{l_i}\rangle \) is defined by
the self-consistent HF method and calculated using the
computer code [14]. The continuum electron states \( |kl\rangle \)
are defined within the frozen-core HF approximation and
evaluated using the computer code [15]. These states are
found in the combined field of the nucleus and the HF
potential of the frozen electron core. So the photoelec-
tron scattering phase \( \delta_i(E) \) delivered by this method con-
tains both the long-range Coulomb and the short-range
Hartree-Fock components.

We note that the reduced matrix element (3) is real and
thus the complex phase of the dipole matrix element (2)
is defined by the scattering phases \( \delta_i \pm \epsilon \). According
to the Fano’s propensity rule [16], the dipole transition with
the increased momentum \( l = l_i + 1 \) is usually dominant
and thus the photoemission time delay is simply \( \tau_l = d\delta_l/dE \).

2. Inter-shell correlation

To include inter-shell correlation effects, we employ the
RPA model [13]. In this approximation, the reduced
dipole matrix element (3) is replaced by its correlated
counterpart \( \langle kl||D||n_{l_i}\rangle \) which accounts for correlation
between different atomic shells. This correlated matrix
element is found as a solution of the system of the integral
equations:

\[
\langle kl||D||n_{l_i}\rangle = \langle kl||d||n_{l_i}\rangle
\]

\[
+ \frac{1}{3} \lim_{\varepsilon \to 0} \sum_{p \neq l} \langle p||D||n_{l_j}\rangle \langle n_{l_j}||kl||V||p||n_{l_i}\rangle
\]

\[
\times \int e^{i\delta(E)l_j} \left( \begin{array}{ccc} l & 1 & l_i \\ m & 0 & m_i \end{array} \right) \langle kl||d||n_{l_i}\rangle
\]

\[
\times \left( \begin{array}{ccc} l_j & 1 & l_i \\ m_j & 0 & m_i \end{array} \right) \langle n_{l_j}||D||p||l'\rangle \langle p||kl||V||n_{l_j}||n_{l_i}\rangle
\]

\[
\times \frac{1}{\omega - p^2/2 + \epsilon - i\varepsilon} .
\]

These equations are represented graphically in Fig. 1.
Here the straight line with an arrow to the left or right
represents electron (continuum) or hole (bound) states,
respectively. The wavy line exhibits the Coulomb inter-
action, which contains both the direct and the exchange
parts. That explains the term exchange in the name
RPA(E). The dashed line is used to display a photon of
the frequency \( \omega \). The shaded circle is used to represent
the correlated dipole matrix element whereas the bare
matrix element is exhibited by a three-pronged vertex.

The Coulomb interaction matrices \( \langle n_{l_i}||kl||V||p||n_{l_i}\rangle \) and
\( \langle p||kl||V||n_{l_i}||n_{l_j}\rangle \) describe the so-called time-forward
and time-reverse correlation processes which are exhibit-
ed by the second and third diagrams (from left to right).
We solve the system of integral equations (5) using a slightly modified version of the computer code [17]. The energy integration in the time-forward term of Eq. (5) (second line) contains a pole and the RPA matrix element acquires an imaginary part and therefore an extra phase arg$(kl||D||nl_i)$ . However, this phase does not enter the partial photoionization cross section $\sigma_{nl_i\rightarrow kl}$ which is obtained from the squared matrix element (5):
\[
\sigma_{nl_i\rightarrow kl} = \frac{4}{3} \pi^2 \alpha_0^2 \omega |(kl||D||nl_i)|^2 . \tag{6}
\]
To get access to the phase information, one has to evaluate the angular asymmetry parameter defined as
\[
\beta_{nl_i\rightarrow kl} = \left[ (2l + 1) [(D_{l+1}|^2 + |D_{l-1}|^2) \right]^{-1} \times \left\{ (l+2)|D_{l+1}|^2 + (l-1)|D_{l-1}|^2 + 6\sqrt{l(l+1)} Re(D_{l+1}D_{l-1}e^{i(\delta_{l+1}-\delta_{l-1})}) \right\} . \tag{7}
\]
Here we used a shortcut $D_l$ for the RPA matrix element (5). The angular asymmetry parameter $\beta$ contains the phase difference between the two photoionization channels $l_i \pm 1$ when $l_i \neq 0$. The photoelectron group delay, which is the energy derivative of the phase of the complex photoionization matrix element, gives an alternative access to the phase information. It is evaluated as the imaginary part of the logarithmic derivative
\[
\tau = Im\left[ f'(E)/f(E) \right] \tag{8}
\]
where
\[
f(E) \propto \sum_{i=l_i, l_i \pm 1} \sum_{m=-m_i} e^{i\delta_i} Y_{lm}(\hat{k}) \times \left( \begin{array}{ccc} l & 1 & l_i \\ m & 0 & m_i \end{array} \right) (kl||D||nl_i) \tag{9}
\]
\[
\begin{array}{c}
\omega \\
kl_i \\
p'l' \\
i
\end{array} \quad \begin{array}{c}
\omega \\
kl_j \\
p' \\
j
\end{array}
\]


III. NUMERICAL RESULTS

A. Neon 2s and 2p shells

On the top panel of Fig. 2 we present the partial photoionization cross-sections of valence shell photoionization of Ne. The HF cross-sections (4) are shown by the dashed (blue) lines and the RPA cross-sections (6) are exhibited by the solid (red) line. The recommended experimental data by Bizau and Wüilleumier [18] are displayed with error bars. In the RPA calculation, we substitute the HF bound state energies with the experimental ionization thresholds $\epsilon_{2p_{3/2}} = 21.56$ eV and $\epsilon_{2s} = 48.47$ eV [19] which are indicated on the upper boundary of the panel. We see that account for the RPA correlation between the 2s and 2p shells improves the calculated cross-sections and makes them closer to the experimental data.

FIG. 2: (Color online) Top: the partial photoionization cross-sections of the 2s and 2p shells of Ne. The HF and RPA calculations are shown by the dashed (blue) and solid (red) lines, respectively. The recommended experimental data by Bizau and Wüilleumier [18] are displayed with error bars. Middle: elastic scattering phases in the field of the Ne$^+$ ion for the 2s $\rightarrow$ Ep and the dominant 2p $\rightarrow$ Ed channels (dotted blue line) and the RPA phases (solid red line). The thin dotted line visualizes the Coulomb phase with $Z = 1$. Bottom: the phase derivatives are converted to the units of the group delay. The vertical bar at the photon energy of 106 eV visualizes the relative time delay between the 2p and 2s shells of 21 as measured by Schultze et al [1]

On the middle panel, we show the elastic scattering phases in the field of the Ne$^+$ ion for the 2s $\rightarrow$ Ep and the
in the $d$-partial wave which is driven by the Coulomb logarithmic singularity. The situation is different in the $2s \rightarrow E_p$ channel. Here the HF phase crosses over from the Coulomb behavior at low photoelectron kinetic energy to the Levinson behavior at larger energies. In result, the phase derivative and, consequently, the time delay change their sign from positive and negative towards the larger photon energies. The RPA correction to the time delay is always negative. Hence the photoemission from the $2s$ shell seems to be ahead of that of the $2p$ shell at around 100 eV photon energy mark where the measurement of Schultze et al [1] was taken (shown as a vertical bar in the figure). However, the combined HF and RPA result of 8.4 as is less than a half of the reported experimental value of $21 \pm 5$ as.

### 1. Argon 3s and 3p shells

An analogous set of data for Ar 3s and 3p shells is shown in Fig. 3. On the top panel we make a comparison of the HF (dashed blue line) and the RPA (solid red line) partial photoionization cross-sections with the experimental data by Möbus et al [21] for 3s shell and by Samson and Stolte [22] for the sum of 3s and 3p shells. The experimental ionization thresholds $E_{3p_{1/2}} = 15.76$ eV and $E_{3s} = 29.24$ eV [19] are indicated on the upper boundary of the panels. These partial photoionization cross-sections are qualitatively different from those of Ne shown in Fig. 2. Firstly, the 3p cross-section in Ar displays the Cooper’s minimum whereas the nodeless 2p orbital does not [23]. Second, the inter-shell correlation changes completely the 3s cross-section which also display a deep Cooper-like minimum at a slightly smaller photon energy. The RPA calculation reproduce these features in good agreement with the experiment.

The HF phases in Ar behave similarly to the analogous case of Ne except that the $3s \rightarrow E_p$ phase would tend to $2\pi$ in the absence of the Coulomb singularity as there are two occupied $p$-shells in the $Ar^+$ ion. The RPA phases in Ar are very different from Ne. When the cross-section goes through the Cooper’s minimum, the corresponding phase makes a jump of $\pi$ in the $3s \rightarrow E_p$ amplitude, and $-\pi$ in the $3p \rightarrow E_d$ amplitude. This jump is easy to understand. If the amplitude was real and had a node, it would simply change its sign which would amount to adding a phase factor of $\pi$ in the complex number representation.

This jump of $\pi$ has a dramatic effect on the time delay which is shown on the bottom panel of Fig. 3. It drives the time delay in the $3s$ shell to very larger numbers in several hundreds of attoseconds. The situation is less dramatic for the $3p$ shell. Here the normally weak transition $3p \rightarrow E_s$ takes over near the Cooper’s minimum of the strong $3p \rightarrow E_d$ transition and the resulting time delay does not go below $-100$ as. We note that there is a strong variation of phase near the autoionization resonances in the $3p$ photoionization which is seen on the...
and Kr behaves similarly to the 3p shell of Ar. The 4s translation changes this ordering completely. With the RPA, this is delayed more than the 3p delay. In the HF approximation, the 3p photoemission is delayed more than the 3p. This is an important, strong and qualitative result which see that at this photon energy range, the RPA correction in the two-photon interferometric experiments [2, 6] we to 22 to 26 of the titanium:sapphire laser at 800 nm used cate the photon photon energies corresponding to the SB 22 to 26 of the experiment [6]. We do not show this variation in the phase and time delay plots for clarity of presentation. Anyway, this resonances are far too narrow to be detected in time delay measurements at present energy resolution.

On the upper boundary of the bottom panel, we indicate the photon photon energies corresponding to the SB 22 to 26 of the titanium:sapphire laser at 800 nm used in the two-photon interferometric experiments [2, 6]. We see that at this photon energy range, the RPA correction changes completely the sign of the relative 3p/3s time delay. In the HF approximation, the 3p photoemission is delayed more that the 3s ones. The inter-shell correlation changes this ordering completely. With the RPA correction, it is the 3s that is delayed more than the 3p. This is an important, strong and qualitative result which is related to the Cooper’s minima in the corresponding partial photoionization cross-sections.

This strong modification of the relative time delay between the 3p and 3s shells in Ar is more clearly seen in Table I where we present the time delay difference \( \tau_{3s} - \tau_{3p} \) in the HF and RPA approximations and compare it with the experimental data of Guenot et al. [6]. Even a fairly large uncertainty of \( \pm 50 \) as cannot reconcile the experimental data with neither of the calculations.

### Table I: Relative time delay between the photoemission

<table>
<thead>
<tr>
<th>SB</th>
<th>22</th>
<th>24</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega ) (eV)</td>
<td>34.1</td>
<td>37.2</td>
<td>40.3</td>
</tr>
<tr>
<td>( \tau_{3s} - \tau_{3p} ) (as)</td>
<td>HF 3</td>
<td>-36</td>
<td>-38</td>
</tr>
<tr>
<td>RPA 76</td>
<td>53</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>Expt 70</td>
<td>-30</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

2. Krypton 4p, 4s and 3d shells

Our results for the 4p, 4s and 3d photoionization of Kr are displayed in Fig. 4. On the top panel we make a comparison of the HF (dashed blue line) and the RPA (solid red line) partial photoionization cross-sections with the experimental data of Ehresmann et al. [24] for 4s and of Samson and Stolte [22] for 4p + 3d (error bars). The data from Aksela et al. [25] for 3d are displayed with asterisks. The experimental ionization thresholds \( \epsilon_{4p} = 14.00 \) eV, \( \epsilon_{4s} = 27.51 \) eV [19] and \( \epsilon_{3d} = 93.83 \) eV [26] are indicated on the upper boundary of the panel. The 4p and 4s cross-sections in Kr behave similarly to the 3p and 3s cross-sections in Ar (see the top panel of Fig. 3). The 4p \( \rightarrow Ed \) cross-section goes through its Cooper’s minimum which is offset somewhat by the weaker 4p \( \rightarrow Es \) channel. So the total 4p cross-section displays a shoulder rather than a true minimum. The 4s cross-section is driven strongly by its inter-shell correlation with 4p to a very deep minimum which is missed completely in the HF approximation. The 3d cross-section from its threshold displays a strong maximum associated with its shape resonance. This resonance is known to be due to electron correlation within a single shell [27] and indeed the 3d photoionization cross-section is well described by the HF approximation.

The HF phases in Kr (middle panel of Fig. 4) behave similarly to the analogous cases of Ne and Ar except that the 4s \( \rightarrow Ep \) phase would tend to \( \pi \) and the 4p \( \rightarrow Ed \) phase would tend to \( \pi \) in the absence of the Coulomb singularity. The RPA phases in Kr are also similar to Ar. Every time the cross-section goes through the Cooper’s minimum, the corresponding phase makes a jump of \( \pi \):
upwards in the 4s → Ep amplitude and downwards in the 4p → Ed amplitude. The RPA phase in the 3d → Ef transition is rather stationary.

This behavior of the phases translates into the corresponding time delays plotted on the bottom panel of Fig. 4. The RPA time delay in 4p shell is not dramatically different from the HF calculation. Even though the dominant 4p → Ed transition displays a Cooper’s minimum, it is offset by the weak 4p → Es transition and is not as prominent in the total 4p cross-section as in the 3p cross-section of Ar. There are some variation of the time delay near the autoionizing resonances close to the 4s threshold which are seen in the RPA calculation but not in HF one. The time delay in the 3d shell is almost entirely due to intra-shell effects and the HF and RPA results are very close. The situation is very different in the 4s shell where the time delay is strongly affected by the inter-shell correlation with the 4p shell and reaches 300 as in its peak. Similarly to Ar, there is a complete reversal of the relative time delay between the 4p and 4s shells in the RPA calculation in comparison with the HF one.

3. Xenon 5p, 5s and 4d shells

The analogous set of data for the 5p, 5s and 4d shells of Xe is presented in Fig. 5. On the top panel we compare the partial photoionization cross-sections in the HF (dashed blue line) and RPA (solid red line) approximations with the experimental data [28, 29] which are shown with the blue asterisks for 5s and error bars for 5p and 4d. The experimental ionization thresholds ε5p/2 = 12.13 eV, ε5d/2 = 23.40 eV [19] and ε4d/2 = 67.50 eV [30] are indicated on the upper boundary of the panel.

Below the 4d ionization threshold, the 5s and 5p partial photoionization cross-sections are rather structureless and there is no significant time delay variations. A phase jump of π, smoothed by the interaction between the two channels, has already been observed both theoretically and experimentally by analyzing the anisotropy parameter in photoionization of Xe 5p shell [31]. According to Eq. (7), this parameter contains the phase shift between the two photoionization channels with \( l = l_i \pm 1 \). In the case of 5p photoionization, these are 5p → Ed and 5p → Es transitions. Their partial photoionization cross-sections and the relative phase shift are presented on the top and bottom panels of Fig. 6. On both panels, we show the present RPA and HF calculations displayed with the solid red and blue dotted lines.
FIG. 5: (Color online) Top: the partial photoionization cross-sections of Xe. The HF and RPA calculations are shown by the dashed (blue) and solid (red for 5s, 5p and green for 4d) lines, respectively. The experimental data from Becker et al. [28] and Fahlman et al. [29] are shown with asterisks for 5s and error bars for 5p and 4d. Middle: elastic scattering phases in the field of the Ar+ ion for the 5s → Ep and the dominant 5p → Ed and 4d → Ef channels (dotted blue line) and the RPA phases (solid red line). Bottom: the phase derivatives are converted to the units of the group delay.

respectively. On the bottom panel, we exhibit the RPA (open circles) and HF (filled circles) phase shifts reported by [31].

On the top panel of Fig. 6 we observe a significant shift of the Cooper’s minimum in the 5p → Ed channel towards the lower photon energies and appearance of the secondary minimum due to the correlation with the 4d shell. In the meantime, the inter-shell correlation does not change the 5p → Es partial photoionization cross-section in such a dramatic way. Accordingly, on the bottom panel of Fig. 6, we see a strong variation of the RPA phase shift with the two successive π jumps near the Cooper’s minima of the 5p → Ed cross-section. In the meantime, the HF calculation returns quite a smooth and monotonous phase shift. Agreement between the two sets of calculations, the present and the one reported by [31], is very good.

FIG. 6: (Color online) Top: Partial photoionization cross-sections of Xe in the 5p → Ed and 5p → Es channels in the RPA (solid red line) and HF (dotted blue line) approximations. Bottom: Phase shift between the partial 5p → Ed and 5p → Es waves. The present RPA and HF calculations (solid red and blue dotted lines, respectively) are compared with the RPA and HF calculations reported in Zimmermann et al. [31] (open and filled circles, respectively).

IV. CONCLUSION

In the present work, we perform a systematic study of the photoemission time delay from the valence shells of noble gas atoms in sequence from Ne to Xe. We cover the photon energy range from the ionization threshold to 200 eV. We test the accuracy of our calculation by making comparison with available partial photoionization cross-sections. We derive the complex phase of the photoionization matrix element in the non-relativistic HF and RPA calculations and convert it to the photoelectron group delay by taking the energy derivative.

The time delay results display a very diverse landscape due to an interplay of three major factors. The first two are the logarithmic Coulomb singularity and the Levinson theorem which drive the photoelectron scattering phase in the field of the singly charged ion. The third factor is the phase jump of π near the Cooper’s minimum which is smoothed by the inter-shell interaction. The two former factors are revealed in the HF calculations whereas the third one is most vividly reflected in the RPA calculations. Experimentally, photoionization measurements near the Cooper’s minima may be challenging but it is the area where the time delay effects are expected to be largest.

These time delay results are compared with experimental data derived from the attosecond streaking mea-
measurement [1] and the two-photon interferometric technique [6]. This comparison is inconclusive as the difference between the theoretical and experimental results clearly exceeds the reported error bars. We are fairly confident about the accuracy of the present calculation which is tested by comparison of the partial photoionization cross-sections with a large set of independent experimental data. In the case of Xe, a direct comparison with the scattering phase shift is also performed. Even for this heaviest of the atoms studied in the present work, the relativistic effects are not expected to change considerably the complex phase [6] and hence the associated time delay. It is therefore an open question why the time delay results cannot be verified experimentally. Such a verification would be a very welcoming development both for the attosecond time delay measuring techniques and the complete theory of atomic photoionization.

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