for the $3p^+$ state of $Z = 40$. Relativistic Hartree-Fock and present-model wave functions (using the parameters given in Table I) are exhibited. Clearly the agreement is very good. Results for other atoms are similar. Table II shows our results for a random selection of elements ($Z = 10, 20, \ldots, 90$). In each case the top entry is the experimentally determined value, the second entry is our fit to it [with $p = 1$ in (7)], resulting in the parameters indicated on the left, while the bottom entries are relativistic Hartree-Fock energies shown for purposes of comparison. The numerical (FORTRAN IV) programs used to obtain these results are available on request.

The results presented above indicate that a simple analytical potential can yield as good a description of ground-state atoms as a numerically generated one from self-consistent field methods. For application purposes, the former has obvious advantages. It is evident, in particular, that the two-parameter analytical potential of Green, Sellin, and Zachor serves as well for relativistic calculations as it did for the nonrelativistic independent-particle-model work.

We would like to thank Dr. J. B. Mann for providing us with some of his relativistic Hartree-Fock results for atoms, prior to publication.

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Spin-Exchange Effects on Density-Matrix Elements*

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The work of Balling, Hanson, and Pipkin on the density-matrix equations for spin-exchange collisions is extended and is simplified in the case of ${}^2S_{1/2}$ atoms. The results allow straightforward calculation of the detailed effects of spin exchange on the density-matrix elements. The equations are useful when dealing with an ensemble of atoms such as in the hydrogen maser, in the rubidium maser, and in optical pumping cells.

I. INTRODUCTION

Spin exchange[1,2] is one of the dominant mechanisms effecting changes in the spin states of colliding atoms having unpaired electrons. For an ensemble of atoms, the characterization of the spin coordinates can be conveniently made by a density matrix. The effect of spin exchange on the elements of this density matrix is an important consideration when dealing with systems of colliding atoms, such as in the hydrogen maser,[3] in the rubidium maser,[4] or in optical pumping cells.[5]

The result of exchange of electron spin coordinates can be derived by considering elastic scattering from a spin-dependent potential. Balling, Hanson, and Pipkin (BHP)[5] have used this method to calculate the effect of spin exchange on the density matrix. Their theory ignores spin-orbit interactions and direct magnetic interactions between the colliding atoms. As shown below, a simplification of their result can be made in the case of spin exchange between ${}^2S_{1/2}$ atoms, wherein the effect of spin exchange on the density matrix of each system is only through the electron polarization of the other, and is not dependent on the specific population of each hyperfine level.

II. DENSITY MATRIX RATE EQUATION

Consider the two-body collision involving an atom of type A and an atom of type H. (A may be the same as or different from H.) The joint density matrix for this composite system is

TABLE I. Matrix elements of $\vec{\sigma}$ for hydrogen.

$F,\ m_F$	1, 1	1, 0	1, −1	0, 0	$F,\ m_F$
$\sigma_x(\mathrm{H}) = \frac{1}{\sqrt{2}}$	0	1	0	−1	1, 1
	1	0	1	0	1, 0
	0	1	0	1	1, −1
	−1	0	1	0	0, 0
$i\sigma_y(H) = \frac{1}{\sqrt{2}}$	0	1	0	−1	
	−1	0	1	0	
	0	−1	0	−1	
	1	0	1	0	
$\sigma_z(H) =$	1	0	0	0	
	0	0	0	1	
	0	0	−1	0	
	0	1	0	0	

$$\rho(A, H) = \rho(A) \times \rho(H). \tag{1}$$

The effect of spin exchange is introduced by means of a scattering matrix that adds independent phase shifts to the singlet and triplet states of the colliding system:

$$\rho(A, H)_{\mathrm{final}} = S\rho(A, H)_{\mathrm{initial}} S^{\dagger}. \tag{2}$$

This method of treating spin exchange has been used by BHP. They derive a result for the effect of spin-exchange collisions on the density matrix in terms of a spin-flip cross section σ_{SF} and a shift parameter K. As shown in BHP, these parameters can be expressed as sums which are dependent on the singlet and triplet phase shifts. If small terms contributed by the possible nuclear identity of A and H are neglected, then the result is [BHP, Eq. (27)]

$$\begin{aligned}\dot{\rho}(H) = \tfrac{1}{4} V_{\mathrm{rel}}(H, A)\, n(A)\, \sigma_{\mathrm{SF}}(H, A)\, TR_A[&-3\rho(A, H) \\ &+ \{1 + 2iK(H, A)\}\vec{\sigma}_H \cdot \vec{\sigma}_A \rho(A, H) + \{1 - 2iK(A, H)\} \\ &\times \rho(A, H)\vec{\sigma}_H \cdot \vec{\sigma}_A + \vec{\sigma}_H \cdot \vec{\sigma}_A \rho(A, H) \vec{\sigma}_H \cdot \vec{\sigma}_A].\end{aligned} \tag{3}$$

If T_{HA} is a time characterizing relaxation of H population differences by spin-exchange collisions with A, then

$$\frac{1}{T_{HA}} = n(A)\, V_{\mathrm{rel}}(H, A)\, \sigma_{\mathrm{SF}}(H, A). \tag{4}$$

In both Eqs. (3) and (4), $n(A)$ is the density of atoms A and $V_{\mathrm{rel}}(H, A)$ is the average relative velocity of A and H. The spin-exchange cross section for collisions between H and A is given by $\sigma_{\mathrm{SF}}(H, A)$; $K(H, A)$ is the shift parameter and reflects the fact that spin-exchange collisions introduce a shift in addition to a relaxation. The trace indicated in Eq. (3) is taken over the hyperfine states of A. Into Eq. (3) can be put the density matrices for A and H, where attention has been restricted to the case of the diagonal elements and only one pair of nonzero off-diagonal elements,

$$\begin{aligned}\rho^{(A)}_{n'n''} &= \rho^{(A)}_{n'n'}\delta_{n'n''} + \rho^{(A)}_{ab}\delta_{n'a}\delta_{n''b} + \rho^{(A)}_{ba}\delta_{n'b}\delta_{n''a}, \\ \rho^{(H)}_{m'm''} &= \rho^{(H)}_{m'm''} + \rho^{(H)}_{cd}\delta_{m'c}\delta_{m''d} + \rho^{(H)}_{dc}\delta_{m'd}\delta_{m''c}.\end{aligned} \tag{5}$$

The subscripts n for A and m for H represent any of the possible F, m_F hyperfine states. The subscripts a, b for A and c, d for H stand for the particular hyperfine states connected by the off-diagonal element. This form of the density matrix frequently arises when a resonant frequency is being applied to an ensemble of colliding atoms such as one finds in optical pumping and hydrogen masers.

When the above expressions are substituted into Eq. (3), the matrix multiplications can be examined explicitly and simplified. The properties of the σ matrices are used,

$$\sigma_i \sigma_j = \delta_{ij} + i\sum_k \epsilon_{ijk}\sigma_k . \tag{6}$$

A useful combination of matrix elements can be defined as the electron polarization,

$$\epsilon(A) = \sum_n \langle n | \sigma_z(A) | n \rangle \rho_{nn}(A), \tag{7}$$

where n represents the possible F, m_F states in the hyperfine spectrum of A. Not all terms will survive when time averaged, i.e., rapidly oscillating terms are eliminated.

Only those terms that have the correct time dependence need be retained to give the final quasistationary solution. As indicated in the subsequent equation, there arise additional terms having the correct time dependence if A and H are the same atom. They are not to be confused with terms con-

TABLE II. Matrix elements of $\vec{\sigma}$ for deuterium.

$F,\ m_F$	$\frac{3}{2}, \frac{3}{2}$	$\frac{3}{2}, \frac{1}{2}$	$\frac{3}{2}, -\frac{1}{2}$	$\frac{3}{2}, -\frac{3}{2}$	$\frac{1}{2}, -\frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}$	$F,\ m_F$
$\sigma_x(\mathrm{D}) = \frac{1}{3}$	0	$\sqrt{3}$	0	0	$-\sqrt{6}$	0	$\frac{3}{2}, \frac{3}{2}$
	$\sqrt{3}$	0	$\sqrt{4}$	0	0	$\sqrt{2}$	$\frac{3}{2}, \frac{1}{2}$
	0	$\sqrt{4}$	0	$\sqrt{3}$	$-\sqrt{2}$	0	$\frac{3}{2}, -\frac{1}{2}$
	0	0	$\sqrt{3}$	0	0	$-\sqrt{6}$	$\frac{3}{2}, -\frac{3}{2}$
	$\sqrt{6}$	0	$-\sqrt{2}$	0	0	−1	$\frac{1}{2}, -\frac{1}{2}$
	0	$\sqrt{2}$	0	$-\sqrt{6}$	−1	0	$\frac{1}{2}, \frac{1}{2}$
$i\sigma_y(\mathrm{D}) = \frac{1}{3}$	0	$\sqrt{3}$	0	0	$\sqrt{6}$	0	
	$-\sqrt{3}$	0	$\sqrt{4}$	0	0	$\sqrt{2}$	
	0	$-\sqrt{4}$	0	$\sqrt{3}$	$\sqrt{2}$	0	
	0	0	$-\sqrt{3}$	0	0	$\sqrt{6}$	
	$-\sqrt{6}$	0	$-\sqrt{2}$	0	0	−1	
	0	$-\sqrt{2}$	0	$-\sqrt{6}$	1	0	
$\sigma_z(D) =$	1	0	0	0	0	0	
	0	$\frac{1}{3}$	0	0	$-\frac{1}{3}\sqrt{8}$	0	
	0	0	$-\frac{1}{3}$	0	0	$-\frac{1}{3}\sqrt{8}$	
	0	0	0	−1	0	0	
	0	$-\frac{1}{3}\sqrt{8}$	0	0	$-\frac{1}{3}$	0	
	0	0	$-\frac{1}{3}\sqrt{8}$	0	0	$\frac{1}{3}$	

tributed by *nuclear* identity. The problem of spin exchange of identical particles where symmetrization of the nuclear wave functions is taken into account has not been considered here. It has been tacitly assumed that the colliding particles can be identified by their nuclear coordinates, and that symmetrization is important only for the overlapping electron wave functions. Since the overlap of nuclear wave functions is small, the amount contributed by terms due to nuclear identity can be neglected.

The terms contributing only when the two atoms are the same species arise because of the possibility of coherent transfer of oscillation from one atom to another. These terms are contained in square brackets in Eq. (8).

It is convenient to group the terms into those affecting the diagonal elements and those affecting the off-diagonal element. With the foregoing qualifications, the effect of spin exchange on the density-matrix-elements can be given as[6]

$$\dot{\rho}_{rr}(H)=\frac{1}{4T_{HA}}\Big\{-3\rho_{rr}+2\epsilon(A)\langle r|\sigma_z|r\rangle\rho_{rr}+\sum_m\rho_{mm}\Big\}\sum_{i=x,y,z}|\langle m|\sigma_i|r\rangle|^2+\epsilon(A)\big(\langle m|\sigma_x|r\rangle\langle r|i\sigma_y|m\rangle$$
$$-\langle m|i\sigma_y|r\rangle\langle r|\sigma_x|m\rangle\big)\Big\}+\Big[2\sum_{i=x,y,z}|\langle c|\sigma_i|d\rangle|^2(\delta_{rc}+\delta_{rd})$$
$$+\sum_{i,j=x,y,z}\big(\langle r|\sigma_i|c\rangle\langle c|\sigma_j\sigma_i|d\rangle\langle d|\sigma_j|r\rangle+\langle r|\sigma_i|d\rangle\langle d|\sigma_j\sigma_i|c\rangle\langle c|\sigma_j|r\rangle\big)\Big]\rho_{cd}\rho_{dc}\Big\}\,,$$
$$\dot{\rho}_{cd}(H)=\frac{1}{4T_{HA}}\Big[-3+\epsilon(A)\{(1+2iK)\langle c|\sigma_z|c\rangle+(1-2iK)\langle d|\sigma_z|d\rangle\}+\langle c|\sigma_z|c\rangle\langle d|\sigma_z|d\rangle \tag{8}$$
$$+\Big(\sum_{i=x,y,z}|\langle c|\sigma_i|d\rangle|^2\{(1+2iK)\rho_{dd}+(1-2iK)\rho_{cc}\}$$
$$+\sum_{i,j=x,y,z}\big(\langle d|\sigma_j\sigma_i|c\rangle\sum_m\rho_{mm}\langle c|\sigma_i|m\rangle\langle m|\sigma_j|d\rangle\big)\Big)\Big]\rho_{cd}\ .$$

TABLE III. Matrix elements of $\vec{\sigma}$ for Rb^{87}.

$F,\ m_F$	2, 2	2, 1	2, 0	2, −1	2, −2	1, −1	1, 0	1, 1	$F,\ m_F$
$\sigma_x(\mathrm{Rb}^{87})=\frac{1}{2\sqrt{2}}$	0	$\sqrt{2}$	0	0	0	0	0	$\sqrt{6}$	2, 2
	$\sqrt{2}$	0	$\sqrt{3}$	0	0	0	$\sqrt{3}$	0	2, 1
	0	$\sqrt{3}$	0	$\sqrt{3}$	0	1	0	-1	2, 0
	0	0	$\sqrt{3}$	0	$\sqrt{2}$	0	$-\sqrt{3}$	0	2, −1
	0	0	0	$\sqrt{2}$	0	$-\sqrt{6}$	0	0	2, −2
	0	0	1	0	$-\sqrt{6}$	0	-1	0	1, −1
	0	$\sqrt{3}$	0	$-\sqrt{3}$	0	-1	0	-1	1, 0
	$\sqrt{6}$	0	-1	0	0	0	-1	0	1, 1
$i\sigma_y(\mathrm{Rb}^{87})=\frac{1}{2\sqrt{2}}$	0	$\sqrt{2}$	0	0	0	0	0	$\sqrt{6}$	
	$-\sqrt{2}$	0	$\sqrt{3}$	0	0	0	$\sqrt{3}$	0	
	0	$-\sqrt{3}$	0	$\sqrt{3}$	0	1	0	1	
	0	0	$-\sqrt{3}$	0	$\sqrt{2}$	0	$\sqrt{3}$	0	
	0	0	0	$-\sqrt{2}$	0	$\sqrt{6}$	0	0	
	0	0	-1	0	$-\sqrt{6}$	0	1	0	
	0	$-\sqrt{3}$	0	$-\sqrt{3}$	0	-1	0	1	
	$-\sqrt{6}$	0	-1	0	0	0	-1	0	
$\sigma_z(\mathrm{Rb}^{87})=$	1	0	0	0	0	0	0	0	
	0	$\frac{1}{2}$	0	0	0	0	0	$-\frac{1}{2}\sqrt{3}$	
	0	0	0	0	0	0	-1	0	
	0	0	0	$-\frac{1}{2}$	0	$-\frac{1}{2}\sqrt{3}$	0	0	
	0	0	0	0	-1	0	0	0	
	0	0	0	$-\frac{1}{2}\sqrt{3}$	0	$\frac{1}{2}$	0	0	
	0	0	-1	0	0	0	0	0	
	0	$-\frac{1}{2}\sqrt{3}$	0	0	0	0	0	$-\frac{1}{2}$	

As mentioned earlier, terms inside [ ] contribute only if A and H are identical atoms. The identification of A or H has been dropped on the right-hand side of the equations since the only manner in which the A system affects the equations is through the single parameter $\epsilon(A)$. A similar conclusion has been given by Grossetête.[7] This substantiates the suspicion that it is, after all, only the expectation value of the electron spin polarization that is important in spin exchange. The nuclear spin only increases the number of hyperfine spin states among which this polarization is distributed. The appearance of $\epsilon(A)$ in Eqs. (8) also indicates the manner in which spin exchange serves as a "polarization detector" between two types of atoms. This effect has already been used extensively.[3,5,8] Furthermore, the off-diagonal part of Eqs. (8) enables one to readily determine the form of the spin-exchange shift for a particular resonant atomic system.

III. CONCLUSIONS

As shown by the form of the equations for the diagonal and off-diagonal elements, the only manner in which the A system affects the time evolution of $\rho(H)$ is through the particular combination of density-matrix elements $\epsilon(A)$ and not through the specific population of each hyperfine level. Although the final equations appear complex at first glance, they are much easier to deal with than the matrix equation that was the starting point. Only the matrix elements of σ_x, σ_y, and σ_z for the systems of interest are needed to give quickly the equations of motion for spin exchange. For example, since Rb^{87} has eight hyperfine levels, using Eq. (3) directly would mean manipulating 64×64 matrices, and the simplification of this calculation is particularly evident.[9] Equation (8), of course, reproduces previously published results for the cases of hydrogen-hydrogen spin exchange,[3,5,10] hydrogen-deuterium spin exchange,[3] deuterium-deuterium spin exchange,[3] rubidium-rubidium spin exchange,[9] and rubidium-hydrogen spin exchange.[6] The matrix elements of $\vec{\sigma}$ for these calculations are displayed in Tables I–III.[11]

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Addendum to "Potential-Scattering Model for Electrons on Helium and Other Atoms"*

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It is shown, as an extension to Ref. 1, that a relatively simple analytic potential, which was obtained from studies of bound electron states in atoms, gives differential cross sections in good agreement with experimental values for the rare gases Ar, Kr, and Xe.

A relatively simple analytic potential for describing the elastic scattering of electrons by atoms was proposed by the present authors.[1] The model is based on a single-particle model for bound states of electrons in atoms.[2]

The purpose of the work done in Ref. 1 was to study the feasibility of the approach by considering the case of electrons on helium, although the more general problem was discussed somewhat. In this paper, the results of applying the model to argon, krypton, and xenon are shown and compared with recent experimental data. Our main purpose is to show that the simple modification given in Ref. 1 of the analytical form used in Ref. 2 is sufficient to account for the main features of the observed cross sections without further adjustment of the parameters involved.

The solid curves shown in Fig. 1 for Ar, Fig. 2