Study of Exchange in Collisions of Polarized Electrons with Atoms and Molecules

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Exchange collisions of electrons with Na and Hg atoms and O_2 and NO molecules have been studied by means of polarized electrons for energies between 4 and 15 eV and scattering angles ranging from 0° to 110°. While significant exchange effects have been observed for collisions of electrons with Na and Hg atoms, in agreement with theoretical predictions, differential spin-exchange cross sections for elastic collisions from the open-shell molecules O_2 and NO are much smaller. This was not anticipated before. A satisfactory explanation of this different behavior is still missing.

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The dynamics of low-energy electron collisions with atoms, molecules, and surfaces is, in general, strongly influenced by exchange collisions. The inclusion of exchange in calculations of low-energy electron scattering very often changes the magnitude of cross sections dramatically; see, for example, Fig. 6 of a review of Lane.[1] Thus a proper treatment of exchange collisions in numerical calculations, which can be tested by experimental results, is very important. The interpretation of a comparison of theoretical and experimental cross sections is complicated by the fact that several different physical effects such as correlation and charge-cloud polarization are important, particularly for low energies. Therefore, direct observation of exchange processes is desirable.

Experimentally, we can only observe exchange processes directly if spin is transferred to or from the target, i.e., if the spin quantum number M_S of the target has been changed by the collision. This will result in a change of polarization for the scattered particles. Over the years, there have been several different types of experiments designed to measure spin transfer. The first experiments of this kind were performed with polarized atoms at the end of the fifties.[2-5] Bederson[6] used polarized beams of alkali atoms at the target and observed the angular distribution of the change of the spin state of the recoil atoms. Differential cross sections for exchange collisions were thus obtained. A somewhat different experiment was reported by Hils *et al.*[7] who also used polarized alkali atoms, but observed the polarization of the scattered electrons. Polarized electrons were used by Hanne and Kessler[8,9] who measured the change of the polarization of scattered electrons in electron-impact excitation of Hg, but only for forward scattering. Recently, Ratliff *et al.*[10] used a similar method to measure spin-exchange cross sections for elastic scattering of polarized electrons from O_2 and NO molecules at thermal energies. Exchange effects have also been observed in experiments where polarized electrons and polarized targets are used simultaneously if the spin-parallel–antiparallel asymmetries of scattered electrons,[11-14] ions,[11,15-18] or photons are measured.[14] The transfer of spin polarization to atomic orientation by exchange in inelastic collisions can be observed by measurement of the circular polarization of fluorescence radiation.[19-22] Finally, we note that, in conjunction with the fine-structure interaction within the target, exchange processes cause spin asymmetries even if only one collision partner is polarized.[23,24]

While exchange effects in electron-atom collisions have been studied for more than thirty years, the first measurements for molecules were performed just recently by Ratliff *et al.*,[10] and these were measurements of average spin-exchange cross sections at thermal energies for collisions of electrons with O_2 and NO molecules. These measurements correspond to spin-exchange cross sections integrated over all scattering angles and integrated over the spread of thermal energies of the electrons. Here we report the first measurement of relative differential spin-exchange cross sections for elastic scattering from molecules. When we started this project it was anticipated that differential spin-exchange cross sections for elastic collisions of electrons from the open-shell molecules O_2 ($X\,^3\Sigma_g^-$) and NO ($X\,^2\Pi$) should be comparable to those for elastic scattering from Na ($3\,^2S$), where significant exchange effects were predicted up to an energy of 15 eV. However, we find no similarity between the corresponding atomic and molecular cases as described in the following.

We report here on investigations in which the change of the electron polarization has been measured to determine relative spin-exchange cross sections. A schematic diagram of the apparatus is shown in Fig. 1. Spin-polarized photoelectrons, with polarization $P \approx 0.3$, are released from a GaAsP crystal by irradiation with circularly polarized light from a He-Ne laser.[25] The polarization can be reversed by means of a Pockels cell. To convert the longitudinal polarization of the electrons into transversal polarization the electron beam passes through an electrostatic 90° deflector. A lens system is used to focus the electron beam onto the target, which is either a beam of Hg or Na atoms from an oven system or a beam of O_2 or NO molecules from a gas inlet system. The energy of the electrons is varied from 4 to 15

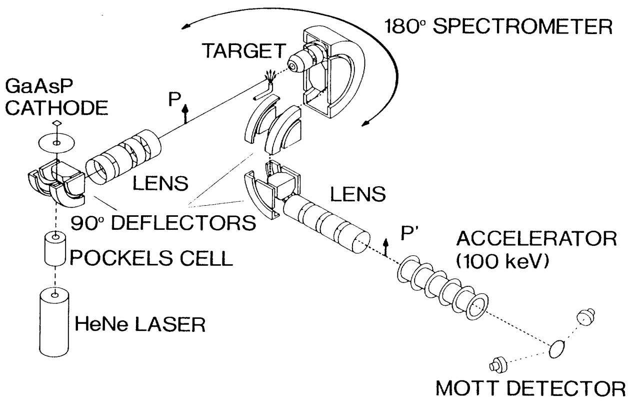

FIG. 1. Scheme of the experiment.

eV. Some electrons are scattered through an angle θ and pass through a system of lenses and electrostatic deflectors. These can be rotated to select arbitrary scattering angles, where the 180° deflector serves as an energy analyzer. After that the electrons are accelerated to 100 keV, the energy at which the Mott analyzer operates. The Mott analyzer is used to measure the polarization P' after scattering as well as the initial polarization P (target off).

With the geometry of Fig. 1 the polarization P' is given by[26,27]

$$P' = (S_P + T_\perp P)/(1+S_A P)\,, \tag{1}$$

where P is the initial polarization oriented perpendicular to the scattering plane. The three parameters S_P, S_A, and $T_\perp$ can be determined independently by measuring P' according to Eq. (1), by evaluating Eq. (1) for initially unpolarized electrons ($P=0$) which gives $P'=S_P$, and by measuring the spin-up-down asymmetry which yields S_A. Since S_P and S_A have been determined frequently for various targets,[28,29] their results from the present investigation are not shown here. Here we are interested in the determination of the parameter $T_\perp$, which describes the contraction of the original polarization P. The parameters S_P and S_A describe spin-orbit effects, whereas significant deviations from $T_\perp = 1$ can, in any case, only be caused by exchange collisions. It is well known that the spin-orbit interaction alone will cause $T_\perp = 1$ for elastic collisions,[28] and only very small deviations from $T_\perp = 1$ for inelastic collisions.[27]

For scattering from targets with low-Z nuclei like Na, O, and N, spin-orbit effects can be neglected; i.e., we have $S_P = S_A = 0$. In that case Eq. (1) reduces to

$$\begin{aligned} P' = T_\perp P &= \frac{\sigma(\uparrow\uparrow)+\sigma(\downarrow\downarrow)-\sigma(\uparrow\downarrow)-\sigma(\downarrow\uparrow)}{\sigma(\uparrow\uparrow)+\sigma(\downarrow\downarrow)+\sigma(\uparrow\downarrow)+\sigma(\downarrow\uparrow)}P \\ &= (1-2w_{\rm SF})P\,. \end{aligned} \tag{2}$$

In Eq. (2) we denote the probability for spin-exchange ("spin-flip") collisions by

$$w_{\rm SF} = \frac{\sigma(\uparrow\downarrow)+\sigma(\downarrow\uparrow)}{\sigma(\uparrow\uparrow)+\sigma(\downarrow\downarrow)+\sigma(\uparrow\downarrow)+\sigma(\downarrow\uparrow)}\,,$$

where, e.g., $\sigma(\uparrow\downarrow)$ is the spin-exchange cross section for electrons that change spin from orientation "up" to orientation "down," etc. In the absence of spin-exchange collisions ($w_{\rm SF}=0$) we have $T_\perp = 1$.

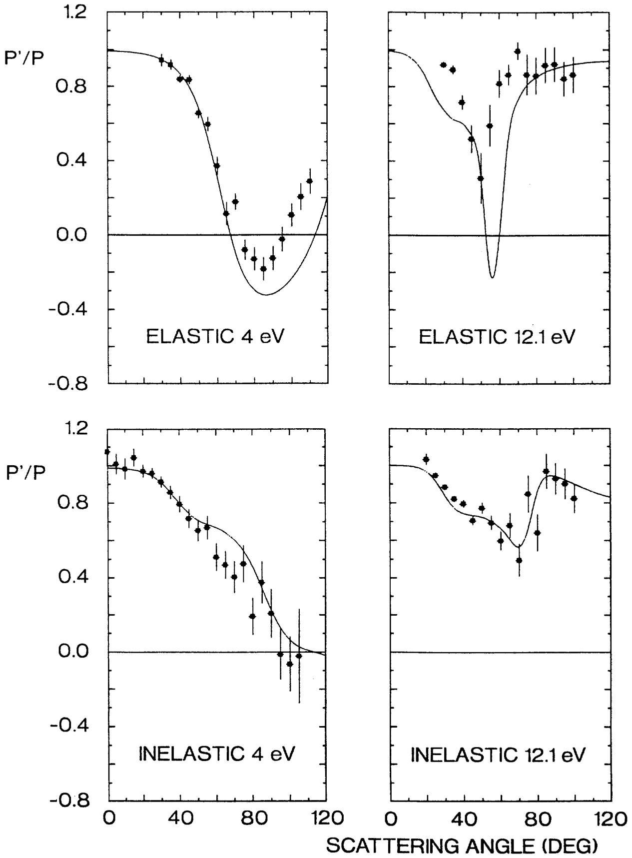

FIG. 2. Results of P'/P plotted against scattering angle for elastic and inelastic (3^2P excitation) collisions of polarized electrons from Na atoms at 4 and 12.1 eV. ●, experimental results; ——, theory, 4 eV (Ref. 30), 12.1 eV (Ref. 31).

The results of our measurements are shown in Figs. 2-4. The error bars represent the statistical uncertainty (1 standard deviation) of the determination of P' and P. For elastic and inelastic (3^2P excitation) collisions from Na atoms, significant deviations from $P'/P=1$ are observed (Fig. 2) which are, as expected, more pronounced at 4 than at 12.1 eV. For elastic collisions from light one-electron atoms we have $2w_{\rm SF} = |g|^2/\sigma$, where g is the exchange amplitude and σ is the differential cross section, and thus Eq. (2) yields[26,28]

$$P'/P = T_\perp = 1 - |g|^2/\sigma\,. \tag{3}$$

We have used the close-coupling results of Moores and Norcross[30,31] to obtain $T_\perp$ for elastic and inelastic

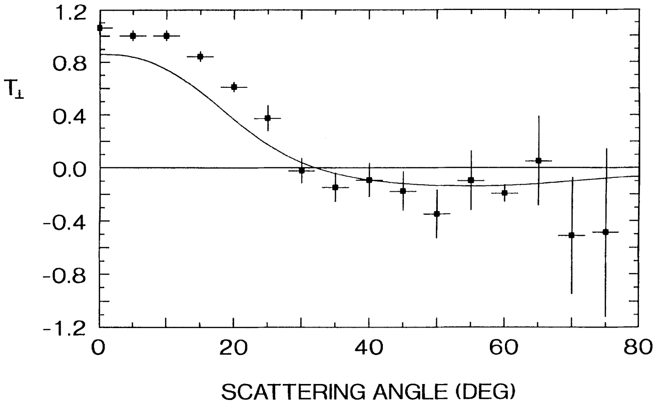

FIG. 3. Spin parameter $T_\perp$ [Eq. (2)] plotted against scattering angle for electron-impact excitation of the 6^3P states of Hg at 15 eV. ●, experimental results; ——, theory (Ref. 32).

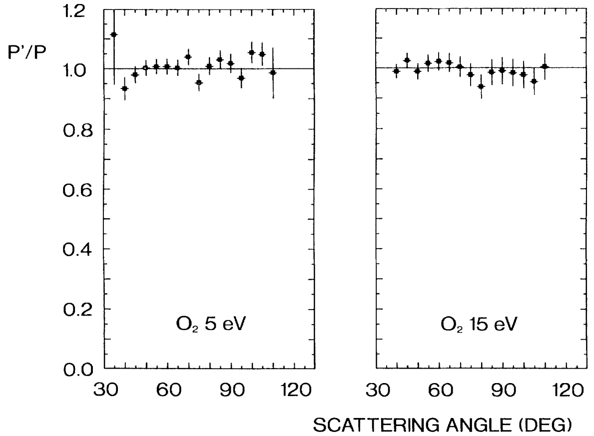

FIG. 4. Experimental results of P'/P plotted against scattering angle for elastic collisions of polarized electrons from O_2 molecules at 5 and 15 eV.

scattering using Eq. (3) and these results are shown in Fig. 2. While experiment and theory are in reasonable agreement for elastic scattering, at 12.1 eV the minimum observed in $P'/P = T_\perp$ is less pronounced and shifted towards smaller scattering angles than predicted. The agreement between theory[31] and experiment is very good for inelastic collisions, where a summation over the magnetic sublevels has been performed.

For Hg the excitation of the 6^3P states (mean energy loss of 4.9 eV) has been studied as an extension of a previous investigation for forward scattering at energies between 4.9 and 11.5 eV.[8] In Fig. 3 the results of $T_\perp$ at 15 eV and scattering angles ranging from 0° to 75° are shown. From the discussion of Eq. (1) we note that, even for heavy targets such as Hg, $T_\perp$ deviates from unity only by exchange collisions. At 15 eV exchange effects are very small at small scattering angles, but these become significant at angles larger than 20°. Similar to our previous investigation,[8] the fine-structure splitting of the $6^3P_{0,1,2}$ states is not resolved. The dominant contribution, however, will come from the 6^3P_1 state since the mean energy loss of 4.9 eV corresponds to the excitation of this state. Bartschat and Madison[32] calculated first-order distorted-wave Born (DWB1) results for each of the $6^3P_{0,1,2}$ states. To compare experiment and theory, a deconvolution of the energy resolution of the experiment was made to determine the relative weights for the 6^3P_1 (energy loss of 4.89 eV), 6^3P_0 (4.67 eV), and 6^3P_2 (5.46 eV) states, respectively. These relative weights were then used to convolute the theoretical results for comparison with experiment. Although the theory overestimates the relative influence of exchange collisions at small scattering angles, the agreement with the experimental data is satisfactory. Note that the tendency $P'/P \to 1$ at small scattering angles must be attributed to the singlet admixture which, in the intermediate-coupling scheme, is added to the triplet part of the wave function of the 6^3P_1 state.[8,9]

The measurements shown in Figs. 2 and 3 demonstrate that the experimental method works. Another purpose of our investigation is the measurement of relative spin-exchange cross sections for scattering of electrons from open-shell molecules like O_2 and NO. To our surprise, the relative spin-flip cross sections are much smaller than those found for Na and Hg atoms at all energies (5-15 eV) and scattering angles studied so far. This is illustrated in Fig. 4, which shows some typical results for the O_2 target. In a recent measurement Ratliff *et al.*[10] have determined the averaged spin-flip cross section for scattering of electrons from O_2 and NO molecules at thermal energies. They found *averaged* cross sections that are significantly smaller than those found for scattering from alkali or hydrogen atoms. While small average cross sections do not necessarily imply small differential spin-exchange cross section our results demonstrate that the *differential* spin-exchange cross sections are also small, even at large scattering angles where they are, in general, most likely to occur.

Evidently, spin exchange of continuum electrons with target electrons in the valence orbitals of O_2 and NO —which are π^* orbitals—is much less important than exchange with the s orbitals of alkali atoms. This would not have been anticipated, however, since it is known that exchange with the σ_g orbital in electron-H_2 collisions significantly influences the magnitude of cross sections.[1] Unfortunately, exchange cannot be observed directly for elastic scattering of electrons from closed-shell molecules like H_2 and N_2. A possible explanation for the experimental findings is that the coupling of the electron spins to other angular momenta (spin-orbit coupling, rotational coupling) suppresses exchange of electrons with opposite spins from molecular π^* orbitals. Theoretical results investigating this phenomenon should be available soon.[33,34] While a preliminary calculation[35] confirmed that spin-exchange cross sections for these molecules were small, no explanation was provided. More experimental and, in particular, theoretical work is required to provide further insight into the strange behavior observed so far. Experimental work will be continued in our laboratory, and we hope that the publication of these first results will stimulate the discussion about the significance of exchange collisions in electron-molecule collisions.

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