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Spin Exchange in Collisions between Atoms*

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Polarization phenomena in collisions between one-electron (alkali-like) atoms are calculated with density-matrix techniques. The kinetic energies for which this treatment is valid are limited from above by the use of the Born–Oppenheimer approximation, and from below by the assumed degeneracy of the hyperfine states. The basic mechanism for polarization changes is the electron-exchange effect, as suggested by Purcell and Field and by Wittke and Dicke. The special situation of unpolarized targets is treated in some detail. In this case, there are two numbers which characterize the scattering through any angle: the absolute values of certain direct and exchange scattering amplitudes, F_d and F_x. All cross sections must be expressible in terms of $|F_d|$ and $|F_x|$, and this is explicitly carried out in two cases of special interest. One refers to the case in which only the electron-spin polarization is measured, and the other to measurements of the polarization of the hyperfine states of the scattered atom. Effects of the identity of the atoms are also studied in detail.

I. INTRODUCTION

COLLISIONS between atoms in which angular momentum is transferred are an important relaxation mechanism in paramagnetic gases. If the atoms have unpaired electrons, then the most important feature of the process is the identity of the electrons. This gives rise to the exchange of electrons between the colliding atoms, the so-called *spin-exchange scattering*. In this paper, the polarization phenomena in spin-exchange scattering are studied in some detail. In a second paper with S. A. Lebedeff, the problem of calculating the relevant scattering amplitudes is examined.[1]

There has been much interest in this process in connection with the polarization of hyperfine states of alkali atoms in their ground electronic states. A simple theory for spin exchange between hydrogen atoms was developed by Purcell and Field[2] and by Wittke and Dicke.[3] The former pair of authors was concerned with the intensity of the 21-cm line in radio astronomy, the latter with line broadening in a precision measurement of the hyperfine structure of atomic hydrogen. Spin exchange has also been observed with optical pumping[4,5] and electron-spin resonance[6,7] techniques, particularly in alkali vapors.

Attempts are now being made in many laboratories to measure spin-exchange cross sections with sufficient accuracy to be of use in the theory of interatomic forces. The best method, and one which is also very difficult, is to scatter two polarized atomic beams. In principle, this can give all of the scattering amplitudes as a function of scattering angle and relative kinetic energy. The most interesting case, from the point of view of the theory, is the collision of two hydrogen atoms, for here there is some hope of making a complete theory starting from the full four-body problem.

The purpose of these papers is to present a more complete theory of spin-exchange scattering than has been available in the past. The dynamical basis of the theory is actually very similar to the first work by Purcell and Field[2] and by Wittke and Dicke,[3] and a more recent version by Dalgarno.[8] In particular, the collision of one-electron atoms will be considered for relative energies much greater than the hyperfine splittings, but small enough for the Born-Oppenheimer approximation to be valid. This means that the collision time must be much greater than the electronic periods, but much less than the period associated with the hyperfine splittings. For two hydrogen atoms, this restricts the relative energy to the range (measured in degrees) from approximately 10 to 10^5 °K. By a one-electron atom is meant, of course, an atom with a single s electron outside closed shells. Neglecting all magnetic moment interactions,[9] the above restrictions on the relative kinetic energy imply that the scattering can be reduced to an elastic scattering problem. In this approximation, the atoms interact through a spin-dependent central potential $V_S(r)$, where r is the distance between the atoms, and S is the quantum number for the total electronic spin, equal to 0 or 1. Associated with the potentials $V_S(r)$ are scattering amplitude $f_S(\theta)$, which are obtained in the usual way by solving the Schrödinger equation.

The present development of this model attempts to improve on previous work by giving a more general and complete description of the polarization effects in spin-exchange scattering. This is largely accomplished by use of the density matrix. Effects of the identity of

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[9] For the heavier atoms, the most important correction is probably the coupling between the electronic-spin and the nuclear orbital angular momentum. This interesting problem is not examined in this paper.

the atoms are also considered. The statistical problem of the relaxation of a collection of such atoms is not studied in this paper at all, although the results are expected to be useful in analyzing such problems. The results should be most directly applicable to cross-section measurements made with crossed polarized atomic beams, i.e., where a truly two-body encounter is of interest. The problem of calculating the various cross sections and scattering amplitudes is treated in another paper.[1]

The plan of the paper is as follows: The theoretical basis of the model is presented in Sec. II. The discussion here is quite general and includes the use of the density matrix, the effects of identity of the atoms, and the definition of a general spin-exchange cross section. The remaining sections are devoted to specific applications, with special emphasis on the situation where the target atoms are unpolarized and measurements are made only on the incident atom before and after scattering. In Sec. III, results are presented for the situation in which only the polarization of the electron spin is measured, a case relevant to electron spin-resonance experiments. The various cross sections of interest are then independent of the nuclear spin except when the atoms are identical. In Sec. IV, it is assumed that the polarization in the atomic hyperfine states is measured and that the atoms are not identical. A simple closed-form expression is then derived which gives the cross section for scattering from any hyperfine state to any other, provided the target is unpolarized. The effects of the identity of the atoms is most fully investigated in Sec. V, which deals with the collision of two hydrogen atoms.

Although the discussion of this paper is directed toward collisions between normal one-electron atoms, it also applies to other situations in which electron exchange is important. These include electron scattering from normal one-electron atoms and collisions in which one (or both) partners is an ion with one electron outside of closed shells.

II. GENERAL THEORETICAL BASIS

The general features of the scattering of two non-identical one-electron atoms will be given first. As mentioned in the Introduction, the kinetic energies considered are high enough to justify ignoring the hyperfine splittings but low enough to use the Born-Oppenheimer approximation. The interaction between the two atoms, which have electronic spins $s_1=s_2=\frac{1}{2}$ and nuclear spins i_1 and i_2, is

$$V=\sum_S V_S(r)P_S, \tag{2.1}$$

where V_S is the potential and P_S is the projection operator for states of total electronic spin S. The scattering from such a potential is familiar from nuclear physics, and Dalgarno has discussed the structure of the scattering amplitude for the present case.[8] In particular, the scattering can be calculated from an operator in the spin space of the two atoms,

$$\mathfrak{F}=\sum_S f_S(\theta)P_S, \tag{2.2}$$

where $f_S(\theta)$ is the usual scattering amplitude associated with the potential $V_S(r)$, θ being the center-of-mass scattering angle. If the two atoms are initially in the spin state $|\alpha_1\alpha_2\rangle$, then the differential cross section for scattering through the center-of-mass angle θ to the spin state $|\alpha_1'\alpha_2'\rangle$ is

$$\sigma(\alpha_1\alpha_2,\alpha_1'\alpha_2';\theta)=|\langle\alpha_1'\alpha_2'|\mathfrak{F}|\alpha_1\alpha_2\rangle|^2. \tag{2.3}$$

The operator $\mathfrak{F}$ is diagonal in the representation in which the total nuclear spin and the total electronic spin are diagonal. However, this is not the one used to describe measurements, which are usually made on isolated atoms. Of greatest practical importance are the states in which the total angular momentum of each atom is diagonal. The analysis of this paper will, however, avoid the complexities of the transformation coefficients $\langle\alpha_1\alpha_2|IM_ISM_S\rangle$ between the states of physical interest $|\alpha_1\alpha_2\rangle$ and the states in which $\mathfrak{F}$ is simple (i.e., diagonal) $|IM_ISM_S\rangle$.[10]

The scattering operator can be put into a convenient form by using the familiar expressions for the projection operators,

$$\begin{aligned}P_0&=\tfrac{1}{4}(1-\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2),\\ P_1&=\tfrac{1}{4}(3+\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2).\end{aligned} \tag{2.4}$$

The result is

$$\mathfrak{F}=F_d+F_x\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2, \tag{2.5}$$

where

$$F_d=\tfrac{1}{4}f_0+\tfrac{3}{4}f_1, \tag{2.6a}$$

$$F_x=\tfrac{1}{4}(f_1-f_0). \tag{2.6b}$$

The amplitudes F_d and F_x are called the direct amplitude and exchange amplitudes, respectively. As will be seen below, F_d never contributes to scattering in which the spin-state changes, if the atoms are different.

Pure states are seldom realized in scattering experiments, so it is necessary to consider statistical ensembles. In the kind used in this paper, the state of relative momentum is pure, but the spin state is completely general. If the density matrix for the initial

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[10] Such coefficients are discussed in great detail in the literature, e.g., A. de-Shalit and I. Talmi, *Nuclear Shell Theory* (Academic Press Inc., New York, 1963). In the case where α is fm, the quantum numbers for the square and one projection of the total angular momentum of a single atom, the transformation coefficients are

$$\begin{aligned}&\langle f_1m_1f_2m_2|IM_ISM_S\rangle\\ &\quad=[(2f_1+1)(2f_2+1)(2I+1)(2S+1)]^{1/2}\\ &\qquad\times\sum_{JM}(f_1m_1f_2m_2|JM)(IM_ISM_S|JM)X(i_2i_2I|\tfrac{1}{2}\tfrac{1}{2}S|f_1f_2J),\end{aligned}$$

where $(f_1m_1f_2m_2|JM)$, for example, is a Clebsch-Gordan coefficient and X is a 9-j symbol.

state is normalized to unity[11]

$$\mathrm{Tr}[\rho_{\mathrm{in}}]=1\,, \tag{2.7}$$

the density matrix for the beam scattered through the angle θ is

$$\rho_{\mathrm{sc}}(\theta)=\mathfrak{F}\rho_{\mathrm{in}}\mathfrak{F}^{\dagger}\,. \tag{2.8}$$

With this normalization, the differential cross section for scattering into *all* final spin states is just the trace of $\rho_{\mathrm{sc}}(\theta)$. Any property of the incident or scattered beams can be calculated in the standard way from the appropriate density matrix ρ,

$$\bar{O}=\mathrm{Tr}[\rho O]/\mathrm{Tr}[\rho]\,, \tag{2.9}$$

where O is the observable in question.

The result of any scattering experiment can be calculated with this general formalism once the initial density matrix is specified. Some interesting special results can be found with comparative ease for experiments in which no measurements are made on one of the atoms, so that its polarization may be assumed to be completely random. Although a complete analysis of the scattering process does require such measurements, most experiments in the near future will involve unpolarized targets. In this case, it is useful to define spin-exchange cross sections $\sigma(\alpha,\alpha';\theta)$ for scattering of the incident atom from an initial spin state α to a final spin state α'. Associated with these states are projection operators $P_1(\alpha)$ with the usual properties,[11]

$$P_1^2=P_1\,, \qquad P_1^{\dagger}=P_1\,,$$
$$\mathrm{tr}[P_1]=1\,, \quad \textstyle\sum_{\alpha} P_1(\alpha)=1\,.$$

The subscript 1 stands for the incident atom and the subscript 2 will represent the other (unpolarized) atom. The spin-exchange cross section is defined as

$$\sigma(\alpha,\alpha';\theta)=\mathrm{Tr}[\rho_{\mathrm{sc}}(\theta)(P_1(\alpha')\times I_2)]\,, \tag{2.10a}$$

with the incident density matrix given by

$$\rho_{\mathrm{in}}=(1/g_2)P_1(\alpha)\times I_2\,, \tag{2.10b}$$

and, therefore, the above definition is

$$\sigma(\alpha,\alpha';\theta)=(1/g_2)\times\mathrm{Tr}[\mathfrak{F}(P_1(\alpha)\times I_2)\mathfrak{F}^{\dagger}(P_1(\alpha')\times I_2)]\,. \tag{2.11}$$

Here I_2 is the identity matrix for the spins of the target atom of order $g_2=2(2i_2+1)$. This definition embodies the usual averaging over unmeasured initial spin states and summing over unmeasured final spin states. The spin states are always defined with respect to the same quantization axis, both before and after scattering.

When the explicit form for $\mathfrak{F}$ given in Eq. (2.5) is substituted into the spin-exchange cross section, four terms are obtained. Two of these are zero, however, because they are linear in the target-atom Pauli operators which, of course, have zero trace. The result may thus be written

$$\sigma(\alpha,\alpha';\theta)=\frac{1}{g_2}\mathrm{Tr}\Big[|F_d|^2P_1(\alpha)P_1(\alpha') + |F_x|^2\sum_{i=1}^{3}\sigma_{1i}P_1(\alpha)\sigma_{1i}P_1(\alpha')\Big]\,. \tag{2.12}$$

This equation is completely devoid of spin operators for the target atom, so all reference to it can be eliminated[11]:

$$\sigma(\alpha,\alpha';\theta)=|F_d|^2\,\mathrm{tr}[P(\alpha)P(\alpha')] + |F_x|^2\sum_{i=1}^{3}\mathrm{tr}[\sigma_iP(\alpha)\sigma_iP(\alpha')]\,. \tag{2.13}$$

As pointed out by Wichmann,[12] this result can be generalized to arbitrary statistical ensembles, not just the particular initial and final states involved in the spin-exchange cross section. If $\rho_{\mathrm{in}}(1)$ and $\rho_{\mathrm{sc}}(1)$ are *effective* density matrices for the initial and final states, then Eq. (2.13) implies the relation

$$\rho_{\mathrm{sc}}(1)=|F_d|^2\rho_{\mathrm{in}}(1)+|F_x|^2\sum_{i=1}^{3}\sigma_i\rho_{\mathrm{in}}(1)\sigma_i\,. \tag{2.14}$$

The average value of any observable $o(1)$ of the scattered atoms is then

$$\bar{o}_{\mathrm{sc}}(1)=\mathrm{tr}[\rho_{\mathrm{sc}}(1)o(1)]\,.$$

Most of the analysis of this paper is based on Eq. (2.13) or its equivalent, Eq. (2.14). From them it can be seen that experiments with unpolarized targets depend only on the absolute values of F_d and F_x. To obtain complete information about the scattering process, i.e., to measure the relative phase of F_d and F_x, obviously requires polarization studies of both atoms. In resonance experiments, where only polarization changes are observed, only $|F_x|$ can be measured. This follows from the fact that the first term of Eq. (2.13) vanishes unless $\alpha=\alpha'$. Although only two numbers determine the spin-exchange cross section at each angle, there are $[2(2i_1+1)]^2$ spin-exchange cross sections according to the definition of Eq. (2.11). One of the main objectives of this paper is to relate these cross sections, which are clearly not all independent, to the quantities $|F_d|$ and $|F_x|$.

This analysis can be extended to identical atoms by properly symmetrizing the scattering amplitudes. If Q_n and Q_e are the operators which interchange the two electronic and the two nuclear spins, respectively, then

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[11] Some explanation of the matrix notation of this paper is in order. First of all, $\mathrm{Tr}[O]$ stands for the trace of O in the spin space of *both* atoms, i.e., in the vector space formed from the product of the four spin spaces of both electrons and both nuclei. The symbol $\mathrm{tr}[o(1)]$ is the partial trace carried out in the spin space of just one atom, i.e., in the vector space formed from the product of the spin space of the electron and the spin space of the nucleus of this atom; the operator $o(1)$ is an observable for the atom. The matrix O is frequently the direct product $o(1)\times o(2)$ of matrices referring to the individual atoms. The cross notation, as well as identity matrices, will frequently be suppressed if the meaning of an equation is clear without them.

[12] E. Wichmann (private communication).

their basic properties follow from the equations,

$$Q_e|IM_ISM_S\rangle=(-)^{S+1}|IM_ISM_S\rangle,$$
$$Q_n|IM_ISM_S\rangle=(-)^{I+2i}|IM_ISM_S\rangle.$$

Therefore, the scattering operator must now be

$$\mathfrak{F}=\sum_S[f_S(\theta)+(-)^{2i+1}Qf_S(\pi-\theta)]P_S, \quad (2.15)$$

where $Q=Q_nQ_e$ interchanges both the electronic and the nuclear spins. The factor $(-)^{2i+1}$ is even for half-integral i and odd for integral i, corresponding to the boson and fermion character of the *atoms* for half and whole integral values of the nuclear spin, respectively. In the representation in which the total nuclear and the total electronic spin are both diagonal, $\mathfrak{F}$ is diagonal with the eigenvalues

$$(IM_ISM_S|\mathfrak{F}|IM_ISM_S)=f_S(\theta)+(-)^{I+S}f_S(\pi-\theta).$$

Most of the remaining analysis parallels the previous discussion for nonidentical atoms. For identical atoms, Eq. (2.3) gives the differential cross section for collisions in which two identical atoms in spin states α_1 and α_2 are scattered into the spin states α_1' and α_2'. The angle θ refers to the direction of motion of the atom in the spin state α_1', measured relative to the incident direction which is defined by the motion of the atom in spin state α_1. Using the familiar form for Q_e,

$$Q_e=P_1-P_0=\tfrac{1}{2}(1+\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2), \quad (2.16)$$

Eq. (2.15) becomes

$$\mathfrak{F}=[f_0(\theta)-(-)^{2i+1}Q_nf_0(\pi-\theta)]P_0 \\ +[f_1(\theta)+(-)^{2i+1}Q_nf_1(\pi-\theta)]P_1.$$

The generalization of Eq. (2.5) for $\mathfrak{F}$ to identical atoms is, therefore,

$$\mathfrak{F}=G_d+G_x\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2, \quad (2.17)$$

where G_d and G_x are the nuclear spin operators

$$G_d(\theta)=\tfrac{1}{4}[f_0(\theta)-(-)^{2i+1}Q_nf_0(\pi-\theta)] \\ +\tfrac{3}{4}[f_1(\theta)+(-)^{2i+1}Q_nf_1(\pi-\theta)], \quad (2.18\text{a})$$

$$G_x(\theta)=\tfrac{1}{4}[f_1(\theta)+(-)^{2i+1}Q_nf_1(\pi-\theta)] \\ -\tfrac{1}{4}[f_0(\theta)-(-)^{2i+1}Q_nf_0(\pi-\theta)], \quad (2.18\text{b})$$

The alternative forms,

$$G_d(\theta)=F_d(\theta)+F_d'(\pi-\theta)(-)^{2i+1}Q_n, \quad (2.19\text{a})$$

$$G_x(\theta)=F_x(\theta)+F_x'(\pi-\theta)(-)^{2i+1}Q_n, \quad (2.19\text{b})$$

emphasize the connection with the previous treatment for nonidentical atoms. The amplitudes F_d' and F_x' are obtained from F_d and F_x of Eq. (2.6) by simply changing f_0 to $-f_0$:

$$F_d'(\theta)=-\tfrac{1}{4}f_0(\theta)+\tfrac{3}{4}f_1(\theta), \quad (2.20\text{a})$$

$$F_x'(\theta)=\tfrac{1}{4}f_1(\theta)+\tfrac{1}{4}f_0(\theta). \quad (2.20\text{b})$$

These amplitudes share with F_d and F_x the useful property

$$|F_d'(\theta)|^2+3|F_x'(\theta)|^2=|F_d(\theta)|^2+3|F_x(\theta)|^2 \\ =\tfrac{1}{4}|f_0(\theta)|^2+\tfrac{3}{4}|f_1(\theta)|^2. \quad (2.20\text{c})$$

The spin-exchange cross section, Eq. (2.11), can now be written in a form analogous to Eq. (2.12) for nonidentical atoms,

$$\sigma(\alpha,\alpha';\theta)=\frac{1}{g_2}\,\mathrm{tr}[G_dP_1(\alpha)G_d^\dagger P_1(\alpha') \\ +\sum_{i=1}^{3}G_x\sigma_{1i}P_1(\alpha)G_x^\dagger\sigma_{1i}P_1(\alpha')]. \quad (2.21)$$

Once again there is no mixing of direct and exchange amplitudes because the scattering operator is linear in $\boldsymbol{\sigma}_2$. This expression may be further developed by using Eq. (2.19) for G_d and G_x. For this purpose, it helps to recognize that[13]

$$\mathrm{Tr}[Q_n]=4(2i+1) \quad (2.22)$$

and to then express Q_n as

$$Q_n=(2i+1)^{-1}I+Q_n', \quad (2.23)$$

where

$$\mathrm{Tr}[Q_n']=0. \quad (2.24)$$

Equation (2.19) then becomes

$$G_d(\theta)=J_d(\theta)+K_d(\theta)Q_n', \quad (2.25\text{a})$$

$$G_x(\theta)=J_x(\theta)+K_x(\theta)Q_n', \quad (2.25\text{b})$$

where

$$J_d(\theta)=F_d(\theta)+[(-)^{2i+1}/2i+1]F_d'(\pi-\theta), \quad (2.26\text{a})$$

$$K_d(\theta)=(-)^{2i+1}F_d'(\pi-\theta), \quad (2.26\text{b})$$

and

$$J_x(\theta)=F_x(\theta)+[(-)^{2i+1}/2i+1]F_x'(\pi-\theta), \quad (2.27\text{a})$$

$$K_x(\theta)=(-)^{2i+1}F_x'(\pi-\theta). \quad (2.27\text{b})$$

Detailed use of these expressions will be made in Secs. III and IV, where the effects of identity are studied for some specific kinds of spin exchange.

To conclude this section, the unpolarized scattering is calculated from Eq. (2.8), starting with the initial density matrix

$$\rho_{\text{in}}=[4(2i_1+1)(2i_2+1)]^{-1}I. \quad (2.28)$$

For nonidentical atoms, Eq. (2.2) is used for $\mathfrak{F}$,

$$\sigma(\theta)=[4(2i_1+1)(2i_2+1)]^{-1}\sum_S\mathrm{Tr}[|f_S(\theta)|^2P_S],$$

with the expected result

$$\sigma(\theta)=\tfrac{3}{4}|f_1(\theta)|^2+\tfrac{1}{4}|f_0(\theta)|^2. \quad (2.29)$$

For identical atoms, Eq. (2.15) must be used,

$$\sigma(\theta)=\frac{1}{4(2i+1)^2}\sum_S\mathrm{Tr}[\{|f_S(\theta)|^2+|f_S(\pi-\theta)|^2 \\ +(-)^{2i+1}2\,\mathrm{Re}f_S^*(\theta)f_S(\pi-\theta)Q_nQ_e\}P_S],$$

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[13] This follows from the fact that the ratio of symmetric to antisymmetric states under interchange of nuclear spins is $(i+1)/i$, the total number states of course being $[2(2i+1)]^2$.

with the result,

$$\sigma(\theta)=\tfrac{1}{4}\left[|f_0(\theta)|^2+|f_0(\pi-\theta)|^2-\frac{(-)^{2i+1}}{2i+1}2\,\mathrm{Re}f_0^*(\theta)f_0(\pi-\theta)\right]$$
$$+\tfrac{3}{4}\left[|f_1(\theta)|^2+|f_1(\pi-\theta)|^2+\frac{(-)^{2i+1}}{2i+1}2\,\mathrm{Re}f_1^*(\theta)f_1(\pi-\theta)\right]. \quad (2.30)$$

These expressions for the unpolarized differential cross section also follow from the alternative expressions for $\mathfrak{F}$ given in Eqs. (2.5) and (2.17) and the simple relation $(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2)^2=3-2(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2)$, i.e., for nonidentical atoms

$$\begin{aligned}\sigma(\theta)&=[4(2i_1+1)(2i_2+1)]^{-1}\,\mathrm{Tr}[|F_d(\theta)|^2+3|F_x(\theta)|^2]\\&=|F_d(\theta)|^2+3|F_x(\theta)|^2,\end{aligned}\quad (2.31)$$

and for identical atoms

$$\begin{aligned}\sigma(\theta)&=[4(2i+1)^2]^{-1}\,\mathrm{Tr}[G_d(\theta)G_d^\dagger(\theta)+3G_x(\theta)G_x^\dagger(\theta)]\\&=|F_d(\theta)|^2+3|F_x(\theta)|^2+|F_d(\pi-\theta)|^2+3|F_x(\pi-\theta)|^2\\&\quad+[(-)^{2i+1}/2i+1]2\,\mathrm{Re}[F_d^*(\theta)F_d'(\pi-\theta)\\&\qquad+3F_x^*(\theta)F_x'(\pi-\theta)].\end{aligned}\quad (2.32)$$

In the approximation that the interference term can be neglected, e.g., for large nuclear spin or for amplitudes peaked in the forward direction, the cross section in Eq. (2.32) reduces to a form appropriate to classical scattering theory.

III. CROSS SECTION FOR ELECTRON SPIN EXCHANGE

A first simple application of the above theory is to collisions in which the initial and final states are characterized by the polarization of the electron spin. Assuming unpolarized targets, the initial density matrix is

$$\rho_{\mathrm{in}}(1)=\tfrac{1}{2}(I_e+\boldsymbol{\sigma}\cdot\mathbf{p})\times[(2i_1+1)^{-1}I_n], \quad (3.1)$$

where $\mathbf{p}$ is the initial electron polarization and I_e and I_n are the identities in the electron and nuclear spin spaces. The length of $\mathbf{p}$ is restricted to $0\leq p\leq 1$, a pure state being characterized by $p=1$ and a completely unpolarized state by $p=0$. The final density matrix is easily obtained by substituting this expression into Eq. (2.14), the result being

$$\rho_{\mathrm{sc}}(1)=\sigma(\theta)\tfrac{1}{2}(I_e+\boldsymbol{\sigma}\cdot\mathbf{p}')\times[(2i_1+1)^{-1}I_n]. \quad (3.2)$$

The cross section $\sigma(\theta)$ is just the unpolarized cross section given in Eq. (2.29). This expression has the usual form of a density matrix describing electron polarization and, thus, the quantity $\mathbf{p}'$,

$$\mathbf{p}'=\frac{|F_d|^2-|F_x|^2}{|F_d|^2+3|F_x|^2}\mathbf{p}, \quad (3.3)$$

is the final electron polarization. The final polarization is parallel to the initial polarization, and always smaller in magnitude.

Possessing a complete solution of this problem, a number of special cases can easily be studied. For example, if the initial state is unpolarized ($p=0$), the final state is also

$$\rho_{\mathrm{sc}}(1)=\sigma(\theta)(\tfrac{1}{2}I_e)\times[(2i_1+1)^{-1}I_n], \quad (3.4)$$

and the trace of $\rho_{\mathrm{sc}}(1)$ in this case is the unpolarized cross section $\sigma(\theta)$. More generally, the cross section for finding the scattered electron completely polarized in the direction $\hat{n}$ is

$$\sigma(\mathbf{p};\hat{n},\theta)=\mathrm{Tr}[\rho_{\mathrm{sc}}(1)\tfrac{1}{2}(I_e+\boldsymbol{\sigma}\cdot\hat{n})\times I_n], \quad (3.5)$$

the second factor being the projection operator for this pure polarization state. Using Eq. (3.2), this is simply

$$\sigma(\mathbf{p};\hat{n},\theta)=\tfrac{1}{2}(1+\mathbf{p}'\cdot\hat{n})\sigma(\theta), \quad (3.6a)$$

or, with Eq. (3.3),

$$\sigma(\mathbf{p};\hat{n},\theta)=\tfrac{1}{2}(1+\mathbf{p}\cdot\hat{n})|F_d|^2+\tfrac{1}{2}(3-\mathbf{p}\cdot\hat{n})|F_x|^2. \quad (3.6b)$$

Defining the cross section for no spin change as

$$\sigma_d(\theta)=\sigma(\hat{n},\hat{n};\theta), \quad (3.7a)$$

and the cross section for a spin-flip as[14]

$$\sigma_x(\theta)=\sigma(\hat{n},-\hat{n};\theta), \quad (3.7b)$$

Eq. (3.6b) leads to the following formulas for these cross sections,

$$\sigma_d=|F_d|^2+|F_x|^2, \quad (3.8a)$$

$$\sigma_x=2|F_x|^2. \quad (3.8b)$$

These cross sections do not depend on the nuclear spin, which seems natural, since they refer to experiments in which only the electron spin is measured–and also since the potential [Eq. (2.1)] arises from electron exchange. It can also be checked [using Eq. (2.13)] that, if measurements are also made on the nuclear spin, the cross section vanishes unless the initial and final nuclear-spin states are the same. This justifies the use of the name, "electron spin exchange," for the kind of cross section under discussion.

The identity of the atoms may be accounted for by using Eq. (2.21) and averaging and summing over the unmeasured nuclear spins. The cross section for scattering from a state in which the electron has the polariza-

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[14] This is a factor of two smaller than the spin-flip cross section used by R. M. Mazo, J. Chem. Phys. **34**, 169 (1959), who has analyzed linewidths in electron paramagnetic resonance in gaseous hydrogen. The cross sections used here are the same as introduced by Purcell and Field (Ref. 2) and by Dalgarno (Ref. 8).

tion $\mathbf{p}$ to a state in which it is completely polarized in the direction $\hat{n}$ is

$$\begin{aligned}\sigma(\mathbf{p},\hat{n};\theta)&\\ =[8(2i+1)^2]^{-1}\{&\mathrm{Tr}[G_d(I_e+\boldsymbol{\sigma}_1\cdot\mathbf{p})G_d^\dagger(I_e+\boldsymbol{\sigma}_1\cdot\hat{n})]\\ &+\sum_{i=1}^{3}\mathrm{Tr}[G_x\sigma_{1i}(I_e+\boldsymbol{\sigma}_1\cdot\mathbf{p})G_x^\dagger\sigma_{1i}(I_e+\boldsymbol{\sigma}_1\cdot\hat{n})]\}\,. \quad (3.9)\end{aligned}$$

This expression reduces considerably because the terms linear in the Pauli operators have zero trace and because G_d and G_x commute with the electron spin operators:

$$\begin{aligned}\sigma(\mathbf{p},\hat{n};\theta)=\frac{1}{4(2i+1)^2}\{&\tfrac{1}{2}(1+\mathbf{p}\cdot\hat{n})\ \mathrm{Tr}[G_dG_d^\dagger]\\ &+\tfrac{1}{2}(3-\mathbf{p}\cdot\hat{n})\ \mathrm{Tr}[G_xG_x^\dagger]\}\,. \quad (3.10)\end{aligned}$$

This result is the generalization of Eq. (3.6b) for identical atoms. In fact, comparison with this equation indicates that all of the results of the preceding analysis can be extended to this case, if the following replacements are made:

$$\begin{aligned}|F_d|^2\rightarrow\frac{1}{4(2i+1)^2}&\mathrm{Tr}[G_dG_d^\dagger]\\ &=|F_d(\theta)|^2+|F_d'(\pi-\theta)|^2\\ &\quad+\frac{(-)^{2i+1}}{2i+1}2\ \mathrm{Re}(F_d^*(\theta)F_d'(\pi-\theta)], \quad (3.11\mathrm{a})\\ |F_x|^2\rightarrow\frac{1}{4(2i+1)^2}&\mathrm{Tr}[G_xG_x^\dagger]\\ &=|F_x(\theta)|^2+F_x'(\pi-\theta)|^2\\ &\quad+\frac{(-)^{2i+1}}{2i+1}2\ \mathrm{Re}[F_x^*(\theta)F_x'(\pi-\theta)]. \quad (3.11\mathrm{b})\end{aligned}$$

This transcription may be made to obtain the effective density matrix from Eq. (3.2), the polarization after scattering from Eq. (3.3), the cross section for a pure polarization state from Eq. (3.6a), and the cross sections for no spin change and for a spin flip from Eqs. (3.8a) and (3.8b), respectively. For example, σ_x is twice the expression given in Eq. (3.11b), and σ_d is the sum of Eqs. (3.11a) and (3.11b). The polarization after scattering $\mathbf{p}'$ is parallel to the initial polarization $\mathbf{p}$ and the ratio of their magnitudes is the difference of Eq. (3.11b) and (3.11a) divided by Eq. (2.32) for the unpolarized scattering cross section. All of these quantities differ in magnitude from the values appropriate to nonidentical atoms. They will also now depend explicitly on the nuclear spin through the factor $(2i+1)^{-1}\times(-)^{2i+1}$ which is associated with the "exchange amplitudes" F_d' and F_x'. The differences with the results for nonidentical atoms persist even in the limit of neglecting the interference terms in Eq. (3.11). As already pointed out in Sec. II, the unpolarized cross section reduces to the classical form, but all of the other quantities of physical interest here do not. For example, the ratio of the polarizations tends in this limit to

$$\frac{p'}{p}=\frac{|F_d(\theta)|^2-|F_x(\theta)|^2+|F_d'(\pi-\theta)|^2-|F_x'(\pi-\theta)|^2}{|F_d(\theta)|^2+3|F_x(\theta)|^2+|F_d(\pi-\theta)|^2+3|F_x(\pi-\theta)|^2}.$$

IV. CROSS SECTIONS FOR CHANGES IN THE TOTAL ANGULAR-MOMENTUM QUANTUM NUMBERS

There are many kinds of experiments in which electron spin exchange manifests itself through changes in the polarization of the atomic hyperfine states. One example is relaxation studies in paramagnetic gases using radio-frequency spectroscopy and various polarization techniques, e.g., optical pumping. The statistical analysis necessary for understanding such experiments is not developed in this paper, however, but only the properties of some of the two-body scattering events occurring in these gases. The results are, therefore, more directly applicable to scattering experiments with crossed polarized atomic beams. The cross sections for the various polarization changes observable in atomic-beam experiments will now be calculated with the density-matrix techniques developed in previous sections.

Restricting the analyses of this section to nonidentical atoms, the cross section for a change in hyperfine state from fm to $f'm'$, on scattering from unpolarized atoms, is [using Eq. (2.13)]

$$\begin{aligned}\sigma(fm,f'm';\theta)&\\ =|F_d|^2\ &\mathrm{tr}[P(fm)P(f'm')]\\ &+|F_x|^2\sum_{i=1}^{3}\mathrm{tr}[\sigma_iP(fm)\sigma_iP(f'm')]. \quad (4.1)\end{aligned}$$

The operators $P(fm)$ are the projection operators for the hyperfine states of the incident atom. The first term vanishes unless the initial and final states are the same. The second term, which expresses the effect of spin-exchange scattering on the hyperfine states, is determined by the quantity[15]

$$\Delta(fm,f'm')\equiv\sum_i\mathrm{tr}[\sigma_iP(fm)\sigma_iP(f'm')]. \quad (4.2)$$

By evaluating the trace in the fm representation, this expression may be rewritten as

$$\Delta(fm,f'm')=\sum_{i=1}^{3}|(f'm'|\sigma_i|fm)|^2,$$

---

[15] The dependence of $\sigma(fm,f'm';\theta)$ in Eq. (4.1) and $\Delta(fm,f'm')$ in Eq. (4.2) on the magnitude i_1 of the nuclear spin of the incident atom (and on the electron spin$=\frac{1}{2}$) has been suppressed here. This is also true of various other quantities derived from these.

and by transforming to the spherical basis $\sigma_\mu(\mu=1, 0, -1)$,[16]

$$\sigma_0=\sigma_z \quad \sigma_{\pm1}=\mp\frac{1}{\sqrt{2}}(\sigma_x\pm i\sigma_y)\,,$$

it becomes

$$\Delta(fm,f'm')=\sum_{\mu=-1}^{1}|(f'm'|\sigma_\mu|fm)|^2.$$

This is a form suitable for applying the Wigner-Eckart theorem[17]

$$(f'm'|\sigma_\mu|fm)=(fm1\mu|f'm')(\tfrac{1}{2}if'\|\sigma\|\tfrac{1}{2}if)\,,$$

where the first factor is the usual Clebsch-Gordan coefficient, and the second is the reduced matrix element of the Pauli spin operator. Thus, Δ of Eq. (4.2) may be written as

$$\Delta(fm,f'm')=|(\tfrac{1}{2}if'\|\sigma\|\tfrac{1}{2}if)|^2\sum_\mu(fm1\mu|f'm')^2. \quad (4.3)$$

Summing over magnetic quantum numbers and using the orthogonality of the Clebsch-Gordan coefficients lead to

$$\Delta(f,f')\equiv\sum_{mm'}\Delta(fm,f'm')$$
$$=(2f'+1)|(\tfrac{1}{2}if'\|\sigma\|\tfrac{1}{2}if)|^2, \quad (4.4)$$

and the possibility of eliminating the reduced matrix element in Eq. (4.3), i.e.,

$$\Delta(fm,f'm')=\tfrac{1}{3}\Delta(f,f')\sum_\mu(fmf'-m'|1-\mu)^2. \quad (4.5)$$

At the same time, the spin-exchange cross section becomes

$$\sigma(fm,f'm';\theta)=\delta_{ff'}\delta_{mm'}|F_d|^2+\tfrac{1}{3}\Delta(f,f')$$
$$\times\sum_\mu(fmf'-m'|1-\mu)^2|F_x|^2. \quad (4.6)$$

This expression fulfills one of the important aims of this paper, which is to relate the $[2(2i+1)]^2$ spin-exchange cross sections to the absolute values, $|F_x|$ and $|F_d|$, of the two basic scattering amplitudes. The essential step was the application of the Wigner-Eckart theorem to the quantity $\Delta(fm,f'm')$ of Eq. (4.2). From this result, the "selection rules" for the process can also be ascertained:

$$\Delta f=|f'-f|=0 \text{ or } 1 \quad (4.7\text{a})$$

$$\Delta m=m'-m=1,\ 0,\ \text{or } -1\,, \quad (4.7\text{b})$$

which follow from the fact that the process occurs by a unit change in the projection of the electron spin.

TABLE I. Values of $\Delta(f,f')$ from Eq. (4.13).

$f'\backslash f$	$i+\frac{1}{2}$	$i-\frac{1}{2}$
$i+\frac{1}{2}$	$\dfrac{(2i+2)(2i+3)}{(2i+1)}$	$\dfrac{8i(i+1)}{2i+1}$
$i-\frac{1}{2}$	$\dfrac{8i(i+1)}{2i+1}$	$\dfrac{(2i-1)(2i)}{(2i+1)}$

The factor $\Delta(f,f')$, which is essentially the square of a reduced matrix element, may be evaluated directly from an alternative form of its definition in Eq. (4.4):

$$\Delta(f,f')=\sum_{i=1}^{3}\text{tr}[\sigma_iP(f)\sigma_iP(f')]. \quad (4.8)$$

The operator $P(f)$ is the sum of the $2f+1$ projection operators $P(fm)$,

$$P(f)=\sum_{m=-j}^{j}P(fm)\,, \quad (4.9)$$

i.e., it is a projection operator for any state with total angular momentum f. For the two hyperfine states $f=i\pm\frac{1}{2}$, these operators [which are the obvious generalizations of the familiar singlet and triplet projection operators of Eq. (2.4)] may be written as

$$P(i+\tfrac{1}{2})=(2i+1)^{-1}(i+1+\boldsymbol{\sigma}\cdot\mathbf{I})\,, \quad (4.10\text{a})$$

$$P(i-\tfrac{1}{2})=(2i+1)^{-1}(i-\boldsymbol{\sigma}\cdot\mathbf{I})\,, \quad (4.10\text{b})$$

or, in one equation,

$$P(f)=(2i+1)^{-1}[(f+\tfrac{1}{2})+(-)^{f-i-\frac{1}{2}}\boldsymbol{\sigma}\cdot\mathbf{I}]. \quad (4.11)$$

Substituting these operators into Eq. (4.8) for $\Delta(f,f')$ and dropping the terms linear in the Pauli operators (which have zero trace), leads to

$$\Delta(f,f')=\frac{1}{(2i+1)^2}\sum_{i=1}^{3}\text{tr}[(f+\tfrac{1}{2})(f'+\tfrac{1}{2})\sigma_i^2$$
$$+(-)^{f-f'}\sigma_i\boldsymbol{\sigma}\cdot\mathbf{I}\sigma_i\boldsymbol{\sigma}\cdot\mathbf{I}]. \quad (4.12)$$

The traces can easily be evaluated and the result is

$$\Delta(f,f')=(2/2i+1)$$
$$\times[3(f+\tfrac{1}{2})(f'+\tfrac{1}{2})-(-)^{f-f'}i(i+1)]. \quad (4.13)$$

The spin-exchange cross section is now finally given by

$$\sigma(fm,f'm')=\delta_{f'f}\delta_{m'm}|F_d|^2$$
$$+\frac{\frac{2}{3}}{2i+1}[3(f+\tfrac{1}{2})(f'+\tfrac{1}{2})-(-)^{f-f'}i(i+1)]$$
$$\times\sum_\mu(fmf'-m'|1-\mu)^2|F_x|^2. \quad (4.14)$$

For convenience, the coefficients $\Delta(ff')$ are tabulated in Table I.

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[16] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1950), p. 64.

[17] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1950), p. 85.

One of the first uses of this formula is to check the results of the preceding section on electron spin exchange by simply setting the nuclear spin to zero in Eq. (4.14):

$$\sigma(\tfrac{1}{2}m,\tfrac{1}{2}m')=\delta_{mm'}|F_d|^2 +2(\tfrac{1}{2}m\tfrac{1}{2}-m'|1m-m')^2|F_x|^2. \quad (4.15)$$

The square of the Clebsch-Gordan coefficient is $\frac{1}{2}$ for $m'=m$, and 1 for $m'=-m$, and thus

$$\sigma(\tfrac{1}{2}m,\tfrac{1}{2}m)=|F_d|^2+|F_x|^2=\sigma_d, \quad (4.16a)$$

and

$$\sigma(\tfrac{1}{2}m,\tfrac{1}{2}-m)=2|F_x|^2=\sigma_x, \quad (4.16b)$$

in agreement with Eqs. (3.8a) and (3.8b).

The situation for nuclear spin $i=\frac{1}{2}$ is not much more complicated, and the sixteen spin-exchange cross sections are listed in Table II. The cross section for an actual change in angular momentum state is $|F_x|^2$ in this case, in contrast to $2|F_x|^2$ for nuclear spin zero. The sum of the entries in any row or in any column of Table II is equal to the unpolarized cross section of Eq. (2.31). Both of these results can be understood as special cases of some general properties of the spin-exchange cross sections which will now be proved.

TABLE II. The sixteen spin-exchange cross sections for nuclear spin $i=\frac{1}{2}$.

	$f=1,\ m=1$	$f=1,\ m=0$	$f=1,\ m=-1$	$f=0,\ m=0$
$f'=1,\ m'=1$	$\lvert F_d\rvert^2+\lvert F_x\rvert^2$	$\lvert F_x\rvert^2$	0	$\lvert F_x\rvert^2$
$f'=1,\ m'=0$	$\lvert F_x\rvert^2$	$\lvert F_d\rvert^2$	$\lvert F_x\rvert^2$	$\lvert F_x\rvert^2$
$f'=1,\ m'=-1$	0	$\lvert F_x\rvert^2$	$\lvert F_x\rvert^2+\lvert F_d\rvert^2$	$\lvert F_x\rvert^2$
$f'=0,\ m'=0$	$\lvert F_x\rvert^2$	$\lvert F_x\rvert^2$	$\lvert F_x\rvert^2$	$\lvert F_d\rvert^2$

It is useful to define the average cross section

$$\sigma(f,f')=\frac{1}{2f+1}\sum_{mm'}\sigma(fm,f'm'), \quad (4.17)$$

which, from Eq. (4.6), is equal to

$$\sigma(f,f')=\delta_{f,f'}|F_d|^2+(2f+1)^{-1}\Delta(f,f')|F_x|^2. \quad (4.18)$$

The quantity $\Delta(f,f')$ is given by Eq. (4.13) and also in Table I; the four values of $\sigma(f,f')$ are also listed for convenience in Table III. In the limit of very large nuclear spin, the average cross sections approach the ones for $i=0$ in Eq. (4.16) and also the cross sections for "pure electron spin exchange" in Eqs. (3.8a) and (3.8b):

$$\lim_{i\to\infty}\sigma(f,f)=\sigma_d, \quad (4.19a)$$

$$\lim_{i\to\infty}\sigma(f,f'\neq f)=\sigma_x. \quad (4.19b)$$

Summing the general spin-exchange cross section in Eq. (4.6) over just one magnetic quantum number is actually sufficient to give the average cross section

$$\sum_{m'}\sigma(fm,f'm')=\sigma(f,f'), \quad (4.20a)$$

$$\sum_{m}\sigma(fm,f'm')=\frac{2f+1}{2f'+1}\sigma(f,f'). \quad (4.20b)$$

From Table III or from Eq. (4.18), it can be shown that the average cross section satisfies certain sum rules:

$$\sum_{f}\sigma(f,f)=2\sigma_d, \quad (4.21a)$$

$$\sum_{f'}\sigma(f,f')=\sigma, \quad (4.21b)$$

$$\sum_{f}\sigma(f,f'\neq f)=2\sigma_x, \quad (4.21c)$$

$$\sum_{f,f'}\frac{2f+1}{2(2i+1)}\sigma(f,f')=\sigma, \quad (4.21d)$$

where σ, σ_d, and σ_x are the cross sections previously introduced in Eq. (2.31) and Eqs. (3.8a) and (3.8b).

The sum of the spin-exchange cross section $\sigma(fm,f'm')$ over all possible final states can easily be obtained from Eqs. (4.20a) and (4.21b):

$$\sum_{f'm'}\sigma(fm,f'm')=\sigma. \quad (4.22)$$

As a further application of Eq. (4.20a) and Table III, the cross section for a change in spin state, such that the initial and final values of the total spin are different, is

$$\frac{1}{2f'+1}\sum_{m'}\sigma(fm,f'\neq fm') =\frac{1}{2f'+1}\sigma(f,f'\neq f)=\frac{2}{2i+1}|F_x|^2. \quad (4.23)$$

TABLE III. The average cross section $\sigma(f,f')$ given by Eqs. (4.17) and (4.18).

	$f=i+\frac{1}{2}$	$f=i-\frac{1}{2}$
$f'=i+\frac{1}{2}$	$\left[(\lvert F_d\rvert^2+\lvert F_x\rvert^2)+\dfrac{2}{2i+1}\lvert F_x\rvert^2\right]$	$\left[\dfrac{4(i+1)}{2i+1}\lvert F_x\rvert^2\right]$
$f'=i-\frac{1}{2}$	$\left[\dfrac{4i}{2i+1}\lvert F_x\rvert^2\right]$	$\left[(\lvert F_d\rvert^2+\lvert F_x\rvert^2)-\dfrac{2}{2i+1}\lvert F_x\rvert^2\right]$

This conforms to the results previously stated for nuclear spin zero and one half. Combining Eqs. (4.23) and (4.22), the probability for a change to a spin state with a different value of the total (hyperfine) angular momentum f is

$$w(i)=\frac{2}{2i+1}\,\frac{|F_x|^2}{|F_d|^2+3|F_x|^2}. \tag{4.24}$$

V. HYDROGEN-HYDROGEN SCATTERING

The special problem of spin-exchange scattering between hydrogen atoms will now be treated, taking full account of the identity of the atoms. This aspect of the problem can be studied in great detail for this case because of the simple form of the nuclear spin-exchange operator,

$$Q_n=\tfrac{1}{2}(I_n+\boldsymbol{\tau}_1\cdot\boldsymbol{\tau}_2), \tag{5.1}$$

$\boldsymbol{\tau}_1$ and $\boldsymbol{\tau}_2$ being the Pauli operators for the proton spins. The traceless operator Q', defined in Eq. (2.23), is now

$$Q_n'=\tfrac{1}{2}\boldsymbol{\tau}_1\cdot\boldsymbol{\tau}_2. \tag{5.2}$$

The partial trace of Q_n' in the spin space of either proton is also zero. The appropriate form of the spin-exchange cross section of Eq. (2.21) is

$$\begin{aligned}\sigma(fm,f'm')&\\ =\tfrac{1}{4}\,&\mathrm{Tr}[(J_d+Q_n'K_d)P_1(fm)(J_d^*+Q_n'K_d^*)P_1(f'm')]\\ &+\tfrac{1}{4}\sum_{i=1}^{3}\mathrm{Tr}[(J_x+Q_n'K_x)\sigma_{1i}P_1(fm)\\ &\qquad\times(J_x^*+Q_n'K_x^*)\sigma_{1i}P_1(f'm')],\end{aligned} \tag{5.3}$$

using the notation of Eq. (2.25) for the scattering amplitudes. The special properties of the operator Q_n' cited above lead to the vanishing of all traces linear in Q_n', and thus to the expression

$$\begin{aligned}\sigma(fm,f'm')=\mathrm{tr}[&|J_d|^2P(fm)P(f'm')\\ &+|J_x|^2\sum_i\sigma_iP(fm)\sigma_iP(f'm')]\\ &+|K_d|^2\tfrac{1}{4}\sum_i\mathrm{tr}[\tau_iP(fm)\tau_iP(f'm')]\\ &+|K_x|^2\tfrac{1}{4}\sum_i\sum_j\mathrm{tr}[\tau_i\sigma_jP(fm)\tau_i\sigma_jP(f'm')].\end{aligned} \tag{5.4}$$

The first two lines are just the cross section analyzed in Sec. IV for nonidentical atoms with F_d and F_x replaced by J_d and J_x. Of the two new kinds of terms, the one in the third line can also be evaluated with the results of the preceding section, and so only the term proportional to $|K_x|^2$ requires detailed consideration here. In particular, Eq. (5.4) is now written as[18]

$$\begin{aligned}\sigma(fm,f'm')=\delta_{ff'}\delta_{mm'}|J_d|^2+\tfrac{1}{3}\Delta(\tfrac{1}{2}f,\tfrac{1}{2}f')&\\ \times[|J_x|^2+\tfrac{1}{4}|K_d|^2]\sum_\mu(fmf'-m'|1-\mu)^2&\\ +|K_x|^2\tfrac{1}{4}\Gamma(\tfrac{1}{2}fm,\tfrac{1}{2}f'm'),&\end{aligned} \tag{5.5}$$

where Γ is the generalization of the Δ introduced in Eq. (4.2):

$$\Gamma(\tfrac{1}{2}fm,\tfrac{1}{2}f'm')=\sum_i\mathrm{tr}[\tau_i\sigma_jP(fm)\tau_i\sigma_jP(f'm')]. \tag{5.6}$$

The basic idea in the analysis is to again apply the Wigner-Eckart theorem to obtain the dependence of Γ on its magnetic quantum numbers. For this purpose, the spherical basis is used, but now the tensor which will be of interest $\sigma_\mu\tau_\nu(\mu,\ \nu=1,0,-1)$ is reducible into the various tensor products $(\sigma\otimes\tau)_L$, which are irreducible spherical tensors of rank $L=0$, 1, and 2:

$$\sigma_\mu\tau_\nu=\sum_{LM}(1\mu1\nu|LM)(\sigma\otimes\tau)_{LM}. \tag{5.7}$$

Transforming Γ from Eq. (5.6) to the spherical basis

$$\begin{aligned}\Gamma(\tfrac{1}{2}fm,\tfrac{1}{2}f'm')&=\sum_{i,j=1}^{3}|(f'm'|\sigma_i\tau_j|fm)|^2\\ &=\sum_{\mu,\nu=-1}^{1}|(f'm'|\sigma_\mu\tau_\nu|fm)|^2,\end{aligned}$$

and using Eq. (5.7) leads to the reduced form

$$\Gamma(\tfrac{1}{2}fm,\tfrac{1}{2}f'm')=\sum_{LM}|(f'm'|(\sigma\otimes\tau)_{LM}|fm)|^2. \tag{5.8}$$

Application of the Wigner-Eckart theorem now leads to

$$\begin{aligned}\Gamma(\tfrac{1}{2}fm,&\tfrac{1}{2}f'm')\\ &=\sum_L|(f'\|(\sigma\otimes\tau)_L\|f)|^2\sum_M(fmLM|f'm')^2.\end{aligned} \tag{5.9}$$

The reduced matrix element of $(\sigma\otimes\tau)_L$ can be related to those of σ and τ (in the representations of their own eigenvectors) with the 9-j or X coefficient, and the result is

$$\begin{aligned}(\tfrac{1}{2}\tfrac{1}{2}f'\|&(\sigma\otimes\tau)_L\|\tfrac{1}{2}\tfrac{1}{2}f)\\ &=[36(2L+1)(2f+1)]^{1/2}X(\tfrac{1}{2}\tfrac{1}{2}f'|\tfrac{1}{2}\tfrac{1}{2}f|11L).\end{aligned} \tag{5.10}$$

Recalling how Γ enters into the cross section of Eq. (5.5), the three tensors $(\sigma\otimes\tau)_L$ ($L=0$, 1, 2) each contribute to the scattering in a characteristic way. The zero rank tensor adds to the nonspin flip scattering

TABLE IV. The four values of $\Gamma(\tfrac{1}{2}f,\tfrac{1}{2}f')$ which enter into the spin-exchange cross section for two hydrogen atoms in Eq. (5.5).

f' \ f	1	0
1	21	6
0	6	3

---

[18] The value of the nuclear spin $i=\tfrac{1}{2}$ has been inserted in the quantities Δ and Γ to distinguish the results of this section from the previous one.

($f'=f$, $m'=m$), since it cannot lead to any angular-momentum change at all. The first rank tensor gives a contribution similar to the spin-flip scattering for nonidentical atoms discussed in the previous section. In this case, however, the transition $f\rightarrow f'=f$ is forbidden, since the corresponding reduced matrix element vanishes.[19] The second-rank tensor contributes only to transitions in which $f=1\rightarrow f'=1$. The transition $f=1$, $m=1\rightarrow f'=1, m'=-1$ is allowed; it occurs by the exchange of an entire atom on collision with another of the opposite polarization.

Using explicit values for the X coefficients, the spin-exchange cross sections for hydrogen atoms scattered from unpolarized hydrogen atoms is

$$\begin{aligned}\sigma(fm,f'm')=\delta_{ff'}\delta_{mm'}[|J_d|^2+\tfrac{3}{4}(2f+1)^{-2}|K_x|^2] \\ +\{\tfrac{1}{3}\Delta(\tfrac{1}{2}f,\tfrac{1}{2}f')[|J_x|^2+\tfrac{1}{4}|K_d|^2]+\tfrac{1}{2}\delta_{|f-f'|,1}|K_x|^2\}\sum_M(fmf'-m'|1-M)^2 \\ +\delta_{f,f'}\delta_{f,1}|K_x|^2\sum_M(1m1-m'|2-M)^2. \quad (5.11)\end{aligned}$$

where $\Delta(\frac{1}{2}f,\frac{1}{2}f')$ is given by Eq. (4.13) and $\Gamma(\frac{1}{2}f,\frac{1}{2}f')$ by Eq. (5.14). This cross section is summarized in Table V.

In treating the average cross section

$$\sigma(f,f')=\frac{1}{2f+1}\sum_{m,m'}\sigma(fm,f'm'),$$

the quantity

$$\Gamma(\tfrac{1}{2}f,\tfrac{1}{2}f')=\sum_{ij}\operatorname{tr}[\sigma_i\tau_jP(f)\sigma_i\tau_jP(f')] \quad (5.12a)$$

$$=\sum_{m,m'}\Gamma(\tfrac{1}{2}fm,\tfrac{1}{2}f'm'), \quad (5.12b)$$

will prove useful. Inserting the appropriate operators from Eq. (4.11) with $i=\frac{1}{2}$,

$$P(f)=\tfrac{1}{4}[2f+1-(-)^f\boldsymbol{\sigma}\cdot\boldsymbol{\tau}], \quad (5.13)$$

the trace in Eq. (5.12a) is easily evaluated to yield

$$\Gamma(\tfrac{1}{2}f,\tfrac{1}{2}f')=\tfrac{3}{4}[3(2f+1)(2f'+1)+(-)^{f+f'}], \quad (5.14)$$

and the four values of Γ are listed for convenience in Table IV. These values are in agreement with those obtained from Eq. (5.12b) and Eq. (5.9),

$$\Gamma(\tfrac{1}{2}f,\tfrac{1}{2}f')=(2f'+1)\sum_L|(\tfrac{1}{2}\tfrac{1}{2}f'\|(\sigma\otimes\tau)_L\|\tfrac{1}{2}\tfrac{1}{2}f)|^2. \quad (5.15)$$

When the reduced matrix elements are evaluated from Eq. (5.10) with appropriate values for the X coefficients, the average cross section is now

$$\begin{aligned}\sigma(f,f')=\delta_{ff'}|J_d|^2+(2f+1)^{-1}\Delta(\tfrac{1}{2}f,\tfrac{1}{2}f')[|J_x|^2+\tfrac{1}{4}|K_d|^2] \\ +(2f+1)^{-1}\Gamma(\tfrac{1}{2}f,\tfrac{1}{2}f')\tfrac{1}{4}|K_x|^2, \quad (5.16)\end{aligned}$$

The various amplitudes which occur in this analysis are given by Eqs. (2.26) and (2.27) for $i=\frac{1}{2}$:

$$J_d(\theta)=F_d(\theta)+\tfrac{1}{2}F_d'(\pi-\theta), \quad (5.17a)$$

$$K_d(\theta)=F_d'(\pi-\theta), \quad (5.17b)$$

$$J_x(\theta)=F_x(\theta)+\tfrac{1}{2}F_x'(\pi-\theta), \quad (5.17c)$$

$$K_x(\theta)=F_x'(\pi-\theta), \quad (5.17d)$$

which in turn are expressible in terms of f_0 and f_1. Unlike the situation for nonidentical atoms, interference terms now occur, but always between amplitudes referring to different scattering angles θ and $(\pi-\theta)$–as is characteristic for identical systems.

It is interesting to compare the average cross sections with those for "electron spin exchange" discussed in Sec. III. From Eqs. (3.11) and (5.17), it is found that

$$\sigma_d=(|J_x|^2+|J_d|^2)+\tfrac{3}{4}(|K_d|^2+|K_x|^2), \quad (5.18a)$$

$$\sigma_x=2(|J_x|^2+\tfrac{3}{4}|K_x|^2). \quad (5.18b)$$

The sum of these is the unpolarized cross section of Eq. (2.32), i.e.,

$$\begin{aligned}\sigma=\sigma_x+\sigma_d=(|J_d|^2+3|J_x|^2) \\ +\tfrac{3}{4}(|K_d|^2+3|K_x|^2). \quad (5.19)\end{aligned}$$

TABLE V. The average spin-exchange cross sections for two hydrogen atoms from Eq. (5.16).

$f'\diagdown f$	1	0
1	$[\|J_d\|^2+2\|J_x\|^2+\frac{1}{2}\|K_d\|^2+(7/4)\|K_x\|^2]$	$[3(\|J_x\|^2+\frac{1}{4}\|K_d\|^2+\frac{1}{2}\|K_x\|^2)]$
0	$[\|J_x\|^2+\frac{1}{4}\|K_d\|^2+\frac{1}{2}\|K_x\|^2]$	$[\|J_d\|^2+\frac{3}{4}\|K_x\|^2]$

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[19] It may also be noted that the "exchange direct amplitude" $K_d(\theta)=F_d'(\pi-\theta)$ enters into the spin-flip part of the cross section, which indicates that the subscript d and the name direct amplitude are not so appropriate for identical atoms.

Comparing these expressions with Table V, it is found that two of the "sum rules" valid for nonidentical atoms, Eqs. (4.21a) and (4.21c), do *not* hold in this case. All the other relations, Eqs. (4.20a), (4.20b), (4.21b), (4.21d), and (4.22), still are valid.

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Effect of Hydrogen-Hydrogen Exchange Collisions

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Exchange collisions between ground-state hydrogen atoms are considered. The density matrix after collision is calculated for pairs of atoms which initially had the same density matrix. The result is applied to the hydrogen maser with the assumption that only exchange collisions and the escape of atoms from the storage bulb influence the linewidth for the field-independent hyperfine transition. Under normal operating conditions a frequency shift of roughly 5% of the exchange collision contribution to the linewidth is predicted.

1. INTRODUCTION

THE effect of exchange collisions between ground-state hydrogen atoms has been treated by a number of authors.[1–6] In particular, Wittke and Dicke considered a case where departures from thermal equilibrium were small and the only nonzero off-diagonal elements of the density matrix for the ground-state sublevels were those corresponding to the magnetic field-independent $(F=1,\ M_F=0)\rightarrow(F=0,\ M_F=0)$ component of the hyperfine transition. The nuclear spins and all magnetic interaction energies can be neglected during collisions and the electron wave functions for the two colliding atoms can be combined to form triplet and singlet states. The effect of a collision is to multiply the triplet and singlet parts of the wave function by $e^{-i\Delta_T}$ and $e^{-i\Delta_S}$ respectively. Δ_T is the integral of $(E_T/\hbar)$ over the time of the collision, where E_T is the triplet state hydrogen-hydrogen interaction energy, and Δ_S is defined similarly. Wittke and Dicke made the approximation that only "strong" collisions were important, where "strong" collisions are those in which the relative phase shift $\Delta=\Delta_T-\Delta_S$ is large enough so that the relative phase after the collision can be considered random.

In the present paper the approximations of strong collisions and of small departures from equilibrium are removed. The effect on the density matrix of a single hydrogen-hydrogen collision for each atom in the sample is given in Sec. 2. The resulting effect on operation of the hydrogen maser[7] is discussed in Sec. 3. The expected frequency shift is estimated in Sec. 4 using straight-line paths with the triplet and singlet interaction potentials of Dalgarno and Lynn.[4,8] A shift in the field-independent hyperfine transition of up to 5% of the exchange collision contribution to the linewidth is predicted.

2. EFFECT OF A SINGLE COLLISION WITH ARBITRARY PHASE SHIFT

The initial 4×4 density matrix[9] ρ^i for the magnetic sublevels of ground-state hydrogen atoms is written in the F, M_F representation:

$$\rho^i=\begin{array}{c|cccc} F,M_F \diagdown F,M_F & 1,1 & 1,0 & 1,-1 & 0,0\\ \hline 1,1 & a & e^* & f^* & h^*\\ 1,0 & e & b & g^* & j^*\\ 1,-1 & f & g & c & k^*\\ 0,0 & h & j & k & d \end{array} \tag{1}$$

The 16×16 density matrix σ^i for a pair of colliding atoms just before collision in the $F_1M_{F_1}F_2M_{F_2}$ representation is the direct product of ρ^i with itself. σ^i is transformed by a unitary transformation Γ to a representation SM_SIM_I where the two electron spins and

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