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Spin-polarized photoelectrons from half-filled-shell atoms

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A spin-polarized beam of photoelectrons of significant intensity from a closed ns^2-subshell of a spin-aligned atom having a multielectron half-filled subshell in its ground state is predicted. The polarization results from the specific properties of a half-filled shell atom due to the unbalanced exchange interaction between spin-up and spin-down electrons in the atom, both at the independent-particle and multielectron correlation levels. This mechanism causing the preferable spin orientation of outgoing photoelectrons differs from the commonly known mechanisms yielding spin-polarized photoelectrons from atoms. Calculated results for the photoionization of the valence $4s^2$ subshell of a spin-up oriented Mn($4s^2\ {}^6S$) atom employing spin-polarized Hartree-Fock and random-phase approximation with exchange are presented, but the results are inherent properties of any half-filled subshell atom. The importance of electron correlation effects is emphasized.

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I. INTRODUCTION

Sources of spin-polarized electrons have attracted much attention because spin-polarized electrons are used in fundamental experimental studies in the area of photon-atom, electron-atom, and electron-molecular collisions. Commonly known mechanisms that yield spin-polarized photoelectrons upon photoionization of atoms are (i) the Fano mechanism [1], where spin-polarized electrons are produced upon photoionization of a closed ns^2 subshell by a circularly polarized light in a region of a Cooper minimum in the ns-photoionization cross section due to the spin-orbit interaction in final ϵp continuum, (ii) Cherepkov's mechanism [2,3], where, due to the spin-orbit interaction in an atomic nl subshell with $l>0$, high spin-polarization is produced at certain ejected photoelectron angles, and (iii) the production of spin-polarized photoelectrons resulting from photoionization of the valence electron in spin-aligned alkali atoms [4]. Overall, to date, the area of research related to spin-polarized electrons has been developed to a high degree [3,5], including the contribution of nondipole corrections to the photoelectron angular distribution [6–9].

In the present paper, we exploit the idea of producing spin-polarized electrons upon photoionization of spin-aligned atoms; but the atoms of interest here are not alkali atoms but those with a multielectron d^5 or f^7 half-filled subshell, and we focus on the yield of spin-polarized photoelectrons not from an unpaired ns electron, but from a closed valence ns^2 subshell in the atom. The aim of this paper is to show that photoionization of the valence ns^2 subshell in a spin-aligned half-filled shell atom can serve as a source of highly spin-polarized photoelectrons, due to the specifics of the electronic structure of the atom itself and electron-electron correlation in the atom. As an example, consider spin-up-aligned Mn ($3d^5 4s^2\ {}^6S$) atoms for a case study. We show that $4s$ photoelectrons are 100% spin-down polarized (i.e., $s_z=-\hbar/2$, s_z being the z projection of the spin of an electron) at the photon energies $I_{4s}({}^7S)<\hbar\omega<I_{4s}({}^5S)$, where $I_{4s}({}^5S)$ and $I_{4s}({}^7S)$ are the Mn $4s$ ionization thresholds with the Mn$^+$ residual ion in the final ${}^5S$ or ${}^7S$ state, respectively. At greater photon energies, $I_{4s}({}^5S)<\hbar\omega<I_{3d}$, $4s$ photoelectrons may be almost all spin-down or spin-up ($s_z=+\hbar/2$) polarized depending on $\hbar\omega$. At yet greater photon energies, $\hbar\omega>I_{3d}$ but below ionization thresholds of inner shells, the outgoing photoelectrons will be almost 100% spin-up polarized, because the photoionization probability of the spin-up-aligned $3d^5$ subshell of the atom far exceeds the photoionization probability of the valence $4s^2$ subshell in this energy region. These findings are properties not merely of the Mn atom itself but are inherent properties of any atom containing a d^5 or f^7 half-filled subshell.

The impetus for this study comes from our older [10–14] and more recent [15,16] work showing that, for randomly oriented half-filled shell atoms, photoionization cross sections of ns^2 subshells depend strongly on a final state term of the residual ion, due to features of electron correlation in these kinds of atoms. As is shown in the present paper, this leads directly to strongly preferential spin polarization of the photoelectrons from a closed ns^2 subshell upon photoionization of a half-filled shell atom, providing the atom is initially spin aligned.

II. ELEMENTS OF THEORY

The degree of spin-polarization of outgoing ns photoelectrons, $P_{ns}(\omega)$, as a function of the photon energy $\hbar\omega$, is defined in the conventional manner as follow:

$$P_{ns}(\omega)=\frac{\mathcal{I}_{ns}^{\downarrow}(\omega)-\mathcal{I}_{ns}^{\uparrow}(\omega)}{\mathcal{I}_{ns}^{\uparrow}(\omega)+\mathcal{I}_{ns}^{\downarrow}(\omega)}. \qquad (1)$$

Here, $\mathcal{I}_{ns}^{\uparrow}$ and $\mathcal{I}_{ns}^{\downarrow}$ is the intensity of a beam of photoelectrons with a z projection of spin $s_z=+\hbar/2$ and $s_z=-\hbar/2$, respectively, termed *spin-up* (↑) and *spin-down* (↓) electrons. Assuming that all of the half-filled shell atoms in the sample being ionized are 100% spin-up aligned, the intensities $\mathcal{I}_{ns}$ in

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the above equation can be replaced by the corresponding photoionization cross sections $\sigma_{ns\uparrow\downarrow}(\omega)$;

$$P_{ns}(\omega) = \frac{\sigma^{\downarrow}_{ns}(\omega) - \sigma^{\uparrow}_{ns}(\omega)}{\sigma^{\uparrow}_{ns}(\omega) + \sigma^{\downarrow}_{nl}(\omega)} = \frac{1-\gamma_{ns}(\omega)}{1+\gamma_{ns}(\omega)}. \tag{2}$$

Here, $\gamma_{ns}(\omega)=\sigma_{ns\uparrow}(\omega)/\sigma_{ns\downarrow}(\omega)$ is the branching ratio of related photoionization cross sections [17]

$$\sigma_{ns\uparrow\downarrow}(\omega) = \frac{4\pi^2\alpha a_0^2}{3}\omega|D_{ns\uparrow\downarrow}(\omega)|^2. \tag{3}$$

In this equation, α is the fine-structure constant, a_0 is the first Bohr radius, ω is the photon energy (in atomic units), and $D_{ns\uparrow\downarrow}(\omega)$ is the reduced amplitude of a dipole photoionization transition $ns\uparrow\downarrow \rightarrow \epsilon p\uparrow\downarrow$ taken in the length form,

$$D_{ns\uparrow\downarrow}(\omega) \equiv (\epsilon p\uparrow\downarrow\|\hat{D}\|ns\uparrow\downarrow), \tag{4}$$

where $\hat{D}$ is the operator of the electron-photon interaction in the atom, and ϵ is the photo-electron energy.

To determine the photoionization amplitudes $D_{ns\uparrow\downarrow}(\omega)$, we first note that spins of all electrons in the half-filled subshell of an atom are aligned in accordance with Hund's rule. Assume that, in the spin-aligned atom, they are pointing upward (↑), i.e., each of the electrons in the half-filled subshell has a spin projection $s_z=+\hbar/2$. Then, according to Slater [18] each closed subshell in the atom splits into two half-filled subshells of opposite spin orientations. For the Mn ($3d^5 4s^2\ {}^6S$) atom, we thus have $1s\uparrow 1s\downarrow 2s\uparrow 2s\downarrow 2p^3\uparrow 2p^3\downarrow 3s\uparrow 3s\downarrow 3p^3\uparrow 3p^3\downarrow 3d^5\uparrow 4s\uparrow 4s\downarrow$ (${}^6S$). Both the binding energies and wave functions of $nl\uparrow$ and $nl\downarrow$ electrons are the solutions of the "spin-polarized" Hartree-Fock (SPHF) equations [18]. The binding energies and wave functions of $nl\uparrow$ and $nl\downarrow$ electrons are different from one another due to the presence of Coulomb exchange interaction between $nl\uparrow$ electrons with spin-up electrons from a half-filled $3d^5\uparrow$ subshell and the absence of such interaction for $nl\downarrow$ electrons because of the orthogonality of spin functions with different s_z's. Correspondingly, ejection of an $ns\uparrow$ electron from the atom will result in the yield of spin-up photoelectrons that leaves the Mn$^+$ residual ion in an ns^{-1}, ${}^5S$ final state, and we assume $\sigma_{ns\uparrow}=\sigma_{ns}({}^5S)$. Alternatively, ejection of an $ns\downarrow$ electron from the atom will result in yield of spin-down photoelectrons and an ns^{-1}, ${}^7S$ final-state term of the Mn ion remainder, so that $\sigma_{ns\downarrow}=\sigma_{ns}({}^7S)$.

Before proceeding, it is of importance to inquire as to the accuracy of the correspondence $\sigma_{ns\uparrow}\leftrightarrow\sigma_{ns}({}^5S)$ and $\sigma_{ns\downarrow}\leftrightarrow\sigma_{ns}({}^7S)$. This point was investigated earlier [10,11,13,14]. In studies employing this approach, combined with accounting for electron-electron correlation, a convincing interpretation, and explanation both of the experimentally observed cross sections $\sigma_{4s}({}^{5,7}S)$ and $\sigma_{3s}({}^{5,7}S)$ and branching ratios $\sigma_{4s}({}^5S)/\sigma_{4s}({}^7S)$ [19–21], and $\sigma_{3s}({}^5S)/\sigma_{3s}({}^7S)$ [22] in the Mn atom was presented. Also, a transparent interpretation [14] of the experimentally established [23] extreme narrowness of the $3d\rightarrow np$ dipole resonances in the $4s$ photoionization cross section of Cr, in contrast to those in Mn and other $3d$ transition metal atoms, was provided.

III. RESULTS AND DISCUSSION

To obtain the degree of spin-polarization of photoelectrons upon photoionization of $4s\uparrow$ and $4s\downarrow$ electrons in the Mn atom, a knowledge of the $\sigma_{4s\downarrow}$ and $\sigma_{4s\uparrow}$ photoionization cross sections, or the branching ratio $\gamma_{4s}(\omega)$ [see Eq. (2)] is required in the photon energy region between the $4s\uparrow$ and $3d\uparrow$ ionization thresholds. Experimental data are not available for either of them, to the best of our knowledge, so theory is required. To calculate $\sigma_{4s\downarrow}$ and $\sigma_{4s\uparrow}$, both the uncorrelated spin-polarized Hartree-Fock (SPHF) and spin-polarized random-phase-approximation with exchange (SPRPAE) [13,17,24] methodologies are employed; performing calculations within the framework of both approximations is of interest because this allows us to pinpoint the effects of electron-electron correlation. Since these methodologies are discussed in detail in the literature in the above references, we omit their discussion in this paper. In addition, in a recent article [16], calculated $4s\uparrow$ and $4s\downarrow$ photoionization cross sections of the Mn atom along with the discussion of details of SPRPAE calculations are presented. For this paper, only two important details related to the calculations are mentioned. First, according to [16] the SPRPAE interchannel interaction between the transitions from $4s\uparrow$, $4s\downarrow$, and $3d^5\uparrow$ subshells is very strong and dominates over interchannel interactions with deeper subshells; for this reason interchannel interactions with deeper subshells are neglected in the present work as they were in Ref. [16]. Second, as in [16], experimental values [25] for ionization thresholds $I_{4s}({}^5S)=8.61$ eV, $I_{4s}({}^7S)=7.44$ eV, and $I_{3d}({}^5D)=14.30$ eV were substituted into SPRPAE calculations in place of needed $I_{4s\uparrow}$, $I_{4s\downarrow}$, and $I_{3d\uparrow}$. The equivalency between these two different viewpoints on the ionization thresholds in the Mn atom (and in other half-filled shell atoms) was demonstrated earlier [24] where it was shown that SPRPAE correlated data for the spin-up and spin-down ionization thresholds ($I_{4s\uparrow}=8.59$, $I_{4s\downarrow}=7.51$, and $I_{3d\uparrow}=14.10$ eV) reproduce the experimental ionization thresholds quite accurately.

Our recently calculated SPRPAE and SPHF results for the cross sections $\sigma_{4s\downarrow}$ and $\sigma_{4s\uparrow}$ [16] in the photon energy domain between 9 and 13.4 eV, where there are both a Cooper minimum and $3d\uparrow\rightarrow 5p\uparrow$, $6p\uparrow$ autoionizing resonances arising in the cross sections, are shown in Fig. 1. One can see strong differences between the cross sections both in the region of the Cooper minimum and autoionizing resonances. This is primarily due to unbalanced multielectron exchange correlation in the atom, as was detailed recently [16]. In addition, it is seen that the SPRPAE results are dramatically different from the SPHF, thereby demonstrating that the effects of electron-electron correlation dominate these cross sections. In a somewhat different photon energy region, namely, from the lowest $4s\downarrow$ ionization threshold to below the $3d\uparrow\rightarrow 5p\uparrow$, $6p\uparrow$ autoionizing resonances, the calculated $\sigma_{4s\downarrow}$ and $\sigma_{4s\uparrow}$ cross sections are presented in Figs. 2(a)–2(c). These calculations demonstrate that there is a strong $3d\uparrow\rightarrow 4p\uparrow$ autoionizing resonance in the $\sigma_{4s\downarrow}$ photoionization cross section in the near threshold region where $\sigma_{4s\downarrow}$ is increased mightily, up to almost 200 Mb. This resonance is absent in $\sigma_{4s\uparrow}$ since the resonance occurs at a photon energy which is quite a bit below the $4s\uparrow$ ionization threshold. In

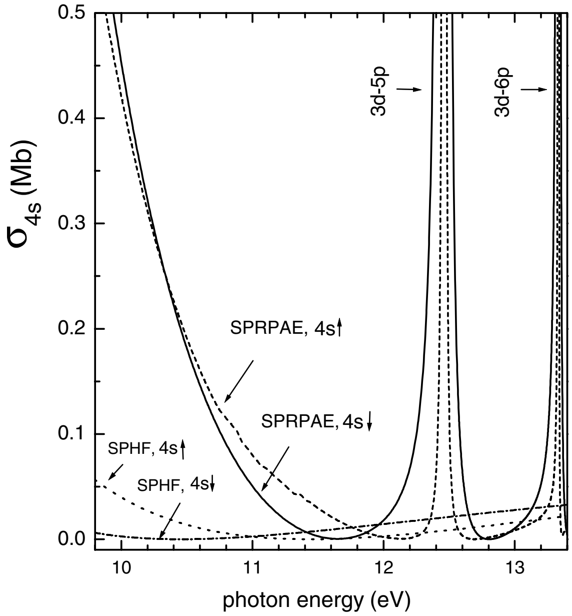

FIG. 1. SPHF and SPRPAE results for $4s\uparrow$ and $4s\downarrow$ photoionization cross sections $\sigma_{4s\uparrow}(\omega)$ and $\sigma_{4s\downarrow}(\omega)$ of a spin-up-aligned Mn atom in the photon energy region between 9.8 and 13.4 eV [16].

any case, in the photon energy region from 7.44 to 8.61 eV, i.e., from the $4s\downarrow$ ionization threshold to the $4s\uparrow$ threshold, the photoelectrons from a spin-up-aligned Mn atom will be 100% spin-down polarized; and, away from the $3d\uparrow \rightarrow 4p\uparrow$ resonances at about 7.4 eV, the cross section (and therefore, the intensity of spin-polarized yield) will be huge. In this threshold region, electron-electron correlation is even more dominant than at the slightly higher energies discussed above. At the $4s\downarrow$ ionization threshold, 7.44 eV, for example, the SPRPAE cross section is seen to be a factor of 500 larger than the SPHF result.

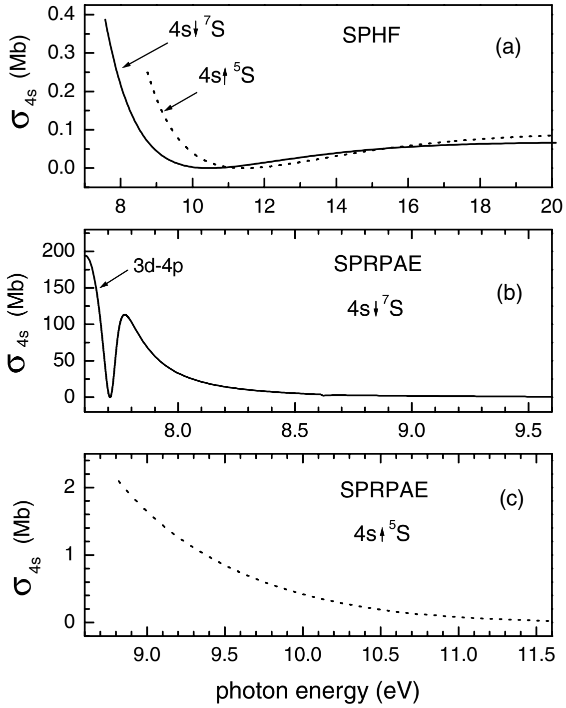

FIG. 2. SPHF [panel (a)] and SPRPAE [panels (b) and (c)] results for $4s\uparrow$ (dotted line) and $4s\downarrow$ (solid line) photoionization cross sections $\sigma_{4s\uparrow}(\omega)$ and $\sigma_{4s\downarrow}(\omega)$ of a spin-up-aligned Mn atom in the photon energy region between 7.5 and 11.6 eV. The near-threshold resonance structure in the photoionization cross section $\sigma_{4s\downarrow}(\omega)$ is due to a $3d\uparrow \rightarrow 4p\uparrow$ autoionizing resonance.

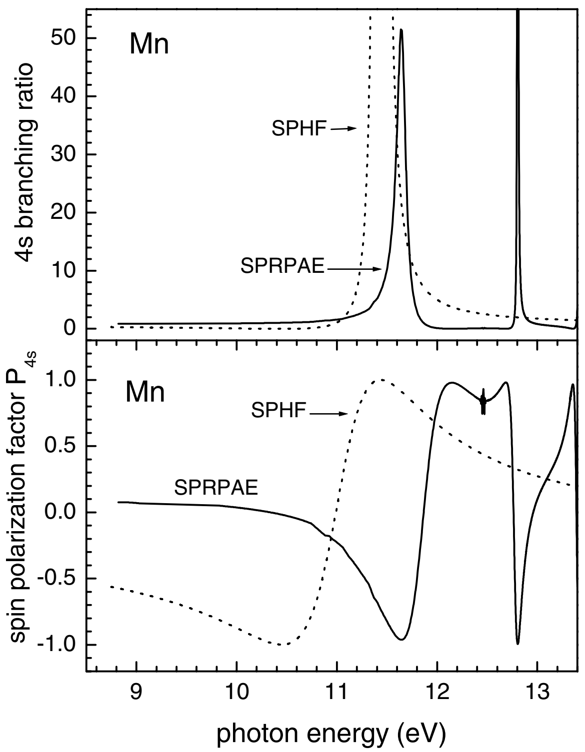

FIG. 3. The $\gamma_{4s}(\omega)=\sigma_{4s\uparrow}(\omega)/\sigma_{4s\downarrow}(\omega)$ branching ratio (upper panel) and the spin-polarization factor $P_{4s}(\omega)$ (lower panel) showing the yield of spin-polarized photoelectrons upon $4s$ photoionization of *spin-up-aligned* Mn atoms calculated within the framework of SPRPAE (solid line) and SPHF (dotted line).

In the photon energy region $I_{4s\uparrow} < \hbar\omega < I_{3d\uparrow}$, i.e., between the $4s^{-1}\ {}^5S$ and the first $3d$ thresholds, the $4s$ branching ratio is shown in Fig. 3 where significant structure is seen. The peak at about 11.6 eV is due to the Cooper minimum in the $4s\downarrow$ (^7S) photoionization channel, and the higher energy peak is due to the near-zero in the same channel between the two resonances shown in Fig. 1. The importance of correlation is also manifested by the significant differences between the SPHF and SPRPAE results. The resultant $P_{4s}(\omega)$, the spin-polarization of photoelectrons resulting from $4s$ photoionization of spin-up-aligned Mn atom is obtained from Eq. (2) using the cross sections and branching ratio discussed above, and the results are also presented in Fig. 3. Note, however, that this is the *total* spin-polarization of all photoelectrons, summed over both channels (^7S and ^5S); thus the photoelectrons are not monoenergetic. It is seen that, as a consequence of the major differences both in the magnitude and energy dependence between $\sigma_{4s\downarrow}(\omega)$ and $\sigma_{4s\uparrow}(\omega)$, the spin-polarization factor $P_{4s}(\omega)$ acquires a complicated energy dependence in the entire energy region, and there are clearly seen broad domains where the ejected photoelectrons are nearly 100% spin-up ($P_{4s} \approx 1$) or spin-down ($P_{4s} \approx -1$) polarized. Furthermore, it is evident that the degree of spin-polarization is crucially affected by electron correlation, as can be judged by comparing SPRPAE and SPHF calculated results for $P_{4s}(\omega)$.

IV. CONCLUSION

In summary, it has been shown that even photoionization of *closed* valence ns^2 subshells in spin-aligned half-filled subshell atoms can be an effective source of highly spin-polarized photoelectron beams. This source of spin-polarized electrons has certain advantages over some of the previous spin-polarization mechanisms because the degree of spin-polarization, in the present case, depends neither on polarization of the incoming radiation nor on the angular distribution of emitted photoelectrons. Moreover, the mechanism for producing spin-polarized electrons discussed herein exhibits much larger cross section, and therefore, intensity, as compared to the Fano mechanism [1]. Indeed, the latter exploits the small difference between final states $\epsilon p_{1/2}$ and $\epsilon p_{3/2}$ due to the spin-orbit interaction in continuum that causes the Cooper minimum in a photoionization channel $\epsilon p_{1/2}$ to be slightly different from that in $\epsilon p_{3/2}$ that, in turn, causes a nonzero spin-polarization of outgoing photoelectrons. However, electron correlation in the Mn atom induces a much stronger difference between $\sigma_{4s\downarrow}(\omega)$ and $\sigma_{4s\uparrow}(\omega)$, even in the region of Cooper minima in the cross sections. Finally, Cherepkov's mechanism is not relevant to this case since we deal not with a subshell with $l > 0$ but with a subshell with $l = 0$ where there is no spin-orbit interaction.

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