Electron elastic scattering off a semifilled-shell atom: The Mn atom

V. K. Dolmatov,[1] M. Ya. Amusia,[2,3] and L. V. Chernysheva[3]
[1]*University of North Alabama, Florence, Alabama 35632, USA*
[2]*Racah Institute of Physics, Hebrew University, 91904 Jerusalem, Israel*
[3]*A. F. Ioffe Physical-Technical Institute, 194021 St. Petersburg, Russia*
(Received 13 August 2013; published 11 October 2013)

The impact of both exchange interaction and electron correlation, as well as their combined impact, on electron elastic scattering off a semifilled-shell Mn($\dots 3d^5 4s^2$, ^6S) atom are theoretically studied in the electron energy range of $\epsilon = 0$–25 eV. Corresponding elastic-scattering phase shifts $\delta_\ell(\epsilon)$ as well as partial $\sigma_\ell(\epsilon)$ and total $\sigma(\epsilon)$ cross sections are found to be subject to a strong correlation impact. The latter is shown to drastically differ for oppositely spin-polarized scattered electrons in some cases, thereby bringing significant differences in corresponding $\delta_\ell(\epsilon)$s, $\sigma_\ell(\epsilon)$s, and $\sigma(\epsilon)$s between these electrons. This is proven to be an inherent feature of electron scattering off a semifilled-shell atom in general. Electron correlation is accounted for in the framework of the self-energy part Σ of the Green function of a scattered electron concept. The latter is calculated both in the second-order perturbation theory in the Coulomb interelectron interaction as well as beyond it by solving the Dyson equation for Σ. The significance of the "Dyson" correlation corrections in $e^- +$Mn scattering is unraveled. They are shown to noticeably increase the inherent differences between elastic-scattering phase shifts and cross sections of spin-up ($\uparrow$) and spin-down ($\downarrow$) polarized electrons scattered off a spin-polarized Mn atom, in some cases. In particular, the existence of a narrow resonant maximum in $\sigma^\downarrow(\epsilon)$ near $\epsilon \approx 8$ eV but the absence of such in $\sigma^\uparrow(\epsilon)$ in $e^- +$Mn scattering is predicted.

DOI: 10.1103/PhysRevA.88.042706 PACS number(s): 34.80.Bm, 31.15.V−, 34.80.Nz

I. INTRODUCTION

The $3d^5$ semifilled-shell Mn($\dots 3d^5 4s^2$, ^6S) atom has long served as the bridge to, and touchstone for, a better understanding of the interaction of transition-metal atoms with x-ray and vacuum-ultraviolet radiation from the early days (see, e.g., the works by Connerade *et al.* [1], Davis and Feldkamp [2], Amusia *et al.* [3]) to now (see review papers by Sonntag and Zimmermann [4], Martins *et al.* [5], as well as some of the most recent papers by Frolov *et al.* [6], Osawa *et al.* [7], Hirsch *et al.* [8], and references therein). The structure and spectra of the Mn atom are of self-interest as well, in view of the found abundance of unique features associated with its semifilled $3d^5$ subshell.

In contrast, studies of another process of the basic and applied significance—electron scattering off the Mn atom—are too scarce. The Mn atom presents a special interest for studying electron-scattering processes. This is because it belongs to a class of atoms with the highest spin multiplicity. The latter is due to codirected spins of all five electrons in the Mn $3d^5$ subshell, due to Hund's rule. As of today, understanding of electron scattering off Mn is rudimentary. The only available experimental data relate to corresponding $e^- +$Mn differential scattering cross sections (DSC) measured at a *single* value of the electron energy $\epsilon = 20$ eV by Williams *et al.* [9] and Meintrup *et al.* [10]. The same stands for theoretical studies as well. Thus, to understand and interpret the experiment, Amusia and Dolmatov [11] calculated the 20-eV $e^- +$Mn elastic DCS in the framework of a multielectron simplified "spin-polarized" random-phase approximation with exchange (SPRPAE) [12]; Meintrup *et al.* [10] did it in a R-matrix framework; and, recently, Remeta and Kelemen [13] performed their calculations of the DCS in the framework of a local spin density approximation but, again, only at discrete values of the electron energies of 10 and 20 eV.

Whatever interesting effects were found in the above cited works, they provide only a limited insight into a problem, since things might work quite differently at other, especially lower, electron energies but only the 10- and 20-eV energies. Clearly, studying the scattering process through a continuum spectrum of electron energies is a way toward a deeper understanding of, as well as discovering new trends in, $e^- +$Mn elastic scattering, in particular, and $e^- +$ *any semifilled-shell atom*, in general. However, no such study has been performed to date, to the best of these authors' knowledge. Its performance is, thus, not merely a wish but necessity.

It is the ultimate aim of the present paper to study $e^- +$Mn elastic scattering through a continuum spectrum of electron energies to fill in an important gap in the current knowledge on this process. To meet this end, we focus on calculations of $e^- +$Mn elastic-scattering phase shifts $\delta_\ell(\epsilon)$ and the corresponding total cross section $\sigma(\epsilon)$ in the electron energy range of 0–25 eV.

The performed calculations, following the work in Ref. [12], utilize a concept of the reducible self-energy part $\tilde{\Sigma}(\epsilon)$ of the Green function G of an incoming electron. The calculations are carried out in three consequentially growing levels of sophistication. First, this is a one-electron "spin-polarized" Hartree-Fock (SPHF) approximation [14] which is the zero-order approximation in perturbation theory in the Coulomb interelectron interaction V for the Green function. In Refs. [11,13], SPHF was adapted, as well as proven to be applicable, to the description of elastic electron scattering off semifilled-shell atoms. Second, $\tilde{\Sigma}(\epsilon)$ is calculated in the second-order approximation in perturbation theory in V to account for electron correlation in the system. This approximation is known as a simplified random-phase approximation with exchange [12] and, with SPHF being chosen as the zero-order approximation with respect to electron correlation interactions, is referred to as SPRPAE1 in the present paper. Third, for a more complete account of electron correlations in electron scattering, $\tilde{\Sigma}(\epsilon)$ is determined beyond the SPRPAE1 approximation by solving the Dyson equation for $\tilde{\Sigma}(\epsilon)$ of a scattered electron, as in Ref. [12]. Such an approximation is referred to as SPRPAE2 in the paper. By comparing results obtained in the framework of each of the SPHF, SPRPAE1, and SPRPAE2 approximations we unravel several important trends in $e^- +$Mn scattering; these have already been noted in the abstract and are subject to a detailed discussion in text. Atomic units (a.u.) are used throughout the paper unless specified otherwise.

II. REVIEW OF THEORY

A. SPHF

A convenient starting point to study the structure and spectra of semifilled-shell atoms is a "spin-polarized" Hartree-Fock (SPHF) approximation [14]. Over the years, SPHF has been extensively and successfully exploited by the authors of this paper and their colleagues (see, e.g., Refs. [3,15–18]) by using it directly or utilizing it as the zero-order approximation for a multielectron random-phase approximation with exchange (RPAE) [12] to study photoionization of these atoms and their ions. As noted earlier, SPHF was also used successfully by Amusia and Dolmatov [11] to provide the initial understanding and interpretation of experimental data of Williams *et al.* [9] on the 20-eV $e^- +$Mn elastic DCS. Recently, SPHF has been employed by Remeta and Kelemen [13] to adapt a local density approximation to electron scattering off semifilled-shell atoms, including Mn, to provide a further understanding of results of experiments [9,10].

The quintessence of SPHF is as follows. It accounts for the fact that spins of all electrons in a semifilled subshell of the atom (e.g., in the $3d^5$ subshell of Mn) are codirected, in accordance with Hund's rule. It will be assumed in the present paper that spins of these electrons point upward ($\uparrow$). This results in splitting of each of other closed $n\ell^{2(2\ell+1)}$ subshells in the atom into two semifilled subshells of opposite spin orientations, $n\ell^{2\ell+1}\uparrow$ and $n\ell^{2\ell+1}\downarrow$. This is in view of the presence of exchange interaction between $nl\uparrow$ electrons with spin-up electrons in the original semifilled subshell of the atom but absence of such for $nl\downarrow$ electrons. Thus, the atom of concern of this paper—the Mn atom—has the following SPHF configuration: Mn$(\ldots 3p^3\uparrow 3p^3\downarrow 3d^5\uparrow 4s^1\uparrow 4s^1\downarrow,\ ^6S)$. SPHF equations for the ground or excited states of a semifilled-shell atom differ from ordinary HF equations for closed-shell atoms (see, e.g., Ref. [12]) by accounting for exchange interaction only between electrons with the same spin orientation ($\uparrow,\uparrow$ or $\downarrow,\downarrow$).

By solving SPHF equations, one determines radial parts $P^{\uparrow}_{\epsilon\ell}(r)$ and $P^{\downarrow}_{\epsilon\ell}(r)$ of the wave functions of spin-up and spin-down electrons in the ground, excited, or scattering state of the atom. For the continuum energy spectrum of scattered electrons, $P^{\uparrow(\downarrow)}_{\epsilon\ell}(r)$ have the well-known asymptotic behavior at large $r \gg 1$ as follows:

$$P^{\uparrow(\downarrow)}_{\epsilon\ell}(r) \approx \frac{1}{\sqrt{\pi k}} \sin\left(kr - \frac{\pi\ell}{2} + \delta^{(0)\uparrow(\downarrow)}_{\ell}(\epsilon)\right). \quad (1)$$

Here, k, ℓ, ϵ, and $\delta^{\mathrm{SPHF}\uparrow(\downarrow)}_{\ell}(\epsilon)$ are the momentum, orbital momentum, energy, and the phase shift of a scattered electron, respectively. The total electron elastic-scattering cross sections of spin-up ($\sigma^{\uparrow}$) and spin-down ($\sigma^{\downarrow}$) electrons are determined as

$$\sigma^{\uparrow(\downarrow)}(k) = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta^{\mathrm{SPHF}\uparrow(\downarrow)}_{\ell}(k). \quad (2)$$

B. SPRPAE1

A simplified random-phase approximation with exchange, version-1 (SPRPAE1), accounts for electron correlation in a $e^- + A$ system in the second-order perturbation theory in the Coulomb interelectron interaction V between the incoming and atomic electrons [12]. The approximation exploits the concept of the reducible self-energy part of the one-electron Green function $\tilde{\Sigma}(\epsilon)$ of a spin-up, $\tilde{\Sigma}^{\uparrow}(\epsilon)$, or spin-down, $\tilde{\Sigma}^{\downarrow}(\epsilon)$, scattered electron. In the framework of SPRPAE1, $\tilde{\Sigma}^{\uparrow(\downarrow)}(\epsilon)$ is illustrated with the help of Feynman diagrams in Fig. 1.

In Fig. 1, diagrams (a) and (c) are called "*direct*" diagrams, in contrast to "*exchange*" diagrams, Figs. 1(b) and 1(d). The latter two are due to exchange interaction in a $e^- + A$ system. Basically, the diagrams in Fig. 1 illustrate how an incoming electron "ϵ_ℓ" polarizes a j subshell in the atom by causing actual or virtual excitations $j \to m$ from the subshell, and couples with these excited states itself via the Coulomb interaction. Note that the exchange diagrams (b) and (d) in Fig. 1 vanish whenever spin directions of an incoming electron and polarized subshell of the atom are opposite, due to orthogonality of electron spin functions. We do not account for spin-flip effects since they are negligible in $e^- +$Mn scattering [10] at the energies of interest.

Once $\tilde{\Sigma}^{\uparrow(\downarrow)}$ is calculated, the elastic electron-scattering phase shifts of spin-up and spin-down electrons are determined as [12]

$$\delta^{\uparrow(\downarrow)}_{\ell} = \delta^{\mathrm{SPHF}\uparrow(\downarrow)}_{\ell} + \Delta\delta^{\uparrow(\downarrow)}_{\ell}. \quad (3)$$

Here $\Delta\delta^{\uparrow(\downarrow)}_{\ell}$ is the correlation correction term to the SPHF-calculated phase shift $\delta^{\mathrm{SPHF}\uparrow(\downarrow)}_{\ell}$,

$$\Delta\delta^{\uparrow(\downarrow)}_{\ell} = \tan^{-1}\left(-\pi\langle\epsilon\ell^{\uparrow(\downarrow)}|\tilde{\Sigma}^{\uparrow(\downarrow)}|\epsilon\ell^{\uparrow(\downarrow)}\rangle\right). \quad (4)$$

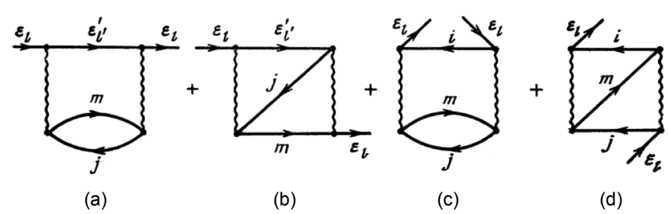

FIG. 1. The reducible self-energy part $\tilde{\Sigma}^{\mathrm{SPRPAE1}\uparrow(\downarrow)}(\epsilon)$ of the Green function of a scattered electron as defined in SPRPAE1. Here a line with a right arrow denotes an electron, whether a scattered electron (lines marked by ϵ_l, $\epsilon'_{l'}$) or an atomic excited electron (a line m), a line with a left arrow denotes a vacancy (hole) in the atom (lines j and i), and a wavy line denotes the Coulomb interelectron interaction V. On the other hand, the notations ϵ_l, $\epsilon'_{l'}$, m, j, and i themselves stand for corresponding electronic states: $|\epsilon_l\rangle$, $\langle j|$, and so on.

A mathematical expression for the matrix element $\langle \epsilon\ell^{\uparrow(\downarrow)}|\tilde{\Sigma}^{\uparrow(\downarrow)}|\epsilon\ell^{\uparrow(\downarrow)}\rangle$ is obtained with the help of the many-body correspondence rules [12]; we refer the reader for details to Ref. [12].

When the energy of a scattered electron exceeds the ionization threshold of the atom scatterer, the term $\Delta\delta_\ell^{\uparrow(\downarrow)}$ and, thus, the phase shift $\delta_\ell^{\uparrow(\downarrow)}$ itself become complex [12]. Correspondingly,

$$\delta_\ell^{\uparrow(\downarrow)} = \lambda_\ell^{\uparrow(\downarrow)} + i\mu_\ell^{\uparrow(\downarrow)}. \quad (5)$$

Here $\lambda_\ell^{\uparrow(\downarrow)}$ and $\mu_\ell^{\uparrow(\downarrow)}$ are the real and imaginary parts of $\delta_\ell^{\uparrow(\downarrow)}$, respectively,

$$\lambda_\ell^{\uparrow(\downarrow)} = \delta_\ell^{\mathrm{SPHF}\uparrow(\downarrow)} + \mathrm{Re}\Delta\delta_\ell^{\uparrow(\downarrow)}, \quad \mu_\ell^{\uparrow(\downarrow)} = \mathrm{Im}\Delta\delta_\ell^{\uparrow(\downarrow)}. \quad (6)$$

The total electron elastic-scattering cross section is then determined [12] by

$$\sigma = \frac{2\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)(\cosh 2\mu_\ell - \cos 2\lambda_\ell)\mathrm{e}^{-2\mu_\ell}. \quad (7)$$

In the context of the present paper, $\sigma \equiv \sigma^{\uparrow(\downarrow)}$, $\mu_\ell \equiv \mu_\ell^{\uparrow(\downarrow)}$, and $\lambda_\ell \equiv \mu_\ell^{\uparrow(\downarrow)}$.

C. SPRPAE2

Version 2 of the simplified random-phase approximation with exchange (SPRPAE2) provides a fuller account for electron correlation. There, the reducible self-energy part of the one-electron Green function of a scattered electron is sought as the solution of corresponding Dyson equation [12]. The latter, in an operator form, in terms of spin-up and spin-down electrons, is

$$\hat{\tilde{\Sigma}}^{\uparrow(\downarrow)} = \hat{\Sigma}^{\uparrow(\downarrow)} - \hat{\Sigma}^{\uparrow(\downarrow)}\hat{G}^{\mathrm{SPHF}\uparrow(\downarrow)}\hat{\tilde{\Sigma}}^{\uparrow(\downarrow)}. \quad (8)$$

Here $\hat{\Sigma}^{\uparrow(\downarrow)}$ and $\hat{\tilde{\Sigma}}^{\uparrow(\downarrow)}$ are the operators of the irreducible and reducible self-energy components of the Green-function operator for an incoming electron, respectively, and $\hat{G}^{\mathrm{SPHF}\uparrow(\downarrow)}$ is the operator of the Green function in the framework of SPHF: $\hat{G}^{\mathrm{SPHF}\uparrow(\downarrow)} = (\hat{H}^{\mathrm{SPHF}\uparrow(\downarrow)} - \epsilon)^{-1}$, where $\hat{H}^{\mathrm{SPHF}\uparrow(\downarrow)}$ is the SPHF Hamiltonian operator of the system.

In SPRPAE2, to avoid tremendous calculation difficulties, the general Dyson equation, Eq. (8), is simplified [12]. This is achieved by replacing the operator of the irreducible self-energy component of the Green function $\hat{\Sigma}^{\uparrow(\downarrow)}$ by $\tilde{\Sigma}^{\mathrm{SPRPAE1}\uparrow(\downarrow)}$ (see Fig. 1) to a good approximation. As in SPRPAE1, corresponding SPRPAE2 phase shifts $\delta_\ell^{\uparrow(\downarrow)}$ and total cross sections $\sigma^{\uparrow(\downarrow)}$ are determined by Eqs. (3)–(7).

III. RESULTS AND DISCUSSION

A. Elastic-scattering phase shifts

In the present paper, $e^- + \mathrm{Mn}$ elastic electron scattering is investigated in the electron energy range between approximately 0 and 25 eV as a case study. This is because core-polarization effects in $e^- + \mathrm{Mn}$ elastic electron scattering are expected to be particularly strong at low electron energies. A trial calculation showed that, at the given energies, accounting for contributions of only s, p, d, and f partial waves to the total elastic-scattering cross section, as well as accounting for only monopole, dipole, quadrupole, and octupole excitations of the atomic core in calculations of $\hat{\tilde{\Sigma}}^{\uparrow(\downarrow)}$ is an excellent approximation. SPHF-, SPRPAE1-, and SPRPAE2-calculated data for real ($\lambda_\ell^{\downarrow}$) and imaginary ($\mu_\ell^{\downarrow}$) parts of elastic-scattering phase shifts $\delta_\ell^{\downarrow}(\epsilon)$ of spin-down electronic waves are depicted in Figs. 2 and 3, and those for $\lambda_\ell^{\uparrow}$ and $\mu_\ell^{\uparrow}$ of $\delta_\ell^{\uparrow}$ for spin-up electronic waves in Figs. 4 and 5.

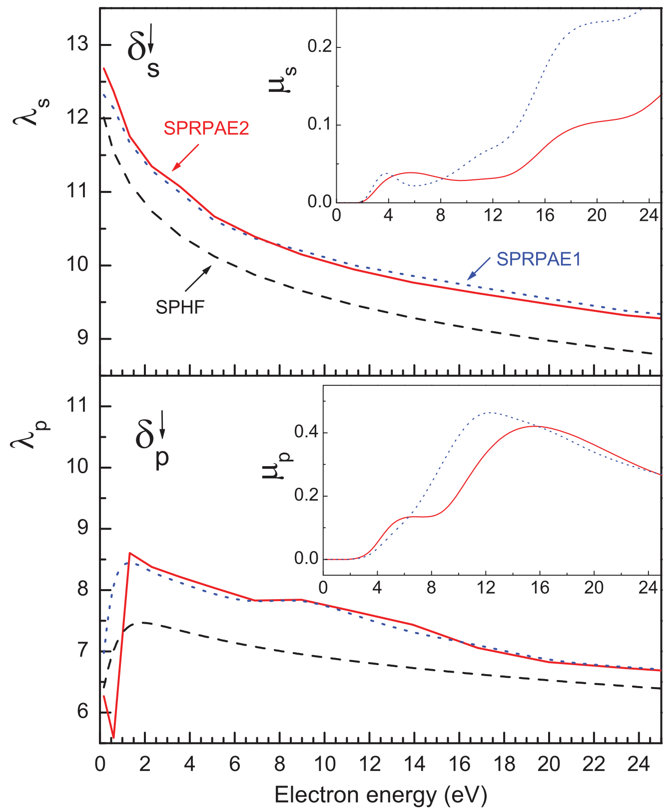

FIG. 2. (Color online) SPHF- (dashed line), SPRPAE1- (dotted line), and SPRPAE2- (solid line) calculated data (in units of radians) for real ($\lambda_\ell^{\downarrow}$) and imaginary ($\mu_\ell^{\downarrow}$) parts of the $e^- + \mathrm{Mn}$ elastic-scattering phase shifts $\delta_\ell^{\downarrow}(\epsilon) = \lambda_\ell(\epsilon) + i\mu_\ell(\epsilon)$ of s and p spin-down electronic waves versus the electron energy ϵ.

The depicted data unravel important trends in low-energy $e^- + \mathrm{Mn}$ elastic scattering which are detailed below.

1. *The effects of electron correlation in $e^- + \mathrm{Mn}$ elastic scattering*

First, one can see from Figs. 2–5 that both SPRPAE1 and SPRPAE2 correlations affect strongly all phase shifts quantitatively and in a number of cases—for p, d, and f partial waves—even qualitatively compared to SPHF-calculated data. Thus, the utter importance of electron correlation in the $e^- + \mathrm{Mn}$ low-energy elastic electron scattering is revealed.

Second, notice how SPRPAE2-calculated data for low-energy $\delta_d^{\uparrow\downarrow}(\epsilon)$ phase shifts differ drastically from calculated data obtained in the framework of SPRPAE1. Indeed, the SPRPAE2-calculated phase shift $\delta_d^{\downarrow}(\epsilon)$ (Fig. 3) drops abruptly,

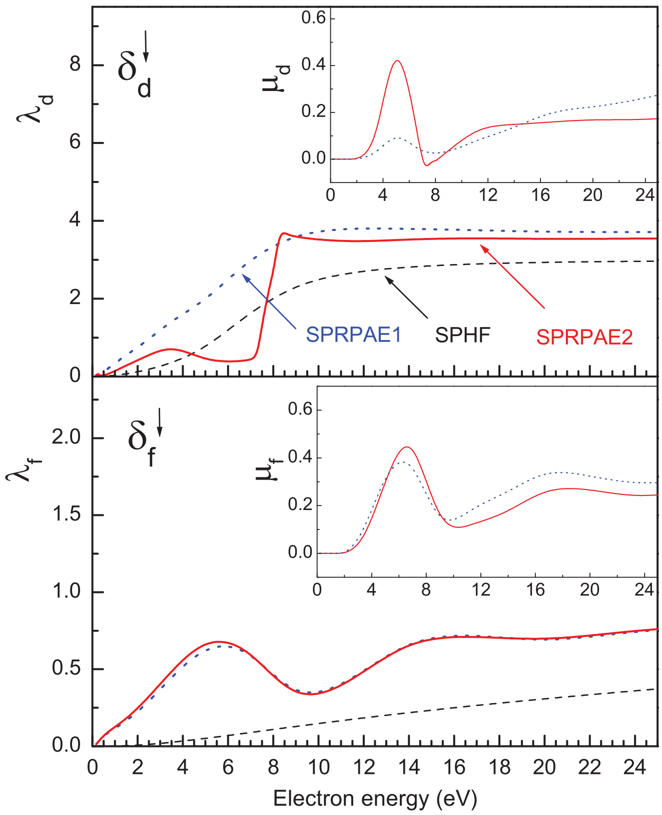

FIG. 3. (Color online) SPHF- (dashed line), SPRPAE1- (dotted line), and SPRPAE2- (solid line) calculated data (in units of radians) for real ($\lambda_\ell^\downarrow$) and imaginary ($\mu_\ell^\downarrow$) parts of the $e^- + \text{Mn}$ elastic-scattering phase shifts $\delta_\ell^\downarrow(\epsilon)$ of d and f spin-down electronic waves.

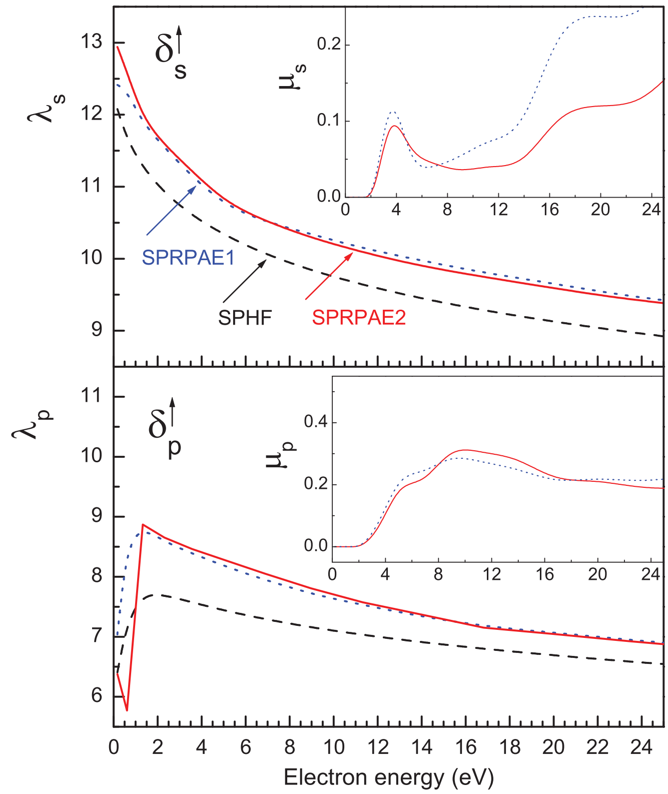

FIG. 4. (Color online) SPHF- (dashed line), SPRPAE1- (dotted line), and SPRPAE2- (solid line) calculated data (in units of radians) for real ($\lambda_\ell^\uparrow$) and imaginary ($\mu_\ell^\uparrow$) parts of the $e^- + \text{Mn}$ elastic-scattering phase shifts $\delta_\ell^\uparrow(\epsilon)$ of s and p spin-up electronic waves.

with decreasing electron energy, from $\delta_d^\downarrow(\epsilon) \approx 3.5$ to $\delta_d^\downarrow(\epsilon) \approx 0.5$ rad between 8 and 7 eV, and then develops a maximum at yet lower energies, after which it approaches its final value of $\delta_d^\downarrow(\epsilon) \approx 0$ at $\epsilon = 0$. Clearly, the described behavior of SPRPAE2-calculated $\delta_d^\downarrow(\epsilon)$ has little in common with that obtained in the framework of SPRPAE1. Strong quantitative differences take place between SPRPAE1- and SRPAR2-calculated data for $\delta_d^\uparrow(\epsilon)$ as well; see Fig. 5. Also, notice abrupt changes in SPRPAE2-calculated phase shifts $\delta_p^{\uparrow\downarrow}(\epsilon)$ between approximately 0 and 2 eV, in opposition to those calculated in SPRPAE1. The found drastic differences between SPRPAE2- and SPRPAE1-calculated phase shifts is a novel result; it was not observed in previous similar calculations performed for other atoms. Thus, the present work reveals, and generally proves, the necessity for a fuller account (as in SPRPAE2) of correlation beyond the second-order approximation (SPRPAE1) for an adequate understanding of $e^- + \text{Mn}$ scattering.

Third, which is of significant importance, notice differences between phases of scattered electronic waves with the same ℓs but opposite spin orientations, $\delta_\ell^\downarrow$ versus $\delta_\ell^\uparrow$. These differences are drastic for ϵd as well as ϵf spin-up and spin-down waves in all three SPHF, SPRPAE1, and SPRPAE2 approximations (see Figs. 3 and 5). For other spin-up and spin-down waves, the differences in question are less spectacular but, nevertheless, exist as well. Thus, it is revealed in the present study that, generally, scattering of oppositely spin-polarized electrons off the Mn atom take different routes.

Below, we provide reasons for the predicted trends in the $e^- + \text{Mn}$ electron-scattering phase shifts.

2. The origin of the zero-order (SPHF) difference between scattering of spin-up and spin-down electrons off Mn

In SPHF, the dependence of $e^- + \text{Mn}$ scattering phase shifts on a spin-orientation of a scattered electron is a straightforward effect. It is due to the presence or absence of exchange interaction between, respectively, $\epsilon\ell\uparrow/\epsilon\ell\downarrow$ incoming electrons and primarily five $3d\uparrow$ electrons in the semifilled $3d^5\uparrow$ subshell in the atom. This is a characteristic feature of elastic electron scattering off any semifilled-shell atom, for an obvious reason.

Next, since no stable negative Mn ion exists with the ground-state atomic core configuration [19], the number $q_{d\uparrow}$ of bound $d\uparrow$ states in the atom is $q_{d\uparrow} = 1$ (due to the presence of $3d^5\uparrow$ subshell in the atom), whereas corresponding $q_{d\downarrow} = 0$. Consequently, in accordance with the generalized Levinson's theorem [$\delta_\ell(\epsilon) \to (n_\ell + q_\ell)\pi$ as $\epsilon \to 0$, n_ℓ being the number of bound states with given ℓ in the field of an atom and q_ℓ being the number of occupied ℓ states in the atom itself] [20], $\delta_d^{\text{SPHF}\uparrow}(\epsilon) \to \pi$, whereas $\delta_d^{\text{SPHF}\downarrow}(\epsilon) \to 0$ as $\epsilon \to 0$. This translates into the initial drastic quantitative and qualitative differences between SPHF-calculated phase shifts

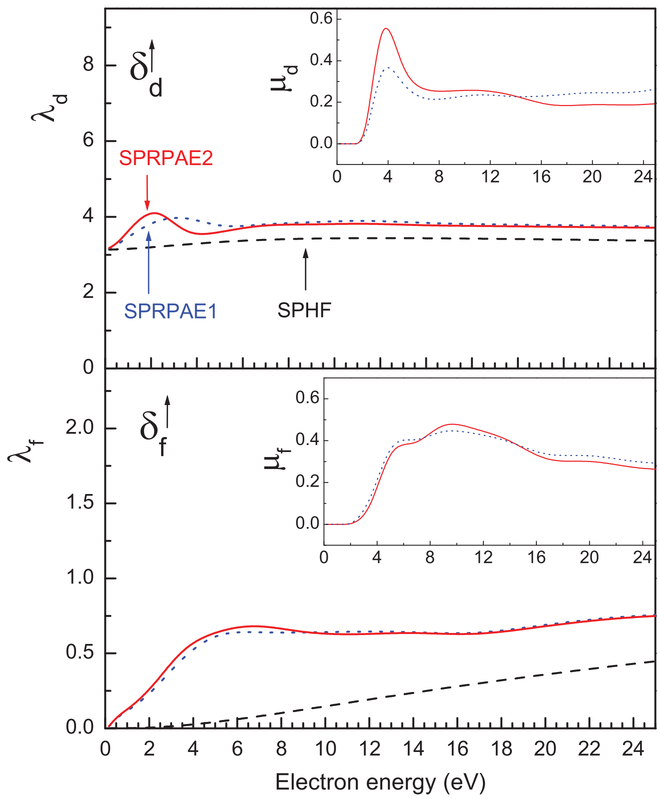

FIG. 5. (Color online) SPHF- (dashed line), SPRPAE1- (dotted line), and SPRPAE2- (solid line) calculated data (in units of radians) for real ($\lambda_\ell^\uparrow$) and imaginary ($\mu_\ell^\uparrow$) parts of the $e^- +$Mn elastic-scattering phase shifts $\delta_\ell^\uparrow(\epsilon)$ of d and f spin-up electronic waves.

$\delta_d^{\mathrm{SPHF}\downarrow}(\epsilon)$ (Fig. 3, dashed line) and $\delta_d^{\mathrm{SPHF}\uparrow}(\epsilon)$ (Fig. 5, dashed line).

3. The origin of the second-order (SPRPAE1) difference between scattering of spin-up and spin-down electrons off Mn

In SPRAE1, compared to SPHF, differences between $\delta_d^\downarrow$ and $\delta_d^\uparrow$ scattering phases become even more spectacular. Indeed, one can see (Fig. 3, dotted line) that the SPRPAE1-calculated real part $\lambda_d^\downarrow$ of $\delta_d^\downarrow$ is a monotonic function of ϵ in the interval of 8 to 0 eV, but the real part $\lambda_d^\uparrow$ of $\delta_d^\uparrow$ (Fig. 5, dotted line) is not. The latter now has a well-developed minimum followed by an appreciable maximum with decreasing energy 8 $\to$ 0 eV. This results, partly, in an additional, compared to SPHF, quantitative as well as qualitative difference between $\delta_d^\downarrow$ and $\delta_d^\uparrow$, due to the effects of electron correlation.

Next, when SPRPAE1 correlation is accounted for, no lesser spectacular differences also emerge between the calculated $\delta_f^\downarrow$ and $\delta_f^\uparrow$ scattering phases. Indeed, SPRPAE1 correlation is seen to induce strong differences between the real parts $\lambda_f^\downarrow$ (Fig. 3, dotted line) and $\lambda_f^\uparrow$ (Fig. 5, dotted line) of phase shifts $\delta_f^\downarrow$ and $\delta_f^\uparrow$: $\lambda_f^{\mathrm{SPRPAE1}\downarrow}$ turns into an oscillating function of ϵ, whereas $\lambda_f^{\mathrm{SPRPAE1}\uparrow}$ does not.

A trial calculation showed that the SPRPAE1 correlation-induced differences between $\lambda_\ell^{\mathrm{SPRPAE1}\downarrow}$ and $\lambda_\ell^{\mathrm{SPRPAE1}\uparrow}$ are due primarily to polarization of the $3d^5\!\uparrow$ subshell by an incoming $\epsilon\ell$ electron. Thus, when the incoming electron is a spin-up electron, exchange diagrams (b) and (d) with $j = |3d\uparrow\rangle$ in Fig. 1 contribute to phase shifts, whereas their contributions vanish for a spin-down incoming electron, as was explained earlier in text.

4. The higher-order (SPRPAE2) correlation difference between scattering of spin-up and spin-down electrons off Mn

Higher-order SPRPAE2 correlation corrections, compared to SPRPAE1, induce additional significant changes, primarily in $\delta_d{}^\downarrow$ and $\delta_d{}^\uparrow$ scattering phases. While the impact of these corrections on a real part $\lambda_d{}^\uparrow(\epsilon)$ of $\delta_d{}^\uparrow$ (Fig. 5, solid line) results mostly in its quantitative change compared to corresponding SPRPAE1 data, it (the impact) makes a real part $\lambda_d{}^\downarrow(\epsilon)$ of $\delta_d{}^\downarrow$ to become both quantitatively and qualitatively different from $\lambda_d{}^{\mathrm{SPRPAE1}\downarrow}$ (Fig. 3, solid line).

The found different impact of SPRPAE2 correlation on $\delta_d{}^\downarrow$ compared to $\delta_d{}^\uparrow$ is because the SPRPAE2 equation for the reducible self-energy part of the Green function, Eq. (8), contains many cross-product terms between terms associated with each of the diagrams depicted in Fig. 1. Note that there are no cross-products terms in the framework of SPRPAE1 at all. Since the number of $3d$ electrons in the Mn atom is a 100% unbalanced in favor of $3d\uparrow$ electrons, many SPRPAE2 cross-product terms, involving various excitations of $3d\uparrow$ electrons, vanish for an incoming spin-down electron but remain for a spin-up scattered electron. This aggravates the difference between the SPRPAE2 correlation impact on the scattering of spin-up compared to spin-down electrons off the atom compared to the difference emerging in SPRPAE1 calculations. For ϵd incoming electrons, this difference is huge, as was illustrated above.

Thus, the study carried out reveals that the lower-order SPRPAE1 approximation is clearly insufficient for a proper understanding of electron scattering off a semifilled -shell atom. This is an important finding.

Note, the demonstrated fast variation of the SPRPAE2 $\delta_d^\downarrow$ phase with energy in a quite narrow energy region near 8 eV can be interpreted as a prominent time delay of the partial $\epsilon d\downarrow$ wave while crossing the atomic region. Indeed, long ago, Wigner [21] connected the time of quantum mechanical reaction procedure τ_r with the derivative on the phase over energy. In the considered case of up and down electrons, one has

$$\tau_{r\ell}^{\uparrow(\downarrow)} = \frac{d\delta_\ell^{\uparrow(\downarrow)}}{d\epsilon}. \tag{9}$$

With the help of this expression, one can estimate not only the time duration of the scattering process of a given $\epsilon\ell$ wave but also the time duration difference $\Delta\tau_\ell^{\uparrow\downarrow}$ for up and down partial waves ℓ. For the $\epsilon d\uparrow$ and $\epsilon d\downarrow$ waves in $e^- +$Mn scattering near $\epsilon \approx 8$ eV, we find that $\Delta_d^{\uparrow\downarrow} \approx 2\ 10^{-15}$ s, in the framework of SPRPAE2.

B. Total $e^- +$Mn elastic-scattering cross section

To get insight into both the individual correlation and exchange interaction impacts, as well as their combined effect, on *observable* elastic electron-scattering characteristics, we calculated the $e^- +$Mn total spin-up $\sigma^\uparrow$ and spin-down $\sigma^\downarrow$

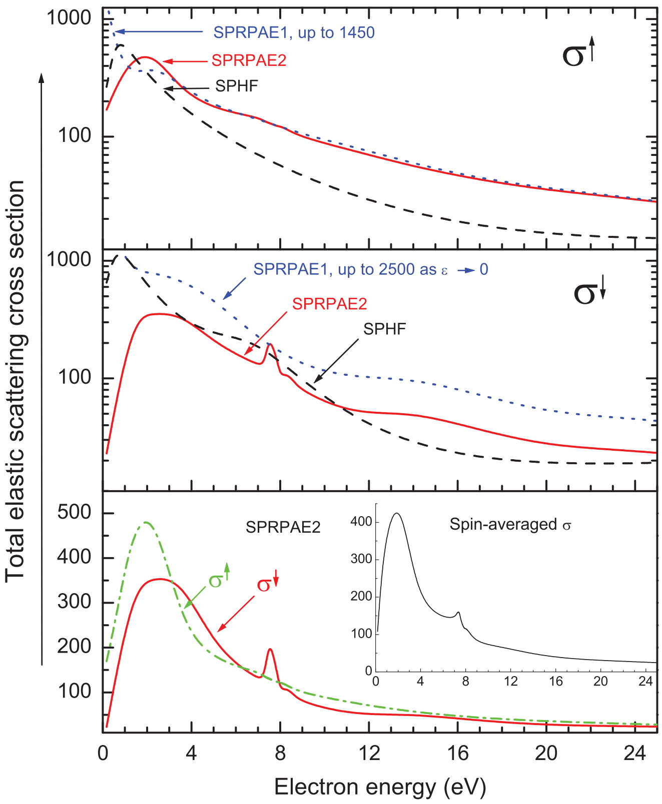

FIG. 6. (Color online) Top panel: SPHF- (dashed line), SPRPAE1- (dotted line), and SPRPAE2- (solid line) calculated data (in a.u.) for the total elastic-scattering cross section $\sigma^{\uparrow}(\epsilon)$ of spin-up electrons off the Mn atom. Middle panel: The same as in the upper panel but for $\sigma^{\downarrow}(\epsilon)$ of spin-down electrons. Bottom panel: Individual data (in a.u.) for $\sigma^{\uparrow}(\epsilon)$ and $\sigma^{\downarrow}(\epsilon)$ calculated in the framework of SPRPAE2 (for a clearer comparison of these two final results). Inset: The total spin-averaged elastic-scattering cross section $\sigma^{\text{avrg}}(\epsilon)$ (in a.u.), see Eq. (10), calculated in the framework of SPRPAE2.

elastic-scattering cross sections in the framework of SPHF, SPRPAE1, and SPRPAE2. The performed calculations utilized the above presented data for phase shifts. The thus-calculated $\sigma^{\uparrow}$ and $\sigma^{\downarrow}$ are depicted in Fig. 6.

The depicted results are self-illustrating in the demonstration of the found significance of correlation impacts on $e^- + \text{Mn}$ elastic electron-scattering cross sections of spin-up and spin-down electrons. Clearly, a fuller account of correlation, secured by the SPRPAE2 approximation, is seen to be decisive.

Of significant interest is the unraveling of the existence of a narrow resonance in $\sigma^{\downarrow}$ near $\epsilon = 8$ eV in the framework of SPRPAE2 (see the middle and bottom panels in Fig. 6). This resonance has an interesting nature which is associated both with a semifilled-shell structure of, and electron correlation in, the Mn atom.

Indeed, as was discussed and demonstrated above, Fig. 3, it is because of the semifilled-shell structure of the Mn atom that the elastic-scattering phase shift $\delta_d^{\text{SPHF}\downarrow}$ as well as real parts $\lambda_d^{\downarrow}$ of both $\delta_d^{\text{SPRPAE1}\downarrow}$ and $\delta_d^{\text{SPRPAE2}\downarrow}$ phase shifts drop to a zero at $\epsilon = 0$. On the way to a zero, $\delta_d^{\downarrow}$ as well as $\lambda_d^{\downarrow}$ pass through the value of $\delta_d^{\downarrow}(\lambda_d^{\downarrow}) = \pi/2$, at certain values of the electron energy. Correspondingly, at such energy, a resonance emerges in a partial $\sigma_d^{\downarrow}$ elastic-scattering cross section both in SPHF, where $\sigma_d^{\downarrow} \propto \sin^2 \delta_d^{\downarrow}$, Eq. (2), and SPRPAE1 or SPRPAE2, where $\sigma_d^{\downarrow}$ depends on $\cos 2\lambda_d^{\downarrow}$, Eq. (7). Naturally, the existence of this resonance in partial $\sigma_d^{\downarrow}$ translates into its emergence in the total elastic-scattering $\sigma^{\downarrow}$ cross section at the same electron energy as well. Indeed, as seen in Fig. 6, the resonance in question is present in $\sigma^{\text{SPHF}\downarrow}$ and $\sigma^{\text{SPRPAE2}\downarrow}$ at $\epsilon \approx 8$ eV, as well as in $\sigma^{\text{SPRPAE1}\downarrow}$ at $\epsilon \approx 5$ eV. The resonance is broad and weakly developed both in the SPHF- and SPRPAE1-calculated cross sections. In contrast, it is sharp and well developed in $\sigma^{\text{SPRPAE2}\downarrow}$. SPRPAE2, without doubt, is a more complete approximation than either of the SPHF or SPRPAE1 approximations. Prediction based on the basis of SPRPAE2 should, thus, match reality better than those in the framework of SPHF or SPRPAE1. The SPRPAE2-calculated results in question, thus, allow us to claim the discovery of the *actual* existence of the 8-eV *sharp* resonance in the $e^- + \text{Mn}$ total elastic electron-scattering cross section. Furthermore, as follows from the discussion, the resonance in question can exist neither without the semifilled-shell nature of the Mn atom nor without accounting for electron correlation in the $e^- + \text{Mn}$ scattering process. This permits us to speak about the discovery of a novel type of a resonance in electron-atom scattering which we name the *semifilled-shell-correlation* resonance, to stress its uniqueness.

Note, the semifilled-shell-correlation resonance shows up not only in the total elastic electron-scattering cross section $\sigma^{\downarrow}$ of spin-down electrons but in the corresponding spin-averaged total cross section σ^{avrg} as well; see the inset in the bottom panel of Fig. 6. The latter (σ^{avrg}) was calculated as

$$\sigma^{\text{avrg}}(\epsilon) = A_{S_A+s}\sigma^{\uparrow}(\epsilon) + A_{S_A-s}\sigma^{\downarrow}(\epsilon), \tag{10}$$

where

$$A_{S_A \pm s} = \frac{2(S_A \pm s) + 1}{(2S_A + 1)(2s + 1)}, \tag{11}$$

with S_A being the spin of the atom ($S_A = 5/2$ for the Mn atom) and $s = 1/2$ being the electron spin.

IV. CONCLUSION

In summary, it is demonstrated in the present paper that (a) SPRPAE1 and SPRPAE2 electron correlations affect significantly $e^- + \text{Mn}$ electron elastic-scattering phase shifts and cross sections; (b) correlations may affect, and in the case of the Mn atom do affect, drastically differently scattering phase shifts of electrons with opposite spin orientations; (c) a fuller account of correlation (as in SPRPAE2) beyond the second-order approximation of perturbation theory in the Coulomb interelectron interaction (SPRPAE1) may be, and in the case of $e^- + \text{Mn}$ scattering is, crucial for an adequate understanding of the spectrum of corresponding phase shifts and cross sections versus the electron energy; and (d) a combined impact of the semifilled-shell nature of the Mn atom and electron correlation results in the emergence of a novel type of the resonance—the semifilled-shell-correlation resonance—in the $e^- + \text{Mn}$ total elastic-scattering cross section. We urge experimentalists and other theorists to verify the made predictions.

Furthermore, the physics behind the discovered effects in $e^- + \mathrm{Mn}$ scattering is so clear that the present authors have little doubt that most of the effects are inherent features of electron elastic scattering off any multilectron semifilled-shell atom in general, not just off the Mn atom. The predicted effects should even be stronger for atom-scatterers with a higher spin multiplicity (than that of Mn), such as the Cr($\ldots 3d^5\uparrow 4s^1\uparrow, {}^7S$) or Eu($\ldots 4f^7\uparrow 6s^1\uparrow 6s^1\downarrow, {}^8S$) atoms, or similar. We are currently undertaking such a study.

ACKNOWLEDGMENTS

V.K.D. acknowledges the support of NSF Grants No. PHY-0969386 and No. PHY-1305085.

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