# Attosecond time delay in the photoionization of Mn in the region of the 3p→3d giant resonance

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

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## Abstract

The initial insight into time delay in Mn photoionization in the region of the $3p \to 3d$ giant autoionization resonance is gained in the framework of the "spin-polarized" random phase approximation with exchange. The dramatic effect of the 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 [$Mn^+(4s^1,^5S)$ vs. $Mn^+(4s^1,^7S)$] is discovered. It is shown that photoionization time delay in the autoionizing resonance region is explicitly associated with the resonance lifetime, which can, thus, be directly measured in attosecond time delay experiments. Similar features are expected to emerge in photoionization time delays of other transition-metal and rare-earth atoms with half-filed subshells that possess giant autoionization resonances as well.

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## I. INTRODUCTION

Atomic photoionization time delay is characterized by a slight temporal offset in the release of the photoelectron wave-packet upon absorption by an atom of a short electromagnetic pulse. Since the first experimental and theoretical demonstration that atomic photoionization time delay can be measured using a single attosecond pulse (SAP) [1], it has become an active topic of investigation. A series of experiments was conducted recently using attosecond pulse trains (ATP) [2–6]. Thus produced experimental results were analyzed using several theoretical models of various degrees of sophistication [7–15]. At the same time, there exists a large body of literature on photoemission time delay in condensed matter but reviewing this literature is outside the framework of the present article.

In essence, photoionization time delay is a direct generalization of the concept of time delay developed by Eisenbud [16] and Wigner [17] for electron scattering and applied recently to atomic photoionization in Ref. [1]. 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 its natural, attosecond time scale. 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 elastic electron 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 $nd^{q<10}$-subshells of these atoms ($n = 3$ for iron-group atoms, like the Mn atom), their photoionization spectra are dominated by the $np \to nd$ giant autoionization resonance which subsequently autoionizes into primarily $nd \to f, p$ channels. The $np \to nd$ 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 Sonntag and Zimmermann [20] and Martins et al. [21], as well as references cited below in this paper).

It is the ultimate aim of the present study to get insight into the impact of the $3p \to 3d$

giant autoionization resonance in the Mn($[\mathrm{Ar}]3d^5 4s^2, ^6S$) atom on time delays in photoionization of the $3d$ and $4s$ valence subshells of the atom.

The effect of resonances on measuring and interpreting atomic photoemission time delay has been studied previously. In Ref. [22] doubly excited states of Ne were scrutinized to explain the discrepancy between experiment and theory reported in Ref. [1]. Similar attempts were made to reconcile the theory and experiment for photoemission time delay near the $3s$ Cooper minimum in Ar [23]. However, neither of these attempts was successful. In Ne, the resonances proved to be too narrow to have any effect on the measured time delay. In Ar, the latest and most accurate set of time delay results [24] was found in disagreement with the theoretical predictions of [23].

There are reasons for choosing Mn for this study. First, $3d$-photoionization of neutral Mn in the region of the $3p \to 3d$ resonance was studied extensively experimentally [20, 21, 25–27]. Thus, Mn is well disposed for experimental photoionization measurements, and there is a reliable experimental information to assess 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) [28–30] designed especially to describe photoionization of half-filled shell atoms. Finally, SPRPAE has been successfully used for the study of the $3p \to 3d$ giant resonance in $3d$ [28] and $4s$ [31, 32] photoionization of Mn, and good quantitative agreement with experiment [20, 25, 26] and MBPT theory [33], was achieved. Thus, SPRPAE is a convenient theoretical method for gaining the initial insight into time delays in 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 [34]. SPHF accounts for the fact that spins of all electrons in a half-filled subshell of the atom (e.g., in the $3d^5$ subshell of Mn) are aligned, in accordance with the Hund's rule, say, all are pointing upward. This results in splitting of a closed $n\ell^{2(2\ell+1)}$ subshell in the atom into

two half-filled subshells of opposite spin orientations, $n\ell^{2\ell+1}\uparrow$ and $n\ell^{2\ell+1}\downarrow$. This is due to the presence of the exchange interaction between $n\ell\uparrow$ electrons with only spin-up electrons of a spin-unpaired half-filled subshell of the atom (e.g., the $3d^5\uparrow$ subshell in the Mn atom), but the absence of such interaction for $n\ell\downarrow$ 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 [28, 34]. Their binding energies $\epsilon_{n\ell\uparrow(\downarrow)}$ and wave functions $P_{\epsilon\uparrow(\downarrow)}(r)$ 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 interactions only between electrons with the same spin-orientation [30, 34]. For the Mn atom, which is the atom of interest of the present paper, the SPHF configuration is $[\mathrm{Ar}]3p^3\uparrow 3p^3\downarrow 3d^5\uparrow 4\mathrm{s}^1\uparrow 4s^1\downarrow$ ($^6S_{5/2}$). The removal of a $3d\uparrow$-electron produces the ion-remainder $\mathrm{Mn}^+(3d^4\uparrow\ 4s^1\uparrow\ 4\mathrm{s}\downarrow,\ ^5D_4)$. A removal of a spin-up $4s\uparrow$ or spin-down $4s\downarrow$ electron from Mn results in ion-remainders having different terms, the $\mathrm{Mn}^+(3d^5\uparrow\ 4s^1\downarrow,\ ^5S_2)$ or $\mathrm{Mn}^+(3d^5\uparrow\ 4s^1\uparrow,\ ^7S_3)$ 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.

The multielectron SPRPAE [28–30] 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 [30] 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 $i$'th subshell of an atom into a continuous state $k$ is depicted graphically in Fig. 1. There, diagrams (c)–(f) represent SPRPAE (RPAE) corrections to the HF photoionization amplitude $\langle k|\hat{d}|i\rangle \equiv d_{ik}$ [diagram (b)]. Diagrams (d) and (f) account for the exchange interaction in the atom, thus being called the exchange diagrams. In SPRPAE, the contribution of the exchange diagrams (d) and (f) 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. The exchange diagrams (d) and (f), in fact, represent an infinite sum over all orders of perturbation theory in the inter-electron interaction. Therefore, the presence of certain series of exchange diagrams in the SPRPAE equation for photoionization of an

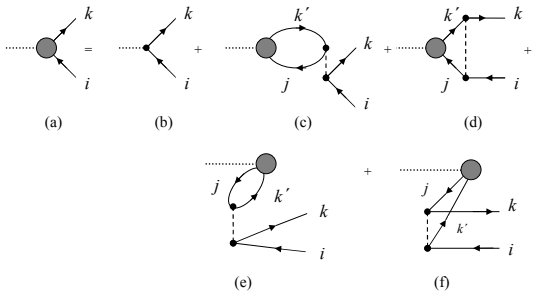


FIG. 1. Feynman diagrammatic representation of the SPRPAE (RPAE) equation for the photoionization amplitude $\langle k|\hat{D}|i\rangle$ of the $i$'th subshell into the $k$'th final state [30]. Here, the time axis is directed from the left to right, the lines with arrows to the left (right) correspond 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.

electron with one spin-polarization (e.g., a spin-up electron) but the absence of this series of exchange diagrams in the corresponding equation for photoionization of an electron with an opposite spin-orientation (spin-down electron, in this example) matters a lot. It enhances the photoionization term-dependence of a half-filled shell atom considerably compared to SPHF 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 [31, 32, 35], but for nondipole photoionization as well [36].

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 [16, 17], time delay in the photoionization of a $n_i l_i$ subshell of the atom is determined by a derivative of the phase $\varphi(E)$ of corresponding photoionization amplitude $T_{n_i l_i} = |T_{n_i l_i}|\, e^{i\varphi(E)}$ [37]. Correspondingly,

$$\varphi(E) = \arg[T_{n_i l_i}(E)], \quad \tau_{n_i l_i} = \frac{d\varphi(E)}{dE}. \tag{1}$$

For a photoionization amplitude $T_{n_i l_i}$ of a $n_i l_i$-state which accounts for both $n_i l_i \to \epsilon(l_i \pm 1)$ dipole transitions, one has [15]:

$$T_{n_i l_i}(E) \propto \sum_{\substack{l=l_i\pm 1 \\ m=m_i}} e^{i\delta_l} i^{-l} Y_{lm}(\hat{\boldsymbol{k}})\,(-1)^m \begin{pmatrix} l & 1 & l_i \\ -m & 0 & m_i \end{pmatrix} \times \langle El\|D\|n_i l_i\rangle. \tag{2}$$

Here, $\hat{\boldsymbol{k}}$ is a unit vector in the direction of the photoelectron momentum $\boldsymbol{k}$, $\delta_l(E)$ is the phase shift of the $l$th outgoing photoelectron wave, and $\langle El\|D\|n_i l_i\rangle$ is the reduced dipole matrix element which is the solution of the RPAE (or SPRPAE, in our work) equation, Fig. 1. Since the matrix element $T_{n_i l_i}$ defined by Eq. (2) depends on the photoelectron emission angles, it will be referred to, when the emphasis is needed, as the angle-dependent matrix element. In the present work, $T_{n_i l_i}(E)$ is evaluated in the forward direction $\boldsymbol{k}\|\hat{z}$, 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 [38, 39].

Summarizing the review of theory, the Eisenbud-Wigner time delay (1) is defined by the complex phase of the stationary ionization amplitude corresponding to a given energy of the ionizing field $\omega$. However, in SAP or ATP measurements, time delay is determined by a combination of the ionizing field and the streaking probe that is used. This introduces the so-called Coulomb-laser coupling corrections [9] (SAP) or continuum-continuum corrections [12] (ATP). The latter reference also demonstrated equivalence of the corrections in the SAP and ATP measurements. In non-resonant photoionization, these corrections should be added to the Eisenbud-Wigner time delay to account for the experimentally measured time delay.

In resonant photoionization, the effect of the measurement on the Eisenbud-Wigner time delay is much more complicated. Indeed, the SAP measurement involves an attosecond pulse of a considerable bandwidth which is required to be much larger than the photon energy of the probing pulse $\Omega \simeq 1.5$ eV [12]. Such wide spectral bandwidth could, at least partially, "mask" an autoionization resonance of comparable width which is manifested in the present Mn $3p \to 3d$ case, so that it might be difficult to employ the SAP technique to verify the made predictions. On the other hand, although the ATP technique is free from the bandwidth limitations, the usual two-frequency modulation of the two-photon interference is strongly distorted by the presence of an autoionizing resonance [40]. Hence a more involved analysis is required that cannot be reduced to adding a unified set of the CC corrections. Recently, an analysis is provided by a general analytical model that accounts for the effect of both intermediate and final resonances on two-photon processes [40]. With the helium atom as the case study, this analysis yields the same result as a solution of the all-dimensional time-dependent Schrödinger equation. Therefore, the ATP technique looks more suitable than SAP to address a resonance problem, although it is not entirely clear how it could

account for the interchannel interference.

## III. RESULTS AND DISCUSSION

### A. Mn $3d$-photoionization

The SPRPAE calculations of Mn $3d$-photoionization in the region of the $3p\downarrow\rightarrow 3d\downarrow$ giant autoionization resonance were performed including interchannel coupling among four $3d\uparrow\rightarrow f\uparrow$, $3d\uparrow\rightarrow p\uparrow$, $3p\downarrow\rightarrow d\downarrow$, and $3p\downarrow\rightarrow s\downarrow$ transitions. Interchannel coupling with other transitions was ignored as negligible. Next, calculated SPHF values for the ionization potentials $I_{3d\uparrow} \approx 17.4$ eV and $I_{3p\downarrow} \approx 60.7$ 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 [28], 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 $3d\uparrow$-photoionization cross section $\sigma_{3d}(\omega)$ and $3d$-angular-asymmetry parameter $\beta_{3d}$ (refer, e.g., to Ref. [30] for the equations for $\sigma_{nl}$ and $\beta_{nl}$) are plotted in Fig. 2(a) and (b) between 25 and 105 eV along with corresponding experimental data from Ref. [25]. One can see reasonable agreement not only between theory and experiment for $\sigma_{3d}(\omega)$ but for $\beta_{3d}$ as well. The angular-asymmetry parameter $\beta_{3d}$ depends not only on the absolute values of the photoionization amplitudes but also on phase shifts of the amplitudes. Therefore, reasonable agreement between the present calculated SPRPAE data and experiment for $\beta_{3d}$ is indicative of reasonably correctly calculated phases of the photoionization matrix elements and, thus, $3d$-time delay $\tau_{3d}$ as well. The calculated SPRPAE phase $\varphi_{3d}(\omega)$ and time delay $\tau_{3d}(\omega)$ in the region of the $3p\downarrow \rightarrow 3d\downarrow$ giant resonance are depicted in Fig. 2c and Fig. 2d, respectively.

Note also how significantly the giant resonance impacts both $\varphi_{3d}(\omega)$ 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

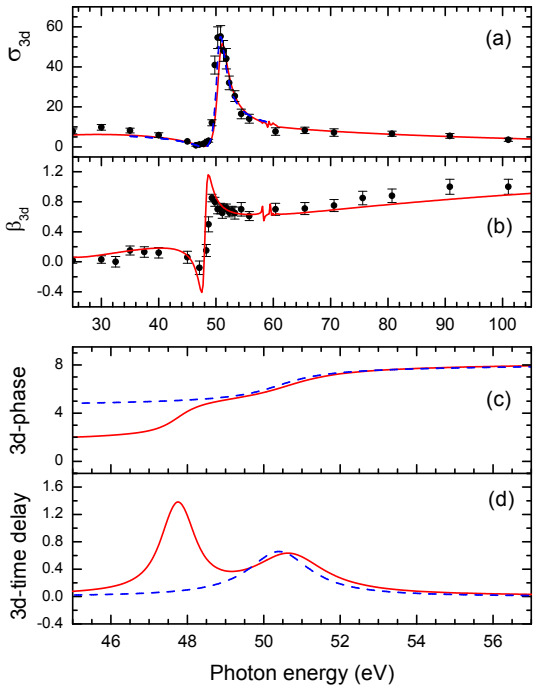


FIG. 2. (Color online) (a): solid line - present calculated SPRPAE data for the Mn $3d\uparrow$-photoionization cross-sections $\sigma_{3d}$ (in units of Mb); dots - experimental data on an absolute scale taken form Table 3 of Ref. [25]; dashed line - SPRPAE $\sigma_{3d}$ calculated previously [28] on the basis of the Fano autoionization formalism in the $3\downarrow \rightarrow 3d\downarrow$ giant resonance region. (b): solid line - present calculated SPRPAE angular-asymmetry parameter $\beta_{3d}$; dots - experimental data from Table 3 of Ref. [25]. (Note, former SPRPAE results for $\beta_{3d}$ [28], obtained on the basis of the Fano formalism in the $3\downarrow \rightarrow 3d\downarrow$ giant resonance region, practically coincide with the present data and not plotted in this figure). (c): solid line - calculated SPRPAE phase $\varphi_{3d}(\omega)$ (in units of radians) of the $3d\uparrow$-photoionization amplitude $T_{3d}$, Eq.(2); dashed line - the same as above but calculated with the help of the single-channel Fano formula, Eq. (3). (d): solid line - calculated SPRPAE time delay $\tau_{3d}(\omega)$ (in units of femtoseconds); dashed line - $\tau_{3d}(\omega)$ calculated with the help of the single-channel Fano formula, Eq. (4).

should facilitate greatly its experimental observation.

It is also instructive to make a simple evaluation of a photoionization amplitude $T_{3d}$, its phase $\varphi_{3d}$, and time delay $\tau_{3d}$ in the $3p\downarrow \rightarrow 3d\downarrow$ giant resonance region within the framework of the Fano theory [41]. A single-channel, single-resonance parametric expressions for the generally dominant matrix element $T_{3d\rightarrow f}(\omega) \equiv T$, Eq. (2), and the photoionization cross

section $\sigma_{3d\to f}(\omega) \equiv \sigma$ read

$$T(\omega) = T_0 \frac{q+\epsilon}{i+\epsilon} \ , \quad \sigma(\omega) = \sigma_0 \frac{(q+\epsilon)^2}{1+\epsilon^2} \ , \quad \epsilon = \frac{\omega - \omega_{\rm r}}{\gamma/2}. \tag{3}$$

Here, $T_0$ and $\sigma_0$ are, respectively, the $3d\uparrow\to f\uparrow$ photoionization amplitude and cross section calculated without accounting for the $3p\downarrow\to 3d\downarrow$ resonance transition, $\omega_{\rm r}$ is the resonance energy, $q$ is the profile index (shape parameter), and $\gamma$ is the resonance width. In Mn, calculated SPRPAE $\gamma \approx 2$ eV, $\omega_{\rm r} \approx 50.4$ eV, $q \approx 2.5$, and $\sigma_0 \approx 7.6$ Mb [28].

With the help of Eqs. (1) and (3) one finds that the time delay $\tau_{3d\to f}$ in a single-resonance, single-channel photoionization Fano formalism is determined as follows:

$$\tau_{3d\to f}(\omega) = \frac{2}{\gamma} \frac{1}{1+\epsilon^2}. \tag{4}$$

It follows from Eq. (4) that single-channel, single-resonance time delay has only one maximum which emerges at $\epsilon = 0$, i.e., at the resonance energy $\omega = \omega_r$. Moreover, one readily finds from Eq. (4) that the resonance width $\gamma = 2/\tau_{\rm max}$. The important implication is that the resonance width $\gamma$ at the half-maximum of the photoionization cross section is explicitly defined by $\tau_{\rm max}$. This opens a unique possibility for measuring the autoionization resonance lifetime directly in attosecond time delay experiments, similar to the corresponding direct measurement of the Kr $3p$-vacancy Auger decay lifetime [45]. Furthermore, it is clear from the above that time delay in the autoionization resonance energy region reaches its maximum where the photoionization cross section $\sigma_{nl} = q^2\sigma_0$. One then concludes that the photoionization time delay is easier to measure in regions of autoionization resonances having large profile indices $q$.

The cross section $\sigma_{3d\to f}$, the phase $\varphi_{3d\to f}$ and the time delay $\tau_{3d\to f}$ calculated within the framework of the Fano formalism, discussed above, were depicted in Fig. 2. They are in a close agreement with the calculated SPRPAE data except for a region near 48 eV. There, the calculated SPRPAE time delay $\tau_{3d}$ has a strong resonance structure where $\tau_{3d}$ steeply rises to more than 1.5 fs below to 48 eV. This resonance is then followed by a broader resonance in $\tau_{3d}$ at higher energies where $\tau_{3d}$ reaches about 0.6 fs near the maximum of $\sigma_{3d}$ at $\omega \approx 50.5$ eV; the latter is in agreement with the Fano formalism.

In order to get insight into the reason for the emergence of the strong 48-eV resonance in $\tau_{3d}$ but the absence of such in $\tau_{3d\to f}$, we plot in Fig. 3 the real and imaginary parts of the corresponding two-channel-weighted photoionization amplitude $T_{3d}(\omega)$ along with those

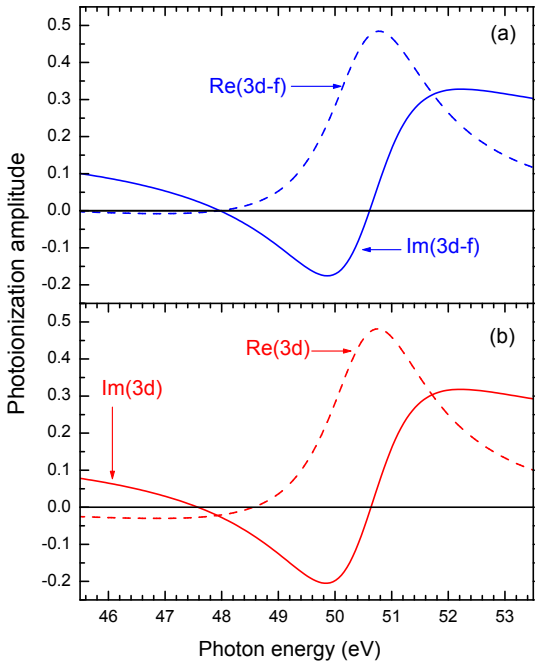


FIG. 3. (Color online) (a) SPRPAE real $\mathrm{Re}T_{3d\to f}$ and imaginary $\mathrm{Im}T_{3d\to f}$ parts (in atomic units) of the dominant $T_{3d\to f}$-photoionization amplitude, Eq. (2), calculated in the region of the giant $3p\downarrow \to 3d\downarrow$ resonance. (b) SPRPAE real $\mathrm{Re}T_{3d}$ and imaginary $\mathrm{Im}T_{3d}$ parts (in atomic units) of the total amplitude $T_{3d}$, calculated as the weighted sum of the two matrix elements $\langle Ef\|D\|3d\rangle$ and $\langle Ep\|D\|3d\rangle$, Eq. (2), in the region of the giant $3p\downarrow \to 3d\downarrow$ resonance.

of the amplitude $T_{3d\to f}(\omega)$. One can see from Fig. 3 that, near 48 eV, the relative behavior of $\mathrm{Re}T_{3d\to f}$ and $\mathrm{Im}T_{3d\to f}$ of the partial $T_{3d\to f}$ amplitude is quite different than the relative behavior of $\mathrm{Re}T_{3d}$ and $\mathrm{Im}T_{3d}$ of the total amplitude $T_{3d}$. Indeed, $\mathrm{Re}T_{3d\to f}$ and $\mathrm{Im}T_{3d\to f}$ take the zero values simultaneously, i.e., at the same energy $\omega \approx 48$ eV, so that their ratio remains about constant through 48 eV, and so are partial $\varphi_{3d\to f}$ and $\tau_{3d\to f}$ as well. In contrast, the zeros of $\mathrm{Re}T_{3d}$ and $\mathrm{Im}T_{3d}$ are separated from each other by the energy interval of about 1 eV inside of which $\mathrm{Re}T_{3d}$ and $\mathrm{Im}T_{3d}$ take equal values at $\omega \approx 48$ eV. This causes a clear variation, which appears to be resonant, in $\tan\varphi(\omega)$ and, thus, in the phase $\varphi(\omega)$, and time delay $\tau_{3d}(\omega)$ as well. As a result, $\tau_{3d}(\omega)$ possesses the additional strong 48-eV resonance but $\tau_{3d\to f}(\omega)$ does not. This finding is both interesting and important since it reveals the necessity for accounting for both a generally dominant $(3d \to f)$ and a generally weaker $(3d \to p)$ transitions in photoionization time delay calculations.

### B. Mn $4s$-photoionization

In this calculation, we use the experimental values [20] $I_{3d\uparrow}(^5D_4) = 14.301$ eV (versus $I^{\rm SPHF}_{3d\uparrow} = 17.43$ eV), $I_{4s\uparrow}(^5S) = 8.611$ eV (versus $I^{\rm SPHF}_{4s\uparrow} = 7.44$ eV), and $I_{4s\downarrow}(^7S) = 7.431$ eV (versus $I^{\rm SPHF}_{4s\downarrow} = 6.15$ eV). This is because the $4s\uparrow$- and $4s\downarrow$-subshells of the Mn atom are significantly closer, in terms of energy, to the multielectron $3d^5\uparrow$-subshell than predicted by the SPHF theory. The use of the calculated SPHF ionization potentials in this case would have resulted in an underestimated coupling between 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 [31, 32] where a Fano single-resonance formalism was exploited.

Results of the present SPRPAE calculation of $\sigma_{4s\uparrow}(^5S)$, $\sigma_{4s\downarrow}(^7S)$, $\varphi_{4s\uparrow}(^5S)$, $\varphi_{4s\downarrow}(^7S)$, as well as $\tau_{4s\uparrow}(^5S)$ and $\tau_{4s\downarrow}(^7S)$ are depicted in Fig. 4. Note the good agreement between experiment and theory for $\sigma_{4s\uparrow}(^5S)$ and $\sigma_{4s\downarrow}(^7S)$. Furthermore, note how the time delays $\tau_{4s\uparrow}(^5S)$ and $\tau_{4s\downarrow}(^7S)$ are dramatically increased in the resonance region. Next, note how $\tau_{4s\uparrow}(^5S)$ and $\tau_{4s\downarrow}(^7S)$ differ strongly from each other in this energy region where $\tau_{4s\uparrow}(^5S)$ exceeds $\tau_{4s\downarrow}(^7S)$ everywhere below an energy of $\omega \approx 54.7$ eV; above this energy the situation changes to the opposite. It is also interesting to note that $\tau_{4s\uparrow}(^5S)$ and $\tau_{4s\downarrow}(^7S)$ differ from each other strongly not only by magnitude but by sign as well, depending on $\omega$. The noted differences between $\tau_{4s\uparrow}(^5S)$ and $\tau_{4s\downarrow}(^7S)$ constitute an interesting finding of a strong term-dependence of time delay in $4s$-photoionization of Mn. This is due to SPRPAE exchange diagrams (d) and (f) of Fig. 1 which contribute to photoionization of $4s\uparrow$-electron differently than to the $4s\downarrow$-electron. For instance (see Fig. 1), if the intermediate excitation "$j - k'$"$\equiv 3d\uparrow \to \epsilon l\uparrow$, then the exchange diagrams (d) and (f) affect photoionization of a $4s\uparrow$-electron, but not a $4s\downarrow$-electron (otherwise the Coulomb interaction would have caused a spin-flip transition). Alternatively, the diagrams (d) and (f) of Fig. 1 do not affect the $4s\uparrow$-electron but do affect the $4s\downarrow$-photoionization amplitude when "$j - k'$"$\equiv 3p\downarrow \to 3d\downarrow$. Thus, in the region of the $3p\downarrow \to 3d\downarrow$ giant resonance, where the impact of interchannel coupling of the $3p\downarrow \to 3d\downarrow$ and $3d\uparrow \to p\uparrow$, $f\uparrow$ channels with each of the $4s\uparrow \to p\uparrow$ and $4s\downarrow \to p\downarrow$ channels is significant, time delay in the $4s$-photoionization of Mn becomes strongly term dependent. This should be a general feature of other transition-metal atoms and ions as well.

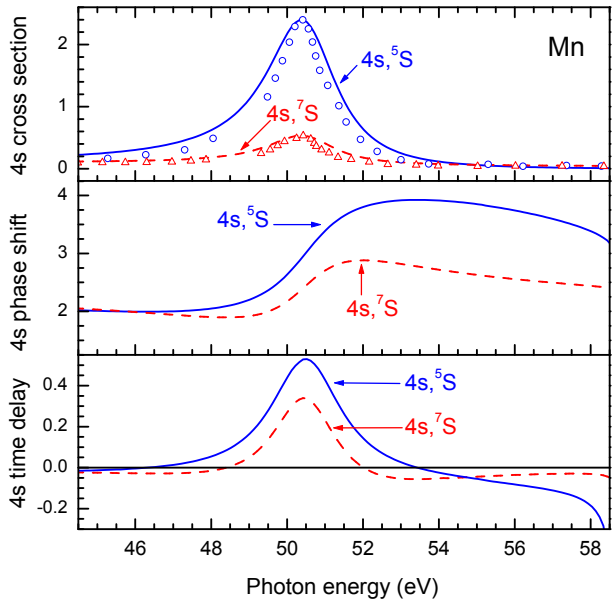


FIG. 4. (Color online) Calculated SPRPAE (present work) and experimentally measured [26] (open circles and triangles) Mn 4$s$-photoionization cross sections (in units of Mb) $\sigma_{4s\uparrow}(^5S)$ and $\sigma_{4s\downarrow}(^7S)$, as well as calculated SPRPAE phase shifts (in units of radians) $\varphi_{4s\uparrow}(^5S)$ and $\varphi_{4s\downarrow}(^7S)$ of the corresponding photoionization amplitudes, Eq. (2), and time delays (in units of femtoseconds) $\tau_{4s\uparrow}(^5S)$, and $\tau_{4s\downarrow}(^7S)$, as marked. Relative experimental data [26] were normalized to the maxima in the calculated SPRPAE $\sigma_{4s\uparrow}(^5S)$ and $\sigma_{4s\downarrow}(^7S)$, respectively, and were shifted by 0.28 eV towards higher energies to match the position of the maxima in the calculated cross sections.

## IV. CONCLUSION

It has been demonstrated in this paper that time delays of the corresponding Mn 3$d$- and 4$s$-photoionization channels are dramatically increased in the region of the $3p \rightarrow 3d$ giant autoionization resonance. Furthermore, by utilizing the Fano formalism, it has been shown that the photoionization time delay in the autoionization resonance region is explicitly associated with the resonance lifetime. The latter, thus, can be determined directly from results of attosecond time delay experiments. Furthermore, it has been found that the time delay of the 4$s$-photoionization channel is strongly term-dependent, resulting in significant differences between time delays $\tau_{4s\uparrow}(^5S)$ and $\tau_{4s\downarrow}(^7S)$. Strong maxima in $\tau_{3d\uparrow}(^4D)$, $\tau_{4s\uparrow}(^5S)$, and $\tau_{4s\downarrow}(^7S)$ emerge at photon energies where the corresponding photoionization cross-sections are large, particularly for 3$d$-photoionization. This should simplify experimental measure-

ments of the phenomena described 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 [43, 44]. This provides the flexibility for experimental verification of the predictions made in this paper. It is expected that the features unraveled 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 features of time delays in Mn photoionization, unveiled in the present paper, 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.

Next, it is important to note that the well-known giant resonance in $4d$-photoionization of Xe, see, e.g., Ref. [30], has found an important application for the induction of a strong enhancement of the high harmonic generation (HHG) process [46]. The autoionization multielectron dynamics can be probed by the HHG technique [47] as well, particularly in the $3p \rightarrow 3d$ giant resonance in Mn, as in recent work by Ganeev et. al. [48], in view of the large value of the Mn $3d$-photoionization cross section in there; the latter 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 [49] and analyzed [50] in the condensed matter phase as well. Solid state Mn is a promising target for such a study.

In conclusion, it would be interesting to study how accounting for a goodly number of other open channels in the Mn $3p \rightarrow 3d$ giant resonance region, omitted in our SPRPAE study, could modify the predicted gross features in $3d$- and $4s$-time delays in this atom (apparently, it does not significantly modify the calculated SPRPAE $\sigma_{3d}$ or $\beta_{3d}$ in Mn). The authors' expectation is that possible alterations should not be drastic, but in the absence of experiment or other theoretical calculations on this subject the question basically remains open. In fact, we consider the photoionization time delay phenomenon in highly correlated atoms as a novel touchstone for a finer testing of existing and to-be-developed many-body theories against experiment. We urge the development of such calculations and experiments, and we hope that the provided in the present paper initial insight into time delay in the Mn photoionization serves as the impetus for such development.

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