Attosecond time delay in the photoionization of Mn in the $3p \rightarrow 3d$ giant resonance region

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The dramatic effect of the $3p \rightarrow 3d$ giant autoionization resonance on time delay of photoemission from the 3d and 4s valence subshells of the Mn atom is unraveled. Strong sensitivity of the time delay of the 4s photoemission to the final-state term of the ion-remainder [Mn$^+(4s^2, 3d^5)$ vs. Mn$^+(4s^2, 3d^5, 3p, 5p, 7p)$] is discovered. The features of time delay uncovered in Mn photoionization are expected to be general properties of transition-metal atoms and ions. The “spin-polarized” random phase approximation with exchange was employed in the study.

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I. INTRODUCTION

Photoionization time delay is characterized by a slight temporal delay in the release of the photoelectron wavepacket upon absorption of a short electromagnetic pulse. It is an active topic investigation as manifested by recent experimental and theoretical studies.

In essence, photoionization time delay is a direct generalization of the concept of time delay developed by Eisenbud and Wigner for electron scattering to atomic photoionization. Normally, the delay is small, of the order of tens to hundreds of attoseconds (1 as = 10$^{-18}$ s). Experimental observation of this phenomenon allows to capture electron motion in atoms, molecules and solids on the attosecond time scale. This has been demonstrated by the attosecond streaking and the RABBITT (Reconstruction of Attosecond Bursts by Ionization of Two-photon Transitions) techniques. In turn, unique experimental accomplishments provide the impetus for advanced theoretical studies of the photoionization time delay phenomenon as well.

To date, to the authors’ best knowledge, photoionization time delay has only been studied in closed shell systems like noble gas atoms. However, there is another interesting group of atoms, the transition-metal atoms, where photoionization time delay has not been studied at all yet; it was only addressed, briefly, for electron elastic scattering off Mn[18]. Meanwhile, time delay in the photoemission spectra of transition-metal atoms presents an especially interesting case. Owing to the open-shell nature of the valence $n^{p<10}$-subshells of these atoms ($n=3$ for iron-group atoms, like the Mn atom), their photoionization spectra are dominated by the $np \rightarrow nd$ giant autoionization resonance which subsequently autoionizes into primarily $nd \rightarrow f, p$ channels. The $np \rightarrow nd$ giant resonance was originally detected experimentally in the 3p-photoabsorption spectrum of Mn by Connerade et. al. [19]. Later, it was experimentally and theoretically studied not only in Mn but in other transition-metal atoms and their ions as well (see review papers by Somntag and Zimmermann and Martins et al., as well as references cited below in this paper). Extensive citation of original publications on this subject, however, goes beyond the scope of the present work.

The ultimate aim of the present study is to uncover the fundamental features of photoionization time delays of transition-metal atoms. To meet this end, it focuses on time delays in photoionization of the 3d and 4s valence subshells of the Mn [Ar]3d$^5$4s$^2$(6S) atom in the $3p \rightarrow 3d$ giant autoionization resonance region, as a case study.

There are reasons for choosing Mn for this study. First, 3d-photoionization of neutral Mn in the region of the $3p \rightarrow 3d$ resonance was studied extensively experimentally. Thus, Mn is well disposable for experimental photoionization measurements, and there is a reliable experimental information to control the quality of corresponding theoretical calculations. Second, Mn is not just an open-shell atom but a half-filled shell atom. This simplifies its theoretical study significantly. In particular, one can employ a multielectron “spin-polarized” random phase approximation with exchange (SPRPAE) designed especially to describe photoionization of half-filled shell atoms. Finally, SPRPAE has been successfully used for the study of the $3p \rightarrow 3d$ giant resonance in 3d and 4s photoionization of Mn, and good quantitative agreement with experiment was achieved. Thus, SPRPAE is a reliable theoretical method to study Mn photoionization. It is, therefore, chosen as the theoretical tool for the present study as well.

Atomic units are used throughout the paper unless specified otherwise.

II. REVIEW OF THEORY

A convenient starting point to account for the structure of a half-filled shell atom is provided by the spin-polarized Hartree-Fock (SPHF) approximation developed by Slater. SPHF accounts for the fact that...
spins of all electrons in a half-filled subshell of the atom (e.g., in the 3d5 subshell of Mn) are aligned, in accordance with the Hund’s rule, say, all are pointing upward. This results in splitting of a closed \( n^2(2f+1) \) subshell in the atom into two half-filled subshells of opposite spin orientations, \( n^2f^{1\uparrow} \) and \( n^2f^{1\downarrow} \). This is due to the presence of the exchange interaction between \( n\uparrow \) electrons with only spin-up electrons of a spin-unpaired half-filled subshell of the atom (e.g., the 3d5\uparrow subshell in the Mn atom), but absence of such interaction for \( n\downarrow \) electrons. Therefore, atoms with half-filled subshells can be treated as having only occupied subshells, filled in only by either one or the other kind of electrons, named “up”- or “down”-electrons depending on their spin orientations, \( \uparrow \) and \( \downarrow \), respectively [23, 31]. Their binding energies \( \epsilon_{n\ell}(\uparrow) \) and wave functions \( P_{\ell m}(r) \) differ from each other, as is clear from the discussion above. They are solutions of the corresponding SPHF equations which differ from the ordinary Hartree-Fock equations by accounting for exchange interaction only between electron with the same spin-orientation [23, 31]. For the Mn atom, which is the atom of interest of the present paper, the SPHF configuration is as follows: \( \{|3p^\uparrow\rangle \uparrow \} \). The removal of a 3d\uparrow-electron produces the ion-remainder Mn\uparrow(3d\uparrow 4s\downarrow 4p\downarrow 5d\downarrow). A removal of a spin-up 4s\uparrow or spin-down 4s\downarrow electron from Mn results in ion-reminders having different terms, the Mn\uparrow(3d\uparrow 4s\downarrow 5d\downarrow) or Mn\uparrow(3d\uparrow 4s\downarrow 5p\downarrow 7S_J) ions, respectively. This makes the photoionization process spin-dependent, or, in other words, term-dependent. In the present paper, “term dependence” and “spin dependence” are used interchangeably.

Multielectron SPRPAE [23, 27] utilizes SPHF as the zero-order independent-particle basis - the vacuum state. This is because the spin-up- and spin-down-subshells of the atom can be regarded as completely filled. Therefore, the well developed random phase approximation with exchange (RPAE) for closed shell atoms [27] can be easily generalized to the case of half-filled shell atoms. Similar to RPAE, the SPRPAE equation for a photoionization amplitude \( \langle k|\hat{D}|i \rangle \equiv D_{ki} \) of the \( \iota \)th subshell of an atom into a continuous state \( k \) is depicted graphically in Fig. 1. There, diagrams (c) and (d) represent SPRPAE (RPAE) corrections to the HF photoionization amplitude \( \langle k|\hat{D}|i \rangle \equiv d_{ki} \) [diagram (b)]. Diagram (d) accounts for the exchange interaction in the atom, thus being called the exchange diagram. In SPRPAE, the contribution of the exchange diagram (d) to the photoionization amplitude is discarded from the equation whenever the corresponding intermediate-state electron-hole pair “\( j-k \)” and the final-state electron-hole pair “\( i-k \)” have opposite spin orientations. For instance, if the intermediate excitation “\( j-k \equiv 3d\uparrow \to \iota \) then diagram (d) affects a 4s\uparrow-photoionization amplitude, but not a 4s\downarrow-photoionization amplitude. In another example, diagram (d) does not affect the 4s\uparrow- but does affect the 4s\downarrow-photoionization amplitude when “\( i-k \equiv 3p\downarrow \to 3d\downarrow \). Exchange diagram (d), in fact, represents an infinite sum over all orders of perturbation theory in the inter-electron interaction. Therefore, the presence or absence of the exchange diagram (d) in the SPRPAE equation for a photoionization amplitude enhances the term-dependence considerably compared to SPHF calculated results. In fact, such term dependence was found to be dramatic not only for dipole photoionization of the outermost ns-subshells in half-filled shell atoms [28, 29, 32], but for nondipole photoionization as well [33].

We now briefly outline the key points of the photoionization time delay concept. In the spirit of the Eisenburg-Wigner theory for time delay in electron scattering [13, 14], time delay in the photoionization of a \( n\ell_i \) subshell of the atom is determined by a derivative of the phase \( \varphi(E) \) of corresponding photoionization amplitude \( T_{n\ell_i} = |T_{n\ell_i}| e^{i\varphi(E)} \) [34]. Correspondingly,

\[
\varphi(E) = \tan^{-1} \left( \frac{\text{Im} T_{n\ell_i}(E)}{\text{Re} T_{n\ell_i}(E)} \right), \quad \tau_{n\ell_i} = \frac{d\varphi(E)}{dE}.
\]  

(1)

For a photoionization amplitude \( T_{n\ell_i} \) of a \( n\ell_i \)-state which accounts for both \( n\ell_i \to \iota (\ell_i \pm 1) \) dipole transitions, one has [12]:

\[
T_{n\ell_i}(E) \propto \sum_{l_i-m_i} e^{i\delta_l} \langle \hat{k}| \psi_{m_i}(\ell_i) (-1)^m \begin{pmatrix} 1 & 1 & \iota \end{pmatrix} \times \langle \text{El}|T|\ell_i \rangle).
\]  

(2)

Here, \( \hat{k} \) is a unit vector in the direction of the photoelectron momentum \( k \), \( \delta_l(E) \) is the phase shift of the \( l \)th outgoing photoelectron wave, and \( \langle \text{El}|T|\ell_i \rangle \) is the reduced dipole matrix element. In the present work, the amplitude \( T_{n\ell_i}(E) \) is evaluated in the forward direction \( k||z \), which is usually the case in the attosecond time delay measurements; this is of importance because the time delay, in general, has an angular dependence [35, 56].

![Figure 1: Feynman diagrammatic representation of the SPRPAE (RPAE) equation for the photoionization amplitude \( \langle k|\hat{D}|i \rangle \) of the \( i \)th subshell into the \( k \)th final state [27]. Here, the time axis is directed from the left to right, the diagrams’ time-topology is not ordered with respect to time, the lines with arrows to the left (right) correspond to holes (electrons) in the atom, a dotted line represents an incoming photon, a dashed line represents the Coulomb interaction \( V(r) \) between charged particles, and a shaded circle marks the effective operator \( \hat{D} \) for the photon-atom interaction which accounts for electron correlation in the atom.](image)
III. RESULTS AND DISCUSSION

A. Mn 3d-photoionization

The SPRPAE calculations of Mn 3d-photoionization in the region of the 3p↓→3d↓ giant autoionization resonance were performed including interchannel coupling among four 3d↑→f↑, 3d↑→p↑, 3p↓→d↓, and 3p↓→s↓ transitions. Interchannel coupling with other transitions was ignored as negligible. Next, calculated SPHF values for the ionization potentials $I_{3d↑} \approx 17.4$ eV and $I_{3p↓} \approx 60.7$ eV, as well as binding energies of discrete excitations were used in this calculation. This is because the use of HF (SPHF) ionization potentials is conceptually consistent with RPAE (SPRPAE) theory. Moreover, earlier [25], the use of SPHF ionization thresholds in the calculated SPRPAE 3d-photoionization cross section of Mn in the $3p \rightarrow 3d$ resonance region was shown to result in a good agreement between theory and experiment.

The present calculated SPRPAE results for the 3d↑-photoionization cross section, $\sigma_{3d}(\omega)$, obtained from the amplitude, Eq. (2), its phase $\varphi_{3d}(\omega)$, Eq. (1), and the time delay $\tau_{3d}(\omega)$, Eq. (1) in the region of the 3p↓→3d↓ giant resonance are shown in Fig. 2. Note the good agreement between experiment and theory for $\sigma_{3d}$. This is indicative of the quality of the present calculations. Note how significantly the giant resonance changes not only $\sigma_{3d}(\omega)$, but also $\varphi_{3d}(\omega)$ and $\tau_{3d}(\omega)$, compared to the region away from the resonance. Specifically, the giant resonance enhances the time delay, $\tau_{3d}(\omega)$, by more than one order of magnitude compared to its nonresonance value, both at $\omega \approx 48$ and 50.5 eV. It is important to note that the latter enhancement of $\tau_{3d}(\omega)$ occurs in the photon energy region where the cross-section is large, $\sigma_{3d} \approx 55$ Mb. This should facilitate greatly its experimental observation.

Note also that the two regions of dramatic enhancement of the time delay result from changes of the phase of the matrix element by about $\pi$ in each of those small energy regions. The lower energy phase change, near 48 eV, results from a near-zero in the dipole matrix element. At the higher energy enhancement, near 50.5 eV, the phase change is the ordinary scattering phase in the neighborhood of a resonance. Both of these phase changes result from the $3d↑ \rightarrow f↑$ photoionization channel which dominates over the $3d↓ \rightarrow p↑$ channel.

It is also instructive to make a simple evaluation of a photoionization amplitude $T_{3d}$, cross-section $\sigma_{3d}$, and time delay $\tau_{3d}$ in the $3p↓ \rightarrow 3d↓$ giant resonance region in the framework of the Fano theory [37]. A single-channel, single-resonance parametric expression for the amplitude reads

$$f(\epsilon) = f_0 \frac{q + \epsilon}{i + \epsilon}, \quad \sigma(\epsilon) = \sigma_0 \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \quad \epsilon = \frac{E - E_0}{\gamma/2}. \quad (3)$$

Here, $f \equiv T_{3d \rightarrow f}$, $\sigma \equiv \sigma_{3d \rightarrow f}$, whereas $f_0$ and $\sigma_0$ are the $3d↑ \rightarrow f↑$-photoionization amplitude and cross section, respectively, calculated without taking account of the $3p↓ \rightarrow 3d↓$ resonance, $q$ is the profile index (shape parameter), and $\gamma$ is the resonance width. In SPRPAE, $\sigma_0 = 7.6$ Mb, $q = 2.5$, and $\gamma = 2$ eV [25]. The phase of the photoionization amplitude $f$ and associated time delay are expressed as follows:

$$\arg f(\epsilon) = \arg \frac{1}{i + \epsilon} = -\arctan \frac{1}{\epsilon}$$

$$\tau(\epsilon) = \frac{d \arg f(\epsilon)}{d\epsilon} = \frac{1}{1 + \epsilon^2} \quad (4)$$

with the energy scaling $d/dE = (2/\gamma) d/d\epsilon$. This equates the time delay at its maximum $\tau = 2/\gamma$ with the resonant width $\gamma$ at half maximum of the cross-section [38]. One concludes from the above that time delay near an autoionization resonance reaches its maximum where the photoionization cross-section $\sigma_{nl}$ is $q^2 \sigma_0$. Hence the photoionization time delay is easier to measure in regions of autoionization resonances having large profile indices $q$. The cross-section $\sigma_{3d \rightarrow f}$, the phase shift $\varphi_{3d \rightarrow f}$ and the time delay $\tau_{3d \rightarrow f}$ calculated in the framework of Fano formalism are depicted in Fig. 2. They are in a close agreement with the calculated SPRPAE data except for a region of the autoionization minimum near 48 eV, where...
the SPRPAE phase makes a jump of approximately one unit of $\pi$. All in all, calculated SPRPAE $\tau_{3d}$ reaches about 600 as near the maximum of $\sigma_{3d}$ and steeply rises to more than 1500 as near the autoionization minimum; the latter is not reproduced by the single-channel Fano expressions (3) and (4).

**B. Mn 4s-photoionization**

In this calculation, we use the experimental values $I_{5d^1(5D_4)} = 14.301$ eV, $I_{4s^1(5S)} = 8.611$ eV, and $I_{4s^1(5S)} = 7.431$ eV [20]. This is because the $4s^{-}$- and $4s\downarrow$-subshells of the Mn atom are significantly closer, in terms of energy, to the multielectron $3d^3\uparrow$-subshell than predicted by the SPHF theory. The use of the calculated SPHF ionization potentials in this case would have resulted in an underestimated contribution to the $4s$- and $3d$-ionization channels. Note that, as in the above case of the $3d$-photoionization, the calculated SPRPAE data for the $4s$-photoionization amplitudes were obtained by a direct solution of the SPRPAE equations, in contrast to work [28, 29] where a Fano single-resonance formalism was exploited.

Results of the present SPRPAE calculation of $\sigma_{4s^1(5S)}$, $\sigma_{4s^1(5S)}$, $\phi_{4s^1(5S)}$, $\phi_{4s^1(5S)}$, as well as $\tau_{4s^1(5S)}$ and $\tau_{4s^1(5S)}$ are depicted in Fig. 3. Note a good agreement between experiment and theory for $\sigma_{4s^1(5S)}$ and $\sigma_{4s^1(5S)}$. Furthermore, note how the time delays $\tau_{4s^1(5S)}$ and $\tau_{4s^1(5S)}$ are dramatically increased in the resonance region. Next, note how $\tau_{4s^1(5S)}$ and $\tau_{4s^1(5S)}$ differ strongly from each other in this energy region. Moreover, note that, in terms of time delay, the $4s^{-}(5S)$-ionization channel generally “outpaces” the $4s\downarrow(7S)$-ionization channel, except at approximately 54.7 eV, when they “run” even (where graphs for $\tau_{4s^1(5S)}$ and $\tau_{4s^1(5S)}$ cross each other). Another significant finding is that these channels can “run”, as it were, in opposite directions as well (since the corresponding time delays have opposite signs). This happens at certain energies, namely, first between approximately 46–48.5 eV and, once again, between approximately 52–53.4 eV. This speaks to a strong term-dependence of time delay in $4s$-photoionization of Mn, in particular, and should be a general feature for other transition-metal atoms and ions.

**IV. CONCLUSION**

It has been demonstrated in this paper that time delays of the corresponding Mn $3d$- and $4s$-photoionization channels are dramatically increased in the region of the $3p \rightarrow 3d$ giant autoionization resonance. Moreover, it has been found that the time delay of the $4s$-photoionization channel is strongly term-dependent, resulting in significant differences between time delays $\tau_{4s^1(5S)}$ and $\tau_{4s^1(5S)}$. Furthermore, strong maxima in $\tau_{4s^1(5S)}$, $\tau_{4s^1(5S)}$, and $\tau_{4s^1(5S)}$ emerge at photon energies where the corresponding photoionization cross-sections are big, particularly for $3d$-photoionization. This should simplify experimental measurements of the described phenomenon in Mn. Moreover, the $3p \rightarrow 3d$ giant autoionization resonance is known to occur in the photoabsorption spectra of Mn$^+$, metallic Mn, molecular MnCl$_2$, and solid MnCl$_2$ as well [39, 40]. This provides the flexibility for experimental verification of the predictions made in this paper. Furthermore, it is expected that the unraveled features in time delays of the Mn photoelectron emission channels will emerge in other $3d$- and $4d$-transitions elements and rare-earths where giant autoionization resonances exist as well. In other words, the unveiled in the present paper features of time delays in Mn photoionization are, in fact, inherent properties of not only the Mn atom, in particular, but other transition-metal and rare-earth atoms, in general. Correspondingly, results of the present paper provide guidance into photoionization time delays in those atoms as well.

Lastly, it is important to note that the well-known giant resonance in $4d$-photoionization of Xe, see, e.g., Ref. [27], has found an important application for the induction of a strong enhancement of the high harmonic generation (HHG) process [41]. The same collective multielectron dynamics can be probed in Mn by the HHG.
technique as well, in view of the large value of the Mn $3d$-photoionization cross section in the region of the $3p \rightarrow 3d$ resonance which is even greater than the Xe $4d$-photoionization cross section. Although experiments with metal vapors and ablation plasmas may be more challenging than with noble gases, HHG experiments can now be performed and analyzed in the condensed matter phase as well. Solid state Mn is a promising target for such a study.

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