Electron elastic scattering off a spin-polarized Cr atom

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Electron elastic scattering off a spin-polarized Cr(...3d^54s^1, 7S) atom is theoretically studied in the region of electron energies up to 15 eV using both a one-electron “spin-polarized” Hartree-Fock and multielectron “spin-polarized” random phase approximation with exchange. It is found that scattering phase shifts of oppositely spin-polarized incoming electrons and corresponding cross sections of the scattering reactions significantly differ from each other, in general, even without accounting for spin-orbit interaction. This is shown to be associated with the presence of two semifilled 3d^5 and 4s^1 subshells in the Cr’s configuration which induce considerably different exchange in the interaction of oppositely spin-polarized incoming electrons with the atom-target. The importance of electron correlation in e^- + Cr elastic scattering process is revealed. Moreover, correlation is shown to induce strong differences between scattering of oppositely spin-polarized electrons off Cr.

A physically transparent interpretation for the latter is provided.

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I. INTRODUCTION

The Cr(...3d^54s^1, 7S) atom is an attractive, even from a purely theoretical point of view, object for studying of delicate exchange and electron correlation interactions in electron-atom scattering. Indeed, Cr is the first atom in the periodic table with the maximum unbalanced number of spin-up and spin-down electrons in its ground-state configuration, owing to its two 3d^5 and 4s^1 semifilled subshells with co-directed electron spin orientations. This unbalance can lead to big differences in the exchange interaction between incoming spin-up and spin-down electrons with the atom. It is of interest and importance to study how this difference can affect electron scattering phases and cross sections both from the viewpoint of pure static exchange (e.g., at a Hartree-Fock approximation level) and electron correlation. Whereas accounting for correlation in electron scattering off atoms with arbitrary open shells encounters serious and not yet entirely resolved difficulties, compared to scattering off closed shell atoms, the situation is greatly simplified for the case of semifilled shell atoms. This is because electrons with opposite spin projections can be treated as two types of different particles, namely “up” (spin-up) and “down” (spin-down) electrons [1, 2]. As a result, electron scattering off Cr inherits intrinsic properties of scattering off both closed shell, on the one hand, and open shell, on the other hand, high spin atoms. This bridges the way from relative “simplicity” in treating closed shell atoms to utter “complexity” in doing so for the cohort of open shell atoms. Furthermore, not the least important, owing to a not too high nuclear charge of Cr, relativistic effects can be discarded, to a good approximation. This greatly simplifies the study of electron scattering off Cr.

To the best of the authors’ knowledge, there have been only two papers dedicated to electron elastic scattering off Cr atom to date [3, 4]. Hanne et. al. [3] measured superelastic scattering of polarized electrons from laser-excited polarized Cr^+ atoms at scattering angles ranging from 10° to 140° but only at two collision energies \( \epsilon = 6.8 \) and 13.6 eV. The above experimental study was followed by a theoretical work [4], where the calculations were performed in the frame of a non-relativistic R-matrix approximation for the same differential scattering cross section at the same two electron energies as in [3]. Thus, obviously, the existing to date results on electron scattering off chromium provide only a limited initial insight into the problem, because only a laser-excited Cr^+-target was chosen and the scattering process itself was explored only at two collision energies.

We are not aware of any work on electron elastic scattering by the ground-state Cr atom. Furthermore, clearly, studying the scattering process through a continuum spectrum of electron energies is a way toward a deeper understanding of electron-atom scattering, including the search for possible shape and correlation resonances. Moreover, not the least important, the study should highlight the role of unbalanced exchange in scattering of spin-up and spin-down electrons off the Cr atom in a physically transparent manner, to the benefit of a better understanding of the role of both exchange and correlation.

It is precisely the aim of this work to conduct the above outlined study in order to get a deeper, clearer insight into electron elastic scattering off Cr through a continuously changing range of electron energies. To meet the goal, a “spin-polarized” Hartree-Fock approximation (SPHF) [5, 6], a concept of the reducible self-energy part \( \Sigma(\epsilon) \) of the Green function \( G \) of an incoming electron, Feynman diagrammatic technique as well as “spin-polarized” random phase approximation with exchange (SPRPAE) [6] are combined together, as in [7],...
in the performed study. The electron energy region of up to 15-20 eV, where most interesting effects occur, is considered.

Atomic units (a.u.) are used throughout the paper unless specified otherwise.

II. THEORY

To learn about exchange effects in $e^- + \text{Cr}$ elastic scattering initially at the simplest static-exchange level, let us use the ideas of the SPHF approximation. SPHF was originally suggested by Slater [3] for the calculation of the structure of semifilled shell atoms. Later, it was extended to the calculation of photoionization of, as well as electron scattering by, semifilled shell atoms, see works [1, 7–9] and references therein. SPHF accounts for the fact that spins of all electrons in semifilled subshells of the ground-state atom - the $3d^5$ and $4s^1$ subshells in Cr - are co-directed, in accordance with Hund’s rule. In the present paper, for the sake of certainty, we consider spins of the the $3d$ and $4s$ electrons in the ground state of Cr being directed upward ($\uparrow$). Then, each of the closed $n\ell^{2(2\ell+1)}$ subshells in the atom splits into two semifilled subshells of opposite spin orientations - $n\ell^{2\ell+1}\uparrow$ and $n\ell^{2\ell+1}\downarrow$ - whose electronic energies $\epsilon_{n\ell\uparrow}$ and $\epsilon_{n\ell\downarrow}$ as well as radial wavefunctions $P_{n\ell\uparrow}(r)$ and $P_{n\ell\downarrow}(r)$ are different. The latter is because of the presence of exchange interaction between corresponding $n\ell\uparrow$ spin-up electrons with the 3$d^5\uparrow$ and 4$s^1\uparrow$ electrons from the half-filled subshells of the atom, but absence of such for $n\ell\downarrow$ electrons. Correspondingly, in SPHF, the Cr’s ground-state configuration takes the following form: Cr(…3p$^3\uparrow$3p$^3\downarrow$3d$^5\uparrow$4s$^1\downarrow$, 7S). SPHF equations for the wavefunctions of the ground and excited states, as well as for the wavefunctions $P_{n\ell\uparrow}(r)$ and $P_{n\ell\downarrow}(r)$ of scattering states of Cr differ from ordinary HF equations for closed shell atoms by accounting for exchange interaction only between electrons with the same spin orientation ($\uparrow$ or $\downarrow$) [3]. The $P_{n\ell\uparrow}(r)$ and $P_{n\ell\downarrow}(r)$ functions have the standard central field asymptotic behavior at large $r \gg 1$:

$$P_{n\ell\pm}(r) \approx \frac{1}{\sqrt{\pi k}} \sin \left( kr - \frac{\pi \ell}{2} + \zeta_{\ell\pm}(\epsilon) \right).$$

(1)

Here, $k$, $\ell$, and $\epsilon$ are the momentum, orbital momentum and energy of a scattered electron, whereas $\zeta_{\ell\pm}(\epsilon)$ are elastic scattering phase shifts of the spin-up(down) electrons, respectively. Corresponding total electron elastic scattering cross sections $\sigma^\uparrow(\epsilon)$ and $\sigma^\downarrow(\epsilon)$ are then determined in the standard for a spherical potential manner, as follows:

$$\sigma^\uparrow(\epsilon) = \frac{4\pi}{k^2} \sum_{\ell=0}^\infty (2\ell + 1) \sin^2 \zeta_{\ell\uparrow}(\epsilon)(k).$$

(2)

In order to take into account the electron correlation in $e^- + \text{Cr}$ elastic scattering, let us exploit the concept of the so-called irreducible self-energy part of the one-electron Green function $\Sigma(\epsilon)$ of a scattering electron (see, e.g., [2, 6, 10, 11] and references therein). In the present paper, the latter will be accounted for in the framework of the random phase approximation with exchange (RPAE) [6, 7]. Many-body RPAE uses the Hartree-Fock atomic ground-state as the vacuum state. Alternatively, RPAE theory, which chooses SPHF as the zeroth-order basis, is termed the “spin-polarized” RPAE (SPRPAE). SPRPAE is a straightforward modification of $\Sigma(\epsilon)^{\text{RPAE}}$ to the case of electron scattering off semifilled shell atoms [7].

In the simplest second-order perturbation theory in the Coulomb interelectron interaction $V$ between the incoming and atomic electrons, to be labeled as SPRPAE1, the irreducible self-energy part of the one-electron Green function of a spin-up $[\Sigma^\uparrow(\epsilon)]$ or spin-down $[\Sigma^\downarrow(\epsilon)]$ scattering electron is depicted with the help of Feynman diagrams in Fig. 1.

The diagrams of Fig. 1 illustrate how a scattered electron “$e^-$” perturbs a $j$-subshell of the atom by causing $j \rightarrow m$ excitations from the subshell and then gets coupled with these excited states itself via the Coulomb interaction. Note that the diagrams (c) and (d) are precisely due to exchange interaction between the scattered and atomic electrons. These diagrams are referred to as the “exchange diagrams” in the present paper. They vanish whenever spins of an incoming electron and the perturbed atomic subshell have opposite directions, due to orthogonality of electron spin-functions. Therefore, the number of diagrams that contribute to scattering of spin-up electrons off Cr differs from the number of corresponding diagrams for spin-down scattering electrons. This is because, in the latter case, no exchange diagrams (c) and (d) exist when the perturbed electrons are those from the semifilled $3d^5\uparrow$ or $4s^1\uparrow$ subshells. One thus immediately arrives at a physically transparent conclusion that unbalanced correlation-exchange in $e^- + \text{Cr}$ scattering adds additional, compared to SPHF static-exchange, differences in scattering of oppositely spin-exchange,
trons off the Cr atom.

For a fuller account for electron correlation in $e^- + Cr$ elastic scattering let us introduce the reducible $\Sigma^{(1)}(\epsilon)$ part of the self-energy part of the one-electron Green function. The latter can be found as the solution of the following simplified Dyson equation \([3]\), to a good approximation:

$$\hat{\Sigma}^{(1)} = \hat{\Sigma}^{(0)}(\epsilon) - \hat{\Sigma}^{(0)}(\epsilon) G^{(0)}(\epsilon) \hat{\Sigma}^{(1)}(\epsilon).$$

The Eq. (3) is written in an operator form, where $\hat{\Sigma}^{(1)}$ is the operator of the irreducible self-energy part of the Green-function operator calculated in the framework of SPRPAE1, $G^{(0)}(\epsilon) = (\hat{H}^{(0)}(\epsilon) - \epsilon)^{-1}$ is the SPHF operator of the electron’s Green function, $\hat{H}^{(0)}(\epsilon)$ is the SPHF Hamiltonian operator of the electron-atom system. As in \([3]\), the approximation \([3]\) will be referred to as SPRPAE2. Clearly, it accounts for an infinite series of diagrams of Fig. A1 at various combinations. Many blocks of these diagrams, namely, those which contain exchange diagrams (c) and (d) of Fig. A1 fall out from the description of spin-down electron scattering. This is for the same reason which was explained above in interpreting the significance of exchange diagrams (c) and (d) of Fig. A1. Thus, SPRPAE2 correlation will additionally induce differences between scattering of spin-up and spin-down electrons off Cr due to more complex spin-dependence of electron correlation in the $e^- + Cr$ system.

In the framework of SPRPAE1 or SPRPAE2, the elastic electron scattering phase shifts $\zeta^{(1)}(\ell)$ are determined as \([6]\)

$$\zeta^{(1)}(\ell) = \delta^{\text{SPHF}}(\ell) + \Delta \delta^{(1)}(\ell).$$

Here, $\Delta \delta^{(1)}(\ell)$ is the correlation correction term to the SPHF calculated phase shift $\delta^{\text{SPHF}}(\ell)$:

$$\Delta \delta^{(1)}(\ell) = \tan^{-1} \left( -\pi \left< \ell \ell^{(1)}(\ell) | \hat{\Sigma}^{(1)}(\ell) | \ell \ell^{(1)}(\ell) \right> \right).$$

The mathematical expression for $\left< \ell \ell^{(1)}(\ell) | \hat{\Sigma}^{(1)}(\ell) | \ell \ell^{(1)}(\ell) \right>$ is cumbersome. The interested reader is referred to \([10]\) for details. The matrix element $\left< \ell \ell^{(1)}(\ell) | \hat{\Sigma}^{(1)}(\ell) | \ell \ell^{(1)}(\ell) \right>$ becomes complex for electron energies exceeding the ionization potential of the atom-target, and so does the correlation term $\Delta \delta^{(1)}(\ell)$ and, thus, the phase shift $\zeta^{(1)}(\ell)$ as well. Correspondingly,

$$\zeta^{(1)}(\ell) = \delta^{(1)}(\ell) + i \mu^{(1)}(\ell),$$

where

$$\delta^{(1)}(\ell) = \delta^{\text{SPHF}}(\ell) + \Re \Delta \delta^{(1)}(\ell), \quad \mu^{(1)}(\ell) = \Im \Delta \delta^{(1)}(\ell).$$

The spin-up(down) total electron elastic scattering cross section $\sigma^{(1)}(\ell)$ is then given by the expression

$$\sigma^{(1)}(\ell) = \sum_{\ell=0}^{\infty} \sigma^{(1)}(\ell),$$

where $\sigma^{(1)}(\ell)$ is the electron elastic scattering partial cross section:

$$\sigma^{(1)}(\ell) = \frac{2 \pi}{k^2} \frac{\cosh 2 \mu^{(1)}(\ell) - \cos 2 \delta^{(1)}(\ell)}{\epsilon^{2} \mu^{(1)}(\ell)}. \quad (9)$$

### III. RESULTS AND DISCUSSION

#### A. $e^- + Cr$ elastic scattering phase shifts $\zeta(\ell)$

A calculation shows that, at electron energies of up to 20 eV, it is sufficient to account for the contributions of only $s, p, d$ and $f$ partial waves to the total elastic scattering cross section. Likewise, accounting for only monopole, dipole, quadrupole and octupole excitations from the $4s^1\uparrow$ and $3d^5\uparrow$ subshells of Cr in calculations of scattering phase shifts is a good approximation as well.

Corresponding SPHF, SPRPAE1 and SPRPAE2 calculated real $\delta^{(1)}(\ell)$ and imaginary $\mu^{(1)}(\ell)$ parts of elastic scattering phase shifts $\zeta^{(1)}(\ell)$ and $\zeta^{(1)}(\ell)$ of s-spin-down and s-spin-up electronic waves are depicted in Fig. 2.

![FIG. 2.](image-url) (Color online) SPHF, SPRPAE1 and SPRPAE2 calculated phase shifts $\zeta(\ell)$ of $e^- + Cr$ elastic scattering, as marked.

First, note how different are the SPHF calculated $\delta^{(1)}(\ell)$ and $\delta^{(1)}(\ell)$ at $\epsilon \to 0$. This finds a ready explanation on the basis of Levinson’s theorem \([12]\) which we write as

$$\delta^{(1)}(\ell)_{\epsilon \to 0} \to (n_{\ell} + q_{\ell}) \pi. \quad (10)$$

Here $q_{\ell}$ is the number of electronic subshells with given $\ell$ in the ground-state configuration of the atom, whereas $n_{\ell}$ is the number of additional bound states with the same $\ell$ in the very field of the neutral atom. As known, the HF field of a neutral atom cannot bind an additional electron. Correspondingly, as $\epsilon \to 0$, the phase shift $\delta^{(1)}(\ell)$ → 4$\pi$, since there are four $ns\uparrow$ subshells in the ground-state of Cr, whereas $\delta^{(1)}(\ell) \to 3\pi$, in view of the absence of $ns\downarrow$ bound states with $n \geq 4$ in the atom. Thus,
the calculation reveals that the inherent to Cr different exchange between spin-up and spin-down incoming electrons with the atomic electrons is significant already in the one-electron SPHF approximation.

Next, note how generally stronger electron correlation affects the s-phase shift of spin-down electrons than that of spin-up electrons over the whole range of considered energies. This provides a numerical support to the suggested in the previous section possibility for a noticeable spin-dependence of correlation in the $e^- + \text{Cr}$ system.

Furthermore, note that SPRPAE2 correlation affects scattering of spin-down electrons stronger than does lower-order SPRPAE1 correlation. This is in contrast to scattering of spin-up electrons, where SPRPAE1 and SPRPAE2 calculated corrections to $\delta^s_1(\epsilon)$ are practically identical. In particular, SPRPAE2 correlation radically, both quantitatively and qualitatively, changes the behavior of $\delta^s_1(\epsilon)$ at $\epsilon \to 0$ compared to SPHF or SPRPAE1 calculated data. As a result, SPRPAE2 calculated $\delta^s_1(\epsilon)$ approaches $4\pi$ rather than $3\pi$ (as in SPHF and SPRPAE1 calculations) at $\epsilon \to 0$. With Levinson’s theorem in mind, this is indicative of the emergence of a correlation induced bound state with $n = 4 \geq 4$ in the field of Cr, i.e., of the formation of a negative chromium ion, possibly of $\text{Cr}^-(3p^33d^64s\uparrow4s\downarrow, 6S)$. As known, see, e.g., [13], the $\text{Cr}^-(3d^54s^2, 7S)$ anion does indeed exist in nature. Clearly, the ability of SPRPAE2 to re-discover the existence of $\text{Cr}^-$ speaks in favor of this approximation. In addition, it underpins, once again, the importance, as well as spin-dependent specificity, of electron correlation in the $e^- + \text{Cr}$ system.

Impressive differences also emerge between calculated electron elastic scattering phase shifts of spin-up and spin-down $ed$-electron waves. Corresponding $\zeta^s_d(\epsilon)$ and $\zeta^d_d(\epsilon)$ are depicted in Fig. 3.

First, note that $\delta^d_1(\epsilon) \to \pi$ whereas $\delta^s_1(\epsilon) \to 0$ at $\epsilon \to 0$ in each of the three approximations. One concludes that, contrary to the s-wave, calculated results demonstrate the incapability of neutral Cr to capture and bind an additional $nd\uparrow$ or $nd\downarrow$ electron. Indeed, in this case, the parameters of Levinson’s theorem take the following values: $n_{d\uparrow} = n_{d\downarrow} = 0$, but $q_{d\uparrow} = 1$, because of the presence of $3d^5\uparrow$ subshell in the Cr structure, whereas $q_{d\downarrow} = 0$, since there is no $nd\downarrow$ bound states in the ground-state of the atom. Consequently, $\delta^s_1(\epsilon) \to \pi$, whereas $\delta^d_1(\epsilon) \to 0$ at $\epsilon \to 0$, exactly as was obtained in the above commented calculation. The fact that calculated $\delta^s_1(\epsilon)$ and $\delta^d_1(\epsilon)$ are in agreement with Levinson’s theorem speaks, once again, to the capability of the used theory to reveal differences between scattering of oppositely spin-polarized electrons off Cr.

Calculated data for $e^- + \text{Cr}$ total spin-up $\sigma^s(\epsilon)$ and spin-down $\sigma^d(\epsilon)$ elastic scattering cross sections are depicted in Fig. 4.

**B. $e^- + \text{Cr}$ elastic scattering cross sections**

Calculated data for the $e^- + \text{Cr}$ total spin-up $\sigma^s(\epsilon)$ and spin-down $\sigma^d(\epsilon)$ elastic scattering cross sections are depicted in Fig. 4.

Note large differences, both quantitative and qualitative, between $\sigma^s(\epsilon)$ and $\sigma^d(\epsilon)$ calculated in each of the three approximations. Furthermore, note how stronger correlation effects are in $\sigma^d(\epsilon)$ than in $\sigma^s(\epsilon)$. Moreover,
FIG. 4. (Color online) SPHF, SPRPAE1 and SPRPAE2 calculated data (in units of radians) for real $\delta_{\mu}^{(\uparrow)}$ and imaginary $\mu_{\mu}^{(\downarrow)}$ parts of the $e^- + \text{Cr}$ elastic scattering phase shifts $\zeta_{\mu}^{(\downarrow)}$, as marked.

FIG. 5. (Color online) SPHF, SPRPAE1 and SPRPAE2 calculated data (in units of radians) for real $\delta_{\mu}^{(\uparrow)}$ and imaginary $\mu_{\mu}^{(\downarrow)}$ parts of the $e^- + \text{Cr}$ elastic scattering phase shifts $\zeta_{\mu}^{(\downarrow)}$, as marked.

FIG. 6. (Color online) SPHF, SPRPAE1 and SPRPAE2 calculated $e^- + \text{Cr}$ total elastic scattering cross sections $\sigma^{(\uparrow)}(\epsilon)$ and $\sigma^{(\downarrow)}(\epsilon)$ for spin-up and spin-down scattering electrons, as marked.

FIG. 7. (Color online) SPRPAE2 calculated $e^- + \text{Cr}$ partial elastic scattering cross sections $\sigma^{(\downarrow)}(\epsilon)$, as marked.

note that, once again, a fuller account of correlation in the calculation of scattering of spin-down than spin-up electrons off Cr.

In order to better understand details of the SPRPAE2 calculated total electron scattering cross section $\sigma^{(\uparrow)}(\epsilon)$ and $\sigma^{(\downarrow)}(\epsilon)$, let us explore corresponding SPRPAE2 calculated partial cross sections $\sigma^{(\downarrow)}(\epsilon)$ and $\sigma^{(\downarrow)}(\epsilon)$. The latter two are plotted in Fig. 7.

By analyzing Figs. 6 and 7 one can see that a sharp narrow maximum in $\sigma^{\text{Sprpae2}}(\epsilon)$ at about 0.5 eV is due primarily to scattering of a $c_p\downarrow$-electronic wave, whereas a shallow maximum between approximately 2 and 5 eV is brought about by a $c_d\downarrow$ scattering wave. Similarly, the maximum in $\sigma^{\text{Sprpae2}}$ at about 1.2 eV is primarily due to scattering of a $c_p\downarrow$-electronic wave. Note the absence of a second shallow maximum in $\sigma^{\text{Sprpae2}}$, which would be similar to that in $\sigma^{\text{Sprpae2}}(\epsilon)$ between 2 and 5 eV. This is because the phase shift $\delta_{\mu}^{(\downarrow)}(\epsilon)$ passes through $\delta_{\mu}^{(\downarrow)}(\epsilon) = \pi/2$ with decreasing energy $\epsilon$, thereby causing the maximum in partial $\sigma^{(\downarrow)}(\epsilon)$, but $\delta_{\mu}^{(\downarrow)}(\epsilon)$ does not. Also note that plotted in Fig. 7 data provide the evidence for sufficiency of accounting for only $s$, $p$, $d$, and $f$ partial waves in the calculation of $e^- + \text{Cr}$ elastic scattering, in the considered region of electron energies.

IV. CONCLUSION

In conclusion, the performed study results in a deeper understanding of electron elastic scattering off Cr, reveals novel interesting features emerging in the scattering process due to unbalanced exchange in the atomic system, as well as provides a physically transparent interpreta-
tion for the unraveled effects at a one-electron and multi-electron levels of sophistication. Furthermore, this paper adds novel concrete data on $e + \text{Cr}$ elastic scattering to the existing database of physics quantities.

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