

## Importance of Nuclear-Spin Effects in Extracting Alkali Spin-Exchange Cross Sections from Zeeman Optical-Pumping Signals\*

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The importance of the nuclear spins in the analysis of alkali spin-exchange experiments employing optical pumping by circularly polarized light and performed in low magnetic fields is demonstrated. Since the exchange interaction is an electronic process, the spin-exchange cross section is expected to be essentially independent of the nuclear spins. However, the hyperfine coupling is sufficient to make the expressions for the signals depend upon the nuclear spins. Failure to include the nuclear-spin effects in the analysis can lead to errors as large as several hundred percent in the deduced cross sections. The signal for general nuclear spin is found for the Franzen-type transient experiment and for the Dehmelt-type steady-state experiment in the limit of low light intensity. The results are quite sensitive to the process assumed for the relaxation of the ground-state populations. The solutions are given for a general process in which randomly oriented disorientation fields interact with the spins of the alkali atom only through the electron spin. The steady-state-signal expression includes the effects of self spin exchange and partial disorientation in the excited state. Only the diagonal elements of the density matrix are included.

### I. INTRODUCTION

RECENTLY, there has arisen considerable interest in utilizing the spin-exchange process to study the forces between atoms and the potentials which describe these forces. The problem of deducing interatomic potential information from spin-exchange cross sections has been studied by Glassgold and Lebedeff, particularly for hydrogen.<sup>1,2</sup> The problem of interest in this paper is that of obtaining the cross sections from optical-pumping experiments.

Optical pumping has been used more than any other technique for determining spin-exchange cross sections. Most of the optical-pumping measurements were made by one of the methods treated in this paper, which involve the determination of a relaxation time and a density. Recently it has been shown that information can be obtained without measuring the density if the linewidth and frequency shift arising from exchange effects are determined.<sup>3,4</sup> The analysis of such experiments requires the inclusion of the off-diagonal density-matrix elements, which is not the case here.

The spin-exchange process is an electronic interaction. Since the collision time is much shorter than a period of the hyperfine precession, the hyperfine coupling has little effect during the collision. Thus the cross section for electron-spin exchange should be essentially independent of the nuclear spins. But in a low magnetic field the electron spin is coupled to the nuclear spin by the hyperfine interaction, and the good quantum num-

bers are  $IJFM$ . Thus the cross sections of interest are between different  $FM$  states; these cross sections depend upon  $I$  even though the interaction is diagonal in  $M_I$ . The optical-pumping signals can then depend upon the nuclear spin because of the hyperfine coupling. Failure to include the nuclear-spin effects can lead to errors of several hundred percent in the values of the spin-exchange cross sections deduced from optical-pumping experiments.

The calculations of this paper apply to spin exchange between two alkali atoms in their ground states. The following assumptions are common to all the calculations:

- (1) The pumping radiation is circularly polarized  $D_1$  light.
- (2) The four hyperfine components in the pumping radiation are of equal intensity.
- (3) The pumping radiation at a given point in the cell is approximately constant.

The rate equations which are used to describe the experiments are given in Sec. II. The following contributions to the rate equations are then discussed: (a) pumping radiation, (b) excited-state disorientation, (c) ground-state relaxation, (d) spin exchange between unlike atoms, and (e) self spin exchange. Solutions to the rate equations of Sec. II are obtained for the Franzen-type<sup>5</sup> transient experiment as applied to spin-exchange measurements in Sec. III; self-exchange effects are neglected. The expression for the signal in the usual Dehmelt-type<sup>6</sup> steady-state spin-exchange experiment is found in Sec. IV in the limit of low light intensity. Applications or comparisons are made to the results of Dehmelt,<sup>6</sup> Jarrett,<sup>7</sup> Balling *et al.*,<sup>4</sup> and Anderson and Ramsey.<sup>8</sup>

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## II. RATE EQUATIONS

Consider the description of the time variation of the populations of two different species of alkali atoms in a static magnetic field of weak intensity. The *ISFM* representation is then best.  $\mathbf{F}$  is the total angular momentum obtained by coupling the nuclear angular momentum  $\mathbf{I}$  to the electronic angular momentum  $\mathbf{S}$  ( $\mathbf{J}=\mathbf{S}$  since  $\mathbf{L}=0$ ).  $M$  is the projection of  $\mathbf{F}$  along the axis de-

finied by the external magnetic field and the incident light beam. Species 1 is optically pumped and has a density in the ground state  $F_1M_1$  of  $p_{F_1M_1}$  and a total density of  $p$ . The second species is disoriented continuously during part or all of the experiment and has a density  $d_{F_2M_2}$  in the ground state  $F_2M_2$  and a total density  $d$ . The first species has a density  $n_{J_1F_1M_1}$  in the excited state  $J_1F_1M_1$ . The time variation of  $p_{F_1M_1}$  can be described as follows:

$$\begin{aligned} \dot{p}_{F_1M_1} = & -p_{F_1M_1} \sum_{J_1'F_1'M_1'q} \int_0^\infty L_q(\nu) P_{\nu q'}(F_1M_1, J_1'F_1'M_1') d\nu \\ & + \sum_{J_1'F_1'M_1'} n_{J_1'F_1'M_1'} P''(J_1'F_1'M_1', F_1M_1) / \tau_{J_1'} - p_{F_1M_1} \sum_{F_1'M_1'} w(F_1M_1, F_1'M_1') \\ & + \sum_{F_1'M_1'} p_{F_1'M_1'} w(F_1'M_1', F_1M_1) - \sum_{\substack{F_1'M_1' \\ F_2M_2 \\ F_2'M_2'}} \int \{ p_{F_1M_1} d_{F_2M_2} Q_E(F_1M_1 F_2M_2, F_1'M_1' F_2'M_2') \\ & - p_{F_1'M_1'} d_{F_2'M_2'} Q_E(F_1'M_1' F_2'M_2', F_1M_1 F_2M_2) \} f(v_E) v_E d^3v_E \\ & - \sum_{\substack{F_1'M_1' \\ F_1''M_1'' \\ F_1'''M_1'''}} \int \{ p_{F_1M_1} p_{F_1'M_1'} Q_{S1}(F_1M_1 F_1'M_1', F_1''M_1'' F_1'''M_1''') \\ & - p_{F_1''M_1''} p_{F_1'''M_1'''} Q_{S1}(F_1''M_1'' F_1'''M_1''', F_1M_1 F_1'M_1') \} f(v_{S1}) v_{S1} d^3v_{S1}. \quad (1) \end{aligned}$$

$\sum_q \int_0^\infty L_q(\nu) P_{\nu q'}(F_1M_1, J_1'F_1'M_1') d\nu$  is the probability per unit time that an atom in the ground state  $F_1M_1$  will absorb a resonance photon and make a transition to the  $F_1'M_1'$  substate of the  ${}^2P_{J_1'}$  excited state;  $L_q(\nu) d\nu$  is the light intensity with polarization  $q$  and with frequencies between  $\nu$  and  $\nu+d\nu$ .  $(1/\tau_{J_1'}) P''(J_1'F_1'M_1', F_1M_1)$  is the probability per unit time for the reverse process;  $\tau_{J_1'}$  is the radiative lifetime of an atom in one of the substates of the  ${}^2P_{J_1'}$  excited state. The quantity  $w(F_1M_1, F_1'M_1')$  is the probability per unit time for an atom in the substate  $F_1M_1$  of the ground state to make a transition to the  $F_1'M_1'$  substate of the ground state by relaxation processes excluding spin exchange. In the last two terms the subscript  $E$  refers to exchange between atoms of different species and  $S$  to exchange between atoms of the same species.  $Q(F_1M_1 F_2M_2, F_1'M_1' F_2'M_2')$  is the cross section for a spin-exchange collision between two atoms in which the first atom makes a transition from  $F_1M_1$  to  $F_1'M_1'$  and the second from  $F_2M_2$  to  $F_2'M_2'$ . The function  $f(v)$  is the distribution of relative velocities  $v$  with the normalization  $\int f(v) d^3v = 1$ . The populations are then affected by (a) the pumping radiation, (b) excited-state disorientation, (c) ground-state relaxation, (d) spin exchange with the second species, and (e) self spin exchange between atoms of the same species.

The form of these equations corresponds to a diagonal density-matrix approach, which should be valid in the absence of coherence-producing interactions. The radio-

frequency fields used in the experiments treated in this paper are ordinarily applied in a manner producing very little coherence. Magnetic field inhomogeneities are usually sufficient to damp out any coherence effects in a time short compared with the other significant times of the problem. A solution of the rate equations including the off-diagonal elements but neglecting nuclear spins has been obtained by other workers; it is discussed in Sec. IV D.

Each of the terms in Eq. (1) will now be discussed and the simplifying assumptions stated. The resulting rate equations are given in Sec. IIF. For the experiments treated in this paper, the  $2(2I+1)$  equations for each species (excluding excited-state equations) reduce to two equations with the variables being the longitudinal electronic polarizations of the various hyperfine levels as defined in (13). However, the particular assumptions made in Secs. III and IV are necessary before this reduction is complete; therefore, the rate equations of IIF are not entirely in that form.

## A. Pumping Radiation

 1. Circularly Polarized  $D_1$  Resonance Radiation

It is assumed that the resonance radiation is filtered with only the  $D_1$  line ( ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ ) incident upon the resonance cell containing two alkali species. It is further assumed that it is circularly polarized so that  $M_1$  must

change by +1 for electric-dipole transitions; i.e.,

$$L_q(\nu)P_{\nu q}'(F_1M_1, J_1'F_1'M_1') = L(\nu)P_{\nu}'(F_1M_1, \frac{1}{2}F_1'M_1+1)\delta_{J_1', 1/2}\delta_{M_1', M_1+1}.$$

2. Equal-Intensity Hyperfine Components Throughout the Cell

It should always be possible to write

$$P_{\nu}'(F_1M_1, \frac{1}{2}F_1'M_1+1) = P'(F_1M_1, \frac{1}{2}F_1'M_1+1)f(\nu - \nu^0_{F_1M_1, F_1'M_1'}),$$

where  $f(\nu - \nu^0_{F_1M_1, F_1'M_1'})$  represents the broadening of the absorption line around the center frequency  $\nu^0_{F_1M_1, F_1'M_1'}$  by, for example, Doppler or pressure effects; furthermore

$$\int_0^\infty f(\nu - \nu^0_{F_1M_1, F_1'M_1'})d\nu = 1.$$

Now assume that

$$\int_0^\infty L(\nu)f(\nu - \nu^0_{F_1M_1, F_1'M_1'})d\nu = L;$$

i.e., over the frequencies for which absorption occurs, the light at each point of the cell is independent of the frequency. Experimental care must be taken to achieve equal hyperfine components in the incident light; this can usually be done by regulating the amount of self-reversal in the lamp bulb, if one is able to monitor the components. Since the hyperfine components often have different absorption coefficients, the absorption must usually be kept low to approximate equal components throughout the cell (see Sec. IIA3).

The first term in (1) contains

$$\sum_q \int_0^\infty L_q(\nu)P_{\nu q}'(F_1M_1, J_1'F_1'M_1')d\nu = L \sum_{F_1'} P'(F_1M_1, \frac{1}{2}F_1'M_1+1) \equiv LP'(F_1M_1), \quad (2)$$

$$P'(F_1M_1) \propto \sum_{F_1'} (|\langle I_1 J_1 F_1 M_1 | r(1,1) | I_1 J_1 F_1' M_1+1 \rangle|^2)_{J_1=1/2}, \quad (3)$$

where  $r(1,q)$  denotes the  $q$ th component of the valence

TABLE I. Values of  $\begin{pmatrix} F_1 & 1 & F_1' \\ M_1 & 1 & -M_1-1 \end{pmatrix}^2$ .

	$F_1'$	
$F_1$	$I_1 + \frac{1}{2}$	$I_1 - \frac{1}{2}$
$I_1 + \frac{1}{2}$	$\frac{2[I_1^2 + 2I_1 + \frac{3}{2} - M_1 - M_1^2]}{(2I_1 + 1)(2I_1 + 2)(2I_1 + 3)}$	$\frac{2[I_1^2 - \frac{1}{2} - 2M_1I_1 + M_1^2]}{4I_1(2I_1 + 1)(2I_1 + 2)}$
$I_1 - \frac{1}{2}$	$\frac{2[I_1^2 + 2I_1 + \frac{3}{2} + (2I_1 + 2)M_1 + M_1^2]}{4I_1(2I_1 + 1)(2I_1 + 2)}$	$\frac{2[I_1^2 - \frac{1}{2} - M_1 - M_1^2]}{(2I_1 - 1)2I_1(2I_1 + 1)}$

electron position vector  $\mathbf{r}$ , which is a tensor of rank 1, see Edmonds,<sup>9</sup> Chap. 5. Using Edmonds' (5.4.1) and (7.1.7), one finds

$$P'(F_1M_1) \propto \sum_{F_1'} \begin{pmatrix} F_1 & 1 & F_1' \\ M_1 & 1 & -M_1-1 \end{pmatrix}^2 \Delta(F_1, F_1'). \quad (4)$$

The squared 3- $j$  symbol in (4) is given in Table I (from Edmonds' Table 2). The quantities

$$\Delta(F_1, F_1') \equiv 6(2F_1+1)(2F_1'+1) \times \begin{Bmatrix} \frac{1}{2} & F_1' & I_1 \\ F_1 & \frac{1}{2} & 1 \end{Bmatrix}^2 = \Delta(F_1', F_1) \quad (5)$$

are given in Table II; they were obtained with the aid of Edmonds' Table 5. Then, for  $F_1 = I_1 \pm \frac{1}{2}$ ,

$$P'(\pm, M_1) = P'(F_1M_1) = C[1 \mp M_1/(I_1+1/2)] = C[1 - 2(F_1 - I_1)M_1/(I_1+1/2)], \quad (6)$$

where  $LP'(F_1M_1)$  is the total probability per unit time that an atom in the substate  $F_1M_1$  will absorb a resonance photon;  $C$  is a constant independent of the quantum numbers of interest.

3. Low Absorption

The experiments analyzed in this paper employ the transmission monitoring technique; the changes in the absorption constitute the signals. The absorption by the cell can be found as follows: The light intensity at frequency  $\nu$  and time  $t$  at a penetration depth of  $x$  into the resonance cell of length  $l$  decreases by

$$dL(\nu, x, t) = -L(\nu, x, t) \sum_{F_1M_1F_1'} \rho_{F_1M_1}(x, t) \times P_{\nu}'(F_1M_1, \frac{1}{2}F_1'M_1+1)h\nu dx \quad (7)$$

between  $x$  and  $x+dx$ ; it is assumed that  $L(\nu, x, t)$  is circularly polarized, so that  $\Delta M_1 = +1$  in absorption. With the assumptions of Sec. IIA2, (7) yields, for the

TABLE II. Values of

$$\Delta(F_1, F_1') = 6(2F_1+1)(2F_1'+1) \begin{Bmatrix} \frac{1}{2} & F_1' & I_1 \\ F_1 & \frac{1}{2} & 1 \end{Bmatrix}.$$

	$F_1'$	
$F_1$	$I_1 + \frac{1}{2}$	$I_1 - \frac{1}{2}$
$I_1 + \frac{1}{2}$	$\frac{(2I_1+2)(2I_1+3)}{2I_1+1}$	$\frac{4I_1(2I_1+2)}{2I_1+1}$
$I_1 - \frac{1}{2}$	$\frac{4I_1(2I_1+2)}{2I_1+1}$	$\frac{2I_1(2I_1-1)}{2I_1+1}$

<sup>9</sup> A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

absorption,

$$A(l,t) = L(0,t) - L(l,t) \\ = \int_0^l L(x,t) \sum_{F_1 M_1} \rho_{F_1 M_1}(x,t) P'(F_1 M_1) h\nu dx. \quad (8)$$

The conditions necessary for maintaining the equality of the hyperfine components throughout the cell can be found by integrating (7):

$$L(\nu, x, t) = L(\nu, 0, t) \exp \left[ - \int_0^x \sum_{F_1 M_1 F_1'} \rho_{F_1 M_1}(x', t) \right. \\ \left. \times P_{\nu'}(F_1 M_1, \frac{1}{2} F_1' M_1 + 1) h\nu dx' \right] \\ = L(\nu, 0, t) \exp \left[ - \int_0^x k_{\nu}(x', t) dx' \right], \quad (9)$$

where  $L(\nu, 0, t)$  is constant over the frequencies for which the absorption is appreciable.  $L(\nu, x, t) \approx L(\nu, 0, t)$  if the absorption is low, i.e.,  $k_0 l \ll 1$  where  $k_0$  is the peak absorption coefficient. But for some cases slightly less stringent requirements are sufficient. For example, if the excited-state hyperfine separation and the Zeeman splittings are much less than the absorption width, the two resolved components are approximately equal to each other at each point of the cell if  $k_0 l / (2I_1 + 1) \ll 1$ . This requirement is satisfactory, since the difference in their absorption rates is only  $1/(2I_1 + 1)$  times the total absorption rate. Experimentally, an extrapolation to zero absorption or a demonstration that the signals are independent of absorption should be made.

With the assumption that the absorbable light at each point in the cell is independent of frequency, the absorption (and the signals) can be expressed as a simple function of

$$\sum_{F_1 M_1} \rho_{F_1 M_1}(x, t) P'(F_1 M_1) \\ = C \rho \left[ 1 - \sum_{F_1 M_1} 2(F_1 - I_1) M_1 \rho_{F_1 M_1} / (I_1 + \frac{1}{2}) \rho \right], \quad (10)$$

which can be expressed as a function of the electronic polarization as follows. It can be shown that  $\langle FM | S_z | FM \rangle = 2(F - I)M / (2I + 1)$ . Then the absorption is

$$A(l, t) \approx k \int_0^l L(x, t) [1 - P(x, t)] dx, \quad (11)$$

with the absorption coefficient  $k = C \rho h\nu$  and

$$P = 2 \langle S_{1z} \rangle = 2 \sum_{F_1 M_1} \rho_{F_1 M_1} \\ \times \langle F_1 M_1 | S_{1z} | F_1 M_1 \rangle / \rho = \sum_{F_1} P_{F_1}, \quad (12)$$

$$P_{F_1 = I_1 \pm 1/2} = P_{\pm} = \pm \sum_{M_1 = -I_1 \mp 1/2}^{I_1 \pm 1/2} M_1 \rho_{F_1 = I_1 \pm 1/2, M_1} / (I_1 + \frac{1}{2}) \rho. \quad (13)$$

Here  $P$  is the longitudinal electronic polarization, and  $P_+$  and  $P_-$  are the contributions to this polarization from the two hyperfine levels. Completely analogous polarizations  $D$ ,  $D_+$ ,  $D_-$  are defined for the second species. Although only  $P$  is needed to define the signal,  $P_+$  and  $P_-$  usually appear in coupled equations and must be solved for separately in order to determine  $P$ . Or, since

$$\langle I_{1z} \rangle = \langle F_{1z} \rangle - \langle S_{1z} \rangle = I_1 P_+ - (I_1 + 1) P_-, \quad (14)$$

the equations for  $\langle S_z \rangle$  and  $\langle I_z \rangle$  can be found and solved instead. In either case the  $2(2I + 1)$  equations for each species reduce to two equations in the cases treated in this paper. Consequently, the rate equations for  $P_+$  and  $P_-$  rather than for  $\rho_{F_1 M_1}$  will be determined. Then the absorption term of (1) gives

$$(\dot{P}_{\pm})_{\text{Abs}} = \mp L \sum_{M_1} M_1 \rho_{F_1 M_1} P'(F_1 M_1) / (I_1 + \frac{1}{2}) \rho, \quad (15)$$

when (2), (6), and (13) are used.

## B. Excited-State Disorientation

It is customary, in analyzing optical-pumping signals in which a buffer gas at a pressure greater than 1 cm of Hg is used, to assume that complete mixing occurs in the excited state. In other words, the excited-state polarization relaxes nonradiatively in a time short compared with the radiative lifetime. Recently, excited-state disorientation cross sections have been reported which are considerably smaller than those found earlier for sodium. Yellin and Marrus<sup>10</sup> report for Rb<sup>87</sup>-Ne collisions a cross section of  $5 \times 10^{-17}$  cm<sup>2</sup>, which implies an excited-state relaxation time of  $T \approx 0.4$   $\mu$ sec for Jarrett's experiment (2.8 cm of Ne at 90°C).<sup>7</sup> The corresponding mixing parameter<sup>11</sup>

$$q = \tau / (T + \tau) \quad (16)$$

(where  $\tau = 2.85 \times 10^{-8}$  sec is the excited-state lifetime against spontaneous emission) is less than 10%, implying that Jarrett's conditions produced very little excited-state mixing. Since one of the primary objectives of this work is to determine the importance of the nuclear spins in Jarrett's experiment, it is of interest to investigate the necessity of the assumption of complete mixing. It will be shown that the signal for Jarrett's experiment (in the limit of low light intensity) is independent of the amount of excited-state disorientation, regardless of the mechanism producing the mixing.

By definition, the probabilities  $P''$  must satisfy

$$\sum_{F_1 M_1} P''(J_1' F_1' M_1', F_1 M_1) = 1. \quad (17)$$

The time rate of change of the density of excited atoms

<sup>10</sup> J. Yellin and R. Marrus, *Bull. Am. Phys. Soc.* **9**, 720 (1964).  
<sup>11</sup> C. O. Alley, Princeton University (unpublished).

in the  $F_1'M_1'$  substate of the  ${}^2P_{J_1'}$  excited state is

$$\dot{n}_{J_1'F_1'M_1'} = L \sum_{F_1M_1} p_{F_1M_1} P'(F_1M_1, J_1'F_1'M_1') \delta_{M_1', M_1+1} \delta_{J_1', 1/2} - n_{J_1'F_1'M_1'} / \tau_{J_1'} \\ - \sum_{J_1''F_1''M_1''} n_{J_1'F_1'M_1'} w_e(J_1'F_1'M_1', J_1''F_1''M_1'') + \sum_{J_1''F_1''M_1''} n_{J_1''F_1''M_1''} w_e(J_1''F_1''M_1'', J_1'F_1'M_1'), \quad (18)$$

where  $w_e(J_1'F_1'M_1', J_1''F_1''M_1'')$  is the probability per unit time that an excited atom in state  $J_1'F_1'M_1'$  will make a transition to the excited state  $J_1''F_1''M_1''$  (without returning to the ground state by emission of a photon). Since the excited-state populations reach equilibrium very rapidly ( $\leq \tau$ ), the equilibrium value of  $n_{J_1'F_1'M_1'}$  can be used in (1). Notice that at equilibrium (18) is of the form

$$R\mathbf{n} = L\mathbf{m}, \quad (19)$$

where  $R$  is a matrix independent of the various populations,  $\mathbf{n}$  is a column vector with components  $n_{J_1'F_1'M_1'}$ , and  $\mathbf{m}$  has components

$$m_{J_1'F_1'M_1'} = \sum_{F_1M_1} p_{F_1M_1} P'(F_1M_1, J_1'F_1'M_1') \\ \times \delta_{M_1', M_1+1} \delta_{J_1', 1/2}. \quad (20)$$

Therefore  $\mathbf{n}$  and  $n_{J_1'F_1'M_1'}$  are proportional to  $L$  or higher order terms in  $L$ . The reemission term of (1), which becomes, when (13) is used,

$$(\dot{P}_{\pm})_{R_0} = \pm \sum_{J_1'F_1'M_1'} n_{J_1'F_1'M_1'} \\ \times \sum_{M_1} M_1 P''(J_1'F_1'M_1', F_1M_1) / (I_1 + \frac{1}{2}) p_{\tau J_1'}, \quad (21)$$

is then proportional to  $L$  or higher order terms in  $L$ . This term vanishes in the transient experiment of Sec. III for which  $L=0$ ; it will be found to be independent of  $P_+$  and  $P_-$  for the Dehmelt-type steady-state experiment of Sec. IV.

### C. Ground-State Relaxation

The most common assumption for the ground-state relaxation in optical-pumping experiments is that it is uniform. It has been suggested that a better assumption is that the electron spin is randomized without affecting the nuclear spin.<sup>11</sup> Recently Bouchiat<sup>12</sup> has carried out a detailed analysis of relaxation on paraffin-coated cells. She assumes that the relaxation arises from the interaction of randomly oriented disorientation fields with the spin of the valence electron. This section contains a short derivation of the contributions to the rate equations from such an interaction which parallels the elegant density-matrix treatment by Bouchiat. A discussion in terms of the assumptions of uniform relaxation and electron randomization is also given.

<sup>12</sup> M. Bouchiat, J. Phys. Radium 24, 379 (1963). This article contains a detailed analysis of relaxation in paraffin-coated cells.

The general relaxation Hamiltonian satisfying the above restrictions can be written

$$\mathcal{H}' = \sum_{kq} \alpha_k (-)^q S(1, q) H(k, -q), \quad (22)$$

where  $H(k, q)$  is the  $q$ th component of a randomly oriented field of rank  $k$  [for example, a scalar contact field ( $k=0$ ) or a tensor dipole field ( $k=2$ ); see Ref. 12] and is independent of the alkali atom spin coordinates.  $S(1, q)$  is the  $q$ th component of the spin of the valence electron of the alkali atom.<sup>9</sup>

Abragam<sup>13</sup> shows that, if  $\mathcal{H}'(t) = AF(t)$ , where  $A$  is an operator acting only on the variables of the alkali, and  $F(t)$  is a random function independent of the alkali, the transition probability from state  $a$  to  $b$  of the alkali is

$$w_{ab} = |(a|A|b)|^2 J(\omega_{ab}), \quad (23)$$

and

$$J(\omega_{ab}) \equiv \int_{-\infty}^{\infty} g(\tau) e^{-i\omega_{ab}\tau} d\tau \\ = 2\tau_c \langle F(t)F(t) \rangle / (1 + \omega_{ab}^2 \tau_c^2) \quad (24)$$

provided that

$$g(\tau) \equiv \langle F(t)F(t+\tau) \rangle = \langle F(t)F(t) \rangle \exp(-|\tau|/\tau_c), \quad (25)$$

i.e., if the interaction can be characterized by a single correlation time  $\tau_c$ .

It should be a good approximation to assume that the Hamiltonian (22) is the sum of several terms each of which satisfies the restrictions of Abragam's derivation. Then

$$w(F_1M_1, F_1'M_1') \\ = \sum_q |(F_1M_1|S(1, q)|F_1'M_1')|^2 J_q(\omega_{F_1M_1, F_1'M_1'}), \quad (26)$$

where  $J_q(\omega_{F_1M_1, F_1'M_1'})$  is proportional to  $\langle \sum_{k'k} \alpha_{k'}^* \alpha_k \times H^*(k', -q)H(k, -q) \rangle$ , which is independent of  $q$ , since the fields are randomly oriented.

In a magnetic field of low intensity the hyperfine energy separation  $\Delta W$  is much larger than the Zeeman separation  $\omega_F$ . Furthermore since the operator  $S(1, q)$  is a tensor of rank one,  $M_1$  can change by at most one unit in each relaxation event. Therefore,  $J(\Delta W)$  and  $J(\omega_F)$  are sufficient to characterize the ground-state relaxa-

<sup>13</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), pp. 272 and 297.

tion. Then one has

$$w(F_1 M_1, F_1' M_1') = \sum_q |(F_1 M_1 | S(1, q) | F_1' M_1')|^2 (\delta_{F_1', F_1} J(\omega_F) + \delta_{F_1', F_1 \pm 1} J(\Delta W)) \quad (27)$$

$$= \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & M_1' - M_1 & M_1 \end{pmatrix}^2 \Delta(F_1, F_1') \{ \delta_{F_1, F_1'} [J(\omega_F) - J(\Delta W)] + J(\Delta W) \} / 4. \quad (28)$$

Equation (28) substituted into the third and fourth terms of (1) yields

$$\begin{aligned} (\sum_{M_1} M_1 \dot{p}_{F_1 M_1})_R &= -[J(\omega_F) - J(\Delta W)] \sum_{M_1} M_1 \dot{p}_{F_1 M_1} / (2I_1 + 1)^2 \\ &\quad - \{ 3 \sum_{M_1} M_1 \dot{p}_{F_1 M_1} / 4 - \sum_{F_1' M_1'} \Delta(F_1, F_1') \Gamma(F_1, F_1', M_1') \dot{p}_{F_1' M_1'} / 4 \} J(\Delta W). \end{aligned} \quad (29)$$

The quantities

$$\Gamma(F_1, F_1', M_1') \equiv \sum_{M_1} M_1 \begin{pmatrix} F_1 & 1 & F_1' \\ M_1 & M_1' - M_1 & -M_1' \end{pmatrix}^2 = M_1' \Gamma(F_1, F_1') \quad (30)$$

are given in Table III, which was found by using Table 2 of Edmonds.<sup>9</sup>

Now define two time constants

$$1/T_1 = [J(\omega_F) - J(\Delta W)] / (2I_1 + 1)^2, \quad (31)$$

$$1/T_1' = J(\Delta W). \quad (32)$$

Equations (13) and (29) give, for the contributions to the rate equations from ground-state relaxation,

$$\begin{aligned} (\dot{P}_+)_R &= -P_+ / T_1 - (2I_1^2 + I_1 + 1) P_+ / (2I_1 + 1)^2 T_1' \\ &\quad - (2I_1 + 2)(2I_1 + 3) P_- / 2(2I_1 + 1)^2 T_1', \end{aligned} \quad (33)$$

$$\begin{aligned} (\dot{P}_-)_R &= -P_- / T_1 - I_1(2I_1 - 1) P_+ / (2I_1 + 1)^2 T_1' \\ &\quad - (2I_1^2 + 3I_1 + 2) P_- / (2I_1 + 1)^2 T_1'. \end{aligned} \quad (34)$$

To gain some insight into the time constants (31) and (32) consider the two limiting cases.

(a) *Zeeman relaxation.* Let  $J(\Delta W) \ll J(\omega_F)$ , i.e.,  $T_1 \ll T_1'$ ; in this case the correlation time is much longer than the hyperfine period  $\tau_{\text{HF}}$ . Relaxation then occurs within the Zeeman sublevels of each hyperfine level, but transitions between hyperfine levels are rare. The longitudinal electronic polarization of each hyperfine level relaxes as a single exponential of time constant  $T_1$ .  $T_1$  is then the characteristic time for Zeeman relaxation in which the electron spin is randomized within each hyperfine level, but no transitions are made between hyperfine levels.

(b) *Relaxation by electron randomization.* Let  $J(\omega_F) \approx J(\Delta W)$ ,  $T_1' \ll T_1$ ,  $\tau_e \ll \tau_{\text{HF}}$ ; in this case both Zeeman and hyperfine transitions occur. The electron spin is completely randomized without affecting the nuclear spin. Such a model has been used by workers at Princeton.<sup>11</sup> The term electron randomization will be used to identify this limit, and  $T_1'$  is the electron randomization relaxation time.

Then in general if the relaxation occurs through random interactions of the alkali electron spin with ran-

domly oriented disorientation fields not involving the alkali spins, the relaxation of the electronic polarization of each hyperfine level can be represented as the sum of two contributions: that from Zeeman relaxation [ $J(\Delta W) \ll J(\omega_F)$ ,  $\tau_e \gg \tau_{\text{HF}}$ ,  $T_1 \ll T_1'$ ] and that from electron randomization [ $J(\Delta W) \approx J(\omega_F)$ ,  $\tau_e \ll \tau_{\text{HF}}$ ,  $T_1' \ll T_1$ ].

Equations (33) and (34) correspond to Eqs. (53) and (54) of Bouchiat<sup>12</sup> if (12) and (14) are recalled and her time constants  $T_e$  and  $T_n$  are related to  $T_1$  and  $T_1'$  by

$$1/T_e = 1/T_1 + 1/T_1',$$

$$1/T_n = 1/T_1 + 2/(2I_1 + 1)^2 T_1'.$$

A Hamiltonian of the form of (22) was taken by Bouchiat to describe relaxation in wall-coated cells. It appears that (22) should also hold for relaxation by collisions with buffer-gas atoms. For example, Bernheim's model for buffer-gas relaxation is of this type.<sup>14</sup> For buffer-gas collisions the correlation time is no longer than the collision time,  $\approx 10^{-12}$  sec, which is much shorter than the hyperfine period. One would then expect disorientation by buffer-gas collisions to satisfy the conditions for electron randomization.

TABLE III. Values of

$$\Gamma(F_1, F_1', M_1') = \sum_{M_1} M_1 \begin{pmatrix} F_1 & 1 & F_1' \\ M_1 & M_1' - M_1 & -M_1' \end{pmatrix}^2 = M_1' \Gamma(F_1, F_1').$$

	$F_1'$	
$F_1$	$I_1 + \frac{1}{2}$	$I_1 - \frac{1}{2}$
$I_1 + \frac{1}{2}$	$\frac{M_1'(4I_1^2 + 8I_1 - 1)}{(2I_1 + 1)(2I_1 + 2)(2I_1 + 3)}$	$\frac{M_1'(2I_1 + 3)}{2I_1(2I_1 + 1)}$
$I_1 - \frac{1}{2}$	$\frac{M_1'(2I_1 - 1)}{(2I_1 + 1)(2I_1 + 2)}$	$\frac{M_1'(4I_1^2 - 5)}{(2I_1 - 1)2I_1(2I_1 + 1)}$

<sup>14</sup> R. A. Bernheim, J. Chem. Phys. **36**, 135 (1962).

There appear to be at least two reasons for retaining uniform relaxation as a decay channel in addition to the mechanism proposed by Bouchiat. First, in cells containing sidearms for controlling the densities of the various alkali vapors, effusion to and from the sidearms constitutes a uniform relaxation process; i.e., when an atom in a given  $F_1M_1$  substate leaves the cell, it is replaced by an atom which has an equal probability of being in any of the  $2(2I_1+1)$  possible substates. Second, if an atom sticks to the wall for a very long time, the relaxation will again be uniform. For example, if the atom undergoes many effective relaxation collisions of the Bouchiat type while on the wall, its initial polarization will be completely destroyed. Imperfections in the coating or small pools of alkali atoms could cause long dwell times.

Uniform relaxation can be included by adding to (28),  $w(F_1M_1, F_1M_1') = 1/2(2I_1+1)T_1''$ , where  $T_1''$  is the uniform relaxation time. Equations (33) and (34) readily become

$$(\dot{P}_+)_R = -P_+/T_1''' - (2I_1^2 + I_1 + 1)P_+ / (2I_1 + 1)^2 T_1' - (2I_1 + 2)(2I_1 + 3)P_- / 2(2I_1 + 1)^2 T_1', \quad (35)$$

$$(\dot{P}_-)_R = -P_- / T_1''' - I_1(2I_1 - 1)P_+ / (2I_1 + 1)^2 T_1' - (2I_1^2 + 3I_1 + 2)P_- / (2I_1 + 1)^2 T_1', \quad (36)$$

where  $1/T_1''' \equiv 1/T_1 + 1/T_1''$  to simplify the subsequent equations. See Sec. IV for a discussion of experimentally determined relaxation times.

#### D. Spin Exchange Between Nonidentical Atoms

The results of Dalgarno's quantum-mechanical treatment of the spin-exchange process are used to describe the spin-exchange collisions between the two species.<sup>15</sup> Atoms 1 and 2 are assumed to be nonidentical and in

doublet spin states. The stationary state of the molecule formed by atoms 1 and 2 is then either a singlet or triplet state. With each of the possible states there is associated a potential which describes the interaction of the two atoms. In the usual manner, the solution of the scattering problem leads to the scattering amplitudes,  $f_s$  and  $f_t$ , where the subscripts refer to singlet and triplet. Spin-orbit interactions are neglected in the collision. For spin-exchange collisions for which the initial states of atoms 1 and 2 are  $A$  and  $B$  and the final states  $A'$  and  $B'$ , the cross section is<sup>15</sup>

$$Q(AB, A'B') = Q_1(A, B)\delta_{A, A'}\delta_{B, B'} + Q_2(AB, A'B'), \quad (37)$$

where

$$Q_1(A, B) = \int \left\{ \left| \frac{f_s + 3f_t}{4} \right|^2 + \frac{1}{2} \operatorname{Re}[(f_s^* + 3f_t^*)(f_t - f_s)] \right. \\ \left. \times \langle AB | \mathbf{S}_1 \cdot \mathbf{S}_2 | AB \rangle \right\} d\Omega, \quad (38)$$

$$Q_2(AB, A'B') = \int |f_t - f_s|^2 d\Omega \\ \times |\langle A'B' | \mathbf{S}_1 \cdot \mathbf{S}_2 | AB \rangle|^2, \quad (39)$$

and  $\mathbf{S}_1$  and  $\mathbf{S}_2$  are the electronic angular momenta of atoms 1 and 2. In the experiments discussed in this paper, contributions from the direct cross section,  $Q_1$ , cancel out because only net changes in state populations are detected. From (39) it is seen that the spin-exchange experiments considered here yield information about the interatomic potentials only through the quantity  $\int |f_t - f_s|^2 d\Omega$ .

The matrix element of  $\mathbf{S}_1 \cdot \mathbf{S}_2$  between  $FM$  states is found as follows: By Edmonds' (5.2.4),<sup>9</sup>

$$\langle F_1' M_1' F_2' M_2' | \mathbf{S}_1 \cdot \mathbf{S}_2 | F_1 M_1 F_2 M_2 \rangle = \sum_q (-)^q \langle F_1' M_1' | S_1(1, q) | F_1 M_1 \rangle \langle F_2' M_2' | S_2(1, -q) | F_2 M_2 \rangle. \quad (40)$$

Then by the Wigner-Eckart theorem, Edmonds' (5.4.1),

$$\langle F_1' M_1' F_2' M_2' | \mathbf{S}_1 \cdot \mathbf{S}_2 | F_1 M_1 F_2 M_2 \rangle \\ = \sum_q (-)^{q+F_1'+F_2'-(M_1'+M_2')} \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & q & M_1 \end{pmatrix} \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & -q & M_2 \end{pmatrix} \langle F_1' || S_1(1) || F_1 \rangle \langle F_2' || S_2(1) || F_2 \rangle. \quad (41)$$

Application of (7.1.7) and (5.4.4) of Edmonds leads to

$$Q_2(F_1 M_1 F_2 M_2, F_1' M_1' F_2' M_2') / \int |f_t - f_s|^2 d\Omega \\ = |\langle F_1' M_1' F_2' M_2' | \mathbf{S}_1 \cdot \mathbf{S}_2 | F_1 M_1 F_2 M_2 \rangle|^2 = (9/4)(2F_1+1)(2F_1'+1)(2F_2+1)(2F_2'+1) \\ \times \sum_q \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & q & M_1 \end{pmatrix}^2 \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & -q & M_2 \end{pmatrix}^2 \left\{ \begin{matrix} \frac{1}{2} & F_1' & I_1 \\ F_1 & \frac{1}{2} & 1 \end{matrix} \right\}^2 \left\{ \begin{matrix} \frac{1}{2} & F_2' & I_2 \\ F_2 & \frac{1}{2} & 1 \end{matrix} \right\}^2. \quad (42)$$

The following selection rules are immediately apparent:  $M_1 + M_2 = M_1' + M_2'$ ,  $|\Delta M_1| \leq 1$ ,  $|\Delta M_2| \leq 1$ . Using (5),

<sup>15</sup> A. Dalgarno, Proc. Roy. Soc. (London) A262, 132 (1961).

one has

$$Q_2(F_1M_1F_2M_2, F_1'M_1'F_2'M_2') = \int \frac{|f_t - f_s|^2}{16} d\Omega \Delta(F_1, F_1') \Delta(F_2, F_2') \sum_q \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & q & M_1 \end{pmatrix}^2 \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & -q & M_2 \end{pmatrix}^2. \quad (43)$$

Then the exchange term in (1) becomes, with (13),

$$(\dot{P}_{\pm})_E = \frac{\mp 1}{4T_{E1}d} \sum_{\substack{F_1'M_1' \\ F_2M_2 \\ F_2'M_2'}} \frac{\Delta(F_1, F_1') \Delta(F_2, F_2')}{(I_1 + \frac{1}{2})\dot{p}} \sum_{qM_1} M_1 \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & q & M_1 \end{pmatrix}^2 \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & -q & M_2 \end{pmatrix}^2 \times (\dot{p}_{F_1M_1} d_{F_2M_2} - \dot{p}_{F_1'M_1'} d_{F_2'M_2'}), \quad (44)$$

where

$$\frac{1}{T_{E1}} = \frac{d}{4} \int \int |f_t - f_s|^2 d\Omega v_E d\Omega v_E f(v_E) d^3v_E = \frac{d}{T_{E2}\dot{p}}. \quad (45)$$

Here  $T_{E1}$  is the time which characterizes the influence of the second species upon the first species through the spin-exchange interaction. Similarly,  $T_{E2}$  indicates the effect upon the second species arising from spin-exchange collisions with atoms of the first species. The normalization is in agreement with accepted convention.<sup>6</sup> Equations (44) are not yet in a useful form because they depend upon the populations and not just upon the polarizations. The further assumptions made for the particular experiments in Secs. III and IV will correct this situation.

A short digression will show that the cross sections derived here agree with the results of Glassgold.<sup>1</sup> From (43) one has, for the case in which the second species is unpolarized,

$$\sum_{\substack{F_2M_2 \\ F_2'M_2'}} Q_2(F_1M_1F_2M_2, F_1'M_1'F_2'M_2') = 2(2I_2 + 1) \int \frac{|f_t - f_s|^2}{16} d\Omega \Delta(F_1, F_1') \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & M_1' - M_1 & M_1 \end{pmatrix}^2, \quad (46)$$

$$= 2(2I_2 + 1) \int \sigma(fm, f'm'; \theta) d\Omega, \quad (47)$$

in the notation of Glassgold with  $f = F_1$  and  $m = M_1$ . The  $\Delta(F_1, F_1')$  defined by (5) and given in Table II are identical to the  $\Delta(f, f')$  of Glassgold, which are listed in his Table I. Therefore, by Edmonds' (3.7.3),

$$\sigma(fm, f'm'; \theta) = \frac{1}{3} \left| \frac{f_1 - f_0}{4} \right|^2 \Delta(f, f') (fmf' - m'|1m - m')^2, \quad (48)$$

where  $f_1 = f_t$  and  $f_0 = f_s$ . Equation (48) agrees with Eq. (4.6) of Glassgold's paper.

If one defines

$$Q_2(F_1M_1F_2M_2, F_1'M_1'F_2'M_2') = \pi S_0^2 \langle | \langle F_1'M_1'F_2'M_2' | P_1 + e^{i\phi} P_0 | F_1M_1F_2M_2 \rangle |^2 \rangle_{\Delta v \text{ over } \phi}, \quad (49)$$

then (44) are still valid if  $1/T_{E1}d$  is replaced by  $\pi S_0^2 \bar{v}/2$ . This substitution places the rate equation in the form used, for example, by Anderson and Ramsey.<sup>8</sup> This approach is similar to the semiclassical description used by Wittke and Dicke<sup>16</sup> and by Purcell and Field.<sup>17</sup>  $P_1$  and  $P_0$  are the projection operators for a total electronic angular momentum of 1 or 0. The relative phase shift,  $\phi$ , between the singlet and triplet parts of the wave function, arises from the difference between the singlet and triplet potentials, which describe the molecule formed by an alkali atom of each kind. For a "strong" collision,  $\phi$  is assumed to be large and random ( $\langle \cos \phi \rangle = 0$ ); collisions not classified as strong are neglected. The maximum impact parameter for which a strong collision occurs,  $S_0$ , is usually taken as the one

for which the particle will have zero velocity at the top of the centrifugal barrier for the singlet potential. Glassgold and Lebedeff have discussed the validity of this approximation.<sup>2</sup>

### E. Self Spin Exchange

Glassgold<sup>1</sup> has shown that the cross section for identical atoms, corresponding to (37), is

$$Q(AA', A''A''') = \int |\langle A''A''' | \mathcal{F} | AA' \rangle|^2 d\Omega / 2, \quad (50)$$

where the first atom in the collision has electronic spin  $\sigma_1/2$  and undergoes a transition from state  $A$  (representing  $F_1M_1$ ) to  $A''$  in an exchange collision with the second atom of spin  $\sigma_1'/2$  which makes a transition

<sup>16</sup> J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620 (1956).

<sup>17</sup> E. M. Purcell and G. B. Field, Astrophys. J. **124**, 542 (1956).

from  $A'$  to  $A'''$ :

$$\mathfrak{F} = F_d(\theta) + F_x(\theta) \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' + (-)^{2i+1} Q [F_d(\pi - \theta) + F_x(\pi - \theta) \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1'], \quad (51)$$

$$F_d = (f_s + 3f_t)/4, \quad (52)$$

$$F_x = (f_t - f_s)/4, \quad (53)$$

$$\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_1'; \quad I_1 = I_1' = i, \quad (54)$$

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_1' = \boldsymbol{\sigma}/2; \quad S_1 = S_1' = \frac{1}{2}. \quad (55)$$

Here  $Q$  is the operator which interchanges both the

electronic and nuclear spins;  $Q = Q_n Q_e$ , where

$$Q_e |IM_TSM_S\rangle = (-)^{S+1} |IM_TSM_S\rangle, \quad (56)$$

$$Q_n |IM_TSM_S\rangle = (-)^{I+2i} |IM_TSM_S\rangle. \quad (57)$$

For a general operator  $O$ ,

$$\langle A''A''' | QO | AA' \rangle = \langle A'''A'' | O | AA' \rangle; \quad (58)$$

the first quantum numbers of each bra or ket always refer to the first atom.

The factor of 2 in (50) is necessary in order to avoid counting final states twice. The cross section is then

$$Q(AA', A''A''') = \int [ |F_d(\theta)|^2 \delta_{A,A'} \delta_{A'',A'''} + |F_x(\pi - \theta)|^2 \delta_{A,A'''} \delta_{A',A''} + (-)^{2i+1} 2 \operatorname{Re} \{ F_d^*(\theta) F_d(\pi - \theta) \delta_{A,A'} \delta_{A'',A'''} + F_d^*(\theta) F_x(\pi - \theta) \langle AA' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle \delta_{A,A'''} \delta_{A',A''} + F_d^*(\pi - \theta) F_x(\theta) \langle A'A' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle \delta_{A,A'''} \delta_{A',A''} + F_x^*(\theta) F_x(\pi - \theta) \langle A''A''' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle \langle A'''A'' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle + 2 \operatorname{Re} F_d^*(\theta) F_x(\theta) \langle AA' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle \delta_{A,A'''} \delta_{A',A''} + 2 \operatorname{Re} F_d^*(\pi - \theta) F_x(\pi - \theta) \langle A'A' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle \delta_{A,A'''} \delta_{A',A''} + |F_x(\theta)|^2 | \langle A''A''' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle |^2 + |F_x(\pi - \theta)|^2 | \langle A'''A'' | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_1' | AA' \rangle |^2 ] d\Omega/2. \quad (59)$$

Fortunately, none of the terms involving deltas contributes to the rate equations, as can be seen by substituting (59) into (1). The  $|F_x(\theta)|^2$  term in (59) is the cross section one would expect between two nonidentical atoms. The  $|F_x(\pi - \theta)|^2$  term arises because no distinction can be made between the incident and target atoms. The  $2 \operatorname{Re} F_d^*(\theta) F_x(\pi - \theta)$  term arises from the quantum-mechanical identity of the two colliding atoms. An estimate of the interference term using the model of Purcell and Field is given in Appendix I and indicates that it is small compared with the other two terms, at least for Rb<sup>87</sup>; it will be neglected entirely in the subsequent calculations. Equation (59) in (1) produces, with the aid of (13) and the fact that  $\int |F_x(\theta)|^2 d\Omega = \int |F_x(\pi - \theta)|^2 d\Omega$ ,

$$(\dot{P}_{\pm})_{S_1} = \frac{\mp 1}{4T_{S_1} \rho} \sum_{\substack{F_1' M_1' \\ F_1'' M_1'' \\ F_1''' M_1'''}} \frac{\Delta(F_1, F_1') \Delta(F_1', F_1''')}{(I_1 + \frac{1}{2}) \rho} \sum_{M_1} M_1 \times \begin{pmatrix} F_1'' & 1 & F_1 \\ -M_1'' & q & M_1 \end{pmatrix}^2 \begin{pmatrix} F_1''' & 1 & F_1' \\ -M_1''' & -q & -M_1' \end{pmatrix}^2 (\rho_{F_1 M_1} \rho_{F_1' M_1'} - \rho_{F_1'' M_1''} \rho_{F_1''' M_1'''}). \quad (60)$$

Here  $T_{S_1}$ , defined by

$$\frac{1}{T_{S_1}} = \frac{\rho}{4} \int \int |f_t - f_s|^2 s_1 d\Omega v_{S_1} f(v_{S_1}) d^3 v_{S_1}, \quad (61)$$

is the self spin exchange time for the first species; for the second species,

$$\frac{1}{T_{S_2}} = \frac{d}{4} \int \int |f_t - f_s|^2 s_2 d\Omega v_{S_2} f(v_{S_2}) d^3 v_{S_2}. \quad (62)$$

## F. Simplified Rate Equations

Combining the results of this section, one has

$$\begin{aligned} \dot{P}_{F_1=I_1 \pm 1/2} = & \mp L \sum_{M_1} \frac{M_1 \rho_{F_1 M_1} \rho'_{(F_1 M_1)}}{(I_1 + \frac{1}{2}) \rho} \pm L \sum_{J_1' F_1' M_1'} \left( \frac{n_{J_1' F_1' M_1'}}{L} \right) \sum_{M_1} \frac{M_1 P''(J_1' F_1' M_1', F_1 M_1)}{(I_1 + \frac{1}{2}) \rho \tau_{J_1'}} \\ & - P_{\pm} / T_1''' - \delta_{F_1, I_1 \pm 1/2} [(2I_1^2 + I_1 + 1) P_+ - (I_1 + 1)(2I_1 + 3) P_-] / (2I_1 + 1)^2 T_1' \\ & - \delta_{F_1, I_1 - 1/2} [I_1(2I_1 - 1) P_+ + (2I_1^2 + 3I_1 + 2) P_-] / (2I_1 + 1)^2 T_1' \\ = & \frac{1}{4T_{S_1} d} \sum_{\substack{F_1' M_1' \\ F_2' M_2'}} \frac{\Delta(F_1, F_1') \Delta(F_2, F_2')}{(I_1 + \frac{1}{2}) \rho} \sum_{q M_1} \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & q & M_1 \end{pmatrix}^2 \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & -q & M_2 \end{pmatrix}^2 \\ & \times M_1 (\rho_{F_1 M_1} d_{F_2 M_2} - \rho_{F_1' M_1'} d_{F_2' M_2'}) \\ = & \frac{1}{4T_{S_1} \rho} \sum_{\substack{F_1' M_1' \\ F_1'' M_1'' \\ F_1''' M_1'''}} \frac{\Delta(F_1, F_1') \Delta(F_1', F_1''')}{(I_1 + \frac{1}{2}) \rho} \sum_{q M_1} \begin{pmatrix} F_1'' & 1 & F_1 \\ -M_1'' & q & M_1 \end{pmatrix}^2 \begin{pmatrix} F_1''' & 1 & F_1' \\ -M_1''' & -q & -M_1' \end{pmatrix}^2 \\ & \times M_1 (\rho_{F_1 M_1} \rho_{F_1' M_1'} - \rho_{F_1'' M_1''} \rho_{F_1''' M_1'''}). \quad (63) \end{aligned}$$

Clearly additional assumptions are necessary before these equations involve only  $P_{\pm}$  and  $D_{\pm}$  and none of the individual populations.

### III. TRANSIENT EXPERIMENT

In this section the rate equations are solved for the case of a Franzen<sup>5</sup> transient experiment applied to the measurement of the spin-exchange cross section in a resonance cell containing the vapors of two alkalis. The first species is optically pumped and the envelope of the decay in the dark of its electronic polarization is traced out, yielding a single relaxation time  $\tau$  if the nuclear spin is neglected. In the presence of the second species, which is continuously disoriented by an rf field, the relaxation time is shortened to

$$1/T = 1/\tau + 1/T_{E1}, \quad (64)$$

neglecting the nuclear spins. A measurement of the density of the second species then permits a determination of the spin-exchange cross section. This transient experiment has the advantage that the density and relaxation times of only one of the two species must be measured, whereas in the steady-state experiments they must be determined for both species.

The transient signal is conveniently defined as

$$S(I_1, t) = \frac{A(\infty) - A(t)}{A(\infty) - A(0)}, \quad (65)$$

where the absorption at time  $t$  is given by (11). Equation (11) becomes, on the assumption that  $P$  is independent of  $x$  and that  $L$  is approximately independent of  $x$  and  $t$ ,

$$A(I_1, t) \approx kl[1 - P(t)]L. \quad (66)$$

In that case,

$$S(I_1, t) \approx P(t)/P(0) = \langle S_{1z}(t) \rangle / \langle S_{1z}(0) \rangle. \quad (67)$$

If the resonance cell contains no buffer gas,  $P$  should be independent of  $x$  because of the rapid motion of the atoms;  $L$  is approximately independent of  $x$  and  $t$  if the absorption is kept small. At any rate, (67) is valid only if experimental care is taken to satisfy (66); otherwise the signal becomes a much more complicated function of the polarization as indicated by (11) and (65).

The continuous application of the rf field at the resonance frequency of the second species,

$$\approx 2.8H_0/(2I_2+1) \text{ Mc/sec}, \quad (68)$$

where  $H_0$  is the static magnetic field strength in gauss, results in equal populations among the substates of each hyperfine state throughout the experiment. One has in (63)

$$d_{F_2, M_2} = d_{F_2} / (2F_2 + 1) \quad (69)$$

and

$$d_{F_2', M_2'} = d_{F_2'} / (2F_2' + 1). \quad (70)$$

(It may take a time " $T_2$ " in paramagnetic-resonance nomenclature for the spins to dephase after the applica-

tion of the rf field; but since the field is applied continuously and is sufficiently strong to overpower the pumping effect of the light, the coherence will not reappear.)

It is necessary to exclude the self-exchange term in (63) from the following solution because of its nonlinear character. Experimentally this is a good approximation whenever  $T_{S1}$  is much longer than the shortest time constants affecting the relaxation; for example, for two alkalis, cross exchange dominates over self exchange when  $d \gg p$ . The importance of self exchange is also reduced because there is no change in the absorption if the two atoms undergoing a collision have both initial and final states in the same hyperfine state:

$$\Delta A \propto \Delta \sum_M M p_{FM} \propto M_1(-1) + M_1'(-1) + M_1''(+1) + M_1'''(+1) = 0, \quad (71)$$

since  $M_1 + M_1' = M_1'' + M_1'''$  always.<sup>5</sup>

With (69), (70),  $T_{S1} = \infty$ , and  $L = 0$  the  $1/T_{E1}$  term in (63) becomes identical in form to the  $T_1'$  term in (29) or (33) and (34). Then

$$\dot{P}_+ = -P_+/T_1''' - (1/T_{E1} + 1/T_1')[(2I_1^2 + I_1 + 1)P_+ + (I_1 + 1)(2I_1 + 3)P_-] / (2I_1 + 1)^2, \quad (72)$$

$$\dot{P}_- = -P_-/T_1''' - (1/T_{E1} + 1/T_1')[I_1(2I_1 - 1)P_+ + (2I_1^2 + 3I_1 + 2)P_-] / (2I_1 + 1)^2. \quad (73)$$

Alternatively, with the aid of (12) and (14),

$$\langle \dot{S}_{1z} \rangle = -(1/T_1''' + 1/T_1' + 1/T_{E1}) \langle S_{1z} \rangle + 2(1/T_1' + 1/T_{E1}) \langle I_{1z} \rangle / (2I_1 + 1)^2, \quad (74)$$

$$\langle \dot{I}_{1z} \rangle = -[1/T_1''' + 2(1/T_1' + 1/T_{E1}) / (2I_1 + 1)^2] \langle I_{1z} \rangle. \quad (75)$$

The solution of the above equations yields, for the signal for a Franzen-type spin-exchange experiment,

$$S(I_1, t) = (1 - a) \exp(-t/\tau_1) + a \exp(-t/\tau_2), \quad (76)$$

where

$$1/\tau_1 = 1/T_1 + 1/T_1' + 1/T_1'' + 1/T_{E1}, \quad (77)$$

$$1/\tau_2 = 1/T_1 + 1/T_1'' + 2(1/T_1' + 1/T_{E1}) / (2I_1 + 1)^2, \quad (78)$$

$$a = 2 \langle I_{1z}(0) \rangle / (4I_1^2 + 4I_1 - 1) \langle S_{1z}(0) \rangle \quad (79)$$

$$= 4[I_1 P_+(0) - (I_1 + 1) P_-(0)] / (4I_1^2 + 4I_1 - 1) P(0), \quad (80)$$

where  $I_1$  is the nuclear spin of the first species,  $T_{E1}$  is defined by (45), and  $T_1, T_1', T_1''$  are the times for Zeeman relaxation, electron randomization, and uniform relaxation, respectively.  $\langle S_{1z} \rangle$  and  $\langle I_{1z} \rangle$  are defined by (12) and (14). Note that for  $I_1 = 0$  or  $I_1 = \frac{1}{2}$ ,  $P_- = 0$ , implying  $\langle I_{1z} \rangle = 2I_1 \langle S_{1z} \rangle$ . For  $T_1'' = T_{E1} = \infty$  these results agree with Bouchiat<sup>12</sup>; for  $T_1 = T_1' = T_1'' = \infty$ , with Grossetête.<sup>18</sup>

<sup>18</sup> For an independent derivation of the results of this section using density matrix techniques, see F. Grossetête, J. Phys. Radium 25, 383 (1964) and Compt. Rend. 258, 3668 (1964).

For a single species, the relaxation of the electronic polarization is a single exponential if the relaxation is by Zeeman or uniform transitions only and is the sum of two exponentials [with characteristic times in the ratio  $(2I_1+1)^2/2$ ] if it is by electron randomization only. The experimental results of Bouchiat and Brossel<sup>19</sup> for Rb<sup>87</sup> in paraffin-coated cells indicate that, at least in some cases, the relaxation is a single exponential; i.e., Zeeman or uniform relaxation is dominant. On the other hand, one would expect buffer gas collisions to produce relaxation by electron randomization, since the correlation time is short compared with the hyperfine period if the collision is elastic.

In summary, the signal for the Franzen-type transient experiment, neglecting self spin exchange, is given by (76). In general, the signal is the sum of two exponentials. For Zeeman or uniform relaxation the ratio of the time constants ranges from 1 to  $(2I_1+1)^2/2$ , depending upon the relative sizes of  $T_1$ ,  $T_1''$ , and  $T_{E1}$ . For the electron randomization case, the ratio is always  $(2I_1+1)^2/2$ .

In either case, the nuclear spin effects must be included in the analysis if correct spin-exchange cross sections are to be deduced.

#### IV. STEADY-STATE EXPERIMENTS IN THE LIMIT OF LOW LIGHT INTENSITY

##### A. Rate Equations

In this section some experiments are analyzed in the limit of low light intensity, for which

$$p_{F_1M_1} = p/2(2I_1+1) + \pi_{F_1M_1}, \quad (81)$$

$$d_{F_2M_2} = d/2(2I_2+1) + \delta_{F_2M_2}, \quad (82)$$

where the deviations  $\pi_{F_1M_1}$  and  $\delta_{F_2M_2}$  of the populations from the depolarized values are small and proportional to  $L$  in first order. Substitution of (81) and (82) into (63), dropping terms proportional to  $L^2$  (e.g.,  $\pi_{F_1M_1}L$ ,  $\pi_{F_1M_1}\delta_{F_2M_2}$ , etc.) immediately, leads to the following rate equations in the limit of low light intensity (see Appendix II for the details):

$$\begin{aligned} \dot{P}_+ \approx & \frac{(2I_1+2)(2I_1+3)}{6(2I_1+1)^2} \left( L_+C + \frac{D_+ + D_-}{T_{E1}} \right) - \left[ \frac{1}{T_1'''} + \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} \right) \frac{2I_1^2 + I_1 + 1}{(2I_1+1)^2} + \frac{2I_1(2I_1-1)}{3(2I_1+1)^2 T_{S1}} \right] P_+ \\ & - \frac{(2I_1+2)(2I_1+3)}{2(2I_1+1)^2} \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{2}{3T_{S1}} \right) P_-, \quad (83) \end{aligned}$$

$$\begin{aligned} \dot{P}_- \approx & \frac{2I_1(2I_1-1)}{6(2I_1+1)^2} \left( L_-C + \frac{D_+ + D_-}{T_{E1}} \right) - \frac{I_1(2I_1-1)}{(2I_1+1)^2} \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{2}{3T_{S1}} \right) P_+ \\ & - \left[ \frac{1}{T_1'''} + \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} \right) \frac{2I_1^2 + 3I_1 + 2}{(2I_1+1)^2} + \frac{(2I_1+2)(2I_1+3)}{3(2I_1+1)^2 T_{S1}} \right] P_-. \quad (84) \end{aligned}$$

The corresponding equations for the second species are found by setting  $L_+ = L_- = 0$ , interchanging  $P_{\pm}$  and  $D_{\pm}$ , and replacing the subscript 1 by 2 in (83) and (84).  $L_+$  and  $L_-$ , defined by (A16), are independent of the polarizations and are linearly proportional to the light intensity  $L$ ;  $L_+ = L_- = L$  for complete mixing. Recall that the hyperfine components in the incident light are equal; i.e.,  $L_+$  and  $L_-$  do not refer to unequal pumping components.

Transforming to the  $\langle S_{1z} \rangle$  and  $\langle I_{1z} \rangle$  representation by using (12) and (14), one finds

$$\begin{aligned} \langle \dot{S}_{1z} \rangle = & [(I_1+1)(2I_1+3)L_+C/2 + I_1(2I_1-1)L_-C/2 + (4I_1^2 + 4I_1 + 3)\langle S_{2z} \rangle / T_{E1}] / 3(2I_1+1)^2 \\ & - \left[ \frac{1}{T_1'''} + \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{4I_1(2I_1+2)}{3(2I_1+1)^2 T_{S1}} \right] \langle S_{1z} \rangle + 2 \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{1}{T_{S1}} \right) \langle I_{1z} \rangle / (2I_1+1)^2, \quad (85) \end{aligned}$$

$$\begin{aligned} \langle \dot{I}_{1z} \rangle = & I_1(2I_1+2)[(2I_1+3)L_+C/2 - (2I_1-1)L_-C/2 + 4\langle S_{2z} \rangle / T_{E1}] / 3(2I_1+1)^2 \\ & + \frac{4I_1(2I_1+2)\langle S_{1z} \rangle}{3(2I_1+1)^2 T_{S1}} - \left[ \frac{1}{T_1'''} + 2 \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{1}{T_{S1}} \right) \right] / (2I_1+1)^2 \langle I_{1z} \rangle. \quad (86) \end{aligned}$$

The corresponding equations for the second species are again found by setting  $L_+ = L_- = 0$  and interchanging the subscripts 1 and 2 in (85) and (86). Thus in the limit of low light intensity the rate equations reduce to four linear equations.

<sup>19</sup> M. Bouchiat and J. Brossel, *Compt. Rend.* **254**, 3650 and 3828 (1962).

##### B. Dehmelt Experiment

The experiment analyzed in this section was first used by Dehmelt to estimate the sodium-electron spin-exchange cross section.<sup>6</sup> A resonance cell contains two atomic species or one atomic species and quasifree electrons. The first species is optically pumped, and the

transmitted resonance radiation is monitored. The signal can be defined as

$$S(I_1, I_2) = [A(0, H_2') - A(0, 0)] / [A(H_1', 0) - A(0, 0)], \quad (87)$$

where  $A(H_1', H_2')$  is the absorption in the presence of two rf fields ( $H_1'$  disorients species 1, etc.). The absorption is given by (11), provided that the incident light is constant over the frequencies for which the absorption is appreciable. It will be assumed that  $L(x, t)$  or  $L(x, H_1', H_2')$  is the same at each point in the cell for arbitrary values of the rf fields; i.e.,  $L(x, H_1', H_2') = L(x, 0, 0) = L(x)$ . This should be a good approximation in the limit of low light intensity, for which—because the polarization is always small—the absorption changes very little with polarization changes. One has  $P(x, H_1', H_2') = f(x)P(H_1', H_2')$ , where  $P(H_1', H_2')$  is in-

dependent of  $x$  and  $f(x)$  is approximately independent of  $H_1'$  and  $H_2'$  since the polarization is small [see (90) below]. Then

$$S(I_1, I_2) \approx 1 - P(0, H_2') / P(0, 0), \quad (88)$$

since  $P(H_1', 0) = 0$ . For  $I_1 = 0$ , (88) is valid for any absorption if the polarization is low.

Applying  $H_2'$  is equivalent to reducing the relaxation time of the second species to zero; therefore,  $P(0, H_2') = P(T_2 = 0)$  and

$$S(I_1, I_2) \approx 1 - P(T_2 = 0) / P(T_2) = 1 - \langle S_{1z}(T_2 = 0) \rangle / \langle S_{1z}(T_2) \rangle. \quad (89)$$

By solving the four simultaneous equations (85) and (86) and the corresponding equations for the second species, one finds, at equilibrium ( $\langle \dot{S}_{1z} \rangle = 0$ , etc.),

$$\langle S_{1z} \rangle \approx \frac{(I_1 + 1)(2I_1 + 3) \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{1}{T_{S1}} + \frac{2I_1 + 1}{2T_1'''} \right) L_+ C - I_1(2I_1 - 1) \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{1}{T_{S1}} + \frac{2I_1 + 1}{2T_1'''} \right) L_- C}{6(2I_1 + 1)[\beta(1) - \alpha(1)\alpha(2)/\beta(2)]}, \quad (90)$$

where

$$\alpha(1) = \frac{1}{T_{E1}} \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{1}{T_{S1}} + \frac{4I_1^2 + 4I_1 + 3}{6T_1'''} \right), \quad (91)$$

$$\beta(1) = \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} \right) \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{1}{T_{S1}} \right) + \frac{4I_1^2 + 4I_1 + 3}{2T_1'''} \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} + \frac{2}{3T_{S1}} \right) + \frac{(2I_1 + 1)^2}{2T_1'''^2}. \quad (92)$$

Then

$$S(I_1, I_2) \approx \alpha(1)\alpha(2)/\beta(1)\beta(2) \quad (93)$$

is the signal for the Dehmelt-type<sup>6</sup> steady-state experiment in the limit of low light intensity.  $I_1$  is the nuclear spin,  $1/T_1''' = 1/T_1 + 1/T_1''$ ,  $T_1$  the Zeeman relaxation time,  $T_1''$  the uniform relaxation time,  $T_1'$  the electron randomization relaxation time, and  $T_{S1}$  and  $T_{E1}$  the self- and cross-exchange times of the pumped species;  $I_2$ ,  $T_2$ ,  $T_2''$ ,  $T_2'$ ,  $T_{S2}$ , and  $T_{E2}$  are the corresponding quantities for the other species.

The signal is independent of  $L_+$  and  $L_-$ , i.e., of any assumptions about excited-state disorientation. But (90) indicates that the electron polarization depends upon the excited-state disorientation. However, the signal is defined as the ratio of two signals, and the disorientation effects cancel out.  $S = 0$  for  $T_2''' = 0$  or  $T_2' = 0$  because the second species is not affected by the rf field, since it is never oriented. Similarly,  $S = 0$  for  $T_1''' = 0$  or  $T_1' = 0$  because the first species is not pumped. For  $T_{E1} = \infty$ ,  $S = 0$ , since disorienting the second species has no effect upon the first species in the absence of spin exchange. Equation (93) is not valid for both  $T_1''' = \infty$  and  $T_1' = \infty$ .

If  $T_1''' = T_2''' = \infty$ , i.e., the relaxation is by electron

randomization only,

$$S(I_1, I_2) |_{T_1''' = T_2''' = \infty} = \frac{1}{T_{E1}T_{E2}} \times \left( \frac{1}{T_1'} + \frac{1}{T_{E1}} \right)^{-1} \left( \frac{1}{T_2'} + \frac{1}{T_{E2}} \right)^{-1}. \quad (94)$$

Also

$$S(0, 0) = \frac{1}{T_{E1}T_{E2}} \left( \frac{1}{T_1'''} + \frac{1}{T_1'} + \frac{1}{T_{E1}} \right)^{-1} \times \left( \frac{1}{T_2'''} + \frac{1}{T_2'} + \frac{1}{T_{E2}} \right)^{-1}, \quad (95)$$

which is identical to (94) in the limit  $T_1''' = T_2''' = \infty$ . Therefore, nuclear spin effects are unimportant if the ground-state relaxation is predominantly by electron randomization.

In order to compare the results above with earlier analyses by other authors, it is useful to compare the rate equations for the case  $I_1 = I_2 = 0$ ; Eqs. (1) become,

with  $n_{F_1, M_1} = n/2(2I_1 + 1)$  for complete mixing,  $C = \frac{1}{2}$ ,

$$T_{S1} = T_{S2} = T_1' = T_2' = \infty, \quad M_S = \pm \frac{1}{2}:$$

$$\begin{aligned} \dot{p}_{1/2} &= L\dot{p}_{-1/2}/2 - (\dot{p}_{1/2} - \dot{p}/2)/T_1''' \\ &\quad - (\dot{p}_{1/2}d_{-1/2} - \dot{p}_{-1/2}d_{1/2})/T_{E1}d, \\ \dot{p}_{-1/2} &= -L\dot{p}_{-1/2}/2 - (\dot{p}_{-1/2} - \dot{p}/2)/T_1''' \\ &\quad - (\dot{p}_{-1/2}d_{1/2} - \dot{p}_{1/2}d_{-1/2})/T_{E1}d, \quad (96) \\ \dot{d}_{1/2} &= -(d_{1/2} - d/2)/T_2''' \\ &\quad - (d_{1/2}\dot{p}_{-1/2} - d_{-1/2}\dot{p}_{1/2})/T_{E1}d, \\ \dot{d}_{-1/2} &= -(d_{-1/2} - d/2)/T_2''' \\ &\quad - (d_{-1/2}\dot{p}_{1/2} - d_{1/2}\dot{p}_{-1/2})/T_{E1}d. \end{aligned}$$

Using  $\dot{p}_{\pm 1/2} = [\dot{p} \pm (\dot{p}_{1/2} - \dot{p}_{-1/2})]/2$ , one has

$$\begin{aligned} \dot{p}_{1/2} - \dot{p}_{-1/2} &= L\dot{p}/2 - \left( \frac{L}{2} + \frac{1}{T_1'''} + \frac{1}{T_{E1}} \right) \\ &\quad \times (\dot{p}_{1/2} - \dot{p}_{-1/2}) + (d_{1/2} - d_{-1/2})/T_{E2}, \quad (97) \\ \dot{d}_{1/2} - \dot{d}_{-1/2} &= - \left( \frac{1}{T_2'''} + \frac{1}{T_{E2}} \right) (d_{1/2} - d_{-1/2}) \\ &\quad + (\dot{p}_{1/2} - \dot{p}_{-1/2})/T_{E1}. \end{aligned}$$

By comparing (97) with the rate equations used by Dehmelt<sup>6</sup> to describe his sodium-electron experiment, one finds that the following identifications must be made:  $\dot{p} = N$ ,  $d = n$ ,  $1/T_{E1} = nvQ$ ,  $T_1''' = \tau(I_0 = 0)$ ,  $T_2''' = T_e$ . Then with  $Qnv \ll 1/\tau$  or  $1/T_e$ , (95) becomes, with  $T_1' = T_2' = \infty$ ,

$$S_D(0,0) = nNT_e\tau v^2 Q^2. \quad (98)$$

Of course,  $I_1$  was actually  $\frac{3}{2}$ , for which (93) becomes, with  $T_1' = T_2' = T_{S1} = T_{S2} = \infty$ ,

$$S_D(3/2,0) = 3nNT_e\tau v^2 Q^2/8 = 3S_D(0,0)/8. \quad (99)$$

Therefore, if the experiment is performed in the limit of low light intensity, the cross section deduced from a given signal becomes  $(8/3)^{1/2} = 1.63$  times as large if nuclear spin is included in the analysis, if the ground-state relaxation of the alkali is by Zeeman or uniform transitions only, and if self exchange is negligible. But if the ground-state relaxation is by electron randomization, (98) is valid (with  $T_e = T_2'$  and  $\tau = T_1'$ ) for arbitrary  $I_1$ .

### C. Jarrett Experiment

Comparison of (96) with Eqs. (12) and (13) of the paper by Jarrett<sup>7</sup> indicates  $1/T_{E1}d = v_r Q_x$ ,  $1/T_1''' = 1/T_2''' = 2R$ ,  $\dot{p} = N$ , and  $d = aN$ ; therefore, with  $T_1' = T_2' = \infty$ , (95) becomes

$$S_J(0,0) = aN^2 v_r^2 Q_x^2 (2R + Nv_r Q_x)^{-1} \times (2R + aNv_r Q_x)^{-1}, \quad (100)$$

which is Jarrett's  $S_x/S$ , as can be verified by solving for the latter from (18) of Jarrett's paper. But from (94)

TABLE IV. Rb<sup>87</sup>-Rb<sup>85</sup> spin-exchange cross sections deduced from the data of Jarrett (Ref. 7).  $Q_J = 1.7 \times 10^{-14}$  cm<sup>2</sup>.

$I_1$	$I_2$	Relaxation: Zeeman, uniform, or electron randomization	Self exchange included?	$Q/Q_J$
0	0	Z or U	Yes or No	1
$\frac{3}{2}$	$\frac{3}{2}$	Z or U	No	4.6
$\frac{3}{2}$	$\frac{3}{2}$	Z or U	Yes	6.8
0	0	ER	Yes or No	1
$\frac{3}{2}$	$\frac{3}{2}$	ER	Yes or No	1

it is seen that if the relaxation is by electron randomization only, (100) is valid for general nuclear spin and includes self exchange (with  $T_1''' = T_2''' = \infty$  and  $1/T_1' = 1/T_2' = 2R$ ). However, if Zeeman or uniform relaxation is dominant, (93) implies a large correction to the deduced cross section for the actual nuclear spins ( $I_1 = \frac{3}{2}$ ,  $I_2 = \frac{3}{2}$ ). These effects may be demonstrated by assuming Jarrett's experimental values of the parameters and signal and then deducing the spin-exchange cross section. This author estimates  $k_0 l/4 \approx \frac{1}{3}$  for Jarrett's experiment; the fact that  $k_0 l/4$  is not much less than 1 [which is the condition that (11) hold in his experiment] is ignored in the following discussion.

For spin exchange between Rb<sup>85</sup> and Rb<sup>87</sup> one has

$$1/T_{S1} \approx \dot{p}/T_{E1}d \quad \text{and} \quad 1/T_{S2} \approx 1/T_{E1}, \quad (101)$$

because  $\int |f_t - f_s|^2 d\Omega$  is only weakly dependent upon nuclear properties. With  $T_{E2} = T_{E1}d/\dot{p}$ ,  $T_2''' = T_1'''$ ,  $T_2' = T_1'$ , in (93), the cross sections  $Q$  are deduced with  $R = 413$  sec<sup>-1</sup>,  $N = 3.33 \times 10^{11}$  cm<sup>-3</sup>,  $a = d/\dot{p} = 2.59$ ,  $v_r = 4.59 \times 10^4$  cm/sec, and  $S_x/S = S_J = 0.107$ . Values of  $Q$  are found for Zeeman or uniform relaxation ( $T_1' = \infty$ ,  $T_1''' = 1/2R$ ) and for relaxation by electron randomization ( $T_1' = 1/2R$ ,  $T_1''' = \infty$ ). By the nature of the measurement, the self-exchange contributions to  $R$  were presumably eliminated.  $Q_J = 1.7 \times 10^{-14}$  cm<sup>2</sup> is the cross section deduced by Jarrett, neglecting the nuclear spins. A comparison of the deduced cross sections for different assumptions is given in Table IV. The nuclear spins are important in the analysis of Jarrett's experiment unless the ground-state relaxation is by electron randomization only.

This author has not determined which relaxation mechanism predominated in Jarrett's experiment. However, the following discussion is pertinent. The relaxation time of the electronic polarization in a cylindrical cell containing a buffer gas can be approximated by<sup>5</sup>

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{wall}}} + \frac{1}{\tau_{\text{buffer}}}, \quad (102)$$

$$\tau_{\text{wall}} = \frac{\dot{p}}{D_0 p_0} \left[ \left( \frac{2.405}{a} \right)^2 + \left( \frac{\pi}{L} \right)^2 \right]^{-1}, \quad (103)$$

$$\tau_{\text{buffer}} = \dot{p}_0 / N_0 \sigma \bar{v} \dot{p}, \quad (104)$$

where  $p$  is the pressure of the buffer gas,  $D_0$  is the diffusion coefficient at atmospheric pressure  $p_0$ ,  $a$  and  $L$  are the radius and length of the cell,  $N_0$  is the density of inert-gas atoms at  $p_0$  and at the temperature of the vapor cell,  $\sigma$  is the disorientation cross section, and  $\bar{v}$  is the mean relative velocity between inert-gas atom and alkali. For Rb in Ne,  $D_0=0.31$  cm<sup>2</sup>/sec,  $\sigma=5.2\times 10^{-23}$  cm<sup>2</sup>, and  $N_0=2.29\times 10^{19}$  cm<sup>-3</sup> at 47°C.<sup>5</sup> For Jarrett's case  $p=2.8$  cm of Ne,  $a=2.5$  cm,  $L=1.43$  cm,  $T=90^\circ\text{C}$ , implying  $\tau_{\text{wall}}\approx 21$  msec and  $\tau_{\text{buffer}}\approx 0.38$  sec. Wall collisions should dominate for Jarrett's experiment, giving  $\tau\approx 21$  msec, but Jarrett found  $\approx 1$  msec. In deriving  $\tau_{\text{wall}}$  it was assumed that every wall collision produces complete disorientation, implying that  $\tau_{\text{wall}}\geq 21$  msec. If, however, the cell contained some impurity in the vapor phase, the relaxation might be greatly accelerated and be dominated by electron randomization. The cross section deduced by Jarrett would then be unchanged by the addition of the nuclear spins into the analysis and would be in agreement with the paramagnetic resonance measurement by Moos and Sands.<sup>20</sup>

#### D. Off-Diagonal Density-Matrix Elements

In the derivation of the general expression (93), the off-diagonal elements of the density matrix were neglected. Balling, Hanson, and Pipkin<sup>4</sup> have carried out an analysis for zero nuclear spin for a general density matrix. It is of interest to compare their result with this work. The polarization for  $I_1=I_2=0$  can be found from (97) or (90) with  $T_{S1}=T_{S2}=T_1'=T_2'=\infty$  and  $L_+=L_-$ :

$$P=P_+=LC \left/ \left[ \frac{1}{T_1'''} + \frac{1}{T_{E1}} - \frac{1}{T_{E1}T_{E2}} \left( \frac{1}{T_2'''} + \frac{1}{T_{E2}} \right)^{-1} \right] \right. \quad (105)$$

Equation (76) of Balling *et al.* is to be compared with the above, with  $P$ ,  $T_1'''$ ,  $T_{E1}$ ,  $T_{E2}$ , and  $T_2'''$  substituted for  $\langle P(R) \rangle$ ,  $T_{1R}$ ,  $T_{eR}$ ,  $T_{ee}$ , and  $T_{1e}$ , respectively:

$$P_{BHP} \propto 1 \left/ \left[ \frac{1}{T_1'''} + \frac{1}{T_{E1}} - \frac{1}{T_{E1}T_{E2}} \times \left( \frac{1}{T_2'''} + \frac{1}{T_{E2}} + \frac{\omega_1^2\tau_2}{1+\tau_2^2(\omega_0-\delta\omega_0-\omega)^2} \right)^{-1} \right] \right. \quad (106)$$

where

$$\omega_1 = -g_J(-\mu_0 H_2'/\hbar), \quad \omega_0 = -g_J(\mu_0 H_0/\hbar),$$

$\delta\omega_0$  is the spin-exchange frequency shift, and

$$1/\tau_2 = 1/T_{2e} + 1/T_{E2}. \quad (107)$$

Here  $T_{2e}$  is essentially the time required for coherence effects to damp out, i.e., the usual " $T_2$ " in magnetic-resonance nomenclature;  $T_{2e}$  should not be confused

with  $T_2$  of this work, which is a " $T_1$ " time for the second species. For  $H_2'=0$  there are no coherence effects, and (105) and (106)<sup>4</sup> agree. For

$$(H_2')^2 \gg \left[ \frac{1}{T_1'''} \left( \frac{1}{T_2'''} + \frac{1}{T_{E2}} \right) + \frac{1}{T_2'''T_{E1}} \right] \times \left( \frac{1}{T_{E2}} + \frac{1}{T_{2e}} \right) / \left( \frac{1}{T_1'''} + \frac{1}{T_{E1}} \right) \left( \frac{g_J\mu_0}{\hbar} \right)^2, \quad (108)$$

(106) agrees with (105) in the limit  $T_2''' \rightarrow 0$ , implying that the second species is completely disoriented. On the assumption that all the time constants are equal to 1 msec, (108) requires  $H_2' \gg 0.4$  milligauss. Thus when the resonance is saturated the polarization, obtained from an arbitrary density matrix, reduces to the diagonal-treatment value at equilibrium. The time required to reach equilibrium is related to  $T_{2e}$  for the off-diagonal contributions. If  $T_{2e}$  is made short—for example, by increasing the inhomogeneity of the static field—the coherence effects are damped out more rapidly, but a larger rf field must be applied to saturate the resonance. In general,  $T_{2e}$  should be made small compared with the period of switching the rf fields;  $H_2'$  is then chosen large enough to saturate the resonance, i.e., satisfy (108).

Although the frequency shifts and line shapes resulting from spin-exchange collisions can be seen and studied, nonetheless, the calculations of this section apply to realizable experiments in which these effects are unimportant. For a much more thorough demonstration of the unimportance of the off-diagonal matrix elements, see Refs. 12 and 18. This problem is difficult to treat in general, but it should be clear that if a state possesses no coherence initially it cannot acquire any by relaxation processes, which are random.

Even though it is unrelated to the discussion of this section, one other aspect of the paper by Balling *et al.*<sup>4</sup> may be worth mentioning. They state that they demonstrate in an appendix that their results are valid for general nuclear spin. However, using their Table IV and their Eq. (24) and making the simplifying assumptions that the second species is disoriented [i.e.,  $P(e)=0$ ] and that  $\rho(e,R)$  is diagonal, this author finds that  $dP_e(\text{Rb}^{87})/dt$  is not proportional to  $P_e(\text{Rb}^{87})$  as in their (A14), but rather arrives at the Eqs. (72) and (73) of Sec. III of this paper with  $I_1=\frac{3}{2}$ ,  $I_2=0$ . They have recently pointed out that their (A14) is in error.<sup>21</sup>

#### E. Anderson and Ramsey

Anderson and Ramsey<sup>8</sup> (AR) have performed an experiment to measure the self-spin-exchange cross section in sodium. The steady-state populations are needed to analyze their experiment, not just the electronic

<sup>20</sup> H. W. Moos and R. H. Sands, Phys. Rev. **135**, A591 (1964).

<sup>21</sup> L. C. Balling, R. J. Hanson, and F. M. Pipkin, Phys. Rev. **135**, AB1 (1964).

TABLE V. Comparison of population differences for the Anderson and Ramsey (AR) experiment (Ref. 8)  
 ( $T_{S1} \equiv 2T_2$ ,  $T_1''' \equiv T_1$ ,  $LC/2 \equiv A$ ,  $I_1 = \frac{3}{2}$ ; see IV E).

Anderson and Ramsey (uniform relaxation)	This work Zeeman or uniform relaxation ( $T_1' = \infty$ )	Electron randomization ( $T_1 = \infty$ )
$\delta_{AR} = \frac{-A \left( \frac{32}{T_1^2} + \frac{5.4}{T_1 T_2} + \frac{3.8}{T_2^2} \right)}{\left( \frac{8}{T_1} + \frac{2.78}{T_2} \right) \left( \frac{32}{T_1^2} + \frac{16.5}{T_1 T_2} \right)}$	$\frac{\pi_-}{p} = \frac{-AT_1}{8} \left( \frac{1}{T_1} + \frac{1}{4T_2} \right) \left( \frac{1}{T_1} + \frac{3}{8T_2} \right)^{-1}$	$\frac{\pi_-}{p} = \frac{AT_1'}{2}$
$(\rho_{1, \pm 1}/p = \frac{1}{8} \pm \delta_{AR})$	$= \frac{-A \left( \frac{32}{T_1^2} + \frac{8}{T_1 T_2} + \frac{4}{T_2^2} \right)}{\left( \frac{8}{T_1} + \frac{3}{T_2} \right) \left( \frac{32}{T_1^2} + \frac{16}{T_1 T_2} \right)}$	
$\beta_{AR} = \frac{A \left( \frac{32}{T_1^2} + \frac{27.6}{T_1 T_2} + \frac{3.8}{T_2^2} \right)}{\left( \frac{8}{T_1} + \frac{2.78}{T_2} \right) \left( \frac{32}{T_1^2} + \frac{16.5}{T_1 T_2} \right)}$	$\frac{\pi_+}{p} = \frac{AT_1}{8} \left( \frac{1}{T_1} + \frac{1}{4T_2} \right) \left( \frac{1}{T_1} + \frac{3}{8T_2} \right)^{-1}$	$\frac{\pi_+}{p} = \frac{\pi_-}{p}$
$(\rho_{2, \pm 1}/p = \frac{1}{8} \pm \beta_{AR})$	$= \frac{A \left( \frac{32}{T_1^2} + \frac{24}{T_1 T_2} + \frac{4}{T_2^2} \right)}{\left( \frac{8}{T_1} + \frac{3}{T_2} \right) \left( \frac{32}{T_1^2} + \frac{16}{T_1 T_2} \right)}$	
$\alpha_{AR} = \frac{A \left( \frac{64}{T_1^2} + \frac{44}{T_1 T_2} + \frac{7.6}{T_2^2} \right)}{\left( \frac{8}{T_1} + \frac{2.78}{T_2} \right) \left( \frac{32}{T_1^2} + \frac{16.5}{T_1 T_2} \right)}$	$\frac{2\pi_+}{p}$	$\frac{2\pi_+}{p}$
$(\rho_{2, \pm 2}/p = \frac{1}{8} \pm \alpha_{AR})$		

polarization. They define  $\rho_{1, \pm 1}/p = 1/8 \pm \delta_{AR}$ ,  $\rho_{2, \pm 1}/p = 1/8 \pm \beta_{AR}$ , and  $\rho_{2, \pm 2}/p = 1/8 \pm \alpha_{AR}$ .

It is shown in Appendix III that, if complete re-orientation occurs in the excited state ( $q \approx 0.8$  for Na in 3 cm of He at 154°C and with  $\sigma = 23 \times 10^{-16}$  cm<sup>2</sup> as determined by Jordan and Franken<sup>22</sup>),

$$\pi_{F_1 M_1} = M_1 \pi_{F_1}, \quad (109)$$

where  $\pi_{F_1 M_1}$  is defined in (81), and that

$$\pi_{\pm} = \pm (I_1 + \frac{1}{2}) p P_{\pm} / \sum_{M_1 = -I_1 \mp 1/2}^{I_1 \pm 1/2} M_1^2. \quad (110)$$

From (83) and (84) with  $T_{E1} = \infty$  (single species) and  $L_+ = L_- = L$  (complete mixing in the excited state), and using (110), one finds that at equilibrium

$$\pi_{\pm} = \frac{LCp \left( \frac{1}{2I_1+1} \left( \frac{1}{T_1'} + \frac{1}{T_{S1}} \pm \frac{2I_1+1}{2T_1'''} \right) \right)}{\frac{1}{T_1'} \left( \frac{1}{T_1'} + \frac{1}{T_{S1}'} \right) + \frac{4I_1^2+4I_1+3}{2T_1'''} \left( \frac{1}{T_1'} + \frac{2}{3T_{S1}'} \right) + \frac{(2I_1+1)^2}{2T_1'''^2}}. \quad (111)$$

Equation (111) as applied to the experiment of Anderson and Ramsey is given in Table V. Notice that if the

ground-state relaxation were by electron randomization only, the signals would be independent of the exchange time. Since they used 3 cm of He buffer gas, one might at first expect electron randomization to dominate.

<sup>22</sup> J. A. Jordan, Jr., and P. A. Franken, Bull. Am. Phys. Soc. 9, 90 (1964).

However, for a spherical cell,<sup>14</sup>

$$\tau_{\text{wall}} = R^2 \bar{p} / \pi^2 D_0 \bar{p}_0 \approx 100 \text{ msec}, \quad (112)$$

$$\tau_{\text{buffer}} = \bar{p}_0 / N_0 \sigma \bar{v} \bar{p} \approx 310 \text{ sec} \quad (113)$$

for Na in 3 cm of He at 154°C [ $D_0 = 1 \text{ cm}^2/\text{sec}$ ,  $\sigma = (3 \pm 4) \times 10^{-26} \text{ cm}^2$ ,  $R = 5 \text{ cm}$ ,  $\bar{v} = 1.6 \times 10^6 \text{ cm/sec}$ ,  $N_0 = 1.7 \times 10^{19} \text{ cm}^{-3}$ ].<sup>8</sup> The measured relaxation time was 87 msec, in excellent agreement with the wall relaxation time. Consequently, Zeeman or uniform relaxation may dominate; such would seem to be the case in light of the reasonable cross section deduced by Anderson and Ramsey assuming uniform relaxation.

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### APPENDIX I: JUSTIFICATION FOR NEGLECTING ONE OF THE SELF-EXCHANGE TERMS

Appendix I compares the quantities

$$I_1 = \int |f_t(\theta) - f_s(\theta)|^2 d\Omega \quad (A1)$$

and

$$I_2 = \int 2 \text{Re}[f_t^*(\theta) - f_s^*(\theta)] \times [f_t(\pi - \theta) - f_s(\pi - \theta)] d\Omega, \quad (A2)$$

which appear in (59). The author wishes to thank Dr. Sergje Lebedeff for outlining the following estimate.

Recall that<sup>2</sup>

$$f_n(\theta) = (1/2ik) \sum_{l=0}^{\infty} (2l+1) [\exp(2i\delta_{l,n}) - 1] P_l(\cos\theta), \quad (A3)$$

where  $n$  refers to  $t$  for triplet or  $s$  for singlet. Using the orthogonality properties of the Legendre polynomials, one finds

$$I_1 = (4\pi/k^2) \sum_l (2l+1) \sin^2(\delta_{l,t} - \delta_{l,s}) \quad (A4)$$

and

$$I_2 = (8\pi/k^2) \sum_l (-)^l (2l+1) \sin^2(\delta_{l,t} - \delta_{l,s}). \quad (A5)$$

In order to proceed with the calculation, one needs a model for estimating the phase shifts. Glassgold and Lebedeff<sup>2</sup> have found that cross sections predicted by the Purcell-Field model<sup>17</sup> agree with the results of

“exact” calculations to within a factor of 2. The Purcell-Field model divides all collisions into two classes: weak collisions ( $l > l_0$ ) for which there is no exchange and  $\langle \sin^2(\delta_{l,t} - \delta_{l,s}) \rangle = 0$ , and strong collisions ( $l < l_0$ ) for which  $\delta_{l,t} - \delta_{l,s}$  is large and random, with the result that  $\sin^2(\delta_{l,t} - \delta_{l,s})$  averages to  $\frac{1}{2}$ . Then

$$I_1 \rightarrow (2\pi/k^2) \sum_{l=0}^{l_0} (2l+1) = (2\pi/k^2)(l_0+1)^2, \quad (A6)$$

$$I_2 \rightarrow (4\pi/k^2) \sum_{l=0}^{l_0} (-)^l (2l+1) = (4\pi/k^2)(-)^{l_0}(l_0+1), \quad (A7)$$

and

$$I_2/I_1 \approx 2(-)^{l_0}/(l_0+1). \quad (A8)$$

Assuming a Lennard-Jones potential of range  $\sigma$  and depth  $\epsilon$ , the range of the strong collisions is approximately<sup>2</sup>

$$r_0 = \sigma \left\{ \frac{1}{5} [1 - (1 - 5K_0/4)^{1/2}] \right\}^{-1/6} \quad (A9)$$

and

$$l_0 + \frac{1}{2} = kr_0 \left\{ (6/5) [1 + (2/5K_0) \times (1 - (1 - 5K_0/4)^{1/2})] \right\}^{1/2}, \quad (A10)$$

where  $K_0 = E/\epsilon$ ,  $E = \hbar^2 k^2 / 2\mu$  is the kinetic energy in the center-of-mass system, and  $\mu$  is the reduced mass. At room temperature, for Rb<sup>87</sup>-Rb<sup>87</sup> collisions,  $E \approx 0.025 \text{ eV}$ ,  $\epsilon \approx 0.5 \text{ eV}$ ,  $\sigma \approx 4A \approx 7.6a_0$ ; then  $K_0 \approx 0.05 \ll 1$ . Therefore,  $r_0 \approx \sigma(8/K_0)^{1/6}$  and  $l_0 + \frac{1}{2} \approx (\frac{3}{2})^{1/2} k \sigma (8/K_0)^{1/6}$ ,

$$(ka_0)^2 = \frac{\mu}{m_e} \left( \frac{E}{\hbar^2 / 2m_e a_0^2} \right) = \frac{87}{2} (1836) \left( \frac{0.025}{13.6} \right),$$

$$ka_0 \approx 12,$$

$$l_0 \approx 260,$$

and

$$I_2/I_1 \approx 0.8\%. \quad (A11)$$

Thus for Rb<sup>87</sup>-Rb<sup>87</sup> collisions the interference term in (59) should be small compared with the other terms and can be neglected to a good approximation.

### APPENDIX II: SIMPLIFICATION OF THE RATE EQUATIONS IN THE LIMIT OF LOW LIGHT INTENSITY

The absorption, re-emission, and exchange terms of (63) are found in the limit of low light intensity, i.e., for  $\pi F_{M_1} \ll \bar{p} / 2(2I_1 + 1)$ .

#### A. Absorption and Re-emission

With

$$L\bar{p}_{F_{M_1}} \approx L\bar{p} / 2(2I_1 + 1), \quad (A12)$$

then

$$(\dot{P}_{\pm})_{\text{Abs}} \approx 2LC \sum_{M_1} M_1^2 / (2I_1 + 1)^3. \quad (A13)$$

TABLE VI. Values of  $\sum_{M_1=-F_1}^{F_1} M_1^2$ .

$F_1$	Values
$I_1 + \frac{1}{2}$	$(2I_1+1)(2I_1+2)(2I_1+3)/12$
$I_1 - \frac{1}{2}$	$(2I_1-1)2I_1(2I_1+1)/12$

Now consider the re-emission term of (63). Equation (20) becomes in the limit of low light intensity, i.e., for (A12),

$$m_{J_1'F_1'M_1'} \approx \frac{\dot{p}}{2(2I_1+1)} \times \sum_{F_1} P'(F_1M_1'-1, J_1'F_1'M_1') \delta_{J_1', 1/2}. \quad (\text{A14})$$

Then (19) indicates that the excited-state populations  $n_{J_1'F_1'M_1'}$  are independent of the deviations  $\pi_{F_1M_1}$  of the ground-state populations from  $\dot{p}/2(2I_1+1)$ , to first order in  $L$ . Therefore, in general, in order to include excited-state mixing of any amount and by any process,

$$(\dot{P}_{\pm})_{\text{Abs+Re}} \approx [2C \sum_{M_1} M_1^2 / (2I_1+1)^3] L_{\pm}. \quad (\text{A15})$$

$$(\dot{P}_{F_1})_E = -3P_{F_1}/4T_{E1} + (1/4T_{E1}) \sum_{F_1'} \Delta(F_1, F_1') \sum_{M_1'=-F_1'}^{F_1'} \frac{\pi_{F_1'M_1'} M_1' \Gamma(F_1, F_1')}{2(F_1-I_1)(I_1+\frac{1}{2})\dot{p}} + \frac{1}{2(F_1-I_1)(2I_1+1)^2 T_{E1} d} \sum_{\substack{F_1'M_1' \\ F_2'M_2' \\ F_2'M_2'M_1}} M_1 (\delta_{F_2'M_2'} - \delta_{F_2M_2}) W(I_1 I_2 F_1 M_1 F_2 M_2 F_1' M_1' F_2' M_2'), \quad (\text{A19})$$

where  $\Delta(F_1, F_1')$  is defined by (5),  $\Gamma(F_1, F_1')$  by (30), and

$$W(I_1 I_2 F_1 M_1 F_2 M_2 F_1' M_1' F_2' M_2') = \frac{\Delta(F_1, F_1') \Delta(F_2, F_2')}{4} \sum_q \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & q & M_1 \end{pmatrix}^2 \begin{pmatrix} F_2' & 1 & F_2 \\ -M_2' & -q & M_2 \end{pmatrix}^2 = W. \quad (\text{A20})$$

Table VII is useful in evaluating the second term in (A19). To evaluate the last term, interchange  $F_2, -M_2$  and  $F_2' M_2'$ :

$$\sum_{\substack{F_1'M_1' \\ F_2M_2 \\ F_2'M_2' \\ M_1}} M_1 \delta_{F_2'M_2'} W = \sum_{\substack{F_1'M_1' \\ F_2M_2 \\ F_2'M_2' \\ M_1}} M_1 \delta_{F_2, -M_2} W, \quad (\text{A21})$$

by Edmonds' (3.7.5). Table VIII contains the values of a quantity  $\alpha(F_1, F_1', q)$  arising in the above sums; then,

$$\sum M_1 \delta_{F_2M_2} W = \sum_{F_2M_2} \delta_{F_2M_2} \sum_{\substack{F_1'F_2' \\ M_1q}} \frac{\alpha(F_1, F_1', q) \alpha(F_2, F_2', -q) M_1}{4(2I_1+1)^2 (2I_2+1)^2}, \quad (\text{A22})$$

$$= \frac{16(F_1-I_1) \sum_{M_1} M_1^2}{(2I_1+1)(2I_2+1)} \sum_{F_2M_2} (F_2-I_2) M_2 \delta_{F_2M_2}. \quad (\text{A23})$$

The quantities

$$L_{\pm} = L \left[ 1 \pm \frac{(2I_1+1)^2}{C \dot{p} \sum_{M_1} M_1^2} \sum_{J_1'F_1'M_1'} \left( \frac{n_{J_1'F_1'M_1'}}{L} \right) \times \sum_{M_1} \frac{M_1 P''(J_1'F_1'M_1', F_1M_1)}{\tau_{J_1'}} \right] \quad (\text{A16})$$

are independent of the ground-state populations to first order in  $L$ . For complete mixing within each  $J_1'$  level,

$$(n_{J_1'F_1'M_1'}) = n_{J_1'} / (2J_1'+1)(2I_1+1); n_{J_1'} = \sum_{F_1'M_1'} n_{J_1'F_1'M_1'},$$

one has  $L_{\pm} = L$ , since  $\sum_{M_1} P''(J_1'F_1'M_1', F_1M_1)$  is independent of  $M_1$  and  $\sum_{M_1} M_1 = 0$ .

Equations (A15) become, if one uses Table VI,

$$(\dot{P}_{+})_{\text{Abs+Re}} = (2I_1+2)(2I_1+3)L_+C/6(2I_1+1)^2, \quad (\text{A17})$$

$$(\dot{P}_{-})_{\text{Abs+Re}} = (2I_1-1)2I_1L_-C/6(2I_1+1)^2. \quad (\text{A18})$$

## B. Cross Exchange

Equations (81) and (82) in (44) yield, to first order in  $L$ ,

TABLE VII. Values of  $(2I_1+1)^2\Gamma(F_1,F_1')\Delta(F_1,F_1')$ .

		$F_1'$	
$F_1$	$I_1+\frac{1}{2}$	$I_1+\frac{1}{2}$	$I_1-\frac{1}{2}$
$I_1+\frac{1}{2}$	$4I_1^2+8I_1-1$	$2(2I_1+2)$	$2(2I_1+3)$
$I_1-\frac{1}{2}$	$4I_1(2I_1-1)$	$4I_1^2-5$	

Substituting (81) into (13), one has

$$P_{F_1} = 2(F_1 - I_1) \sum_{M_1=-F_1}^{F_1} M_1 \pi_{F_1 M_1} / (I_1 + \frac{1}{2}) p, \quad (\text{A24})$$

$$D_{F_2} = 2(F_2 - I_2) \sum_{M_2=-F_2}^{F_2} M_2 \delta_{F_2 M_2} / (I_2 + \frac{1}{2}) d. \quad (\text{A25})$$

Equations (A24) and (A25) in (A19) with (A21) and (A23) gives

$$(\dot{P}_+)_{E1} \approx \frac{(2I_1+2)(2I_1+3)}{6(2I_1+1)^2 T_{E1}} (D_+ + D_- - 3P_-) - \frac{(2I_1^2 + I_1 + 1)}{(2I_1+1)^2 T_{E1}} P_+, \quad (\text{A26})$$

$$(\dot{P}_-)_{E1} \approx \frac{2I_1(2I_1-1)}{6(2I_1+1)^2 T_{E1}} (D_+ + D_- - 3P_+) - \frac{(2I_1^2 + 3I_1 + 2)}{(2I_1+1)^2 T_{E1}} P_-. \quad (\text{A27})$$

### C. Self Exchange

Examination of (63) reveals that

$$(\dot{P}_{\pm})_{S1} = (\dot{P}_{\pm})_E \Big|_{\substack{D_{\pm} = P_{\pm} \\ T_{E1} = T_{S1}}} \approx \frac{-2I_1(2I_1-1)P_+}{3(2I_1+1)^2 T_{S1}} - \frac{(2I_1+2)(2I_1+3)P_-}{3(2I_1+1)^2 T_{S1}}, \quad (\text{A28})$$

in the limit of low light intensity.

TABLE VIII. Values of

$$\alpha(F_1, F_1', q) = (2I_1+1)^2 \Delta(F_1, F_1') \sum_{M_1'} \begin{pmatrix} F_1' & 1 & F_1 \\ -M_1' & q & M_1 \end{pmatrix}^2.$$

$F_1$	$q$	$I_1+\frac{1}{2}$	$F_1'$	$I_1-\frac{1}{2}$
$I_1+\frac{1}{2}$	1	$2(I_1+\frac{3}{2}+M_1)(I_1+\frac{1}{2}-M_1)$	$2(I_1-\frac{1}{2}-M_1)(I_1+\frac{1}{2}-M_1)$	$4(I_1+\frac{1}{2}+M_1)(I_1+\frac{1}{2}-M_1)$
	0	$4M_1^2$	$4(I_1+\frac{1}{2}+M_1)(I_1+\frac{1}{2}-M_1)$	
	-1	$2(I_1+\frac{3}{2}-M_1)(I_1+\frac{1}{2}+M_1)$	$2(I_1+\frac{1}{2}+M_1)(I_1-\frac{1}{2}+M_1)$	
$I_1-\frac{1}{2}$	1	$2(I_1+\frac{3}{2}+M_1)(I_1+\frac{3}{2}+M_1)$	$2(I_1+\frac{1}{2}+M_1)(I_1-\frac{1}{2}-M_1)$	$4M_1^2$
	0	$4(I_1+\frac{3}{2}+M_1)(I_1+\frac{1}{2}-M_1)$	$4M_1^2$	
	-1	$2(I_1+\frac{1}{2}-M_1)(I_1+\frac{3}{2}-M_1)$	$2(I_1+\frac{1}{2}-M_1)(I_1-\frac{1}{2}+M_1)$	

### APPENDIX III: EXPRESSION OF THE POPULATION DIFFERENCES IN TERMS OF THE POLARIZATIONS IN THE LIMIT OF COMPLETE MIXING

In this Appendix it is shown that  $\pi_{F_1 M_1} = M_1 \pi_{F_1}$  in equilibrium if there is complete mixing in the excited state. Since this proof is of interest in connection with the experiment of Anderson and Ramsey<sup>8</sup> in which a single species is present, set  $T_{E1} = \infty$  in (1). Substituting (81) into (1), one finds, with the aid of the discussions of the various terms given in Sec. II,

$$\begin{aligned} \dot{\pi}_{F_1 M_1} &= \alpha(F_1) M_1 + \beta(F_1 M_1) \pi_{F_1 M_1} \\ &+ \sum_{F_1' M_1'} \gamma(F_1' M_1', F_1 M_1) \pi_{F_1' M_1'} = 0, \quad (\text{A29}) \end{aligned}$$

where  $\beta(F_1, -M_1) = \beta(F_1, M_1)$  and  $\gamma(F_1', -M_1'; F_1, -M_1) = \gamma(F_1' M_1', F_1 M_1)$ . Then

$$\begin{aligned} \dot{\pi}_{F_1, -M_1} &= -[\alpha(F_1) M_1 + \beta(F_1 M_1) (-\pi_{F_1, -M_1}) \\ &+ \sum_{F_1' M_1'} \gamma(F_1' M_1', F_1 M_1) (-\pi_{F_1', -M_1'})] = 0. \quad (\text{A30}) \end{aligned}$$

Comparison of (A30) with (A29) reveals  $\pi_{F_1, -M_1} = -\pi_{F_1 M_1}$ ; i.e., an expansion of  $\pi_{F_1 M_1}$  in  $M_1$  must be odd.

Set  $T_{E1} = \infty$  and  $L_+ = L_-$  (complete mixing) in (83) and (84) and find, at equilibrium,

$$P_- = \frac{-2I_1(2I_1-1)}{(2I_1+2)(2I_1+3)} \frac{\left( \frac{1}{T_1'} + \frac{1}{T_{S1}} - \frac{2I_1+1}{2T_1'''} \right)}{\left( \frac{1}{T_1'} + \frac{1}{T_{S1}} + \frac{2I_1+1}{2T_1'''} \right)} P_+, \quad (\text{A31})$$

i.e.,  $\sum_{M_1'} M_1' \pi_{F_1' M_1'} \propto \sum_{M_1} M_1 \pi_{F_1 M_1}$  for both values of  $F_1'$ . Equation (83) or (84) can then be written, for equilibrium,

$$\sum_{M_1} M_1 \pi_{F_1 M_1} = a(F_1) L \sum_{M_1} M_1^2, \quad (\text{A32})$$

where (A15) has been used for the radiation term. Since  $\pi_{F_1 M_1}$  must be an odd function of  $M_1$ , one has

$$\pi_{F_1 M_1} = M_1 \pi_{F_1}, \quad (\text{A33})$$

where  $\pi_{F_1}$  is independent of  $M_1$ . (A33) in (A24) results in

$$\pi_{F_1} = (I_1 + \frac{1}{2}) p P_{F_1} / 2(F_1 - I_1) \sum_{M_1} M_1^2. \quad (\text{A34})$$