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The Role of the Nuclear Spin in Optical Pumping with D_2-Light

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Optical pumping with D_2-light provides an excellent means for studying collisional relaxation in the excited $^2P_{3/2}$-state of alkali atoms. Collisional relaxation of orientations in that state very sensitively affects the spin orientation in the ground state. All these orientations may be easily created by absorption of σ^+- or σ^--light. At a certain strength of the relaxation realized by a certain buffer gas pressure, the spin orientation in the ground state even vanishes, provided D_2-light is used for excitation. The condition for this situation is derived from the set of rate equations which governs the evolution of all the orientations involved. These conditions very markedly depend on the nuclear spin value I. The validity of this dependence has been checked by magnetic decoupling of the nuclear spin and observing the associated shift of the pressure for vanishing spin orientation.

I. Introduction

In 1967, optical pumping with D_2-light was introduced independently by several authors[1-4] as a means for studying relaxation in the lowest $^2P_{3/2}$-state of alkali-like spectra. For the evaluation of the experimental results frequently an analysis is used which generously ignores the presence of a nuclear spin in those spectra. Unfortunately, this analysis has been accepted by the learned literature[5] notwithstanding that the disregard of the role played by the nuclear spin in optical pumping dynamics, may give rise to severe errors. This was demonstrated, for instance, by the history of spin relaxation in the $^2S_{1/2}$-ground state. As pointed out by Bouchiat[6], earlier depolarizing cross sections which were derived under disregard of the nuclear spin, had to be corrected by multipliers as large as $(2I+1)^2/2$ when the nuclear spin I was correctly taken into account. In the considerations which lead to those multipliers, the nuclear spin plays the role of an additional reserve of polarization

1 Franz, F. A., Franz, J. R.: Phys. Rev. **148**, 82 (1966).
2 Fricke, J., Haas, J., Lüscher, E., Franz, F. A.: Phys. Rev. **163**, 45 (1967).
3 Elbel, M., Naumann, F.: Z. Physik **204**, 501 (1967); **208**, 104 (E) (1967).
4 Violino, P.: Nuovo Cimento **54**B, 61 (1968).
5 Massey, H. S. W.: Electronic and ionic impact phenomena, vol. 3. Oxford 1971.
6 Bouchiat, M. A.: J. Phys. Radium **24**, 379, 611 (1963); **26**, 415 (1965).

accessible only through hyperfine interaction with the electronic spin. In sudden collisions only the electronic spin is depolarized with a subsequent redistribution of polarization among the systems of spin and nuclear spin by hyperfine interaction. This hyperfine interaction takes place during the long periods between successive collisions. Thus the presence of a nuclear spin obscures the proper relaxation of the electronic angular momentum. In particular, it may effect a considerable slowing-down of the relaxation up to several times, depending on the relative size of the electronic and the nuclear spin.

II. Analysis of the Optical Pumping Process Including Nuclear Spin

The afore-mentioned principles must be carefully considered when analyzing the optical pumping process with D_2-light. Fig. 1 displays the

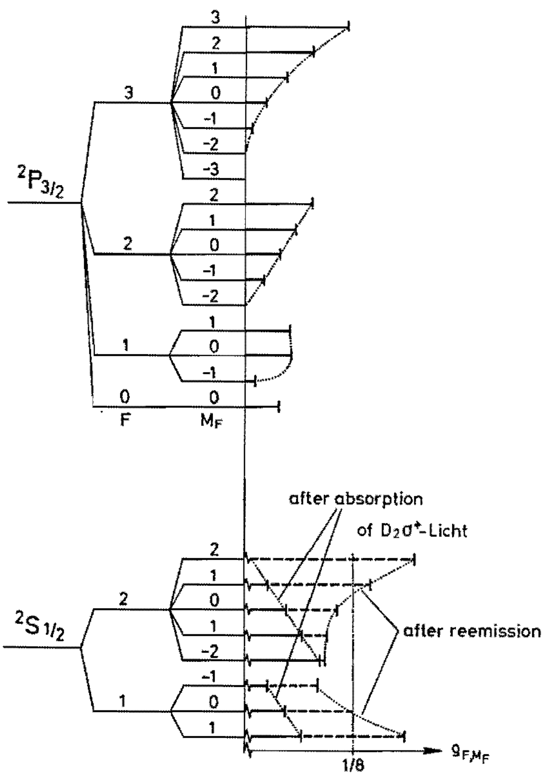

Fig. 1. Populations of the sublevels of the ground state $^2S_{1/2}$ and the excited state $^2P_{3/2}$ after absorption of a $D_2\sigma^+$-light pulse (solid lines) and after decay of the excited state (broken lines)

hyperfine sublevels of both the states involved. The nuclear spin is chosen 3/2. Normally any of the eight ground state sublevels is occupied by 1/8 of the total number of alkali atoms. On shining in a short pulse of $D_2\sigma^+$-light, the ground state sublevels are depleted to the degree indicated by the solid lines and the sublevels of the excited state are occupied. The structure of the occupation of the different F-levels implies strong orientations and alignments. Quantities $\langle F_z\rangle_F = \sum m_F \rho_{F,m_F}$ will be used for describing the orientations in the excited state, whereas the orientation of the spin system $\langle S_z\rangle$ and the nuclear spin system $\langle I_z\rangle$ will be preferred for the description of the ground state orientations. The quantity $\langle S_z\rangle$ in the ground state bears particular importance for being proportional to the difference of the absorption of σ^+ and σ^- quanta of either resonance line. Hence this quantity is easy to observe. The spin orientation of the residual population of the ground state has negative sign. If, however, the population of the excited state undergoes spontaneous decay, the sublevels of the ground state are reoccupied to the degree which corresponds to the broken lines. This population clearly gives rise to a positive spin orientation $\langle S_z\rangle$.

If, however, depolarizing collisions completely destroy the orientations which exist in the excited substates during their life time, then the orientation of the residual population in the ground state will last even after recoccupation. Hence we may conclude that the sign and the size of the quantity $\langle S_z\rangle$ in the ground state provide a sensitive measure for the degree of the relaxation in the excited state.

The degree of relaxation in the excited state can be varied when changing the buffer gas pressure in the pumping cell. On doing so, the inversion of the quantity $\langle S_z\rangle$ can be observed and the particular pressure can be determined where $\langle S_z\rangle$ passes through zero. This case may be studied in more detail by writing down rate equations for $\langle S_z\rangle$ in the ground state, on the one hand, and the various orientations $\langle F_z\rangle_F$ in the excited state, on the other hand.

Ground State $^2S_{1/2}$:

$$\frac{d}{dt}\langle S_z\rangle = -\frac{4I^2+4I+3}{2I+1}\cdot\frac{2}{9T_p} + \frac{4}{(2I+1)\tau}\sum_f\sum_F(-1)^{f+I+\frac{1}{2}} \cdot \frac{F(F+1)+f(f+1)-2}{2F(F+1)}(2f+1)\,W^2(jJfF,1I)\langle F_z\rangle_F \tag{1}$$

$j, f \rightarrow$ Quantum numbers: ground state

$J, F \rightarrow$ Quantum numbers: excited state

Excited State $^2P_{3/2}$:

$$\begin{aligned}\frac{d}{dt}\langle F_z\rangle_F = & \frac{F(F+1)+J(J+1)-I(I+1)}{2}\,\frac{2(2F+1)}{9T_p} \\ & -\left(\frac{1}{\tau}+\frac{1}{T_c}\right)\langle F_z\rangle_F \\ & +\frac{F(F+1)+I(I+1)-J(J+1)}{2I(I+1)}\,\frac{(2F+1)}{(2I+1)(2J+1)T_c} \\ & \cdot\sum_{F'}\frac{(F'(F'+1)+I(I+1)-J(J+1))\langle F_z\rangle_{F'}}{2F'(F'+1)}.\end{aligned} \tag{2}$$

The set of rate equations which governs the evolution of the $\langle F_z\rangle_F$ of the hyperfine sublevels of the excited state, consists of three terms. The first term accounts for gains by excitation through absorption of $D_2\sigma^+$-quanta. T_P denotes any arbitrarily chosen pumping time. The dependence on the quantum numbers results from a straight-forward evaluation of the probabilities for excitation of the sublevel M_F of F from the ground state. They are weighed with $\langle FM_F|\,F_z\,|FM_F\rangle$ and traced over M_F for the purpose of obtaining the rate at which $\langle F_z\rangle_F$ is built-up on account of the absorption process. The second term stands for losses through spontaneous decay and collisional depolarization. τ and T_c denote the mean life of the level $^2P_{3/2}$ and the time constant of collisional relaxation of $\langle J_z\rangle_{J=3/2}$, respectively. The third term describes collisional mixing of the hyperfine states on account of the very suddenness of the collisional process when compared to hyperfine interaction. The particulars of the consideration which led to the formulation of this term, are given in Appendix B.

The first equation which deals with the evolution of the spin orientation $\langle S_z\rangle$ in the ground state, consists of two terms, as spin exchange is neglected. Obviously, $\langle S_z\rangle$ is being built by absorption of $D_2\sigma^+$-quanta and by a transfer of orientation from the excited state through spontaneous decay. The particulars of the second term are given in Appendix A.

One may solve the latter three equations to obtain stationary solutions for the $\langle F_z\rangle_F$ and subsequently substitute those solutions into the rate equation for $\langle S_z\rangle$ for the purpose of finding a condition for vanishing $d\langle S_z\rangle/dt$. Vanishing $d\langle S_z\rangle/dt$ implies that no build-up of $\langle S_z\rangle$ occurs in course of time by optical pumping of the ground-state sublevels which are initially populated at random.

We are then led to the conditions Eq. (3)–(6) which are indeed strongly dependent on the nuclear spin I. The dependence consists in a sudden drop of the ration T_c/τ occurring when a nuclear spin $I=3/2$ is introduced, and in a slow rising of that ratio if the nuclear spin proceeds to even higher values.

$$I=0, \qquad \frac{T_c}{\tau}=1.50, \tag{3}$$

$$I=\frac{3}{2}, \qquad \frac{T_c}{\tau}=0.75, \tag{4}$$

$$I=\frac{5}{2}, \qquad \frac{T_c}{\tau}=1.05, \tag{5}$$

$$I=\frac{7}{2}, \qquad \frac{T_c}{\tau}=1.18. \tag{6}$$

III. Comparison with Experiment

a) Sodium

In sodium, a nuclear spin $I=3/2$ is present which in ${}^2P_{3/2}$-state is coupled so weakly to the electron spin that a magnetic field of a few ten Oersteds suffices for breaking this coupling. Thus over a range of a few ten Oersted, Eq. (4) loses validity and Eq. (3) takes its place. With T_c independent of hyperfine coupling, since

$$T_c=\frac{1}{N v_r \sigma_{\text{relax}}(\langle J_z \rangle_J)} \tag{7}$$

we may conclude that the buffer gas density N for vanishing $\langle S_z \rangle$ is shifted to half its initial value if the nuclear spin is decoupled. This prediction can be checked experimentally. This has been done with an experimental set-up displayed in Fig. 2. A sodium vapor which is contained in a cell, is irradiated with $D_2 \sigma^+$-light. A detector beam about hundred times less intense, serves for the detection of the spin orientation $\langle S_z \rangle$ which is known to be proportional to the absorption difference for $D_1 \sigma^+$- and $D_1 \sigma^-$-light. A variable magnetic field which is slightly tilted against the light beams, serves for the decoupling of the nuclear spin. In Fig. 3 the signal which is proportional to the spin orientation, is plotted versus the buffer gas pressure in the cell. The magnetic field is used as a parameter. A drop of the pressure for vanishing $\langle S_z \rangle$ occurs with rising field, as predicted. In Fig. 4, the pressures of vanishing $\langle S_z \rangle$ are plotted versus magnetic field for the various noble gases. The ratios of the initial and the asymptotic pressure values slightly deviate from the predicted value of two. They amount to 2.35 for the three lighter noble gases proceeding to even higher values for Kr and Xe. From the asymptotic values, the cross-sections for the relaxation of $\langle J_z \rangle_{J=3/2}$ are derived for the various

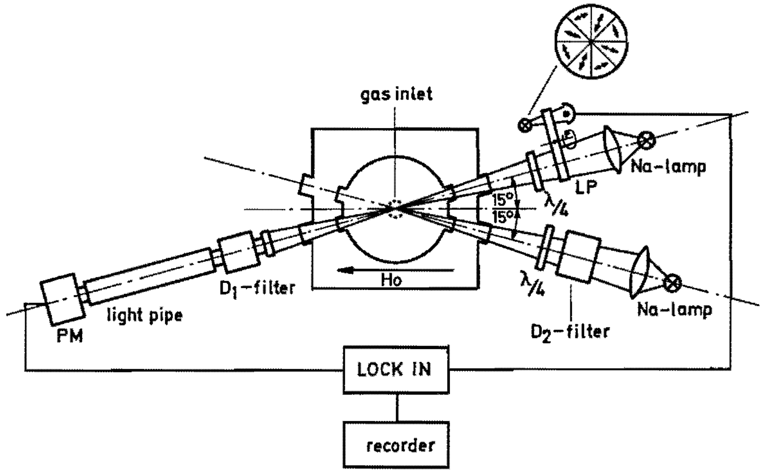

Fig. 2. Apparatus for optical pumping of sodium vapor with D_2-light. A second light beam is used for the detection of $\langle S_z \rangle$ in the ground state. The circular sense of the polarization of the latter beam is changed periodically and the transmission signal yielded by a photomultiplier is detected by lock-in techniques. The signal hence becomes proportional to the difference of the absorption for $D_1\sigma^+$- and for $D_1\sigma^-$-light

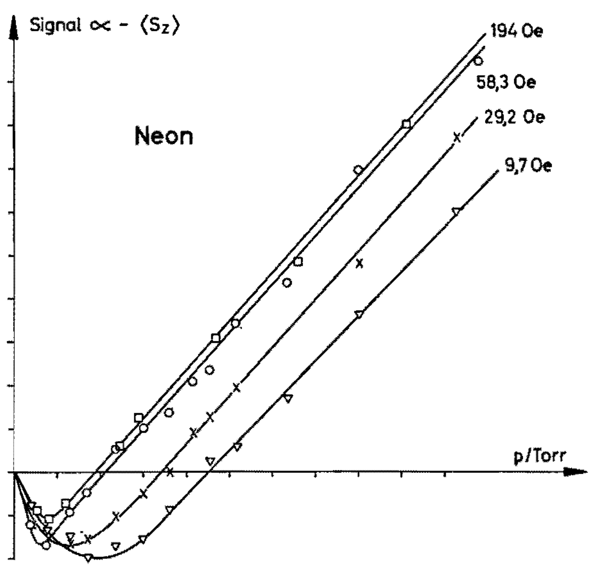

Fig. 3. The signal yielded by the lock-in set as plotted against the foreign-gas pressure in the cell. The strength of the magnetic field is used as a parameter. The shift of the intercept with the p-axis associated with the increasing field-strength is demonstrated

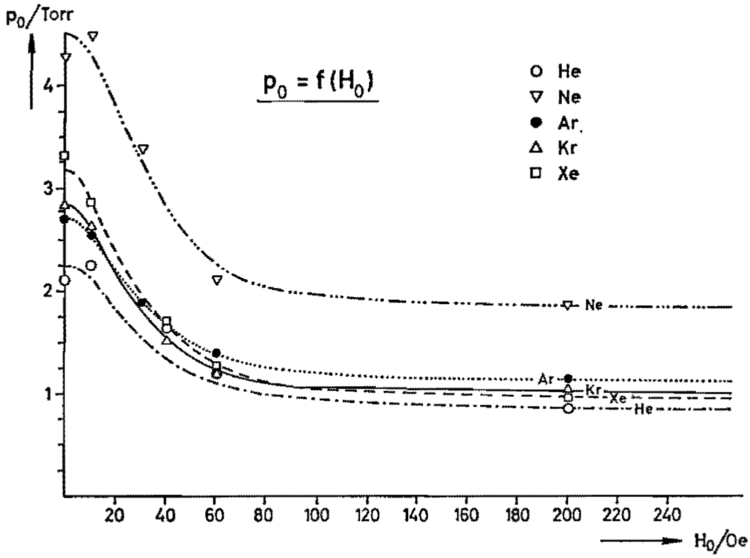

Fig. 4. The intercepts of the signal with the p-axis as a function of the magnetic field-strength. Various noble gases are used as foreign gases

noble gases utilizing Eqs. (3) and (7). They are displayed in Table 1. For Helium a striking agreement with a theoretical value given by Masnou and Roueff [7] is obtained.

b) Rubidium

Two isotopes exist with $I=3/2$ (Rb^{87}) and $I=5/2$ (Rb^{85}). According to Eq. (4) and (5), the pressure of vanishing $\langle S_z \rangle$ for Rb^{87} would differ from the one for Rb^{85} by a multiplier of 1.40. Shitnikov and co-

Table 1. Cross-sections for the relaxation of $\langle J_z \rangle_J$ in state $3\,^2P_{3/2}$ of sodium by collisions with various buffer gases

Noble gas	$\sigma_{\text{relax}}(\langle J_z \rangle_{3/2})$ (exp.)	$\sigma_{\text{relax}}(\langle J_z \rangle_{3/2})$ (theory) [7]
He	128 Å^2	110 Å^2
Ne	107 Å^2	
Ar	205 Å^2	
Kr	243 Å^2	
Xe	281 Å^2	

7 Masnou-Seeuws, F., Roueff, E.: Vième Colloque sur la Physique des Collisions Atomiques et Electroniques, Liège 1972.

workers[8] measured multipliers which range from 1.20 to 1.29 for the various noble gases. Meanwhile doubts have been raised concerning the suitability of magnetic induction for the measurement of $\langle S_z \rangle$. For this reason Shitnikov and co-workers[9] have measured the pressures for the disappearance of another ground-state orientation, namely

$$\langle F_z \rangle_{f=I+1/2}.$$

We have written down the rate equation which governs the evolution of the latter quantity, and found

$$\frac{d\langle F_z \rangle_{f=I+1/2}}{dt} = -\frac{(4I+6)(I+1)}{9T_P} + \frac{1}{\tau} \sum_F \frac{F(F+1)+f(f+1)-1\cdot 2}{2F(F+1)} \tag{8}$$
$$\cdot (2J+1)(2f+1)\, W^2(jJfF, 1I) \langle F_z \rangle_F.$$

Hence we have deduced conditions for vanishing $\langle F_z \rangle_{f=I+1/2}$, which read

$$I=3/2: \quad \frac{T_c}{\tau} = 0.375, \tag{9}$$

$$I=5/2: \quad \frac{T_c}{\tau} = 0.190. \tag{10}$$

Eqs. (9) and (10) predict that, for Rb^{87}, $\langle F_z \rangle_{f=I+1/2}$ passes through zero at a pressure which exceeds the one for Rb^{85} by a multiplier of 1.97. The authors of Ref.[9] have measured multipliers which range from 1.43 to 1.60. At any rate, Shitnikovs results show the same tendency as do our theoretical predictions, although quantitive agreement might be improved.

Meanwhile, Franz and co-worker[10] have repeated Shitnikov's measurements. However, no satisfactory agreement was obtained neither with Shitnikov's nor with our results. The authors have also done numerical computations which support their findings. The reason for the discrepancy is beyond our understanding, the more so as the applied methods are hard to compare. At least one equation in Franz's paper (Eq. (21)) differs from our Eq. (1) by one sign which might lead to the inconsistency of our results.

8 Shitnikov, R. A., Kuleshov, I. P., Okunevich, A. I.: Phys. Lett. **29** A, 239 (1969).

9 Shitnikov, R. A., Kuleshov, I. P., Okunevich, A. I., Sevastyanov, B. N.: Soviet Phys. JETP **31**, 445 (1970). Theoretical considerations in this publication are based on: Okunevitch, A. I., Perel, V. I.: Soviet Phys. JETP **31**, 356 (1970).

10 Papp, J. F., Franz, F. A.: Phys. Rev. A**5**, 1763 (1972).

c) Cesium

Fricke and Haas[2] have measured the pressures for vanishing $\langle S_z \rangle$ and have hence derived cross-sections. In so far as their calculation was based on Eq. (3) which does not hold except for $I=0$, it ought to be repeated with Eq. (6) which pertains to the nuclear spin value 7/2 of Cs^{133}. This means multiplying their results with the ratio of Eqs. (3) and (6), namely 1.27, which is not much of a correction.

Anyhow, for the sake of lucidity, the measurements for Rubidium and Cesium ought to be repeated with the nuclear spin decoupled magnetically. Respective measurements are under way.

IV. Conclusions

A striking dependence of collisional relaxation on hyperfine coupling which is known for $J=1/2$-levels since a long time[6,11], is revealed now for $J=3/2$-levels. It is shown both theoretically and experimentally, how this dependence affects optical-pumping dynamics, in particular if D_2-light is used. Theoretically, the buffer gas density for vanishing transmission signal was predicted to be dependent on the nuclear spin value and, experimentally, this dependence could be proved by magnetic decoupling of the nuclear spin during optical pumping. Moreover, cross-sections could be derived from the high-field measurements for sodium which can be unambiguously assigned now to the relaxation of $\langle J_z \rangle$ in the $^2P_{3/2}$-state.

Appendix A

Transfer of Orientation to the Ground State through Spontaneous Decay of the Excited State

Consider any two sets of quantum numbers J, F, M_F and j, f, m_f denoting substates of the excited state and of the ground state, respectively. The rate at which the atomic density of the latter state is replenished through spontaneous decay of the former state, follows from well-known theory of electric dipole radiation as

$$\begin{aligned} \frac{d\langle jfm_f|\,\rho\,|jfm_f\rangle}{dt} \propto \sum_{M_F} &\langle jfm_f|\,\mathfrak{r}\,|JFM_F\rangle \\ &\cdot \langle JFM_F|\,\rho\,|JFM_F\rangle \\ &\cdot \langle JFM_F|\,\mathfrak{r}\,|jfm_f\rangle . \end{aligned} \tag{11}$$

11 Bulos, B. R., Happer, W.: Phys. Rev. A4, 849 (1971).

Multiplying of this relation with $\langle jfm_f|\, \boldsymbol{F}_z\, |jfm_f\rangle$ and tracing over m_f yields a rate equation for $\langle \boldsymbol{F}_z\rangle_f$

$$\begin{aligned}\frac{d\langle \boldsymbol{F}_z\rangle_f}{dt} \propto \sum_{M_F}\sum_{mf} &\langle FM_F|\, f\, 1\, m_f\, M_F - m_f\rangle^2 \\ &\cdot \sqrt{f(f+1)}\,\langle f m_f|\, f\, 1\, m_f\, 0\rangle \\ &\cdot \left|\langle JF\|\, \mathfrak{r}\,\| jf\rangle\right|^2 \langle FM_F|\,\rho\,|FM_F\rangle.\end{aligned} \tag{12}$$

The summation on the right hand side of this relation is led over three Clebsch-Gordan-coefficients. It may be carried through by utilizing the contraction of $3j$-symbols (c.f. Brink-Satchler, Angular Momentum, Appendix III), yielding

$$\begin{aligned}\frac{d\langle \boldsymbol{F}_z\rangle_f}{dt} &\propto \sqrt{\frac{f(f+1)(2f+1)(2F+1)}{F(F+1)}}\, W(1fF1, fF) \\ &\quad\cdot \left|\langle JF\|\, \mathfrak{r}\,\| jf\rangle\right|^2 \langle F_z\rangle_F \\ &\propto \frac{f(f+1)+F(F+1)-1\cdot 2}{2F(F+1)} \left|\langle JF\|\, \mathfrak{r}\,\| jf\rangle\right|^2 \langle \boldsymbol{F}_z\rangle_F.\end{aligned} \tag{13}$$

The latter relation elucidates the distribution of the initial orientation $\langle \boldsymbol{F}_z\rangle_F$ among the radiation field and the final atomic state. On further reducing the matrix element of $\mathfrak{r}$ we are led to

$$\begin{aligned}\frac{d\langle \boldsymbol{F}_z\rangle_f}{dt} &\propto \frac{f(f+1)+F(F+1)-1\cdot 2}{2F(F+1)} \\ &\quad\cdot (2f+1)(2J+1)\, W^2(JjFf, 1I)\left|\langle J\|\, \mathfrak{r}\,\| j\rangle\right|^2 \cdot \langle \boldsymbol{F}_z\rangle_F.\end{aligned} \tag{14}$$

On substituting the reciprocal mean life $1/\tau$ for $|\langle J\|\,\mathfrak{r}\,\|j\rangle|^2$, equality is established among both sides of this relation. Hence our final result arises

$$\begin{aligned}\frac{d\langle \boldsymbol{F}_z\rangle_f}{dt} &= \frac{f(f+1)+F(F+1)-1\cdot 2}{2F(F+1)}\,(2f+1)(2J+1) \\ &\quad\cdot W^2(JjFf, 1I)\,\langle \boldsymbol{F}_z\rangle_F/\tau.\end{aligned} \tag{15}$$

Appendix B

Collisional Coupling Among Hyperfine States

In the initial state $|i\rangle$ an atom may occupy the sublevels m_F of a hyperfine level F with amplitudes α_{F,m_F}

$$|i\rangle = \sum_{m_F} \alpha_{F,m_F}\, |F, m_F\rangle. \tag{16}$$

We rewrite this state in terms of decoupled wave functions

$$|i\rangle = \sum_{m_F} \alpha_{F,m_F} \sum_{m_I, m_J} \langle m_I\, m_J|F\, m_F\rangle\, |m_I\rangle\, |m_J\rangle.$$

A collision which depolarizes J substitutes all substates $|m'_J\rangle$ with random amplitudes for $|m_J\rangle$. Be $\boldsymbol{S}$ the scattering operator, then its action on $|i\rangle$ may be understood as follows

$$\begin{aligned} \boldsymbol{S}\,|i\rangle = \frac{1}{\sqrt{2J+1}} \sum_{m_F} \alpha_{F,m_F} \sum_{m_I,m_J} \langle m_I\, m_J | F\, m_F\rangle\, |m_I\rangle \\ \cdot \sum_{m'_J} \exp(i\,\varphi_{m_J,m'_J}) \cdot |m'_J\rangle. \end{aligned} \tag{17}$$

The amplitude of any desired final state

$$|f\rangle = |F', m_{F'}\rangle$$

in the scattered state is readily obtained on projecting the scattered state on that final state. The absolute square of that amplitude when averaged over the scattering phases $\varphi_{m'_J,m_J}$ and the α_{F,m_F} of a great number of atoms, provides an expression for the density matrix element

$$\langle F', m_{F'}|\,\rho\,|F', m_{F'}\rangle.$$

One is led at once to the result

$$\begin{aligned} &\langle F', m_{F'}|\,\rho\,|F', m_{F'}\rangle_{\text{after collision}} \\ &= \sum_{m_F} \overline{|\alpha_{F,m_F}|^2} \cdot \sum_{m_I,m_J} \langle F, m_F | m_I, m_J\rangle^2 \frac{\langle m_I, m'_J | F', m_{F'}\rangle^2}{2J+1}. \end{aligned} \tag{18}$$

When calculating $\langle F_z\rangle_{F'}$ using these density matrix elements and applying the contraction theorem for $3j$-symbols one finally is led to the result

$$\begin{aligned} \frac{d}{dt}\langle F_z\rangle_{F'} = \frac{(2F'+1)}{(2J+1)(2I+1)} \frac{I(I+1)+F'(F'+1)-J(J+1)}{2I(I+1)} \\ \cdot \frac{F(F+1)+I(I+1)-J(J+1)}{2F(F+1)} \langle F_z\rangle_F / T_C. \end{aligned} \tag{19}$$

The coefficient on the right hand side of this equation suggests the following interpretation. If a collision destroys the orientation in the J-system, only the orientation in the I-system survives. Hence we understand the projection of F on I. If hyperfine interaction sets in after the collision, states F' are reestablished whose orientations are derived from the orientation in the I-system. Hence the projection of I on F' results.

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