

## Effect of spin exchange on the ground-state density matrix of alkali-metal and hydrogen atoms

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A comparison of various methods of calculation of the effect of spin-exchange interaction on the density matrix of hydrogen and alkali-metal atoms in their ground state is made. The elements connected to the  $(F, m_F=0) \leftrightarrow (F-1, m_F=0)$  transition are calculated. Matrices necessary for the calculation of any other element are also given.

### INTRODUCTION

When two atoms are close to each other, the identity of their electrons gives rise to the phenomenon of spin exchange. This phenomenon has been studied extensively both theoretically and experimentally by the magnetic resonance technique in hydrogen and vapors of alkali-metal atoms in their ground state.<sup>1</sup> The effect of spin exchange is to alter the population of the various  $(F, m_F)$  sublevels and to produce a small displacement of these levels. The calculation of these effects can be made in several ways. Many articles have been published on the subject. Unfortunately, the connection between these various calculations has not been made clear. In this paper some of these methods of calculation are summarized and their interconnection is made explicit. We also make comments on the relative difficulty of these calculations, give the general expression for the frequency shift in the  $(F, m_F=0) \leftrightarrow (F-1, m_F=0)$  transition, and give tables of matrices which are useful in the calculation. Some of these matrices have been published before<sup>2</sup> but appear to contain errors.

### METHODS OF CALCULATION

The effect of spin exchange on the wave function and density matrix of hydrogen and alkali-metal atoms can be obtained by means of the spin-exchange operator  $E_x$  defined as

$$E_x = F_d + F_x \sigma_1 \cdot \sigma_2, \tag{1}$$

where  $F_d$  and  $F_x$  are the direct and exchange scattering amplitudes of the wave function  $\psi$  and  $\sigma_1$  and  $\sigma_2$  are the Pauli matrices of the electron spin of the two colliding atoms. Neglecting the identity of the nuclei, which is a good approximation at high temperatures, a partial-wave analysis gives

$$F_d = \frac{1}{4} f_s + \frac{3}{4} f_t, \tag{2a}$$

$$F_x = \frac{1}{4} (f_t - f_s), \tag{2b}$$

with

$$f_{s,t} = \frac{1}{2ik} \sum_{l=0}^{\infty} (2l+1) (e^{2i\eta_{l,t}} - 1) P_l(\cos\theta), \tag{3}$$

where  $\eta_l^s$  and  $\eta_l^t$  are the phase shifts introduced in the partial wave  $l$  by the singlet and triplet potentials, respectively. Under the effect of  $E_x$  we have

$$\psi^c = E_x \psi^i, \tag{4}$$

$$\rho^c = E_x \rho^i(1, 2) E_x^\dagger, \tag{5}$$

where  $E_x^\dagger$  is the adjunct matrix of  $E_x$ . The superscript  $i$  is used to identify the state of the atoms before collision and  $c$  refers to the state after collision. The density matrix  $\rho^i(1, 2)$  stands for the direct product:

$$\rho^i(1, 2) = \rho_1 \times \rho_2, \tag{6}$$

where  $\rho_1$  and  $\rho_2$  are the initial density matrices of the individual atoms. If each matrix is of order  $n$  the combined matrix is of order  $n^2$ . The final effect of the spin exchange is obtained by taking the trace of the resulting matrix, over one of the atoms:

$$\rho_1^c = \text{Tr}_2 \rho^c. \tag{7}$$

#### A. Matrix multiplication method

In the first method that was used in this field, the calculations are done directly with Eq. (5). The numerical value of the matrix elements are made explicit for each particular case considered. The matrix multiplications are then developed in detail. The size of the matrices that need to be handled goes up rapidly with the nuclear spin of the atom studied. For example, in the case of hydrogen-hydrogen collisions with  $I = \frac{1}{2}$  the matrices are  $16 \times 16$ . In the case of rubidium-rubidium collisions, one deals with

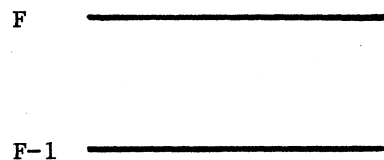


FIG. 1. Notation used for identifying the levels.

64 × 64 matrices and the calculations are extremely tedious. Nevertheless, such a calculation has been performed for several matrix elements of interest in the field of atomic frequency standards.<sup>3</sup>

### B. Analytical method

In the second method the spin matrices are left in their analytical form. The contraction is done without making explicit the actual numerical values of the matrix elements. The expression obtained is somewhat complicated but the size of the matrices to be handled is more reasonable. The resulting expression is

$$\rho'_i = \left[ \frac{1}{4} \left( 4 - 3 \sin^2 \frac{\delta}{2} \right) \rho_1 + \frac{1}{4} \sin^2 \frac{\delta}{2} \sum_{\beta} \sigma_{\beta} \rho_1 \sigma_{\beta} + \frac{1}{4} \left( \sin^2 \frac{\delta}{2} \right) \sum_{\beta} (\sigma_{\beta} \rho_1 + \rho_1 \sigma_{\beta}) \text{Tr}_2(\sigma_{\beta} \rho_2) \right. \\ \left. - \frac{1}{4} \left( \sin^2 \frac{\delta}{2} \right) \sum_{\alpha} i (\sigma_{\alpha} \rho_1 \sigma_{\beta} - \sigma_{\beta} \rho_1 \sigma_{\alpha}) \text{Tr}_2(\sigma_{\gamma} \rho_2) \right] + i \left[ \frac{1}{4} (\sin \delta) \sum_{\beta} (\sigma_{\beta} \rho_1 - \rho_1 \sigma_{\beta}) \text{Tr}_2(\sigma_{\beta} \rho_2) \right] , \quad (8)$$

where  $\delta$  stands for  $2(\eta'_i - \eta_i)$  and the Greek index on  $\sigma$  stands for  $x, y,$  or  $z$ . In the fourth term it is understood that a permutation of  $\alpha, \beta,$  and  $\gamma$  is to be made.

At this stage two approaches are possible.

(1) In the first approach, one evaluates each matrix element  $\rho_{ij}$ .<sup>4</sup> The matrix elements required are then those of the Pauli matrices in the  $(F, m_F)$  representation. They can be obtained from a table published by Feld and Lamb.<sup>5</sup> They are given in Table I,<sup>4</sup> the notation used being that made explicit in Fig. 1. In many applications, the effect of spin exchange on the  $(F, 0) \leftrightarrow (F-1, 0)$  transition is desired. This is the case, for example, of atomic frequency standards in which the reference frequency is derived from the so-called magnetic-field-independent transition. A direct application of Eq. (8) using the matrix elements of the Pauli matrices shown in Table I gives for the time evolution of the population difference of the two levels involved, for a single species of atoms

$$\frac{d}{dt} (\rho_{F,0;F,0} - \rho_{F-1,0;F-1,0}) = -n\bar{v}_r \bar{\sigma}_{\text{ex}} (\rho_{F,0;F,0} - \rho_{F-1,0;F-1,0}) , \quad (9)$$

where  $n$  is the density,  $\bar{v}_r$  the relative speed of the atoms, and  $\bar{\sigma}_{\text{ex}}$  stands for  $\langle \sigma \sin^2(\delta/2) \rangle$ , the spin-exchange cross section. The average is made over all  $\delta$ 's. It is observed that the time evolution of the population difference of the  $(F, 0), (F-1, 0)$  levels is exponential, independent of the coherence existing between them, and also independent of the nuclear spin.

For the coherence we have, in the interaction picture,

$$\frac{d}{dt} (\rho'_{F,0;F-1,0}) = -n\bar{v}_r \left[ \bar{\sigma}_{\text{ex}} \left( \frac{3}{4} - \frac{F+1}{8F} (\rho_{F,1;F,1} + \rho_{F,-1;F,-1}) - \frac{F-1}{8F} (\rho_{F-1,1;F-1,1} + \rho_{F-1,-1;F-1,-1}) \right) \right. \\ \left. - \frac{1}{4} (\rho_{F,0;F,0} + \rho_{F-1,0;F-1,0}) \right] - i\bar{\lambda}_{\text{ex}} (\rho_{F,0;F,0} - \rho_{F-1,0;F-1,0}) \rho'_{F,0;F-1,0} . \quad (10)$$

The imaginary term produces a small frequency shift in the transition considered. The parameter  $\bar{\lambda}_{\text{ex}}$  stands for,  $\langle \frac{1}{4} \sigma \sin \delta \rangle$ , the frequency shift spin-exchange cross section.

These results are in complete agreement with those reported by one of the authors in Ref. 3, in which the first method was used to obtain the effect of spin exchange in <sup>87</sup>Rb in a very lengthy calculation.

(2) In the second avenue, which may be qualified as intermediate between the first method (A), and the analytical one just presented, the  $\sigma$  matrices are first calculated in the  $(F, m_F)$  representation. This is the approach proposed by Valberg,<sup>2</sup> who has given the spin matrices up to the case  $I = \frac{3}{2}$ . Unfortunately some of the matrices given by the author<sup>2</sup> are not exact. This may cause some confusion if one wants to use them in a particular calculation. We give, in Table II, an example for the case  $I = 1$ .<sup>6</sup>

### SUMMARY

In the calculation of spin-exchange effects on the density matrix of hydrogen and alkali-metal atoms in their ground state, it appears that much simplification results if the con-

TABLE I. Analytical expression of the Pauli matrices in the  $(F, m_F)$  representation ( $\sigma^+ = \sigma_x + i\sigma_y, \sigma^- = \sigma_x - i\sigma_y$ ) [after Grossetête (Ref. 4) and Feld and Lamb (Ref. 5)].

$\langle F, m   \sigma^z   F, m \rangle = m/F$
$\langle F, m   \sigma^z   F-1, m \rangle = -(F^2 - m^2)^{1/2}/F$
$\langle F, m   \sigma^-   F, m+1 \rangle = [(F-m)(F+m+1)]^{1/2}/F$
$\langle F, m   \sigma^-   F-1, m+1 \rangle = -[(F-m)(F-m-1)]^{1/2}/F$
$\langle F, m   \sigma^+   F, m-1 \rangle = [(F+m)(F-m+1)]^{1/2}/F$
$\langle F, m   \sigma^+   F-1, m-1 \rangle = [(F+m)(F+m-1)]^{1/2}/F$
$\langle F-1, m   \sigma^z   F-1, m \rangle = -m/F$
$\langle F-1, m   \sigma^z   F, m \rangle = -(F^2 - m^2)^{1/2}/F$
$\langle F-1, m   \sigma^-   F-1, m+1 \rangle = -[(F-m-1)(F+m)]^{1/2}/F$
$\langle F-1, m   \sigma^-   F, m+1 \rangle = [(F+m)(F+m+1)]^{1/2}/F$
$\langle F-1, m   \sigma^+   F-1, m-1 \rangle = -[(F+m-1)(F-m)]^{1/2}/F$
$\langle F-1, m   \sigma^+   F, m-1 \rangle = -[(F-m)(F-m+1)]^{1/2}/F$

TABLE II. Example of Pauli spin matrices in the  $\{F, m_F\}$  representation used in spin-exchange calculation for the case  $I=1$ .

$F$	$m$		$\sigma_x$					
			$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
			$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$
		$\frac{1}{3} \times$	$\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 & 0 & \sqrt{6} \\ \sqrt{3} & 0 & 2 & 0 & \sqrt{2} & 0 \\ 0 & 2 & 0 & \sqrt{3} & 0 & -\sqrt{2} \\ 0 & 0 & \sqrt{3} & 0 & -\sqrt{6} & 0 \\ 0 & \sqrt{2} & 0 & -\sqrt{6} & 0 & -1 \\ \sqrt{6} & 0 & -\sqrt{2} & 0 & -1 & 0 \end{pmatrix}$					
		$\frac{1}{3} \times$	$\begin{pmatrix} 0 & \sqrt{3} & 0 & 0 & 0 & \sqrt{6} \\ -\sqrt{3} & 0 & 2 & 0 & \sqrt{2} & 0 \\ 0 & -2 & 0 & \sqrt{3} & 0 & \sqrt{2} \\ 0 & 0 & -\sqrt{3} & 0 & \sqrt{6} & 0 \\ 0 & -\sqrt{2} & 0 & -\sqrt{6} & 0 & 1 \\ -\sqrt{6} & 0 & -\sqrt{2} & 0 & -1 & 0 \end{pmatrix}$					
		$\frac{1}{3} \times$	$\begin{pmatrix} 3 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & -2\sqrt{2} \\ 0 & 0 & -1 & 0 & -2\sqrt{2} & 0 \\ 0 & 0 & 0 & -3 & 0 & 0 \\ 0 & 0 & -2\sqrt{2} & 0 & 1 & 0 \\ 0 & -2\sqrt{2} & 0 & 0 & 0 & -1 \end{pmatrix}$					

traction to a single atom is made first in an analytical way [method (B)]. In this method the matrices to be used are of order  $4(I + \frac{1}{2})$  rather than  $16(I + \frac{1}{2})^2$  in the case where the contraction is made at the end of the calculation. The method used by Grossetête<sup>4</sup> in which algebraic expressions are obtained for the various matrix elements has the advantage of being general but becomes quite involved if off-diagonal elements are present. On the other hand, the

method proposed by Valberg consists of straightforward matrix multiplication in which any element may be included but may be somewhat lengthy in the case of high values of the nuclear spin. The method to be used has thus to be chosen according to the particular problem at hand. When no coherence exists the algebraic expressions are best to use, while when such coherences are present it appears simpler to use the matrix multiplication method.

<sup>1</sup>For basic work on the subject the reader is referred to the following articles: J. P. Wittke and R. H. Dicke, Phys. Rev. **103**, 620, (1956); P. L. Bender, *ibid.* **136**, 2154 (1964); L. C. Balling, R. J. Hanson, and F. M. Pipkin, *ibid.* **133**, 607 (1964); N. W. Ressler, R. H. Sands, and T. E. Stark, *ibid.* **184**, 102 (1969).

<sup>2</sup>P. A. Valberg, Phys. Rev. A **3**, 505 (1971).

<sup>3</sup>J. Vanier, Phys. Rev. **168**, 129 (1968).

<sup>4</sup>F. Grossetête, Ph.D. dissertation, Université de Paris, 1967 (Centre National de la Recherche Scientifique Reg. No. A01263); J. Phys. **25**, 383 (1964); **29**, 456 (1968).

<sup>5</sup>B. T. Feld and W. E. Lamb, Jr., Phys. Rev. **67**, 15 (1945).

<sup>6</sup>See AIP document No. PAPS PLRAA-31-3967-21 for 21 pages of material which includes a complete set of these matrices for the cases  $I = \frac{1}{2}$  to  $I = \frac{7}{2}$ . Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for microfiche, or \$5.00 for a photocopy up to 30 pages, and \$0.15 for each additional page. Airmail additional. Make checks payable to the American Institute of Physics.