Merging resonant frequencies and changing the sign of the g-factors of different atoms with frequent spin exchange

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Abstract. The paper discusses the high-temperature spin-exchange of a mixture of vapors of alkali metals. It is shown that in a small magnetic field, an increase in temperature can lead to a sharp decrease in the frequency of transverse relaxation and to a significant decrease in the frequency of oscillation of the angular moments of atomic sublevels. Such changes in relaxation and frequency are well known in the case of a vapor of a single alkali metal. New in the case of a mixture was the merging of the resonance frequencies of different atoms into one frequency, which is the frequency of rotation of the total angular momentum of the atoms of the mixture. It also turned out that with an increase in temperature, the sign of the g-factors of atoms changes.

1. Introduction

Almost half a century has passed since Happer and Tang [1] discovered in the experiment a surprising feature of the spin exchange of alkali atoms — a decrease in the transverse relaxation rate with increasing temperature in a small magnetic field. A decrease occurs when the frequency of the spin exchange exceeds the Larmor frequency of the atoms. At the same time [2] a detailed theory of this phenomenon was developed. After a quarter of a century, this phenomenon was used [3–5] to create supersensitive magnetometers and was called SERF (Spin Exchange Relaxation Free - Spin Exchange Without Relaxation). The purpose of this work was to study a similar phenomenon in a mixture of alkali metal vapours.

2. The equation of spin-exchange in a mixture of vapours of alkali metals

The alkali metal atoms in the ground state of the \( ^2S_{1/2} \) state have two sublevels of the superfine structure, differing in the value of the quantum number \( F \) of the total angular momentum: \( F^z = I \pm 1/2 \) (\( I \) is the spin of the nucleus.)

The evolution of the density matrix of alkali atoms due to pair spin-exchange collisions is described by well-known nonlinear kinetic equations [6–9]. The linearization of these equations allows one to obtain the equation [9] for describing the evolution of orientation \( f_{i, q}^A (F_A) \) and \( f_{i, q}^B (F_B) \) of alkali atoms A and B due to their spin-exchange collisions. In the matrix form, these equations have the form:
\[
\left[ \frac{\partial}{\partial t} X^{AB}(q) \right]_{AB} = M^{AB} X^{AB}(q) \tag{1}
\]

\[
M^{AB} = \begin{bmatrix}
\bar{v}_{AA} G^A + \bar{v}_{AB} \Gamma^A & \bar{v}_{AB} T^{AB} \\
\bar{v}_{BA} T^{BA} & \bar{v}_{BB} G^B + \bar{v}_{BA} \Gamma^B
\end{bmatrix}
\tag{2}
\]

The column of unknowns in formula (1) in transposed form looks like this:

\[
\left[ X^{AB}(q) \right]^T = \{ f_{1,q}^A \left( F^+ \right) f_{1,q}^B \left( F^+ \right) \}.
\tag{3}
\]

The cyclic components \((q = 0, \pm 1)\) of orientation vectors are determined by the relation [10]:

\[
f_{1,q}(F) = (2F + 1)^{1/2} \sum_{MM'} (-1)^{F-M} \begin{pmatrix} F & F & 1 \\ M & -M' & q \end{pmatrix} f_{FM,FM'},
\tag{4}
\]

in which \(f_{FM,FM'}\) - the density matrix of the atom in the usual \((FM, F'M')\) - representation.

The matrix \(M^{AB}\) in equation (1) was obtained with allowance for collisions \(A+B, A+A, \text{ and } B+B\). Formula (2) gives the connection of the matrix \(M^{AB}\) with the matrices \(\Gamma^A\) and \(T^{AB}\). These matrices with dimension \(2 \times 2\) are explicitly presented in [9]. In Table 1 of work [9] for the matrix \(\Gamma^A\) there is a typo. To eliminate it, all elements of this table should be divided by 4. The matrix \(\Gamma^A\) in (2) gives equality: \(G^A = \Gamma^A + T^{AA}\).

The formula (2) includes the spin-exchange frequency \(\bar{v}_{AB}\) in collisions of atoms \(A\) and \(B\):

\[
\bar{v}_{AB} = \langle v_{AB} \rangle \sigma_{01} N_B,
\tag{5}
\]

Here \(\langle v_{AB} \rangle = \left(8k_B T / \pi \mu_{AB} \right)^{1/2}\) the average relative velocity of atoms \(A\) and \(B\) (\(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(\mu_{AB}\) is the reduced mass of the atoms \(A\) and \(B\)), \(\sigma_{01}^{AB}\) is the spin-exchange cross section of the atoms \(A\) and \(B\), \(N_B\) is the concentration of atoms \(B\). The remaining spin-exchange frequencies in (2) are obtained from formula (4) by replacing the letters \(A\) and \(B\).

The orientation vector \(f_{1,q}(F)\) of an atom on the \(F\)-sublevel is connected by a simple relation with the average quantum mechanical value \(\hat{F}_q\) of the angular momentum of the atom in the \(F\)-state and the total angular momentum \(\hat{\Phi}_q\) of the atom:

\[
\langle \hat{F}_q \rangle_F = (-1)^q \left[ F (F + 1) \right]^{1/2} f_{1,q}(F), \quad \langle \hat{\Phi}_q \rangle = \sum_F \langle \hat{F}_q \rangle_F.
\tag{6}
\]

The total angular momentum \(\langle \hat{\Phi}_q^{AB} \rangle\) of a mixture of atoms \(A\) and \(B\) can be obtained taking into account the fractions \(\alpha_A = N_A / (N_A + N_B)\) and \(\alpha_B = 1 - \alpha_A\) of these atoms in the mixture:

\[
\langle \hat{\Phi}_q^{AB} \rangle = \alpha_A \langle \hat{\Phi}_q^A \rangle + \alpha_B \langle \hat{\Phi}_q^B \rangle.
\tag{7}
\]

3. The evolution of the orientation of atoms in constant and alternating magnetic fields

The evolution of orientation in an arbitrary magnetic field \(H\) with cyclic components \(H_q(q = 0, \pm 1)\) is described by the equation [11]:

\[
\left[ \frac{\partial}{\partial t} f_{1,q}(F) \right]_H = -ig(F) \mu_0 \left[ \left[ (1 + q)(2 - q) / 2 \right]^{1/2} H_{-1} f_{1,q-1}(F) + q H_0 f_{1,q} - \left[ (1 - q)(2 + q) / 2 \right]^{1/2} H_{-1} f_{1,q+1}(F) \right],
\tag{8}
\]
here \( g \left( F^\pm \right) = \mp 2 / (2I + 1) \) are the g-factors of the \( F^\pm \) states, \( \mu_0 = \mu_B / h \), \( \mu_B \) is the Bohr magneton.

In a constant field \( \mathbf{H} \), directed along the \( z \) axis, this formula gives the equation:

\[
\left[ \frac{\partial}{\partial t} f_{1,q}(F) \right]_{H_0} = -iqg(F)\mu_0H_0f_{1,q}(F).
\] (7)

In this paper, the excitation of resonances by a rotating magnetic field is considered. Such a field, in contrast to the usual oscillating radio frequency (RF) field, makes it possible to observe separately the resonances of paramagnetic materials that differ only in the signs of g-factors.

The right rotating magnetic field \( \mathbf{h}^R \) is given by the relations:

\[
h^R_x = h_0 \sqrt{2} \cos \omega t, \quad h^R_y = h_0 \sqrt{2} \sin \omega t
\] (8)

or in covariant cyclic coordinates:

\[
h^R_0 = \mp h_0 \exp(\pm i\omega t).
\]

Formula (6) for such a field gives the following equation:

\[
\left[ \frac{\partial}{\partial t} f_{1,q}(F) \right]_{h} = -i \left( 1 - \delta_{q,0} \right) g(F)\mu_0 h_0 f_{1,0}(F) \exp(i\omega t).
\] (9)

Replacing \( \omega \rightarrow -\omega \) in formulas (8) and (9) changes the direction of rotation of the field to the opposite, that is, it gives a left-rotating field.

4. Spin exchange in a constant field \( H_0 \)

For a mixture of alkali atoms \( A + B \), formulas (1) and (7) give the equation:

\[
\frac{d}{dt} X^{AB}(q) = \hat{M}^{AB}(q) X^{AB}(q),
\] (10)

\[
\hat{M}^{AB}(q) = M^{AB} - iq\mu_0 H_0 N^{AB},
\] (11)

\[
N^{AB} = \begin{bmatrix} N^A & 0 \\ 0 & N^B \end{bmatrix}, \quad N^A = \begin{bmatrix} g(F^+_A) & 0 \\ 0 & g(F^-_A) \end{bmatrix}, \quad [0]_2 = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}.
\]

5. Spin-exchange under conditions of resonance, excited by a rotating field.

Complementing equation (10) with formula (9), we obtain the following equation for the evolution of transverse orientations in longitudinal and rotating magnetic fields:

\[
\frac{d}{dt} X^{AB}(q) = \hat{M}^{AB}(q) X^{AB}(q) - i \left( 1 - \delta_{q,0} \right) \mu_0 h_0 X^{AB}(0) \exp(i\omega t).
\] (12)

On the right side of the equation is a column \( X^{AB}(0) \) of longitudinal orientations created by the pump light. In addition to light, these orientations depend on the RF field and on the transverse orientations \( X^{AB}(\pm 1) \) it creates. The calculation of all component orientations in an optically dense vapour is a very difficult task.

Therefore, in the present work, the longitudinal orientations will be considered as given by the value of the parameter \( \beta \) of the spin temperature. This is justified [12], when the contribution of spin-exchange collisions to the evolution of the density matrix is much greater than the contribution of pumping light and magnetic fields. Preserving the total moment in a longitudinal magnetic field makes it possible to write the density operator \( \hat{f}^A \) of an ensemble of atoms A in the form

\[
\hat{f}^A = C_A(\beta) \exp(\beta \hat{F}^A_{z}).
\] (13)

From here we get the well-known expression for the diagonal elements of the density matrix
\[ f_{_{A,M_1,M_2}}^A = C_A(\beta) \exp(\beta M_A), \quad C_A(\beta) = \left[ \sum_{M_A} \exp(\beta M_A) \right]^{-1} \]  
\( \text{(14)} \)

and for the longitudinal orientation of the \( F_A \)-sublevel (using formula (3))

\[ f_{_{L,0}}^A(F_A) = C_A(\beta) \left[ F_A(F_A + 1) \right]^{-1/2} \sum_{M_A = -F_A}^{F_A} M_A \exp(\beta M_A). \]

In the case of a mixture of alkali atoms A and B, instead of (13), expression (5) can be applied to the mixture density operator \( \hat{\rho}_{AB} \), which takes into account the proportions of atoms A and B:

\[ \hat{\rho}_{AB} = C_{AB} \exp(\beta \hat{\rho}_{AB}) = C_{AB} \exp(\beta \alpha_A \hat{\rho}_{A}) \exp(\beta \alpha_B \hat{\rho}_{B}). \]

From this expression, a formula is obtained for the density matrix of atoms A:

\[ f_{_{A,M_1,M_2}}^A = C_A(\beta \alpha_A) \exp(\beta \alpha_A M_A), \quad C_A(\beta \alpha_A) = \left[ \sum_{M_A} \exp(\beta \alpha_A M_A) \right]^{-1}. \]  
\( \text{(15)} \)

From the comparison of formulas (14) and (15) it follows that the expression for the density matrix of atoms A in a mixture can be obtained simply by multiplying the parameter \( \beta \) in formulas (14) by the value \( \alpha_A \). The expressions for atoms B in the mixture are obtained from the expressions for atoms A by replacing the letters in them: \( A \rightarrow B \). In the same way, using formula (3), we can also obtain expressions for the longitudinal orientations of atoms A and B in the mixture.

Note that the specification of the values of the longitudinal orientations of the atoms A and B by the parameter \( \beta \) makes the spin-exchange equation (12) non-uniform.

6. Finding solutions to the spin-exchange equations.

The algorithm for solving a system of linear differential equations similar to equation (12) is well known [13].

To solve a system of \( n \) inhomogeneous equations

\[ dX/dt = \tilde{M}X + Ye^{i\omega t} \]

we must first find a solution to the system (10) of homogeneous equations \( d\tilde{X}/dt = \tilde{M} \tilde{X} \). That is, calculate the \( n \) pieces of the eigenvalues \( \lambda_n \) of the matrix \( \tilde{M} \) from the equation

\[ [\tilde{M} - \lambda_n [I_n]] = 0 \]  
\( \text{(17)} \)

and for each value \( \lambda_n \) found, calculate its own \( n \)-dimensional vector

\[ V_n^T = (v_{n,1} v_{n,2} \ldots v_{n,n}) \]

from the system of equations

\[ (\tilde{M} - \lambda_n [I_n])V = 0. \]  
\( \text{(18)} \)

Here \( [I_n] \) is a unit diagonal matrix of dimension \( n \times n \).

The values found \( \lambda_n \) and \( V_n \) allow us to find a solution to the inhomogeneous equation (16). The required column \( X \) is calculated by the formula:

\[ X = (W^T D/\Delta) e^{i\omega t}. \]  
\( \text{(19)} \)

Here
\[ W = \begin{pmatrix} \omega_{1,1} & \ldots & \omega_{1,n} \\
 & \ldots & \ldots \\
 \omega_{n,1} & \ldots & \omega_{n,n} \end{pmatrix}, \quad \Delta = \text{Det} W \ . \]  
\[ D^T = \begin{pmatrix} \Delta_1 & \Delta_2 & \ldots & \Delta_n \\
i\omega - \lambda_1 & i\omega - \lambda_2 & \ldots & i\omega - \lambda_n \end{pmatrix}, \]  
where \( \Delta_p \) is the determinant \( \Delta \), in which the \( \nu \)-th string is replaced by the string \( Y^T = \{ y_1, y_2, \ldots, y_n \} \).

### 7. Results of calculations and their discussion

The calculations were performed for a mixture of Cs \( (I_A = 7/2) \) and Rb\(^{85} \) atoms \( (I_B = 5/2) \). The temperature dependence of the concentration of these atoms was determined by the formulas of [14]. The spin exchange cross sections found in experiments [12] \( \sigma_{cs} = 2.2 \cdot 10^{-14} \) cm\(^2\) and \( \sigma_{cs} = 2.1 \cdot 10^{-14} \) cm\(^2\) were used. For the CsRb collision cross section, the mean value of \( \sigma_{cs} = 2.15 \cdot 10^{-14} \) cm\(^2\) was used, since its experimental value is unknown. The value \( \sigma_{AB} \) of the cross sections in this work is twice the experimental cross sections, since the cross section of the decay rate of \( \{ \vec{S} \cdot T \} \) is usually found in the experiment: \( \sigma_{AB} = \sigma_{AB} / 2 \) [8, 12, 15].

Figure 1 shows the temperature dependence of the eigenvalues \( \lambda_{AB} (q) = \gamma_{AB} (q) + i\omega_{AB} (q) \) of the matrix \( \tilde{M}_{AB} (q) \) for the mixture A + B with the value \( q = +1 \).

From figure 1a it can be seen that at a temperature of 90\(^0\) C, the first decay constant \( \gamma_{AB} (1) \) splits off from the remaining 3 constants with \( n = 2, 3 \) and 4. The constant modulus \( |\gamma_{11} (1)| \) with an increase in temperature decreases sharply from a hundred Hertz at 100\(^0\) C to a few Hertz at 200\(^0\) C. And the modules of other constants \( |\gamma_{21} (1)| \) with \( n \geq 2 \) in this temperature range increase sharply and at 200\(^0\) C exceed a value \( |\gamma_{11} (1)| \) by more than 4 orders of magnitude. So, when \( t \approx 200^0 \) C, the regime of extremely slow decay of the transverse components of the orientations of atoms A and B with a very small rate constant \( |\gamma_{11} (1)| \) is realized. That is, the SERF mode, known [1, 2] for a one-component vapour of alkali atoms, is implemented.

Let us now consider the magnetic resonance signals excited by a rotating RF field. Figure 2 shows the result of calculating the signals of such a resonance at two temperatures of 40\(^0\) and 200\(^0\) C. The values of \( f_{1,1}^A (F_A^+) \) and \( f_{1,1}^B (F_B^+) \) are shown as signals. The calculation was carried out according to the algorithm given by formulas (16) - (21) as applied to equation (12). In this case, the values of the parameters were used: \( q = +1, H_0 = 1 \) mOe, \( h_m = 0.1 \) mOe, \( \beta = 0.1 \).

Figure 2 shows that at a low temperature of 40\(^0\) C there are 4 signals. Two signals exist at positive frequencies: the signal at a frequency of +350 Hz is due to the resonance of Cs atoms at the sublevel \( F_A^+ = 4 \) and the signal at a frequency of +466 Hz from the resonance of Rb\(^{85} \) atoms at the sublevel \( F_B^+ = 3 \). Both of these signals gave sublevels with negative g-factors. It is these resonances that the right-handed RF field should excite. A change in the sign of the frequency \( f \) leads to the replacement of the right-handed field \( h^R \) by a left-handed \( h^L \), which is capable of exciting resonances at sublevels.
The temperature dependence of the matrix $\tilde{M}^{AB}(1)$ eigenvalues $\lambda_n^{AB}(1) = \gamma_n^{AB}(1) + i\omega_n^{AB}(1)$ for a mixture of Cs and Rb$^{85}$ vapours in a magnetic field $H_0 = 1$ mOe.

The bold line is $n = 1$, the points are $n = 2$, the circles are $n = 3$, the thin line is $n = 4$.

Figure 1a - $[-\gamma_n^{AB}(1)/2\pi]$ [Hz], figure 1b - $\omega_n^{AB}(1)/2\pi$ [Hz].

with positive g-factors. This leads to the appearance of the signal of the Cs atom at the sublevel $F_A^- = 3$ at the frequency ($-350$) Hz and the signal of the Rb$^{85}$ atom at the sublevel $F_B^- = 2$ at the frequency ($-466$) Hz.

A weak resonance signal of the orientation $|f_{\pm,1}^B F_{\pm}^B\rangle$ of the Rb$^{85}$ atoms at a cesium resonance frequency $+350$ Hz is also seen in figure 2a. The appearance of such a "cross" signal is possible due to the interrelation of all 4 transverse orientations of the atoms of the mixture through spin-exchange collisions.

At high temperatures of 200° C, as can be seen from figure 2a and figure 2b, all the resonant frequencies of the signals from two atoms merge into one positive frequency of $+146.5$ Hz, which is the frequency of rotation of the total angular momentum $\langle \hat{\Phi}_{\pm,1}^{AB}\rangle$. This means that with increasing temperature, the mixture of atoms A and B turned into a paramagnetic with a negative g-factor. And the reason for such a transformation is the superfrequent spin-exchange, which occurs when all frequencies of spin-exchange collisions become much larger than the Larmor frequencies of the atoms of the mixture. We note that such a merging of resonant frequencies is accompanied by a change in the signs of the g factors in the two lower sublevels of the atoms with the moments $F_A^-$ and $F_B^-$. Note that the fusion of resonant frequencies and the change in the signs of g-factors should also occur in a well-studied high-temperature spin-exchange in a one-element alkali metal vapour. However, in the experiment this has not yet been observed.
Figure 2. The resonances of the modules of the transverse orientations of the Cs (A) and Rb$^{85}$ (B) atoms in the field $H_0 = 1$ mOe.

Figure 2a. Resonances at temperature of 40° C: a thin line - $f_{1+1}^A \left( F^+_A \right)$, dash-dotted - $f_{1+1}^A \left( F^-_A \right)$, dotted - $2f_{1+1}^B \left( F^+_B \right)$, points - $2f_{1+1}^B \left( F^-_B \right)$. The solid line at a frequency of 146.5 Hz is the resonance of the total angular momentum $0.07 \hat{J}_{12}^{AB}$ of the Cs + Rb$^{85}$ mixture at a temperature of 200° C.

Figure 2b. Resonances at 200° C near the frequency $\omega_{1}^{AB} \left( 1 \right) / 2\pi = 146.5$ Hz. The solid line - $\text{Cs} \left( F^+_A \right)$, dotted line - $\text{Rb}^{85} \left( F^+_B \right)$, dash-dotted line - $\text{Cs} \left( F^-_A \right)$, points - $\text{Rb}^{85} \left( F^-_B \right)$. 
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